SUPPLEMENTARY INFORMATION

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General information.

Unless otherwise stated, reactions were performed in oven-dried brand-new Fisherbrand scintillation vials in a nitrogen filled glove box or in flamed-dried Schlenk flasks under argon connected on a Schlenk line using dry, degassed solvents and brand-new stirring bars. Solvents were dried by passage through an activated alumina column under argon.[1] Reaction progress was monitored by thin-layer chromatography (TLC), UHPLC-LCMS or GC-FID analyses. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, phosphomolybdic acid, or $KMnO_4$ staining. Silicycle SiliaFlash P60 Academic Silica gel (particle size 40–63 nm) was used for flash chromatography. ^1H NMR spectra were recorded on Varian Inova 500 MHz and 600 MHz spectrometers in $CDCl_3$ or C_6D_6 and are reported relative to residual solvent peak at δ 7.26 ppm or δ 7.16 ppm respectively. ^{13}C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (125 MHz) in $CDCl_3$ or C_6D_6 and are reported relative to residual solvent peak at δ 77.16 ppm or δ 128.06 ppm respectively. Data for ^1H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septet, m = multiplet, br s = broad singlet, br d = broad doublet, app = apparent. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm). IR spectra were obtained on a Perkin Elmer Spectrum BXII spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). UHPLC-LCMS analyses were obtained on an Agilent 1290 ultra high performance liquid chromatography/mass spectrometry equipped with an Agilent EclipsePlus C18 RRHD 1.8 μM column. GC-FID analyses were obtained on an Agilent 6890N gas chromatograph equipped with a HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent). GC-MS analyses were obtained on an Agilent 6850 gas chromatograph equipped with a HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent). High resolution mass spectra (HRMS) were obtained on an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed ionization mode (MM: ESI-

(1) Pangborn, A. M.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics*, **1996**, *15*, 1518.

APCI+), or were acquired from the California Institute of Technology Mass Spectrometry Facility. ICP-MS analysis was conducted at the California Institute of Technology Mass Spectrometry Facility.

Al_2O_3 was purchased from Aldrich and activated by storing in a 200 °C oven for one week and then heating in a round bottom flask at 200 °C under vacuum (60 millitorr). Silanes were purchased from Aldrich and distilled before use. KO*t*-Bu was purchased from Aldrich (sublimed grade, 99.99% trace metals basis) and used directly. Heteroaromatic substrates were purchased from Aldrich, TCI, or Acros, or synthesized according to literature procedures.[2]

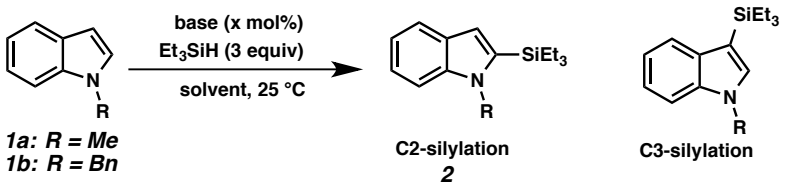
(2) (a) Kong, A.; Han, X.; Lu, X. *Org. Lett*. **2006**, *8*, 1339. (b) Islam, S.; Larrosa, I. *Chem. – Eur. J*. **2013**, *19*, 15093. (c) Huestis, M. P.; Fagnou, K. *Org. Lett*. **2009**, 11, 1357. (d) Mahadevan, I.; Rasmussen, M. *Tetrahedron*, **1993**, *49*, 7337.

Part I. Reaction optimizations, control experiments and trace metal analysis.

1. Reaction optimization.

Procedure for reaction condition optimization: In a nitrogen-filled glovebox, base and indole **1** (0.2 mmol, 1 equiv) were added to a 2 dram scintillation vial equipped with a magnetic stirring bar. Next, Et_3SiH (97 μL, 0.6 mmol, 3 equiv*, filtered through a short pad of activated alumina before use*) and solvent (0.2 mL, unless the reaction was run neat) were added. The vial was sealed and the mixture was stirred at the indicated temperature for the indicated time. Then the vial was removed from the glovebox, diluted with diethyl ether (1 mL) and concentrated under reduced pressure. The regioselectivity (C2 silylation product to C3 silylation product: C2:C3) and yield were determined by ^{1}H NMR or GC analysis of the crude mixture using an internal standard.

Table 1. Condition optimization of direct C–H silylation of indoles.



entry[a]	R	base	solvent	x	*t* (h)	C2:C3[b]	C2 (%)[b]
1	Me	LiO*t*-Bu	THF	100	16	–	0
2	Me	NaO*t*-Bu	THF	100	16	–	0
3	Me	NaOEt	THF	100	16	–	0
4	Me	NaOAc	THF	100	16	–	0
5	Me	KOMe	THF	100	16	–	<5
6	Me	KOEt	THF	100	16	–	14
7	Me	KO*t*-Bu	THF	100	16	>20:1	67
8	Me	KHMDS	THF	100	16	>20:1	44
9	Me	KOAc	THF	100	16	–	0
10	Me	KH	THF	100	72	–	0
11	Me	KOH	THF	100	16	–	0
12	Me	Cs_2CO_3	THF	100	16	–	0
13	Me	DABCO	THF	100	16	–	0

14	Me	TBAF	THF	100	16	–	0
15	Me	CsF	THF	100	16	–	0
16	Me	KF	THF	100	16	–	0
17 [c]	Me	KO*t*-Bu	THF	20	60	4:1	98
18 [c]	Me	KO*t*-Bu	MeO*t*-Bu	20	60	>20:1	89
19 [c]	Me	KO*t*-Bu	DME	20	60	3.4:1	95
20 [c]	**Me**	**KO*t*-Bu**	**neat**	**20**	**48**	**>20:1**	**88**
21 [d]	Me	KHMDS	THF	20	72	17:1	75
22 [c,e]	**Bn**	**KO*t*-Bu**	**THF**	**20**	**61**	**>20:1**	**90**
23 [c,e,f]	Bn	KO*t*-Bu	THF	20	96	>20:1	22
24 [c,e]	Bn	KOTMS	THF	20	72	>20:1	79

[a] Reactions performed with 0.2 mmol of **1** and 0.6 mmol of Et_3SiH in 0.2 mL of solvent. [b] Determined by GC analysis of the crude reaction mixture using an internal standard. [c] At 45 °C. [d] At 35 °C. [e] The ratio of C2:C3 and yield were determined by ^1H NMR analysis of the crude reaction mixture. [f] With 50 mol% of 18-crown-6.

The results from Table 1 reveal that good catalysts for the C–H silylation reaction are categorized by the combination of a bulky basic anion and a potassium cation: KO*t*-Bu proved to be ideal catalyst and operated under neat conditions or in THF and MeO*t*-Bu (Entry 18, 20 and 22), but KHMDS (Entry 21) and KOTMS (Entry 24) were also effective. The complete lack of reactivity with LiO*t*-Bu and NaO*t*-Bu (Entries 1 and 2) as well as the precipitous drop in reactivity when 18-crown-6 is added to KO*t*-Bu (Entry 23) lend support to the crucial, albeit unknown, role of the potassium cation. Conversion roughly correlates with basicity in stoichiometric reactions (i.e., O*t*-Bu > OEt > OMe; Entries 5–7). No product was observed in the absence of catalyst, or when KH, KOH, KOAc and Cs_2CO_3 were employed (Entries 9–12). The organic base DABCO and common fluoride-based activators for silicon – TBAF, CsF, and KF – were also investigated and failed to convert the starting material (Entries 13–16). Headspace GC-TCD analysis of successful silylation reactions indicated the formation of H_2.

2. Control experiments and trace metal analysis.

Careful experiments were conducted in order to rule out catalysis by adventitious transition metal impurities in the reaction mixture [see below (1) – (3)].

*(1) Control reactions with commercially available KO*t*-Bu, re-sublimed KO*t*-Bu, and freshly-prepared KO*t*-Bu.* Three reactions were performed in parallel (THF, 45 °C, 1-methylindole, 20 mol% KO*t*-Bu, 0.2 mmol scale): a) KO*t*-Bu (Aldrich, sublimed grade, 99.99%, trace metal basis) was used as received; b) KO*t*-Bu (Aldrich, sublimed grade, 99.99% trace metal basis) was used after re-sublimation by heating the material under vacuum; and c) KO*t*-Bu, freshly prepared by reaction of potassium metal with anhydrous *t*-BuOH followed by evaporation of the *t*-BuOH and sublimation of the solid, was used. No appreciable differences in conversion and selectivity in these reactions were observed.

(2) Control reaction with KOt-Bu of different grade purchased from different vendors. Four reactions were performed in parallel (THF, 45 °C, 1-benzylindole, 20 mol% KO*t*-Bu, 0.2 mmol scale): a) KO*t*-Bu (Aldrich, sublimed grade, 99.99% trace metal basis), b) KO*t*-Bu (Strem, 98%), c) KO*t*-Bu (TCI, >97%), and d) KO*t*-Bu (Alfa-Aesar, 97%). The reactions were monitored by UHPLC-LCMS and no appreciable differences in conversion and selectivity in these four reactions was observed (Figure 1).

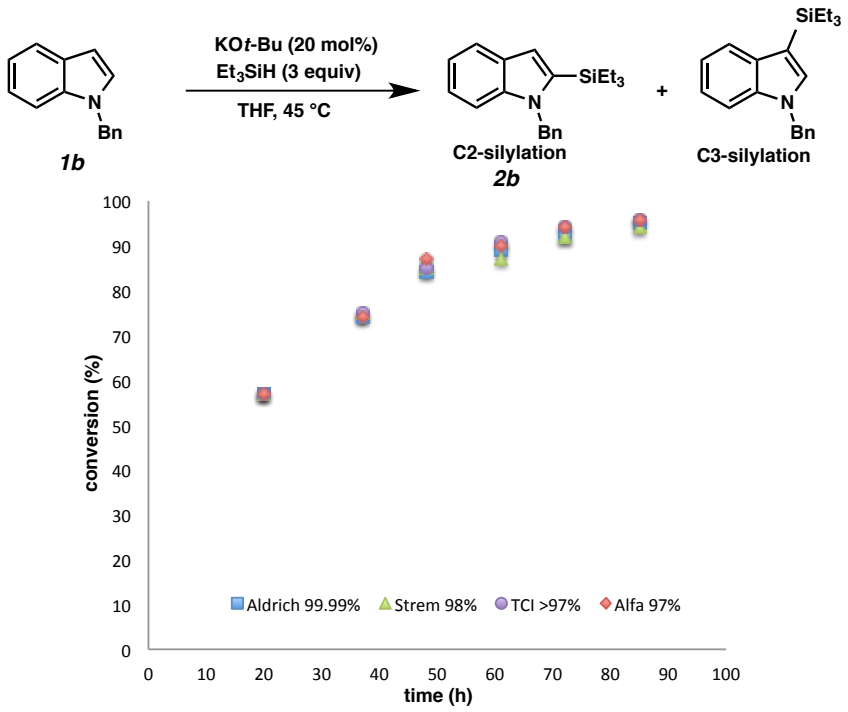


Figure 1. The results of with KO*t*-Bu purchased from different vendors

(3) ICP-MS trace metal analysis of all the reaction components. To provide further support against involvement of adventitious trace metal species in the C–H activation

catalysis, inductively coupled plasma mass spectrometry was performed on samples of KO*t*-Bu from different vendors, 1-benzylindole starting material, THF, Et_3SiH and a standard reaction mixture that was run under optimal conditions in the glove box ("Rxn Mixture" in Table 2). The results from quantitative analysis revealed that most metal contaminants were present below the instrument's lowest limit of detection (i.e., in ppt range or lower). Microgram per liter (ppb) quantities of metal contaminants are given in Table 2.

Table 2. ICP-MS trace metal analysis.

500 mg samples each of KO*t*-Bu from four different vendors (Strem, Aldrich, TCI, Alfa-Aesar), 1-benzylindole, Et_3SiH, THF, and a standard reaction mixture (0.5 mmol scale mixture, prepared following the general procedure with 103.5 mg of 1-Bn-indole, 11.2 mg of KO*t*-Bu from Aldrich, 173.5 mg of Et_3SiH in 0.5 mL of THF and stirred in the glovebox for 72 h.) were analyzed. Each sample was added to a 50 mL DigiTUBE digestion tube (SCP Science) followed by addition of 3.0 mL of Plasma Pure nitric acid (SCP Science) and heating to 75 ^oC for 36 hours. After digestion, each sample was diluted using Milli Q water to 50 mL and sample analysis was performed on an Agilent 7900 ICP-MS spectrometer. LOD indicates that the analyte concentration is below the instrument's *Lowest Limit of Detection*. Values in ppb (*microgram per liter*).

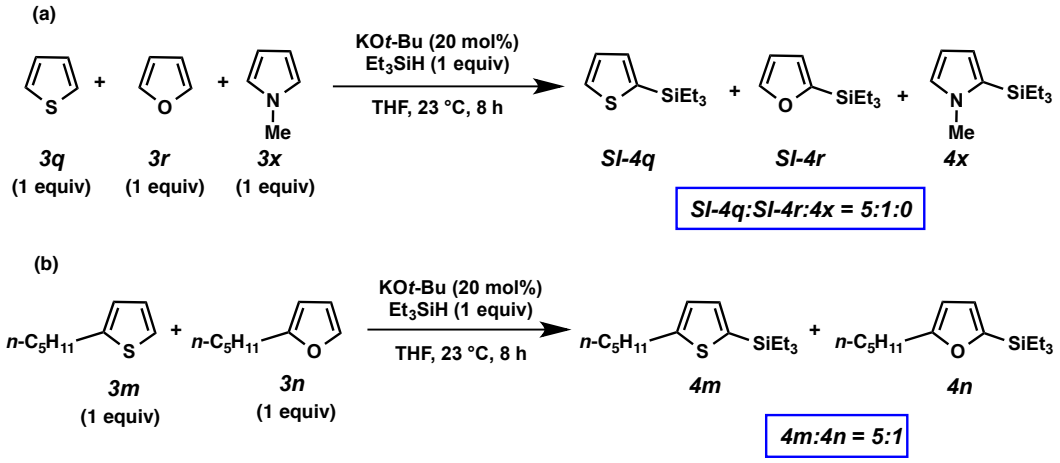
ICPMS Trace Metal Analysis – Agilent 7900 (quantities in ppb)								
Element	**KO*t*-Bu Strem (98%)**	**KO*t*-Bu TCI (>97%)**	**KO*t*-Bu Alpha (97%)**	**KO*t*-Bu Aldrich (99.99%)**	**THF**	**$HSiEt_3$**	**1-Bn-indole**	**Rxn Mixture**
Ti	0.360	0.051	0.138	0.464	LOD	2.073	9.408	31.082
Mn	1.343	1.168	1.338	1.525	LOD	0.177	88.191	LOD
Fe	12.285	10.171	13.080	14.036	1.691	9.531	86.191	LOD
Co	0.005	LOD	0.006	0.008	0.001	0.006	0.416	LOD
Ni	0.064	LOD	0.232	1.418	0.011	LOD	16.540	19.826
Cu	0.134	0.211	1.126	0.366	LOD	0.520	17.936	3.092
Zr	0.038	LOD	LOD	0.633	LOD	0.031	LOD	8.889
Mo	2.005	1.650	1.744	2.243	LOD	LOD	LOD	LOD
Ru	0.002	0.002	0.001	0.008	LOD	0.004	0.146	LOD

Rh	LOD	LOD	LOD	0.001	LOD	LOD	LOD	LOD
Pd	0.014	0.006	0.029	0.116	0.002	0.004	0.070	0.593
Ag	0.001	LOD	0.290	0.015	LOD	0.004	0.055	0.013
Os	0.001	LOD	LOD	0.001	LOD	LOD	0.007	0.016
Ir	0.001	0.001	0.002	0.026	LOD	0.001	0.047	0.041
Pt	0.009	0.004	0.002	0.010	LOD	0.001	LOD	LOD
Au	0.017	0.013	0.013	0.023	0.108	0.024	0.738	1.582

Part II. Competition experiments and evaluation of functional group compatibility.

1. Competition experiments with thiophene, furan and pyrrole.

To investigate the relative reactivities of nitrogen-, oxygen-, and sulfur-containing aromatic heterocycles by KO*t*-Bu-catalyzed C–H silylation, two internal competition experiments were conducted using one equivalent of Et_3SiH and one equivalent of each heteroarene (Scheme 1). Reactions were run to partial consumption of Et_3SiH and relative quantities of silylated heteroarene were determined by ^1H NMR analysis. Results demonstrated that for 5-membered heteroarenes, the relative rate of reactivity trends as: thiophene **3q** > furan **3r** > 1-methylpyrrole **3x** (Scheme 1a). This trend is corroborated in the competition between substituted thiophene **3m** and furan **3n**, as shown in Scheme 1b.

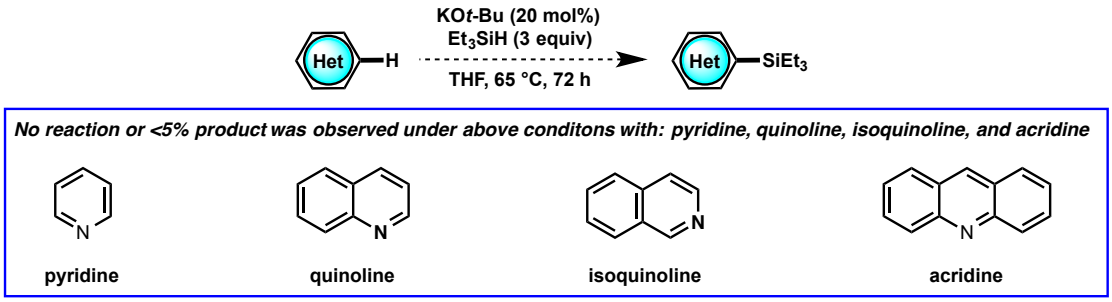


Scheme 1. Competition experiments

Procedures for competition experiments as shown in Figure 1: *For reaction (a)*: In a nitrogen-filled glove box, KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), thiophene **3q** (42.1 mg, 0.5 mmol, 1 equiv), furan **3r** (34.0 mg, 0.5 mmol, 1 equiv) and 1-methylpyrrole **3x**

(40.5 mg, 0.5 mmol, 1 equiv) were added to a 2 dram scintillation vial equipped with a magnetic stirring bar. THF (0.3 mL) and Et_3SiH (81 μL, 0.5 mmol, 1 equiv – *filtered through a short pad of activated alumina before use*) were then added. The vial was sealed and stirred at 23 °C for approximately 8 hours. The vial was removed from the glove box, diluted with diethyl ether (2 mL) and concentrated under reduced pressure. Analysis of the crude reaction mixture by ^{1}H NMR revealed that the ratio of **SI-4q**:**SI-4r**:**4x** was 5:1:0. *For reaction (b):* In a nitrogen-filled glove box, KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 2-pentylthiophene **3m** (77.0 mg, 0.5 mmol, 1 equiv), and 2-pentylfuran **3n** (69.1 mg, 0.5 mmol, 1 equiv) were added to a 2 dram scintillation vial equipped with a magnetic stirring bar. THF (0.3 mL) and Et_3SiH (81 μL, 0.5 mmol, 1 equiv – *filtered through a short pad of activated alumina before use*) were then added. The vial was sealed and stirred at 23 °C for approximately 8 hours. The vial was removed from the glove box, diluted with diethyl ether (2 mL) and concentrated under reduced pressure. Analysis of the crude reaction mixture by ^{1}H NMR revealed that the ratio of **4m**:**4n** was 5:1.

2. Reactions with electron-deficient heteroarenes.

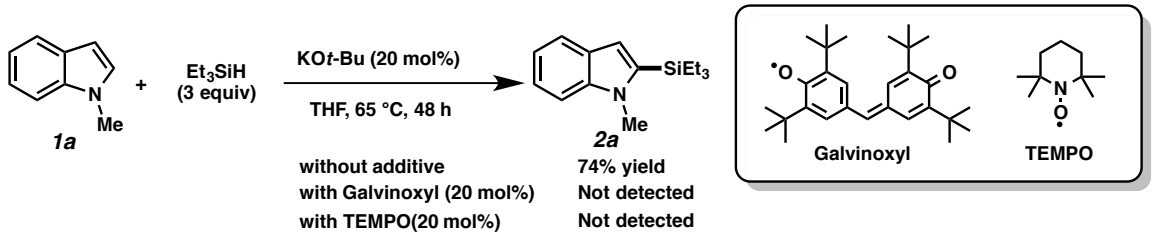


Scheme 2. Examples of unreactive pyridine derivatives

Pyridine derivatives would be expected to react readily if a conventional silyl radical addition process was operational. However, the above substrates were unreactive under the KO*t*-Bu–catalyzed C–H silylation conditions. This observation argues against the likelihood of an elementary Minisci-type mechanism and suggests that the reaction is proceeding by an alternative and presently unidentified pathway.

3. Investigation into the radical nature of the KO*t*-Bu–catalyzed C–H silylation.

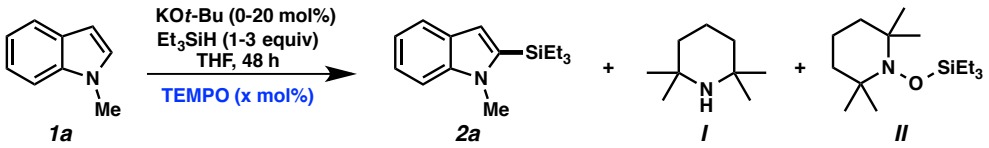
A number of experiments were conducted to gain insight into the reaction mechanism. As a first investigation, we decided to probe whether the silylation reaction was polar or radical in nature. We began by performing our reaction in the presence of the radical traps TEMPO and galvinoxyl. Both additives thwarted the C–H silylation (Scheme 3).



Scheme 3. Control reactions with radical traps

Subsequently, we conducted three control experiments in an attempt to probe the role of TEMPO (Table 3). A trace amount of triethylsilyl protected product **II** was observed at 23 °C with 1 equivalent of TEMPO (entry 5), presumably arising from the radical combination of a silyl radical and TEMPO itself. Product **II** becomes the major component of the mixture when the temperature is raised to 65 °C, lending support to the involvement of silyl radical species in the silylation reaction. In contrast, this protected compound **II** is not observed in the absence of KO*t*-Bu, indicating that the catalyst is critical to generate the silyl radical (entry 2).

Table 3. Control experimental results with TEMPO.

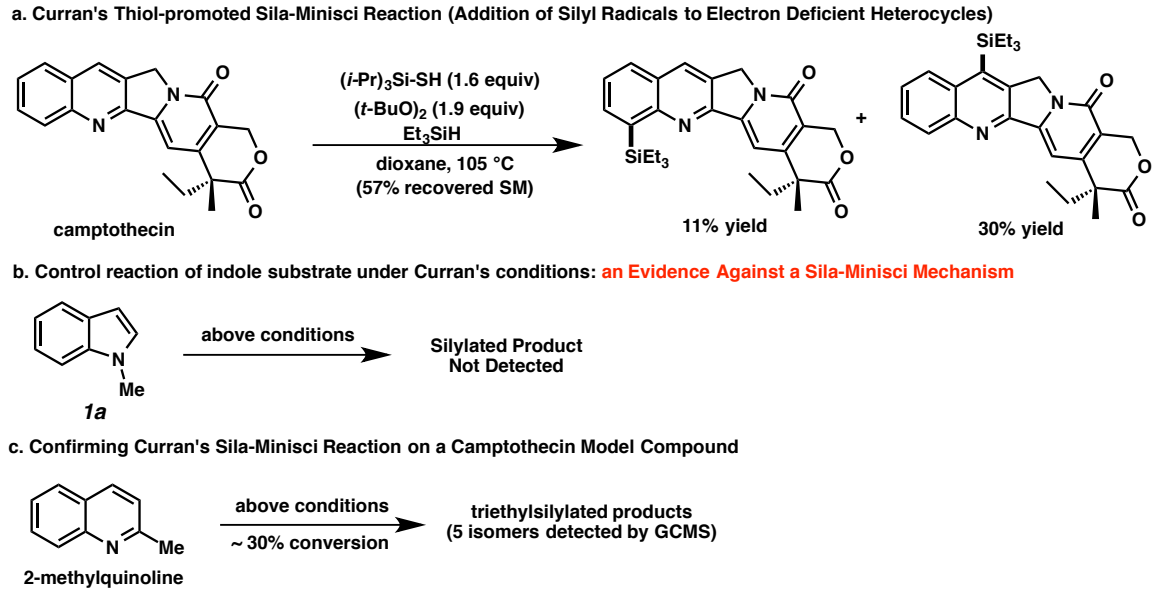


entry	*1a*	TEMPO (mol%)	KO*t*-Bu (mol%)	$HSiEt_3$ (equiv)	Temp (°C)	*2a* (%)	*I*	*II*
1	–	100	–	1	23	ND[a]	ND[a]	ND[a]
2	–	100	–	1	65	ND[a]	ND[a]	ND[a]
3	1	20	20	3	23	ND[a]	ND[a]	ND[a]
4	1	20	20	3	65	ND[a]	ND[a]	ND[a]
5	–	100	20	1	23	ND[a]	trace[b]	trace[b]
6	–	100	20	1	65	ND[a]	minor[b]	major[b]

[a] Not detected; [b] Determined by GCMS analysis.

Although we are unsure as to the mechanism of formation of the putative silyl radical, we considered that if such radical species were formed in appreciable amounts, then the

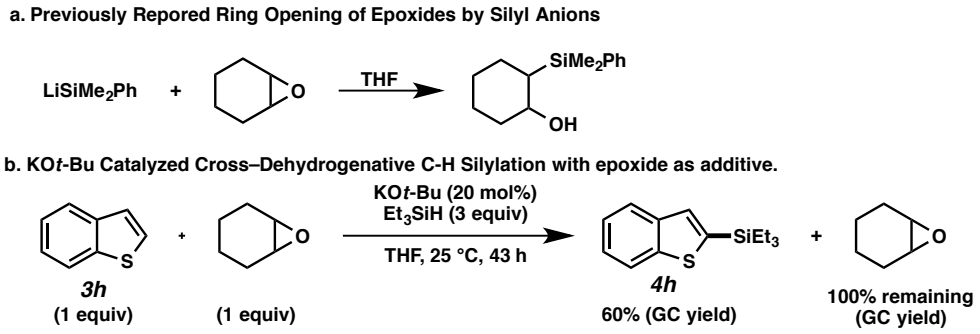
reaction could proceed by an elementary addition of a silyl radical to a heterocycle (i.e., sila-Minisci reaction). To probe this hypothesis, we subjected 1-methylindole **1a** to a mixture of reagents under conditions that are reported by the Curran group[3] to generate discrete silyl radicals (*see Scheme 4a for Curran's conditions, and Scheme 4b for the result of indole **1a** under these conditions*). Interestingly, no silylated product of any kind was detected in this reaction (Scheme 4b). Conversely, we confirmed that the Curran's conditions do silylate with electron poor heterocycles (such as 2-methyl quinoline, Scheme 4c), but our method fails in the case of these substrates (*vide supra*, Supplementary Information Part 12).



Scheme 4. Control experiments under sila-Minisci reaction conditions

To provide further evidence against a polar mechanism (i.e., formation of silyl anions), our KO*t*-Bu–catalyzed reaction with benzothiophene **3h** as a substrate was conducted in the presence of cyclohexene oxide as an additive (epoxides, including cyclohexene oxide, are known to undergo nucleophilic ring opening by silyl anions, Scheme 5a).[4] However, under our conditions, the epoxide is quantitatively recovered after the reaction, and the desired silylation product **4h** was obtained in moderate yield (Scheme 5b), providing evidence against the formation of discrete silyl anions.

(3) Du, W.; Kaskar, B.; Blumbergs, P.; Subramanian, P. K.; Curran, D. P. *Bioorg. Med. Chem.* **2003**, *11*, 451.
(4) Gilman, H.; Aoki, D.; Wittenberg, D. *J. Am. Chem. Soc*. **1959**, *81*, 1107.



Scheme 5. Control experiments with cyclohexene oxide

In summary, based on the results of control reactions with radical traps (Scheme 3) and the observation of TEMPO-$SiEt_3$ **II** (Table 3), we propose that silyl radical species appear to be involved and may be playing an important role in this catalytic C–H silylation reaction. However, based on the results from Scheme 2 and Scheme 4, an elementary radical generation/addition mechanism (i.e., sila-Minisci reaction) is likely not operative. The survival of the epoxide additive (Scheme 5) is inconsistent with the silyl anion pathway. Taken together, these preliminary studies point to a previously unreported (hetero)aromatic C–H functionalization mechanism. Efforts to elucidate the mechanism by experimental and computational methods are underway.

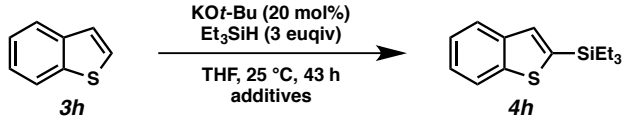
4. Evaluation of functional group compatibility.

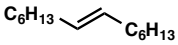
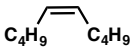
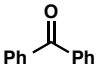
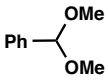
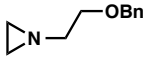
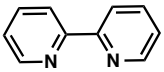
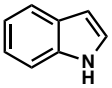
In order to provide a comprehensive treatment of functional group tolerance for the silylation reaction, a "robustness screen" as per the method of Glorius has been performed (Table 4).[5] Certain generalizations can be made from the results. For example, carbonyl groups shut down the reaction (entries 16, 17). Nevertheless, protection as an acetal, such as benzaldehyde dimethyl acetal is well tolerated (entry 18). Aryl-X groups where X = Br, I, CN, NO_2 likewise thwart the reactivity (entries 7, 8, 19 and 20). Intriguingly, these functional groups remain intact in most cases. However, alkene, alkyne, Ar-F, Ar-Cl, Ar-CF_3, tertiary amine, pyridine, and phosphine moieties are compatible (entries 2–6, 9, 11, 23–26). No obvious hydrosilylation or reduction of alkene and alkyne occurs. Even free OH and NH groups are tolerated to some extent

(5) Collins, K. D.; Glorius, F. *Nature Chem*. **2013**, *5*, 597.

presumably due to a fortuitous silylative protection of the heteroatom *in situ*, which was confirmed by using BnOTES as an additive (entries 12, 13, and 15).

Table 4. Examining of the functional groups and heterocycles compatibility.[a]



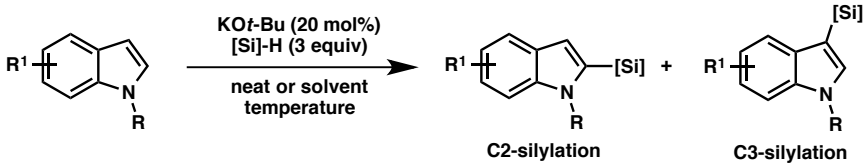
entry	additive (1.0 equiv)	*4h* yield (%)	*3h* remaining (%)	additive remaining (%)	entry	additive (1.0 equiv)	*4h* yield (%)	*3h* remaining (%)	additive remaining (%)
1[b]	_	99	0	_	14	PhOH	0	63	91
2		95	0	95	15	BnOTES	60	37	89
3		67	31	97	16		0	83	91
4		83	26	99	17	$PhCO_2Me$	0	87	84
5	PhF	95	5	N.D.[c]	18		82	0	50[f]
6	PhCl	74	25	100	19	$PhNO_2$	0	86	98
7	PhBr	0	89	100	20	PhCN	0	85	81
8	PhI	0	91	86	21		60	35	100
9	$PhCF_3$	90	10	N.D.[c]	22		40	53	100
10	$PhNMe_2$	80	20	79	23		71	28	N.D.[c]
11	*n*-Bu_3N	38	55	100	24		47	50	100
12		19	73	N.D.[c,d]	25		0	92	99
13	BnOH	31	60	0[e]	26	PPh_3	48	50	97

[a] The reaction was performed with 0.5 mmol of **3h** and 0.5 mmol of additive under the general procedure. 0.5 mmol of tridecane was added as an internal standard at the start of the reaction. Yield of product, remaining amounts of **3h** and additive were determined by GC-FID analyses. [b] Control reaction without the addition of additive. [c] Not determined (overlapped with solvent peak due to the low boiling point). [d] Triethyl silyl protected morpholine was formed and confirmed by GCMS analysis. [e] BnOTES was formed. [f] Acetal partially hydrolyzed to PhCHO.

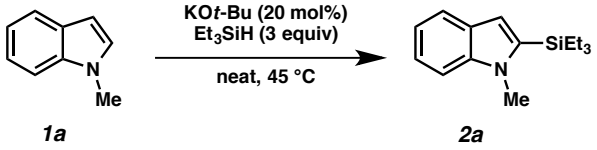
Moreover, epoxide and aziridine are tolerated as well and nucleophilic ring opening of these additives was not observed (entries 21, 22). In conclusion, these results demonstrate that a wide array of versatile organic functionalities is tolerated in the KO*t*-Bu–catalyzed silylation reaction. This is encouraging for the application of the current method to alkaloid natural product synthesis and pharmaceutical science applications either at an early stage or for advanced intermediate functionalization.

Part III. Experimental and analytics.

1. General procedure for KO*t*-Bu–catalyzed silylation and characterization data.

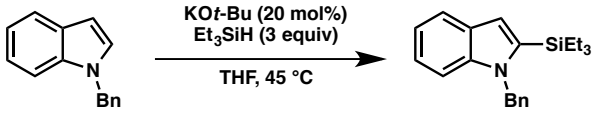


In a nitrogen-filled glove box, KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%) and indole (0.5 mmol, 1 equiv) were added to a 2 dram scintillation vial equipped with a magnetic stirring bar, [*solvent was added if indicated, see the details below*], followed by silane (1.5 mmol, 3 equiv, *filtered through a short pad of activated alumina before use*). Then the vial was sealed and the mixture was stirred at the indicated temperature for the indicated time. The vial was removed from the glove box, the reaction mixture was diluted with diethyl ether (2 mL) and concentrated under reduced pressure. The regioselectivity (C2 silylation product to C3 silylation product: C2:C3) was determined by ^{1}H NMR or GC analysis of the crude mixture. The residue was purified by silica gel flash chromatography to give the desired product.



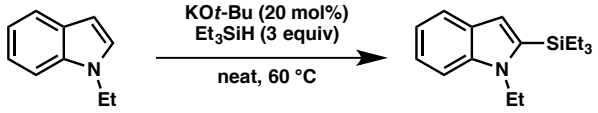
1-Methyl-2-(triethylsilyl)-1*H*-indole 2a: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-methylindole **1a** (65.5 mg, 0.5 mmol, 1 equiv) and Et_3SiH (243 μL, 1.5 mmol, 3 equiv) at 45 °C for 96 h. C2:C3 > 20:1. The desired product **2a** (95.6 mg, 78% yield) was obtained as a colorless

oil after purification by silica gel flash chromatography (gradient elution, 2→3% CH_2Cl_2 in hexanes). R_f = 0.4 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.40 (dq, *J* = 8.3, 1.0 Hz, 1H), 7.30 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.16 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H), 6.81 (d, *J* = 1.1 Hz, 1H), 3.90 (s, 3H), 1.13 – 1.05 (m, 9H), 1.03 – 0.95 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 138.3, 128.7, 122.0, 120.7, 119.1, 113.1, 109.1, 33.1, 7.7, 4.2. IR (Neat Film, NaCl) 2953, 2909, 2874, 1492, 1464, 1415, 1372, 1356, 1299, 1233, 1166, 1101, 1069, 1007, 973, 797 cm^{-1}; HRMS (ESI+) calc'd for $C_{15}H_{24}NSi$ [M+H]$^+$: 246.1673, found 246.1674.



1b *2b*

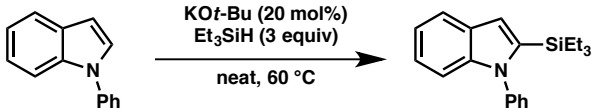
1-Benzyl-2-(triethylsilyl)-1*H*-indole 2b: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-benzylindole **1b** (103.5 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 45 °C for 40 h. C2:C3 > 20:1. The desired product **2b** (132.2 mg, 82% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (10% CH_2Cl_2 in hexanes). R_f = 0.3 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 1H), 7.38 – 7.29 (m, 3H), 7.26 – 7.19 (m, 3H), 7.02 (ddd, *J* = 6.9, 2.2, 1.0 Hz, 2H), 6.97 (s, 1H), 5.59 (s, 2H), 1.08 – 1.04 (m, 9H), 0.94 – 0.89 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 138.5, 138.3, 129.1, 128.7, 127.3, 125.9, 122.3, 120.7, 119.5, 114.1, 110.2, 50.2, 7.5, 4.0. IR (Neat Film, NaCl) 3060, 3029, 2954, 2909, 2875, 1606, 1495, 1466, 1452, 1416, 1377, 1353, 1333, 1300, 1238, 1196, 1164, 1115, 1096, 1014, 798, 734 cm^{-1}; HRMS (ESI+) calc'd for $C_{21}H_{28}NSi$ [M+H]$^+$: 322.1986, found 322.1985.



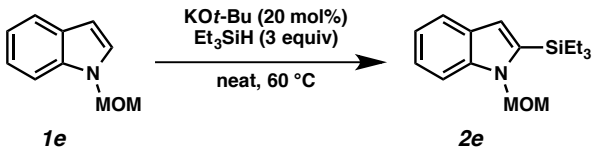
1c *2c*

1-Ethyl-2-(triethylsilyl)-1*H*-indole 2c: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-ethylindole **1c** (72.5 mg, 0.5 mmol, 1 equiv), and Et_3SiH (243 μL, 1.5 mmol, 3 equiv) at 60 °C for 84 h.

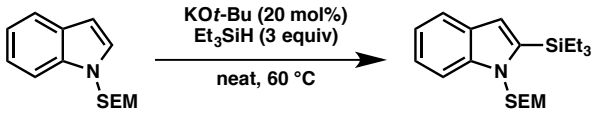
C2:C3 > 20:1. The desired product **2c** (92.4 mg, 71% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (5% CH_2Cl_2 in hexanes). R_f = 0.4 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.40 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.25 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.13 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1H), 6.75 (d, *J* = 1.0 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.08 – 1.04 (m, 9H), 0.99 – 0.92 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 137.4, 129.1, 121.7, 120.7, 119.0, 113.0, 109.4, 41.5, 15.5, 7.5, 4.0. IR (Neat Film, NaCl) 2953, 2909, 2874, 1491, 1466, 1416, 1378, 1347, 1335, 1299, 1218, 1165, 1090, 1069, 1012, 956, 900, 820, 787, 773, 750, 733 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{16}H_{26}NSi$ $[M+H]^+$: 260.1829, found 260.1829.



1-Phenyl-2-(triethylsilyl)-1*H*-indole 2d: The general procedure was followed. The reaction was performed with KO*t*-Bu (7.4 mg, 0.07 mmol, 20 mol%), *N*-phenylindole **1d** (63.2 mg, 0.33 mmol, 1 equiv), and Et_3SiH (160 μL, 1.0 mmol, 3 equiv) at 60 °C for 84 h. C2:C3 > 20:1. The desired product **2d** (45.6 mg, 45% yield) was obtained as a white solid after purification by silica gel flash chromatography (3% CH_2Cl_2 in hexanes). R_f = 0.5 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 1H), 7.58 – 7.47 (m, 3H), 7.44 – 7.36 (m, 2H), 7.21 – 7.12 (m, 2H), 7.12 – 7.05 (m, 1H), 6.93 (d, *J* = 0.9 Hz, 1H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.68 – 0.55 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.6, 140.8, 139.1, 129.2, 128.8, 128.7, 128.3, 122.4, 120.5, 119.8, 114.9, 110.5, 7.5, 4.0. IR (Neat Film, NaCl) 3058, 2952, 2909, 2873, 1597, 1498, 1465, 1428, 1362, 1297, 1237, 1214, 1122, 1071, 1012, 976, 922, 820, 793, 736 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{20}H_{26}NSi$ $[M+H]^+$: 308.1829, found 308.1824.

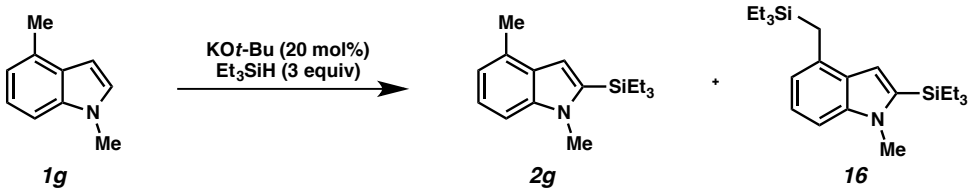


1-(Methoxymethyl)-2-(triethylsilyl)-1*H*-indole 2e: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-methoxymethylindole **1e** (80.5 mg, 0.5 mmol, 1 equiv) and Et_3SiH (243 μL, 1.5 mmol, 3 equiv) at 60 °C for 84 h. C2:C3 = 10:1. The desired product **2e** (75.1 mg, 55% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (3% EtOAc in hexanes). R_f = 0.3 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.53 (dq, *J* = 8.3, 0.9 Hz, 1H), 7.28 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.17 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1H), 6.86 (d, *J* = 0.9 Hz, 1H), 5.55 (s, 2H), 3.30 (s, 3H), 1.10 – 1.01 (m, 9H), 1.01 – 0.92 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 138.3, 129.2, 122.6, 120.8, 120.0, 115.6, 109.8, 76.8, 55.6, 7.5, 4.1. IR (Neat Film, NaCl) 2952, 2908, 2874, 1495, 1466, 1416, 1393, 1344, 1311, 1299, 1224, 1166, 1126, 1104, 1091, 1045, 1004, 961, 913, 797, 762, 735 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{16}H_{26}NOSi$ $[M+H]^+$: 276.1778, found 276.1769.



1f *2f*

2-(Triethylsilyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indole 2f: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-(2-trimethylsilyl-ethoxymethyl)-1*H*-indole **1f** (123.5 mg, 0.5 mmol, 1 equiv) and Et_3SiH (243 μL, 1.5 mmol, 3 equiv) at 60 °C for 84 h. C2:C3 > 20:1. The desired product **2f** (121.4 mg, 67% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (15% CH_2Cl_2 in hexanes). R_f = 0.2 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.50 (dq, *J* = 8.3, 0.9 Hz, 1H), 7.24 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.12 (ddd, *J* = 7.9, 7.0, 0.9 Hz, 1H), 6.80 (d, *J* = 0.9 Hz, 1H), 5.54 (s, 2H), 3.54 – 3.48 (m, 2H), 1.04 – 0.98 (m, 9H), 0.96 – 0.90 (m, 8H), -0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 138.1, 129.1, 122.4, 120.7, 119.9, 115.3, 109.8, 75.2, 65.6, 18.1, 7.6, 4.0, -1.3. IR (Neat Film, NaCl) 2952, 2875, 1495, 1466, 1443, 1417, 1378, 1343, 1312, 1299, 1249, 1167, 1081, 1003, 972, 939, 894, 859, 836, 796, 760, 749, 734 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{20}H_{36}NOSi_2$ $[M+H]^+$: 362.2330, found 362.2340.



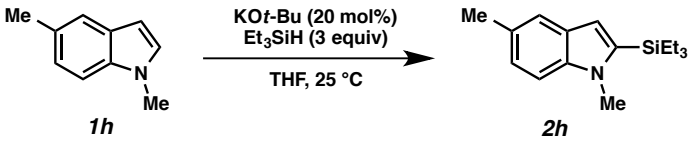
condition A: THF, 25 °C, 120 h:	48%	5%
condition B: neat, 45 °C, 84 h:	69%	–

The general procedure was followed. *For condition A*: The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 4-methyl-*N*-methylindole **1g** (72.5 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 25 °C for 120 h. C2:C3 > 20:1. The desired mono-silylation product **2g** (61.8 mg, 48% yield) and bis-silylation **16** (9.7 mg, 5% yield) were obtained after purification by silica gel flash chromatography (gradient elution, 2→3% CH_2Cl_2 in hexanes). *For condition B*: The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 4-methyl-*N*-methylindole **1g** (72.5 mg, 0.5 mmol, 1 equiv) and Et_3SiH (243 μL, 1.5 mmol, 3 equiv) at 45 °C for 84 h. C2:C3 > 20:1. Only mono silylation product **2g** (89.7 mg, 69% yield) was formed and obtained after purification by silica gel flash chromatography (3% CH_2Cl_2 in hexanes).

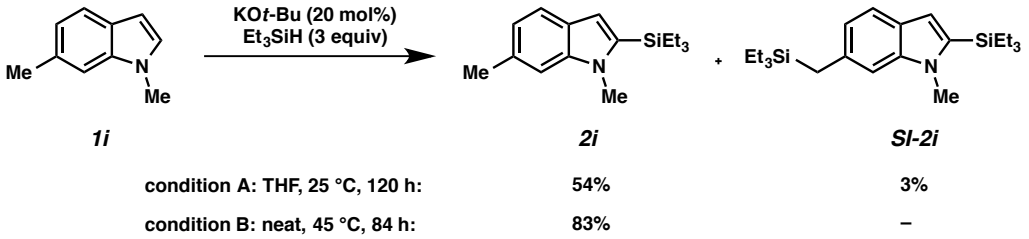
1,4-Dimethyl-2-(triethylsilyl)-1*H*-indole 2g: Colorless oil; R_f = 0.4 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.14 (m, 2H), 6.91 (dt, *J* = 6.7, 1.0 Hz, 1H), 6.75 (d, *J* = 0.9 Hz, 1H), 3.85 (s, 3H), 2.60 (s, 3H), 1.07 – 1.00 (m, 9H), 0.98 – 0.92 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 137.6, 130.2, 128.6, 122.2, 119.4, 111.5, 106.8, 33.2, 18.8, 7.7, 4.3. IR (Neat Film, NaCl) 2953, 2910, 2874, 1586, 1502, 1454, 1415, 1366, 1323, 1280, 1238, 1160, 1140, 1077, 1004, 953, 765, 752, 735 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{16}H_{26}NSi$ $[M+H]^+$: 260.1829, found 260.1823.

1-Methyl-2-(triethylsilyl)-4-((triethylsilyl)methyl)-1*H*-indole 16: Colorless oil; R_f = 0.4 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, C_6D_6) δ 7.28 (dd, *J* = 8.2, 7.1 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.97 – 6.94 (m, 2H), 3.31 (s, 3H), 2.50 (s, 2H), 1.01 (t, *J* = 7.8 Hz, 9H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.83 (q, *J* = 7.8 Hz, 6H), 0.58 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 141.1, 136.0, 133.3, 122.8, 118.9, 113.0, 105.8, 32.9, 19.2, 7.7, 4.5, 4.1. IR (Neat Film, NaCl) 2952, 2909, 2874, 1579, 1498, 1454, 1443, 1414,

1359, 1322, 1285, 1237, 1151, 1070, 1008, 980, 774, 734 cm^{-1}; HRMS (EI+) calc'd for $C_{22}H_{39}NSi_2$ [$M^{\bullet+}$]: 373.2621, found 373.2624.



1,5-Dimethyl-2-(triethylsilyl)-1*H*-indole 2h: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 5-methyl-*N*-methylindole **1h** (72.5 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 25 °C for 96 h. C2:C3 > 20:1. The desired product **2h** (88.7 mg, 68% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (10% CH_2Cl_2 in hexanes). R_f = 0.3 (10% CH_2Cl_2 in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.25 – 7.19 (m, 1H), 7.05 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.63 (d, *J* = 0.8 Hz, 1H), 3.81 (s, 3H), 2.45 (s, 3H), 1.03 – 0.97 (m, 9H), 0.93 – 0.86 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.3, 128.9, 128.3, 123.6, 120.2, 112.4, 108.8, 33.1, 21.5, 7.7, 4.1. IR (Neat Film, NaCl) 2952, 2909, 2873, 1505, 1456, 1358, 1321, 1236, 1181, 1104, 1069, 1003, 833, 788, 736 cm^{-1}; HRMS (ESI+) calc'd for $C_{16}H_{26}NSi$ $[M+H]^+$: 260.1826, found 260.1827.

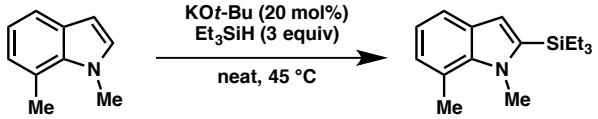


The general procedure was followed. *For condition A*: The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 6-methyl-*N*-methylindole **1i** (72.5 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 25 °C for 120 h. C2:C3 > 20:1. The desired mono silylation product **2i** (69.5 mg, 54% yield) and bis-silylation **SI-2i** (5.2 mg, 3% yield) were obtained after purification by silica gel flash chromatography (gradient elution, 2→3% CH_2Cl_2 in hexanes). *For condition B*: The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 6-methyl-*N*-methylindole **1i** (72.5 mg, 0.5 mmol, 1 equiv) and Et_3SiH (243 μL, 1.5 mmol, 3 equiv) at

45 °C for 84 h. C2:C3 > 20:1. Only mono silylation product **2i** (108.1 mg, 83% yield) was formed and obtained after purification by silica gel flash chromatography (3% CH_2Cl_2 in hexanes).

1,6-Dimethyl-2-(triethylsilyl)-1*H*-indole 2i: Colorless oil; R_f = 0.4 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.18 (s, 1H), 6.98 (ddd, *J* = 8.0, 1.4, 0.7 Hz, 1H), 6.73 (d, *J* = 0.9 Hz, 1H), 3.85 (s, 3H), 2.57 (s, 3H), 1.08 – 1.03 (m, 9H), 0.98 – 0.92 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9, 137.6, 131.8, 126.7, 121.0, 120.3, 113.0, 109.1, 33.0, 22.0, 7.6, 4.2. IR (Neat Film, NaCl) 2953, 2910, 2874, 1617, 1480, 1451, 1413, 1376, 1360, 1333, 1296, 1233, 1065, 1003, 941, 808, 781, 736 cm^{-1}; HRMS (ESI+) calc'd for $C_{16}H_{26}NSi$ $[M+H]^+$: 260.1826, found 260.1823.

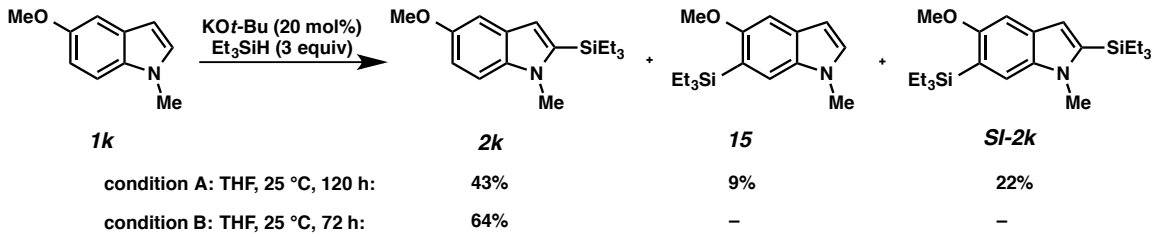
1-Methyl-2-(triethylsilyl)-6-((triethylsilyl)methyl)-1*H*-indole SI-2i: Colorless oil; R_f = 0.4 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, C_6D_6) δ 7.64 (dd, *J* = 7.9, 0.8 Hz, 1H), 6.99 – 6.93 (m, 2H), 6.81 (d, *J* = 0.9 Hz, 1H), 3.41 (s, 3H), 2.31 (s, 2H), 1.02 – 0.93 (m, 18H), 0.79 (q, *J* = 7.7 Hz, 6H), 0.58 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 141.9, 136.3, 134.6, 126.7, 121.2, 120.9, 114.0, 108.3, 32.7, 22.4, 7.8, 7.7, 4.5, 3.7. IR (Neat Film, NaCl) 2952, 2909, 2874, 1615, 1568, 1479, 1463, 1414, 1361, 1336, 1319, 1299, 1234, 1195, 1157, 1090, 1065, 1009, 948, 842, 817, 787, 771, 736 cm^{-1}; HRMS (EI+) calc'd for $C_{22}H_{39}NSi_2$ $[M^{\bullet+}]$: 373.2621, found 373.2609.



1j *2j*

1,7-Dimethyl-2-(triethylsilyl)-1*H*-indole 2j: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 7-methyl-*N*-methylindole **1j** (72.5 mg, 0.5 mmol, 1 equiv) and Et_3SiH (243 μL, 1.5 mmol, 3 equiv) at 45 °C for 84 h. C2:C3 > 20:1. The desired product **2j** (78.9 mg, 61% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (3% CH_2Cl_2 in hexanes). R_f = 0.4 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.7 Hz, 1H), 6.94 – 6.87 (m, 2H), 6.66 (s, 1H), 4.11 (s, 3H), 2.80 (s, 3H), 1.03 – 0.97 (m, 9H), 0.92 – 0.85 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 139.1, 129.7, 125.0, 121.0, 119.4, 119.0, 113.6, 36.8, 20.6, 7.7, 4.2. IR (Neat Film, NaCl) 2953,

2909, 2873, 1503, 1459, 1415, 1396, 1377, 1358, 1340, 1315, 1304, 1238, 1156, 1113, 1086, 1063, 1004, 861, 798, 742 cm^{-1}; HRMS (ESI+) calc'd for $C_{16}H_{26}NSi$ $[M+H]^+$: 260.1826, found 260.1828.



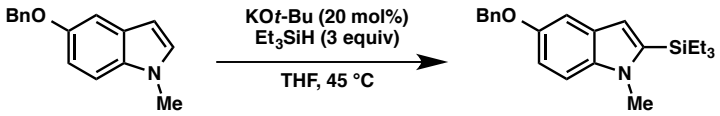
The general procedure was followed. *For condition A*: The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-methyl-5-methoxyindole **1k** (80.7 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 25 °C for 120 h. C2:C3 > 20:1. The C2-silylation product **2k** (58.7 mg, 43% yield), C6-silylation product **15** (12.5 mg, 9% yield), and bis-silylation product **SI-2k** (42.9 mg, 22% yield), were obtained after purification by silica gel flash chromatography (gradient elution, 5→10→25% CH_2Cl_2 in hexanes). *For condition B*: The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-methyl-5-methoxyindole **1k** (80.5 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 25 °C for 72 h. C2:C3 > 20:1. The desired product **2k** (87.6 mg, 64% yield) was obtained after purification by silica gel flash chromatography (gradient elution, 5→10→25% CH_2Cl_2 in hexanes) and a minor amount (<5%) of byproducts were observed.

5-Methoxy-1-methyl-2-(triethylsilyl)-1*H*-indole 2k: White solid; R_f = 0.2 (33% CH_2Cl_2 in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.21 (s, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.63 (d, *J* = 0.8 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 1.03 – 0.96 (m, 9H), 0.93 – 0.86 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.0, 139.0, 135.9, 128.8, 112.6, 112.3, 109.8, 102.0, 56.1, 33.2, 7.7, 4.1. IR (Neat Film, NaCl) 2950, 2909, 2872, 1503, 1450, 1413, 1334, 1237, 1208, 1173, 1147, 1102, 1072, 1027, 997, 843, 801, 735, 716 cm^{-1}; HRMS (ESI+) calc'd for $C_{16}H_{26}NOSi$ $[M+H]^+$: 276.1778, found 276.1776.

5-Methoxy-1-methyl-2,6-bis(triethylsilyl)-1*H*-indole SI-2k: White solid, R_f = 0.6 (33% CH_2Cl_2 in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (s, 1H), 7.01 (s, 1H), 6.64 (d, *J* = 0.8 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 1.06 – 0.97 (m, 18H), 0.95 – 0.86 (m, 12H); ^{13}C

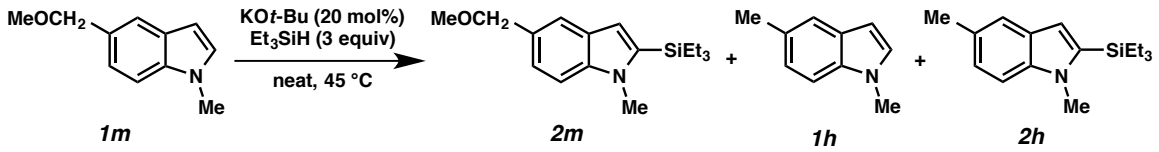
NMR (125 MHz, $CDCl_3$) δ 159.1, 138.9, 136.1, 130.1, 120.8, 116.3, 112.2, 99.7, 55.5, 33.2, 7.9, 7.7, 4.3, 4.1. IR (Neat Film, NaCl) 2952, 2874, 2908, 1608, 1556, 1475, 1454, 1407, 1363, 1337, 1236, 1205, 1172, 1144, 1123, 1072, 1004, 971, 837 cm^{-1}; HRMS (ESI+) calc'd for $C_{22}H_{40}NOSi_2$ $[M+H]^+$: 390.2643, found 390.2632.

5-Methoxy-1-methyl-6-(triethylsilyl)-1*H*-indole 15: Colorless oil; R_f = 0.4 (33% CH_2Cl_2 in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.01 (s, 1H), 7.00 (d, *J* = 3.0 Hz, 1H), 6.38 (dd, *J* = 3.0, 0.8 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 1.00 – 0.94 (m, 9H), 0.91 – 0.83 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 132.5, 130.1, 129.3, 120.2, 116.5, 100.4, 100.3, 55.5, 33.0, 7.9, 4.1. IR (Neat Film, NaCl) 2950, 2908, 2873, 1612, 1554, 1505, 1471, 1414, 1310, 1268, 1231, 1190, 1148, 1123, 1059, 1017, 984, 831 cm^{-1}; HRMS (ESI+) calc'd for $C_{16}H_{26}NOSi$ $[M+H]^+$: 276.1778, found 276.1765.



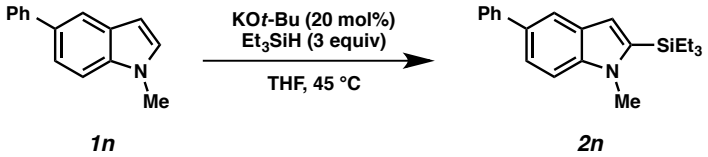
1l *2l*

5-(Benzyloxy)-1-methyl-2-(triethylsilyl)-1*H*-indole 2l: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-methyl-5-benzyloxyindole **1l** (118.5 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 45 °C for 64 h. C2:C3 > 20:1. The desired product **2l** (119.4 mg, 68% yield) was obtained as a yellow solid after purification by silica gel flash chromatography (25% CH_2Cl_2 in hexanes). R_f = 0.4 (5% EtOAc in hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.0 Hz, 2H), 7.41 – 7.36 (m, 2H), 7.35 – 7.29 (m, 1H), 7.22 (d, *J* = 8.9 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 6.97 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.62 (d, *J* = 0.8 Hz, 1H), 5.11 (s, 2H), 3.81 (s, 3H), 1.04 – 0.96 (m, 9H), 0.96 – 0.84 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 139.1, 138.1, 136.2, 129.0, 128.6, 127.8, 127.6, 113.4, 112.5, 109.8, 104.0, 71.3, 33.2, 7.6, 4.2. IR (Neat Film, NaCl) 2951, 2908, 2872, 1492, 1452, 1422, 1336, 1288, 1237, 1192, 1150, 1102, 1075, 1018, 840, 812, 751, 735 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{22}H_{30}NOSi$ $[M+H]^+$: 352.2091, found 352.2093.



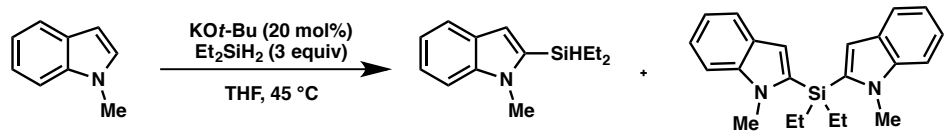
The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 5-(methoxymethyl)-*N*-methylindole **1m** (87.5 mg, 0.5 mmol, 1 equiv) and Et_3SiH (243 μL, 1.5 mmol, 3 equiv) at 45 °C for 84 h. C2:C3 > 20:1. The desired product **2m** (69.3 mg, 48% yield), byproducts **1h** (2.5 mg, 2% yield) and **2h** (11.3 mg, 9% yield) were obtained after purification by silica gel flash chromatography (gradient elution, 25→50% CH_2Cl_2 in hexanes).

5-(Methoxymethyl)-1-methyl-2-(triethylsilyl)-1*H*-indole 2m: Colorless oil, R_f = 0.4 (50% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 0.8 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 0.8 Hz, 1H), 4.59 (s, 2H), 3.85 (s, 3H), 3.38 (s, 3H), 1.06 – 0.99 (m, 9H), 0.96 – 0.90 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0, 138.9, 128.8, 128.5, 122.6, 120.5, 113.0, 109.1, 75.6, 57.6, 33.2, 7.6, 4.1. IR (Neat Film, NaCl) 2952, 2873, 2817, 1504, 1455, 1415, 1357, 1324, 1297, 1236, 1188, 1153, 1137, 1094, 1069, 1004, 971, 878, 840, 798, 783, 726 cm^{-1}; HRMS (ESI+) calc'd for $C_{17}H_{28}NOSi$ $[M+H]^+$: 290.1935, found 290.1948.



1-Methyl-5-phenyl-2-(triethylsilyl)-1*H*-indole 2n: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 5-phenyl-*N*-methylindole **1n** (103.5 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 45 °C for 108 h. C2:C3 > 20:1. The desired product **2n** (77.8 mg, 48% yield) was obtained as a white solid after purification by silica gel flash chromatography (gradient elution, 5→10% CH_2Cl_2 in hexanes). R_f = 0.3 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 6.85 (s, 1H), 3.91 (s, 3H), 1.09 (t, *J* = 7.8 Hz, 9H), 1.03 – 0.95 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 140.0, 139.3, 132.8, 129.2, 128.7, 127.5, 126.3, 122.0, 119.2,

113.5, 109.4, 33.2, 7.6, 4.2. IR (Neat Film, NaCl) 2950, 2908, 2873, 1600, 1485, 1455, 1361, 1325, 1301, 1214, 1162, 1074, 1004, 1086, 887, 820, 807, 787, 759, 733 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{21}H_{28}NSi$ $[M+H]^+$: 322.1986, found 322.1984.

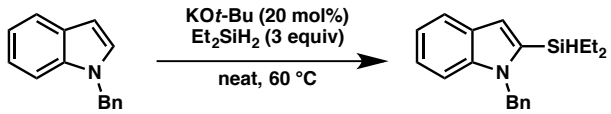


1a ***2o*** ***SI-2o***

The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-methylindole **1a** (65.5 mg, 0.5 mmol, 1 equiv), Et_2SiH_2 (194 µL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 45 °C for 72 h. C2:C3 > 20:1. The silylation product **2o** (73.4 mg, 68% yield) and a minor bisindolyl silane byproduct **SI-2o** were obtained after purification by silica gel flash chromatography (gradient elution, 1→2→5% CH_2Cl_2 in hexanes).

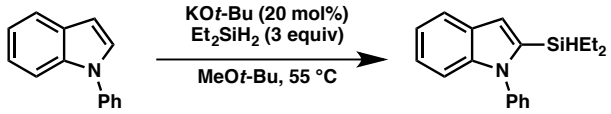
2-(Diethylsilyl)-1-methyl-1*H*-indole 2o: Colorless oil; R_f = 0.4 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.37 (dt, *J* = 8.3, 1.1 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.16 – 7.09 (m, 1H), 6.79 (d, *J* = 0.9 Hz, 1H), 4.50 – 4.43 (m, 1H), 3.88 (s, 3H), 1.14 – 1.06 (m, 6H), 1.00 – 0.93 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 136.6, 128.6, 122.2, 120.8, 119.3, 112.8, 109.3, 32.8, 8.4, 3.7. IR (Neat Film, NaCl) 2954, 2908, 2872, 2110, 1492, 1464, 1412, 1371, 1357, 1327, 1301, 1233, 1166, 1101, 1071, 1009, 974, 987, 815, 785 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{13}H_{20}NSi$ $[M+H]^+$: 218.1360, found 218.1354.

Diethylbis(1-methyl-1*H*-indol-2-yl)silane SI-2o: Colorless oil; R_f = 0.2 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dt, *J* = 7.9, 1.0 Hz, 2H), 7.31 (dt, *J* = 8.3, 1.0 Hz, 2H), 7.25 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 2H), 7.13 (ddd, *J* = 7.9, 6.9, 1.1 Hz, 2H), 6.92 (d, *J* = 0.9 Hz, 2H), 3.57 (s, 6H), 1.31 (q, *J* = 8.4 Hz, 4H), 1.07 (t, *J* = 7.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 136.5, 128.7, 122.5, 120.9, 119.4, 113.8, 109.4, 32.7, 7.5, 4.5. IR (Neat Film, NaCl) 2955, 2874, 1492, 1463, 1414, 1355, 1327, 1299, 1233, 1166, 1101, 1072, 1008, 799, 751 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{22}H_{27}N_2Si$ $[M+H]^+$: 347.1938, found 347.1934.



1b *2p*

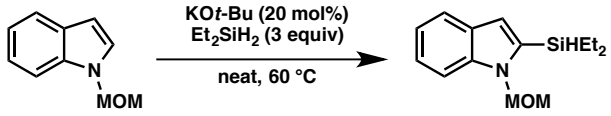
1-Benzyl-2-(diethylsilyl)-1*H*-indole 2p: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-benzyl indole **1b** (103.5 mg, 0.5 mmol, 1 equiv) and Et_2SiH_2 (194 μL, 1.5 mmol, 3 equiv) at 60 °C for 72 h. C2:C3 > 20:1. The desired product **2p** (114.1 mg, 78% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (5% CH_2Cl_2 in hexanes). R_f = 0.5 (25% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.36 – 7.26 (m, 4H), 7.26 – 7.15 (m, 2H), 7.07 – 7.01 (m, 2H), 6.94 (d, *J* = 0.9 Hz, 1H), 5.56 (s, 2H), 4.44 (p, *J* = 3.3 Hz, 1H), 1.12 – 1.03 (m, 6H), 0.94 – 0.79 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 138.5, 136.7, 129.0, 128.7, 127.4, 126.1, 122.5, 120.8, 119.6, 113.7, 110.1, 49.8, 8.3, 3.6. IR (Neat Film, NaCl) 2954, 2873, 2114, 1605, 1494, 1466, 1450, 1413, 1353, 1334, 1301, 1233, 1198, 1164, 1116, 1095, 972, 815 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{19}H_{24}NSi$ $[M+H]^+$: 294.1673, found 294.1668.



1d *2q*

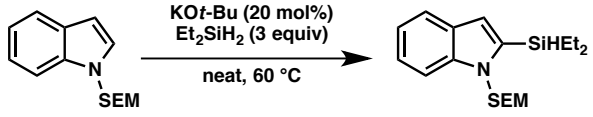
2-(Diethylsilyl)-1-phenyl-1*H*-indole 2q: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-phenyl indole **1d** (96.5 mg, 0.5 mmol, 1 equiv), Et_2SiH_2 (194 μL, 1.5 mmol, 3 equiv), and 0.5 mL of MeO*t*-Bu at 55 °C for 96 h. C2:C3 > 20:1. The desired product **2q** (76.9 mg, 55% yield) was obtained as a yellow oil after purification by silica gel flash chromatography (10% CH_2Cl_2 in hexanes). R_f = 0.6 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.74 (m, 1H), 7.60 – 7.55 (m, 2H), 7.53 – 7.47 (m, 3H), 7.30 – 7.17 (m, 3H), 7.03 (d, *J* = 0.9 Hz, 1H), 4.30 (p, *J* = 3.3 Hz, 1H), 1.02 – 0.98 (m, 6H), 0.79 – 0.63 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 140.3, 137.1, 129.4, 128.8, 128.1, 128.0, 122.8, 120.7, 120.1, 115.1, 110.5, 8.2, 3.4. IR (Neat Film, NaCl) 3058, 2953, 2872, 2117, 1597, 1498, 1466, 1433, 1415, 1363, 1300, 1215, 1202, 1146, 1121, 1072, 1013, 978, 921, 902,

823, 759, 748, 737 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{18}H_{22}NSi$ $[M+H]^+$: 280.1516, found 280.1515.



1e *2r*

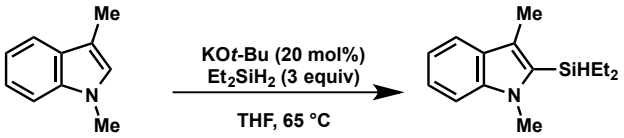
2-(Diethylsilyl)-1-(methoxymethyl)-1*H*-indole 2r: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-methoxymethylindole **1e** (80.5 mg, 0.5 mmol, 1 equiv) and Et_2SiH_2 (193 μL, 1.5 mmol, 3 equiv) at 60 °C for 96 h. C2:C3 > 20:1. The desired product **2r** (81.0 mg, 66% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (3% EtOAc in hexanes). R_f = 0.3 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.54 (ddd, *J* = 8.3, 2.0, 0.9 Hz, 1H), 7.29 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.18 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1H), 6.88 (d, *J* = 0.9 Hz, 1H), 5.60 (s, 2H), 4.49 (p, *J* = 3.3 Hz, 1H), 3.29 (s, 3H), 1.14 – 1.08 (m, 6H), 1.03 – 0.94 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 136.6, 129.2, 122.8, 120.9, 120.2, 115.1, 109.9, 76.6, 55.6, 8.3, 3.8. IR (Neat Film, NaCl) 2954, 2874, 2819, 2115, 1496, 1467, 1443, 1413, 1393, 1360, 1344, 1314, 1300, 1282, 1226, 1190, 1166, 1127, 1102, 1091, 1047, 1009, 974, 914, 896, 818, 749, 736 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{14}H_{22}NOSi$ $[M+H]^+$: 248.1465, found 248.1459.



1f *2s*

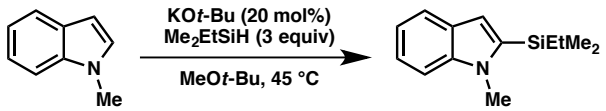
2-(Diethylsilyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indole 2s: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-(2-trimethylsilyl-ethoxymethyl)-1*H*-indole **1f** (123.5 mg, 0.5 mmol, 1 equiv) and Et_2SiH_2 (194 μL, 1.5 mmol, 3 equiv) at 60 °C for 84 h. C2:C3 > 20:1. The desired product **2s** (106.7 mg, 64% yield) was obtained after purification by silica gel flash chromatography (14% CH_2Cl_2 in hexanes) as a colorless oil. R_f = 0.2 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.53 (dt, *J* =

8.3, 0.9 Hz, 1H), 7.27 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.15 (ddd, *J* = 7.9, 7.0, 0.9 Hz, 1H), 6.84 (d, *J* = 0.8 Hz, 1H), 5.61 (s, 2H), 4.48 (p, *J* = 3.3 Hz, 1H), 3.55 – 3.48 (m, 2H), 1.14 – 1.04 (m, 6H), 1.03 – 0.88 (m, 6H), -0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 136.5, 129.1, 122.7, 120.8, 120.1, 114.7, 110.1, 75.0, 65.6, 18.0, 8.4, 3.7, -1.3. IR (Neat Film, NaCl) 2953, 2874, 2116, 1496, 1466, 1443, 1413, 1379, 1343, 1318, 1300, 1249, 1219, 1165, 1081, 1010, 974, 922, 895, 859, 835, 748, 735 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{18}H_{32}NOSi_2$ $[M+H]^+$: 334.2017, found 334.2028.



1t *2t*

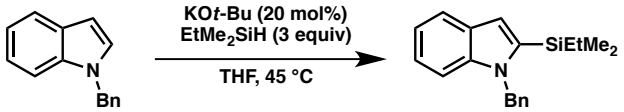
2-(Diethylsilyl)-1,3-dimethyl-1*H*-indole 2t: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 1,3-dimethyl-1*H*-indole **1t** (72.6 mg, 0.5 mmol, 1 equiv), Et_2SiH_2 (193 µL , 1.5 mmol, 3 equiv), and 0.5 mL of THF at 65 °C for 120 h. The desired product **2t** (84.2 mg, 65% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (100% hexanes). R_f = 0.6 (100% hexanes); ^{1}H NMR (500 MHz, C_6D_6) δ 7.67 (d, *J* = 7.9 Hz, 1H), 7.30 (dd, *J* = 8.3, 6.9 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 4.59 (p, *J* = 3.7 Hz, 1H), 3.31 (s, 3H), 2.46 (s, 3H), 0.98 (t, *J* = 7.8 Hz, 6H), 0.77 (qd, *J* = 7.9, 3.9 Hz, 4H); ^{13}C NMR (125 MHz, C_6D_6) δ 140.6, 131.5, 129.8, 122.7, 122.3, 119.4, 119.0, 109.4, 32.4, 10.9, 8.8, 4.7. IR (Neat Film, NaCl) 2952, 2871, 2125, 1509, 1460, 1351, 1317, 1237, 1167, 1138, 1011, 975, 839, 803, 737 cm^{-1}; HRMS (EI+) calc'd for $C_{14}H_{21}NSi$ $[M^{\bullet+}]$: 231.1443, found 231.1446.



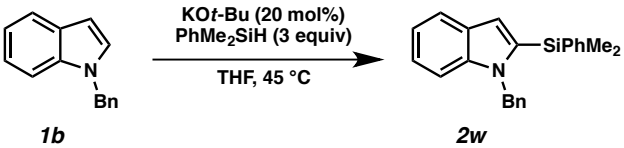
1a *2u*

2-(Ethyldimethylsilyl)-1-methyl-1*H*-indole 2u: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-methylindole **1a** (66.8 mg, 0.5 mmol, 1 equiv), $EtMe_2SiH$ (197 µL, 1.5 mmol, 3 equiv) and 0.5 mL of MeO*t*-Bu at 45 °C for 120 h. C2:C3 > 20:1. The desired product **2u** (58.5

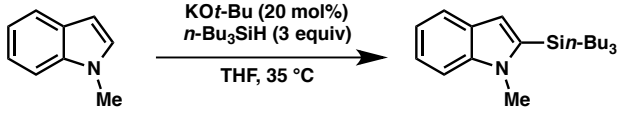
mg, 54% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (3% CH_2Cl_2 in hexanes). R_f = 0.4 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.37 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.28 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.14 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H), 6.77 (d, *J* = 0.9 Hz, 1H), 3.89 (s, 3H), 1.11 – 1.02 (m, 3H), 0.95 – 0.90 (m, 2H), 0.43 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3, 140.2, 128.5, 122.1, 120.7, 119.2, 112.0, 109.1, 33.1, 7.8, 7.6, -2.6. IR (Neat Film, NaCl) 2954, 2908, 2873, 1492, 1464, 1418, 1356, 1326, 1300, 1249, 1233, 1166, 1131, 1101, 1071, 1007, 958, 897, 821 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{13}H_{20}NSi$ $[M+H]^+$: 218.1360, found 218.1353.



1-Benzyl-2-(ethyldimethylsilyl)-1*H*-indole 2v: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-benzylindole **1b** (102.5 mg, 0.5 mmol, 1 equiv), $EtMe_2SiH$ (197 μL, 1.5 mmol, 3 equiv) and 0.5 mL of THF at 45 °C for 96 h. C2:C3 > 20:1. The desired product **2v** (87.9 mg, 60% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (10% CH_2Cl_2 in hexanes). R_f = 0.3 (10% CH_2Cl_2 in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 1H), 7.34 – 7.23 (m, 3H), 7.23 – 7.11 (m, 3H), 6.96 (ddd, *J* = 6.8, 2.2, 1.2 Hz, 2H), 6.88 (s, 1H), 5.54 (s, 2H), 1.00 (t, *J* = 7.9 Hz, 3H), 0.79 (q, *J* = 7.8 Hz, 2H), 0.32 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 140.1, 138.4, 128.9, 128.7, 127.3, 125.9, 122.4, 120.8, 119.6, 112.9, 110.1, 50.1, 7.8, 7.5, -2.6. IR (Neat Film, NaCl) 3060, 3028, 2954, 2910, 2873, 1605, 1495, 1466, 1450, 1377, 1353, 1334, 1300, 1249, 1196, 1164, 1115, 1096, 1014, 958, 823, 780, 725 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{19}H_{24}NSi$ $[M+H]^+$: 294.1673, found 294.1669.

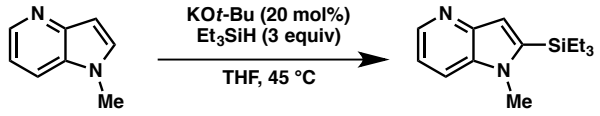


1-Benzyl-2-(dimethyl(phenyl)silyl)-1*H*-indole 2w: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-benzylindole **1b** (103.5 mg, 0.5 mmol, 1 equiv), $PhMe_2SiH$ (230 μL, 1.5 mmol, 3 equiv) and 0.5 mL of THF at 45 °C for 96 h. C2:C3 > 20:1. A mixture of starting material **1b** and product **2w** (*174.5 mg of mixture, contains 133.9 mg of **2w**, 78% yield, calculated based on ^1H NMR*) was obtained after purification by silica gel flash chromatography (2% EtOAc in hexanes). *Analytically pure compound **2w** was obtained as a white solid after subsequent purification by Preparative HPLC (3% EtOAc in hexanes)*. R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 1H), 7.51 – 7.48 (m, 2H), 7.40 – 7.35 (m, 1H), 7.34 – 7.29 (m, 2H), 7.21 – 7.16 (m, 3H), 7.14 – 7.08 (m, 3H), 6.90 (d, *J* = 0.7 Hz, 1H), 6.78 – 6.75 (m, 2H), 5.25 (s, 2H), 0.50 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 139.4, 138.3, 137.5, 134.2, 129.6, 128.9, 128.6, 128.1, 127.2, 125.9, 122.6, 121.0, 119.6, 114.1, 110.2, 50.0, -1.7. IR (Neat Film, NaCl) 3064, 3027, 2956, 1605, 1587, 1494, 1466, 1450, 1427, 1353, 1335, 1301, 1250, 1197, 1164, 1116, 1106, 1096, 1014, 905, 822 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{23}H_{24}NSi$ $[M+H]^+$: 342.1673, found 342.1676.



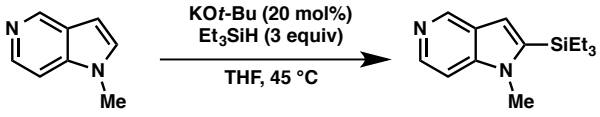
1-Methyl-2-(tributylsilyl)-1*H*-indole 2x: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-methylindole **1a** (65.6 mg, 0.5 mmol, 1 equiv), *n*-Bu_3SiH (385 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 35 °C for 65 h. C2:C3 > 20:1. The desired product **2x** (123.5 mg, 75% yield) was obtained as a white solid after purification by silica gel flash chromatography (100% hexanes). R_f = 0.5 (100% hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.22 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.08 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H), 6.69 (d, *J* = 0.9 Hz, 1H), 3.84 (s, 3H), 1.38 – 1.27 (m, 12H), 0.94 – 0.86 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 139.0, 128.6, 121.7, 120.5, 118.9, 112.7, 108.9, 32.9, 26.6, 26.1, 13.6, 12.7; IR (Neat Film, NaCl) 2955, 2922, 2871, 2855, 1492,

1464, 1411, 1375, 1356, 1325, 1298, 1232, 1196, 1166, 1102, 1070, 897, 885, 799, 788, 749, 732 cm^{-1}; HRMS (EI+) calc'd for $C_{21}H_{35}NSi$ [$M^{\bullet+}$]: 329.2539, found 329.2523



3a ***4a***

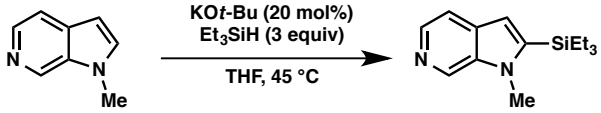
1-Methyl-2-(triethylsilyl)-1*H*-pyrrolo[3,2-*b*]pyridine 4a: The general procedure was followed. The reaction was performed with KO*t*-Bu (4.5 mg, 0.04 mmol, 20 mol%), *N*-methyl-4-azaindole **3a** (26.4 mg, 0.2 mmol, 1 equiv), Et_3SiH (98 μL, 0.6 mmol, 3 equiv) and 0.2 mL of THF at 45 °C for 96 h. C2:C3 = 6:1. *A mixture of C2- and C3-silylation products* (16.2 mg, 33% yield) was obtained after purification by silica gel flash chromatography (50% EtOAc in hexanes). *Analytically pure C2-silylation **4a** was obtained as a colorless oil after subsequent purification by Preparative TLC (50% EtOAc in hexanes).* R_f = 0.1 (33% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 4.6, 1.4 Hz, 1H), 7.60 (dt, *J* = 8.3, 1.2 Hz, 1H), 7.09 (dd, *J* = 8.3, 4.6 Hz, 1H), 6.90 (d, *J* = 0.9 Hz, 1H), 3.83 (s, 3H), 1.03 – 0.97 (m, 9H), 0.96 – 0.89 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 143.0, 142.7, 133.0, 116.4, 116.1, 113.8, 33.1, 7.6, 4.0. IR (Neat Film, NaCl) 2953, 2909, 2874, 1596, 1557, 1455, 1434, 1413, 1355, 1317, 1288, 1237, 1134, 1064, 1004, 800 cm^{-1}; HRMS (ESI+) calc'd for $C_{14}H_{23}N_2Si$ [M+H]$^+$: 247.1625, found 247.1621.



3b ***4b***

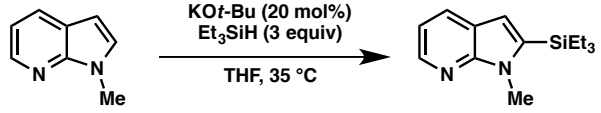
1-Methyl-2-(triethylsilyl)-1*H*-pyrrolo[3,2-*c*]pyridine 4b: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-methyl-5-azaindole **3b** (66.0 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 45 °C for 120 h. C2:C3 > 20:1. The desired product **4b** (37.9 mg, 31% yield) was obtained as a yellow oil after purification by silica gel flash chromatography (100% EtOAc). R_f = 0.2 (100% EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (d, *J* = 1.1 Hz, 1H), 8.28 (d, *J* = 5.9 Hz, 1H), 7.24 – 7.18 (m, 1H), 6.80 (d, *J* = 0.9

Hz, 1H), 3.82 (s, 3H), 1.02 – 0.96 (m, 9H), 0.94 – 0.87 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 143.6, 140.8, 140.4, 125.7, 112.9, 104.5, 32.9, 7.6, 4.0. IR (Neat Film, NaCl) 2953, 2909, 2874, 1597, 1563, 1485, 1463, 1435, 1415, 1368, 1334, 1310, 1291, 1219, 1184, 1123, 1069, 1004, 900, 809 cm^{-1}; HRMS (ESI+) calc'd for $C_{14}H_{23}N_2Si$ $[M+H]^+$: 247.1625, found 247.1626.



3c *4c*

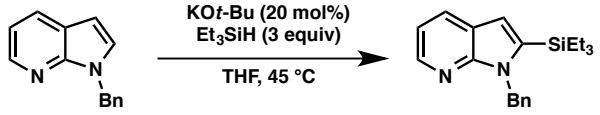
1-Methyl-2-(triethylsilyl)-1*H*-pyrrolo[2,3-*c*]pyridine 4c: The general procedure was followed. The reaction was performed with KO*t*-Bu (5.8 mg, 0.52 mmol, 20 mol%), *N*-methyl-6-azaindole **3c** (35.0 mg, 0.26 mmol, 1 equiv), Et_3SiH (126 μL, 0.78 mmol, 3 equiv), and 0.3 mL of THF at 45 °C for 94 h. C2:C3 > 20:1. The desired product **4c** (32.9 mg, 50% yield) was obtained as a yellow oil after purification by silica gel flash chromatography (gradient elution, 2.5→5% MeOH in CH_2Cl_2). R_f = 0.3 (5% MeOH in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.20 (d, *J* = 5.5 Hz, 1H), 7.47 (dd, *J* = 5.5, 1.1 Hz, 1H), 6.68 (d, *J* = 0.8 Hz, 1H), 3.93 (s, 3H), 1.03 – 0.97 (m, 9H), 0.95 – 0.89 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 138.1, 137.2, 133.0, 132.6, 114.7, 112.0, 33.3, 7.5, 3.9. IR (Neat Film, NaCl) 2952, 2909, 2874, 1594, 1559, 1496, 1475, 1457, 1415, 1358, 1333, 1315, 1286, 1241, 1167, 1120, 1070, 1004, 817, 808 cm^{-1}; HRMS (ESI+) calc'd for $C_{14}H_{23}N_2Si$ $[M+H]^+$: 247.1625, found 247.1620.



3d *4d*

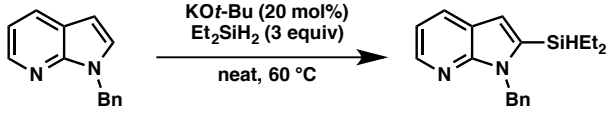
1-Methyl-2-(triethylsilyl)-1*H*-pyrrolo[2,3-*b*]pyridine 4d: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-methyl-7-azaindole **3d** (66 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 35 °C for 63 h. C2:C3 > 20:1. The desired product **4d** (87.1 mg, 71% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (gradient elution, 0→10% EtOAc in hexanes). R_f = 0.3 (10% EtOAc in hexanes); ^{1}H

NMR (500 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.87 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.02 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.67 (s, 1H), 3.95 (s, 3H), 1.04 – 0.97 (m, 9H), 0.96 – 0.88 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 143.2, 139.2, 128.3, 120.7, 115.3, 111.0, 31.4, 7.6, 3.9. IR (Neat Film, NaCl) 3052, 2953, 2910, 2874, 1590, 1570, 1489, 1444, 1403, 1302, 1286, 1226, 1162, 1134, 1107, 1066, 1004, 906, 804, 772, 739 cm^{-1}; HRMS (FAB+) calc'd for $C_{14}H_{23}N_2Si$ $[M+H]^+$: 247.1631, found 247.1637.



3e ***4e***

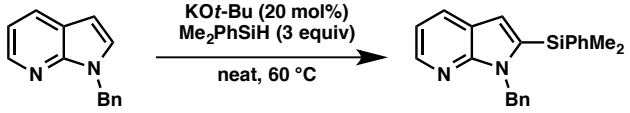
1-Methyl-2-(triethylsilyl)-1*H*-pyrrolo[2,3-*b*]pyridine 4e: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-benzyl-7-azaindole **3e** (104.0 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 45 °C for 144 h. C2:C3 > 20:1. The desired product **4e** (89.4 mg, 56% yield) was obtained as a colorless oil purification by silica gel flash chromatography (gradient elution, 2.5→5% EtOAc in hexanes). R_f = 0.3 (5% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.94 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.25 – 7.16 (m, 3H), 7.07 (dd, *J* = 7.8, 4.6 Hz, 1H), 6.87 – 6.85 (m, 2H), 6.79 (s, 1H), 5.69 (s, 2H), 0.91 – 0.83 (m, 9H), 0.74 – 0.69 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2, 143.7, 139.04, 138.96, 128.6, 128.4, 127.0, 125.9, 120.5, 115.7, 112.2, 47.8, 7.4, 3.7. IR (Neat Film, NaCl) 2954, 2874, 1589, 1570, 1495, 1452, 1439, 1422, 1378, 1357, 1309, 1239, 1157, 1103, 1004, 909, 803, 777 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{20}H_{27}N_2Si$ $[M+H]^+$: 323.1938, found 323.1947.



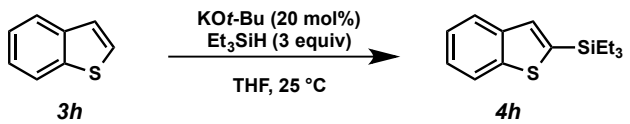
3e ***4f***

1-Benzyl-2-(diethylsilyl)-1*H*-pyrrolo[2,3-*b*]pyridine 4f: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-benzyl-7-azaindole **3e** (104.5 mg, 0.5 mmol, 1 equiv) and Et_2SiH_2 (194 μL, 1.5 mmol, 3 equiv) at 60 °C for 84 h. C2:C3 > 20:1. The desired product **4f** (96.2 mg, 65% yield)

was obtained as a yellow oil after purification by silica gel flash chromatography (3% EtOAc in hexanes). R_f = 0.4 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.30 – 7.16 (m, 3H), 7.09 (dd, *J* = 7.8, 4.6 Hz, 1H), 7.01 – 6.99 (m, 2H), 6.80 (s, 1H), 5.71 (s, 2H), 4.32 (p, *J* = 3.3 Hz, 1H), 0.95 (t, *J* = 7.9 Hz, 6H), 0.78 – 0.63 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.9, 143.8, 138.9, 137.4, 128.6, 128.5, 127.2, 126.6, 120.5, 115.8, 111.7, 47.6, 8.1, 3.4. IR (Neat Film, NaCl) 2955, 2873, 2120, 1590, 1568, 1495, 1453, 1439, 1422, 1358, 1300, 1235, 1156, 1100, 1009, 973, 910, 808 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{18}H_{23}N_2Si$ $[M+H]^+$: 295.1625, found 295.1636.

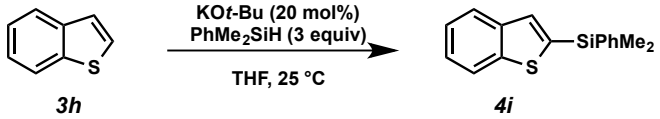


1-Benzyl-2-(dimethyl(phenyl)silyl)-1*H*-pyrrolo[2,3-*b*]pyridine 4g: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), *N*-benzyl-7-azaindole **3e** (103.9 mg, 0.5 mmol, 1 equiv) and $PhMe_2SiH$ (230 μL, 1.5 mmol, 3 equiv) at 60 °C for 96 h. C2:C3 > 20:1. The desired product **4g** (118.0 mg, 69% yield) was obtained as a yellow oil after purification by silica gel flash chromatography (3% EtOAc in hexanes). R_f = 0.4 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.97 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.41 – 7.38 (m, 1H), 7.37 – 7.32 (m, 2H), 7.20 – 7.13 (m, 3H), 7.08 (dd, *J* = 7.8, 4.6 Hz, 1H), 6.84 (s, 1H), 6.77 – 6.68 (m, 2H), 5.46 (s, 2H), 0.42 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 144.0, 140.0, 138.8, 136.9, 134.2, 129.7, 128.8, 128.5, 128.1, 127.0, 126.1, 120.4, 115.9, 112.2, 47.6, -2.0. IR (Neat Film, NaCl) 3050, 3027, 2956, 1589, 1569, 1495, 1439, 1427, 1359, 1309, 1250, 1156, 1107, 1029, 987, 910, 822 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{22}H_{23}N_2Si$ $[M+H]^+$: 343.1625, found 343.1635.

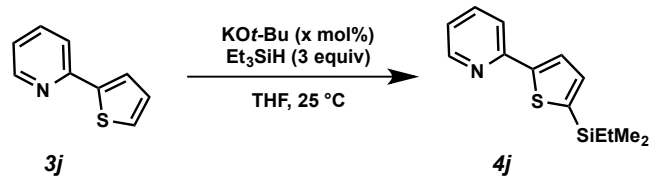


Benzo[*b*]thiophen-2-yltriethylsilane 4h: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), benzo[*b*]thiophene

3h (67.0 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 25 °C for 60 h. The desired product **4h** (120.3, 97% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (100% hexanes). R_f = 0.6 (100% hexanes); this compound is known.[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (m, 1H), 7.87 – 7.81 (m, 1H), 7.49 (m, 1H), 7.41 – 7.29 (m, 2H), 1.07 – 1.03 (m, 9H), 0.96 – 0.85 (m, 6H).



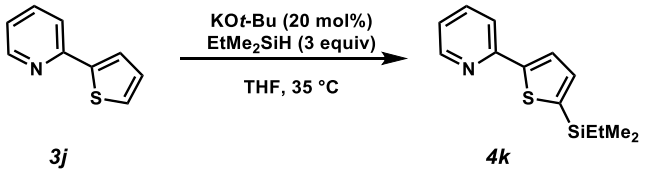
Benzo[*b*]thiophen-2-yldimethyl(phenyl)silane 4i: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), benzo[*b*]thiophene **3h** (67.0 mg, 0.5 mmol, 1 equiv), $PhMe_2SiH$ (230 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 25 °C for 60 h. The desired product **4i** (116.6 mg, 87% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (100% hexanes). R_f = 0.5 (100% hexanes); this compound is known.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 1H), 7.87 – 7.79 (m, 1H), 7.68 – 7.59 (m, 2H), 7.51 (d, *J* = 0.8 Hz, 1H), 7.46 – 7.39 (m, 3H), 7.38 – 7.31 (m, 2H), 0.69 (s, 6H).



2-(5-(Triethylsilyl)thiophen-2-yl)pyridine 4j: The general procedure was followed. *Condition A*: The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 2-(thiophen-2-yl)pyridine **3j** (80.5 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 25 °C for 35 h. The desired product **4j** (129.3 mg, 94% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (5% EtOAc in hexanes). *Condition B*: The reaction was performed with KO*t*-Bu (19.6 mg, 0.18 mmol, 3.5 mol%), 2-(thiophen-2-yl)pyridine **3j** (0.81 g, 5 mmol, 1 equiv),

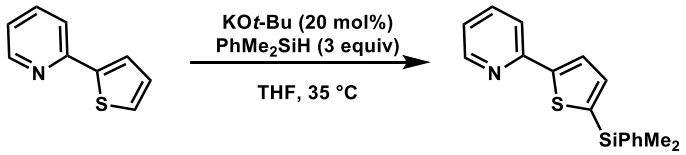
(6) Lu, B.; Falck, J. R. *Angew. Chem. Int. Ed.* **2008**, *47*, 7508

Et_3SiH (2.43 mL, 15 mmol, 3 equiv), and 3.0 mL of THF at 25 °C for 96 h. The desired product **4j** (1.13 g, 82% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (5% EtOAc in hexanes). R_f = 0.3 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.7 Hz, 1H), 7.61 (dt, *J* = 3.9, 1.7 Hz, 3H), 7.23 (d, *J* = 3.3 Hz, 1H), 7.08 (q, *J* = 4.8 Hz, 1H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.82 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 149.8, 149.6, 139.7, 136.6, 135.6, 125.7, 121.8, 119.0, 7.4, 4.5; IR (Neat Film, NaCl) 3054, 3001, 2953, 2909, 2874, 1585, 1563, 1528, 1517, 1464, 1436, 1422, 1377, 1315, 1290, 1238 ,1207, 1151, 1077, 1066, 1047, 1007, 990, 962, 807, 774, 737 cm^{-1}; HRMS (FAB+) calc'd for $C_{15}H_{22}NSSi$ $[M+H]^+$: 276.1242, found 276.1239.



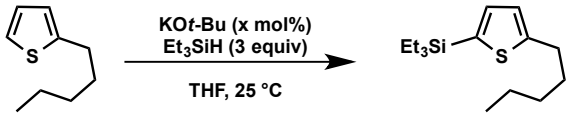
3j *4k*

2-(5-(Ethyldimethylsilyl)thiophen-2-yl)pyridine 4k: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 2-(thiophen-2-yl)pyridine **3j** (80.5 mg, 0.5 mmol, 1 equiv), $EtMe_2SiH$ (198 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 35 °C for 48 h. The desired product **4k** (107.4 mg, 87% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (10% Et_2O in hexanes). R_f = 0.4 (10% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (ddd, *J* = 4.9, 1.8, 1.1 Hz, 1H), 7.72 – 7.63 (m, 2H), 7.62 (d, *J* = 3.5 Hz, 1H), 7.24 (d, *J* = 3.5 Hz, 1H), 7.13 (ddd, *J* = 6.7, 4.9, 2.0 Hz, 1H), 1.05 – 0.96 (m, 3H), 0.78 (qd, *J* = 7.8, 0.8 Hz, 2H), 0.32 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.7, 149.7, 149.6, 141.9, 136.6, 135.0, 125.6, 121.7, 118.9, 8.3, 7.2, -2.5; IR (Neat Film, NaCl) 3054, 3001, 2953, 2909, 2874, 1585, 1563, 1528, 1517, 1464, 1436, 1422, 1315, 1290, 1248, 1207, 1151, 1077, 1066, 1047, 1007, 990, 964, 836, 812, 774, 752, 737, 712 cm^{-1}; HRMS (FAB+) calc'd for $C_{13}H_{18}NSSi$ $[(M+H)^+–H_2]$: 248.0929, found 248.0935.



3j *4l*

2-(5-(Dimethyl(phenyl)silyl)thiophen-2-yl)pyridine 4l: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 2-(thiophen-2-yl)pyridine **3j** (80.5 mg, 0.5 mmol, 1 equiv), $PhMe_2SiH$ (230 μL, 1.5 mmol, 3 equiv), and 1.0 mL of THF at 35 °C for 48 h. The desired product **4l** (118.1 mg, 80% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (10% Et_2O in hexanes). R_f = 0.3 (10% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 – 8.54 (m, 1H), 7.72 – 7.56 (m, 5H), 7.43 – 7.33 (m, 3H), 7.26 (m, 1H), 7.14 (m, 1H), 0.63 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 150.3, 149.5, 140.6, 137.3, 136.6, 136.0, 133.8, 129.3, 127.8, 125.6, 121.8, 118.9, –1.6; IR (Neat Film, NaCl) 3067, 2955, 1586, 1563, 1527, 1463, 1423, 1316, 1290, 1249, 1207, 1151, 1112, 1077, 1005, 989, 963, 807, 773, 731 cm^{-1}; HRMS (FAB+) calc'd for $C_{17}H_{18}NSSi$ $[M+H]^+$: 296.0929, found 296.0938.

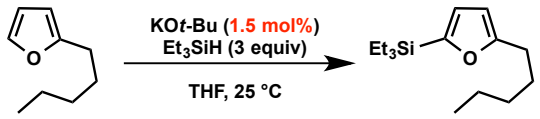


3m *4m*

condition A: 0.5 mmol, 20 mol% KO*t*-Bu, 48 h 96%
condition B: 5 mmol, 1 mol% KO*t*-Bu, 96 h 92%

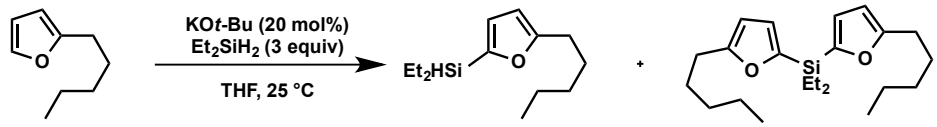
Triethyl(5-pentylthiophen-2-yl)silane 4m: The general procedure was followed. *Condition A*: The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 2-pentylthiophene **3m** (77.0 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 25 °C for 48 h. The desired product **4m** (130.0 mg, 96% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (100% hexanes). *Condition B:* The reaction was performed with KO*t*-Bu (5.6 mg, 0.05 mmol, 1 mol%), 2-pentylthiophene **3m** (770.4 mg, 5.0 mmol, 1 equiv), Et_3SiH (2.43 mL, 15 mmol, 3 equiv), and 3.0 mL of THF at 25 °C for 96 h. The desired product **4m** (1.23g, 92% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (100% hexanes). R_f = 0.6 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (dd, *J* =

3.3, 1.5 Hz, 1H), 6.91 (dt, *J* = 3.3, 1.0 Hz, 1H), 2.90 (td, *J* = 7.7, 1.2 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.48 – 1.36 (m, 4H), 1.06 (t, *J* = 7.8 Hz, 9H), 0.99 – 0.94 (m, 3H), 0.84 (qd, *J* = 7.8, 1.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6, 134.7, 134.1, 125.5, 31.7, 31.6, 30.2, 22.6, 14.1, 7.5, 4.7; IR (Neat Film, NaCl) 3054, 2955, 2934, 2874, 1750, 1528, 1456, 1438, 1413, 1378, 1339, 1235, 1213, 1058, 1011, 988, 799, 736 cm^{-1}; HRMS (FAB+) calc'd for $C_{15}H_{27}SSi$ $[(M+H)–H_2]^+$: 267.1603, found 267.1609.



3n *4n*

Triethyl(5-pentylfuran-2-yl)silane 4n: The general procedure was followed. The reaction was performed with KO*t*-Bu (8.4 mg, 0.075 mmol, 1.5 mol%), 2-pentylfuran **3n** (691 mg, 5.0 mmol, 1 equiv), Et_3SiH (2.43 mL, 15 mmol, 3 equiv), and 3 mL of THF at 25 °C for 96 h. The desired product **4n** (1.15 g, 91% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (100% hexanes). R_f = 0.6 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.53 (d, *J* = 3.0 Hz, 1H), 5.96 (dt, *J* = 3.0, 0.9 Hz, 1H), 2.67 – 2.60 (m, 2H), 1.64 (dq, *J* = 9.4, 7.4 Hz, 2H), 1.36 – 1.28 (m, 4H), 1.05 – 0.95 (m, 9H), 0.92 – 0.85 (m, 3H), 0.74 (qd, *J* = 7.8, 0.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 156.2, 121.5, 104.6, 31.6, 28.3, 27.9, 22.6, 14.1, 7.5, 3.6; IR (Neat Film, NaCl) 3108, 2954, 2933, 2874, 1807, 1721, 1588, 1493, 1459, 1414, 1378, 1340, 1237, 1186, 1173, 1118, 1084, 1011, 962, 923, 782, 736, 724 cm^{-1}; HRMS (FAB+) calc'd for $C_{15}H_{27}OSi$ $[(M+H)–H_2]^+$: 251.1831, found 251.1821.

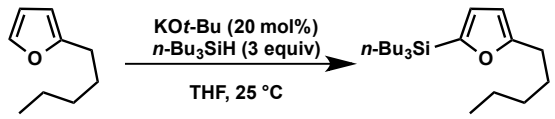


3n *4o* *SI-4o*

The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 2-pentylfuran **3n** (69.1 mg, 0.5 mmol, 1 equiv), Et_2SiH_2 (195 µL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 25 °C for 76 h. The desired product **4o** (87.4 mg, 78% yield) and silicon-tethered product **SI-4o** (12.4 mg, 8% yield) were obtained after purification by silica gel flash chromatography (100% hexanes).

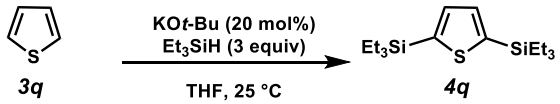
Diethyl(5-pentylfuran-2-yl)silane 4o: Colorless oil, R_f = 0.6 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.63 (d, *J* = 3.1 Hz, 1H), 6.00 (dt, *J* = 3.1, 0.9 Hz, 1H), 4.21 (p, *J* = 3.2 Hz, 1H), 2.75 – 2.64 (m, 2H), 1.73 – 1.62 (m, 2H), 1.38 – 1.32 (m, 4H), 1.11 – 1.04 (m, 6H), 0.95 – 0.90 (m, 3H), 0.88 – 0.81 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8, 153.7, 122.7, 105.0, 31.6, 28.4, 27.9, 22.6, 14.1, 8.1, 3.2; IR (Neat Film, NaCl) 2955, 2931, 2873, 2120, 1588, 1493, 1461, 1233, 1082, 1010, 974, 925, 798, 715 cm^{-1}; HRMS (FAB+) calc'd for $C_{13}H_{23}OSi$ $[(M+H)–H_2]^+$: 223.1518, found 223.1519.

Diethylbis(5-pentylfuran-2-yl)silane SI-4o: Colorless oil, R_f = 0.7 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 (d, *J* = 3.1 Hz, 2H), 5.98 (dt, *J* = 3.1, 0.9 Hz, 2H), 2.69 – 2.61 (m, 4H), 1.70 – 1.59 (m, 4H), 1.36 – 1.30 (m, 8H), 1.08 – 1.01 (m, 6H), 1.01 – 0.93 (m, 4H), 0.93 – 0.81 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 153.7, 122.8, 104.8, 31.4, 28.2, 27.7, 22.4, 13.9, 7.2, 4.2; IR (Neat Film, NaCl) 2955, 2928, 2873, 2859, 1587, 1493, 1461, 1378, 1233, 1187, 1122, 1010, 961, 925, 783, 726 cm^{-1}; HRMS (EI+) calc'd for $C_{22}H_{36}O_2Si$ $[M^{\bullet+}]$: 360.2485, found 360.2468.

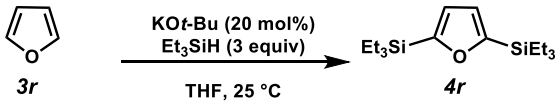


3n ***4p***

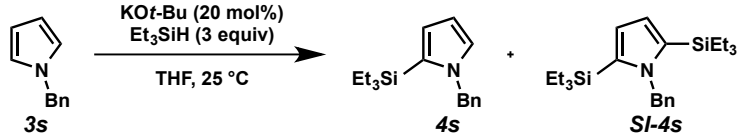
Tributyl(5-pentylfuran-2-yl)silane 4p: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 2-pentylfuran **3n** (69.1 mg, 0.5 mmol, 1 equiv), *n*-Bu_3SiH (386 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 25 °C for 108 h. The desired product **4p** (137.8 mg, 82% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (100% hexanes). R_f = 0.71 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.50 (d, *J* = 3.0 Hz, 1H), 5.95 (d, *J* = 3.0, 1H), 2.67 – 2.60 (m, 2H), 1.69 – 1.59 (m, 2H), 1.39 – 1.24 (m, 16H), 0.94 – 0.83 (m, 12H), 0.79 – 0.69 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0, 156.8, 121.3, 104.7, 31.6, 28.3, 28.0, 26.7, 26.2, 22.6, 14.1, 13.9, 12.3; IR (Neat Film, NaCl) 3107, 2956, 2923, 2871, 2857, 2099, 1677, 1588, 1493, 1464, 1410, 1376, 1341, 1296, 1271, 1217, 1187, 1175, 1082, 1050, 1010, 961, 925, 885, 781, 759, 732 cm^{-1}; HRMS (EI+) calc'd for $C_{21}H_{40}OSi$ $[M^{\bullet+}]$: 336.2848, found 336.2859.



2,5-Bis(triethylsilyl)thiophene 4q: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), thiophene **3q** (42.1 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 25 °C for 72 h. The desired product **4q** (134.2 mg, 86% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (100% hexanes). R_f = 0.6 (100% hexanes); this compound is known.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 2H), 1.02 – 0.99 (m, 18H), 0.83 – 0.79 (m, 12H).



2,5-Bis(triethylsilyl)furan 4r: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), furan **3r** (34.0 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 25 °C for 48 h. The desired product **4r** (106.6 mg, 72% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (100% hexanes). R_f = 0.7 (100% hexanes); this compound is known.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.66 (s, 2H), 1.09 – 0.95 (m, 18H), 0.86 – 0.70 (m, 12H).

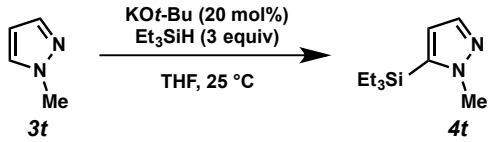


The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 1-benzyl-1*H*-pyrrole **3s** (78.5 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 25 °C for 108 h. The desired product **4s** (100.3 mg, 74% yield) and bis-silylation product **SI-4s** (9.6 mg, 5%) were obtained after purification by silica gel flash chromatography (100% hexanes).

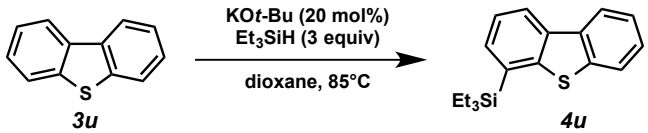
1-Benzyl-2-(triethylsilyl)-1*H*-pyrrole 4s: Colorless oil, R_f = 0.3 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 2H), 7.32 – 7.25 (m, 1H), 7.04 – 6.98 (m, 2H), 6.86 (dd, *J* = 2.4, 1.5 Hz, 1H), 6.51 (dd, *J* = 3.5, 1.5 Hz, 1H), 6.30 (dd, *J* = 3.4, 2.4 Hz,

1H), 5.22 (s, 2H), 0.95 (t, J = 7.8 Hz, 9H), 0.73 (q, J = 7.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 129.9, 128.7, 127.5, 126.62, 126.56, 120.9, 108.9, 53.5, 7.6, 4.2; IR (Neat Film, NaCl) 3088, 3064, 3029, 2952, 2908, 2873, 1516, 1506, 1495, 1454, 1418, 1353, 1329, 1288, 1237, 1175, 1112, 1080, 1008, 969, 760 cm^{-1}; HRMS (EI+) calc'd for $C_{17}H_{25}NSi$ [$M^{\bullet+}$]: 271.1756, found 271.1755.

1-Benzyl-2,5-bis(triethylsilyl)-1*H*-pyrrole SI-4s: Colorless oil, R_f = 0.4 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 2H), 7.21 – 7.15 (m, 1H), 6.72 (dq, J = 7.1, 1.0 Hz, 2H), 6.52 (s, 2H), 5.28 (s, 2H), 0.85 – 0.82 (m, 18H), 0.63 – 0.52 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 135.6, 128.2, 126.9, 125.5, 121.2, 53.3, 7.4, 3.9; IR (Neat Film, NaCl) 3027, 2952, 2909, 2874, 1605, 1498, 1485, 1454, 1416, 1377, 1343, 1277, 1237, 1161, 1075, 1002, 912, 775, 764, 731 cm^{-1}; HRMS (EI+) calc'd for $C_{23}H_{39}NSi_2$ [$M^{\bullet+}$]: 385.2621, found 385.2638.



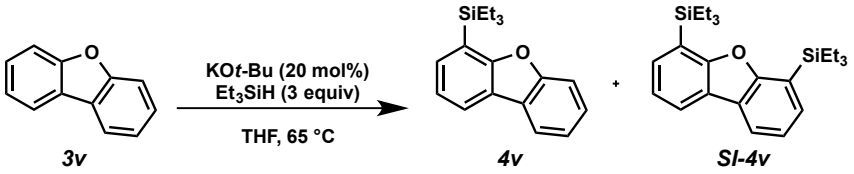
1-Methyl-5-(triethylsilyl)-1*H*-pyrazole 4t: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 1-methyl-1*H*-pyrazole **3t** (41.1 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 25 °C for 120 h. The desired product **4t** (72.6 mg, 74% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (1:1 Et_2O:hexanes). R_f = 0.3 (1:1 Et_2O:hexanes); this compound is known.[7] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 1.9 Hz, 1H), 6.37 (d, J = 1.8 Hz, 1H), 3.95 (s, 3H), 0.96 (m, 9H), 0.83 (m, 6H).



Dibenzo[*b,d*]thiophen-4-yltriethylsilane 4u: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), dibenzothiophene

(7) Despotopoulou, C.; Klier, L.; Knochel, P *Org. Lett.* **2009**, *11*, 3326

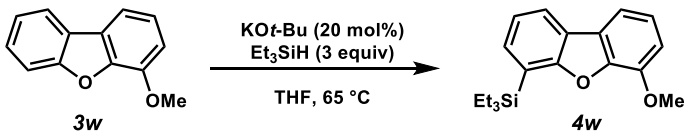
3u (92 mg, 0.5 mmol, 1.0 equiv), Et_3SiH (243 μL, 1.5 mmol, 3.0 equiv), and 3 mL of dioxane at 85 °C for 72 h. The desired product **4u** (55.4 mg, 38% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (100% hexanes). R_f = 0.7 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (m, 2H), 7.86 (m, 1H), 7.58 (m, 1H), 7.45 (m, 3H), 1.10 – 0.93 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 139.3, 135.4, 134.7, 133.7, 131.5, 126.5, 124.2, 123.7, 122.4, 122.2, 121.4, 7.4, 3.2. IR (Neat Film, NaCl) 3060, 2953, 2908, 2873, 1450, 1440, 1415, 1366, 1283, 1250, 1238, 1098, 1080, 1042, 1019, 1003, 972, 812, 749, 733 cm^{-1}; HRMS (EI+) calc'd for $C_{18}H_{22}SSi$ [$M^{\bullet+}$]: 298.1212, found 298.1214.



The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), dibenzo[*b*,*d*]furan **3v** (84.1 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 65 °C for 65 h. Desired product **4v** (100.2 mg, 71% yield) and bis-silylated product **SI-4v** (6.9 mg, 4% yield) were obtained after purification by silica gel flash chromatography (100% hexanes).

Dibenzo[*b,d*]furan-4-yltriethylsilane 4v: Colourless oil, R_f = 0.6 (100% hexanes); This compound is known.[8] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.61 – 7.50 (m, 2H), 7.46 (td, *J* = 7.7, 1.4 Hz, 1H), 7.34 (td, *J* = 7.6, 4.4 Hz, 2H), 1.02 (m, 15H).

4,6-Bis(triethylsilyl)dibenzo[b,d]furan SI-4v: White solid, R_f = 0.7 (100% hexanes); This compound is known.[5] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.6, 1.4 Hz, 2H), 7.54 (dd, *J* = 7.1, 1.4 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 1.12 – 0.96 (m, 30H).



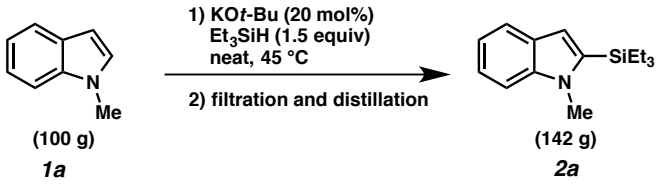
Triethyl(6-methoxydibenzo[*b,d*]furan-4-yl)silane 4w: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 4-

(8) Fedorov, A.; Toutov, A. A.; Swisher, N. A.; Grubbs, R. H. *Chem. Sci.* **2013**, *4*, 1640.

methoxydibenzo[*b*,*d*]furan **3w** (99.0 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 65 °C for 65 h. The desired product **4w** (99.9 mg, 64% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (100% hexanes). R_f = 0.3 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.53 (ddd, *J* = 15.4, 7.4, 1.2 Hz, 2H), 7.37 – 7.30 (m, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 6.99 (dd, *J* = 8.0, 1.0 Hz, 1H), 4.09 (s, 3H), 1.08 – 0.95 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.1, 145.7, 145.3, 133.4, 126.1, 123.0, 122.8, 122.3, 121.5, 120.4, 112.9, 111.0, 56.9, 7.4, 3.5; IR (Neat Film, NaCl) 3052, 2952, 2925, 2873, 2852, 2361, 1627, 1596, 1576, 1497, 1483, 1456, 1432, 1387, 1322, 1308, 1270, 1220, 1180, 1168, 1147, 1125, 1038, 1006, 854, 836, 767, 752, 729 cm^{-1}; HRMS (EI+) calc'd for $C_{19}H_{24}O_2Si$ [$M^{\bullet+}$]: 312.1546, found 312.1555.

2. Multi-gram scale syntheses of 2a, 4h and 4n.

2.1. Procedure for the multi-gram scale synthesis of 2a.



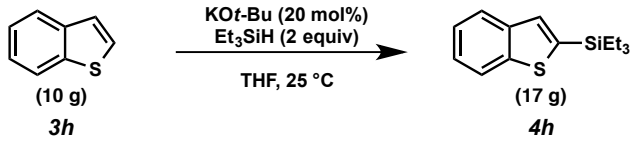
A 500 mL oven-dried Schlenk flask equipped with a stir bar and stoppered with a rubber septum was evacuated and refilled once with argon. KO*t*-Bu (18.8 grams, 167.9 mmols, 20 mol%) was weighed out on the bench and added to the flask under a strong flow of argon. The charged flask was then evacuated and refilled with argon. 1-Methylindole (95% purity, AKSci, undistilled, yellow oil; 95.1 mL, 762.4 mmol, 1.0 equiv) and Et_3SiH (182.6 mL, 1142 mmol, 1.5 equiv), which were previously degassed, were added through the septum by syringe. The mixture was then cooled to –78 °C (dry ice/acetone) and evacuated/backfilled with argon for three cycles. The cooling bath was removed and the flask was allowed to warm to room temperature under a positive pressure of argon. The flask was then transferred to a heating mantle set at 45 °C and stirred for 72 hours. The flask with the resultant deep red-purple solution was removed from heating and allowed to cool to room temperature, diluted with anhydrous Et_2O (50 mL) and filtered to remove solid residue. After the solvent was removed *in vacuo*, a stirbar was added and the transparent deep amber solution was stirred under high vacuum (100 millitorr) for several

hours to remove remaining volatiles. The mixture was then subjected to distillation under vacuum. A thermometer installed at the distillation head measured the temperature of the vapor being distilled.

a) Heating bath to 120 °C, vacuum stabilizes at 300 millitorr as the solution boils. Forerun comes off as pale yellow oil. Thermometer reads 65–80 °C.
b) Vacuum stabilizes at 180 millirtorr. Boiling continues vigorously.
c) As dripping rate in the forerun decreases (ca. one drop every three seconds), increase temperature. Remaining 1-methylindole comes over at 140 °C bath temp and 100 millitorr as a pale yellow oil. Thermometer reads 80–85 °C.
d) Increase temperature to 160 °C, vacuum at 100 millitorr to distil over the desired 2-triethylsilyl-1-methylindole (pale yellow oil). Thermometer reads 110–120 °C.

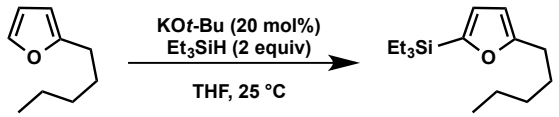
The desired product **2a** is obtained as a pale yellow oil (141.88 g, 76% yield).

2.2. Procedure for the multi-gram scale synthesis of 4h.



In a nitrogen-filled glove box, KO*t*-Bu (1.7 g, 15 mmol, 20 mol%), benzo[*b*]thiophene **3h** (10.1 g, 75 mmol, 1 equiv), Et_3SiH (23.3 mL, 146 mmol, 2 equiv), and 75 mL of THF were added to a 250 mL media jar equipped with a magnetic stir bar and sealed with a polypropylene cap. The reaction mixture was stirred at 25 °C for 60 h. The jar was then removed from the glovebox, opened carefully (*caution: gas released!*), and diluted with anhydrous Et_2O (30 mL). The reaction was filtered, the solvent was removed *in vacuo* and the residual volatiles were removed under high vacuum *(30 millitorr, 23 °C)*. The desired product **4h** (17.3 g, 93% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (100% hexanes).

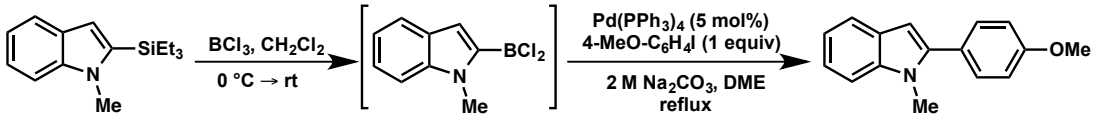
2.3. Procedure for the multi-gram scale synthesis of 4n.



(10 g) ***3n*** (17 g) ***4n***

Followed the same procedure as for the multi-gram scale synthesis of **4h**: The reaction was performed with KO*t*-Bu (1.6 g, 14.6 mmol, 20 mol%), 2-pentylfuran **3n** (10.1 g, 73 mmol, 1 equiv), Et_3SiH (23.3 mL, 146 mmol, 2 equiv), and 73 mL of THF at 25 °C for 72 h. The desired product **4n** (17.4 g, 95% yield) was obtained as a colorless oil after filtration, removal of volatiles under high vacuum (30 millitorr, 23 °C) and purification by silica gel flash chromatography (100% hexanes).

3. One-pot Si-directed *ipso*–substitution/Suzuki–Miyaura cross-coupling.



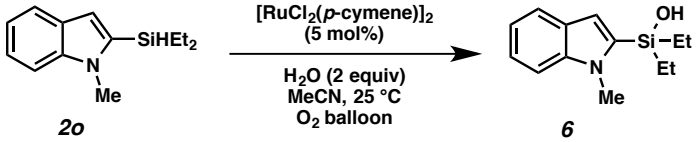
2a ***5***

Followed a modified known procedure:[9] A solution of BCl_3 (1.0 M, 0.48 mL, 0.48 mmol) in CH_2Cl_2 was added by syringe under N_2 to a stirred solution of indolesilane **2a** (98.2 mg, 0.4 mmol) in CH_2Cl_2 (4 mL) at 0 °C. The mixture was stirred at room temperature for 3 h, after which time the solvent was removed *in vacuo*. After the residue was dried under high vacuum for 20 min, 4-iodoanisole (94.0 mg, 0.4 mmol), $Pd(PPh_3)_4$ (23.2 mg, 5 mol%), DME (4 mL, degassed) and 2M Na_2CO_3 aqueous solution (1 mL, degassed) were added and the mixture was stirred under reflux for 5 h. Then the reaction mixture was cooled to room temperature and water (20 mL) was added. The mixture was extracted with Et_2O (3 x 30 mL), the combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. The desired 2-(4-methoxyphenyl)-1-methyl-1*H*-indole **5** (71.9 mg, 76% yield) was obtained as a white solid after purification by silica gel flash chromatography (gradient elution, 10→33% CH_2Cl_2 in hexanes). This compound is known.[10] R_f = 0.4 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.49 – 7.39 (m, 2H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.24 (dt, *J* = 8.2,

(9) Zhao, Z.; Snieckus, V. *Org. Lett*. **2005**, *7*, 2523.
(10) Denmark, S. E.; Baird, J. D. *Org. Lett*. **2004** , *6*, 3649.

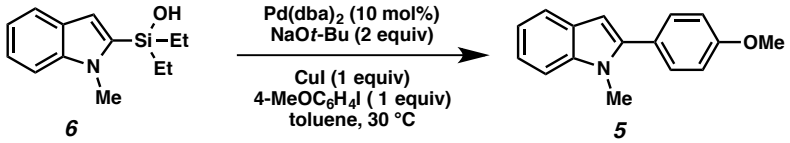
1.2 Hz, 1H), 7.14 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.05 – 6.96 (m, 2H), 6.51 (br s, 1H), 3.88 (s, 3H), 3.73 (s, 3H).

4. Synthesis of a heteroarylsilanol and application in Denmark–Hiyama cross-coupling.



2o *6*

Diethyl(1-methyl-1*H*-indol-2-yl)silanol 6: Followed a modified known procedure.[11] Compound **2o** (44.5 mg, 0.2 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (6.3 mg, 0.01 mmol) were added to a 5 mL flask equipped with a stirring bar. The flask was sealed with a septum and placed under high vacuum for 5 min before being connected with an O_2 balloon and back-filled with O_2, then acetonitrile (1 mL) and H_2O (7.4 μL, 0.4 mmol) were added by syringe through the septum. The reaction mixture was stirred for 12 h at room temperature. The solvent was evaporated and the product **6** (36.0 mg, 77% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (gradient elution, 10→20% EtOAc in hexanes). R_f = 0.2 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.37 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.28 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1H), 7.13 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H), 6.80 (d, *J* = 0.9 Hz, 1H), 3.93 (s, 3H), 2.12 (br s, 1H), 1.12 – 1.05 (m, 6H), 1.02 – 0.95 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 138.1, 128.4, 122.6, 121.1, 119.4, 112.7, 109.4, 33.1, 7.1, 6.7. IR (Neat Film, NaCl) 3315, 2956, 2876, 1493, 1463, 1413, 1357, 1328, 1300, 1234, 1166, 1102, 1075, 1007, 960, 897, 839, 798, 751, 732 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{13}H_{20}NOSi$ $[M+H]^+$: 234.1309, found 234.1305.



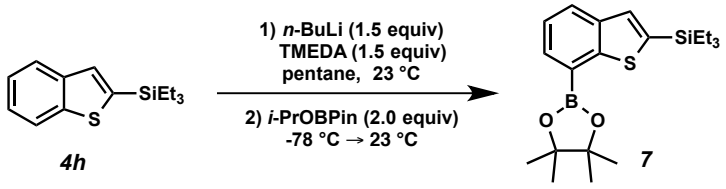
6 *5*

2-(4-Methoxyphenyl)-1-methyl-1*H*-indole 5: Followed a modified known procedure.[10] In a nitrogen-filled glovebox, a 2 dram vial equipped with a stir bar was charged with

(8) Lee, M.; Ko, S.; Chang, S. *J. Am. Chem. Soc*. **2000**, *122*, 12011.

NaO*t*-Bu (26.8 mg, 0.28 mmol) and CuI (26.6 mg, 0.14 mmol), 4-iodoanisole (33.0 mg, 0.14 mmol), $Pd(dba)_2$ (8.2 mg, 0.014 mmol, 10 mol%) and 0.2 mL of toluene. The mixture was sealed with a cap and stirred for 10 min. Then this mixture was transferred by syringe to another 2 dram vial containing silanol **6** (33.1 mg, 0.14 mmol). The vial was washed with toluene (2 x 0.4 mL) and that rinse was added to the reaction mixture. After the reaction was stirred at 30 °C for 4 h, the starting material was completely converted (monitored by TLC). The desired product **5** (28.1 mg, 84% yield) was obtained as a white solid after purification by silica gel flash chromatography (gradient elution, 10→50% CH_2Cl_2 in hexanes).

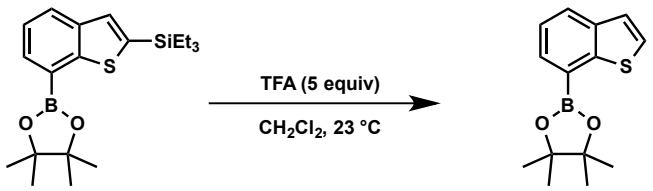
5. Direct C7 lithiation-borylation by a Si-blocking group strategy.



Triethyl(7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[b]thiophen-2-yl)silane 7: Followed a modified known procedure.[12] To a flame-dried, round bottom flask charged with a stir bar, capped with a septum and under a steady stream of argon was added benzo[*b*]thiophen-2-yltriethylsilane **4h** (992 mg, 4.0 mmol, 1 equiv), pentane (5.0 mL) and TMEDA (0.703g, 0.907 mL, 1.5 equiv) at 23 °C. *n*-Butyllithium (1.6 M in hexanes, 3.78 mL, 1.5 equiv) was added dropwise such that the internal temperature remained between 22 and 25 °C (*a thermocouple was inserted through the septum directly into the solution for internal monitoring of the temperature*). The resultant dark brown solution was allowed to stir at 22 °C for 20 h. The solution was then cooled to –78 °C (dry ice/acetone) and *i*-PrOBPin (1.52 g, 1.64 mL, 8.06 mmol, 2.0 equiv) was added as a 1 M solution in THF (8.06 mL) dropwise such that the temperature was kept below –75 °C (*careful temperature control is crucial for reproducibility*). The resulting solution was allowed to stir for 1 h at –78 °C after which time the cooling bath was removed. The solution was allowed to naturally warm to 23 °C and stirred at that temperature for an additional hour. The resulting turbid yellow reaction mixture was carefully quenched

(9) Hansen, M.; Clayton, M.; Godfrey, A.; Grutsch, Jr. J.; Keast, S.; Kohlman, D.; McSpadden, A.; Pedersen, S.; Ward, J.; Xu, Y.-C. *Synlett*, **2004**, *8*, 1351

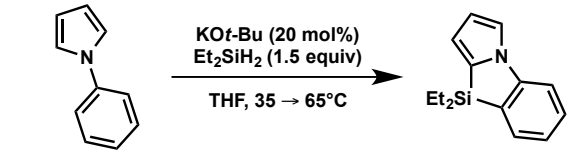
with NH_4Cl (5 mL). The mixture was extracted with Et_2O (3 x 10 mL), the combined organic fractions were washed with brine, dried over $MgSO_4$, filtered, and the solvent was evaporated to give a viscous brown liquid. The desired product **7** (926 mg, 64% yield) was obtained as a colorless solid after purification by silica gel flash chromatography (gradient elution 0→3% EtOAc in hexanes). R_f = 0.2 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.80 (dd, *J* = 7.0, 1.3 Hz, 1H), 7.48 (s, 1H), 7.35 (dd, *J* = 7.9, 7.0 Hz, 1H), 1.42 (s, 12H), 1.10 – 1.00 (m, 9H), 0.89 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 140.8, 139.8, 132.0, 131.4, 126.4, 123.4, 84.3, 25.1, 7.6, 4.4. IR (Neat Film, NaCl) 2955, 2937, 1375, 1367, 1359, 1134, 1059, 854, 735 cm^{-1}; HRMS (EI+) calc'd for $C_{20}H_{31}BSSiO_2$ [$M^{\bullet+}$]: 374.1907, found 374.1907.



7 *8*

2-(Benzo[*b*]thiophen-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8: Followed a modified known procedure.[9] To a vial charged with a magnetic stirbar and triethyl(7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[b]thiophen-2-yl)silane **7** (300 mg, 0.80 mmol) was added CH_2Cl_2 (0.3 mL) and trifluoroacetic acid (306 μL, 4.0 mmol, 5.0 equiv) at room temperature. The reaction was allowed to stir for 3 hours, after which time the mixture was quenched with water (0.5 mL), extracted with Et_2O (3 x 5 mL) and the combined organic fractions were washed with brine (5 mL). The solvents were removed to give **8** (203.8 mg, 98%) as a white solid without further purification. R_f = 0.4 (3% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.83 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.48 (d, *J* = 5.5 Hz, 1H), 7.38 (dd, *J* = 7.9, 7.0 Hz, 1H), 7.34 (d, *J* = 5.5 Hz, 1H), 1.41 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 139.4, 132.0, 127.5, 126.7, 123.7, 123.4, 84.4, 25.1. IR (Neat Film, NaCl) 2977, 1564, 1504, 1461, 1372, 1330, 1300, 1267, 1199, 1165, 1135, 1097, 1038, 969, 851, 829, 801, 714, 672 cm^{-1}; HRMS (EI+) calc'd for $C_{14}H_{17}BSO_2$ [$M^{\bullet+}$]: 260.1042, found 260.1039.

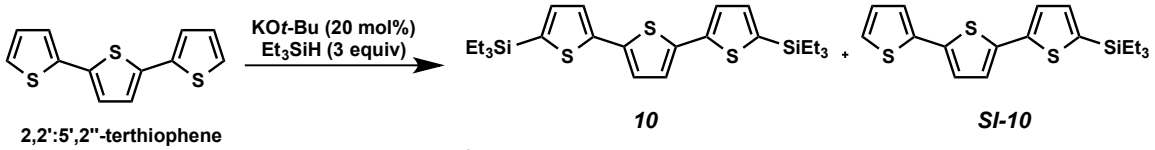
6. Synthesis of a sila-heterocycle by inter-/intramolecular double C–H silylation.



1-phenyl-1*H*-pyrrole — ***9***

9,9-Diethyl-9*H*-benzo[d]pyrrolo[1,2-*a*][1,3]azasilole 9: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 1-phenyl-1*H*-pyrrole (72.0 mg, 0.5 mmol, 1 equiv), Et_2SiH_2 (97 μL, 0.75 mmol, 1.5 equiv), and 0.5 mL of THF at 35 °C for 72 h and then at 65 °C for 72 h. The desired product **9** (48.8 mg, 43% yield) was obtained as colorless needles after purification by silica gel flash chromatography (100% hexanes). R_f = 0.6 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (ddd, *J* = 7.1, 1.4, 0.6 Hz, 1H), 7.46 – 7.33 (m, 2H), 7.31 (dt, *J* = 7.9, 0.7 Hz, 1H), 7.09 (td, *J* = 7.2, 1.0 Hz, 1H), 6.52 (dd, *J* = 3.3, 1.0 Hz, 1H), 6.41 (dd, *J* = 3.3, 2.6 Hz, 1H), 1.05 – 0.96 (m, 6H), 0.96 – 0.79 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 134.1, 130.8, 129.4, 128.5, 123.9, 117.5, 117.1, 113.3, 111.6, 7.5, 4.4; IR (Neat Film, NaCl) 2958, 2921, 2873, 2849, 1658, 1598, 1462, 1471, 1451, 1377, 1332, 1260, 1086, 1017, 799, 755, 717 cm^{-1}; HRMS (FAB+) calc'd for $C_{14}H_{18}NSi$ $[M+H]^+$: 228.1208, found 228.1206.

7. C–H silylation of terthiophene and EDOT.



2,2':5',2''-terthiophene — ***10*** — ***SI-10***

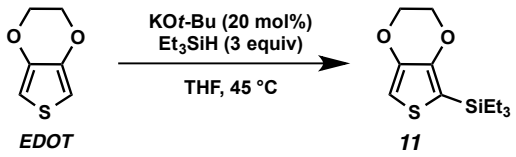
condition A: THF, 25 °C, 40 h — 86% — 13%
condition B: THF, 45 °C, 65 h — 96% — trace

The general procedure was followed. *For condition A*: The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 2,2':5',2''-terthiophene (124 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 25 °C for 40 h. Products **10** (204.7 mg, 86% yield) and **SI-10** (23.5 mg, 13% yield) were obtained after purification by silica gel flash chromatography (100% hexanes). *For condition B:* The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 2,2':5',2''-terthiophene (124 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5

mL of THF at 45 °C for 65 h. Product **10** (228.6 mg, 96% yield) was obtained after purification by silica gel flash chromatography (100% hexanes); **SI-10** was observed as a trace product by ^{1}H NMR and GC-MS, but was not isolated.

5,5''-Bis(triethylsilyl)-2,2':5',2''-terthiophene 10: Yellow oil, R_f = 0.5 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 3.5 Hz, 2H), 7.14 (d, *J* = 3.5 Hz, 2H), 7.10 (s, 2H), 1.03 (m, 18H), 0.82 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 136.7, 136.5, 135.7, 124.9, 124.5, 7.2, 4.4; IR (Neat Film, NaCl) 3057, 2953, 2934, 2908, 2874, 1750, 1455, 1428, 1417, 1377, 1303, 1236, 1212, 1198, 1068, 988, 1009, 911, 892, 792, 736, 723 cm^{-1}; HRMS (EI+) calc'd for $C_{24}H_{36}S_3Si_2$ [$M^{\bullet+}$]: 476.1518, found 476.1534

[2,2':5',2''-Terthiophen]-5-yltriethylsilane SI-10: Yellow oil, R_f = 0.4 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 3.4 Hz, 1H), 7.21 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.17 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.14 (dd, *J* = 3.4, 1.6 Hz, 1H), 7.09 (q, *J* = 3.7 Hz, 2H), 7.02 (dd, *J* = 5.1, 3.6 Hz, 1H), 1.07 – 0.98 (m, 9H), 0.82 (qd, *J* = 7.8, 0.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 137.5, 136.8, 136.6, 136.4, 135.6, 128.0, 125.0, 124.6, 124.5, 124.5, 123.8, 7.5, 4.6; IR (Neat Film, NaCl) 3068, 2953, 2873, 1458, 1425, 1377, 1235, 1195, 1069, 1011, 989, 913, 865, 836, 793, 737 cm^{-1}; HRMS (FAB+) calc'd for $C_{18}H_{23}S_3Si$ [M+H]$^+$: 363.0731, found 363.0742.

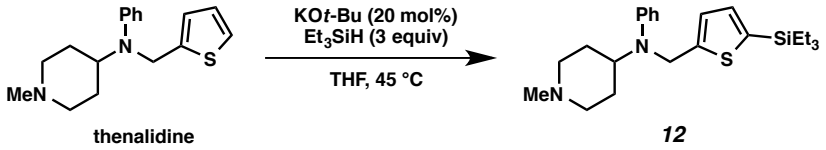


EDOT *11*

(2,3-Dihydrothieno[3,4-b][1,4]dioxin-5-yl)triethylsilane 11: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), EDOT (2,3-dihydrothieno[3,4-b][1,4]dioxine, 71.1 mg, 0.5 mmol), Et_3SiH (240 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 45 °C for 72 h. The desired product **11** (79.3 mg, 62% yield) was obtained after purification by silica gel flash chromatography (gradient elution, 0→5% EtOAc in hexanes) as a cloudy yellow oil. R_f = 0.3 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.56 (s, 2H), 4.17 (s, 4H), 0.98 (td, *J* = 7.8, 0.8 Hz, 9H), 0.84 – 0.74 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5, 142.5, 108.7, 105.0, 64.5, 64.5, 7.4, 3.9; IR (Neat Film NaCl) 2952, 2873, 1468, 1440, 1422, 1361, 1244, 1181, 1151, 1072,

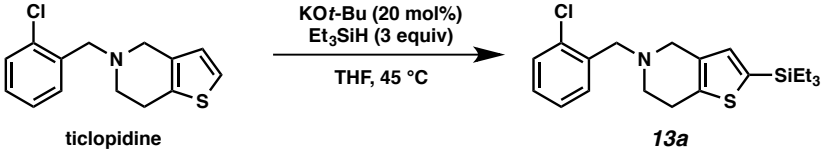
1042, 1009, 899, 721 cm^{-1}; HRMS (EI+) calc'd for $C_{12}H_{21}O_2SSi$ $[M+H]^+$: 257.1032, found 257.1064.

8. Late stage silylation of active pharmaceutical ingredients (APIs).



thenalidine **12**

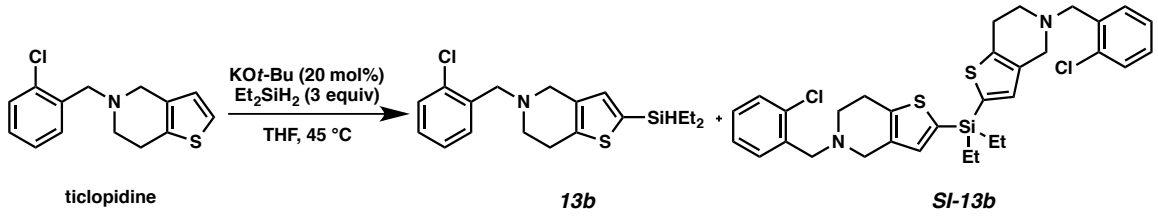
1-Methyl-*N*-phenyl-*N*-((5-(triethylsilyl)thiophen-2-yl)methyl)piperidin-4-amine 12: The general procedure was followed. The reaction was performed with KO*t*-Bu (2.2 mg, 0.02 mmol, 20 mol%), thenalidine (28.2 mg, 0.1 mmol, 1 equiv), Et_3SiH (48 μL, 0.3 mmol, 3 equiv), and 0.1 mL of THF at 45 °C for 72 h. The desired product **12** (24.9 mg, 62% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (hexanes:EtOAc:Et_3N = 100:100:1). R_f = 0.2 (hexanes:EtOAc:Et_3N = 20:20:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 7.05 (d, *J* = 3.4 Hz, 1H), 6.97 (d, *J* = 3.3 Hz, 1H), 6.82 (dt, *J* = 7.8, 1.0 Hz, 2H), 6.72 (tt, *J* = 7.2, 1.0 Hz, 1H), 4.62 (s, 2H), 3.70 (tt, *J* = 11.6, 4.0 Hz, 1H), 2.96 – 2.92 (m, 2H), 2.30 (s, 3H), 2.07 (td, *J* = 11.9, 2.5 Hz, 2H), 1.93 – 1.85 (m, 2H), 1.85 – 1.73 (m, 2H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.76 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 149.0, 135.2, 134.7, 129.3, 125.3, 117.3, 113.8, 55.8, 55.6, 46.4, 46.0, 29.6, 7.5, 4.6. IR (Neat Film, NaCl) 2951, 2873, 2780, 2734, 1597, 1574, 1503, 1459, 1377, 1352, 1278, 1237, 1207, 1131, 1068, 1008, 987, 850, 802, 745 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{23}H_{37}N_2SSi$ $[M+H]^+$: 401.2441, found 401.2460.



ticlopidine **13a**

5-(2-Chlorobenzyl)-2-(triethylsilyl)-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridine 13a: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), ticlopidine (132.5 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 45 °C for 48 h. The desired product **13a** (107.7 mg, 57% yield) was obtained as a colorless oil after purification by silica gel flash chromatography

(gradient elution, 5→10% Et_2O in hexanes). R_f = 0.4 (10% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.37 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.25 (td, *J* = 7.4, 1.5 Hz, 1H), 7.20 (td, *J* = 7.6, 1.9 Hz, 1H), 6.86 (s, 1H), 3.84 (s, 2H), 3.67 (d, *J* = 1.6 Hz, 2H), 2.94 (t, *J* = 5.9 Hz, 2H), 2.87 (t, *J* = 5.4 Hz, 2H), 1.02 – 0.98 (m, 9H), 0.80 – 0.74 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 136.5, 135.6, 134.4, 134.0, 133.2, 130.8, 129.6, 128.3, 126.8, 58.7, 53.3, 51.0, 26.1, 7.5, 4.6. IR (Neat Film, NaCl) 2952, 2908, 2873, 2805, 2763, 1462, 1443, 1413, 1375, 1360, 1347, 1303, 1289, 1234, 1169, 1125, 1106, 1047, 1032, 1018, 991, 907, 835, 752 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{20}H_{29}ClNSSi$ $[M+H]^+$: 378.1473, found 378.1480.

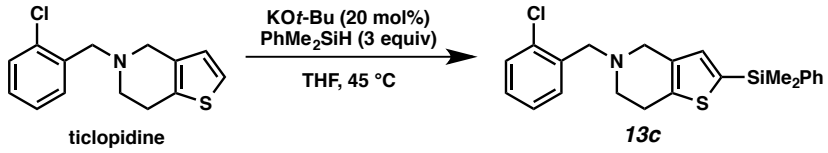


The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), ticlopidine (134.5 mg, 0.5 mmol, 1 equiv), Et_2SiH_2 (194 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 45 °C for 108 h. Products **13b** (97.9 mg, 56% yield) and **SI-13b** (27.3 mg, 18% yield) were obtained after purification by silica gel flash chromatography (gradient elution, 5→50% Et_2O in hexanes).

5-(2-Chlorobenzyl)-2-(diethylsilyl)-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridine 13b: Colorless oil, R_f = 0.4 (10% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.38 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.26 (td, *J* = 7.4, 1.5 Hz, 1H), 7.21 (td, *J* = 7.6, 1.9 Hz, 1H), 6.93 (s, 1H), 4.30 (p, *J* = 3.2 Hz, 1H), 3.84 (s, 2H), 3.67 (t, *J* = 1.7 Hz, 2H), 2.96 – 2.94 (m, 2H), 2.88 – 2.85 (m, 2H), 1.05 (t, *J* = 7.8 Hz, 6H), 0.83 (qd, , *J* = 7.5, 3.3 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0, 136.4, 135.9, 134.4, 134.2, 131.3, 130.8, 129.6, 128.3, 126.8, 58.6, 53.2, 50.9, 26.1, 8.1, 4.5. IR (Neat Film, NaCl) 2953, 2909, 2872, 2805, 2112, 1456, 1447, 1361, 1348, 1303, 1290, 1231, 1169, 1125, 1106, 1048, 1033, 1009, 992, 907, 810, 752 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{18}H_{25}ClNSSi$ $[M+H]^+$: 350.1160, found 350.1155.

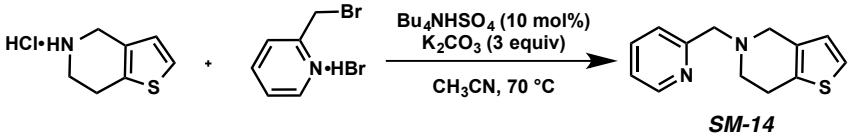
Bis(5-(2-chlorobenzyl)-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridin-2-yl)diethylsilane SI-13b: Colorless oil, R_f = 0.3 (50% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.55

(dd, J = 7.6, 1.8 Hz, 2H), 7.37 (dd, J = 7.8, 1.5 Hz, 2H), 7.25 (td, J = 7.4, 1.5 Hz, 2H), 7.20 (td, J = 7.6, 1.9 Hz, 2H), 6.92 (s, 2H), 3.83 (s, 4H), 3.65 (t, J = 3.3 Hz, 4H), 2.94 (t, J = 5.4 Hz, 4H), 2.86 (t, J = 5.6 Hz, 4H), 1.09 – 0.95 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 136.4, 135.8, 134.53, 134.45, 132.4, 130.9, 129.6, 128.3, 126.8, 58.7, 53.2, 50.9, 26.1, 7.5, 6.5. IR (Neat Film, NaCl) 3059, 2953, 2913, 2868, 2806, 1471, 1453, 1446, 1361, 1289, 1125, 1105, 1033, 989, 907, 839, 805, 753 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{32}H_{37}Cl_2N_2S_2Si$ $[M+H]^+$: 611.1539, found 611.1523.



ticlopidine *13c*

5-(2-Chlorobenzyl)-2-(dimethyl(phenyl)silyl)-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridine 13c: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), ticlopidine (134.5 mg, 0.5 mmol, 1 equiv), $PhMe_2SiH$ (230 μL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 45 °C for 108 h. Product **13c** (135.4 mg, 68% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (3% Et_2O in hexanes). R_f = 0.3 (10% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 3H), 7.39 – 7.34 (m, 4H), 7.25 – 7.18 (m, 2H), 6.87 (s, 1H), 3.82 (s, 2H), 3.64 (t, J = 1.7 Hz, 2H), 2.95 – 2.92 (m, 2H), 2.88 – 2.84 (m, 2H), 0.56 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 138.2, 136.4, 135.9, 135.2, 134.4, 134.1, 133.9, 130.8, 129.6, 129.4, 128.3, 128.0, 126.8, 58.6, 53.2, 50.9, 26.1, -1.1. IR (Neat Film, NaCl) 3067, 2953, 2918, 2806, 2764, 1652, 1471, 1446, 1427, 1361, 1248, 1169, 1109, 1033, 990, 907, 832, 810, 777, 753 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{22}H_{25}ClNSSi$ $[M+H]^+$: 398.1160, found 398.1152.

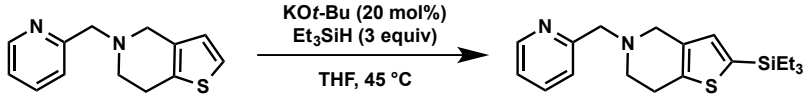


SM-14

5-(Pyridin-2-ylmethyl)-4,5,6,7-tetrahydrothieno[3,2-c]pyridine SM-14: Followed a modified known procedure.[13] To a flame-dried 50 mL Schlenk flask was added 4,5,6,7-

(13) Pan, X.; Huang, R.; Zhang, J.; Ding, L.; Li, W.; Zhang, Q.; Liu, F. *Tetrahedron Lett* **2012**, *53*, 5364.

tetrahydrothieno[3,2-c]pyridine HCl salt (1.0 g, 5.7 mmol), 2-(bromomethyl)pyridine HBr salt (2.18 g, 8.6 mmol, 1.5 equiv), Bu_4NHSO_4 (0.20 g, 0.6 mmol, 10 mol%), K_2CO_3 (3.94 g, 28.5 mmol, 5 equiv), and 10 mL of acetonitrile. The flask was purged with argon and the reaction was stirred at 70 °C for 18 h. The desired product **SM-14** (346.5 mg, 26% yield) was obtained after purification by silica gel flash chromatography (gradient elution, 50→100% Et_2O in hexanes) as a yellow oil. R_f = 0.1 (50% Et_2O in hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ 8.58 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 7.67 (td, J = 7.6, 1.8 Hz, 1H), 7.51 (dt, J = 7.9, 1.0 Hz, 1H), 7.19 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 7.07 (dt, J = 5.1, 0.7 Hz, 1H), 6.70 (d, J = 5.1 Hz, 1H), 3.89 (s, 2H), 3.64 (t, J = 1.7 Hz, 2H), 2.96 – 2.83 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.79, 149.20, 136.52, 133.78, 133.36, 125.22, 123.13, 122.63, 122.13, 63.82, 53.22, 50.89, 25.50; IR (Neat Film, NaCl) 3403, 3062, 2918, 2813, 1648, 1588, 1569, 1473, 1431, 1356, 1320, 1236, 1167, 1109, 1053, 1015, 993, 905, 840, 809, 761 cm^{-1}; HRMS (EI+) calc'd for $C_{13}H_{13}SN_2$ $[(M+H)-H_2]^+$: 229.0799, found 229.0806.

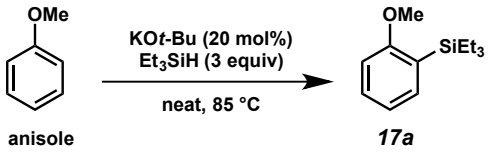


SM-14 ***14***

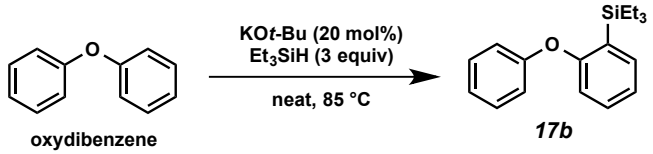
5-(Pyridin-2-ylmethyl)-2-(triethylsilyl)-4,5,6,7-tetrahydrothieno[3,2-c]pyridine 14: The general procedure was followed. The reaction was performed with KO*t*-Bu (4.5 mg, 0.04 mmol, 20 mol%), 5-(pyridin-2-ylmethyl)-4,5,6,7-tetrahydrothieno[3,2-c]pyridine **SM-14** (46.1 mg, 0.2 mmol), Et_3SiH (96 μL, 0.6 mmol, 3 equiv), and 0.2 mL of THF at 45 °C for 72 h. The desired product **14** (49.1 mg, 71% yield) was obtained after purification by silica gel flash chromatography (gradient elution, 75→100% Et_2O in hexanes) as a colourless oil. R_f = 0.5 (75% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 8.56 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.66 (td, *J* = 7.7, 1.8 Hz, 1H), 7.50 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.17 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 6.83 (s, 1H), 3.87 (s, 2H), 3.64 (t, *J* = 1.6 Hz, 2H), 2.94 (tt, *J* = 5.3, 1.5 Hz, 2H), 2.86 (dd, *J* = 5.9, 5.0 Hz, 2H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.74 (qd, *J* = 7.7, 0.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 149.1, 138.9, 136.5, 135.3, 133.8, 133.0, 123.1, 122.1, 63.9, 53.2, 50.9, 25.8, 7.4, 4.4; IR (Neat

Film, NaCl) 3048, 2951, 2873, 2806, 1588, 1569, 1448, 1430, 1361, 1289, 1235, 1169, 1114, 1031, 1005, 992, 908, 835, 757, 735, 718 cm^{-1}; HRMS (EI+) calc'd for $C_{19}H_{29}N_2SSi$ $[M+H]^+$: 345.1821, found 345.1835.

9. Oxygen-directed C(sp^2)–H silylation of anisole derivatives.

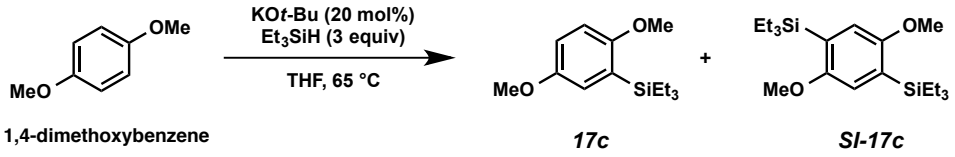


Triethyl(2-methoxyphenyl)silane 17a: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), anisole (54.0 mg, 0.5 mmol, 1 equiv), and Et_3SiH (243 μL, 1.5 mmol, 3 equiv) without any added solvent at 85 °C for 72 h. *ortho*:(*meta* + *para)* > 20:1. The GC yield of desired product **17a** is 65%. The analytically pure product (47.7 mg, 43% yield) was obtained as a colorless oil after evaporation of starting material and volatiles under vacuum (60 millitorr, 23 °C). *Note: compound **17a** is volatile and can be removed under vacuum.* This compound is known.[14] R_f = 0.3 (10% Et_2O in hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 2H), 6.97 (m, 1H), 6.87 – 6.81 (m, 1H), 3.80 (s, 3H), 1.05 – 0.90 (m, 9H), 0.91 – 0.77 (m, 6H).



Triethyl(2-phenoxyphenyl)silane 17b: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), oxydibenzene (85.0 mg, 0.5 mmol), and Et_3SiH (240 μL, 1.5 mmol, 3 equiv) without solvent at 85 °C for 120 h. The desired product **17b** (84.5 mg, 55% yield) was obtained after purification by silica gel flash chromatography (100% hexanes) as a colorless oil. R_f = 0.4 (100% hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 1H), 7.38 – 7.25 (m, 3H), 7.10 (t, *J* = 7.4 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 1H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.85 (q, *J* = 7.9 Hz, 6H). This compound is known.[8]

(14) Yamanoi, Y.; Nishihara, H. *J. Org. Chem.* **2008**, *73*, 6671.

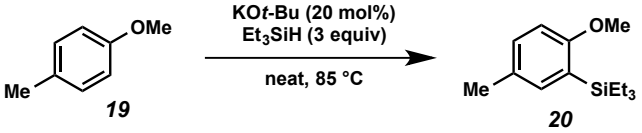


1,4-dimethoxybenzene — ***17c*** — ***SI-17c***

The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 1,4-dimethoxybenzene (69.1 mg, 0.5 mmol), and Et_3SiH (240 μL, 1.5 mmol, 3 equiv), in 0.5 mL of THF at 65 °C for 72 h. The desired product **17c** (53.1 mg, 42% yield) and bis-silylated byproduct **SI-17c** (16.1 mg, 8% yield) were obtained after purification by silica gel flash chromatography (100% hexanes).

(2,5-Dimethoxyphenyl)triethylsilane 17c: Colorless oil, R_f = 0.5 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, *J* = 3.1 Hz, 1H), 6.85 (dd, *J* = 8.8, 3.1 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 0.99 – 0.91 (m, 9H), 0.85 – 0.74 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 153.3, 126.7, 122.2, 122.3, 114.1, 55.7, 55.5, 7.6, 3.7; IR (Neat Film, NaCl) 2952, 2873, 1580, 1478, 1463, 1398, 1272, 1220, 1177, 1050, 1026, 872, 800, 769, 732 cm^{-1}; HRMS (EI+) calc'd for $C_{14}H_{24}O_2Si$ [$M^{+\bullet}$]: 252.1546, found 252.1540.

(2,5-Dimethoxy-1,4-phenylene)bis(triethylsilane) SI-17c: White solid, R_f = 0.8 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (s, 2H), 3.75 (s, 6H), 0.95 (td, *J* = 7.9, 0.9 Hz, 9H), 0.85 – 0.77 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 127.1, 116.9, 55.6, 7.7, 3.8; IR (Neat Film, NaCl) 2948, 2870, 1459, 1418, 1345, 1262, 1203, 1107, 1045, 999, 868, 727, 700 cm^{-1}; HRMS (EI+) calc'd for $C_{20}H_{38}Si_2O_2$ [$M^{+\bullet}$]: 366.2410, found 366.2415.

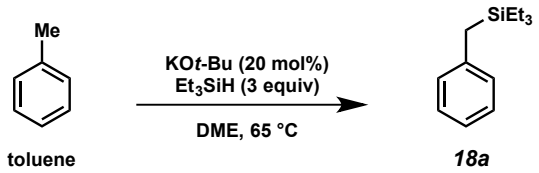


19 — ***20***

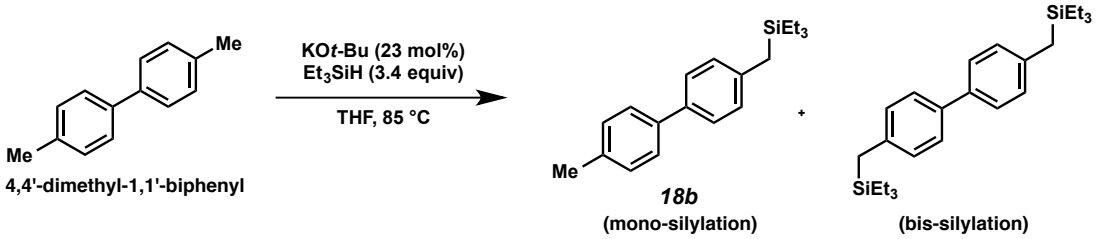
Triethyl(2-methoxy-5-methylphenyl)silane 20: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 1-methoxy-4-methylbenzene **19** (61.0 mg, 0.5 mmol), and Et_3SiH (240 μL, 1.5 mmol, 3 equiv) at 85 °C for 120 h. The desired product **20** (38.5 mg, 32% yield) was obtained after purification by silica gel flash chromatography (100% hexanes) as a colorless oil. R_f = 0.4 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 – 7.08 (m, 2H), 6.74 (dt, *J* = 8.7, 1.3 Hz,

1H), 3.76 (s, 3H), 2.30 (s, 3H), 0.97 – 0.92 (m, 9H), 0.85 – 0.79 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7, 136.7, 130.9, 129.2, 125.0, 109.5, 55.2, 20.8, 7.8, 3.7; IR (Neat Film, NaCl) 2951, 2873, 1595, 1480, 1464, 1385, 1238, 1175, 1147, 1081, 1034, 1004, 876, 806, 708 cm^{-1}; HRMS (EI+) calc'd for $C_{14}H_{24}OSi$ [$M^{+\bullet}$]: 236.1596, found 236.1598.

10. Direct C(sp^3)–H silylation reactions.



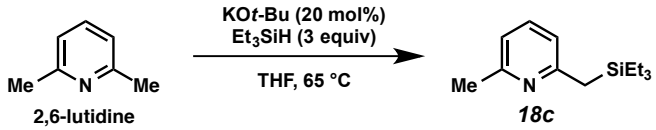
Benzyltriethylsilane 18a: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), toluene (46 mg, 0.5 mmol, 1 equiv), Et_3SiH (243 μL, 1.5 mmol, 3 equiv) and DME (0.5 mL) at 65 °C for 108 h. C(sp^3):C(sp^2) = 18:1. The GC yield of desired product **18a** is 53%. The analytically pure product (25.0 mg, 24% yield) was obtained as a colorless oil after evaporation of starting material and volatiles under vacuum (60 millitorr, 23 °C). *Note: compound **18a** is volatile and readily removed under vacuum.* This compound is known.[15] R_f = 0.8 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (m, 2H), 7.09 – 7.05 (m, 1H), 7.05 – 7.02 (m, 2H), 2.12 (s, 2H), 0.96 – 0.91 (t, 9H), 0.53 (q, *J* = 7.9 Hz, 6H).



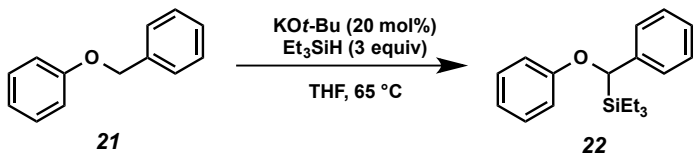
Triethyl((4'-methyl-[1,1'-biphenyl]-4-yl)methyl)silane 18b: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 23 mol%), 4,4'-dimethyl-1,1'-biphenyl (80.0 mg, 0.44 mmol), Et_3SiH (240 μL, 1.5 mmol, 3.4 equiv), and 0.5 mL of THF at 85 °C for 96 h. The ratio of mono-silylation product to bis-silylation product is 16:1. A mixture of desired product **18b** and starting material 4,4'-dimethyl-1,1'-biphenyl (*69.7 mg of mixture, contains 56.6 mg of **18b**, 43% yield, calculated based*

(15) Huckins, J. R.; Rychnovsky, S. D. *J. Org. Chem.* **2003**, *68*, 10135.

on ^1H NMR) was obtained after purification by silica gel flash chromatography (100% hexanes). *A small fraction of analytically pure compound **18b** was obtained as a colorless oil after subsequent purification by silica gel flash chromatography.* R_f = 0.5 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.46 – 7.42 (m, 2H), 7.25 – 7.21 (m, 2H), 7.11 – 7.04 (m, 2H), 2.39 (s, 3H), 2.14 (s, 2H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.54 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.7, 138.5, 136.7, 136.5, 129.6, 128.6, 126.8, 126.7, 21.4, 21.2, 7.5, 3.1; IR (Neat Film, NaCl) 3022, 2951, 2909, 2873, 1610, 1497, 1455, 1416, 1238, 1209, 1153, 1005, 845, 806, 773, 729 cm^{-1}; HRMS (EI+) calc'd for $C_{20}H_{28}Si$ [$M^{+\bullet}$]: 296.1960, found 296.1954.



2-Methyl-6-((triethylsilyl)methyl)pyridine 18c: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%), 2,6-lutidine (53.5 mg, 0.5 mmol), Et_3SiH (240 µL, 1.5 mmol, 3 equiv), and 0.5 mL of THF at 65 °C for 120 h. The desired product **18c** (58.6 mg, 53% yield) was obtained after purification by silica gel flash chromatography (gradient elution, 5%→10% EtOAc in hexanes) as a colorless oil. *Note: compound **18c** is volatile and is readily removed under vacuum.* R_f = 0.3 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.6 Hz, 1H), 6.90 – 6.73 (m, 2H), 2.47 (s, 3H), 2.32 (s, 2H), 0.98 – 0.83 (m, 9H), 0.58 – 0.48 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.8, 157.4, 135.9, 119.0, 118.4, 25.4, 24.5, 7.2, 3.3; IR (Neat Film, NaCl) 3060, 2951, 2874, 1587, 1575, 1450, 1414, 1372, 1269, 1238, 1145, 1078, 1016, 919, 796, 748, 726 cm^{-1}; HRMS (EI+) calc'd for $C_{13}H_{24}NSi$ [M+H]$^+$: 222.1678, found 222.1666.

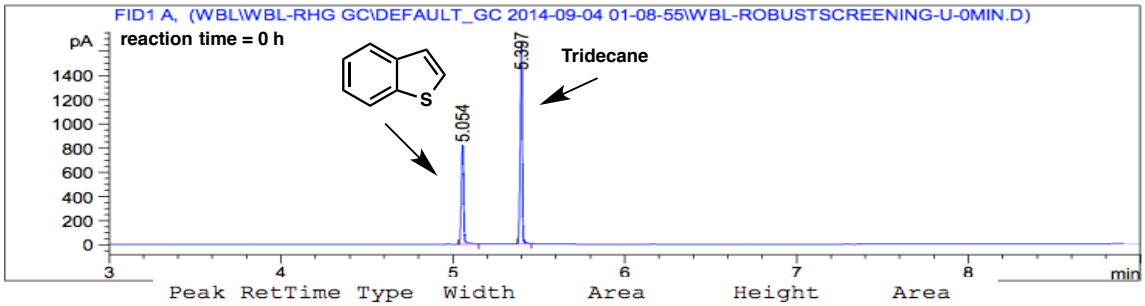


Triethyl(phenoxy(phenyl)methyl)silane 22: The general procedure was followed. The reaction was performed with KO*t*-Bu (11.2 mg, 0.1 mmol, 20 mol%),

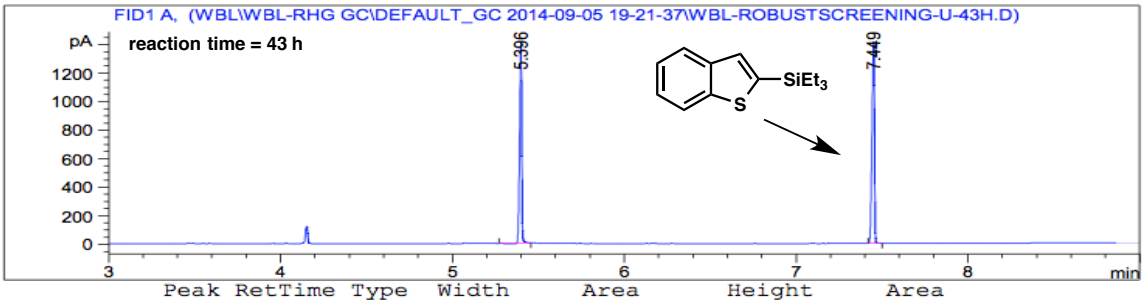
(benzyloxy)benzene **21** (92.0 mg, 0.5 mmol), Et_3SiH (240 μL, 1.5 mmol, 3 equiv), and 0.25 mL of THF at 65 °C for 120 h. The desired product **22** (68.4 mg, 46% yield) was obtained after purification by silica gel flash chromatography (100% hexanes) as a colorless oil. R_f = 0.3 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 4H), 7.38 – 7.28 (m, 4H), 7.30 – 7.20 (m, 2H), 5.80 (s, 1H), 0.92 (t, J = 7.9 Hz, 9H), 0.66 – 0.55 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 128.1, 128.1, 126.9, 126.9, 126.4, 126.3, 6.7, 4.9; IR (Neat Film, NaCl) 3063, 3026, 2954, 2875, 1598, 1492, 1454, 1413, 1302, 1239, 1188, 1090, 1065, 1006, 974, 833, 740, 700 cm^{-1}; HRMS (EI+) calc'd for $C_{19}H_{25}OSi$ $[(M+H)-H_2]^+$: 297.1675, found 297.1668.

Part IV. GC-FID spectra of the robustness screen.

GC-FID spectra of SI-Table 4, entry 1:

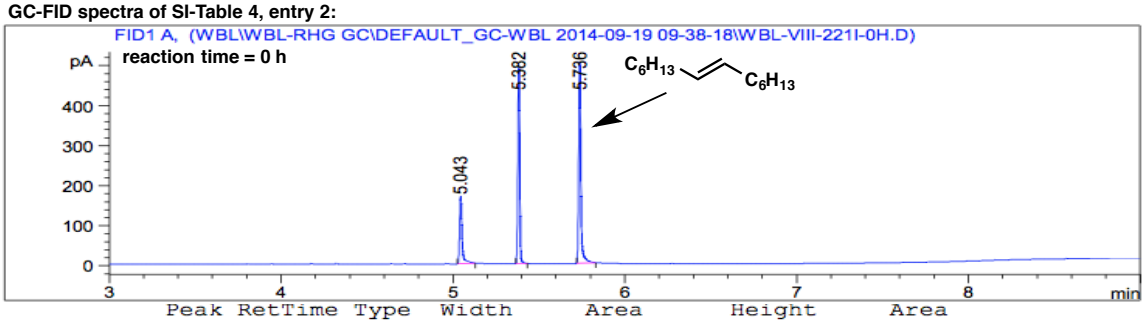


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.054	BB	0.0149	757.81213	813.08362	35.50033
2	5.397	BB	0.0137	1376.85034	1656.54895	64.49967

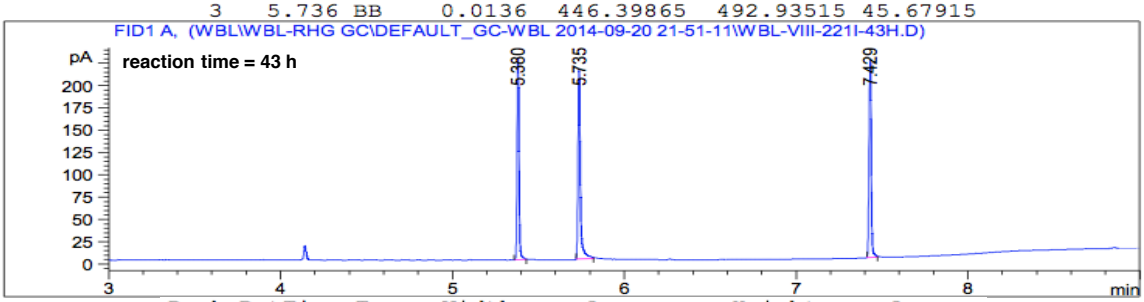


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.396	BB	0.0139	1193.07715	1403.63696	46.17764
2	7.449	BB	0.0161	1390.59131	1344.55493	53.82236

GC-FID spectra of SI-Table 4, entry 2:

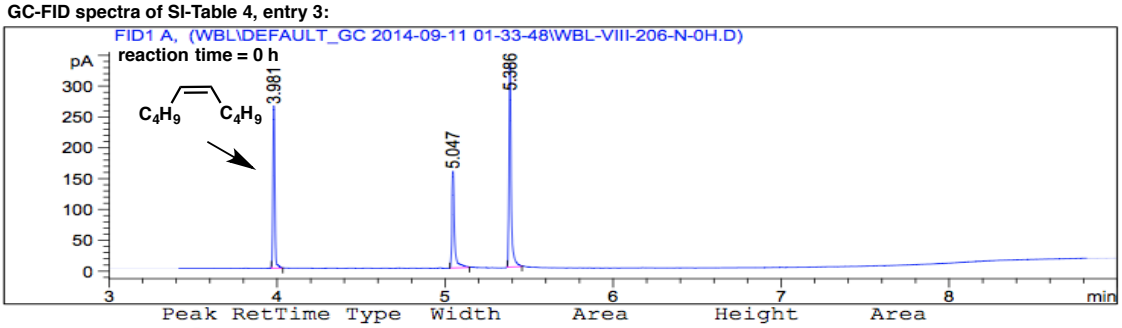


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.043	BB	0.0159	167.35704	164.46207	17.12534
2	5.382	BB	0.0118	363.49246	483.96515	37.19551
3	5.736	BB	0.0136	446.39865	492.93515	45.67915

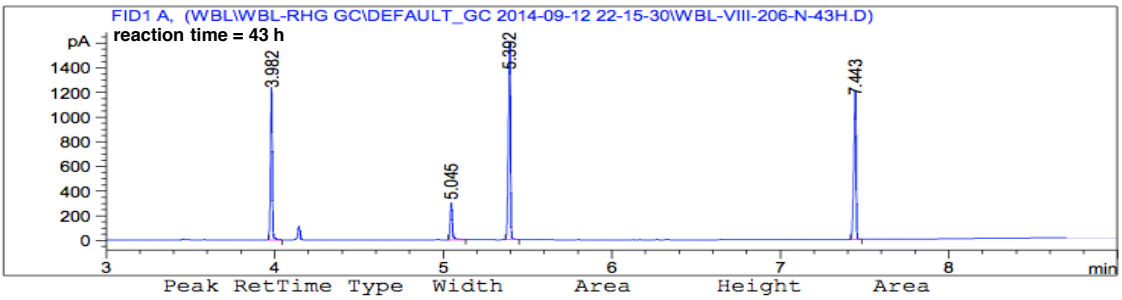


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.380	BB	0.0132	172.35509	218.78630	30.70791
2	5.735	BB	0.0142	200.51813	209.03979	35.72563
3	7.429	BB	0.0142	188.39932	215.53876	33.56646

GC-FID spectra of SI-Table 4, entry 3:

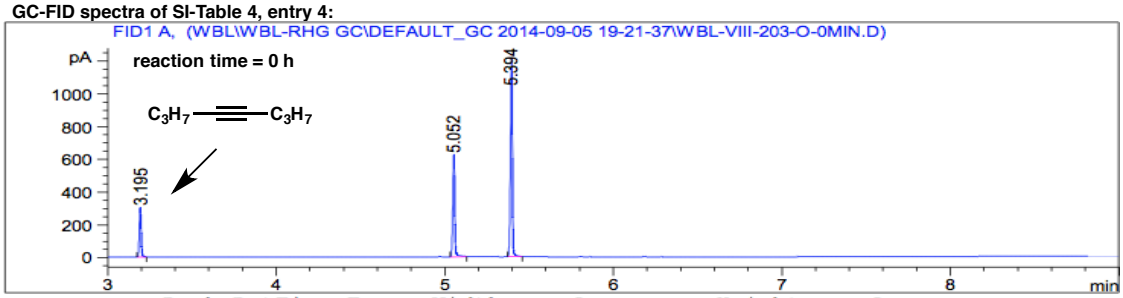


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.981	BB	0.0121	203.23712	259.37045	30.86568
2	5.047	BB	0.0163	163.03261	154.42287	24.75981
3	5.386	BB	0.0147	292.18683	317.25317	44.37450

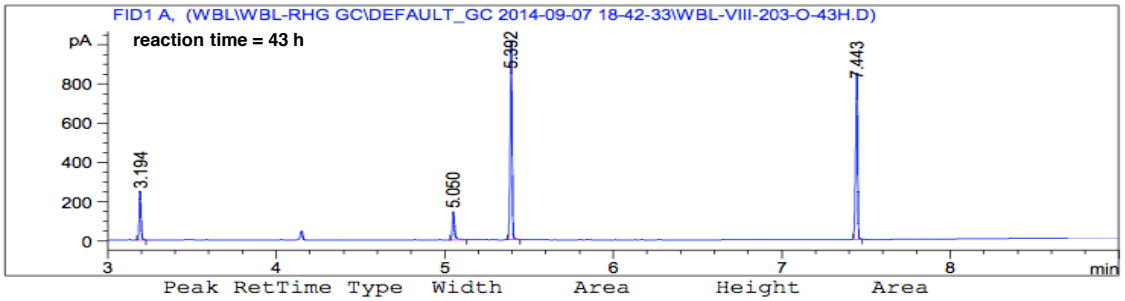


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.982	BB	0.0121	940.36487	1207.33105	25.44243
2	5.045	BB	0.0137	269.47769	293.51743	7.29096
3	5.392	BB	0.0134	1396.98389	1564.41138	37.79667
4	7.443	BB	0.0152	1089.22388	1136.62244	29.46994

GC-FID spectra of SI-Table 4, entry 4:

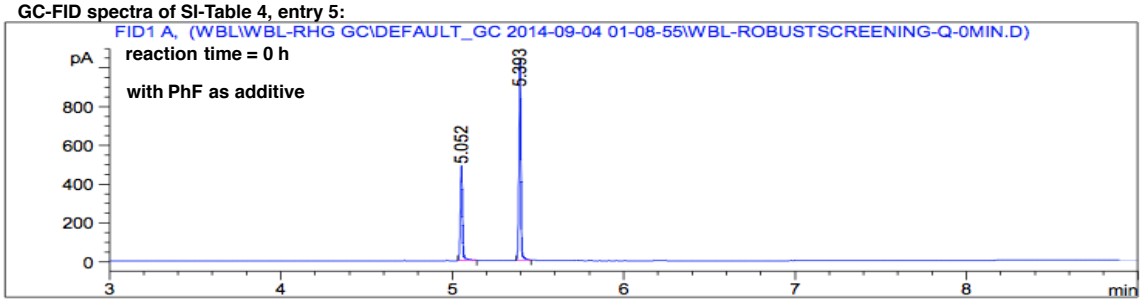


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.195	BB	0.0133	233.26434	293.04001	13.60265
2	5.052	BB	0.0130	527.93085	613.78699	30.78591

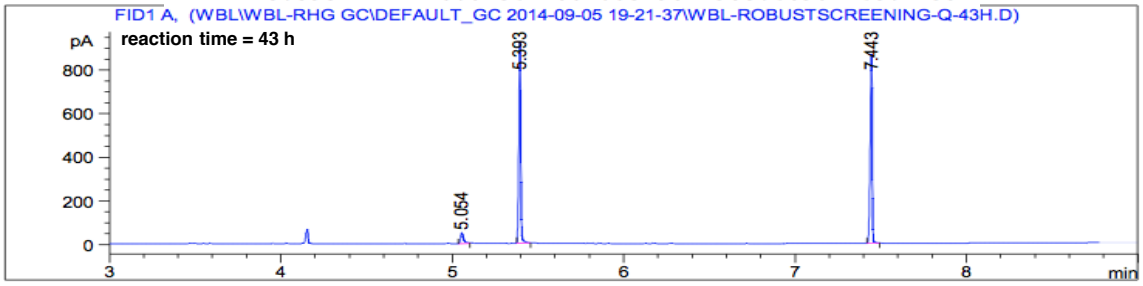


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.194	BB	0.0133	194.81905	244.24142	10.56992
2	5.050	BB	0.0152	135.15347	140.84714	7.33276
3	5.392	BB	0.0126	807.20825	980.40820	43.79512
4	7.443	BB	0.0143	705.96582	803.04401	38.30221

GC-FID spectra of SI-Table 4, entry 5:

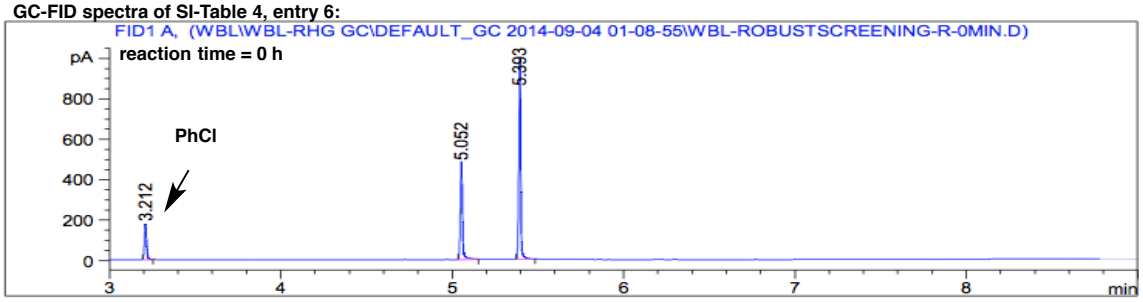


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.052	BB	0.0134	432.28278	483.75388	34.88006
2	5.393	BB	0.0136	807.05798	983.66907	65.11994

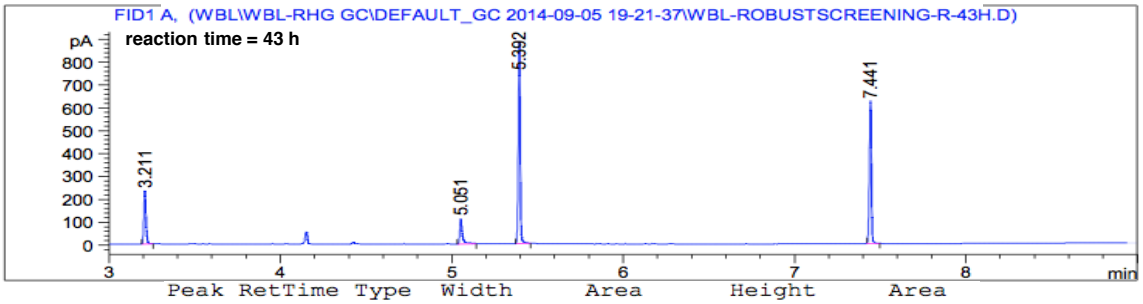


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.054	BB	0.0185	60.12766	48.45945	3.97540
2	5.393	BB	0.0136	724.24512	882.39813	47.88423
3	7.443	BB	0.0138	728.11908	866.32690	48.14036

GC-FID spectra of SI-Table 4, entry 6:

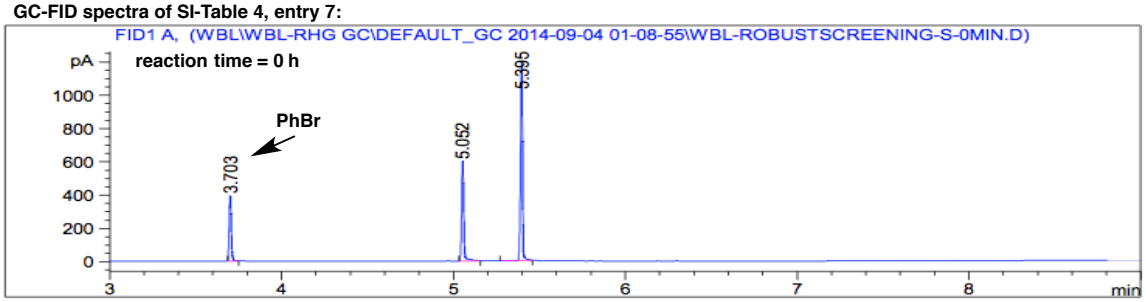


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.212	BB	0.0133	154.23224	173.96222	11.30731
2	5.052	BB	0.0135	425.45627	473.00186	31.19169
3	5.393	BB	0.0134	784.31653	977.44501	57.50100

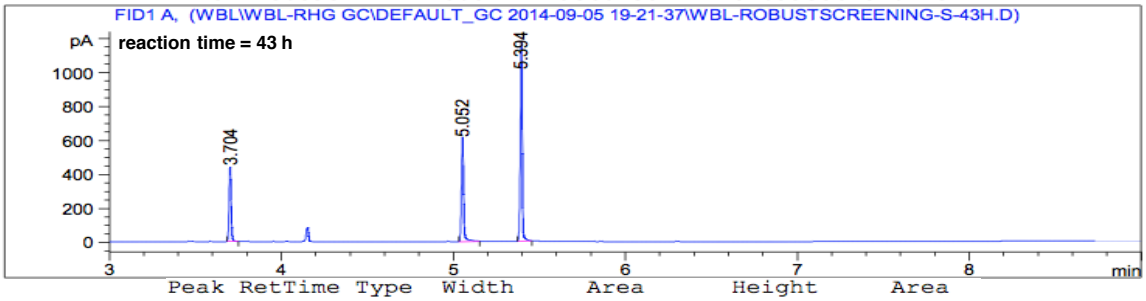


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.211	BB	0.0145	205.19017	229.02733	13.32845
2	5.051	BB	0.0175	123.75800	107.26932	8.03890
3	5.392	BB	0.0124	683.63361	851.12238	44.40650
4	7.441	BB	0.0129	526.90802	619.05310	34.22615

GC-FID spectra of SI-Table 4, entry 7:

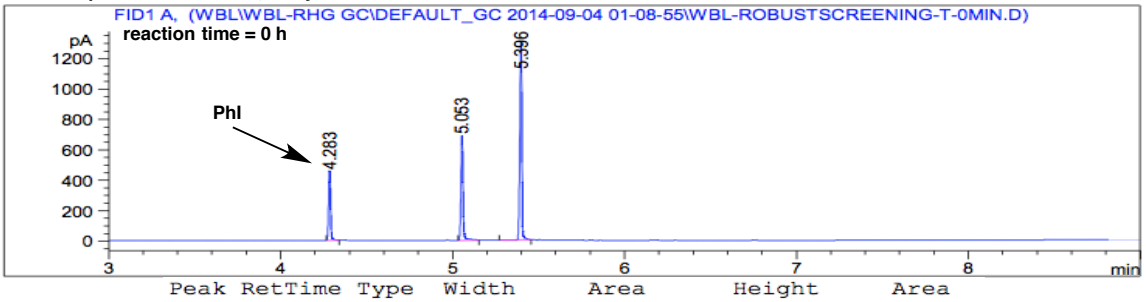


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.703	BB	0.0137	321.18744	384.43445	17.70586
2	5.052	BB	0.0146	536.59937	587.90198	29.58071
3	5.395	BB	0.0124	956.23077	1187.99536	52.71342

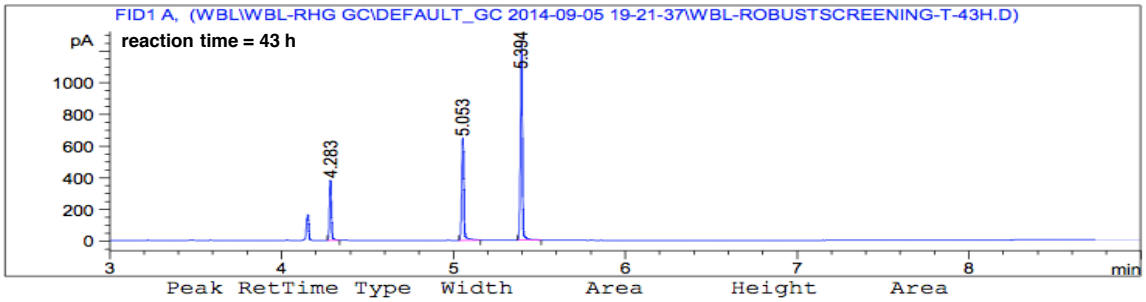


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.704	BB	0.0137	354.46970	425.76340	19.23968
2	5.052	BB	0.0134	533.08838	597.62415	28.93462
3	5.394	BB	0.0136	954.83105	1163.62964	51.82570

GC-FID spectra of SI-Table 4, entry 8:

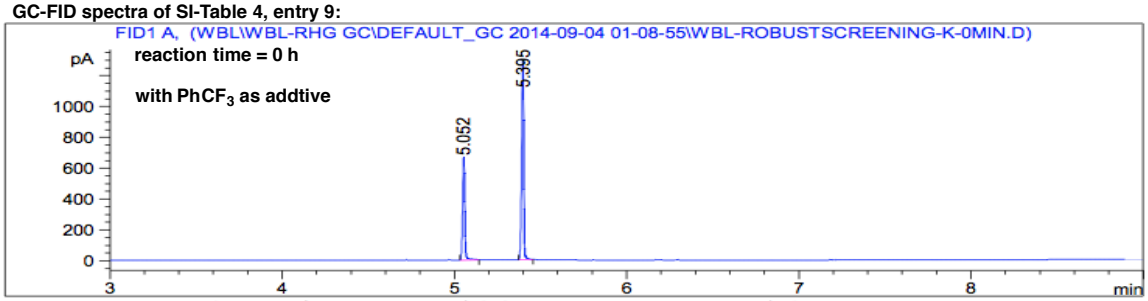


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.283	BB	0.0138	372.08484	444.89694	18.28708
2	5.053	BB	0.0145	604.12518	671.07733	29.69130
3	5.396	BB	0.0127	1058.47729	1274.90295	52.02162

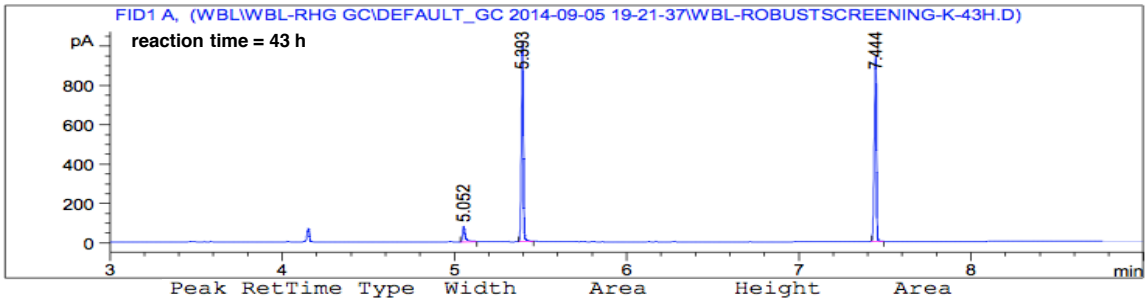


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.283	BB	0.0126	305.44244	372.80069	16.14080
2	5.053	BB	0.0146	577.15674	635.40320	30.49928
3	5.394	BB	0.0135	1009.76276	1238.18677	53.35992

GC-FID spectra of SI-Table 4, entry 9:

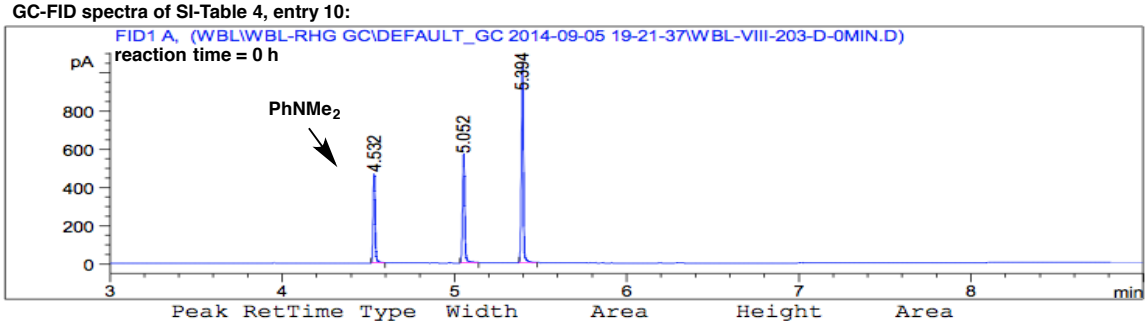


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.052	BB	0.0135	588.29590	655.02374	35.17884
2	5.395	BB	0.0130	1084.00464	1270.07581	64.82116

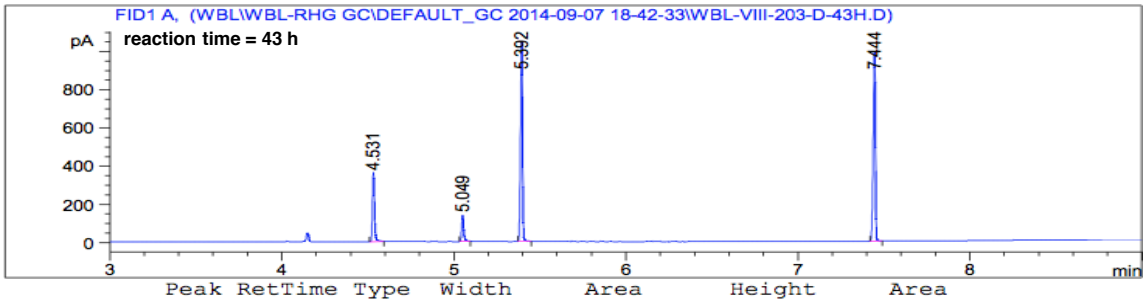


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.052	BB	0.0160	88.95304	79.72253	5.24940
2	5.393	BB	0.0138	804.46118	955.82367	47.47379
3	7.444	BB	0.0139	801.12335	939.42273	47.27681

GC-FID spectra of SI-Table 4, entry 10:

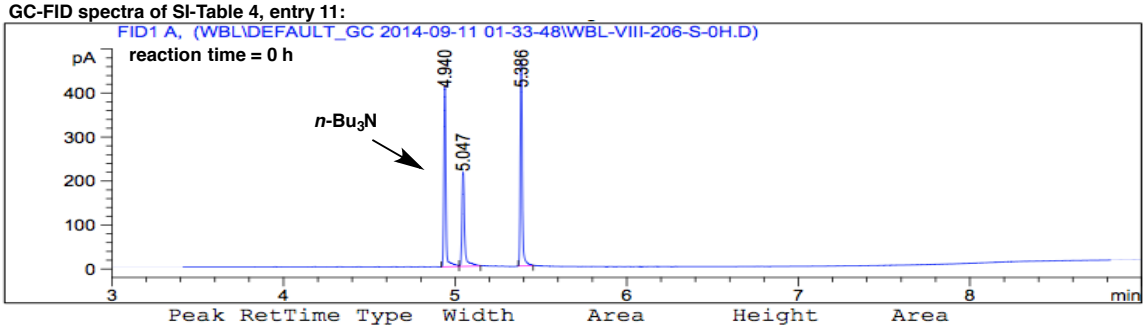


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.532	BB	0.0137	377.70926	454.98398	21.89827
2	5.052	BB	0.0145	499.47571	553.67822	28.95787
3	5.394	BB	0.0126	847.65112	1034.31641	49.14387

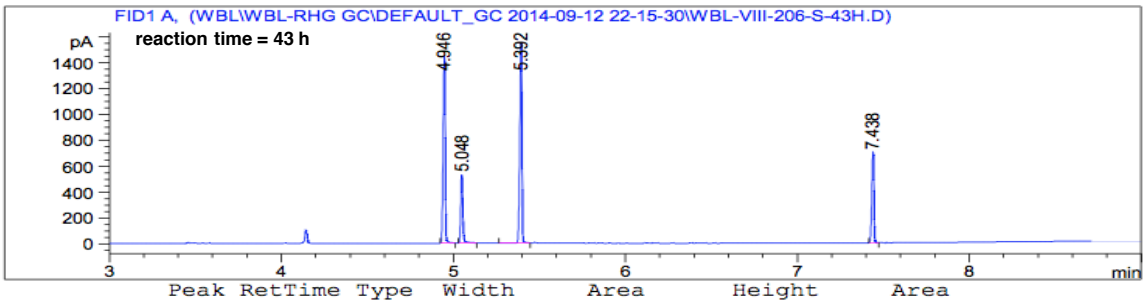


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.531	BB	0.0138	297.83487	354.08572	14.02392
2	5.049	BB	0.0146	121.14701	133.53572	5.70436
3	5.392	BB	0.0127	842.06940	1013.86646	39.64987
4	7.444	BB	0.0142	862.71204	989.58295	40.62185

GC-FID spectra of SI-Table 4, entry 11:

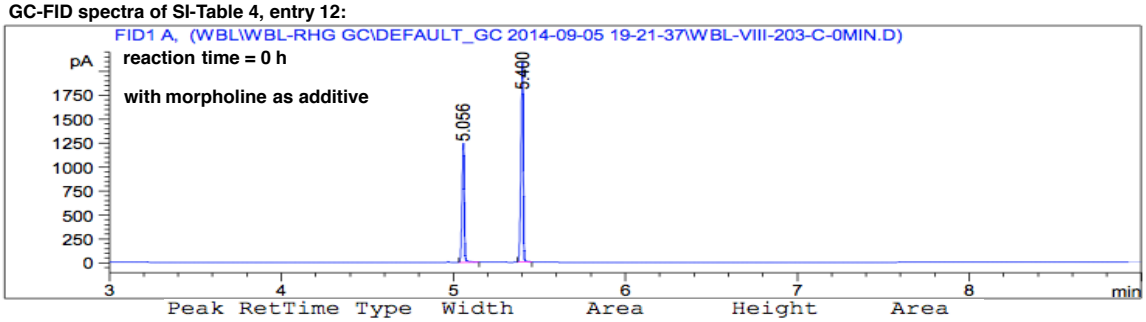


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.940	BV	0.0137	330.20572	398.56238	35.52488
2	5.047	VB	0.0164	219.53682	207.19090	23.61867
3	5.386	BB	0.0127	379.76306	457.34445	40.85646

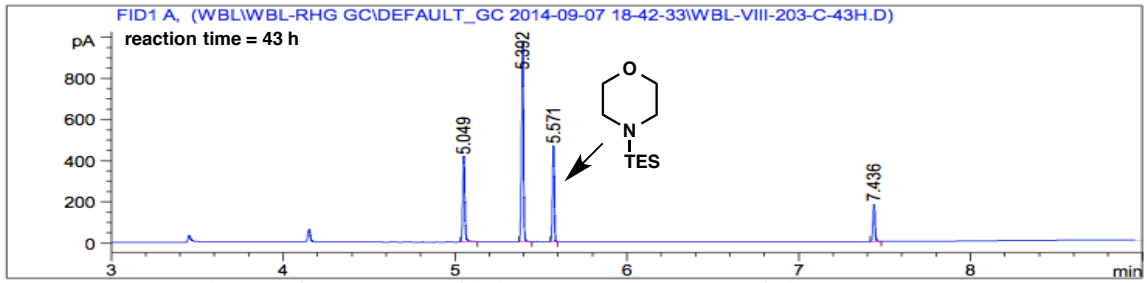


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.946	BB	0.0141	1203.80591	1394.00037	33.46110
2	5.048	BB	0.0145	471.45068	522.15521	13.10449
3	5.392	BB	0.0132	1334.67249	1523.16736	37.09868
4	7.438	BB	0.0129	587.69885	689.41693	16.33573

GC-FID spectra of SI-Table 4, entry 12:

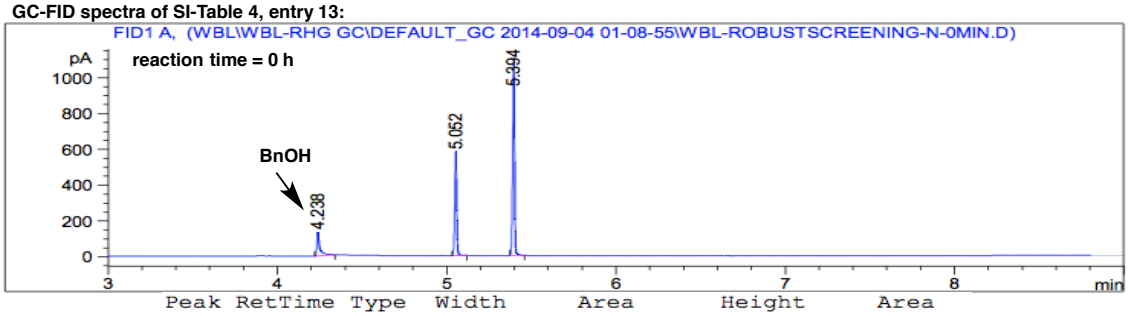


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.056	BB	0.0146	1114.04028	1226.71338	36.92116
2	5.400	BB	0.0154	1903.30896	1953.58960	63.07884

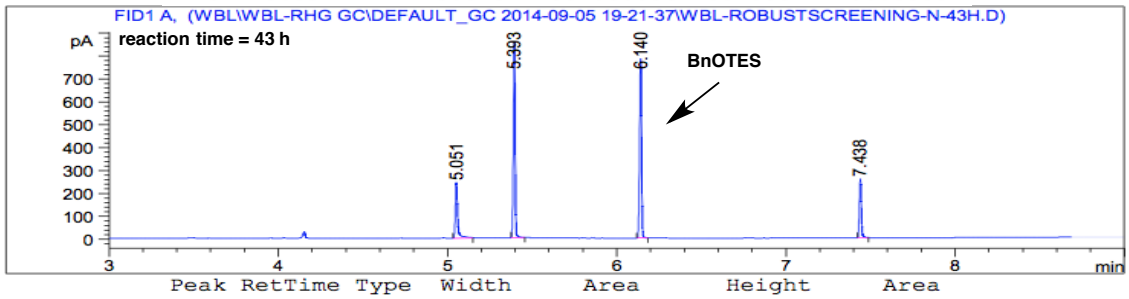


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.049	BB	0.0143	359.11511	406.27972	21.90699
2	5.392	BB	0.0126	783.82477	952.01721	47.81542
3	5.571	BB	0.0116	338.93201	457.76031	20.67577
4	7.436	BB	0.0144	157.39992	176.92252	9.60182

GC-FID spectra of SI-Table 4, entry 13:

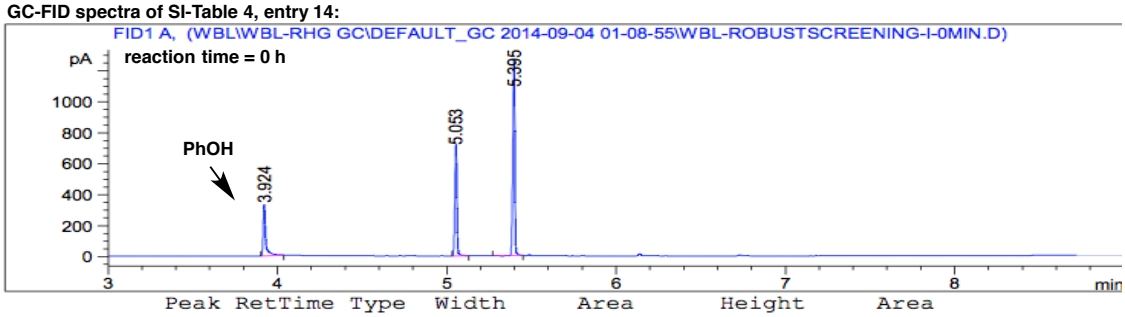


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.238	BB	0.0190	164.34883	127.53644	10.89584
2	5.052	BB	0.0130	489.51434	571.82513	32.45335
3	5.394	BB	0.0132	854.50006	1081.55774	56.65081

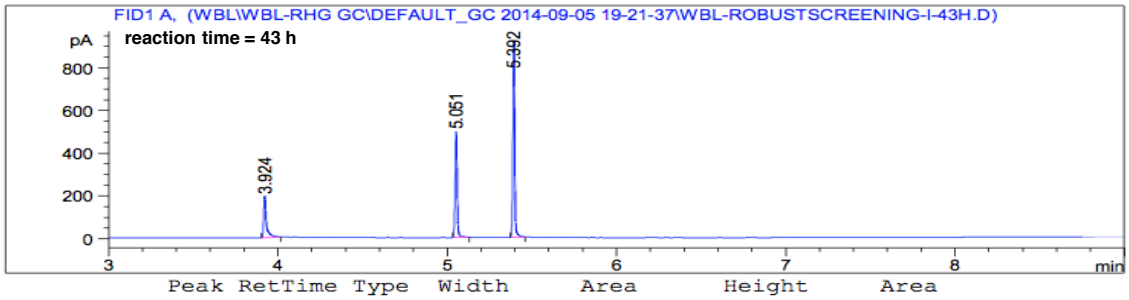


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.051	BB	0.0157	237.87219	237.71118	14.04074
2	5.393	BB	0.0130	629.44916	818.91058	37.15411
3	6.140	BB	0.0137	623.10913	746.75342	36.77988
4	7.438	BB	0.0124	203.72693	254.05693	12.02527

GC-FID spectra of SI-Table 4, entry 14:

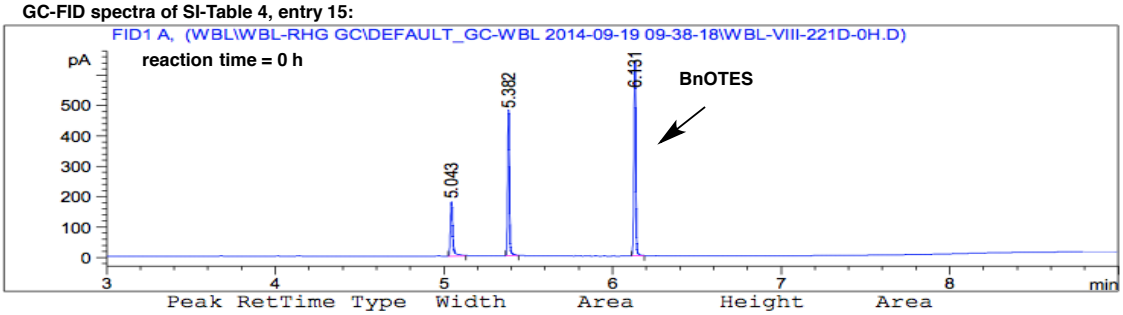


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.924	BB	0.0167	347.61041	318.65836	17.61199
2	5.053	BB	0.0141	596.71674	691.87122	30.23318
3	5.395	BB	0.0129	1029.38770	1215.88281	52.15483

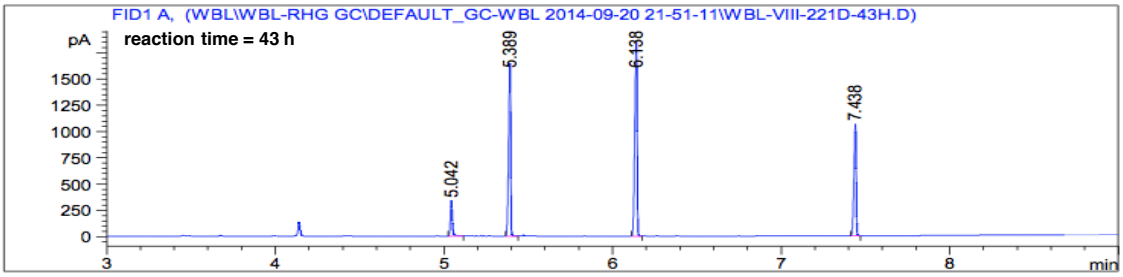


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.924	BB	0.0177	219.71886	186.97559	16.18693
2	5.051	BB	0.0130	419.85248	489.05118	30.93100
3	5.392	BB	0.0124	717.81268	889.42621	52.88206

GC-FID spectra of SI-Table 4, entry 15:

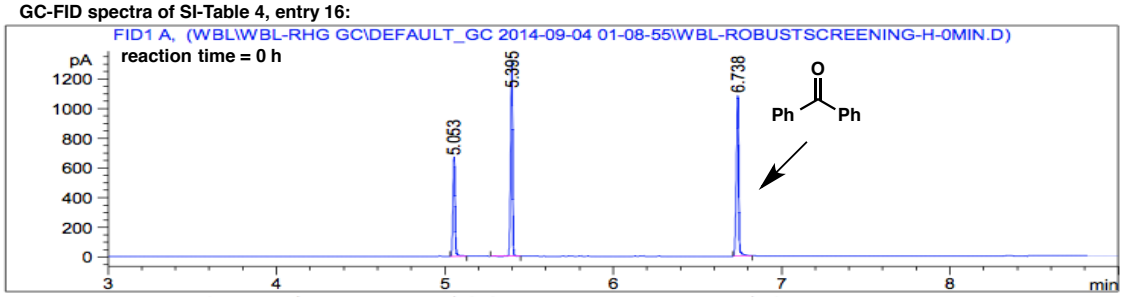


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.043	BB	0.0157	177.43666	176.76627	17.25147
2	5.382	BB	0.0117	350.31625	472.30042	34.05988
3	6.131	BB	0.0132	500.77747	634.92981	48.68864

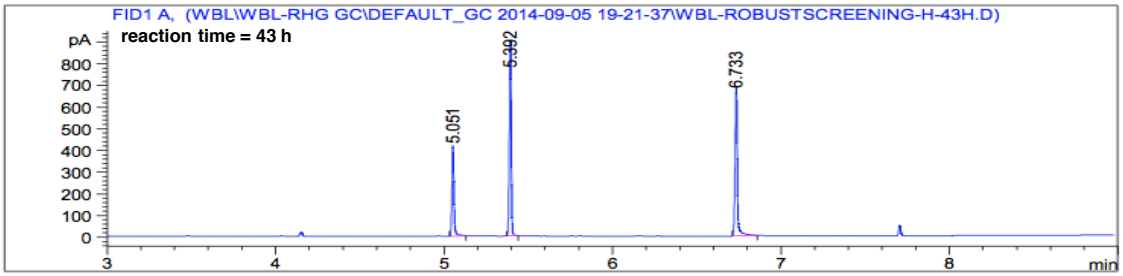


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.042	BB	0.0130	285.85907	334.54684	6.61147
2	5.389	BB	0.0130	1359.89429	1584.62854	31.45222
3	6.138	BB	0.0152	1734.73511	1799.69421	40.12170
4	7.438	BB	0.0144	943.19476	1057.01978	21.81461

GC-FID spectra of SI-Table 4, entry 16:

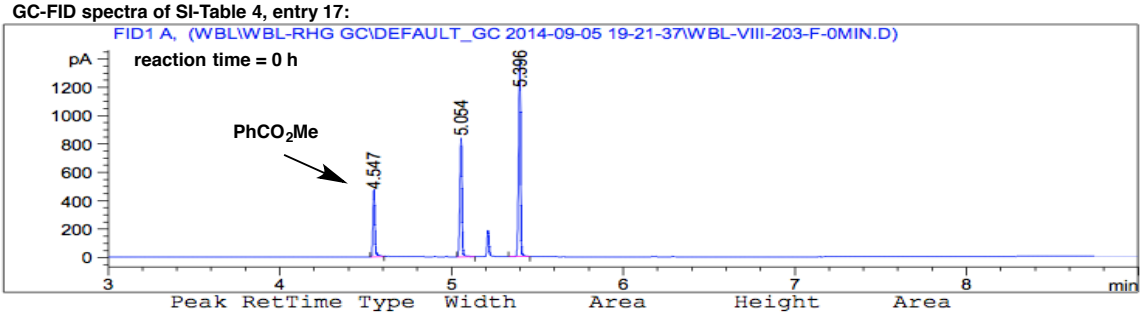


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.053	BB	0.0144	581.33722	653.60175	22.02989
2	5.395	BB	0.0123	1024.88892	1285.39587	38.83837
3	6.738	BB	0.0152	1032.63074	1078.53052	39.13174

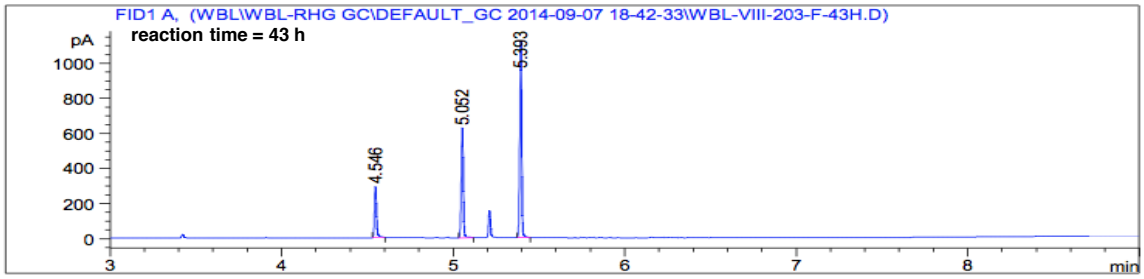


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.051	BB	0.0144	362.96750	408.90005	20.54536
2	5.392	BB	0.0123	701.74109	884.47821	39.72125
3	6.733	BB	0.0153	643.90259	665.52136	36.44737
4	10.496	BB	0.0239	58.05304	35.86992	3.28603

GC-FID spectra of SI-Table 4, entry 17:

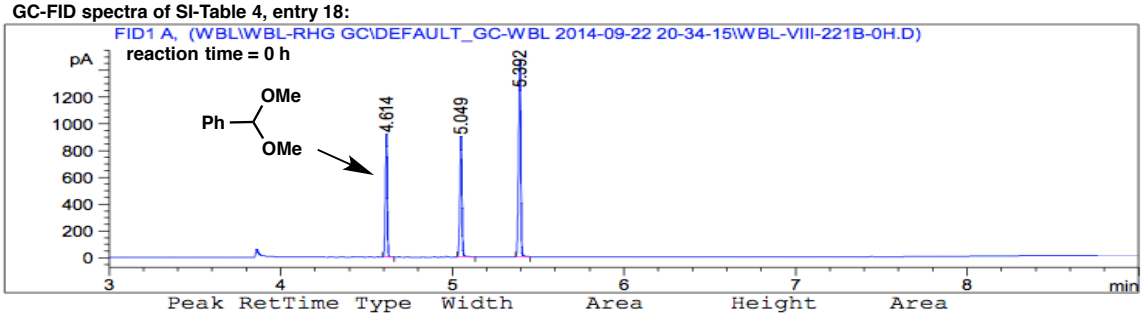


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.547	BB	0.0138	379.91116	454.35962	16.80495
2	5.054	BB	0.0140	708.21655	824.81445	31.32717
3	5.396	BB	0.0144	1172.58264	1309.76538	51.86788

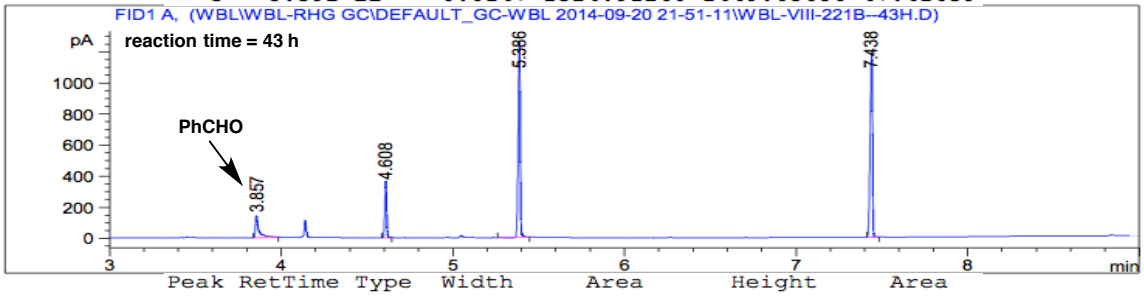


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.546	BB	0.0128	239.78859	286.69708	14.65431
2	5.052	BB	0.0127	514.46545	616.55530	31.44076
3	5.393	BB	0.0137	882.04706	1057.42419	53.90494

GC-FID spectra of SI-Table 4, entry 18:

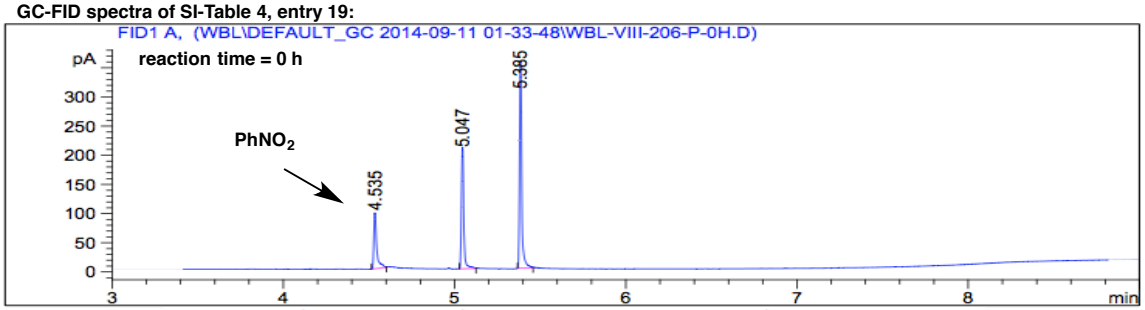


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.614	BB	0.0131	700.10925	902.38428	25.05573
2	5.049	BB	0.0131	769.18634	887.87695	27.52788
3	5.392	BB	0.0147	1324.91260	1449.65686	47.41639

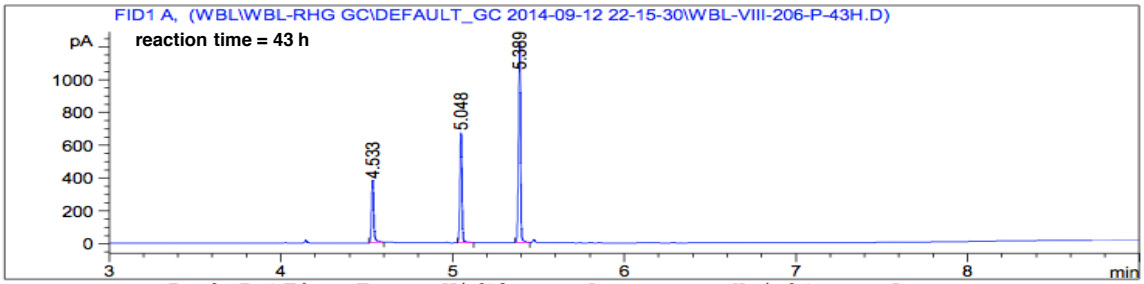


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.857	BB	0.0214	205.34763	137.73538	7.82671
2	4.608	BB	0.0129	268.36557	350.84610	10.22861
3	5.386	BB	0.0127	1024.33691	1225.97473	39.04203
4	7.438	BB	0.0151	1125.62695	1178.64563	42.90265

GC-FID spectra of SI-Table 4, entry 19:

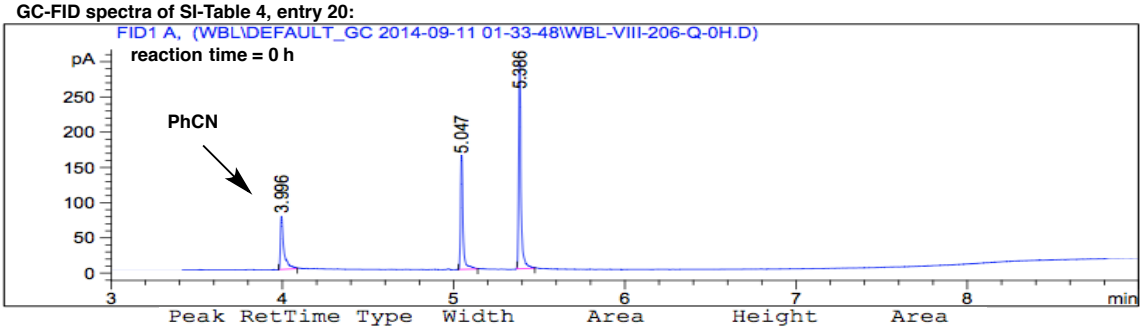


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.535	BB	0.0177	111.61236	94.77935	18.16164
2	5.047	BB	0.0150	190.39711	201.12346	30.98156
3	5.385	BB	0.0134	312.54041	351.13321	50.85680

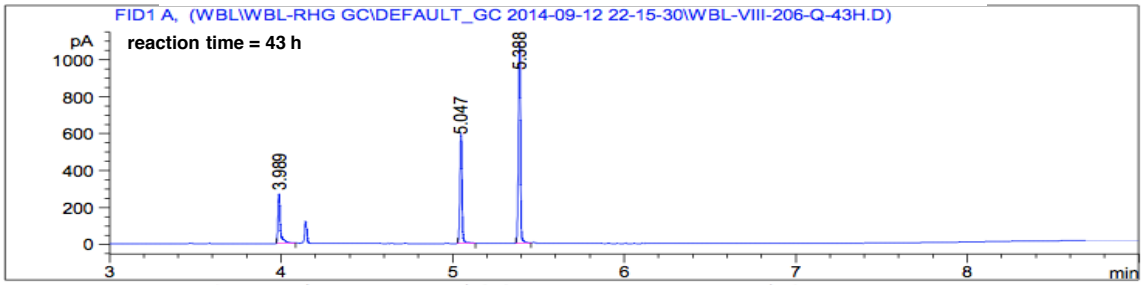


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.533	BB	0.0150	347.16339	367.95538	18.21877
2	5.048	BB	0.0130	570.93298	664.53088	29.96196
3	5.389	BV	0.0141	987.42975	1141.82764	51.81927

GC-FID spectra of SI-Table 4, entry 20:

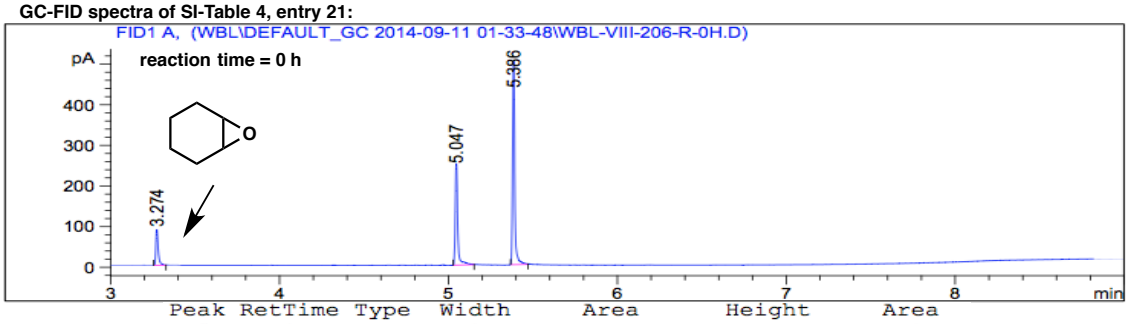


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.996	BB	0.0203	104.37083	74.60351	19.55841
2	5.047	BB	0.0158	161.13466	159.39436	30.19557
3	5.386	BB	0.0149	268.13120	286.23087	50.24602

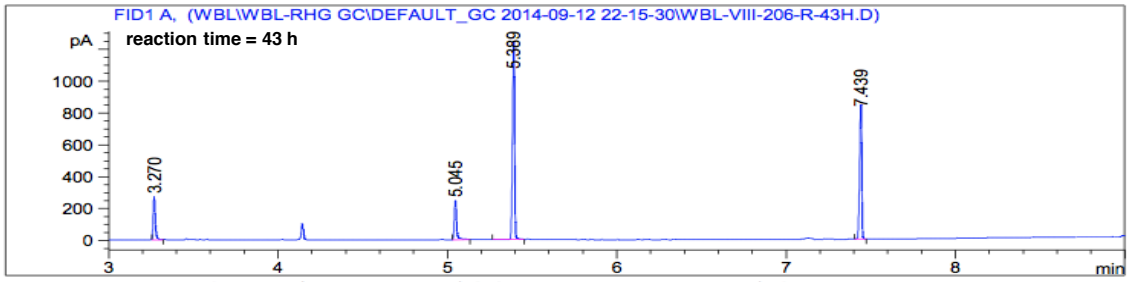


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.989	BB	0.0154	283.01514	267.23007	16.80506
2	5.047	BB	0.0144	506.30051	569.71454	30.06345
3	5.388	BV	0.0137	894.79102	1078.10925	53.13149

GC-FID spectra of SI-Table 4, entry 21:

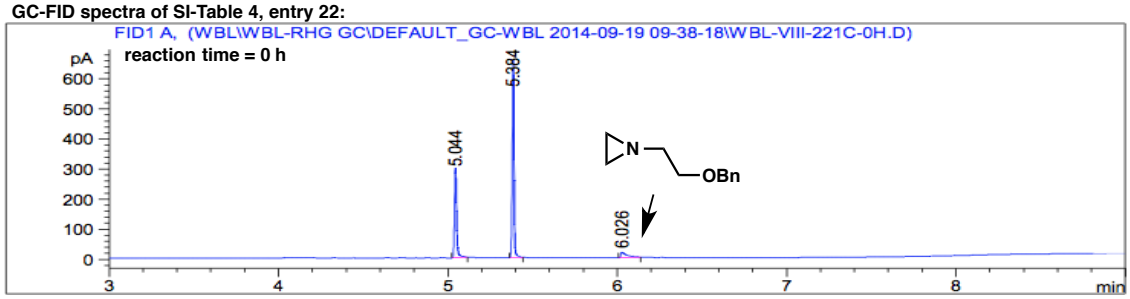


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.274	BB	0.0155	84.74000	86.20313	11.10321
2	5.047	BB	0.0159	247.62512	242.42696	32.44551
3	5.386	BB	0.0143	430.83789	489.86090	56.45128

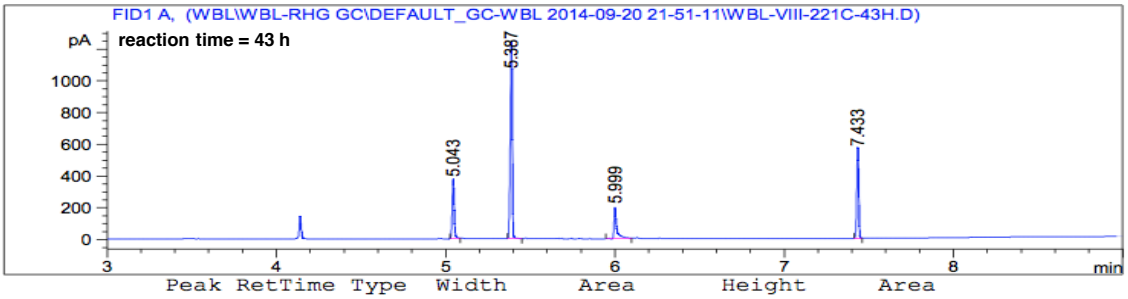


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.270	BB	0.0145	237.99971	264.70377	10.68970
2	5.045	BB	0.0140	228.91533	242.20050	10.28168
3	5.389	BB	0.0141	1037.04797	1199.63281	46.57877
4	7.439	BB	0.0144	722.47601	810.45892	32.44985

GC-FID spectra of SI-Table 4, entry 22:

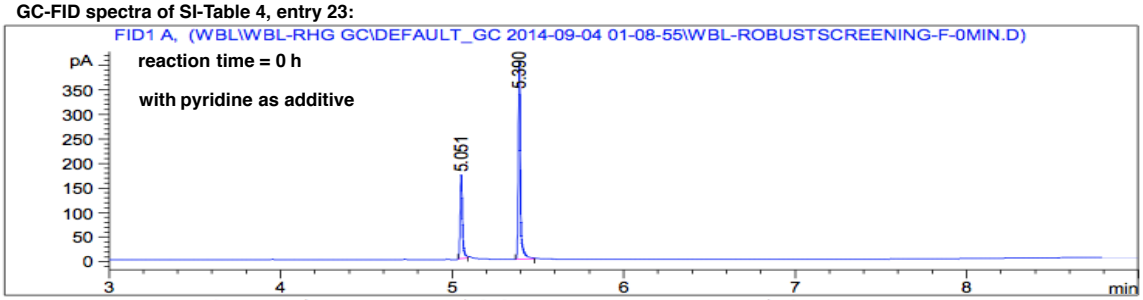


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.044	BB	0.0144	259.58676	290.56866	32.05666
2	5.384	BB	0.0130	503.19037	649.27142	62.13955
3	6.026	BB	0.0314	46.99762	19.29555	5.80379

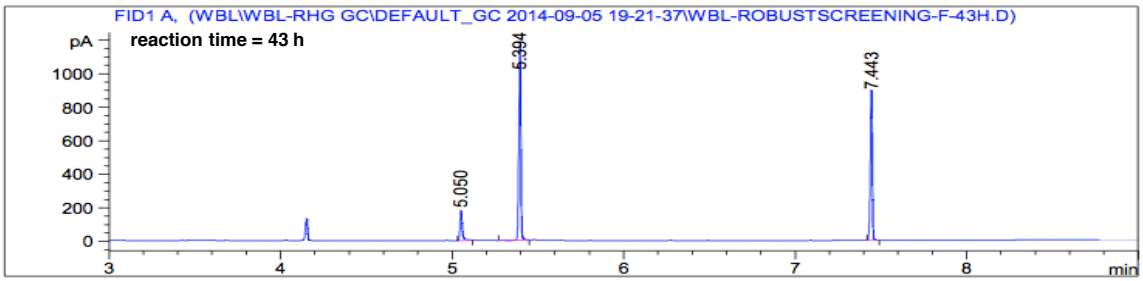


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.043	BB	0.0129	312.46866	367.83182	15.38465
2	5.387	BB	0.0140	1016.13641	1183.95178	50.03032
3	5.999	BB	0.0168	232.78250	197.34129	11.46124
4	7.433	BB	0.0138	469.65353	557.11810	23.12378

GC-FID spectra of SI-Table 4, entry 23:

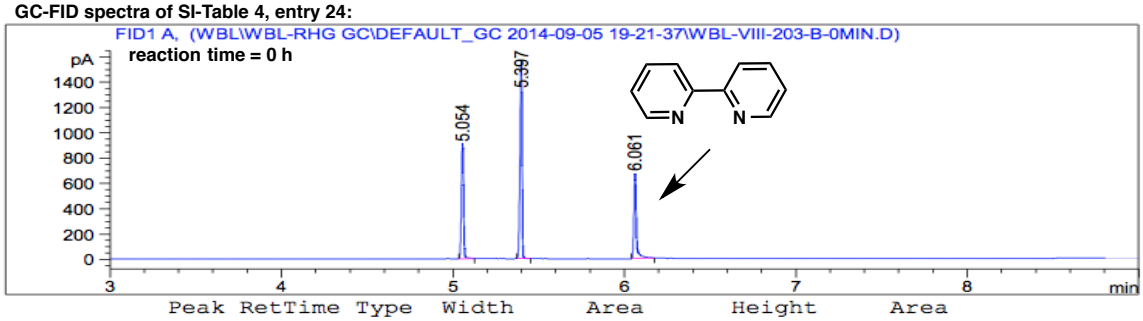


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.051	BB	0.0138	156.20609	168.59203	31.01447
2	5.390	BB	0.0143	347.44943	394.23758	68.98553

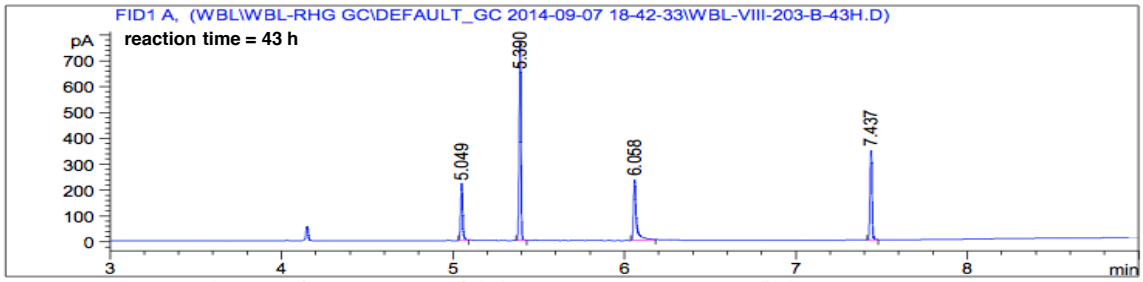


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.050	BB	0.0150	166.53435	176.15463	8.89926
2	5.394	BB	0.0135	951.68530	1171.16174	50.85614
3	7.443	BB	0.0140	753.10858	882.47650	40.24460

GC-FID spectra of SI-Table 4, entry 24:

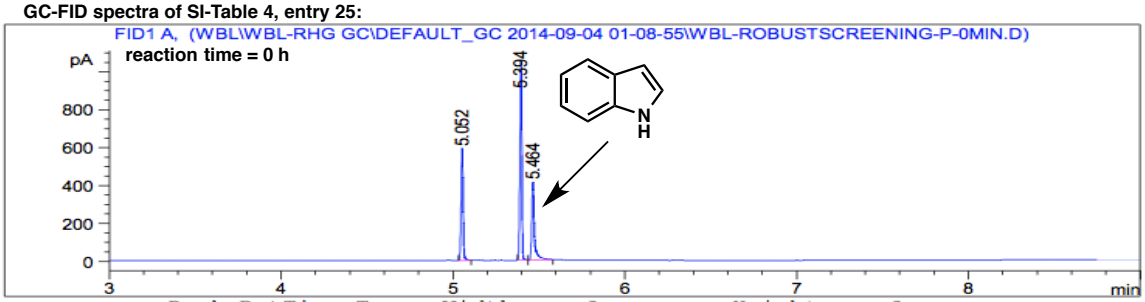


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.054	BB	0.0142	784.29218	899.93848	28.42038
2	5.397	BB	0.0137	1296.84875	1561.22388	46.99389
3	6.061	BB	0.0159	678.47058	665.00964	24.58573

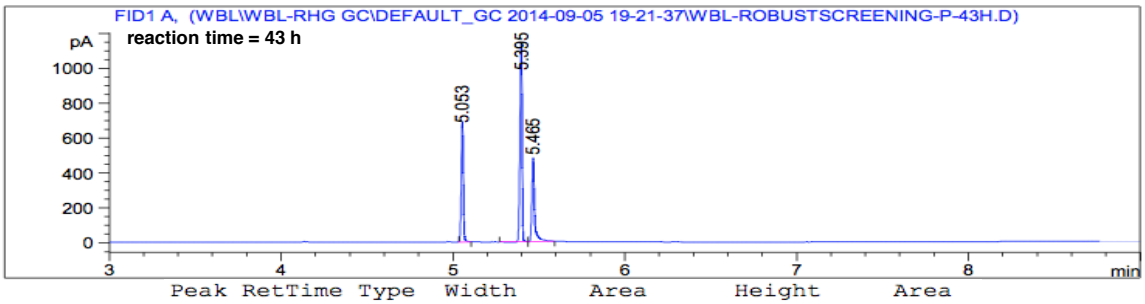


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.049	BB	0.0130	186.29955	217.96092	14.19997
2	5.390	BB	0.0126	550.36261	746.06616	41.94928
3	6.058	BB	0.0183	287.27814	233.70592	21.89667
4	7.437	BB	0.0137	288.03137	347.25116	21.95408

GC-FID spectra of SI-Table 4, entry 25:

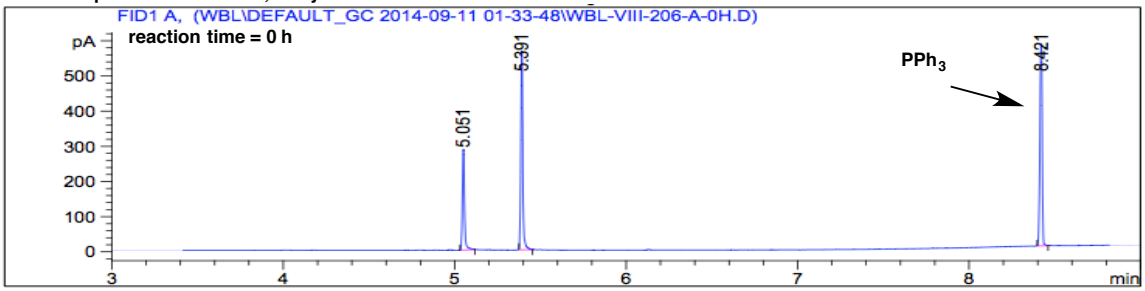


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.052	BB	0.0126	480.47305	581.80505	27.64849
2	5.394	BV	0.0122	819.30896	1037.32178	47.14657
3	5.464	VB	0.0167	438.00916	403.49310	25.20494

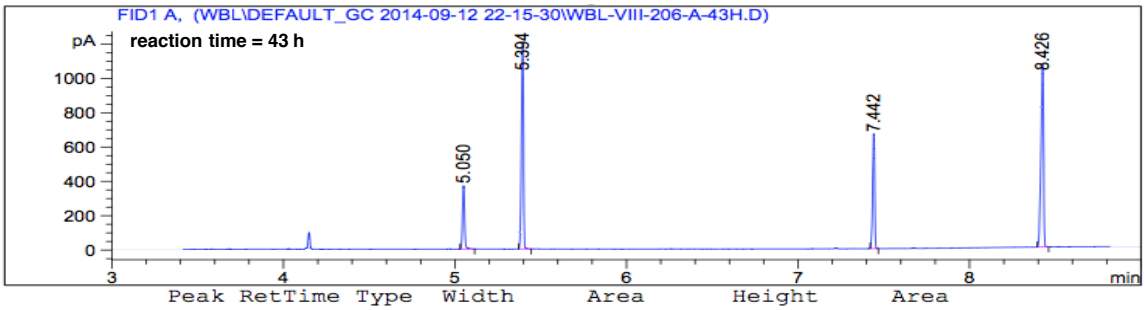


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.053	BB	0.0140	566.89130	664.10944	27.16086
2	5.395	BV	0.0144	991.34656	1110.61658	47.49734
3	5.465	VB	0.0170	528.92432	473.68710	25.34179

GC-FID spectra of SI-Table 4, entry 26:

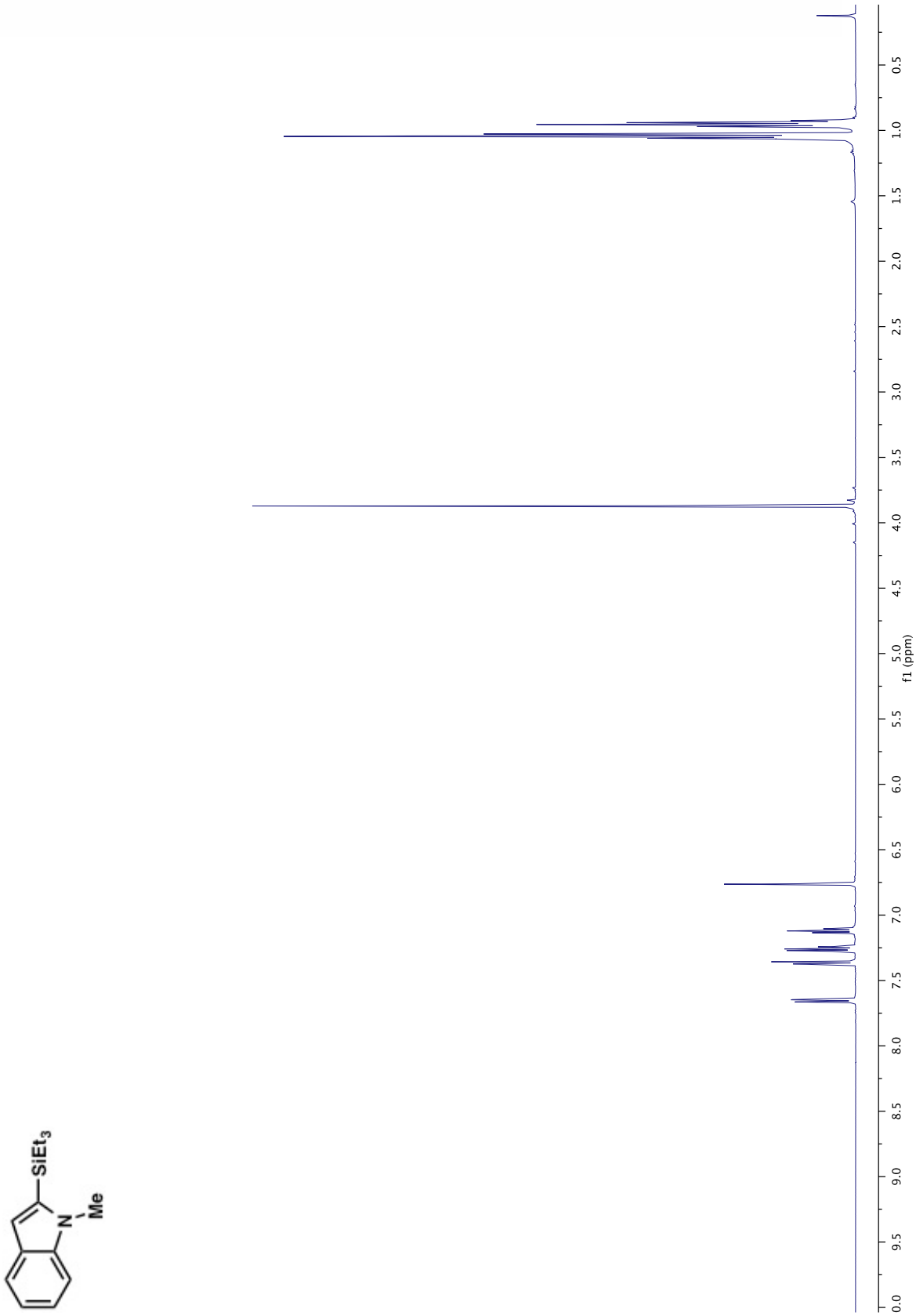


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.051	BB	0.0144	250.97217	282.10843	20.80203
2	5.391	BB	0.0122	436.13669	555.49304	36.14953
3	8.421	BB	0.0146	519.37061	570.63788	43.04844

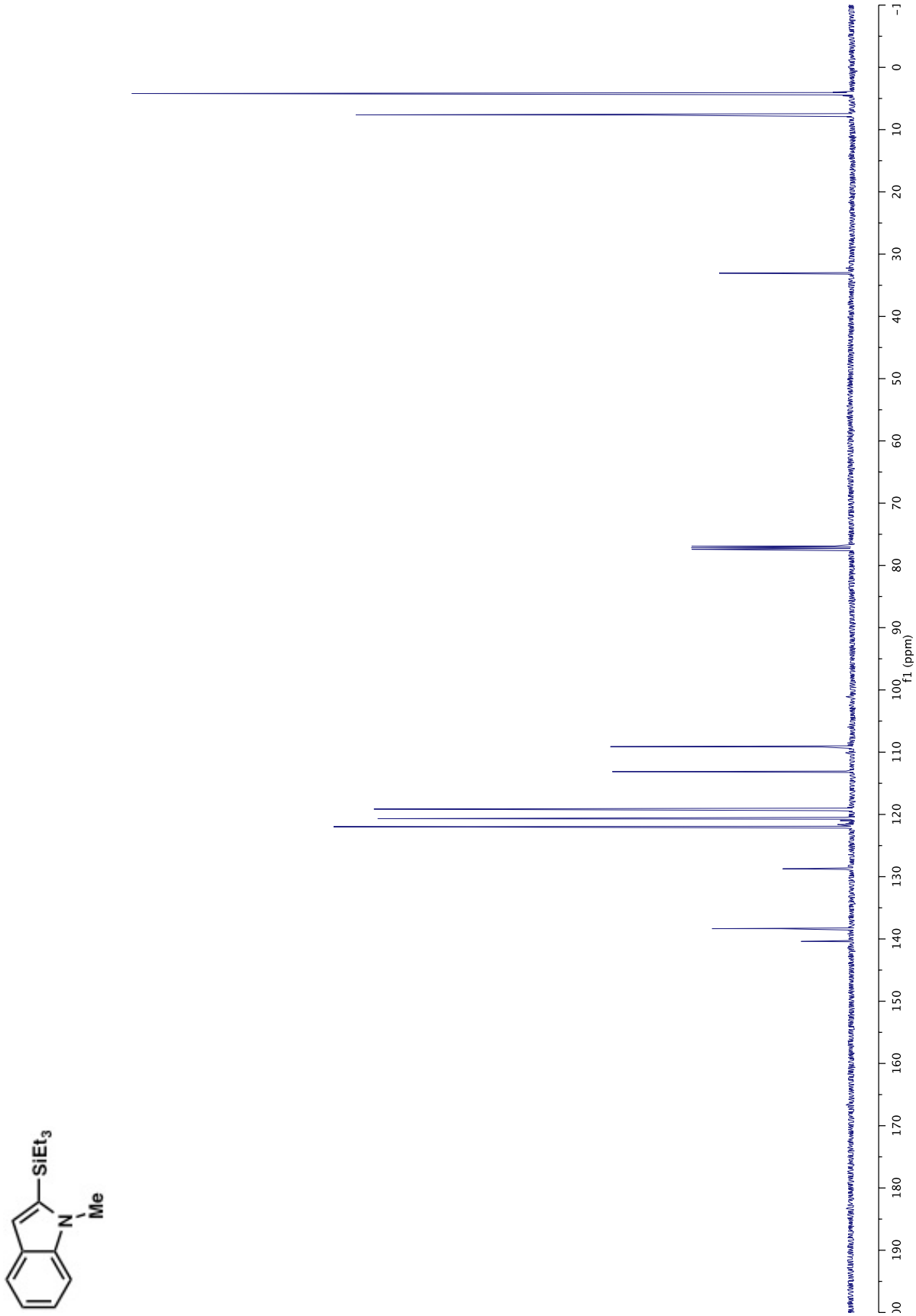


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.050	BB	0.0139	308.54736	363.27356	10.49166
2	5.394	BB	0.0125	970.49554	1192.30505	33.00015
3	7.442	BB	0.0125	535.07501	656.23175	18.19437
4	8.426	BB	0.0168	1126.76465	1028.11218	38.31383

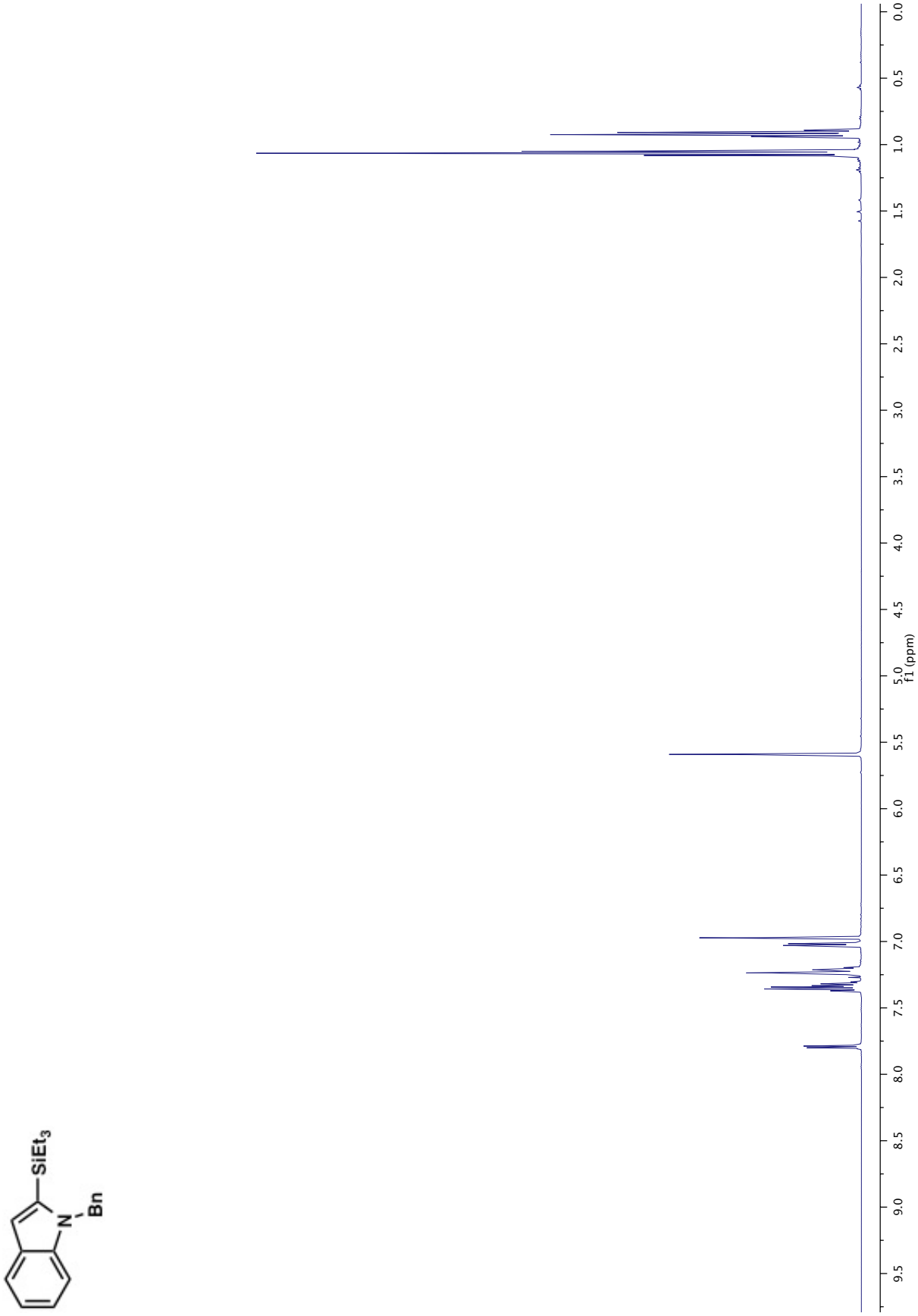
3 ^{1}H NMR and ^{13}C NMR Spectra of New Compounds



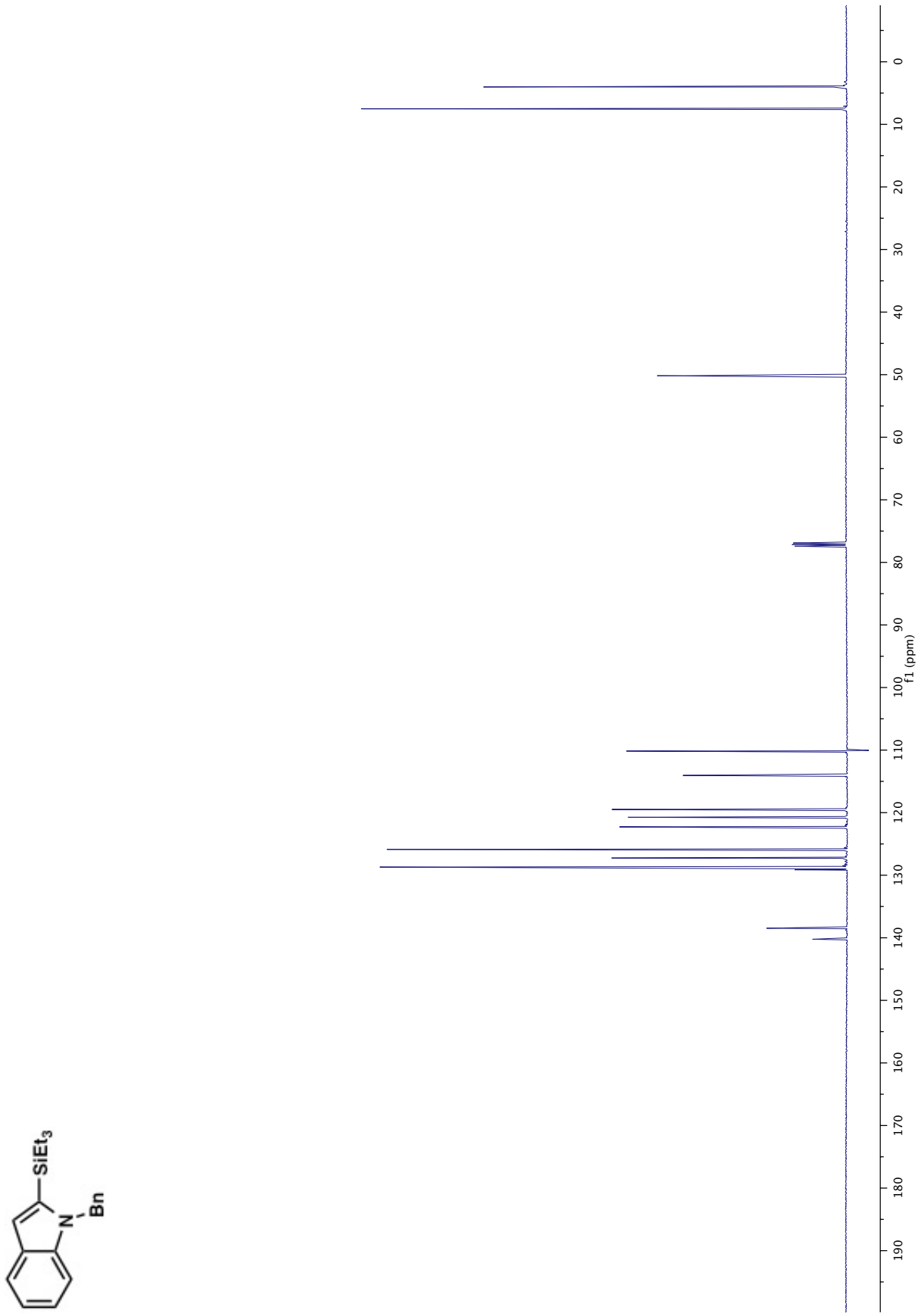
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2a**.



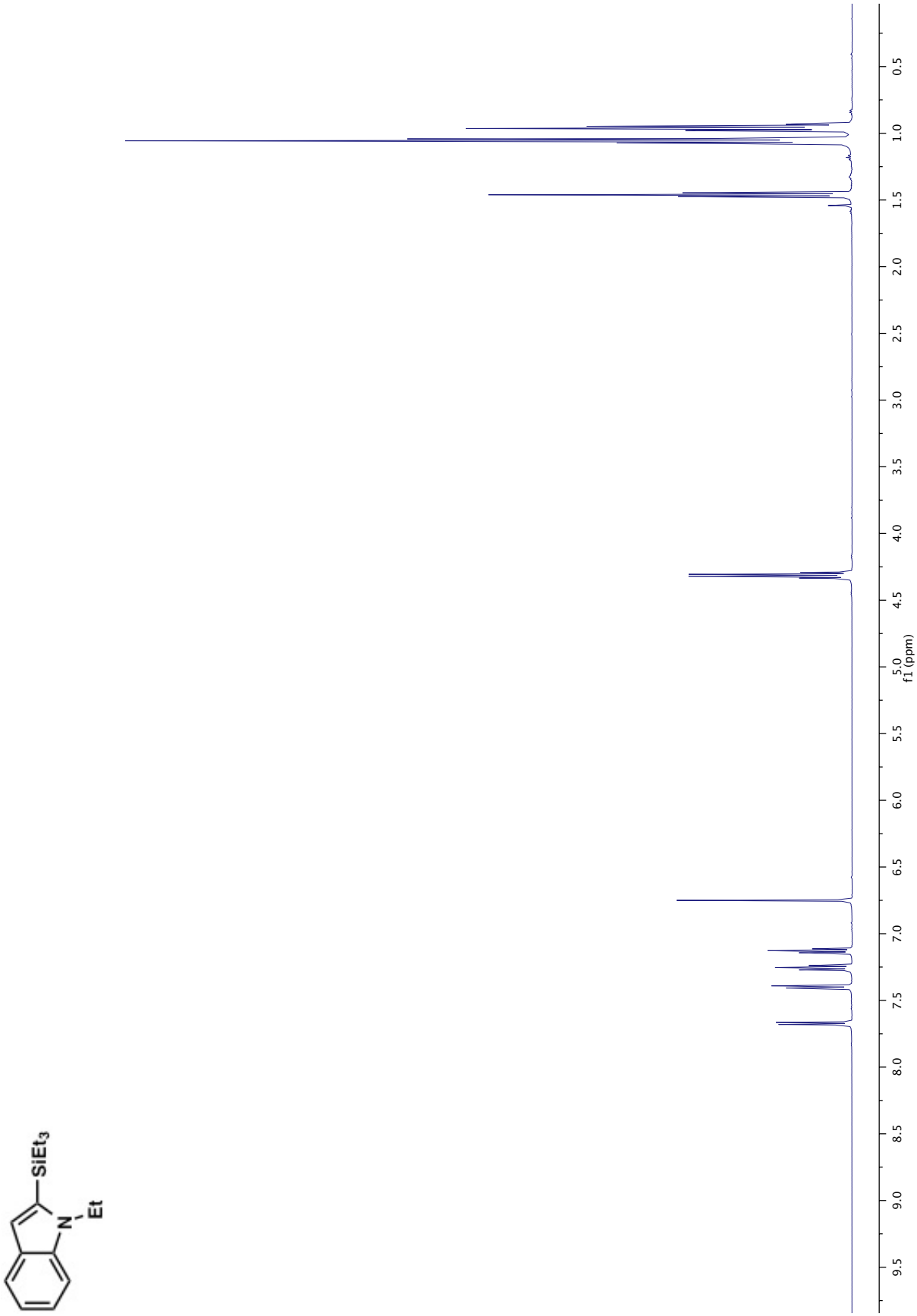
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2a.**



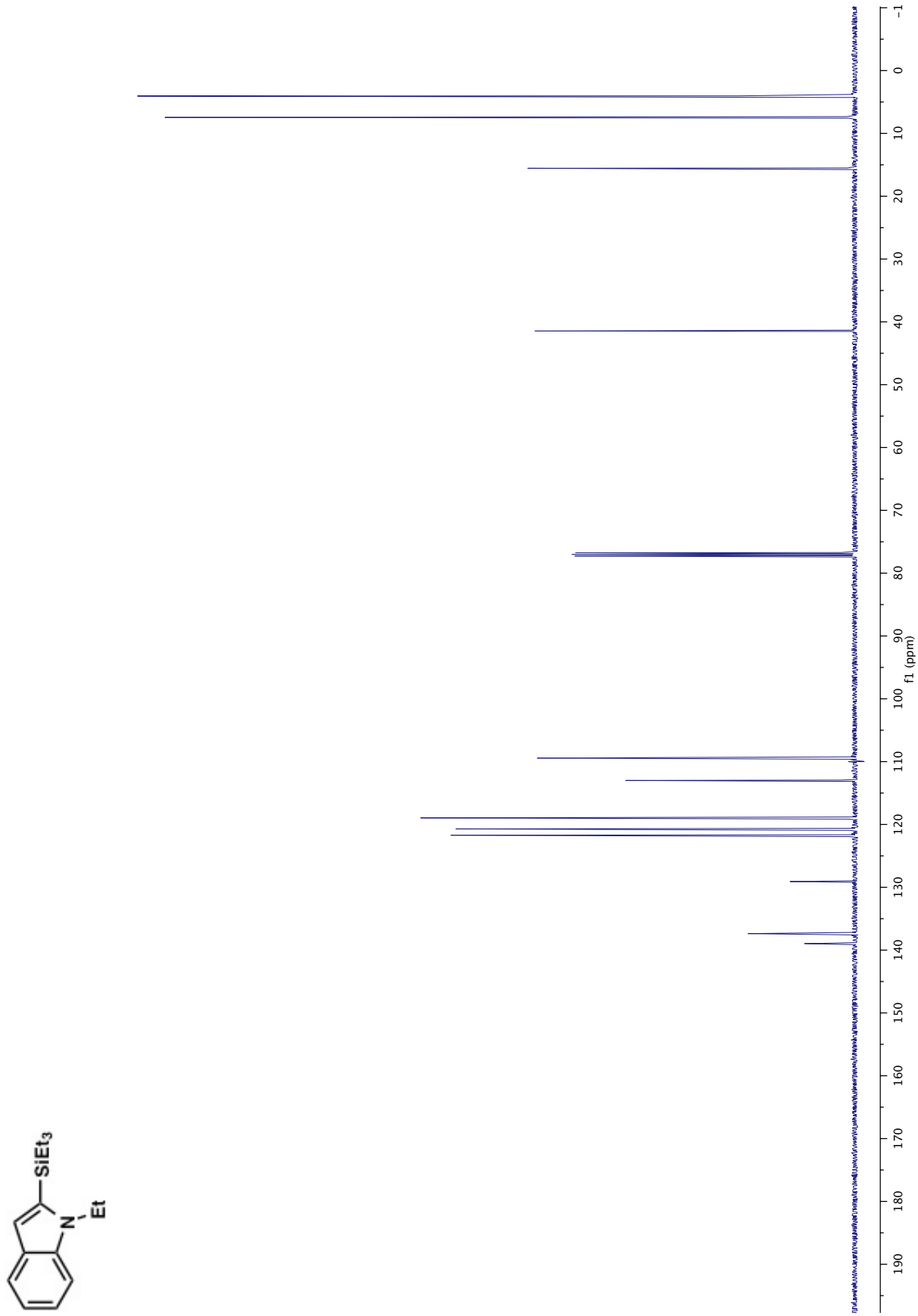
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2b**.



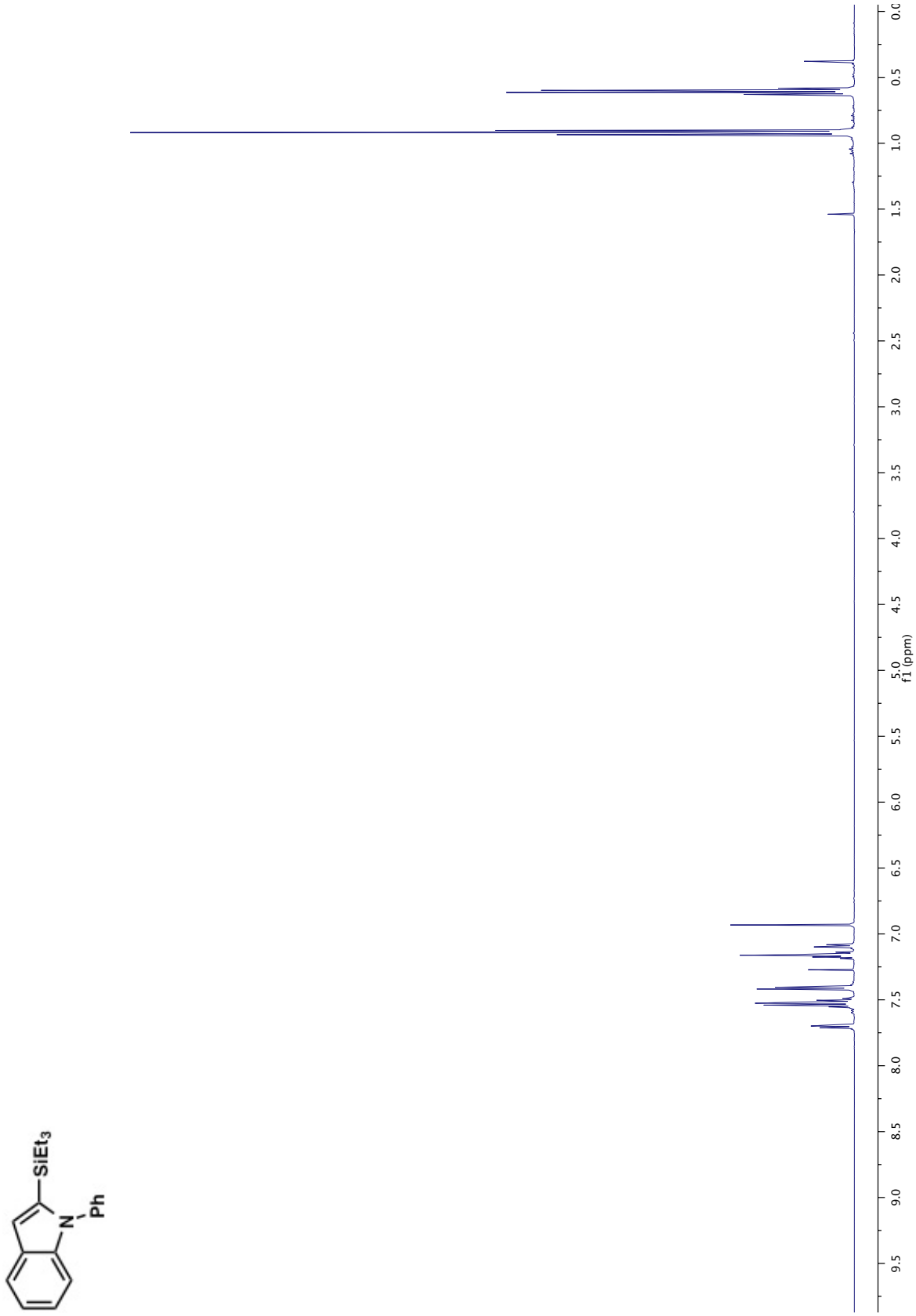
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2b**.



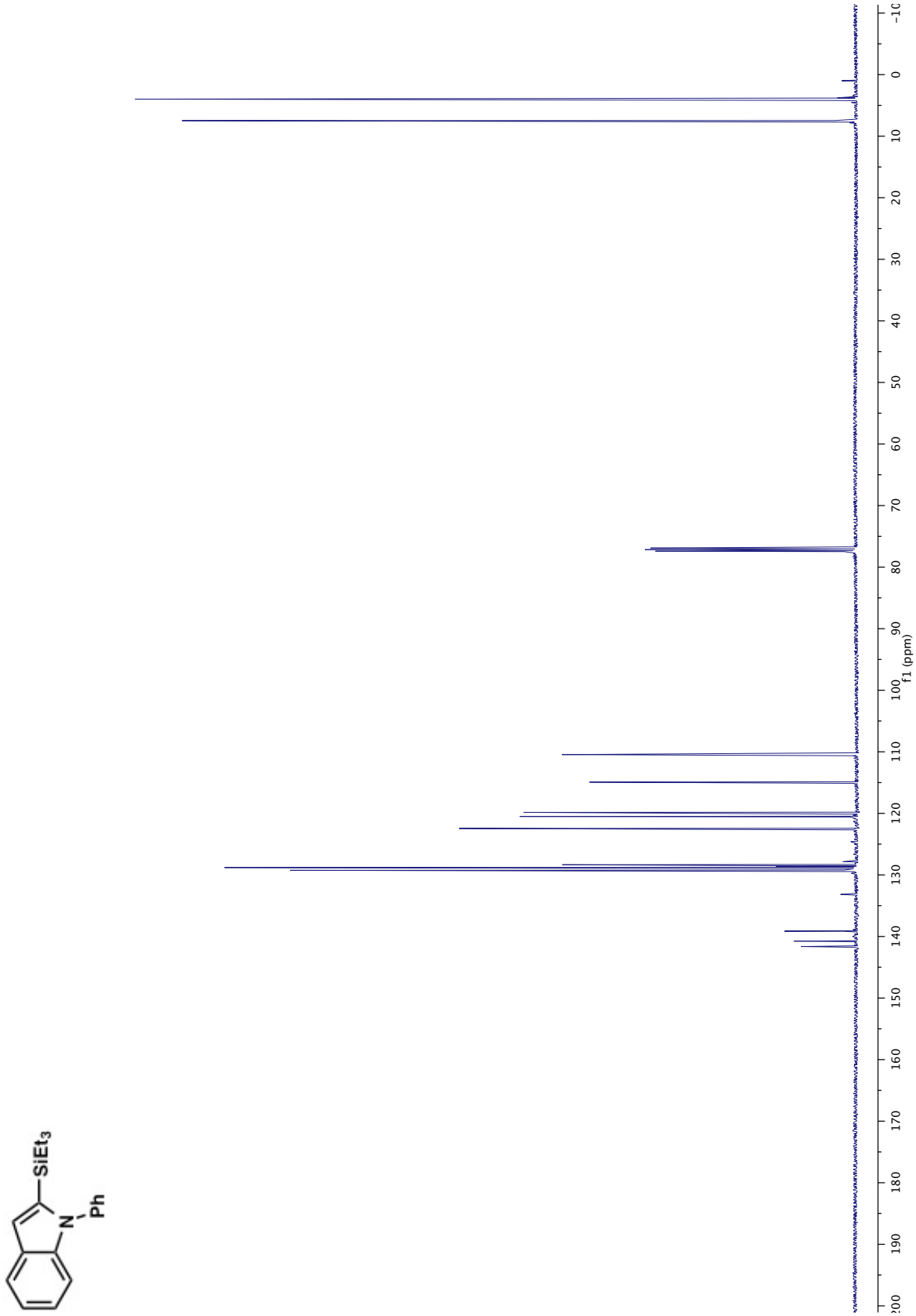
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2c**.



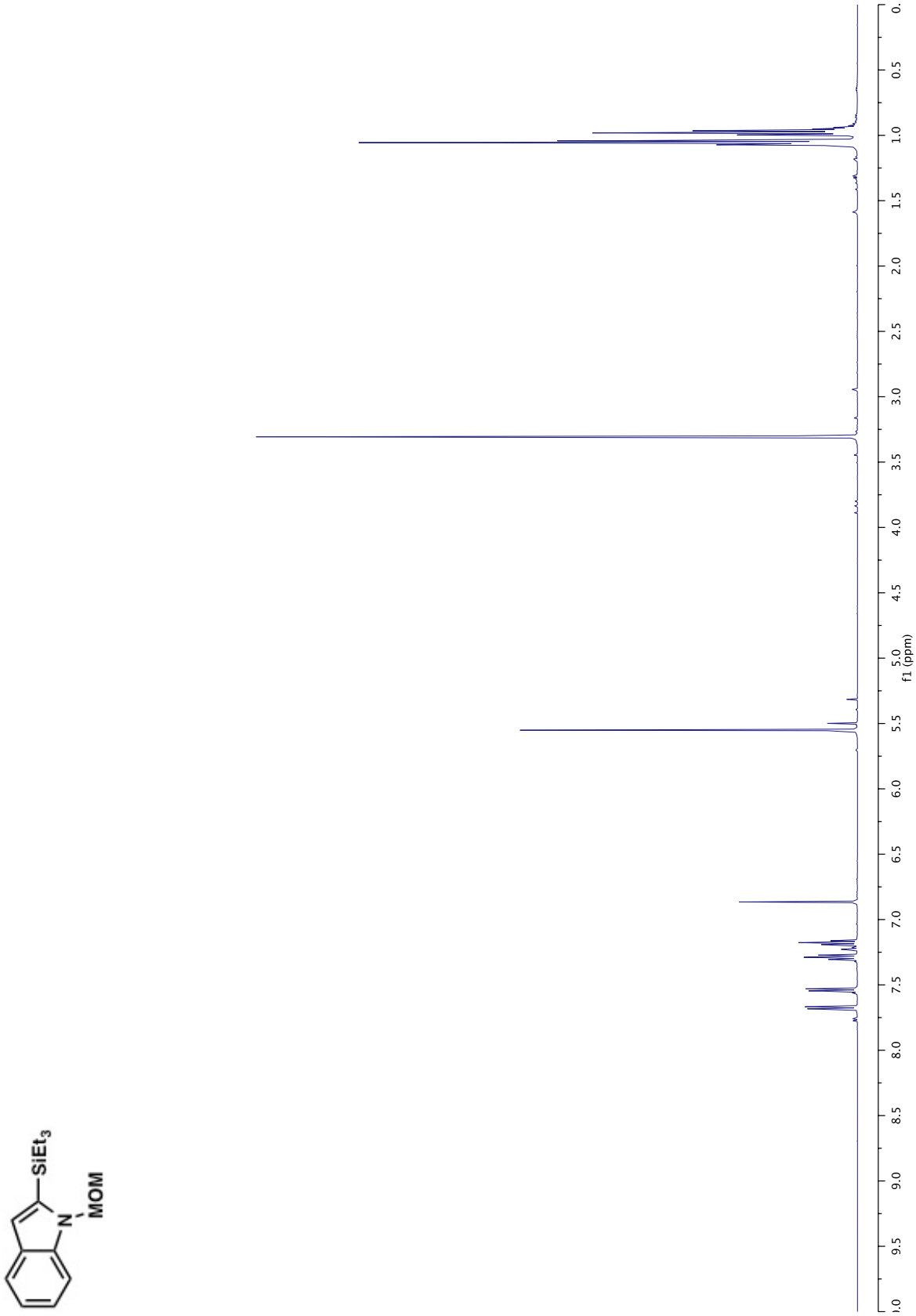
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2c**.



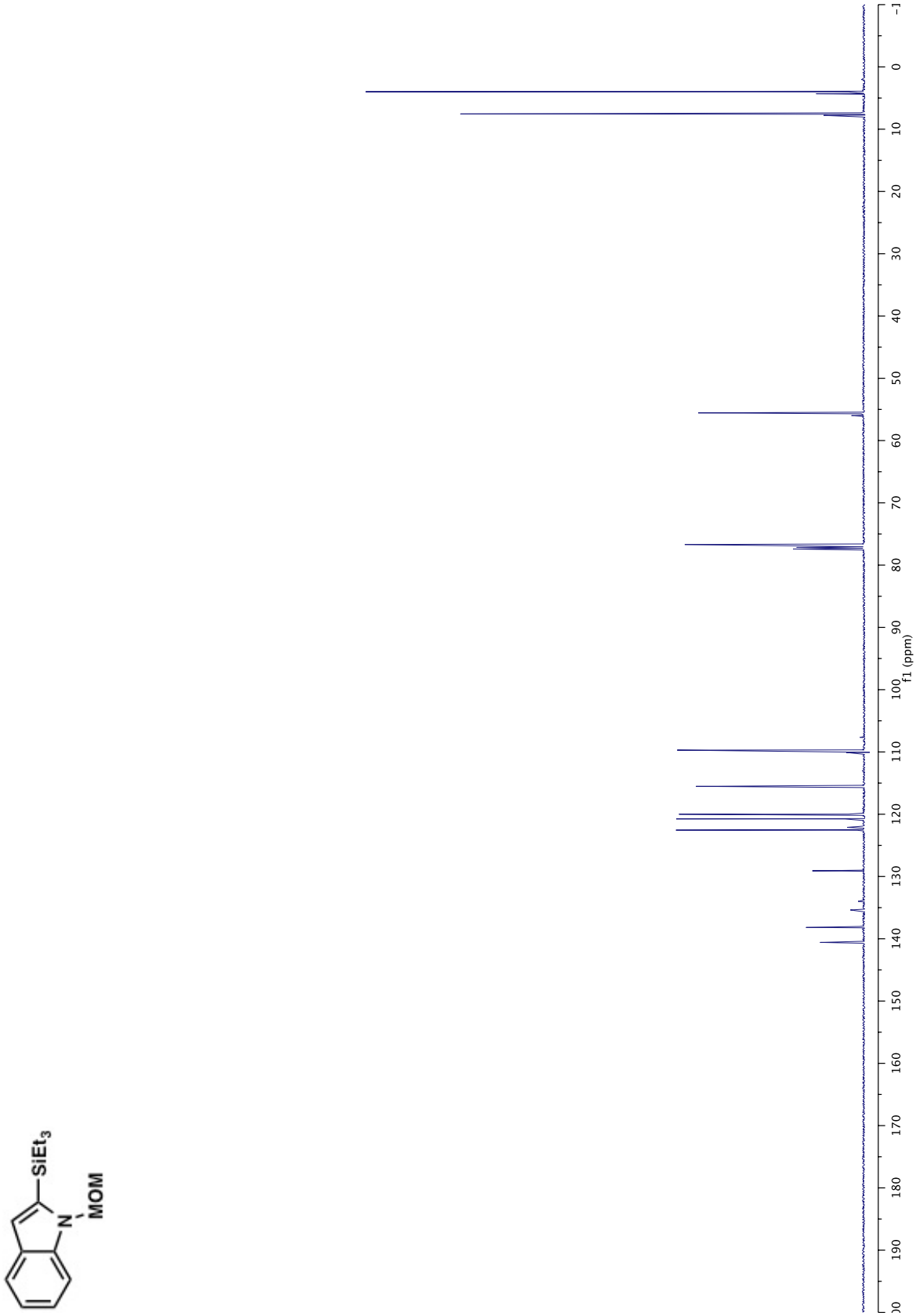
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2d**.



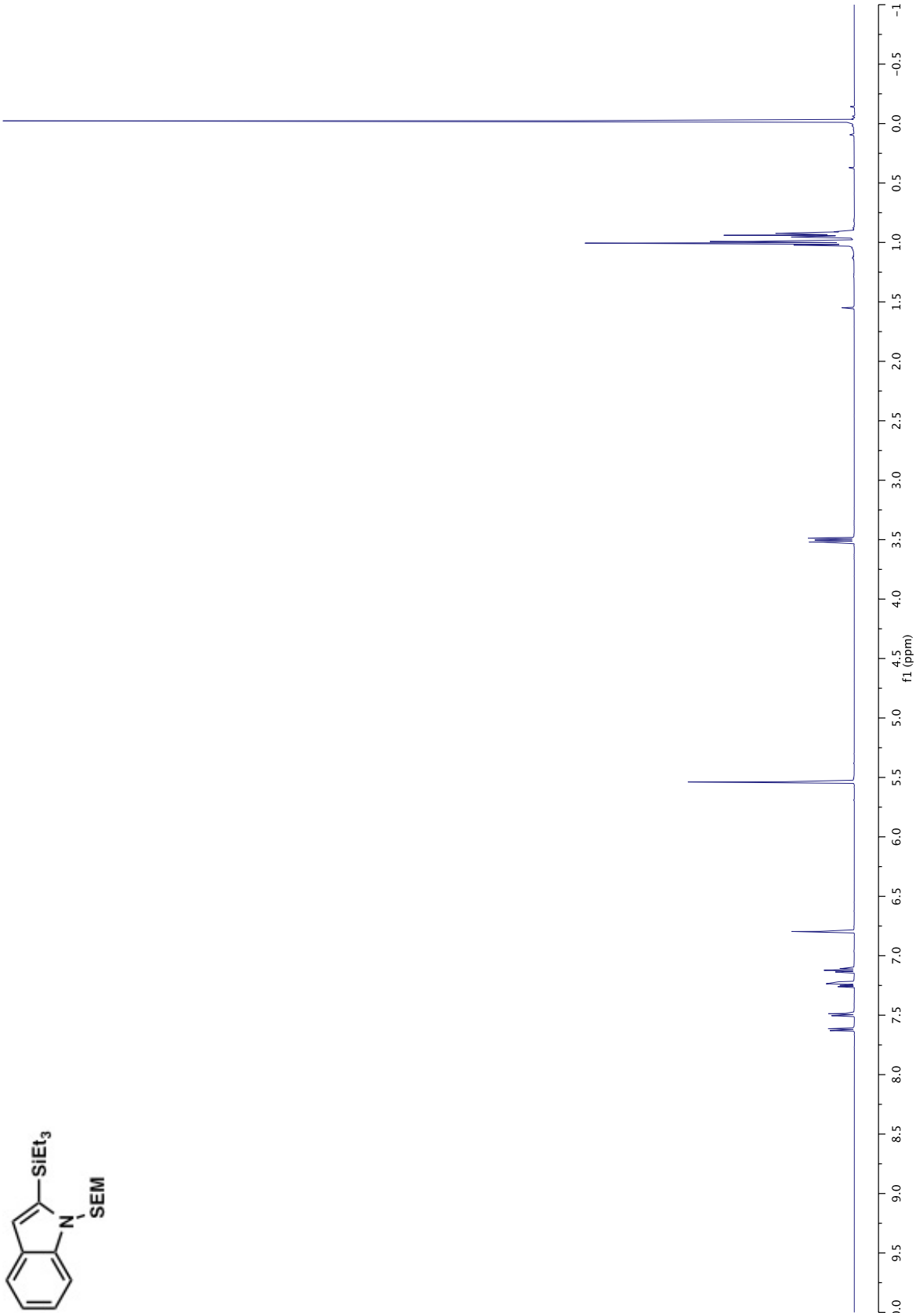
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2d**.



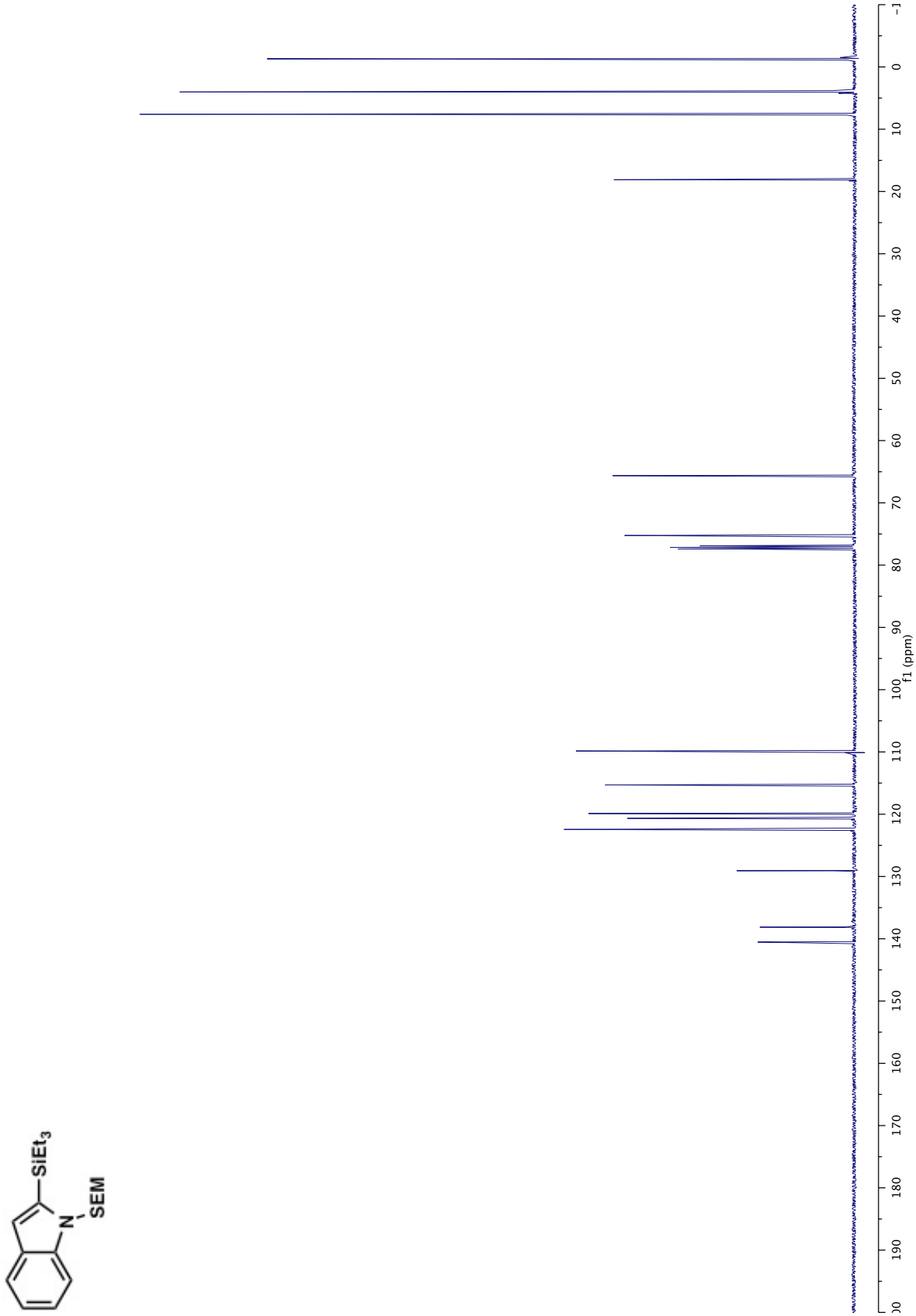
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2e**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **2e**.

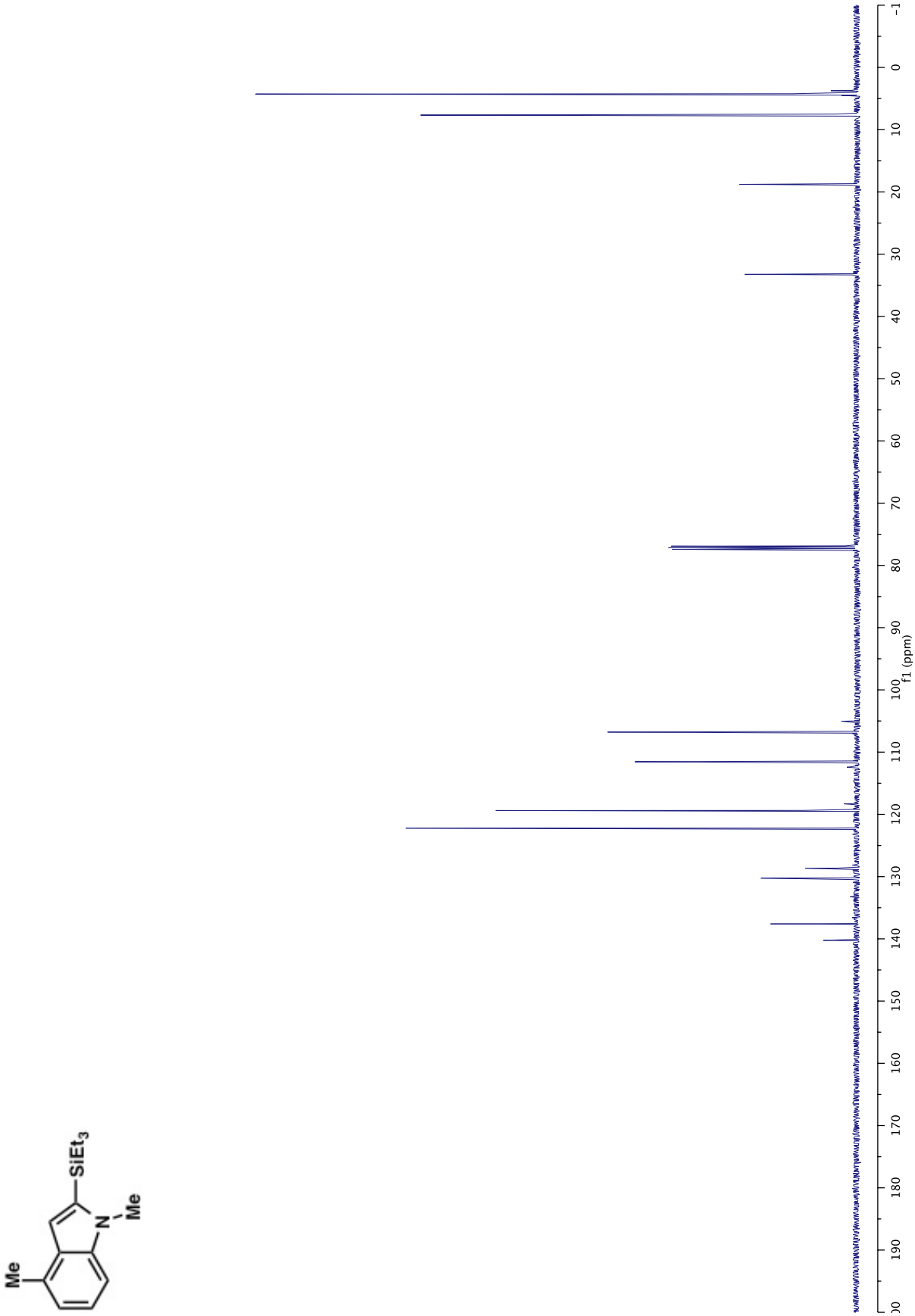


^{1}H NMR (500 MHz, $CDCl_3$) of compound **2f**.

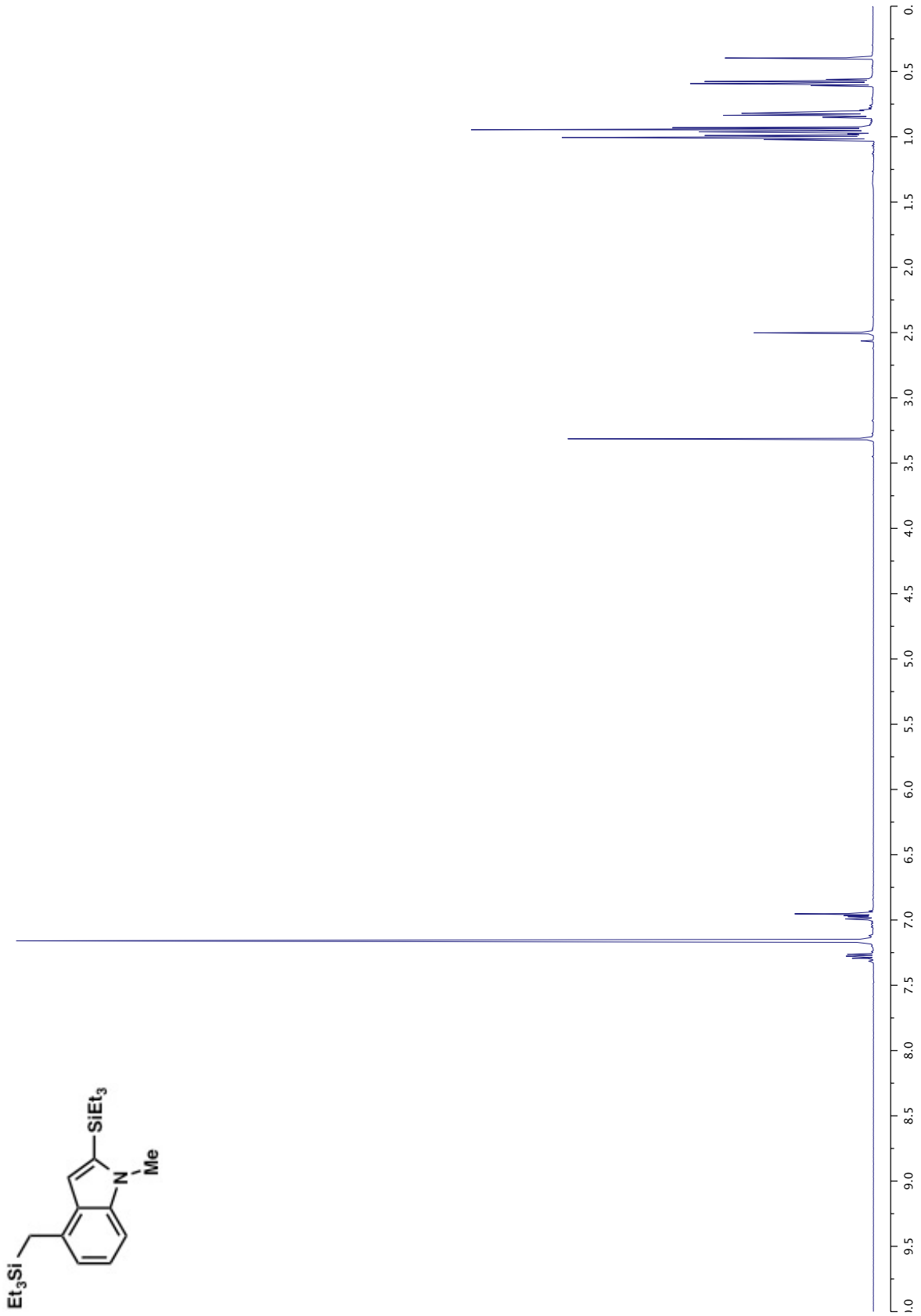


^{13}C NMR (125 MHz, $CDCl_3$) of compound **2f**.

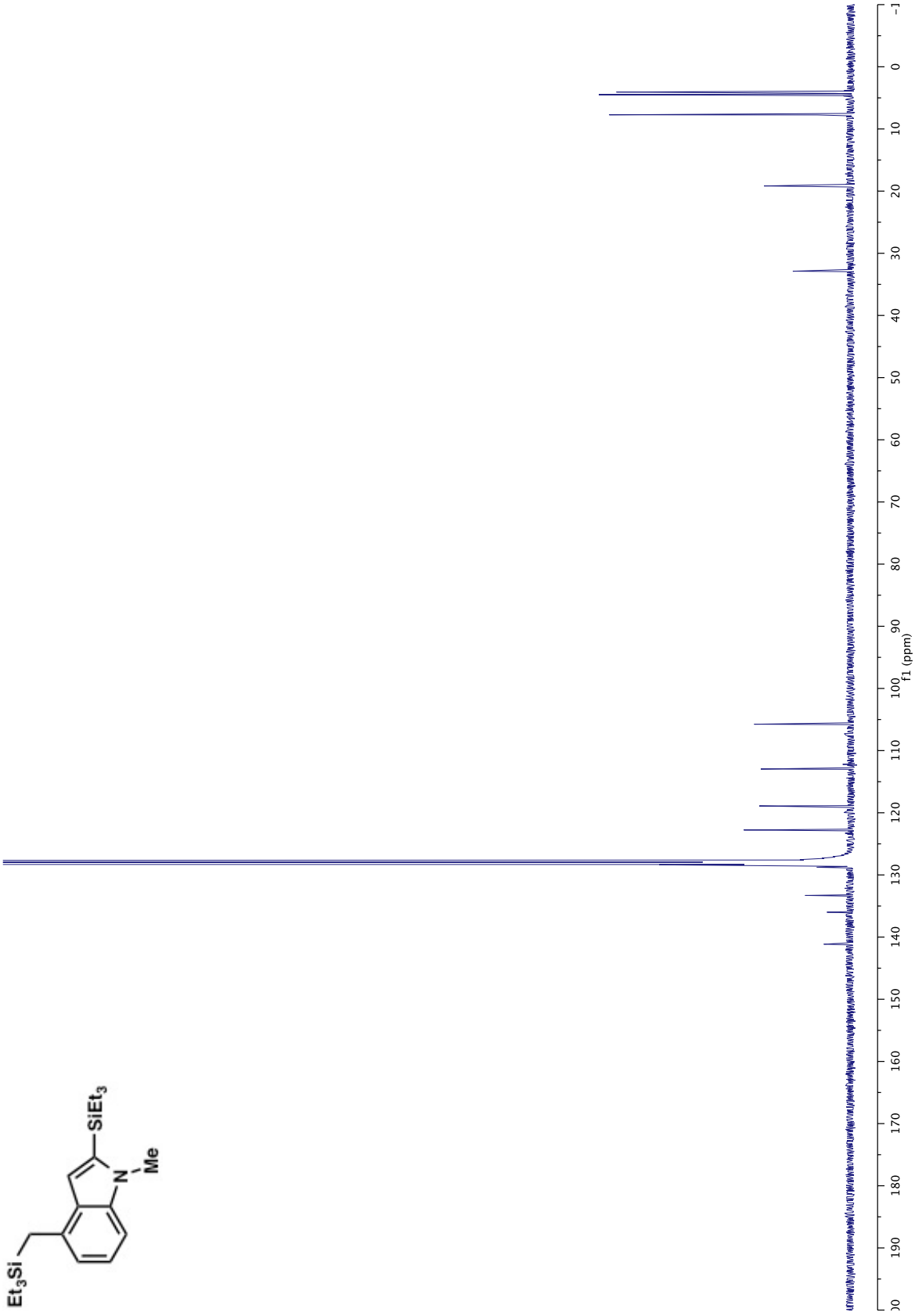
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2g**.



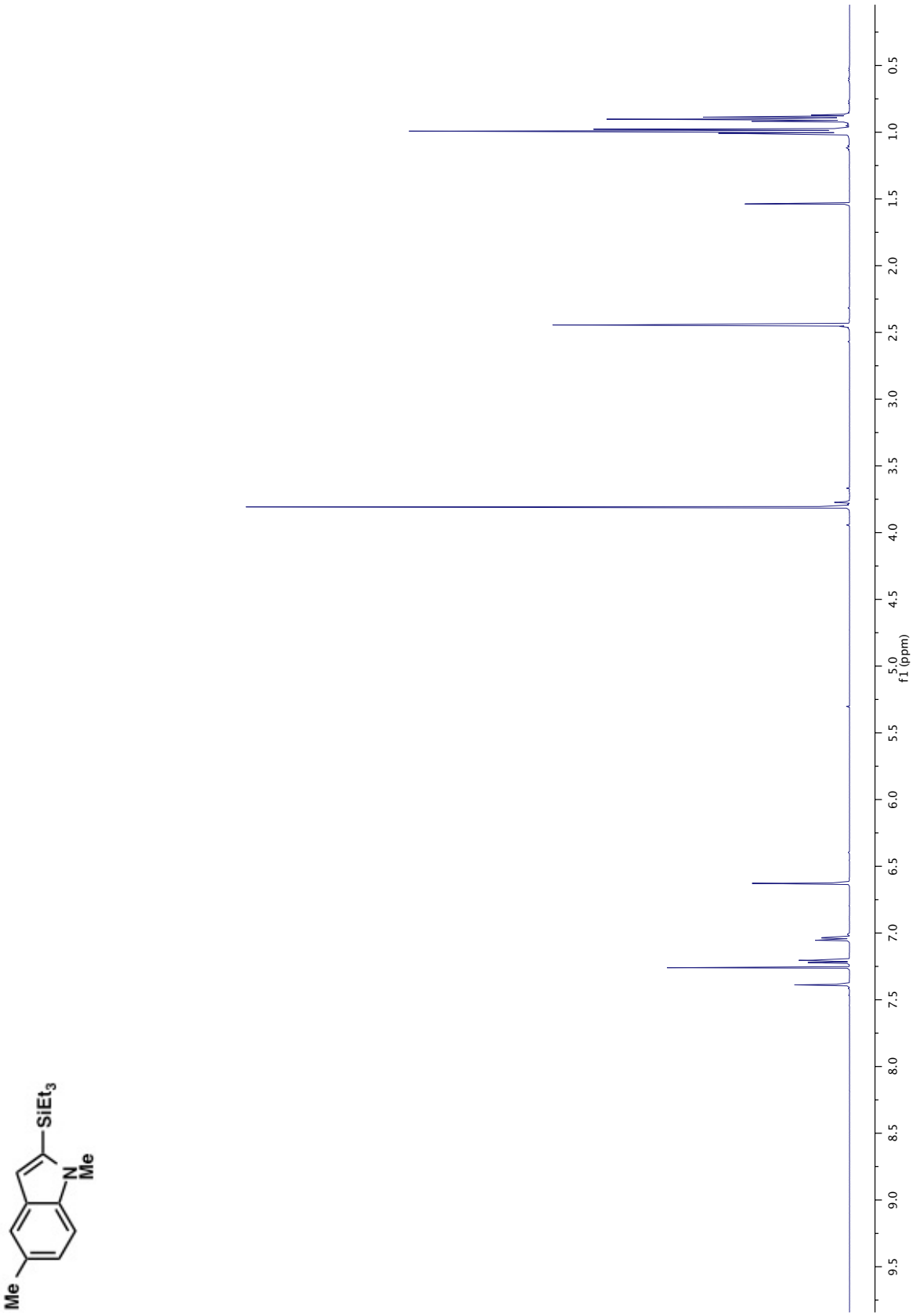
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2g**.



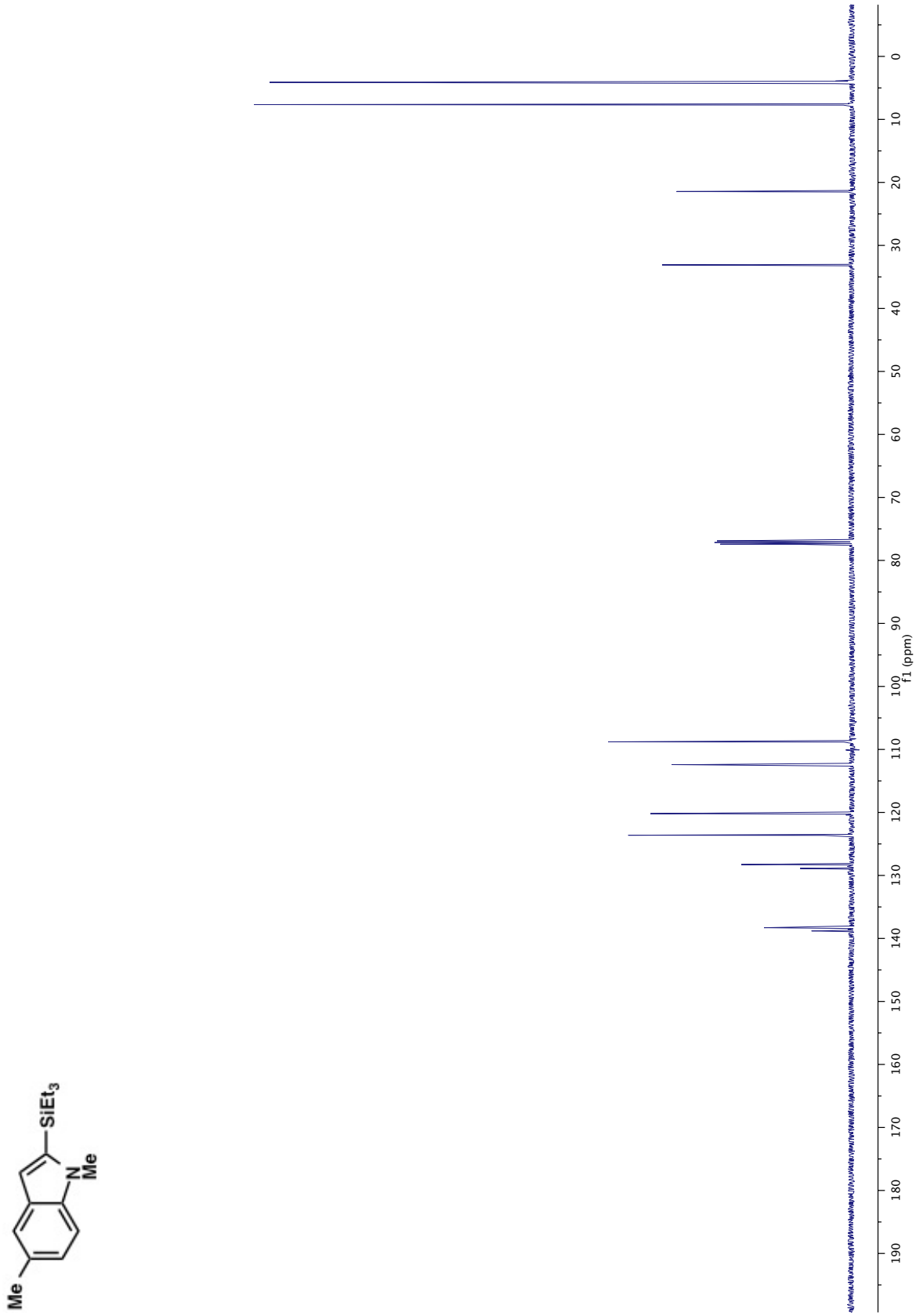
^{1}H NMR (500 MHz, C_6D_6) of compound **16**.



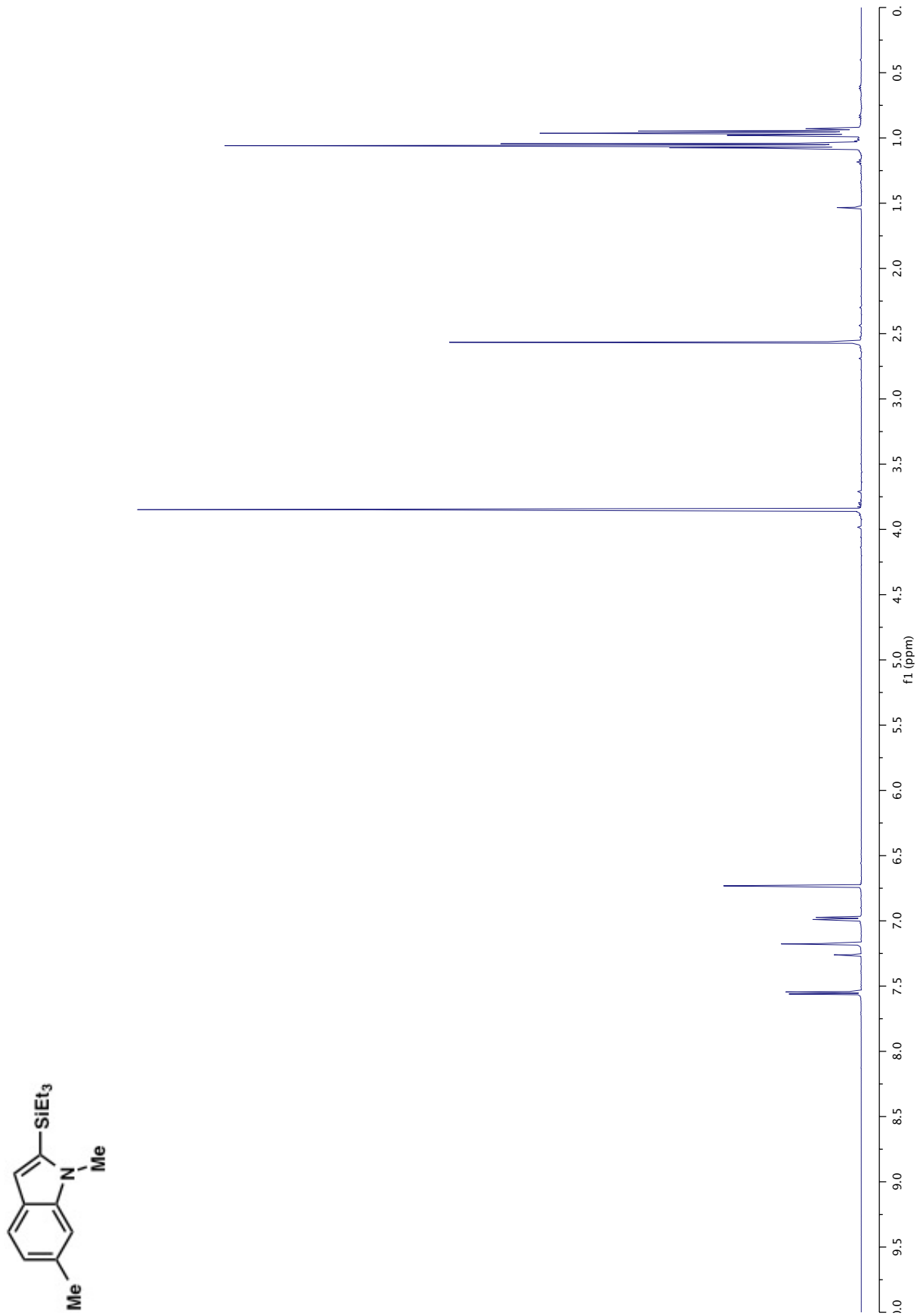
^{13}C NMR (125 MHz, C_6D_6) of compound **16**.



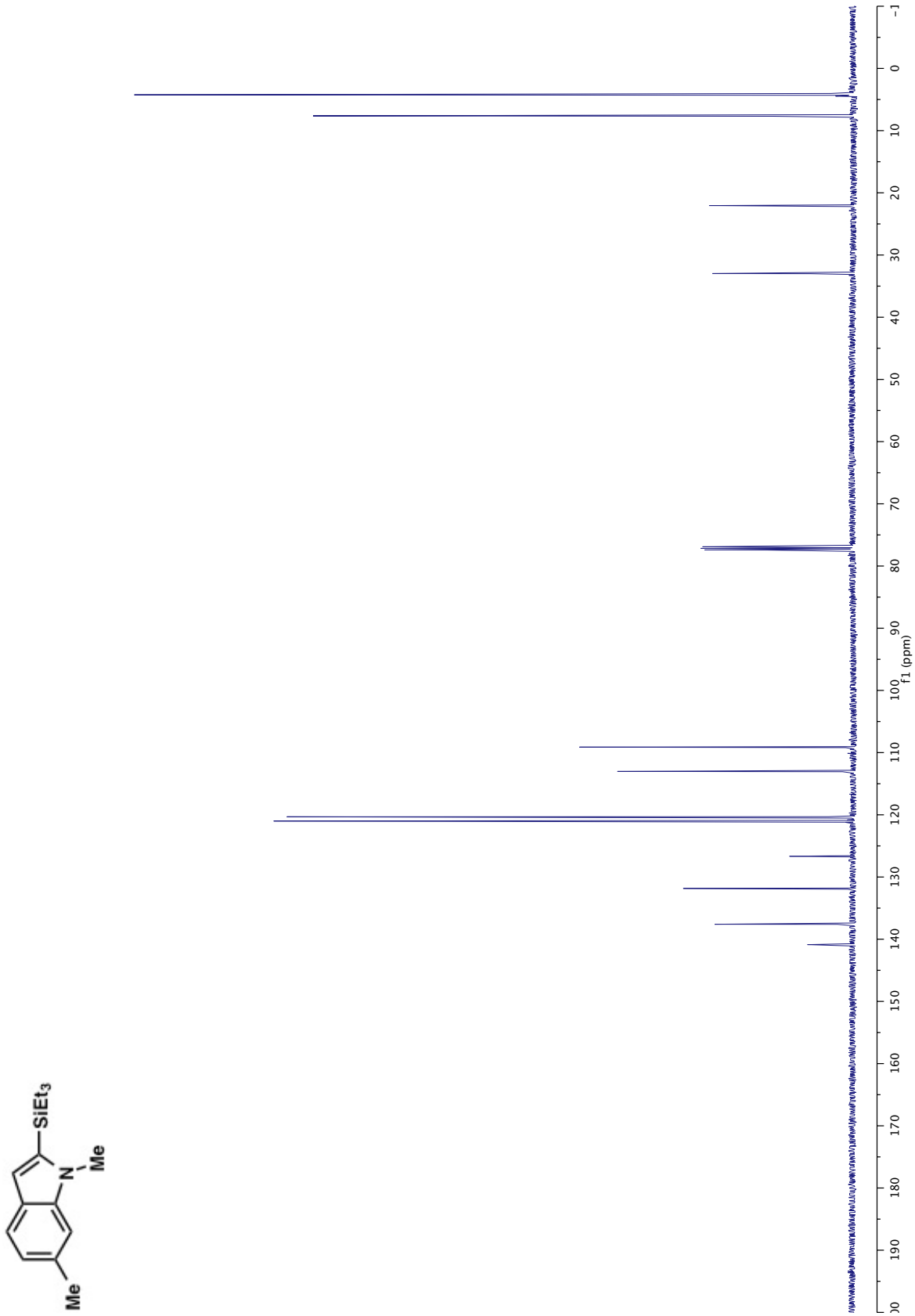
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2h**.



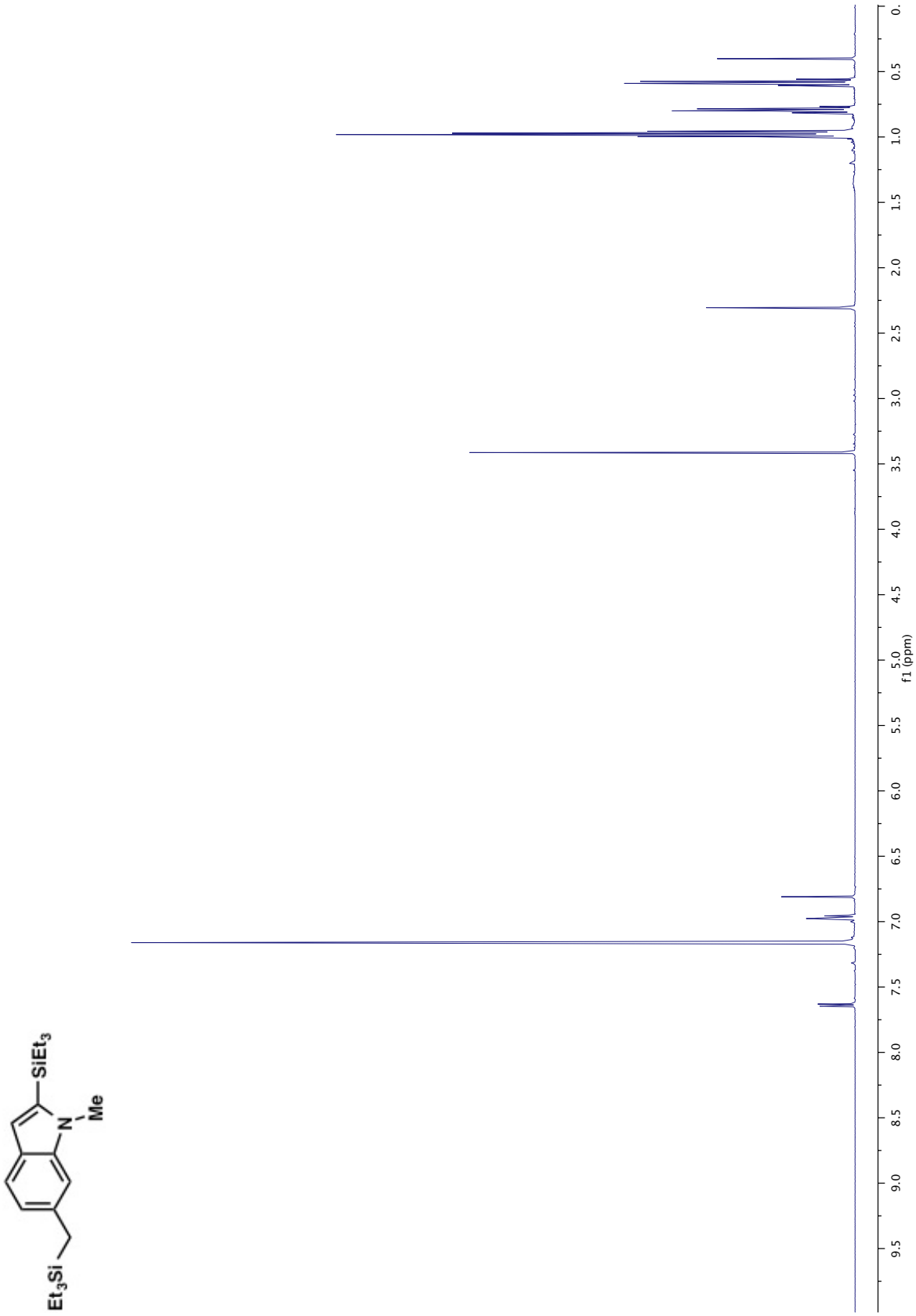
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2h**.



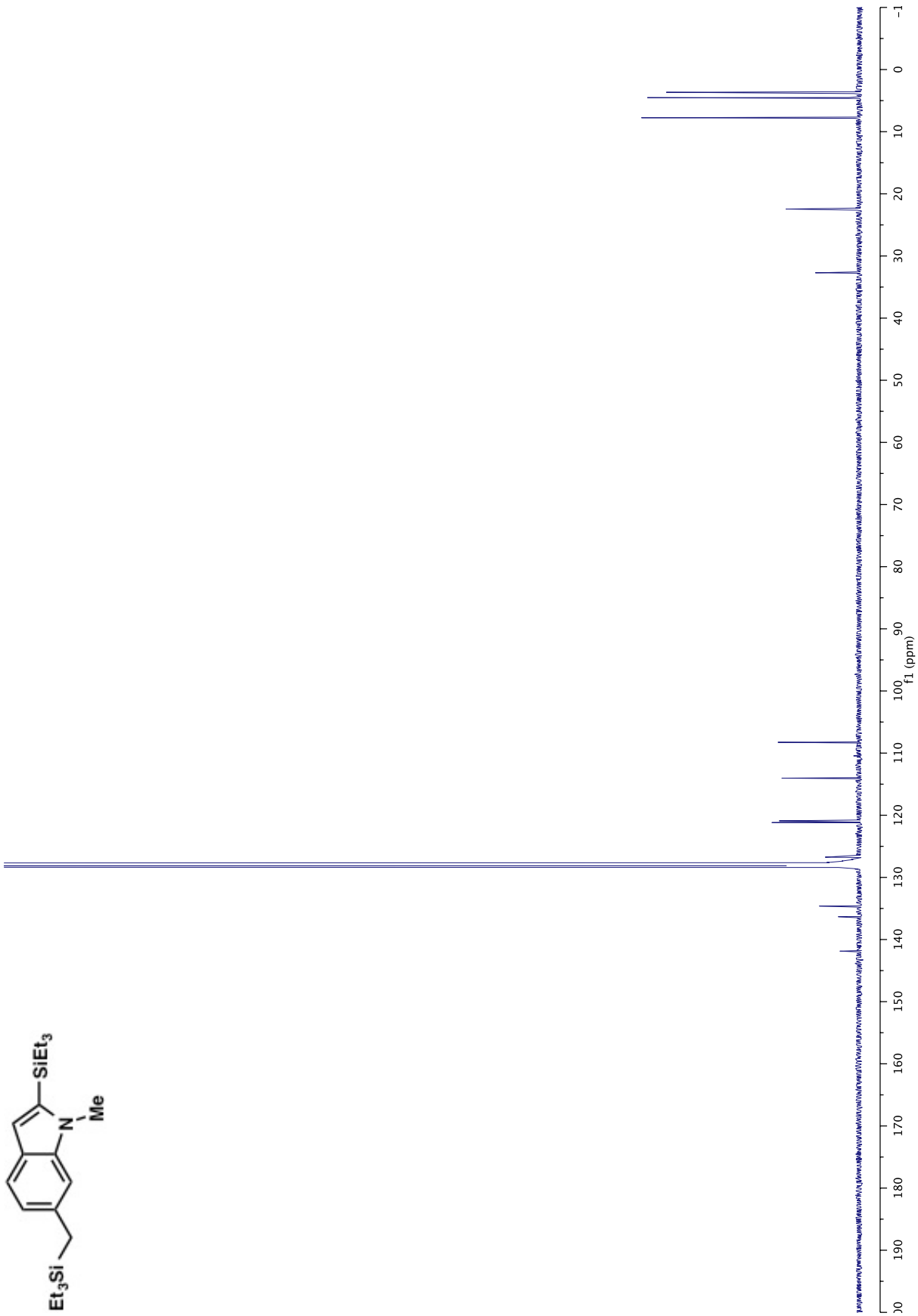
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2i**.



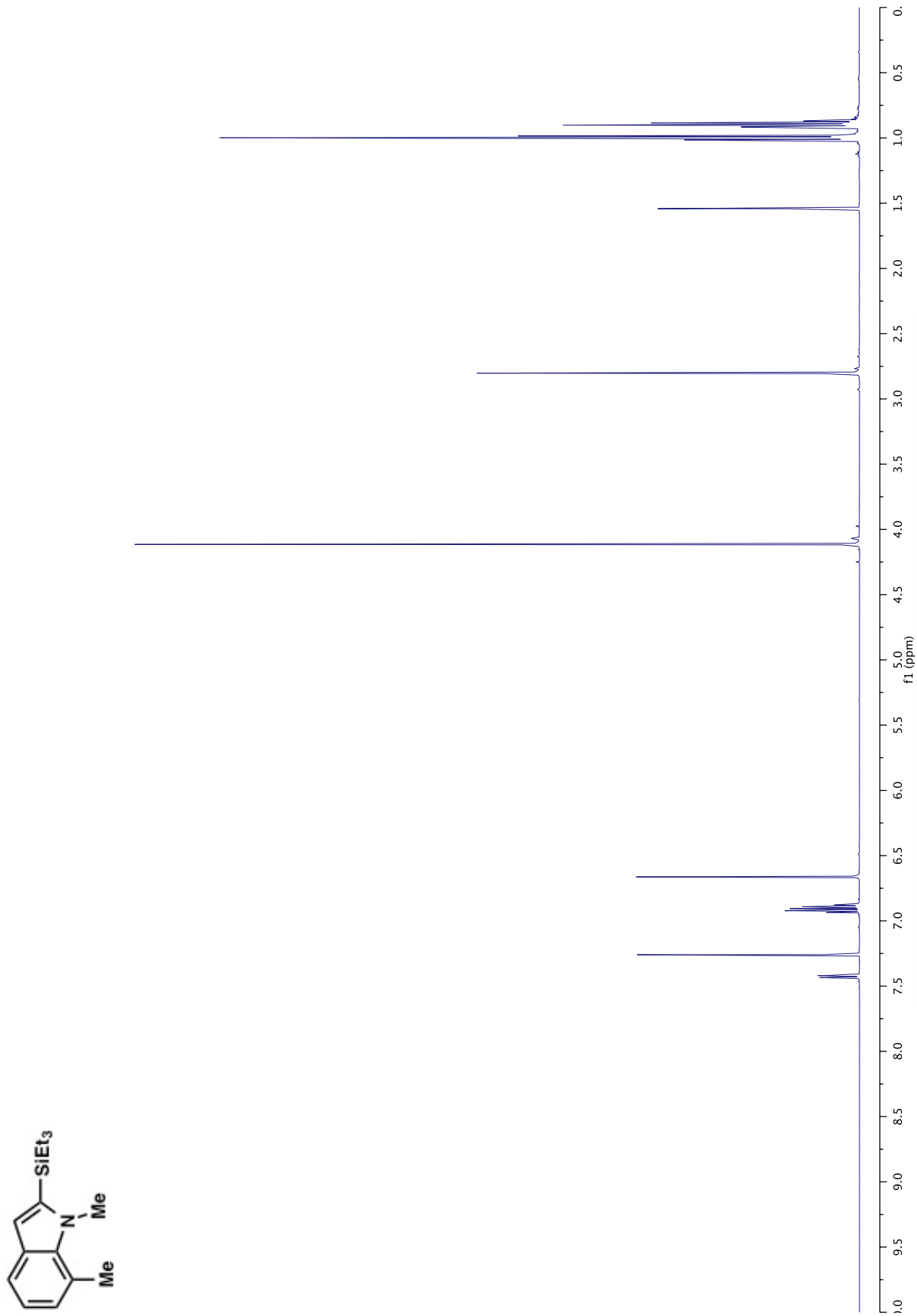
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2i**.



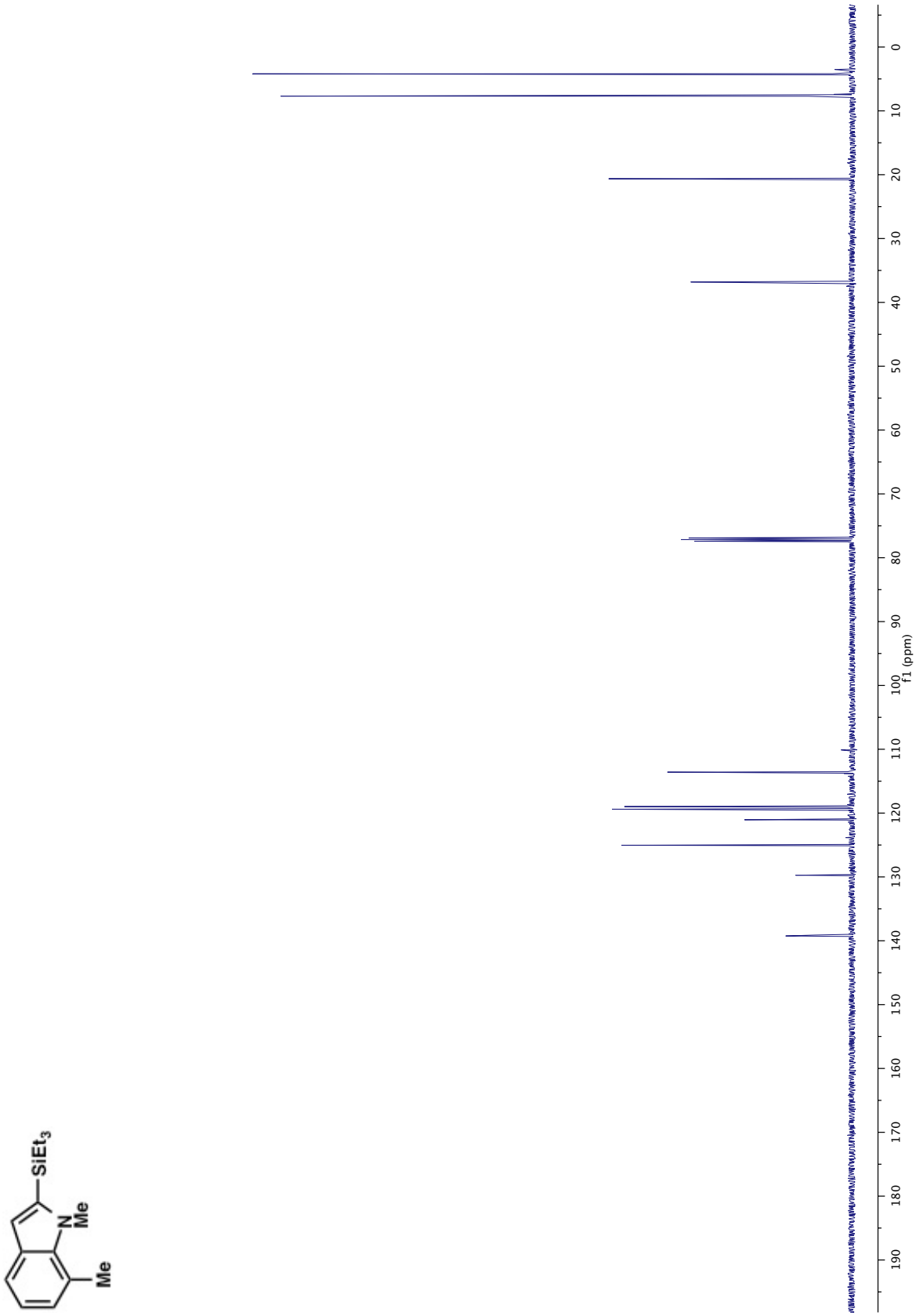
^{1}H NMR (500 MHz, C_6D_6) of compound **SI-2i.**



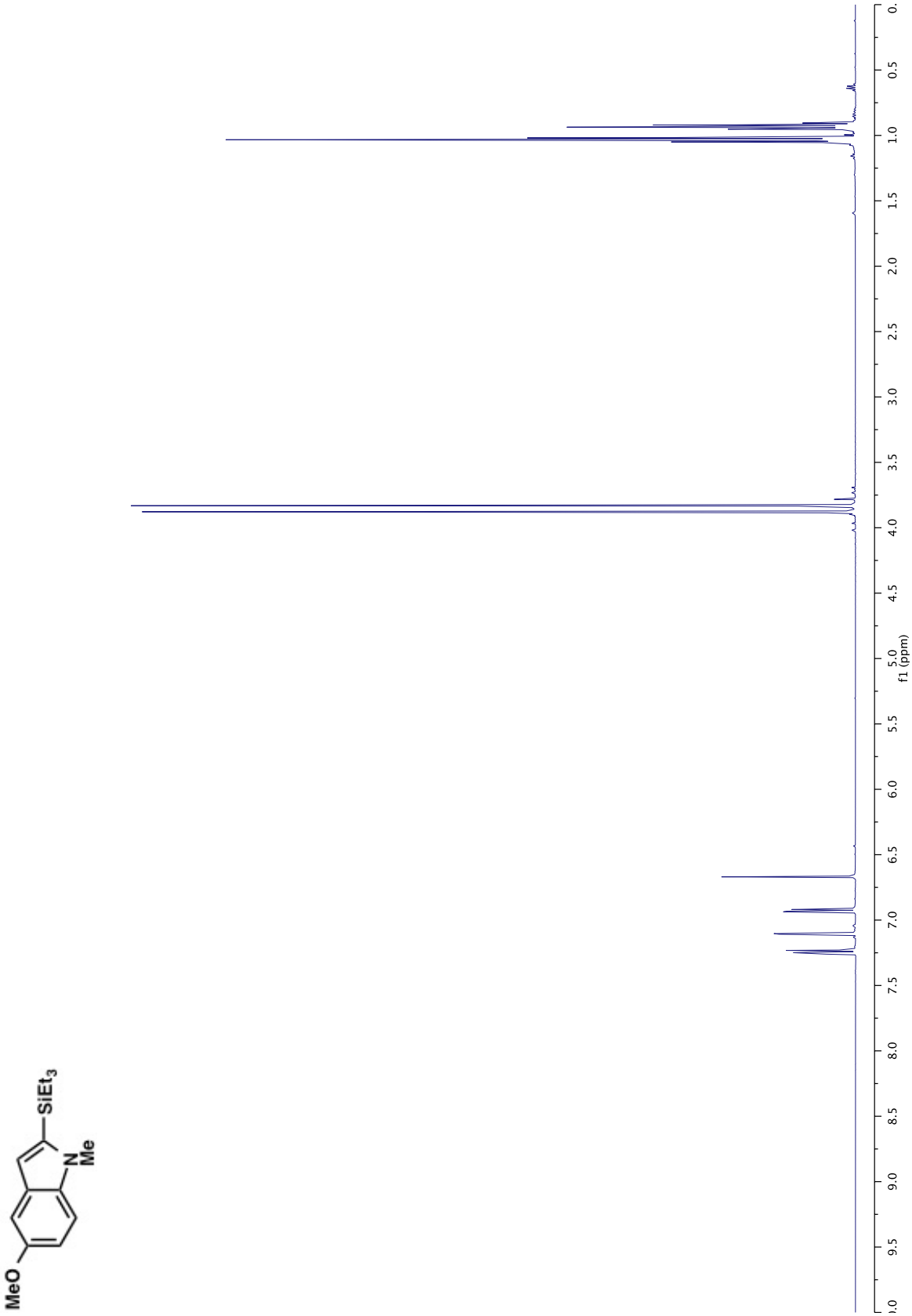
^{13}C NMR (125 MHz, C_6D_6) of compound **SI-2i**.



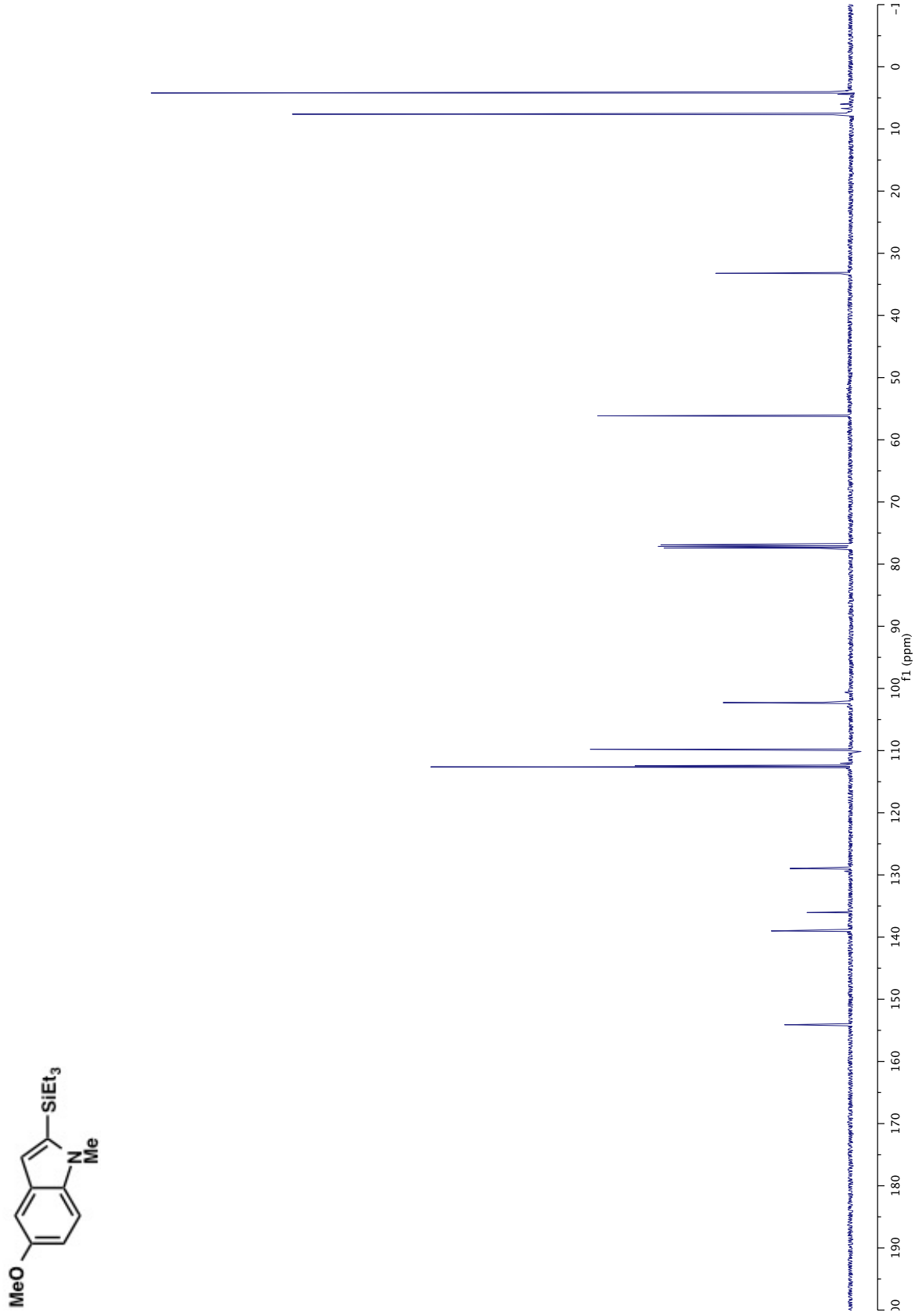
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2j**.



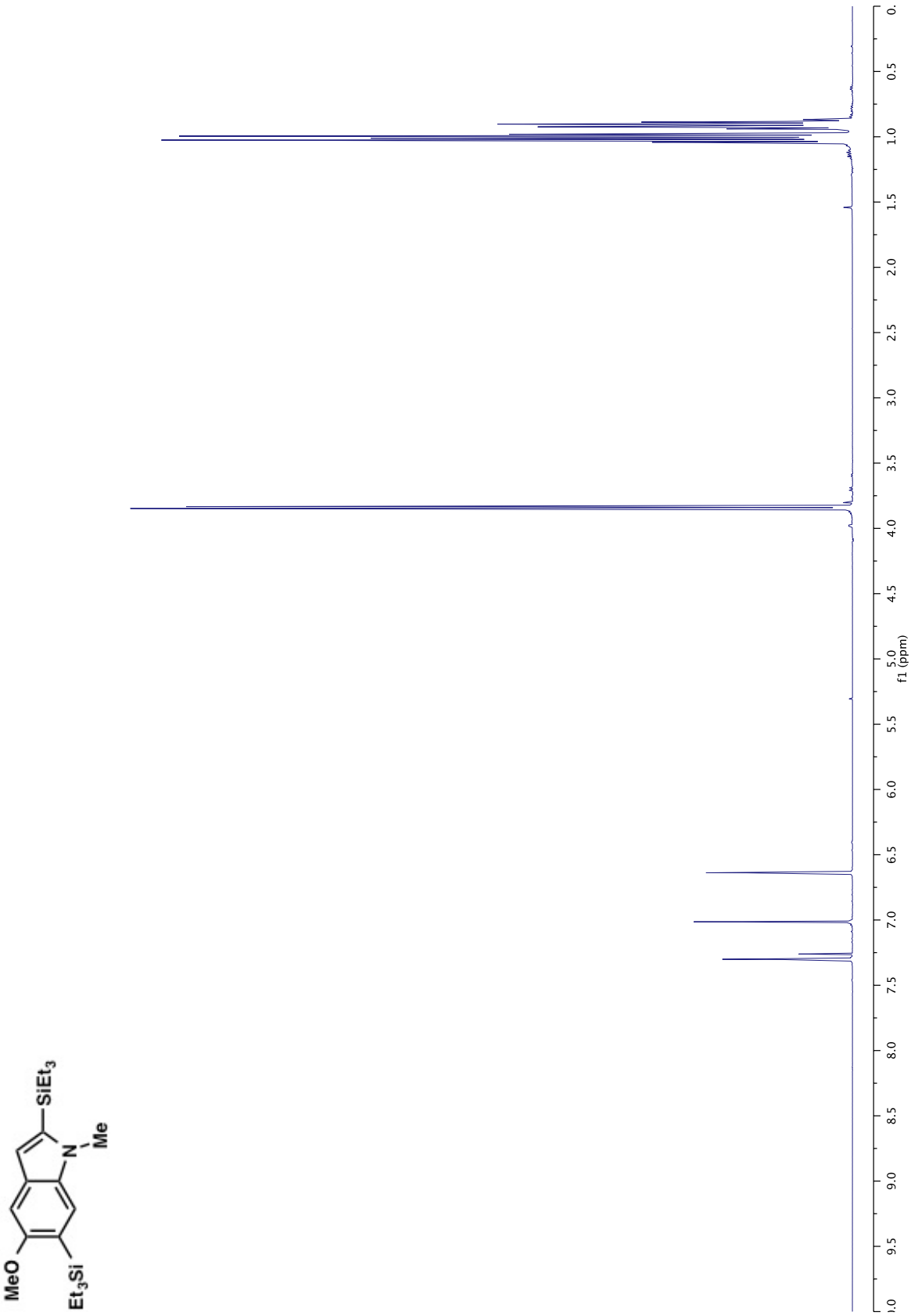
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2j**.



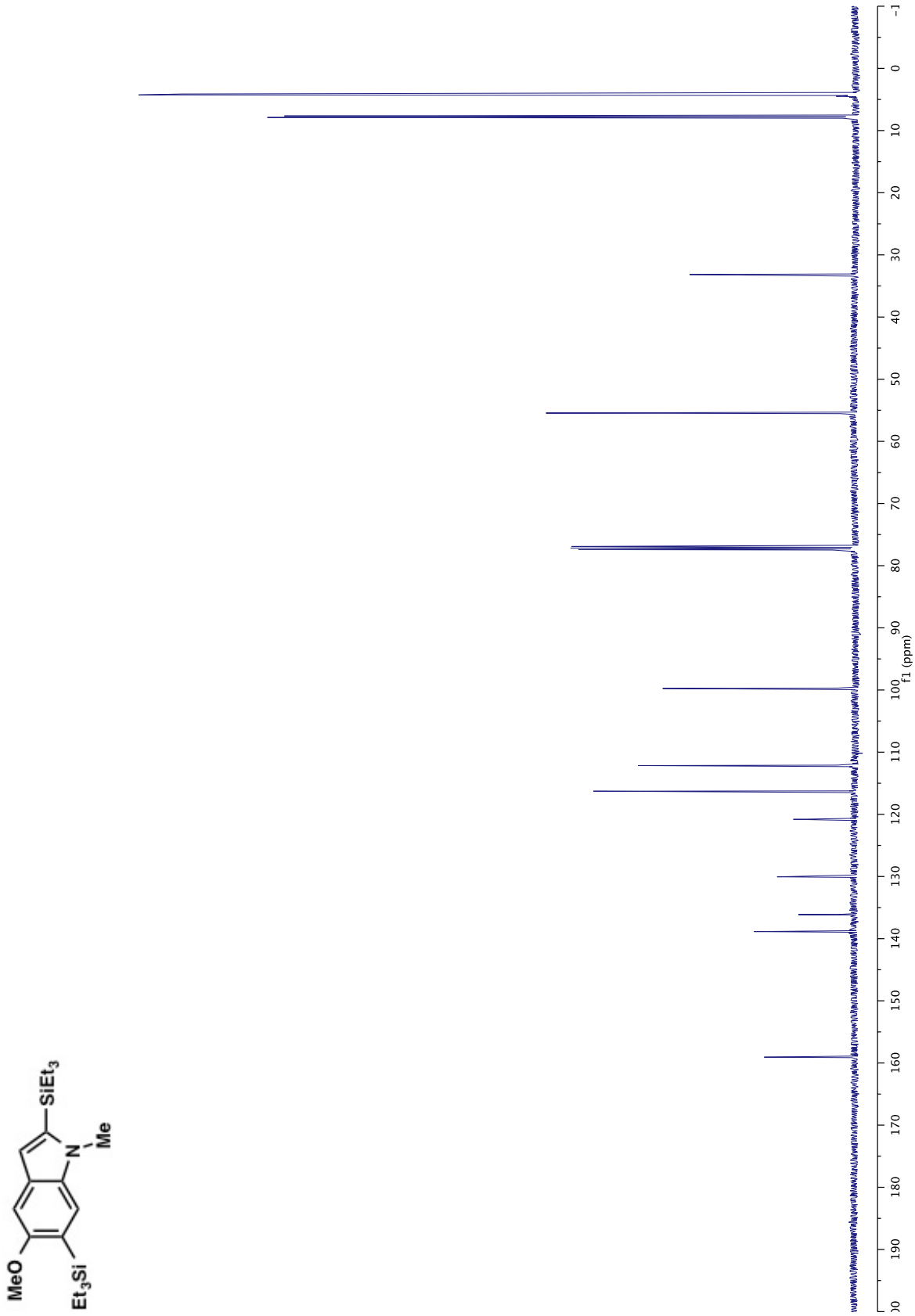
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2k**.



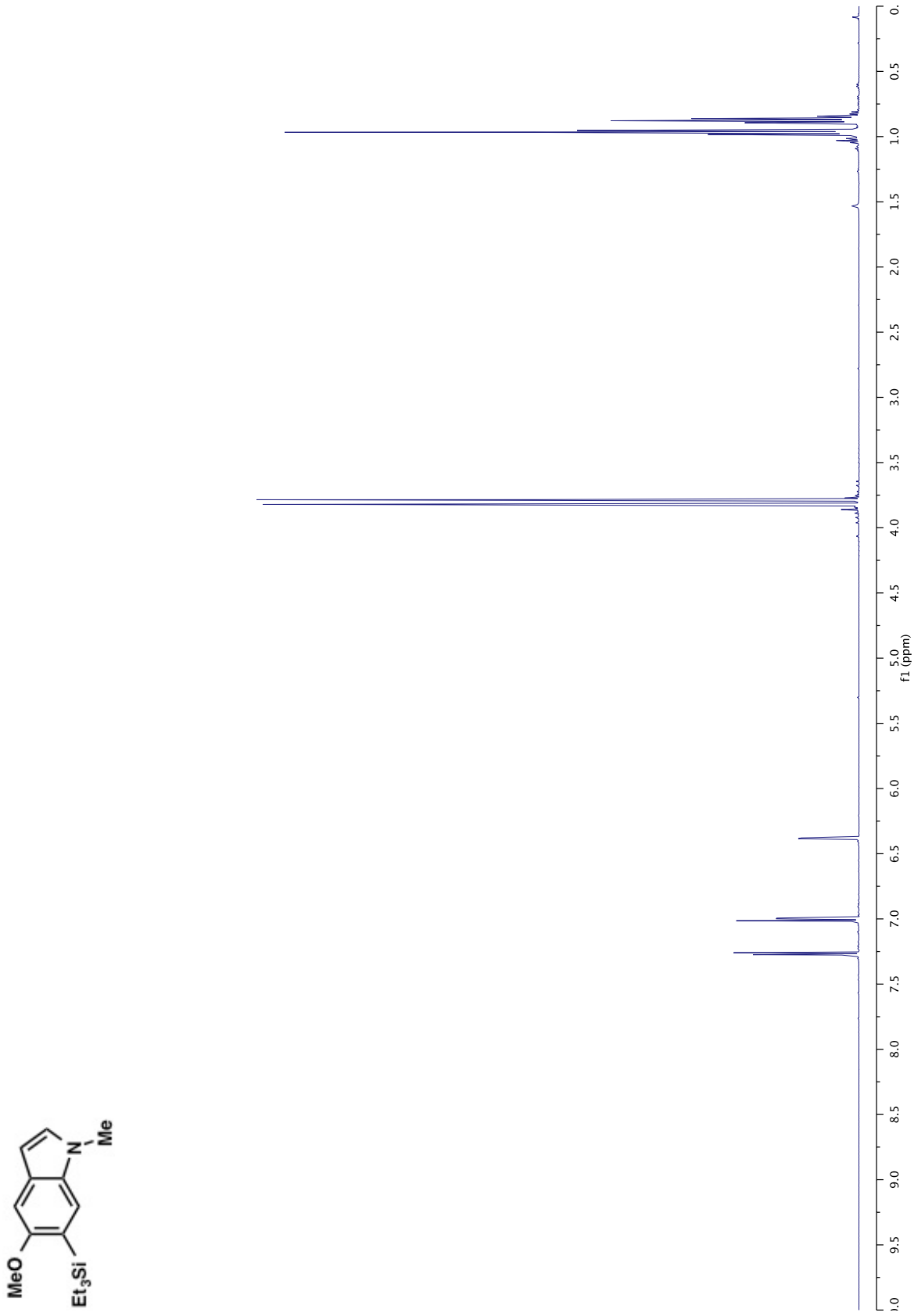
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2k**.



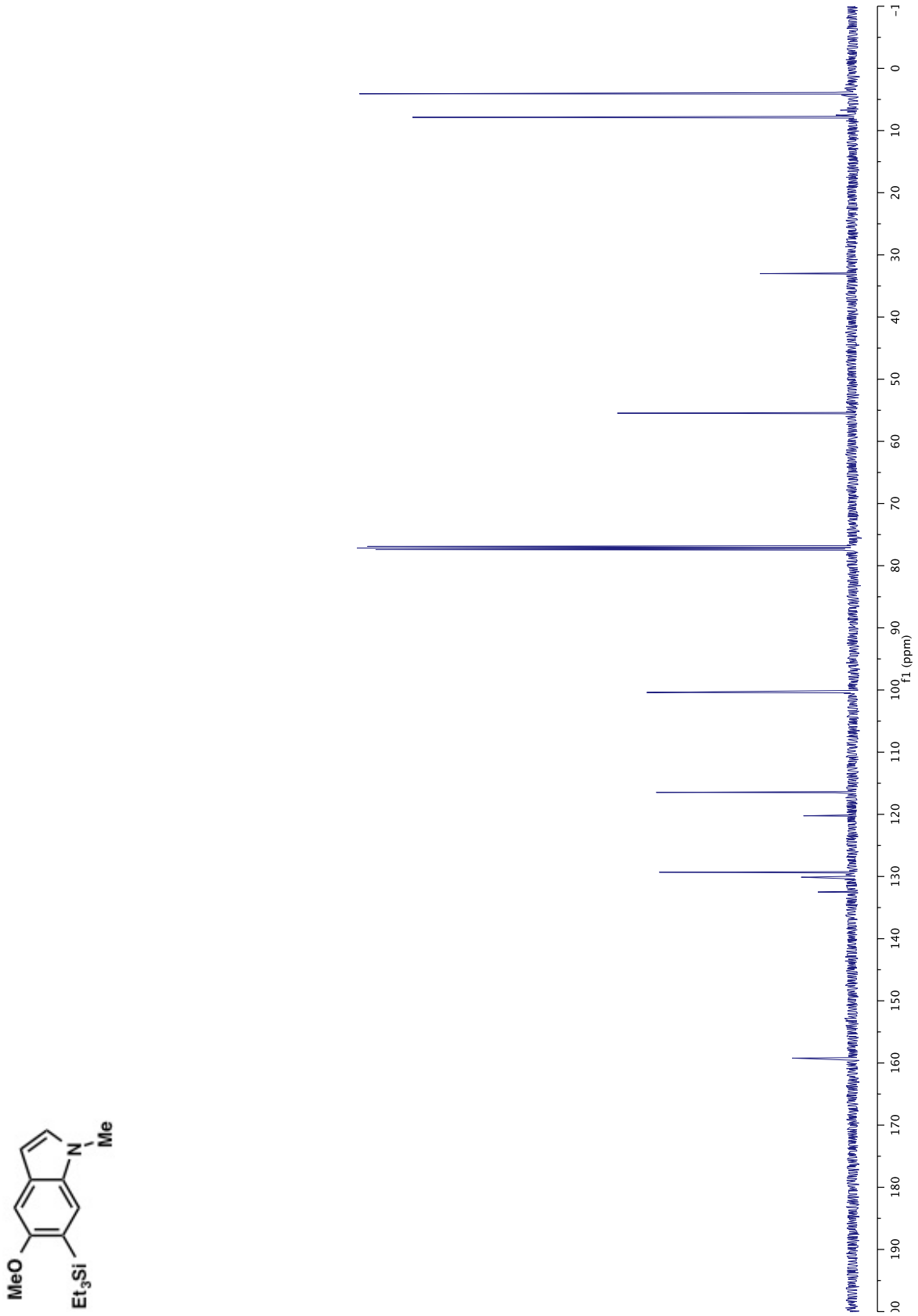
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-2k**.



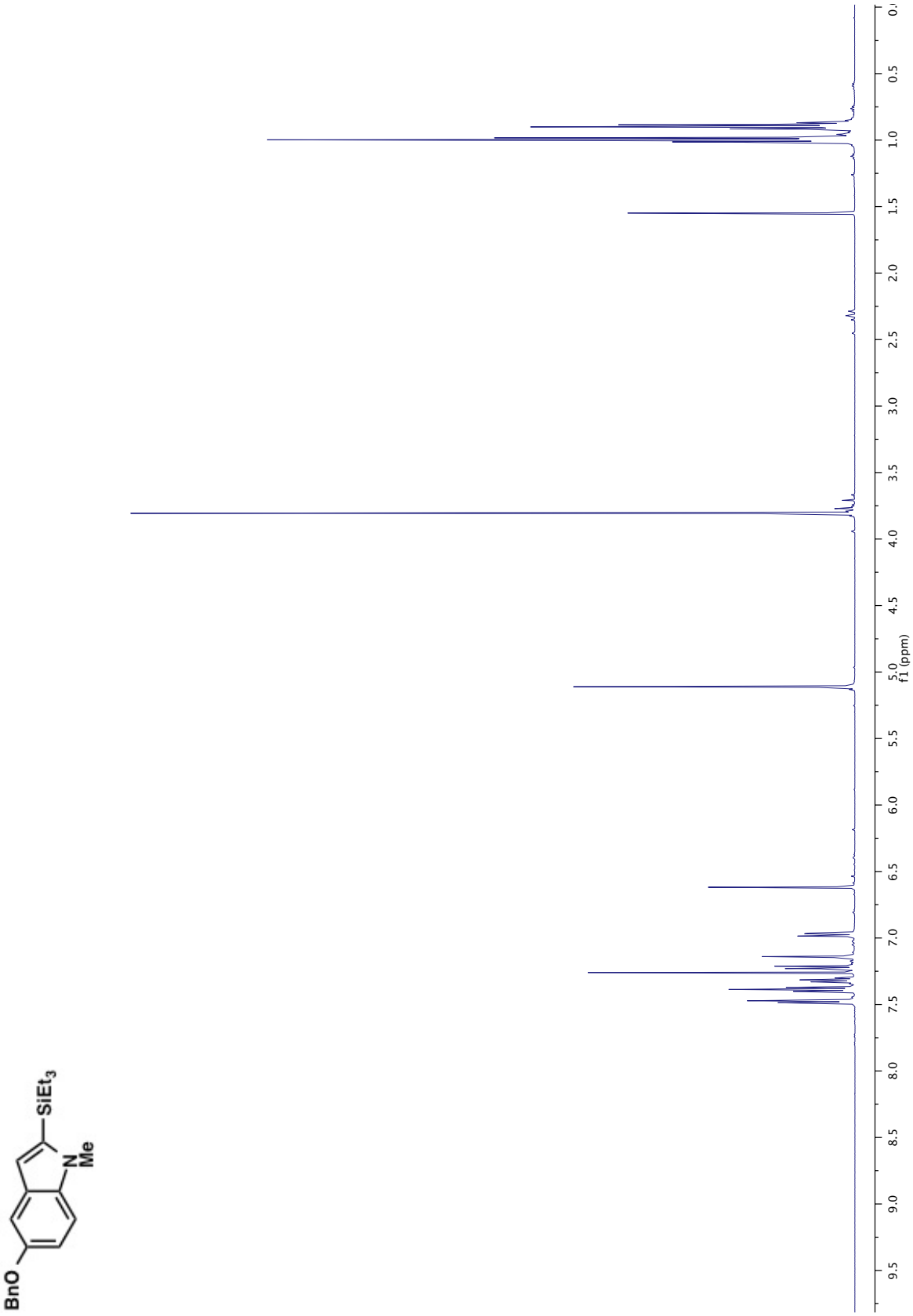
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-2k**.



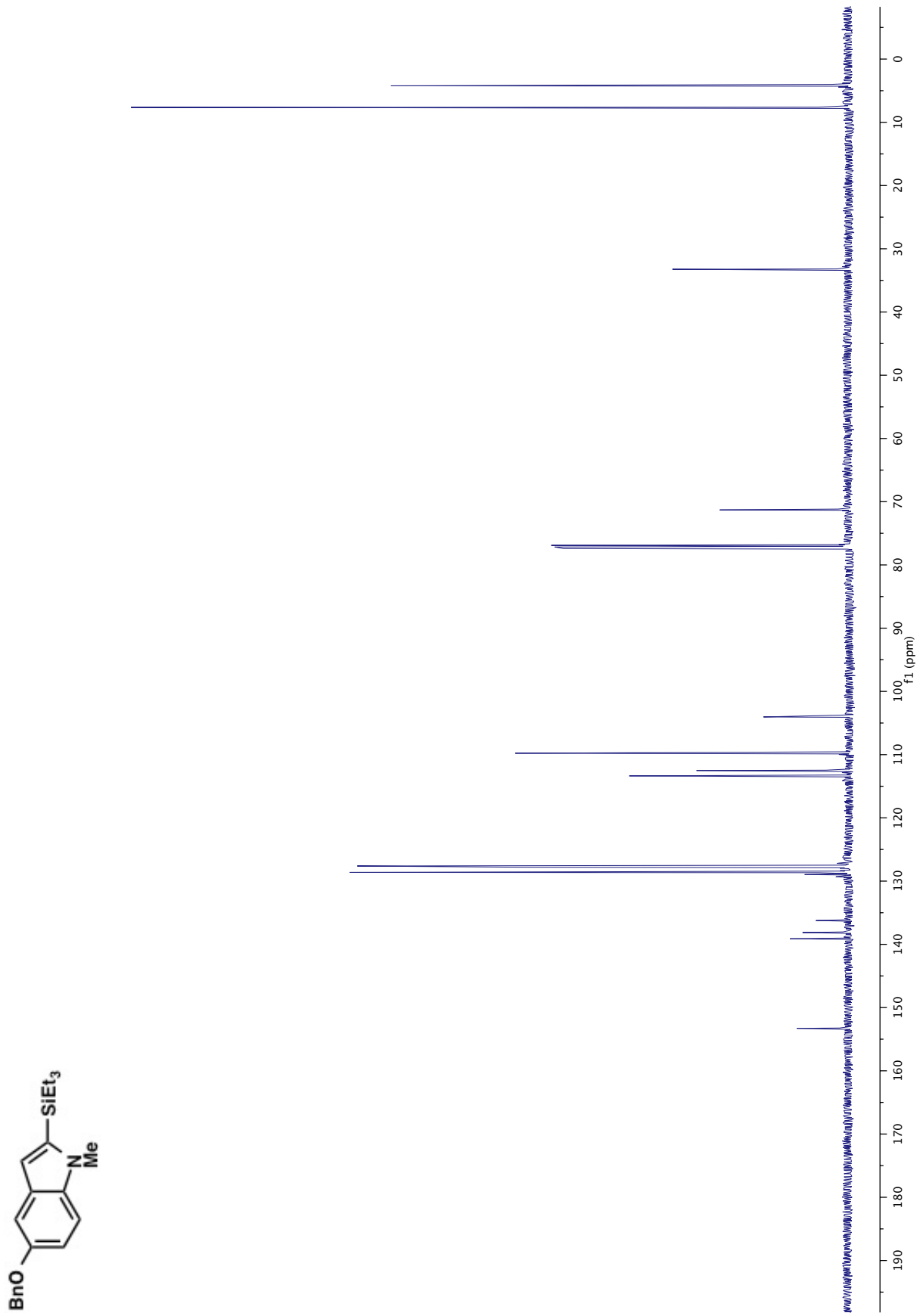
^{1}H NMR (500 MHz, $CDCl_3$) of compound **15**.



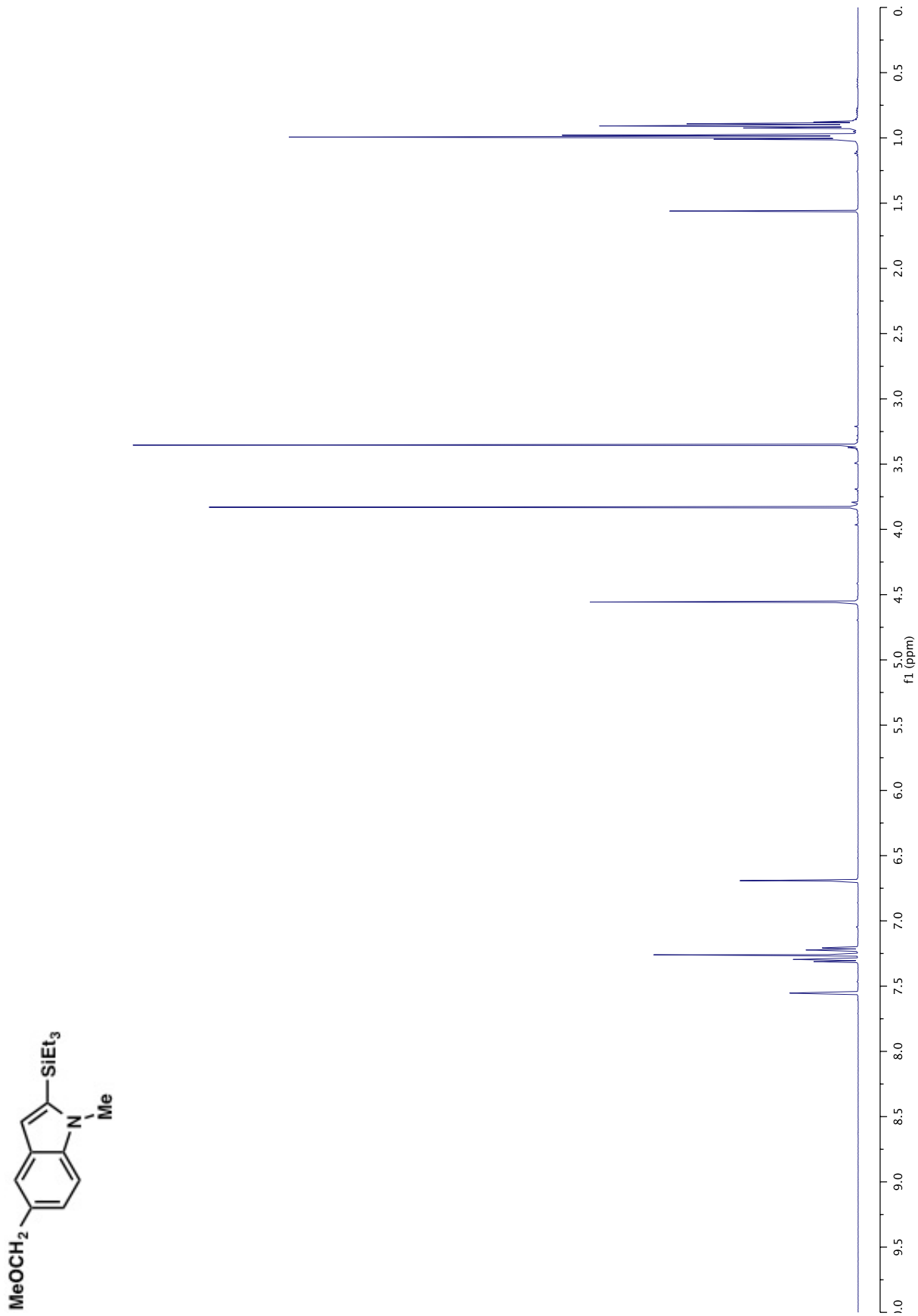
^{13}C NMR (125 MHz, $CDCl_3$) of compound **15**.



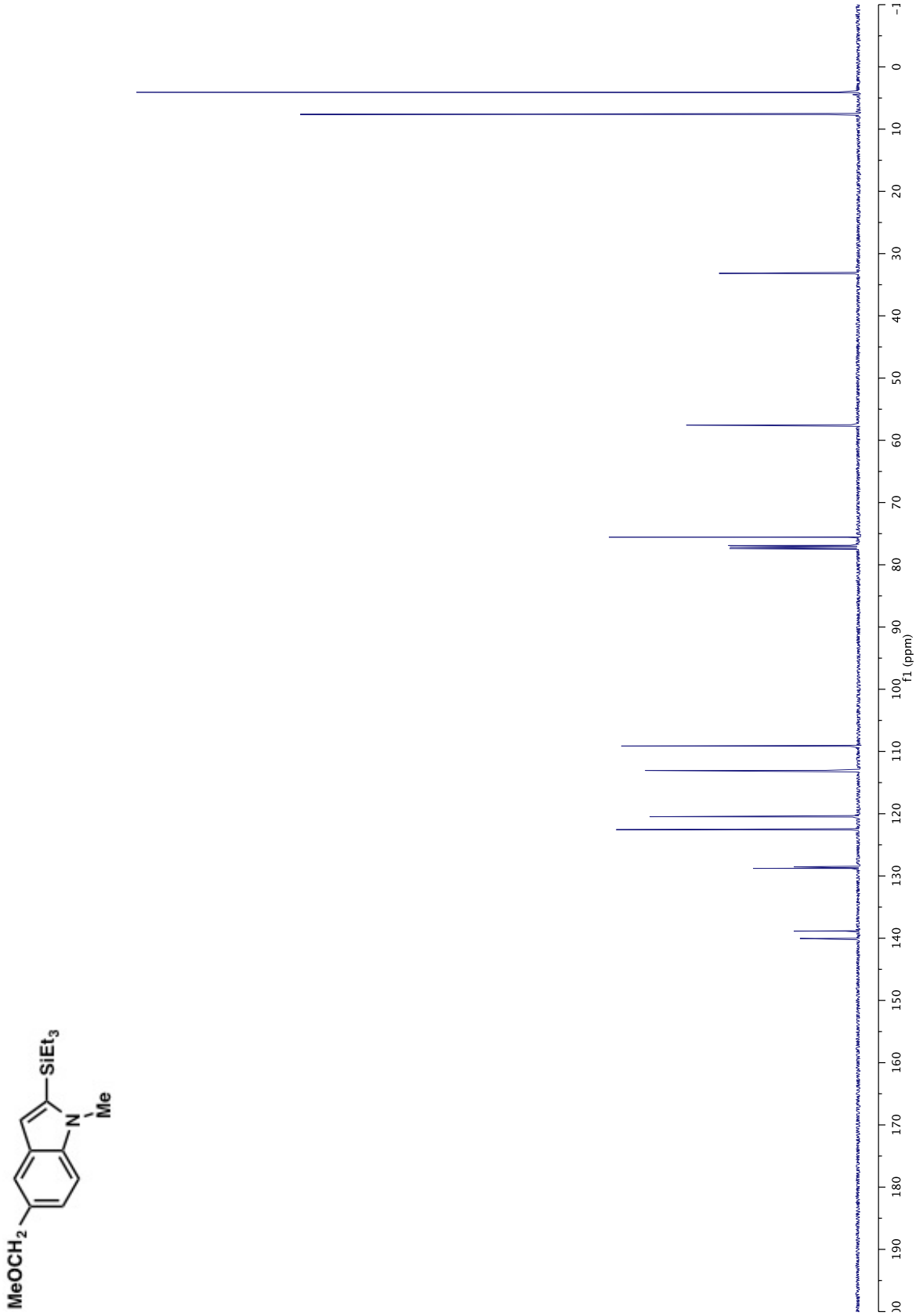
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2l**.



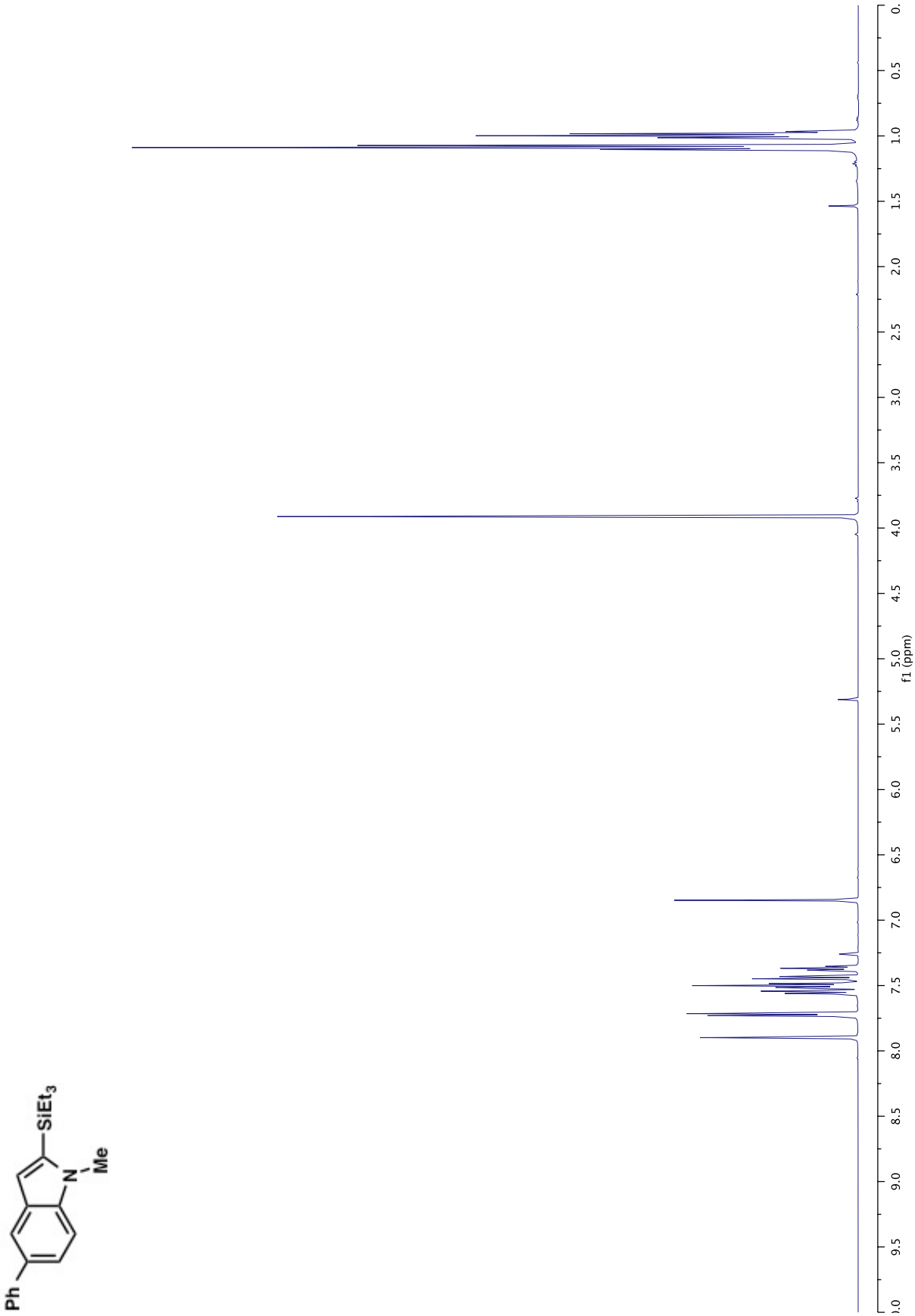
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2l**.



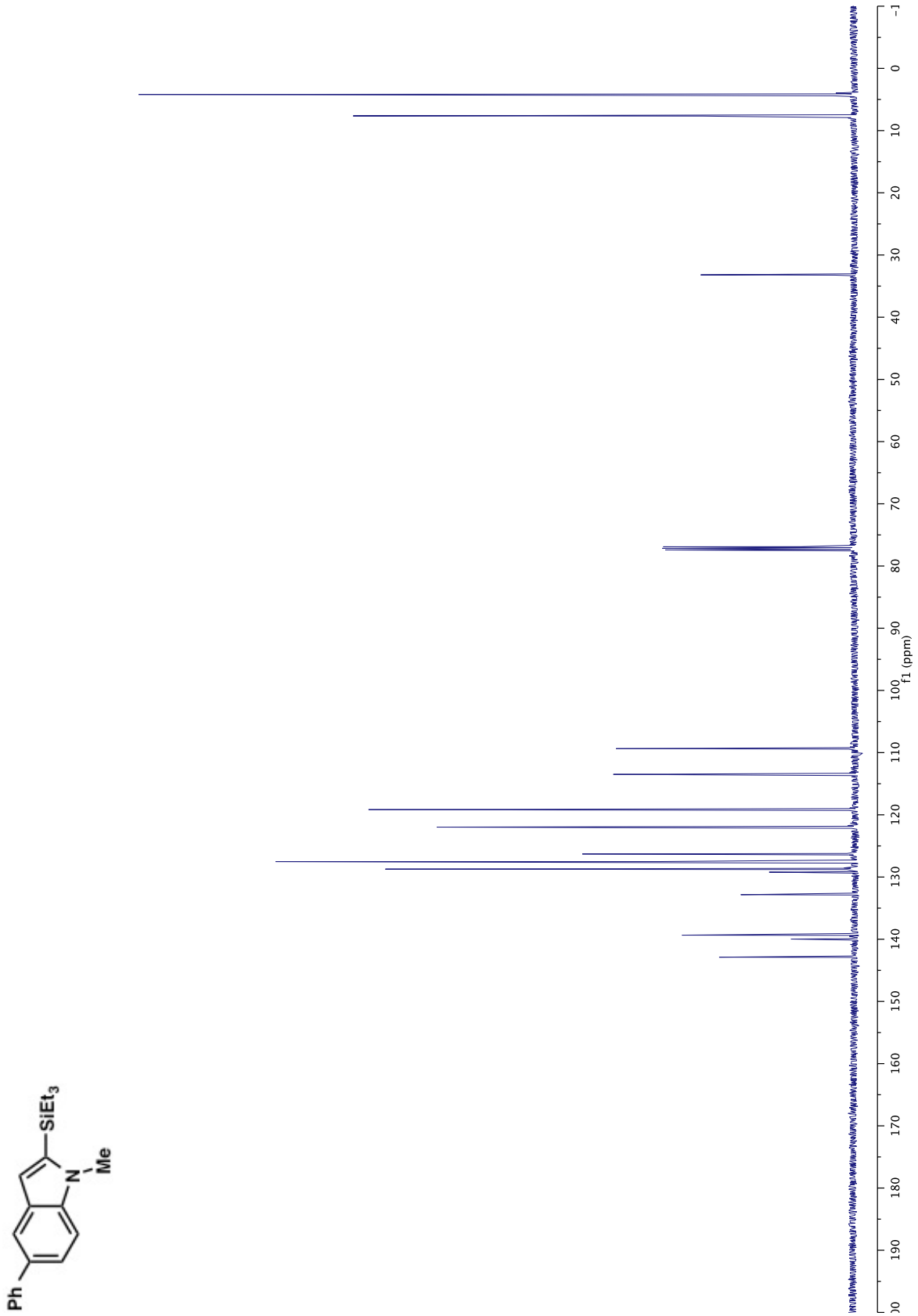
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2m**.



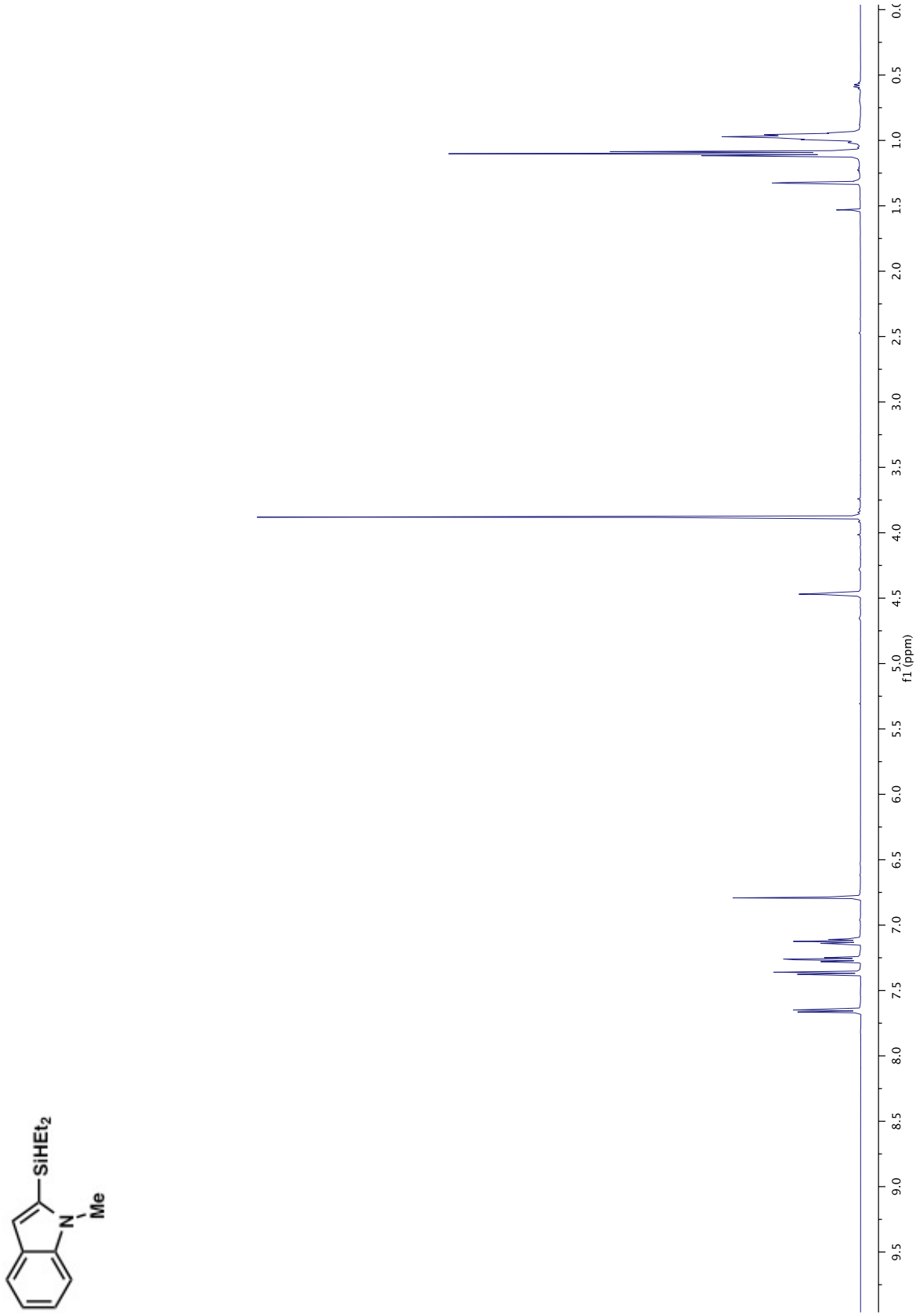
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2m**.



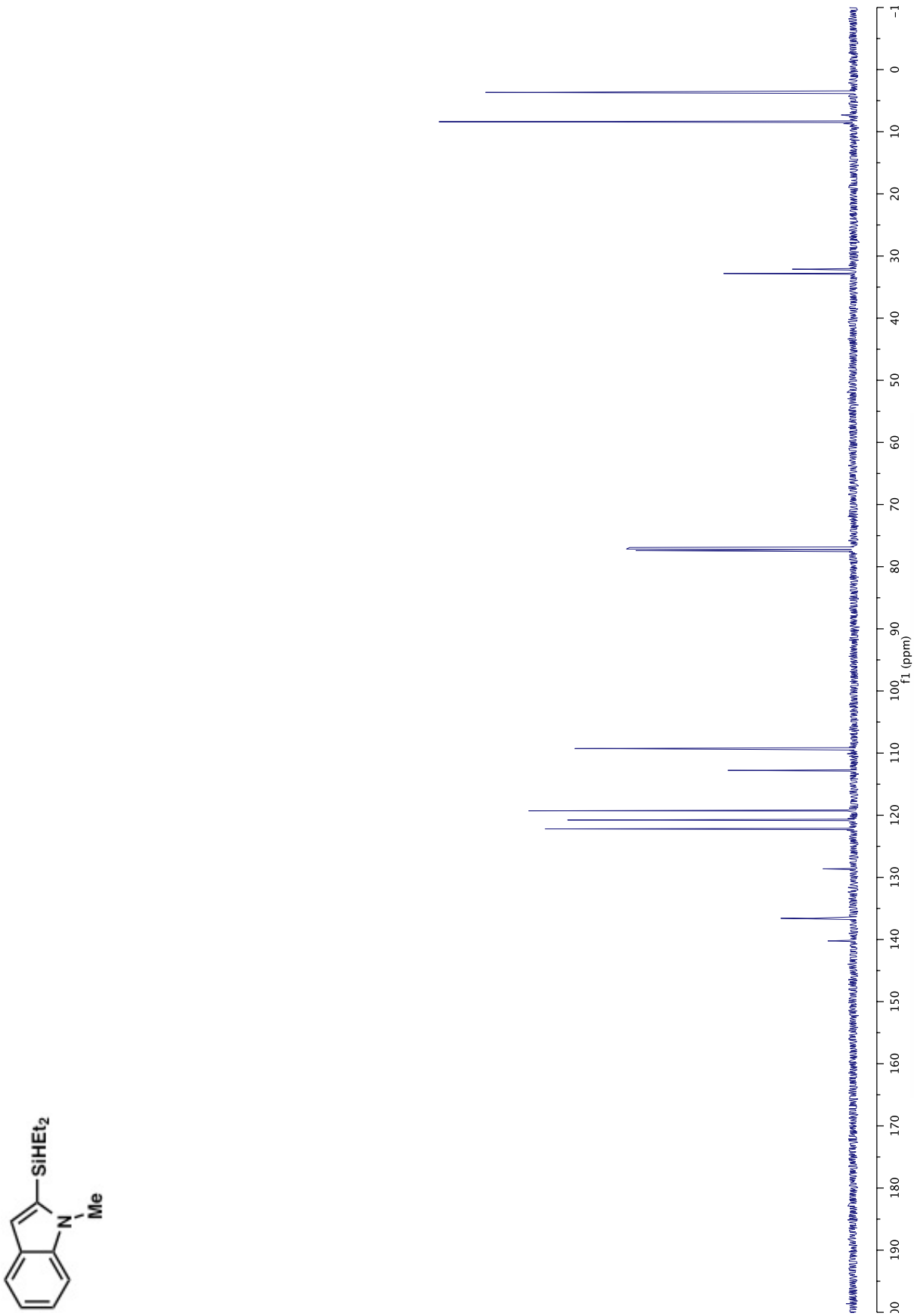
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2n**.



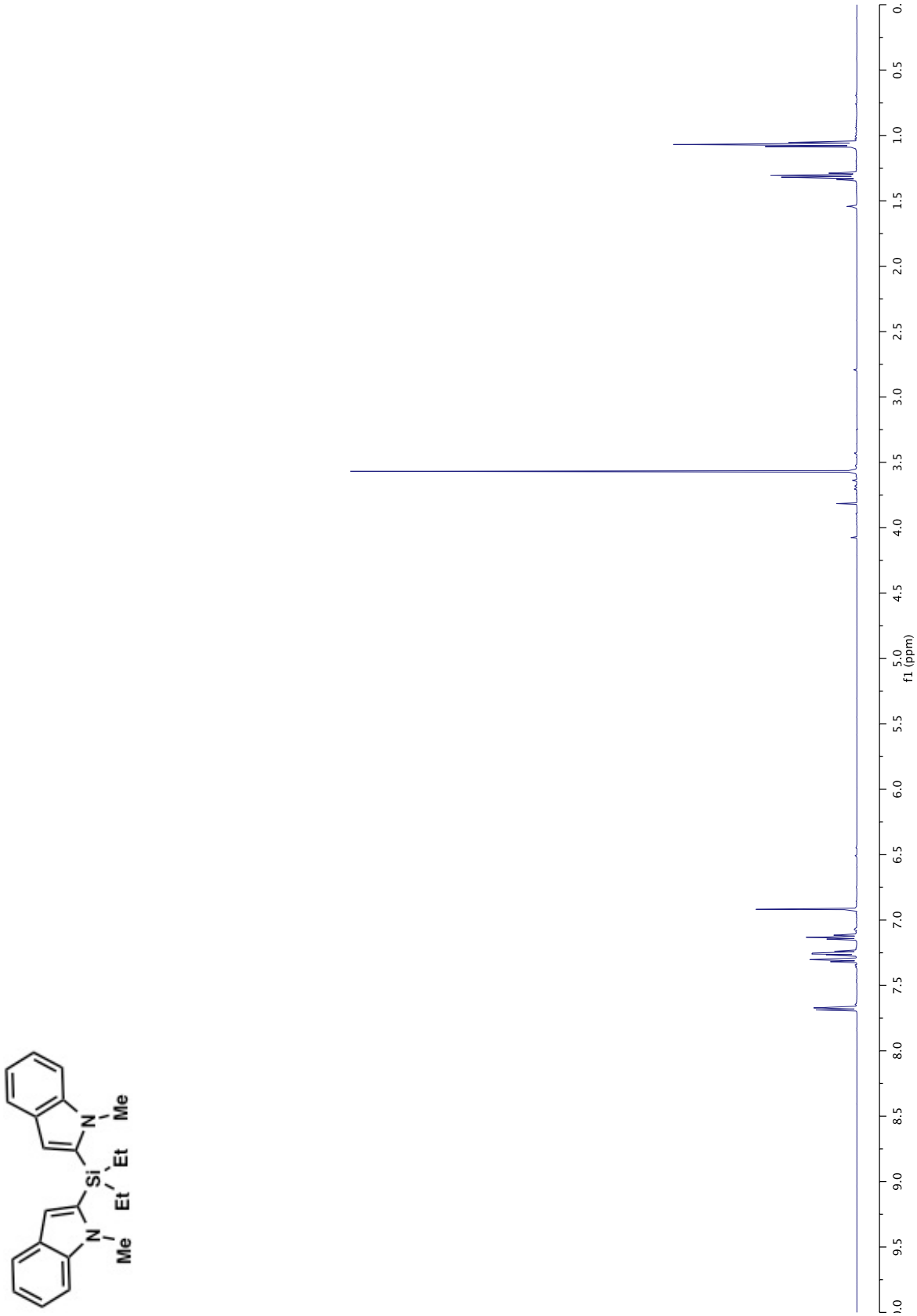
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2n**.



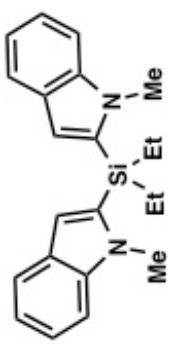
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2o**.

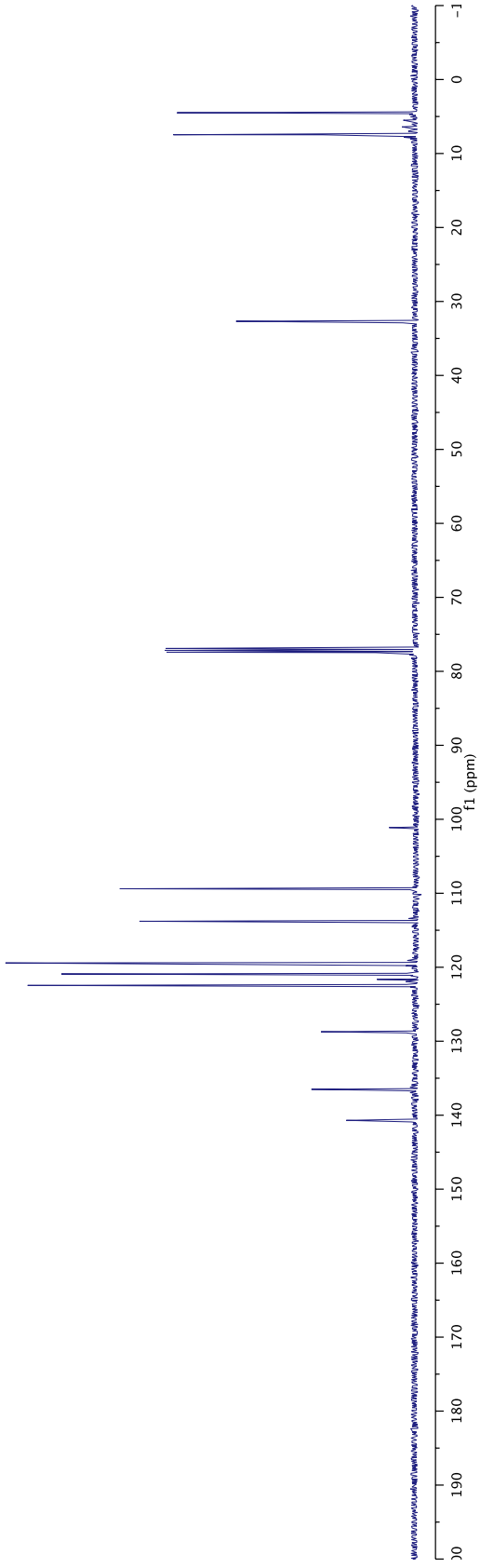


^{13}C NMR (125 MHz, $CDCl_3$) of compound **2o**.

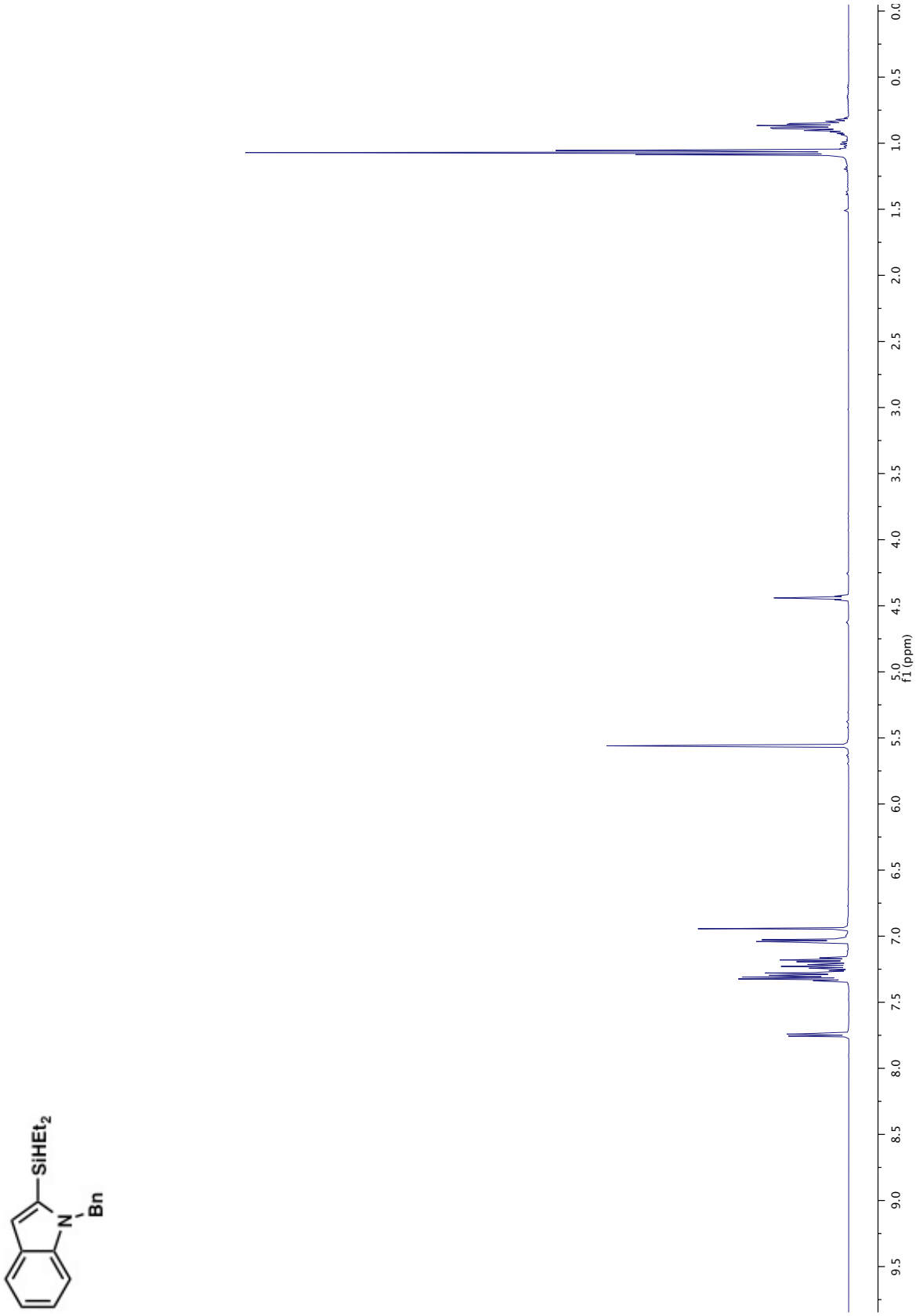


^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-2o**.

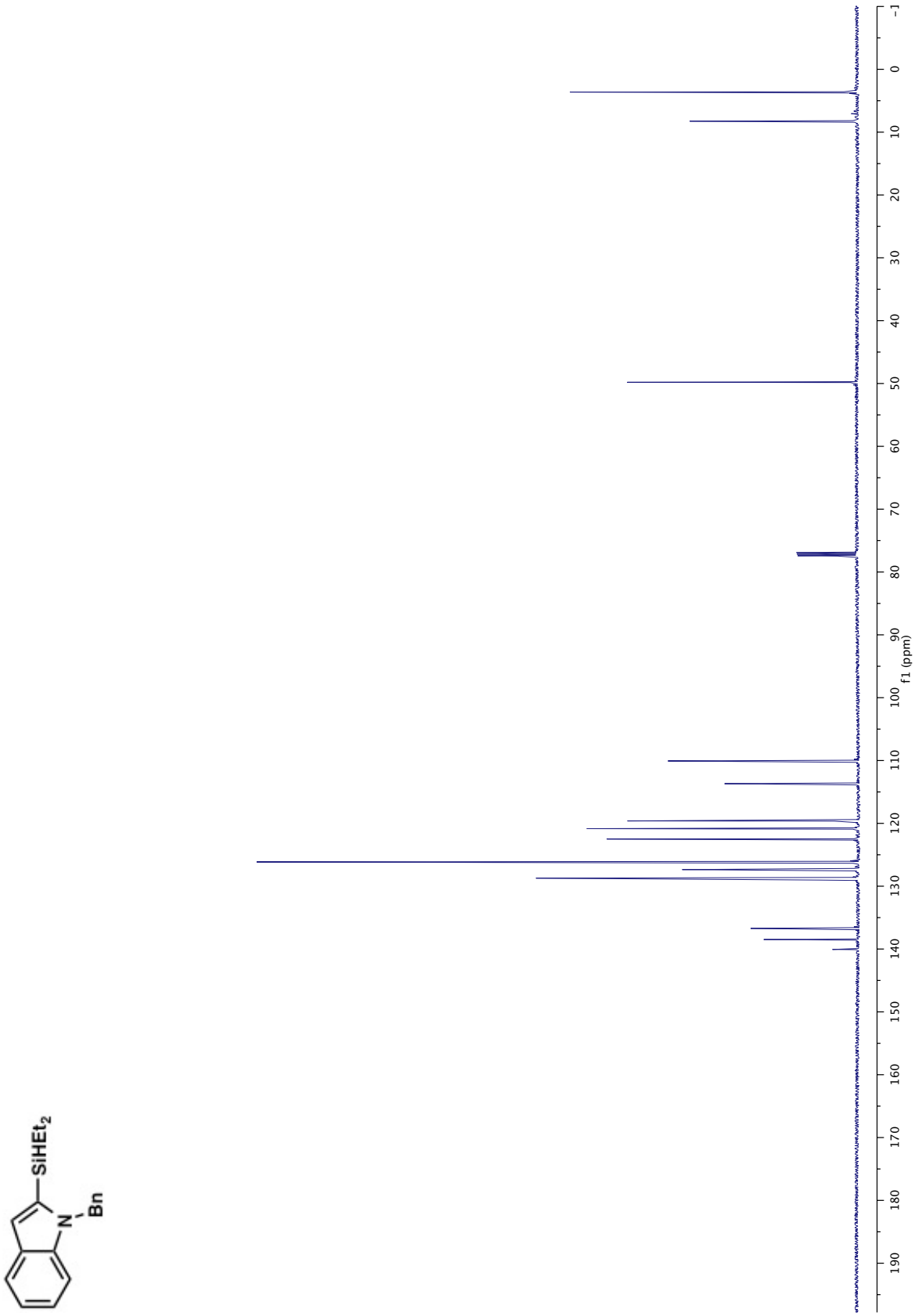




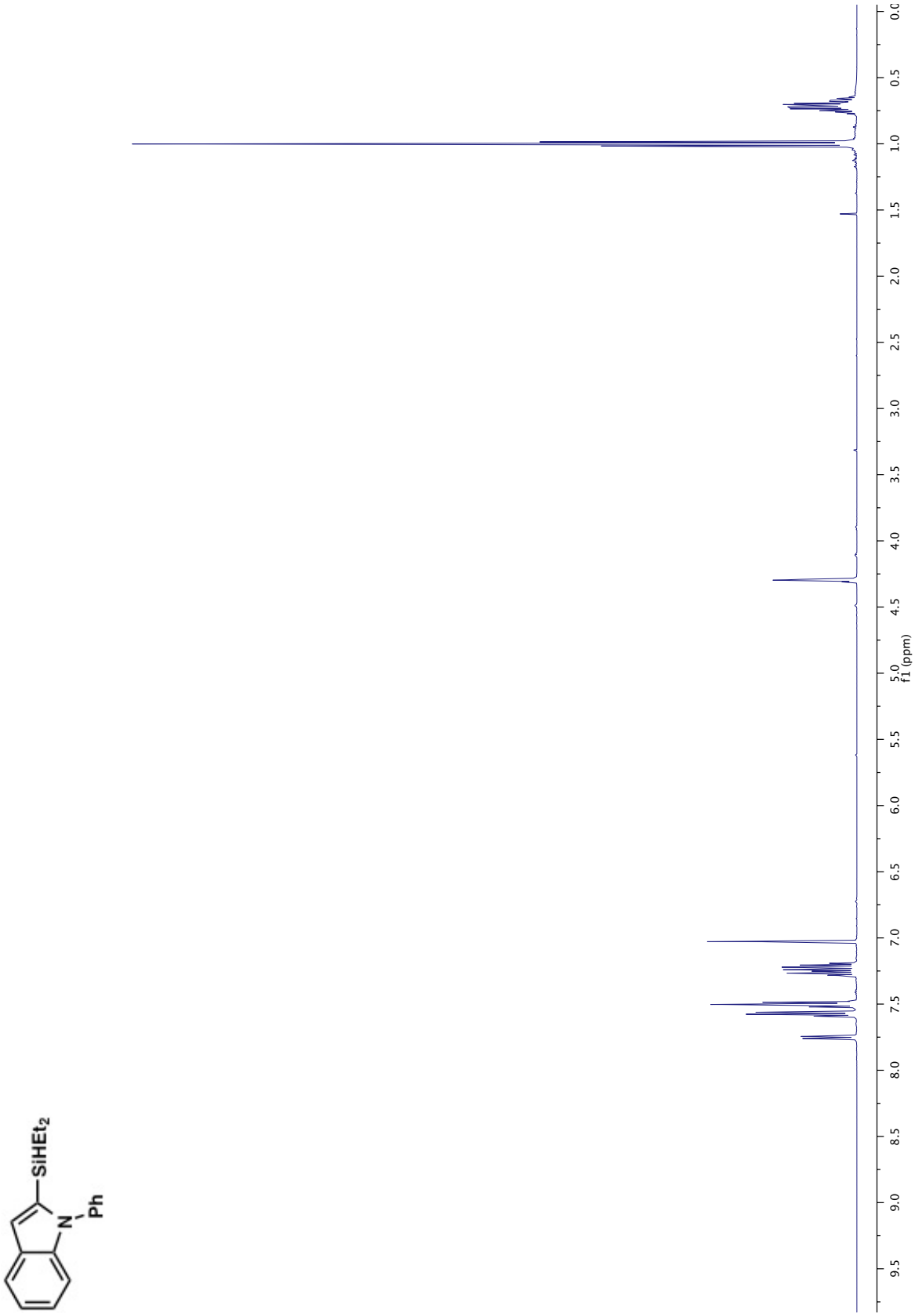
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-2o**.



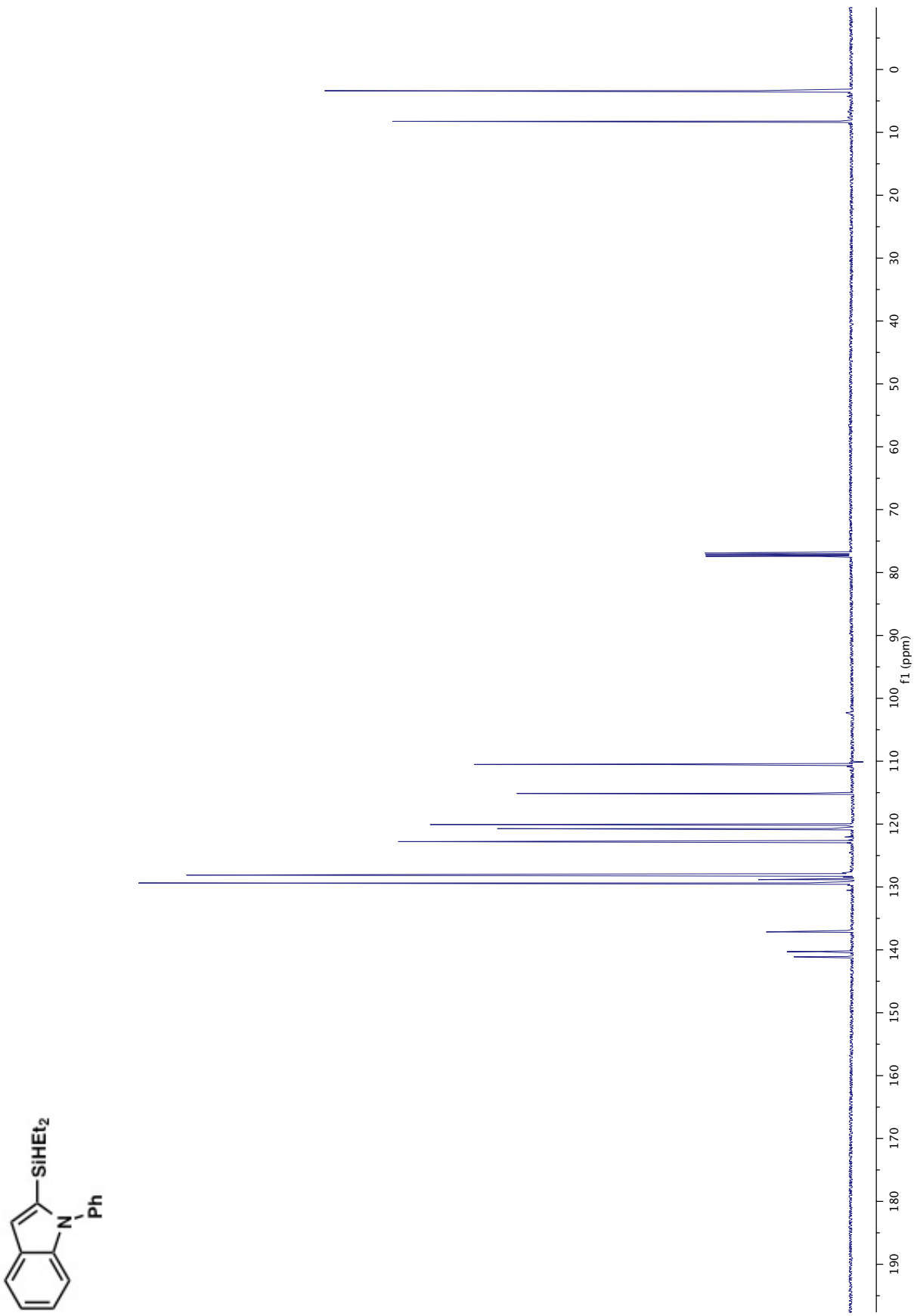
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2p**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **2p**.

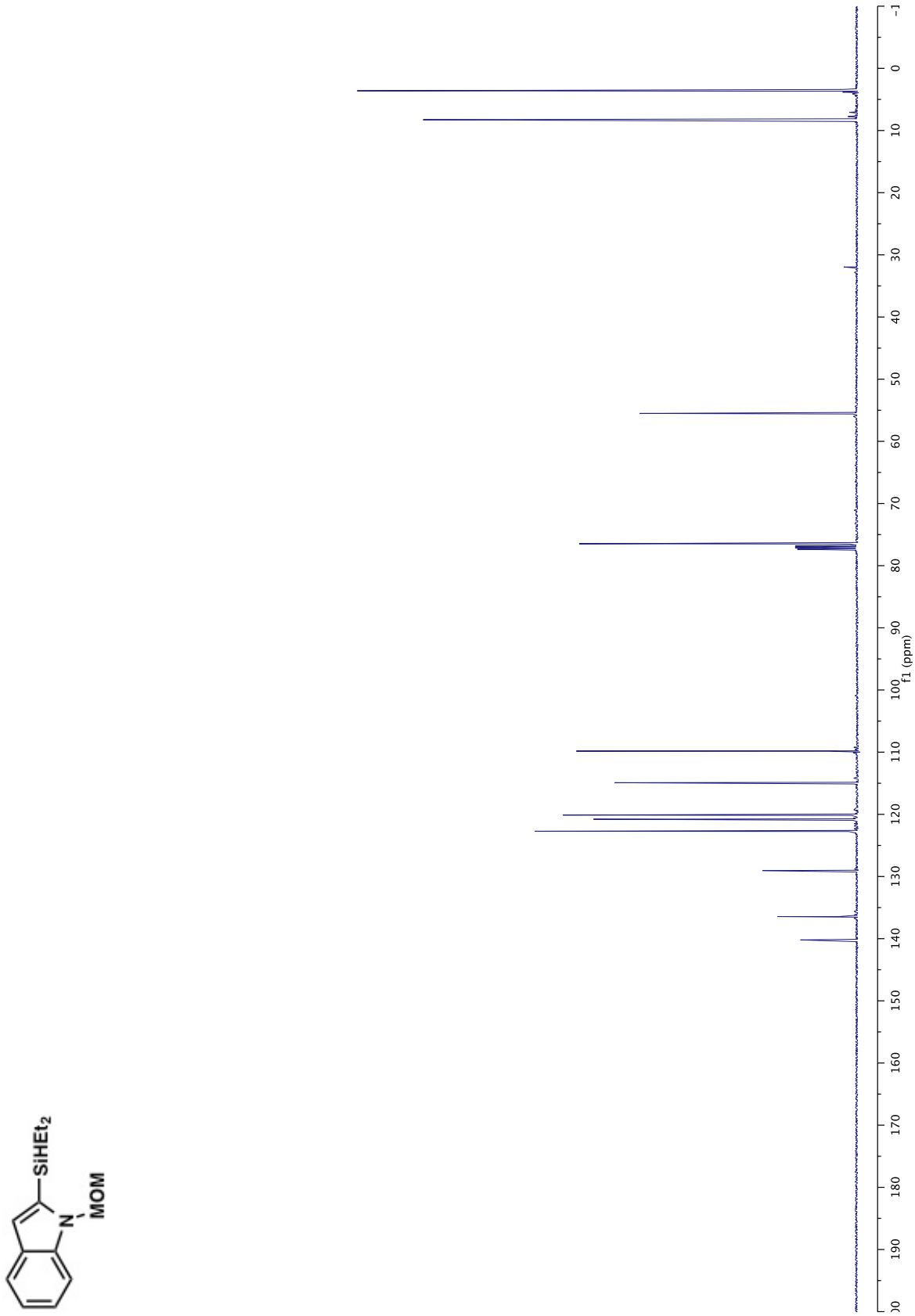


^{1}H NMR (500 MHz, $CDCl_3$) of compound **2q**.

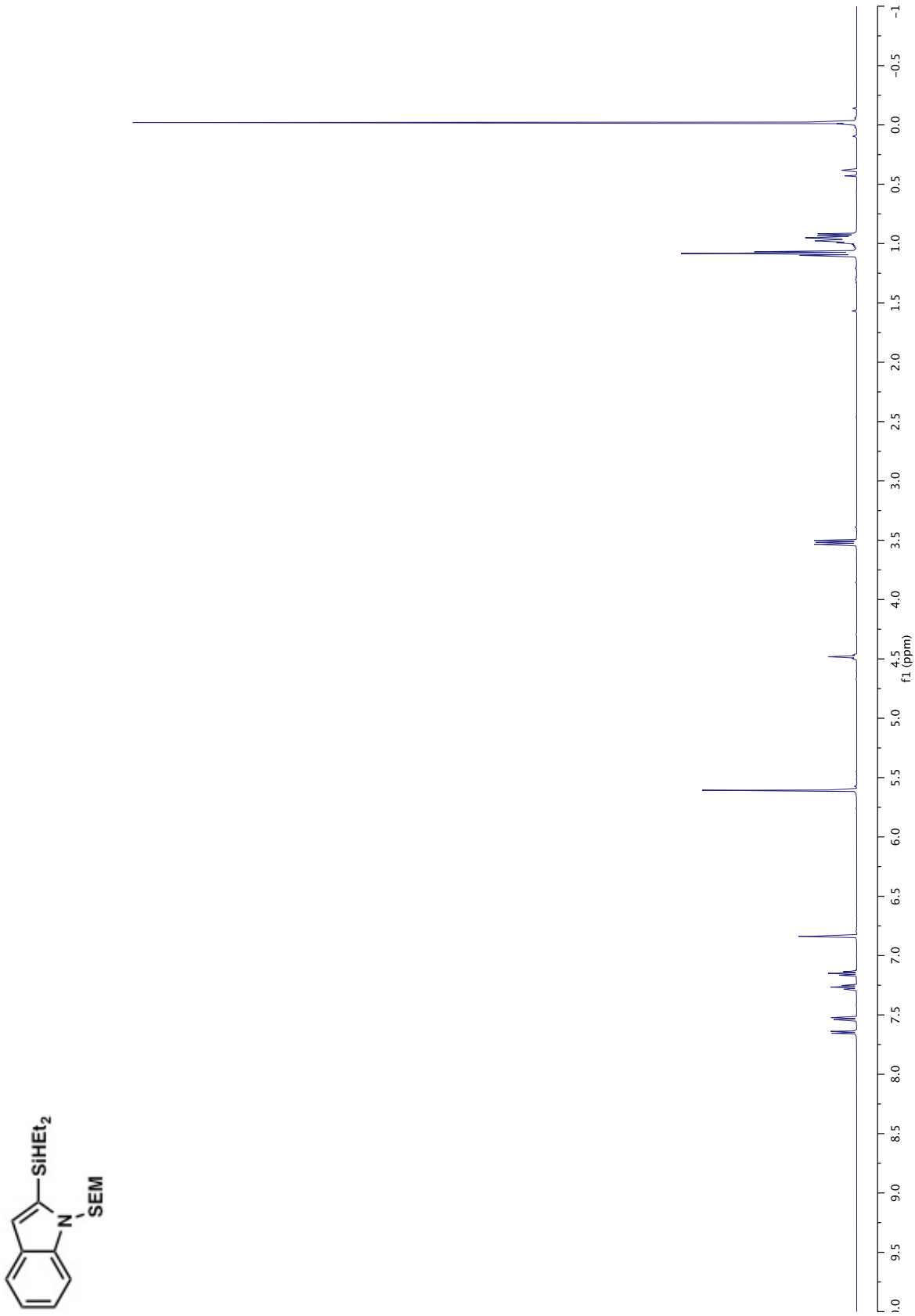


^{13}C NMR (125 MHz, $CDCl_3$) of compound **2q**.

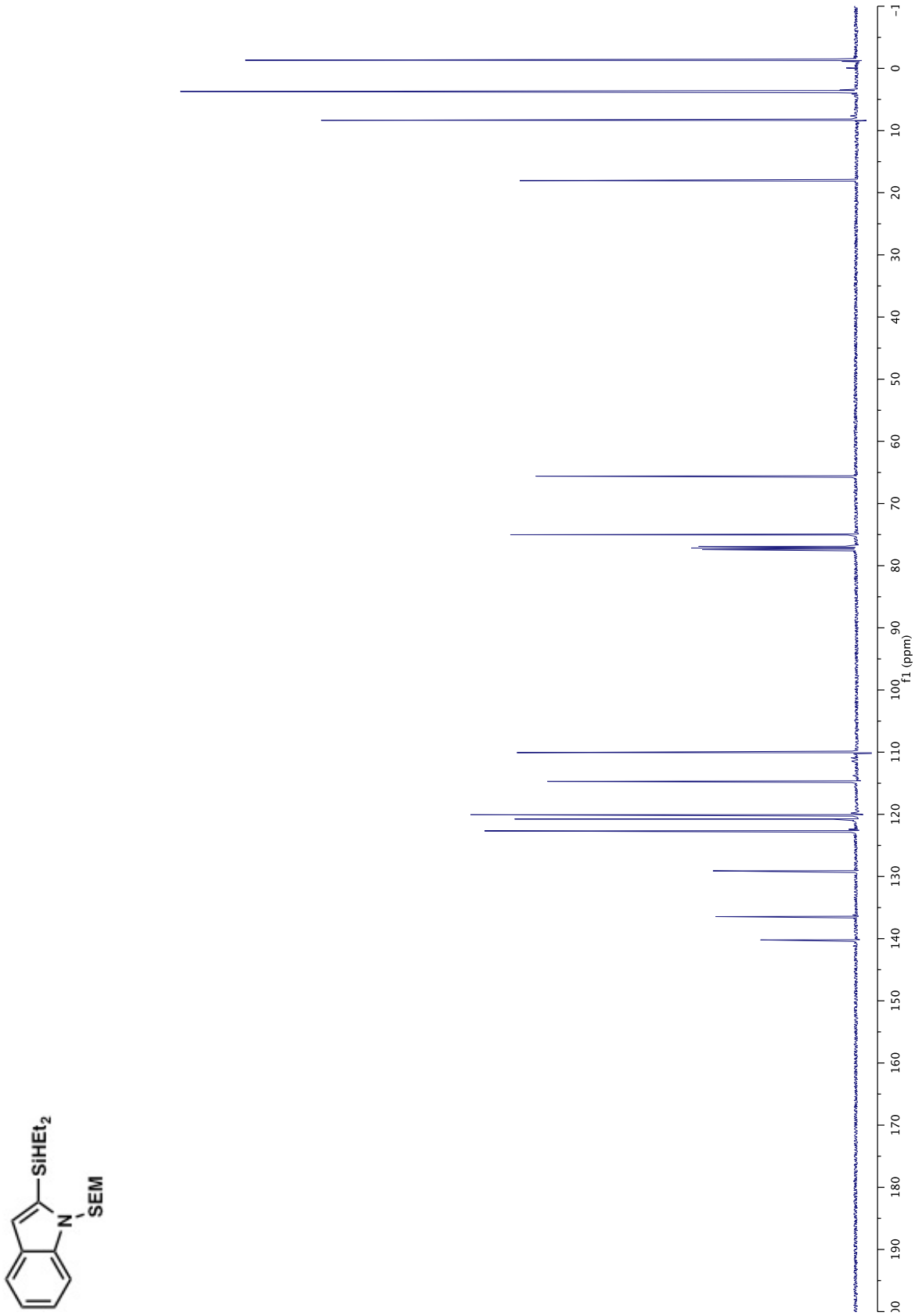
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2r**.



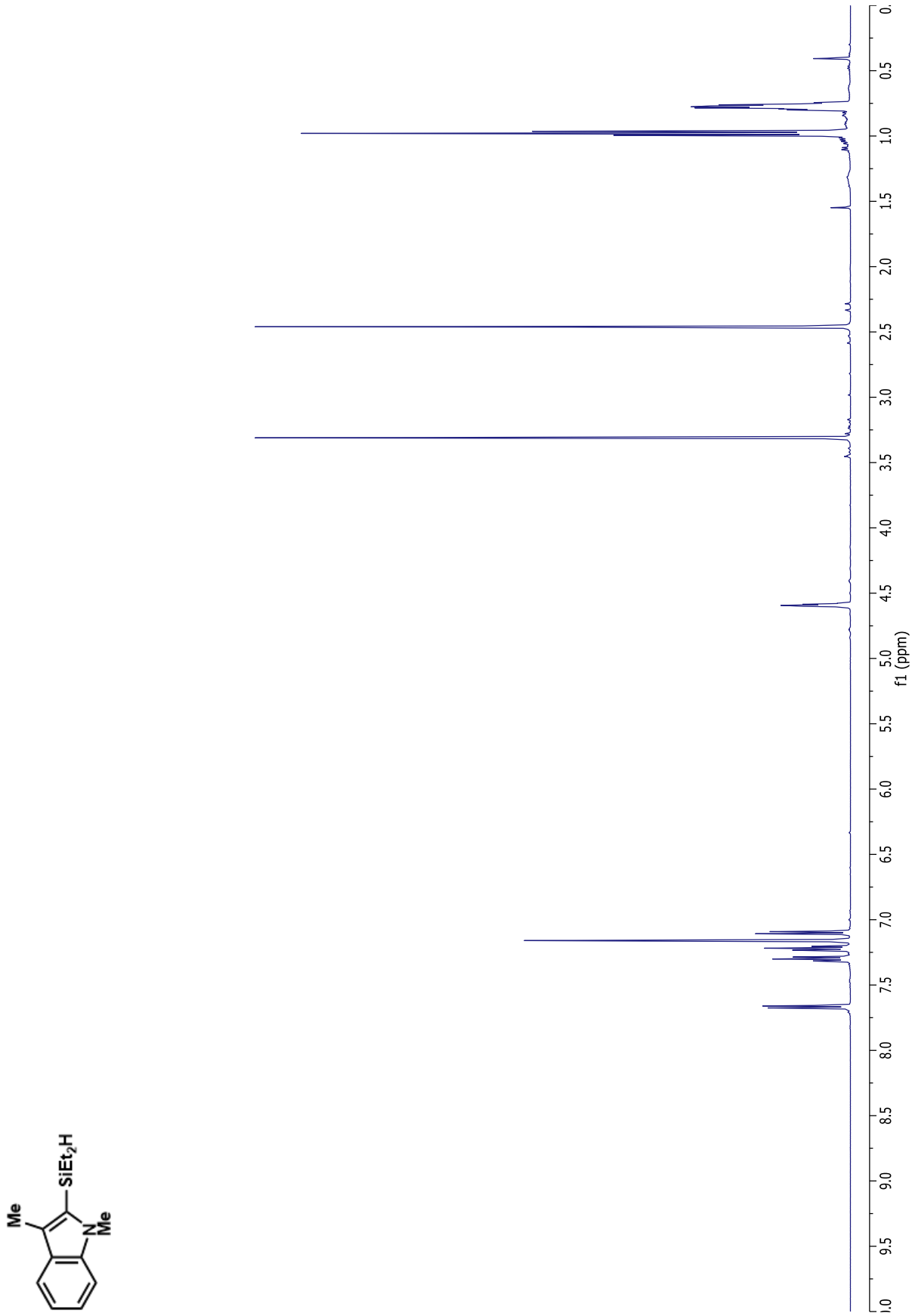
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2r**.



^{1}H NMR (500 MHz, $CDCl_3$) of compound **2s**.

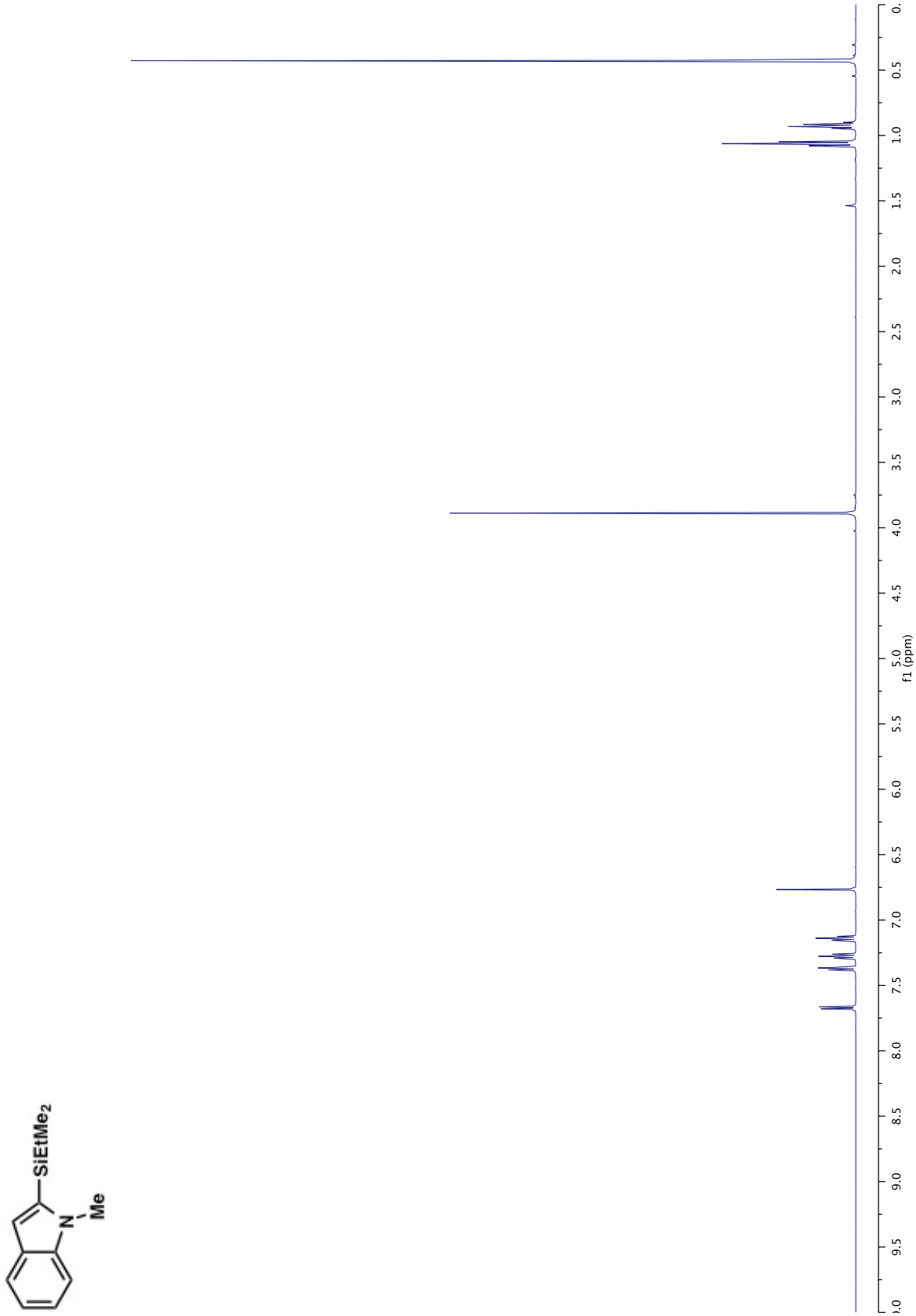


^{13}C NMR (125 MHz, $CDCl_3$) of compound **2s**.

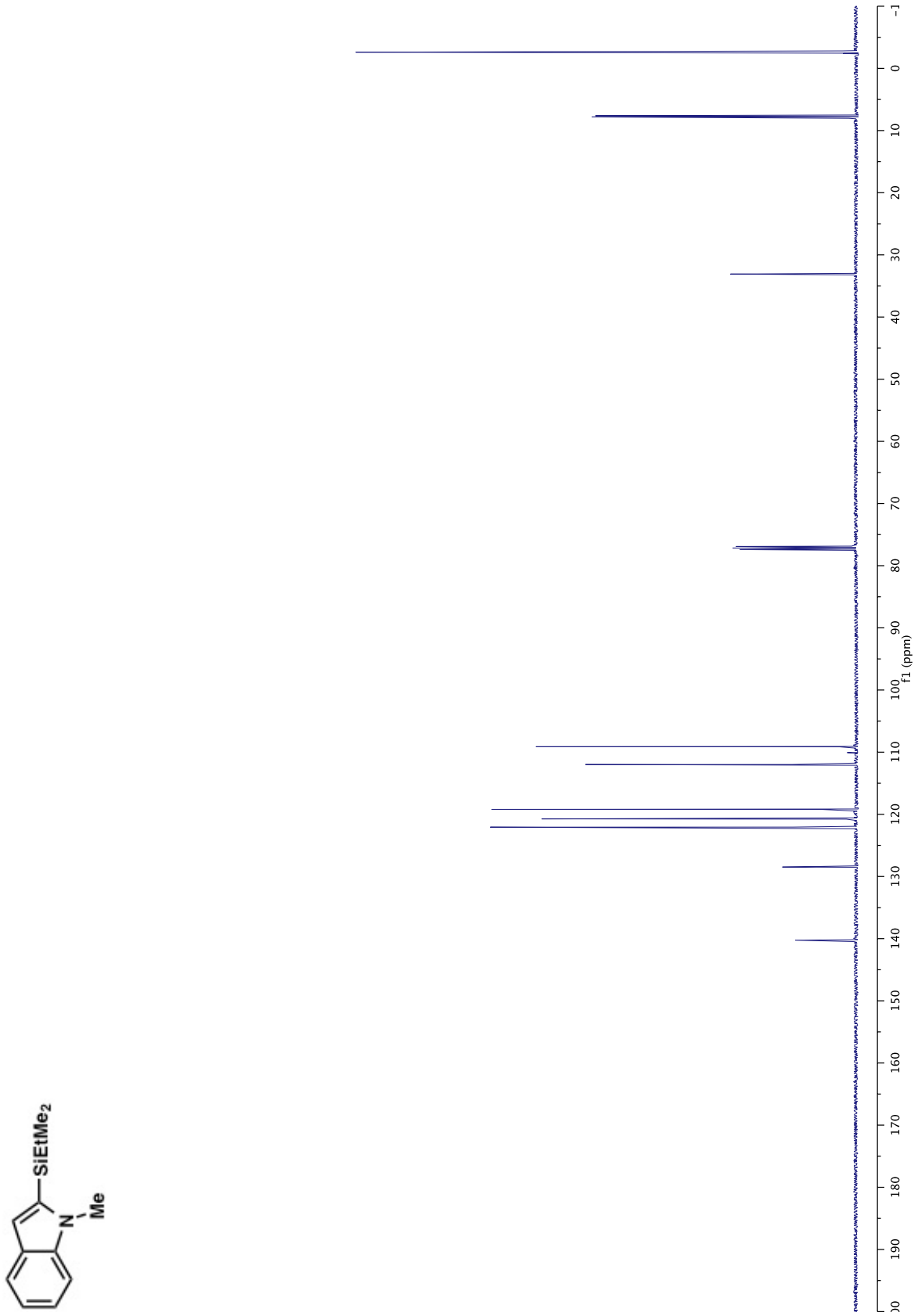


^{1}H NMR (500 MHz, C_6D_6) of compound **2t**.

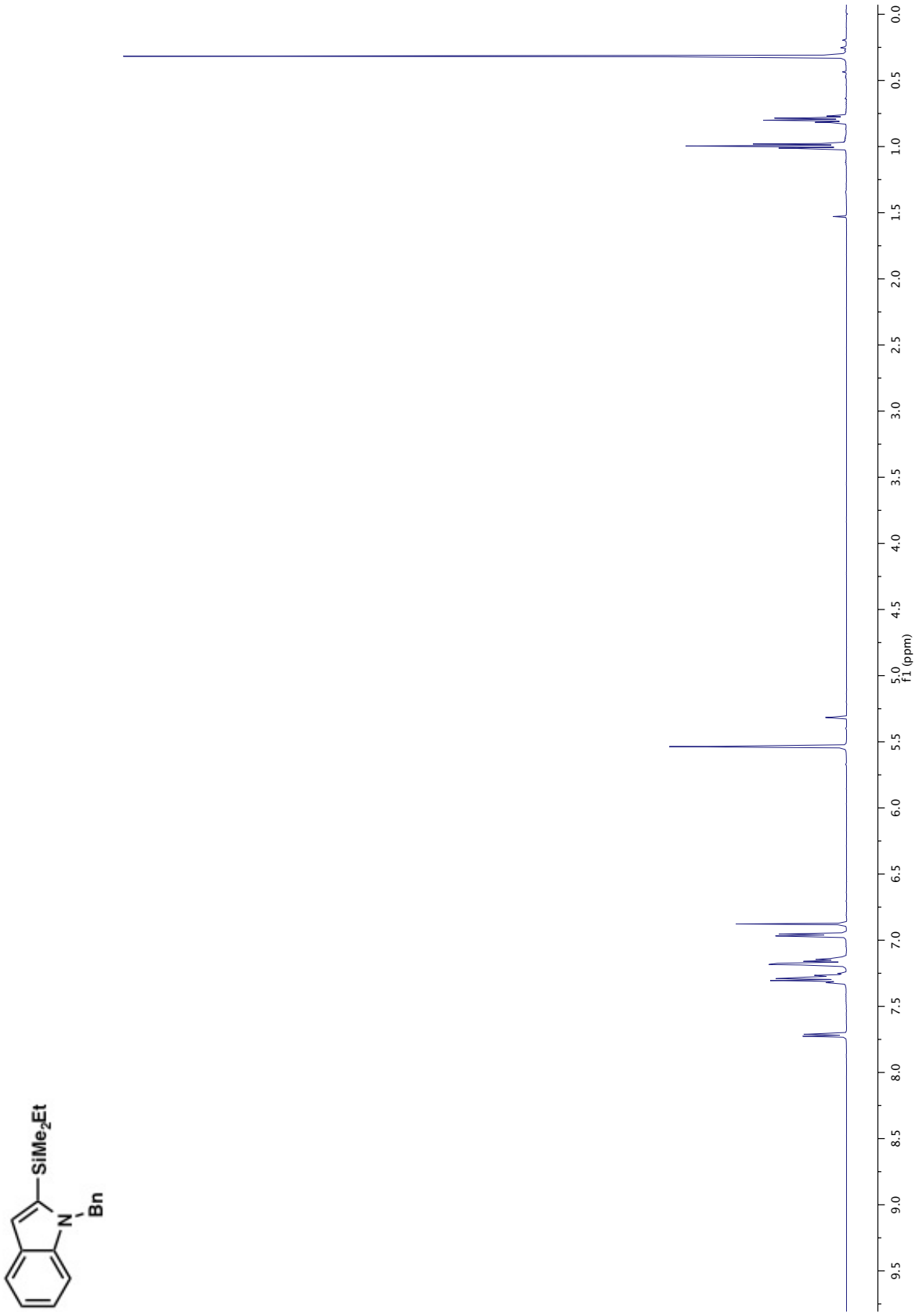
^{13}C NMR (125 MHz, C_6D_6) of compound **2t**.



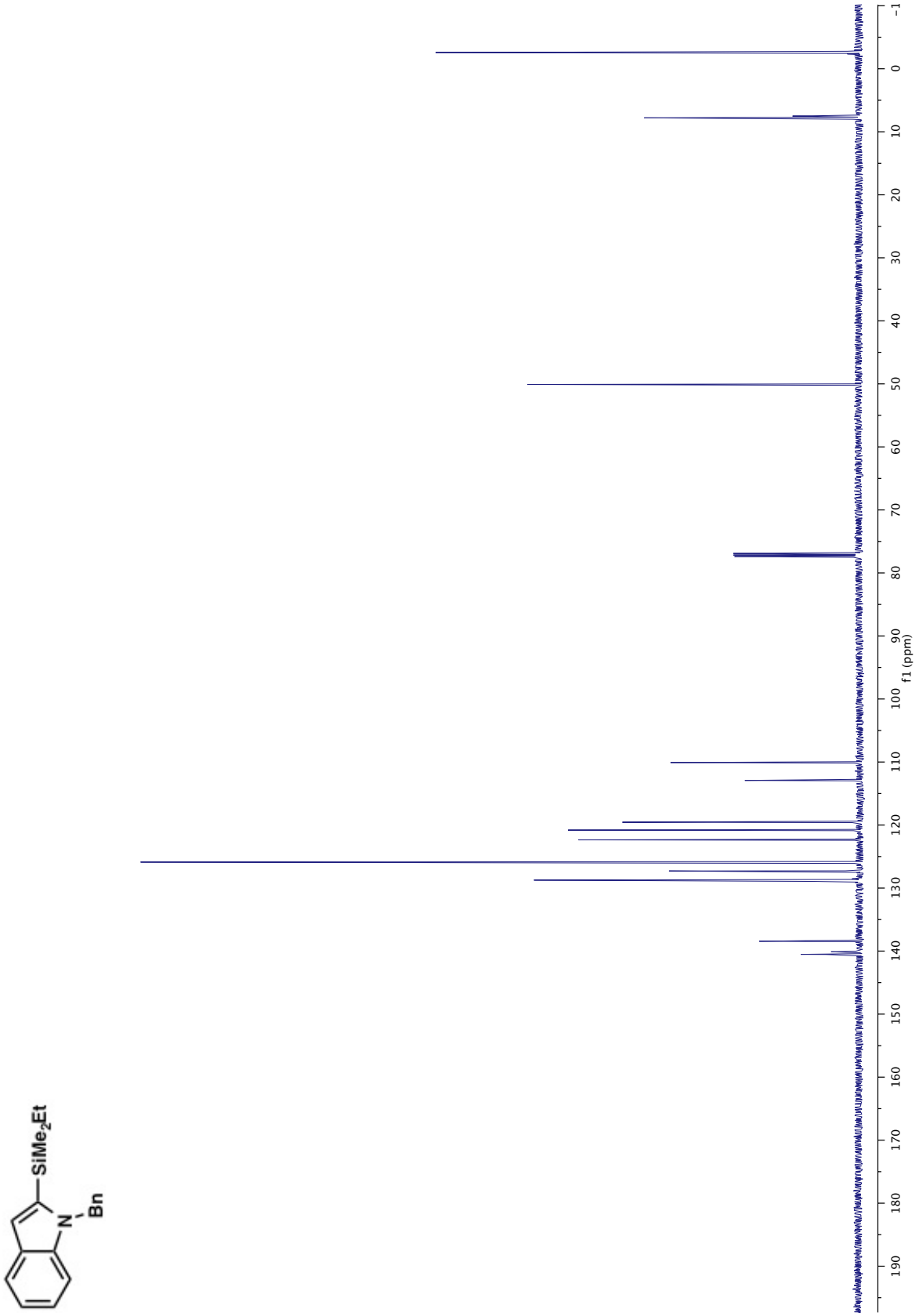
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2u**.



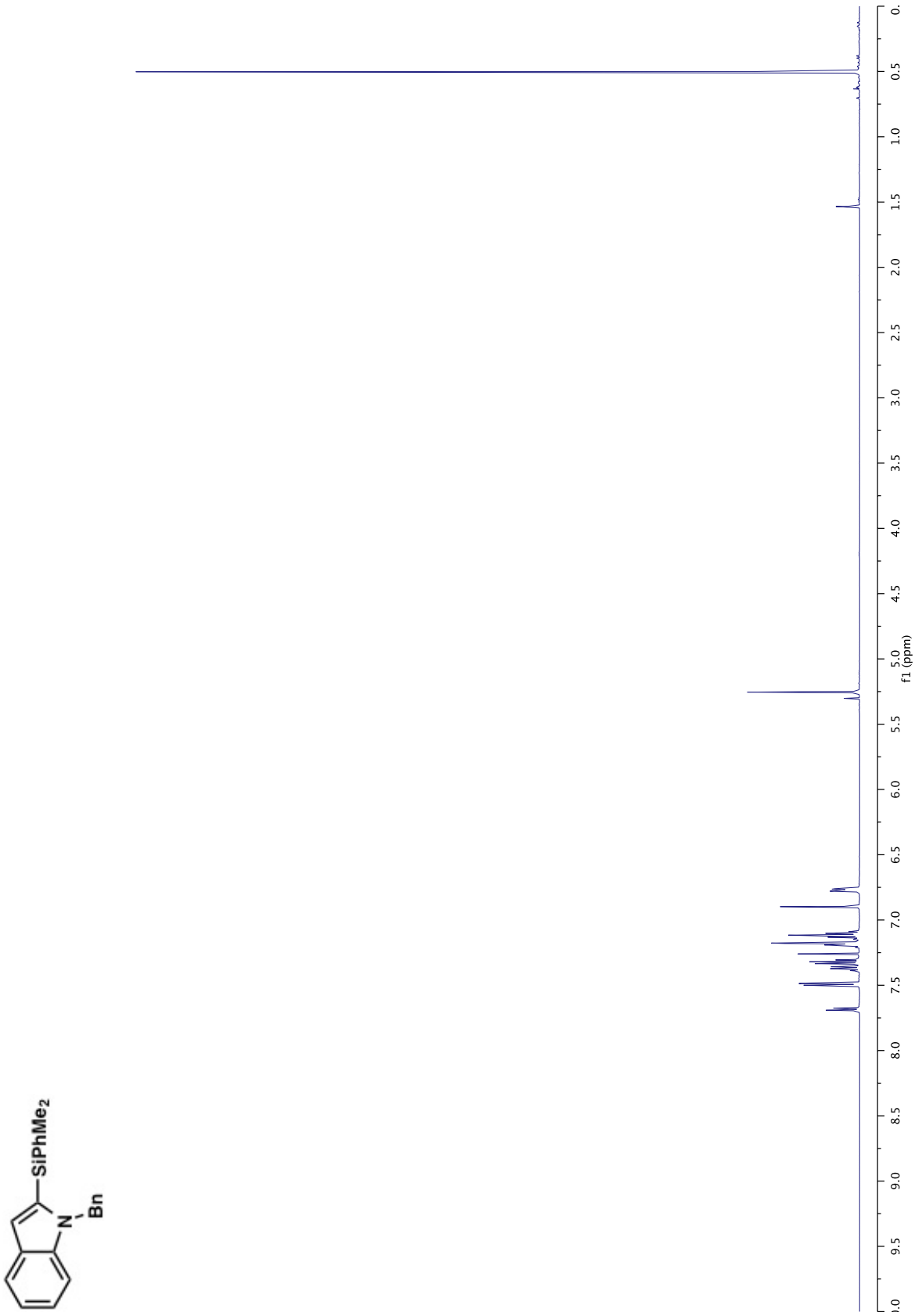
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2u**.



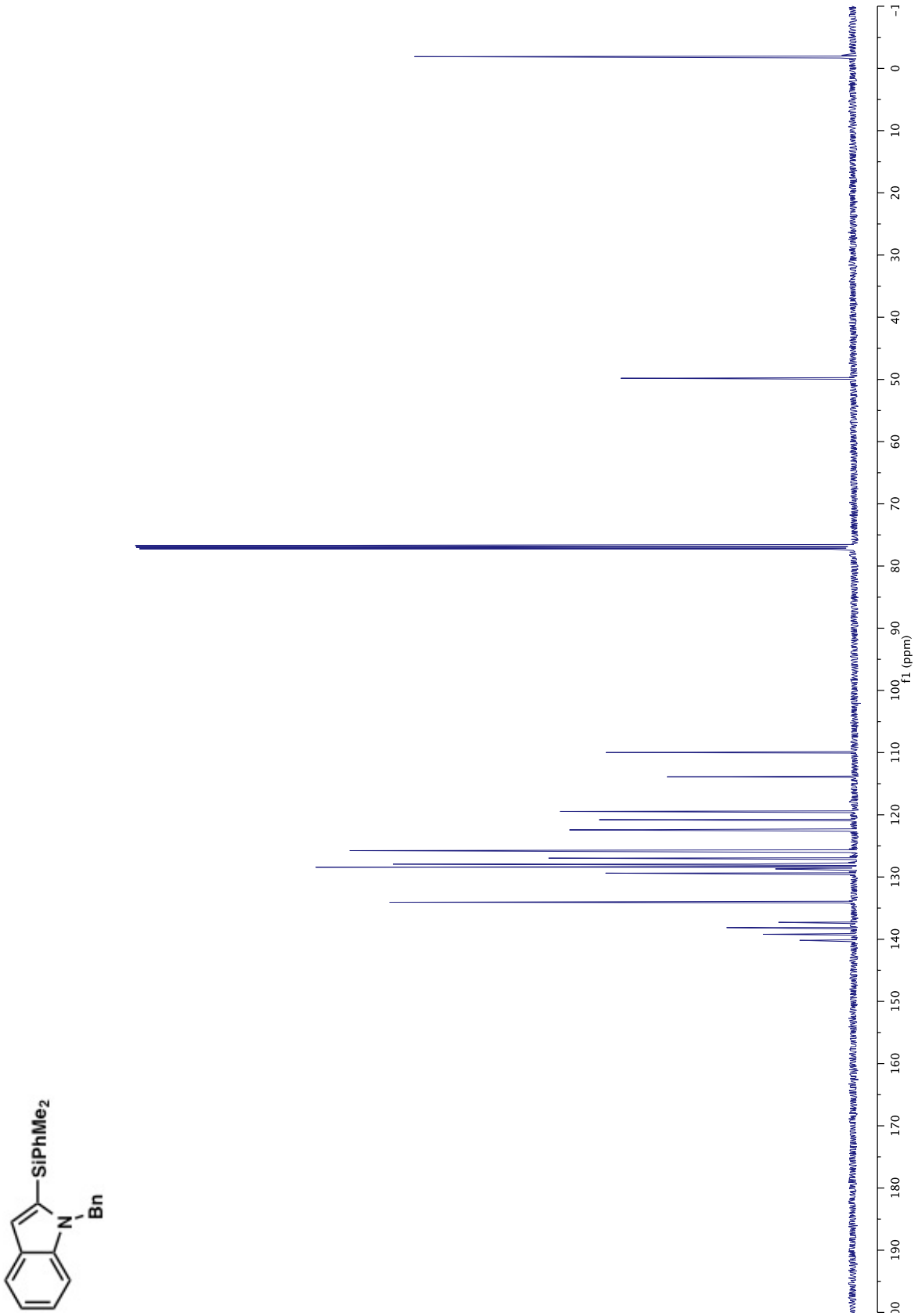
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2v**.



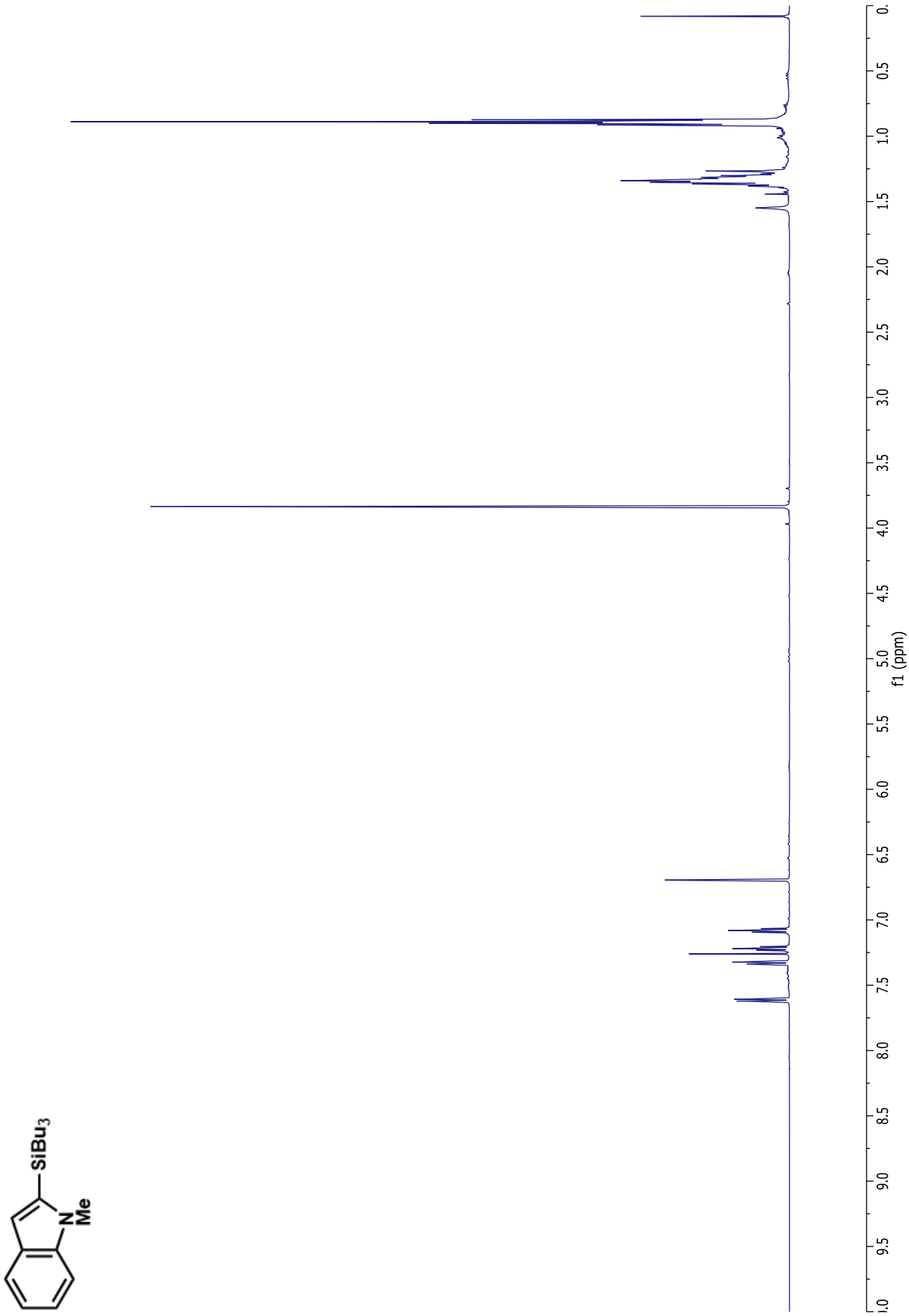
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2v**.



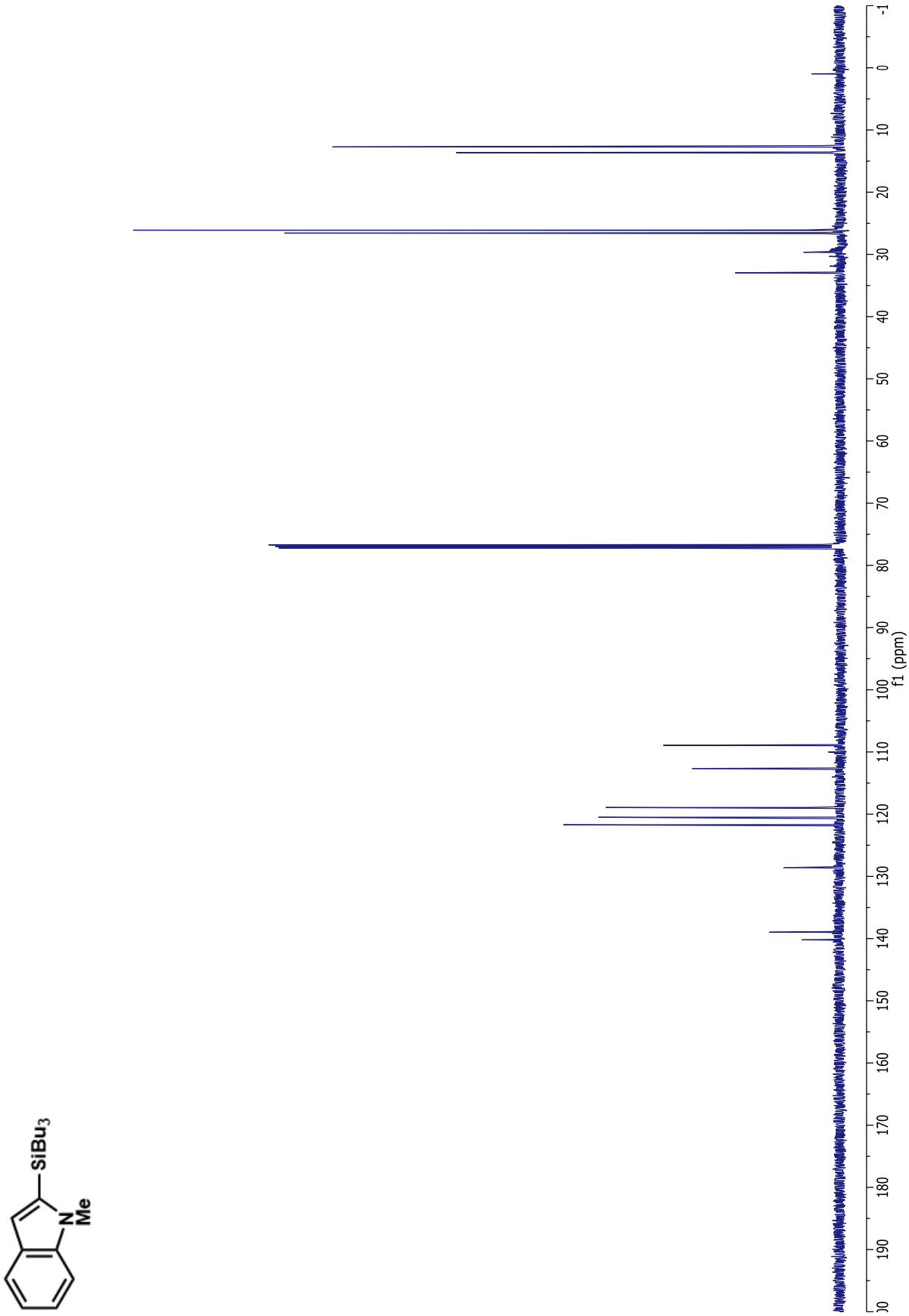
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2w**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **2w**.

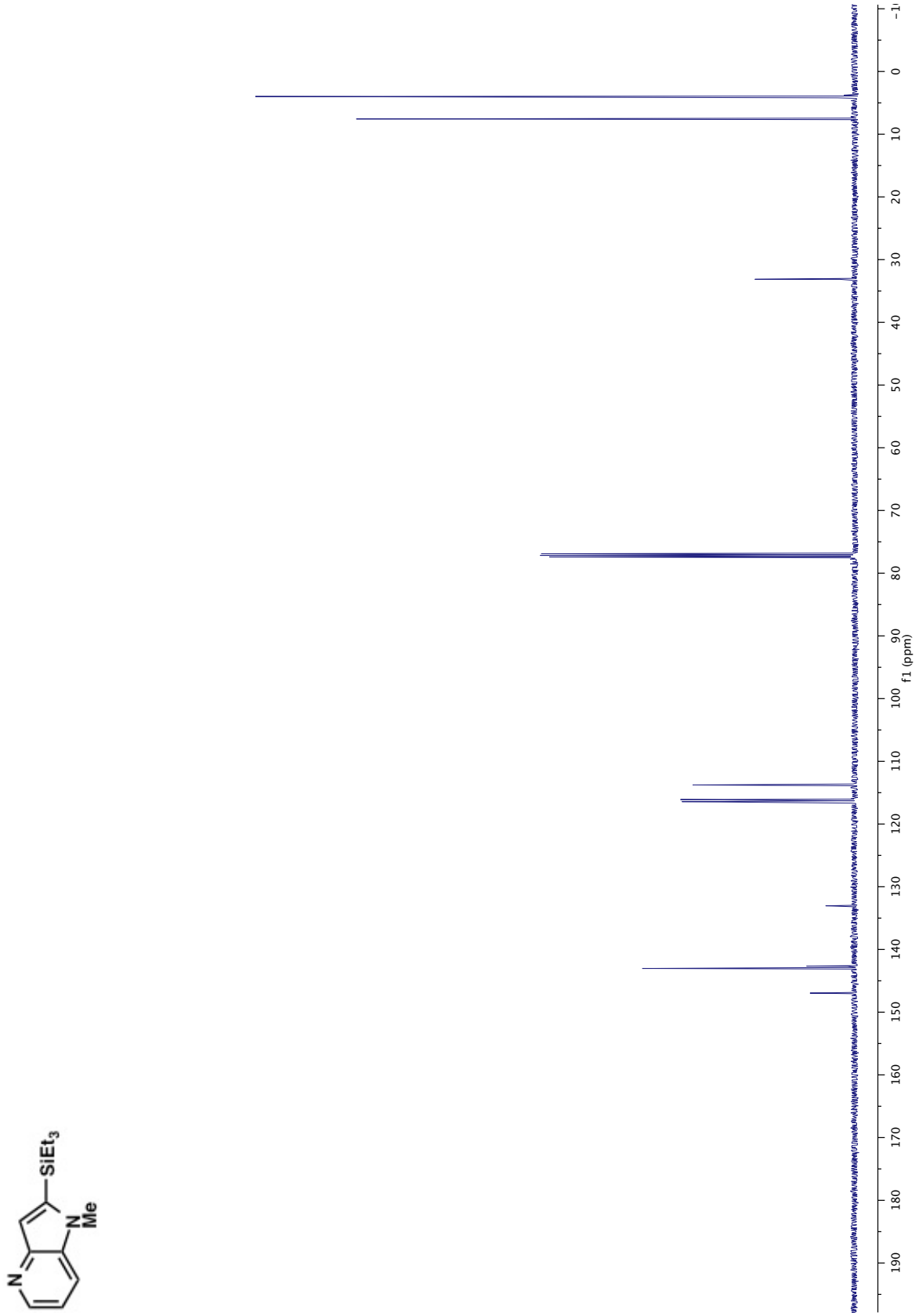


^{1}H NMR (500 MHz, $CDCl_3$) of compound **2x**.

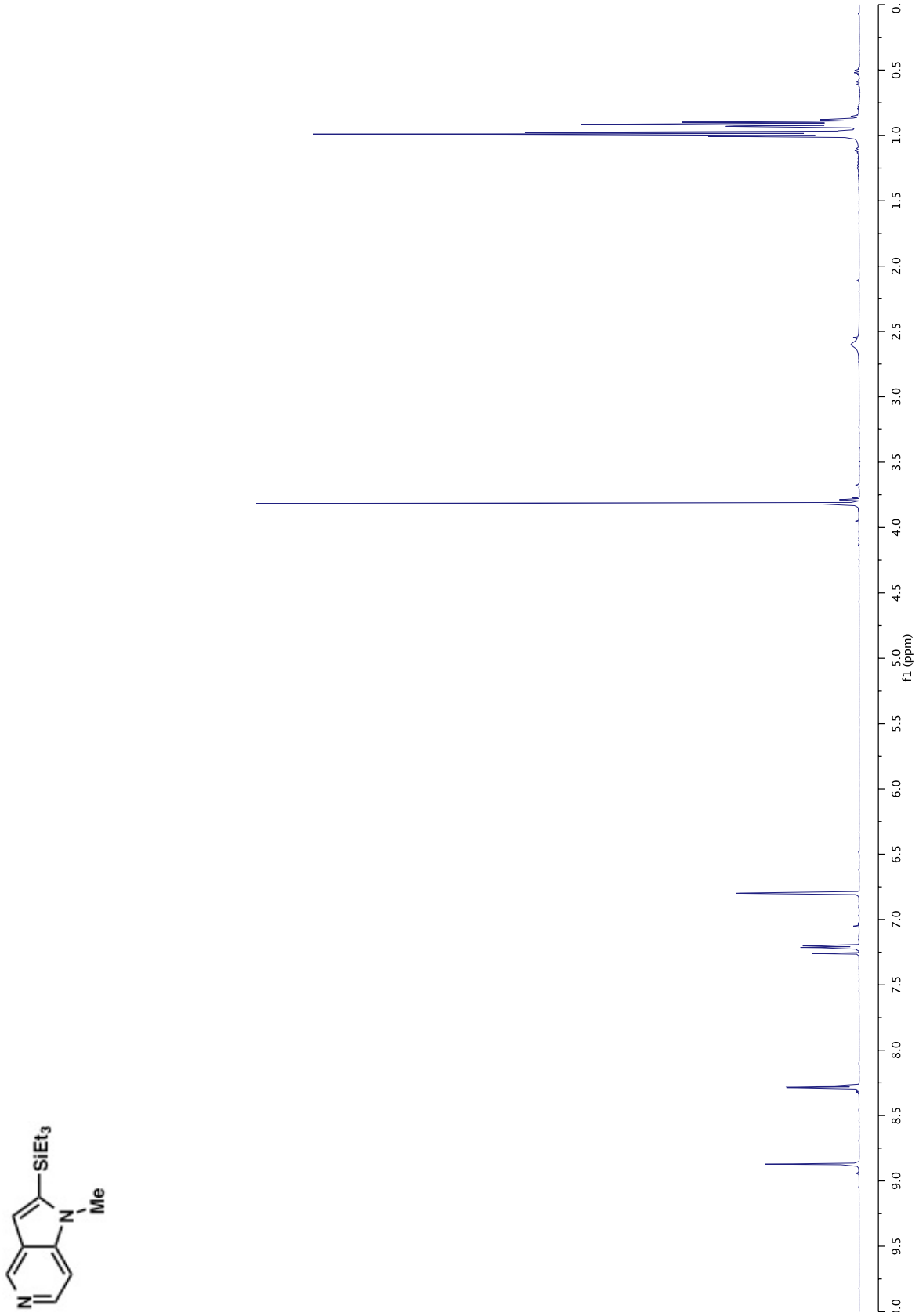


^{13}C NMR (125 MHz, $CDCl_3$) of compound **2x**.

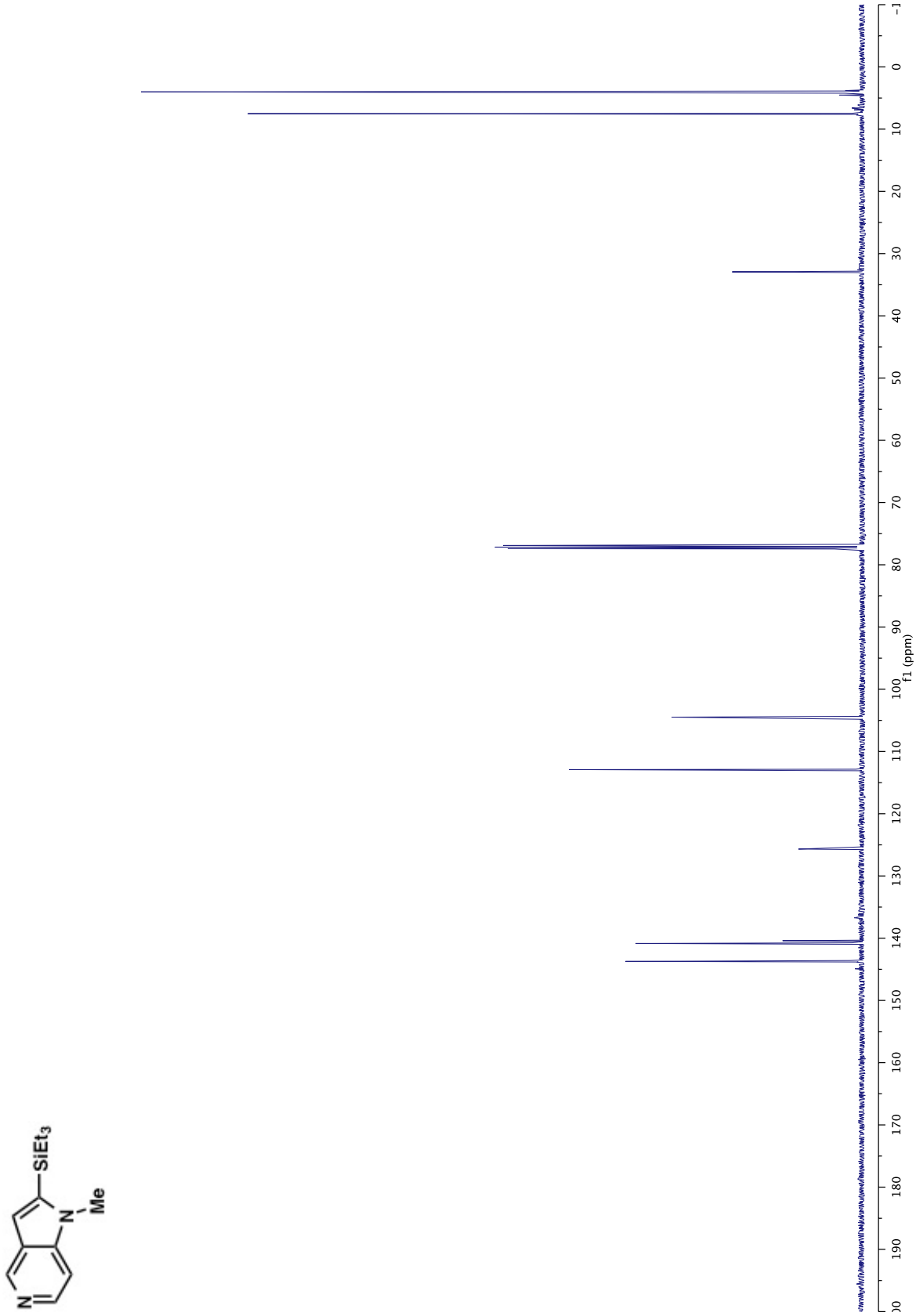
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4a.**



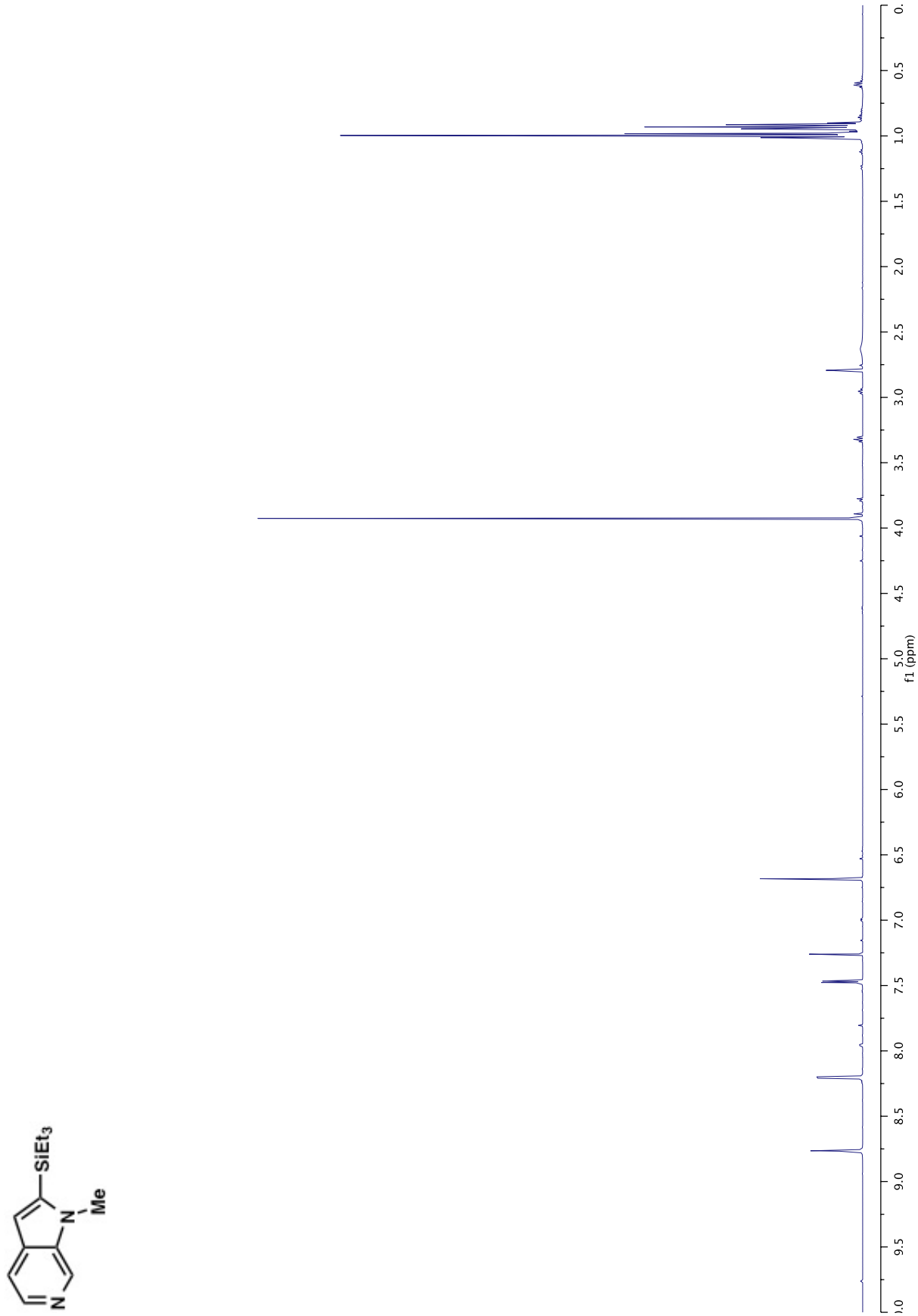
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4a**.



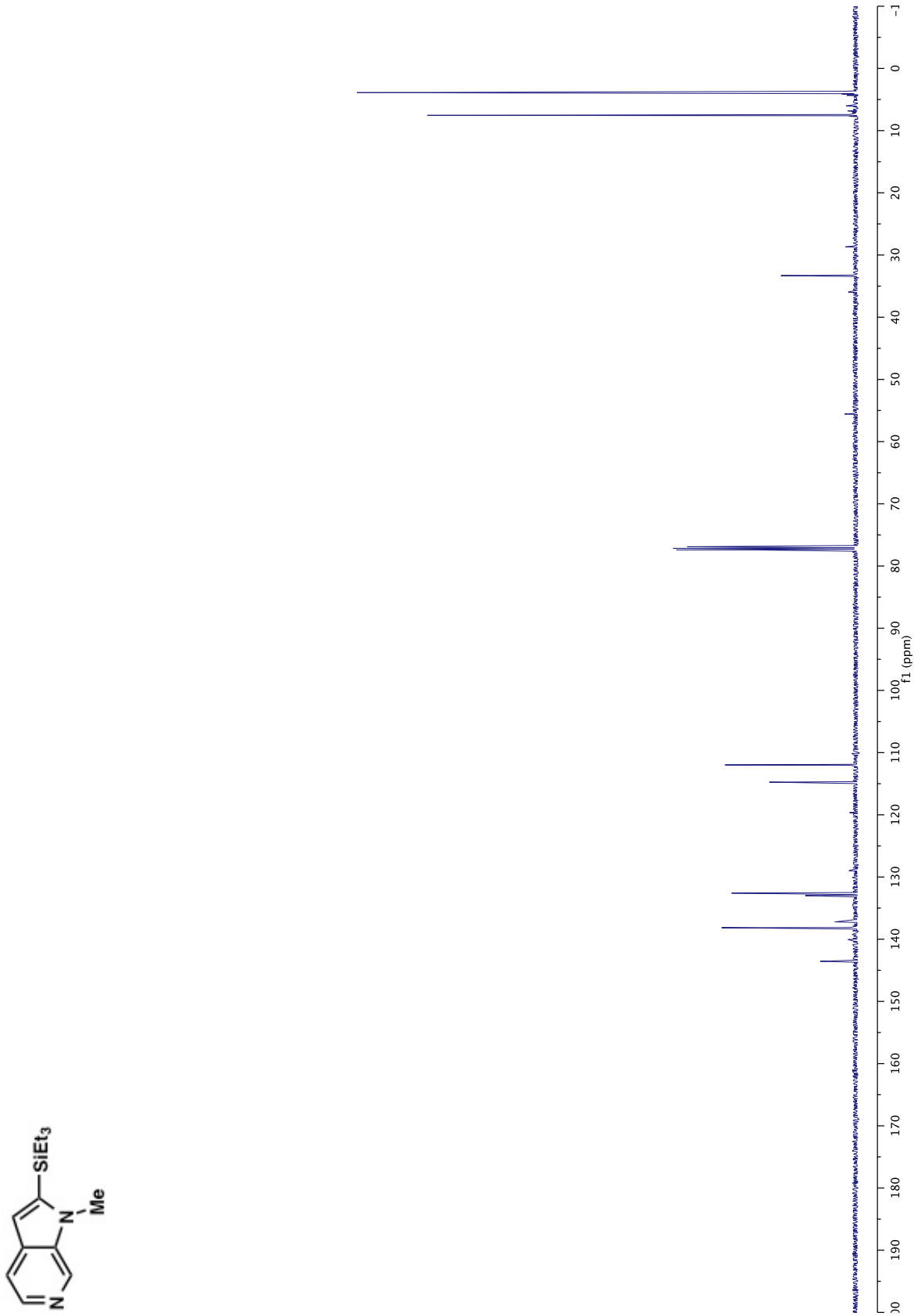
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4b.**



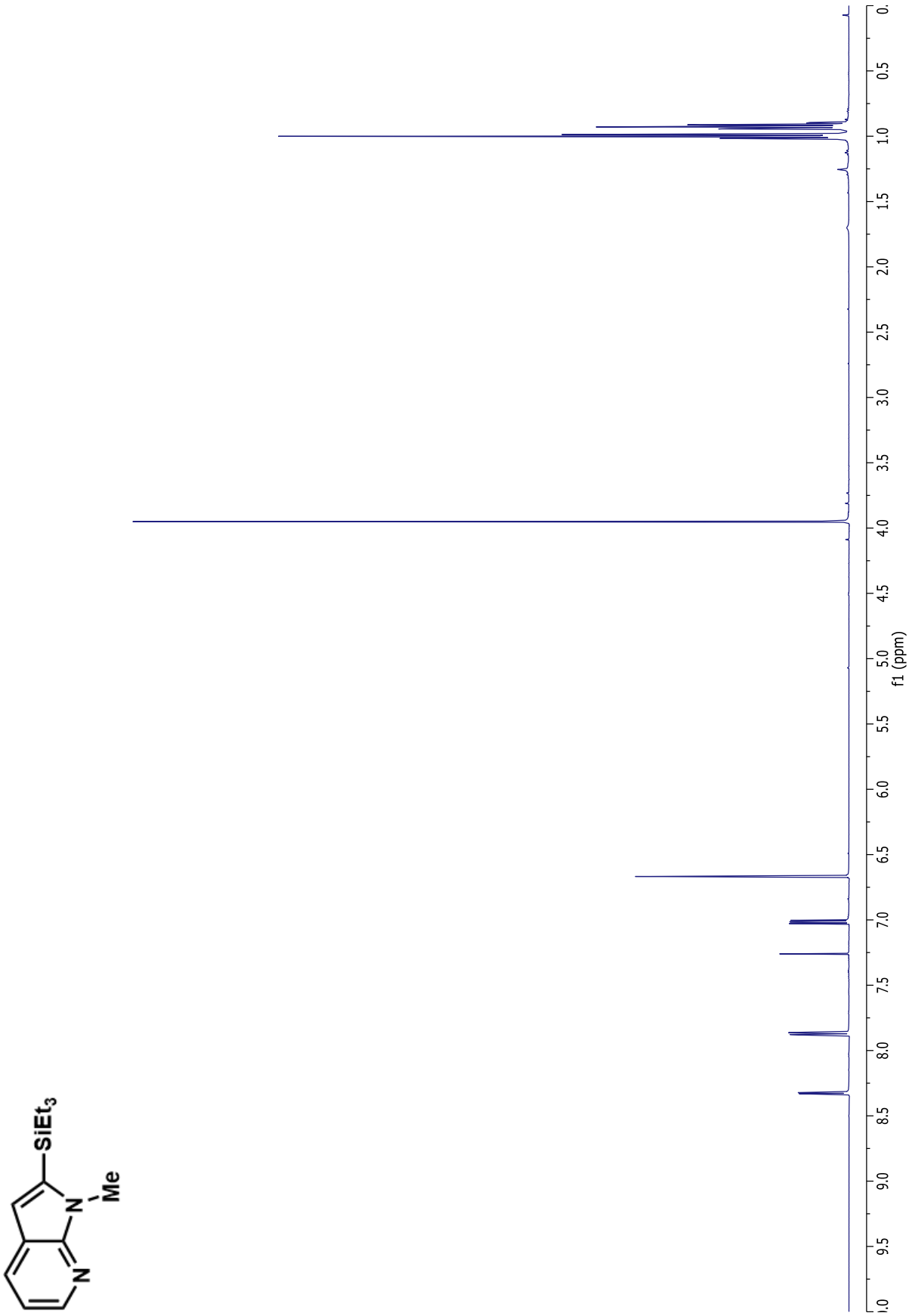
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4b.**



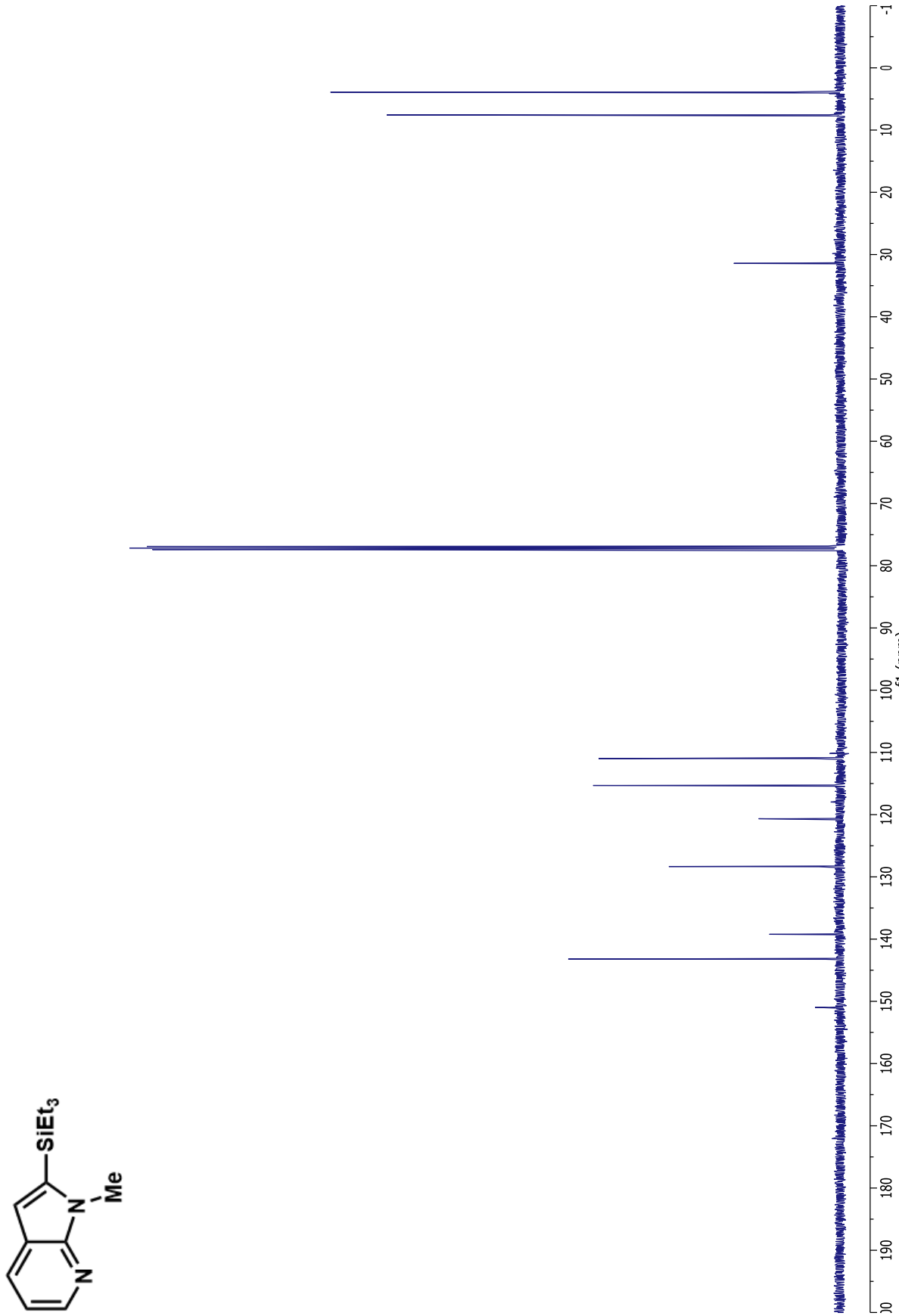
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4c**.



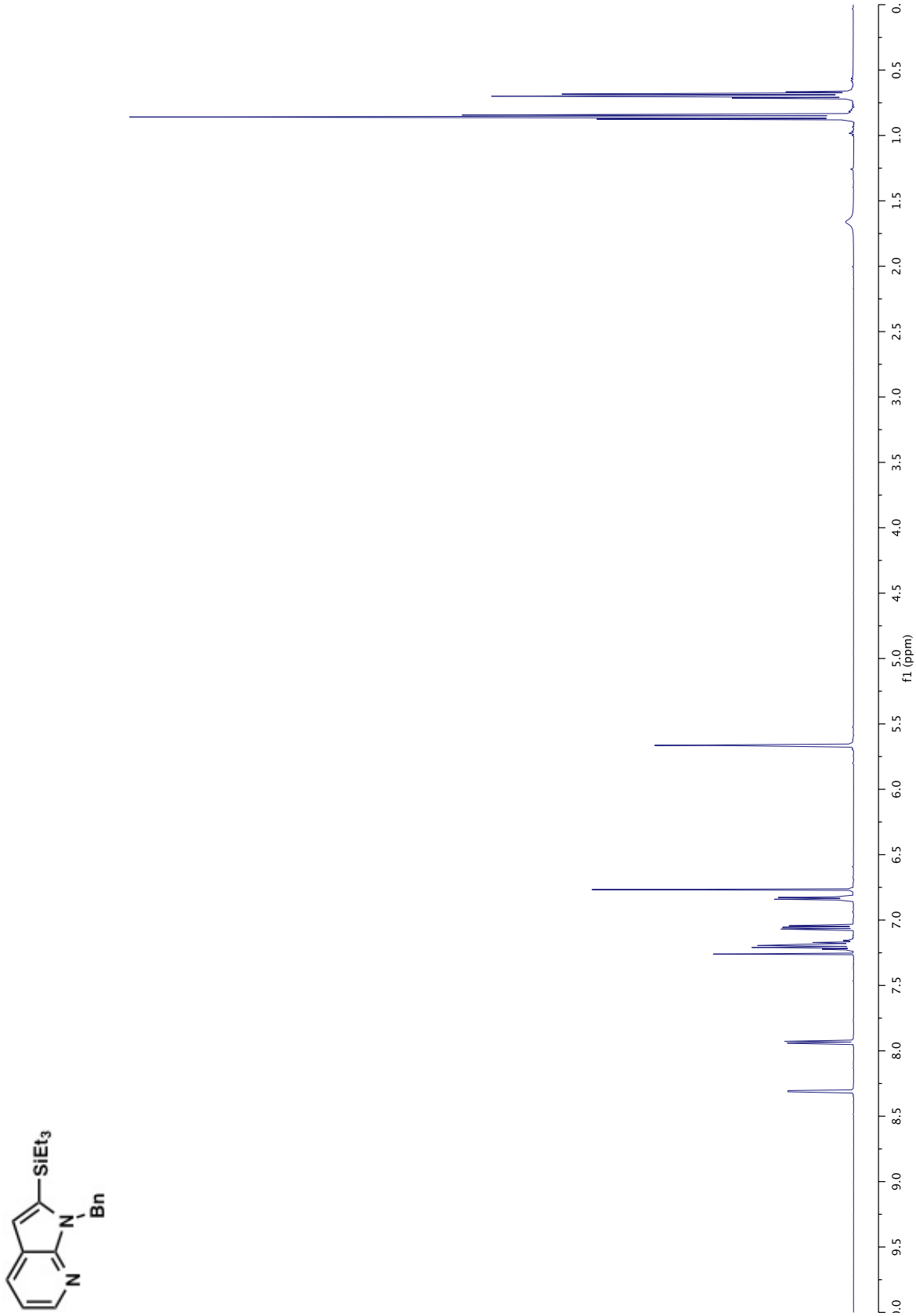
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4c**.



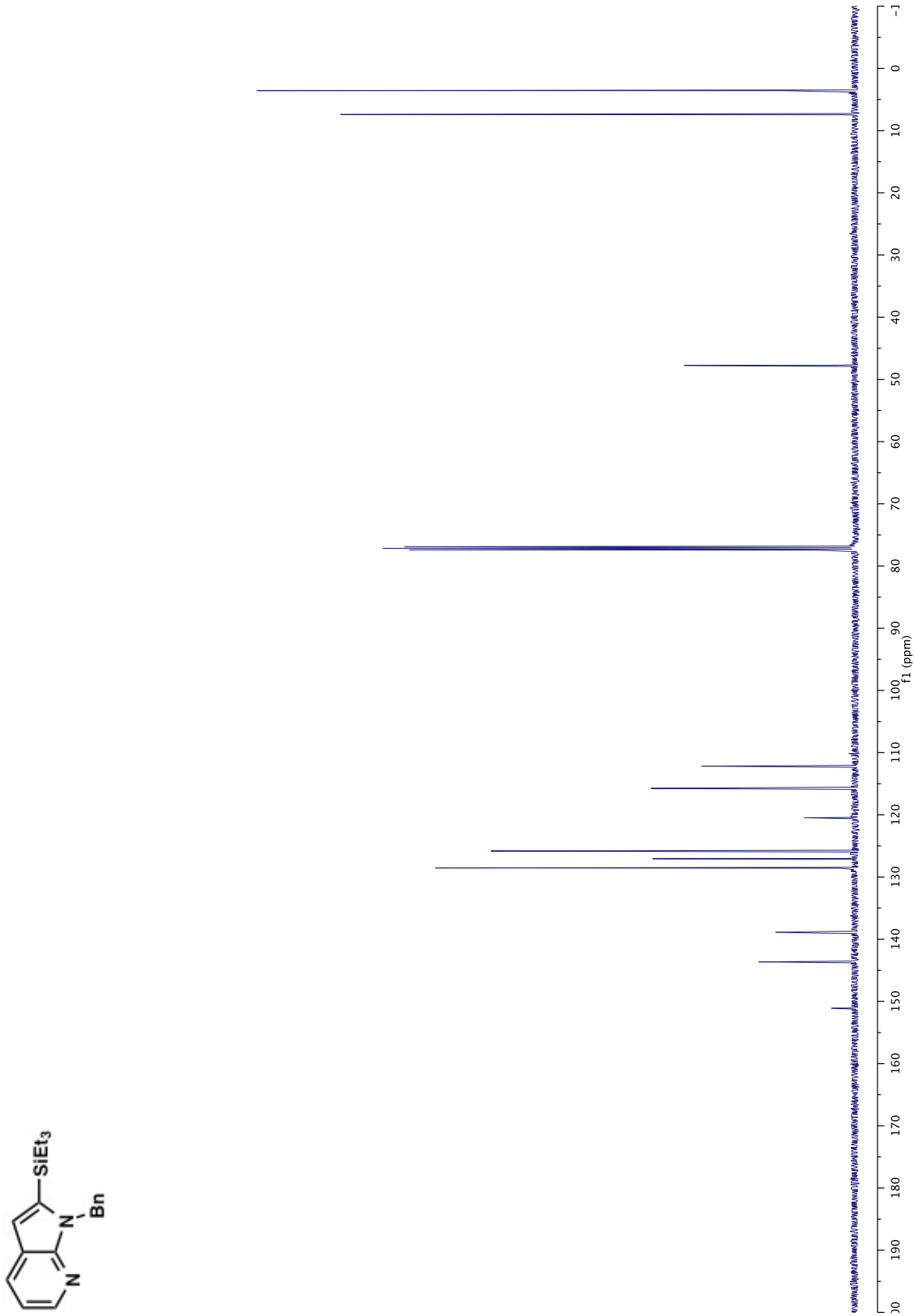
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4d**.



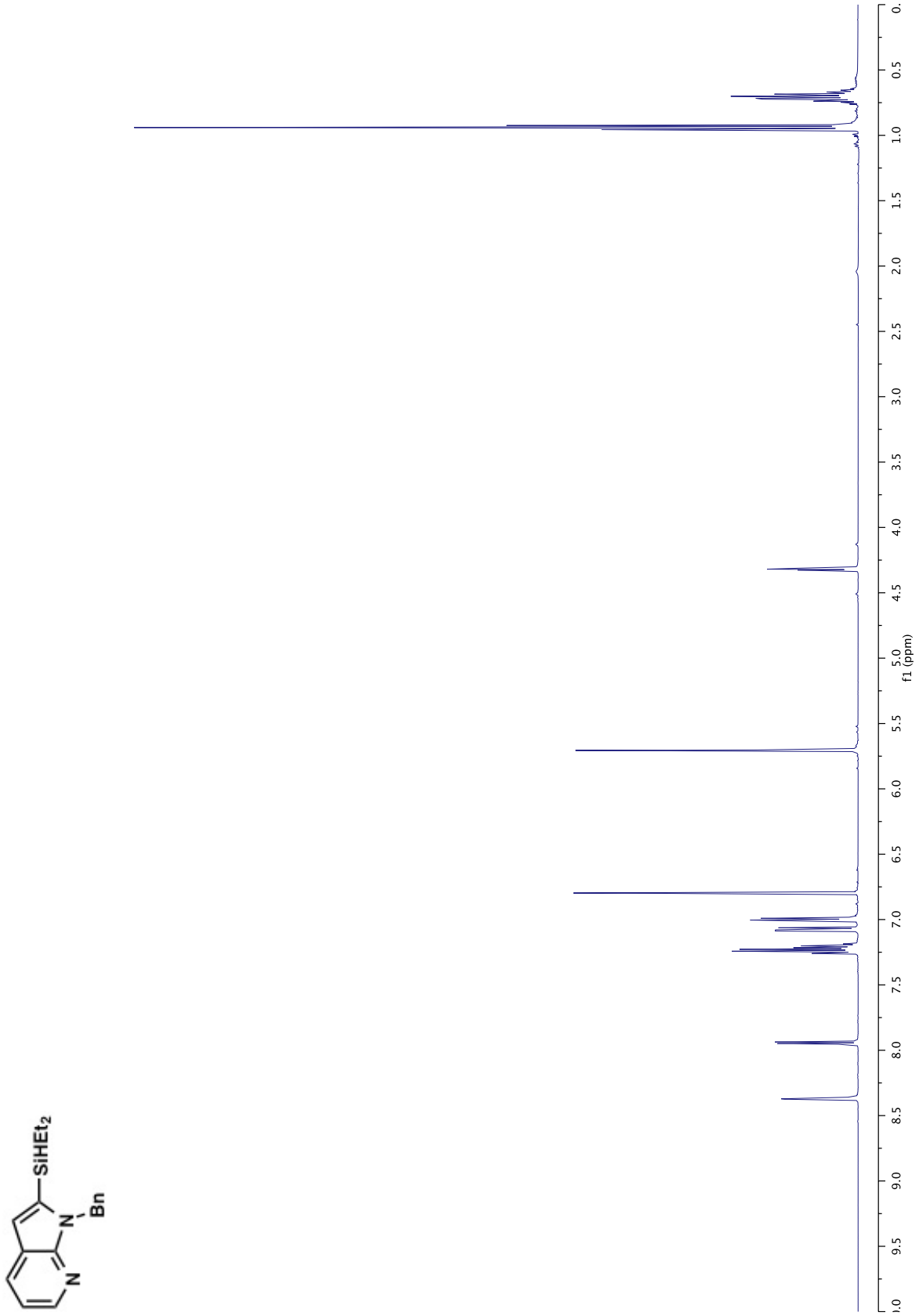
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4d**.



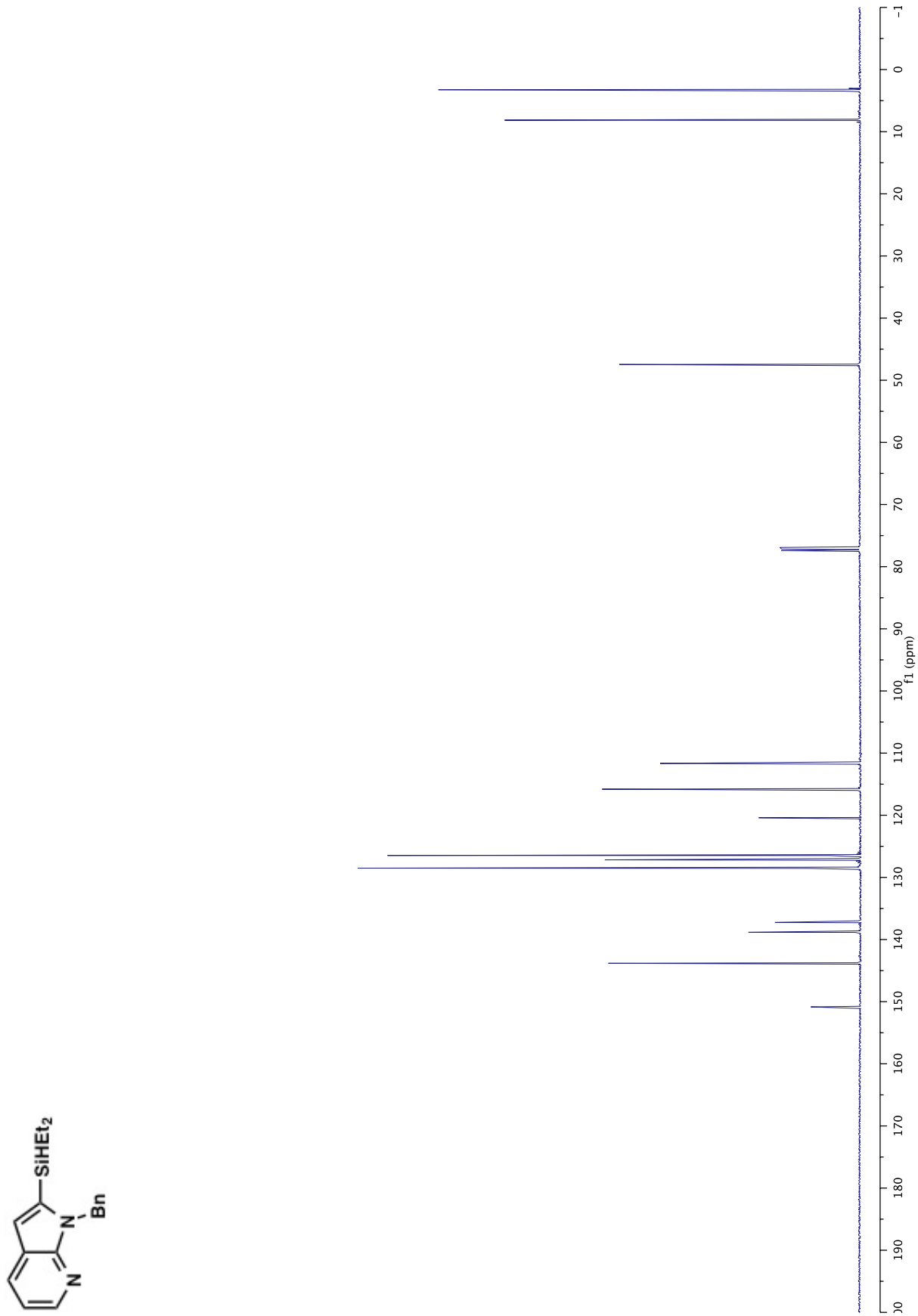
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4e**.



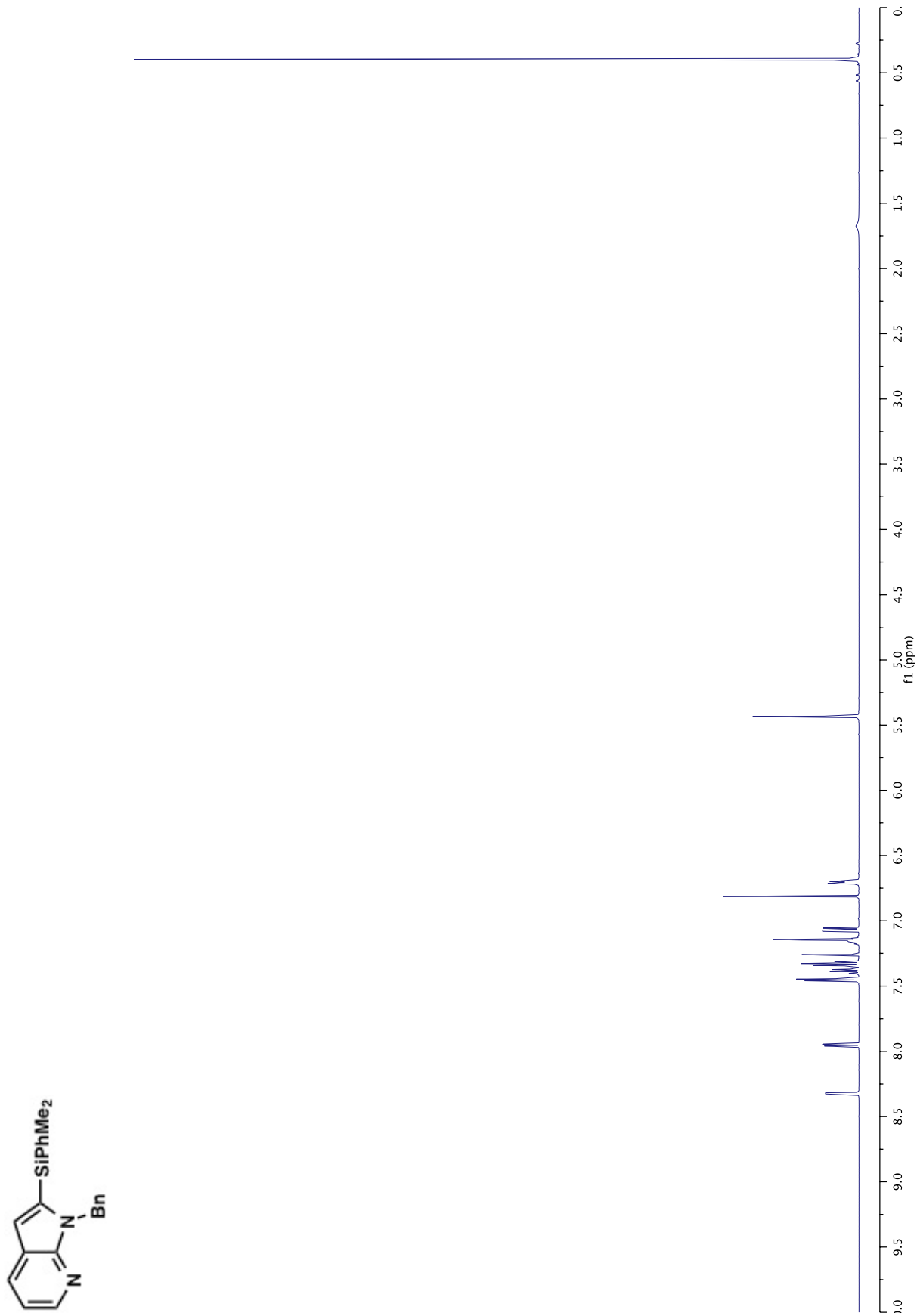
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4e.**



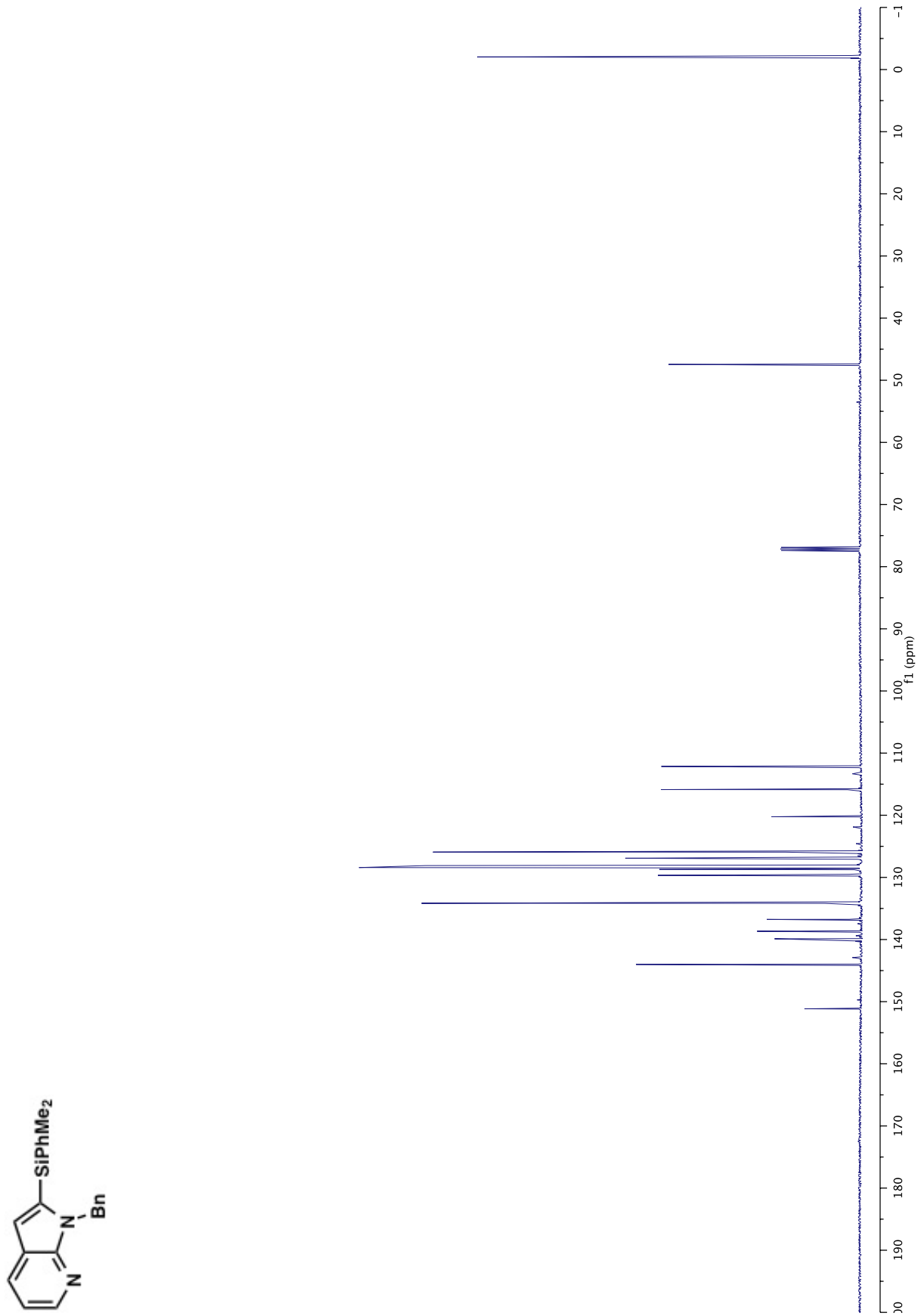
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4f**.



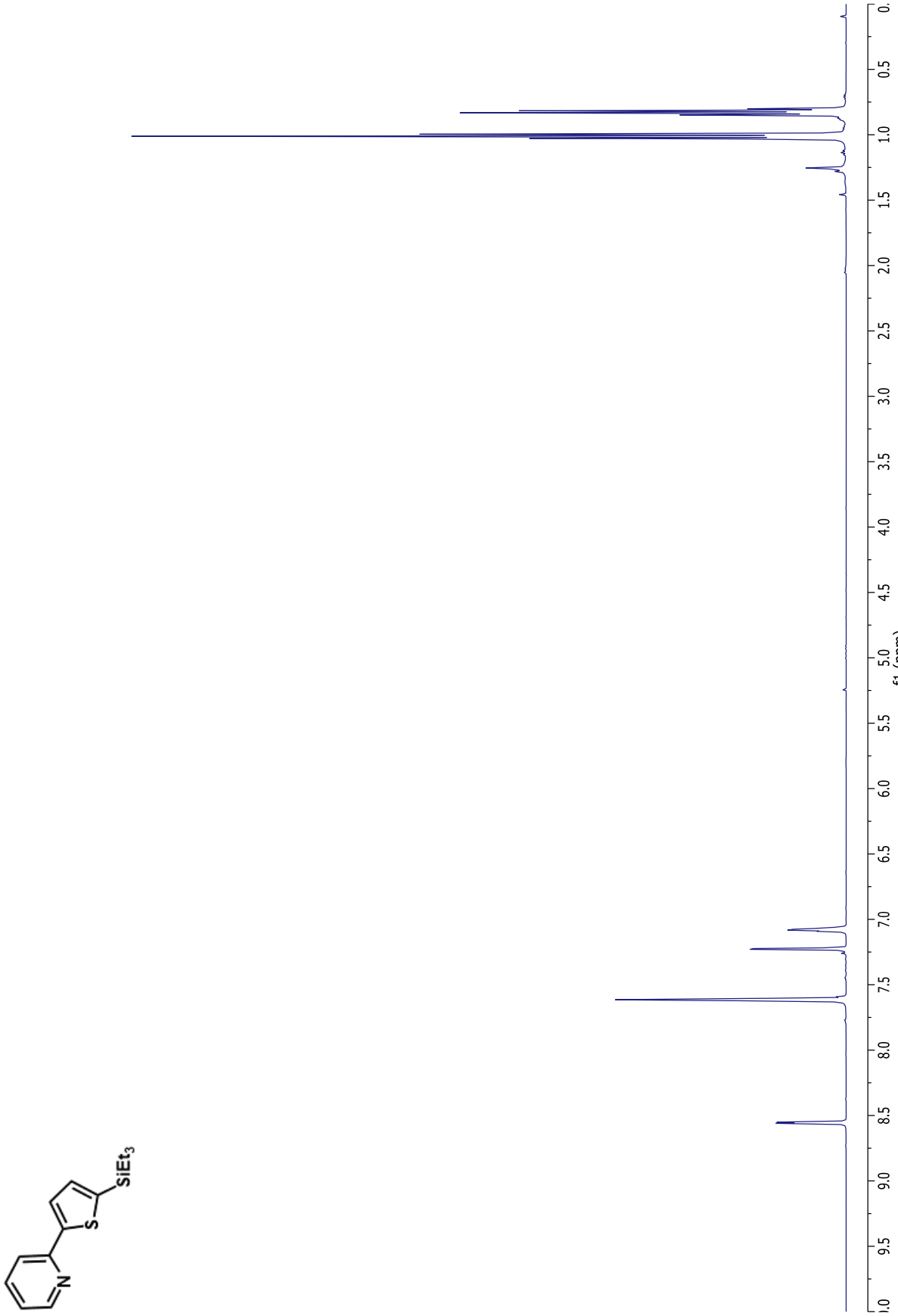
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4f**.



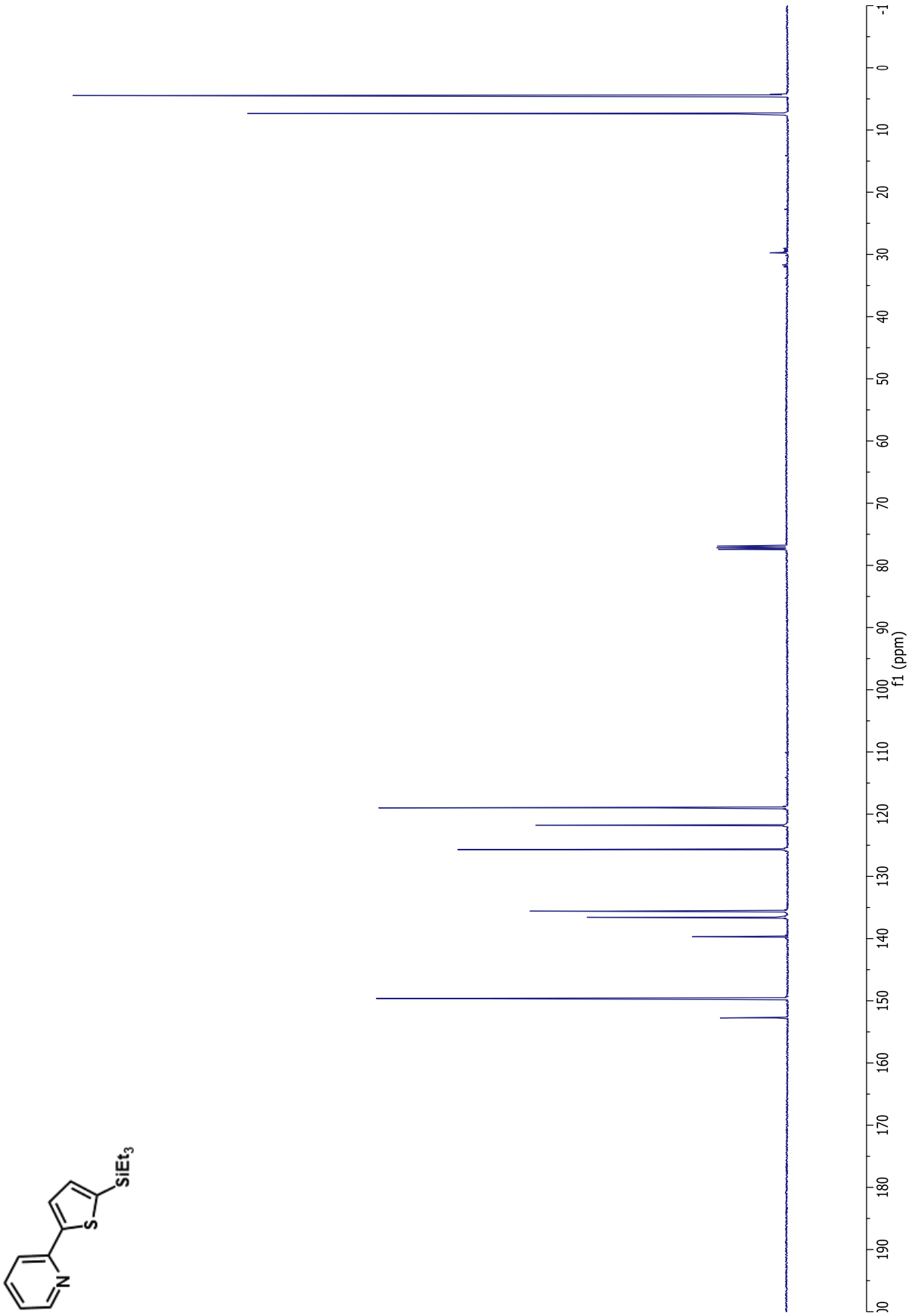
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4g**.



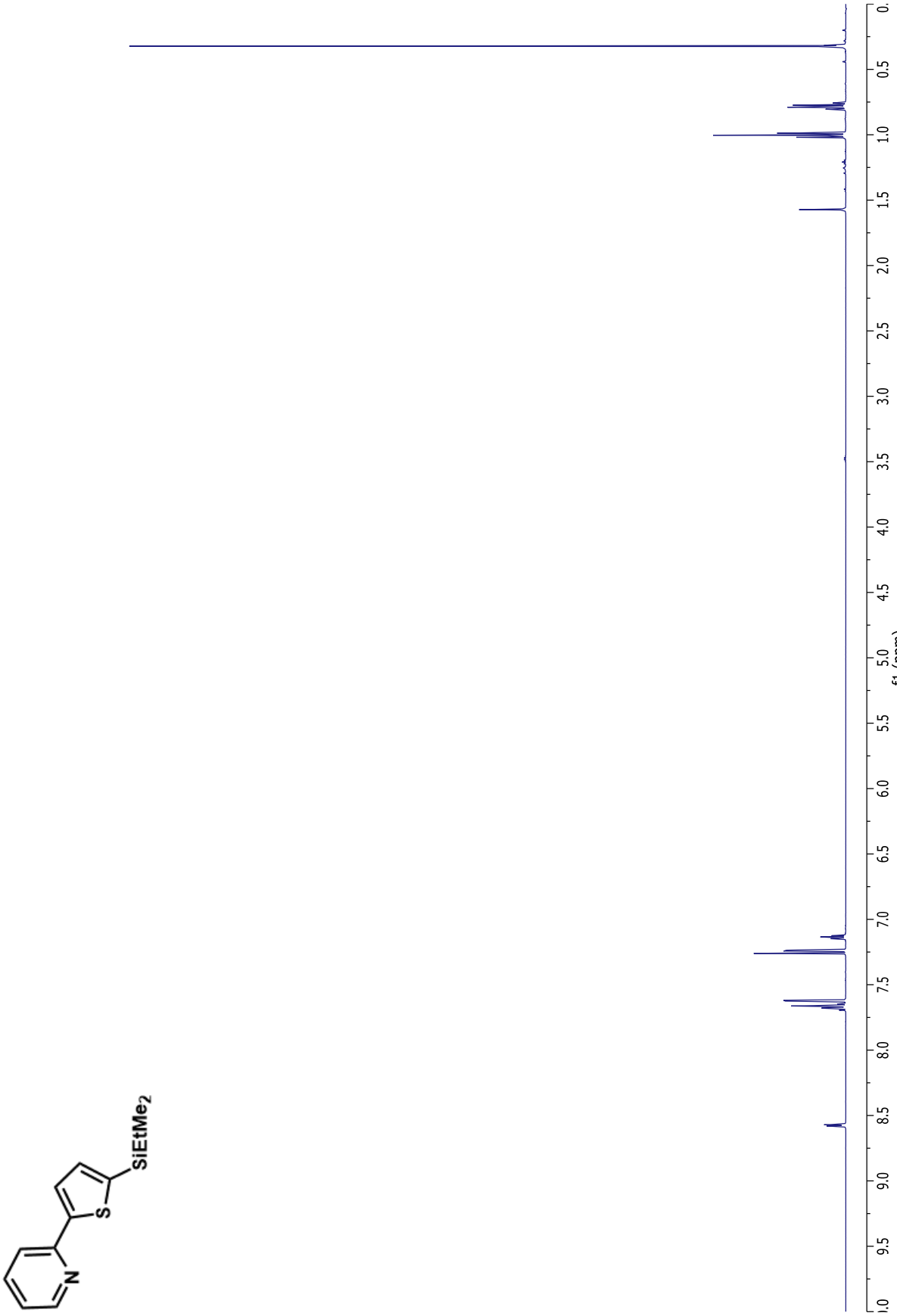
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4g**.



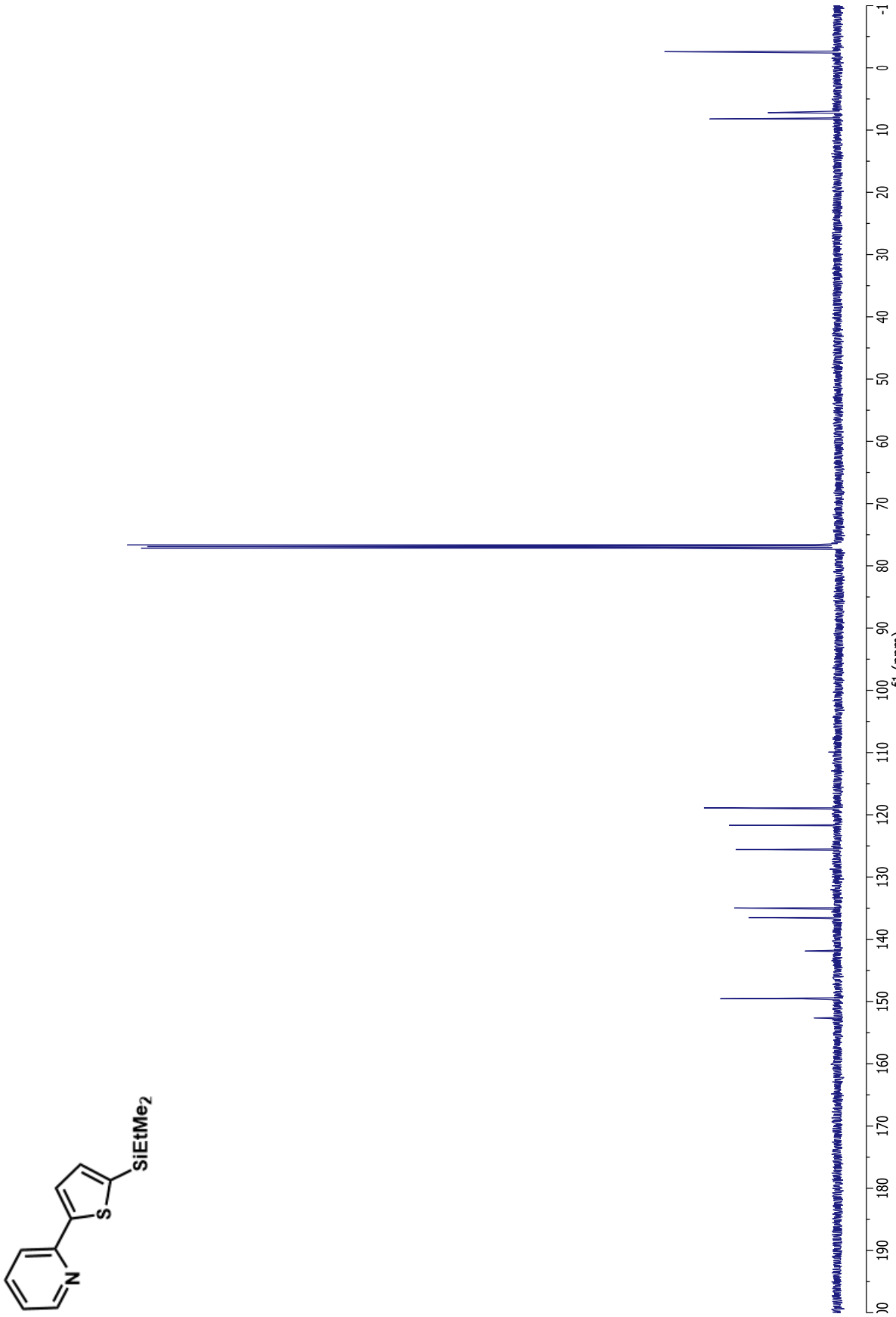
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4j**.



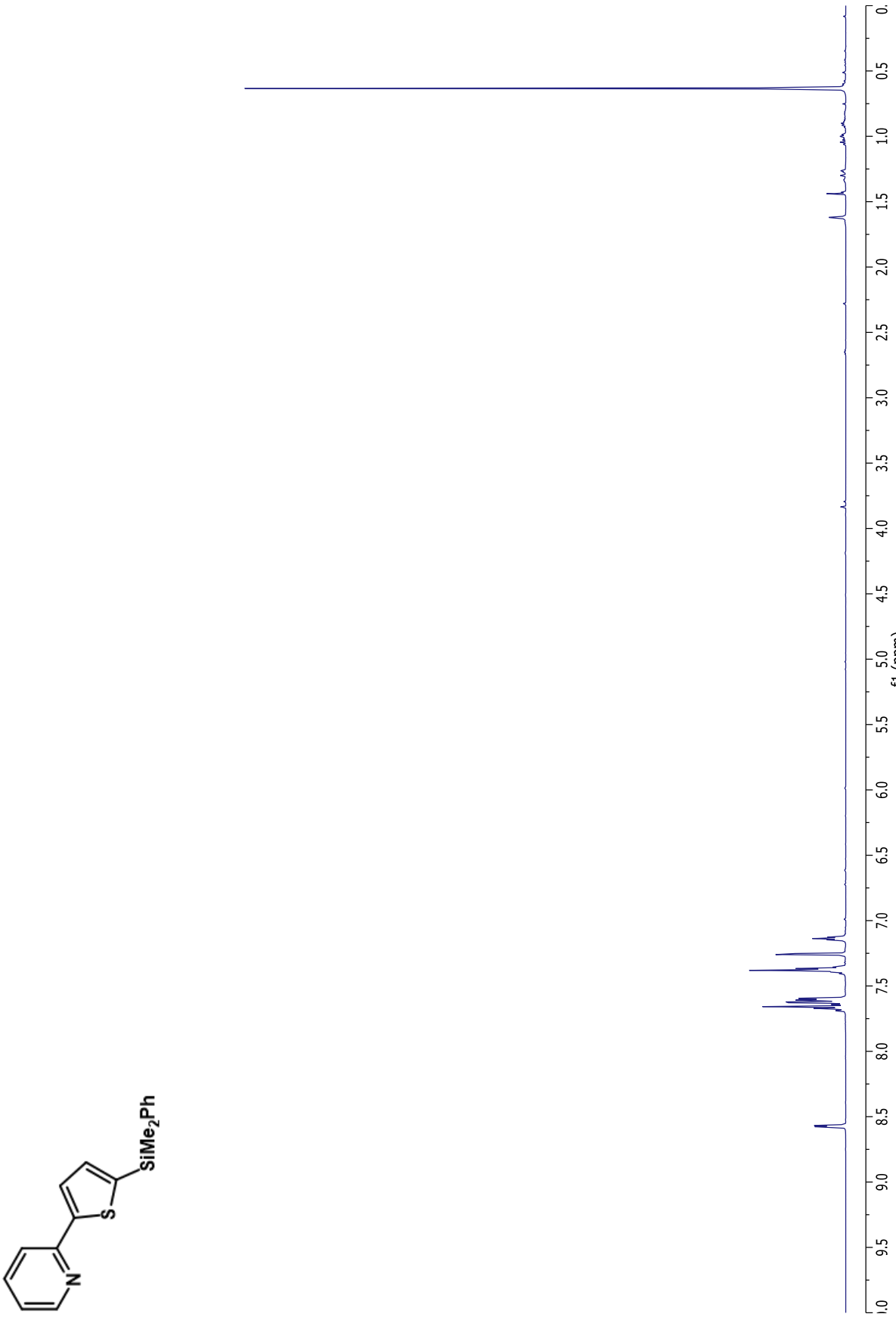
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4j**.



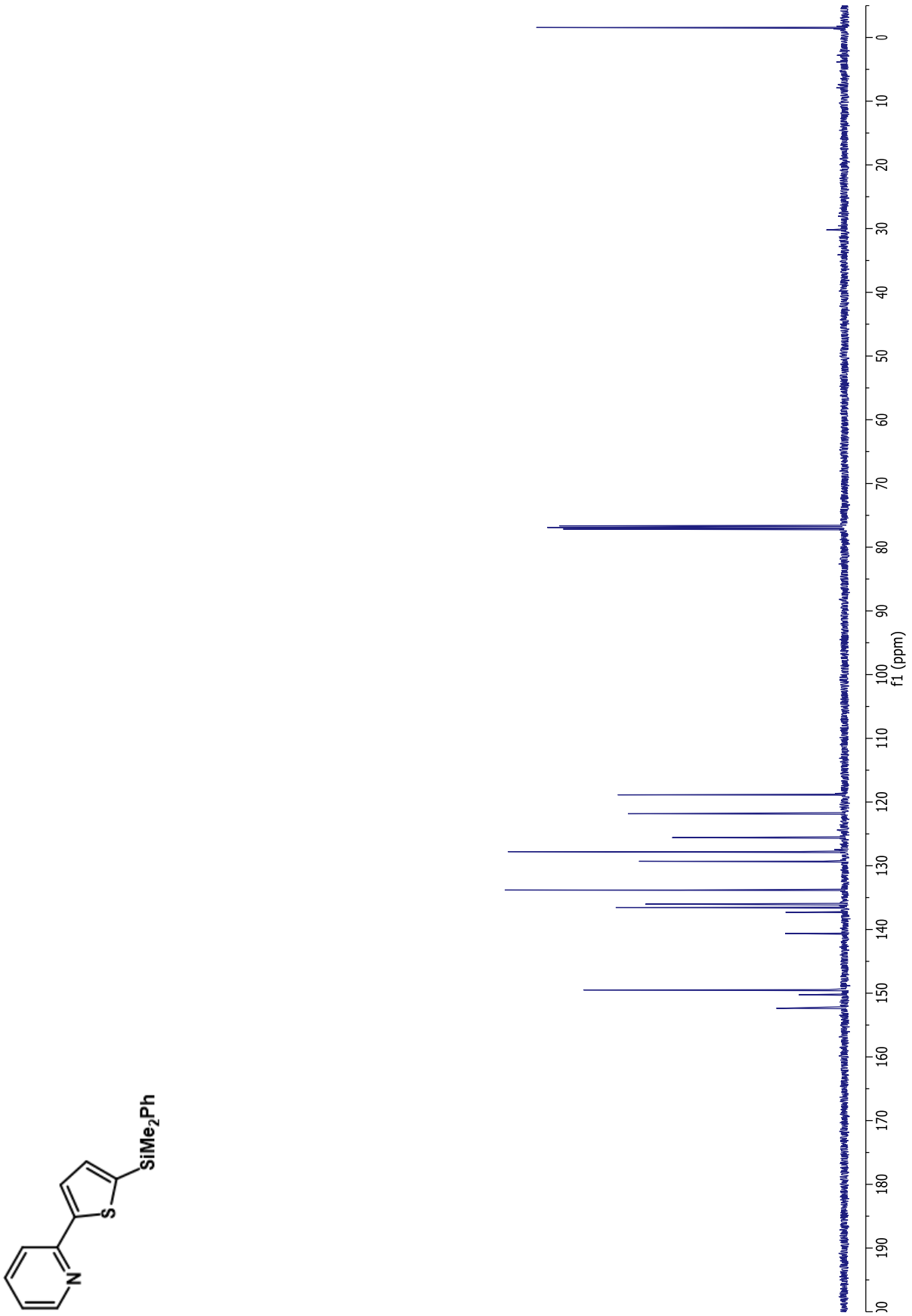
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4k**.



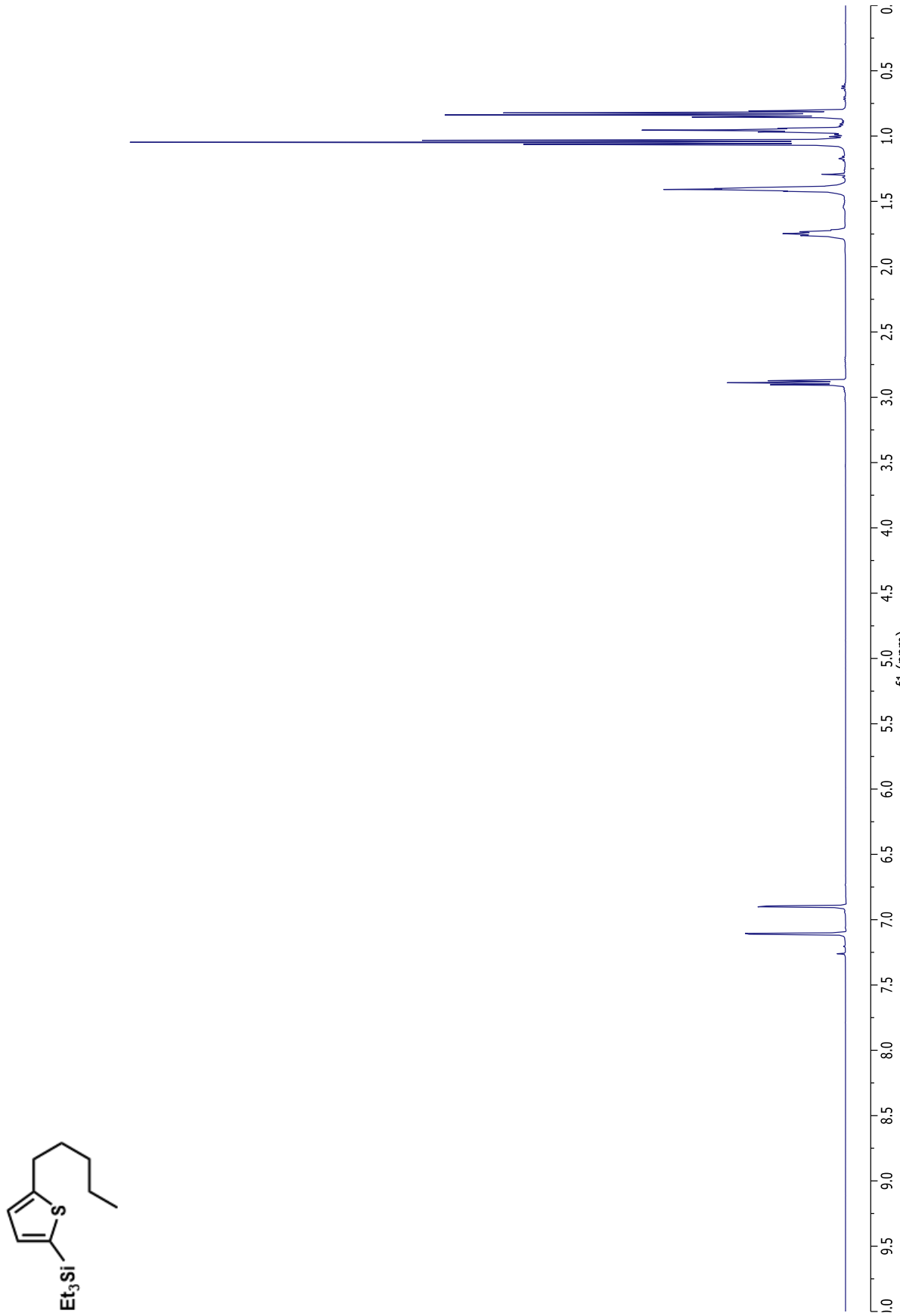
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4k**.



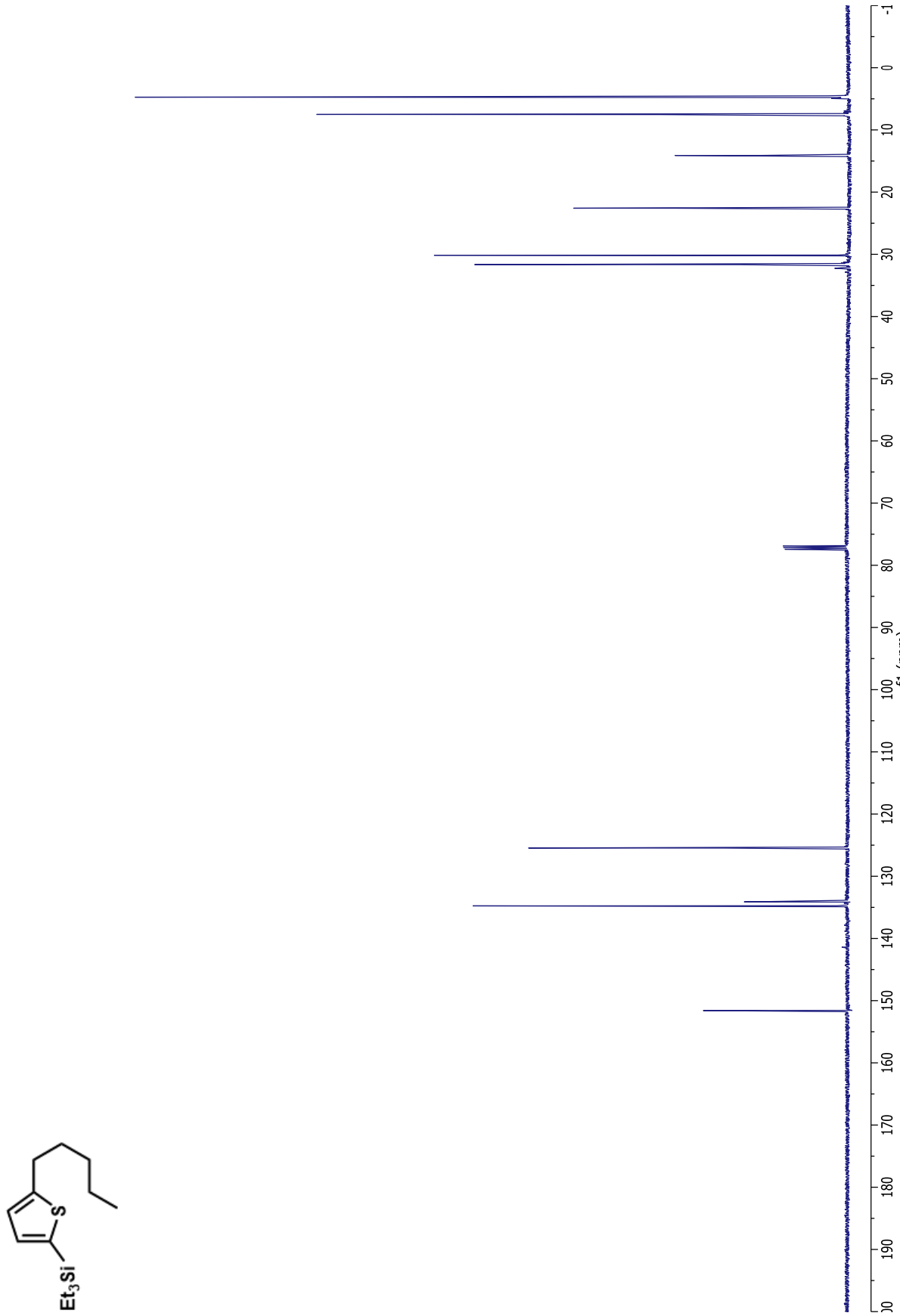
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4l**.



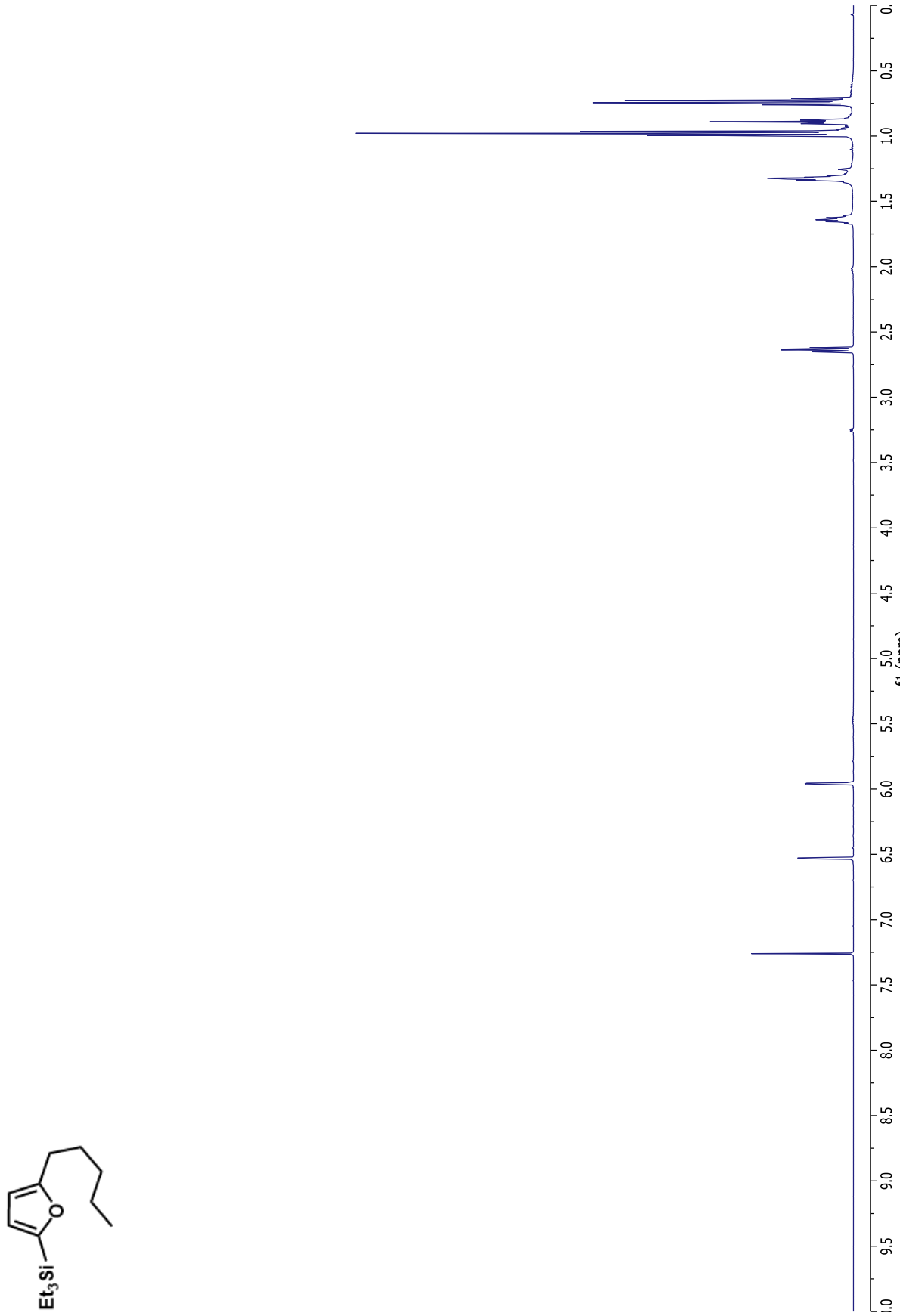
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4l**.



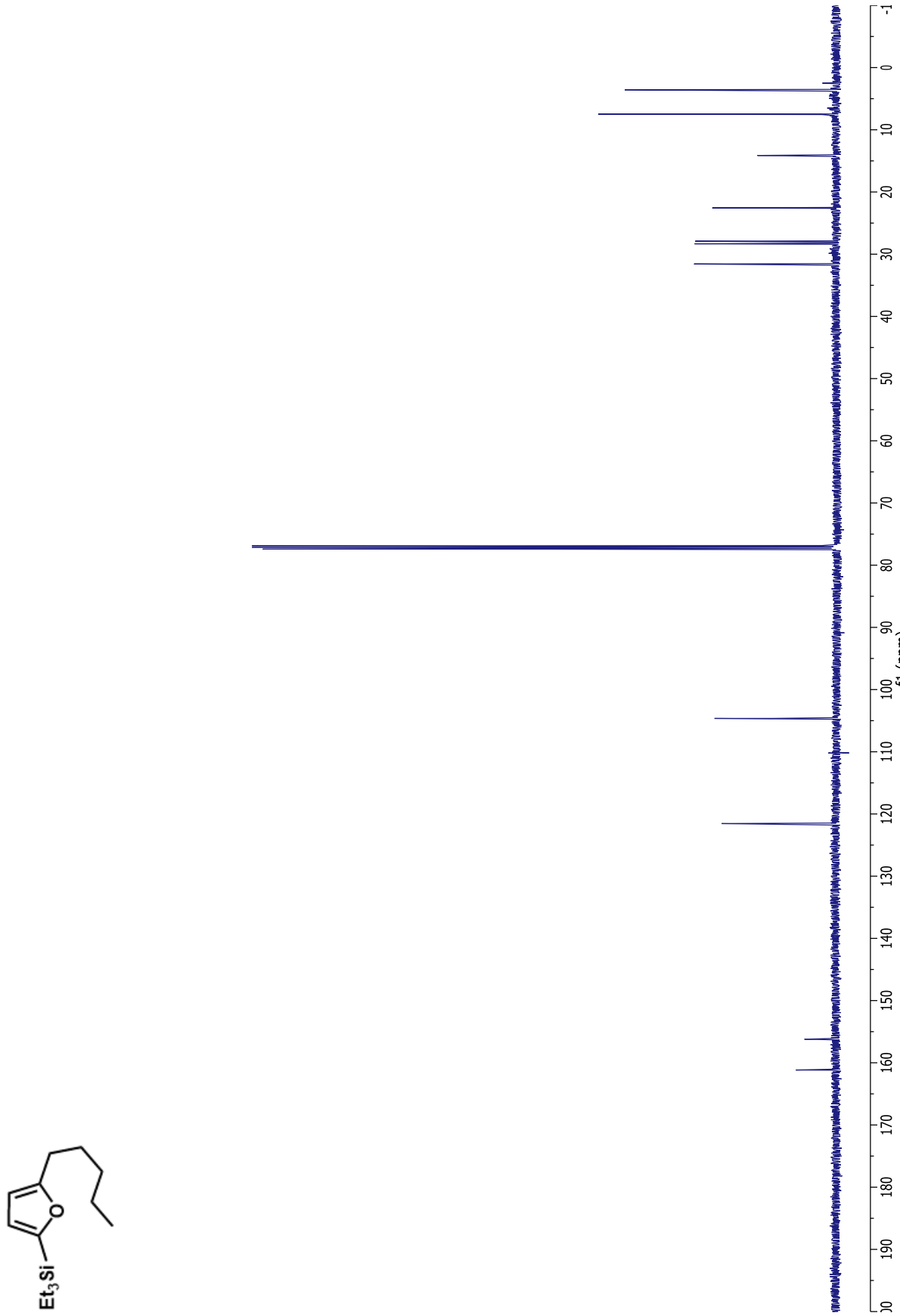
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4m**.



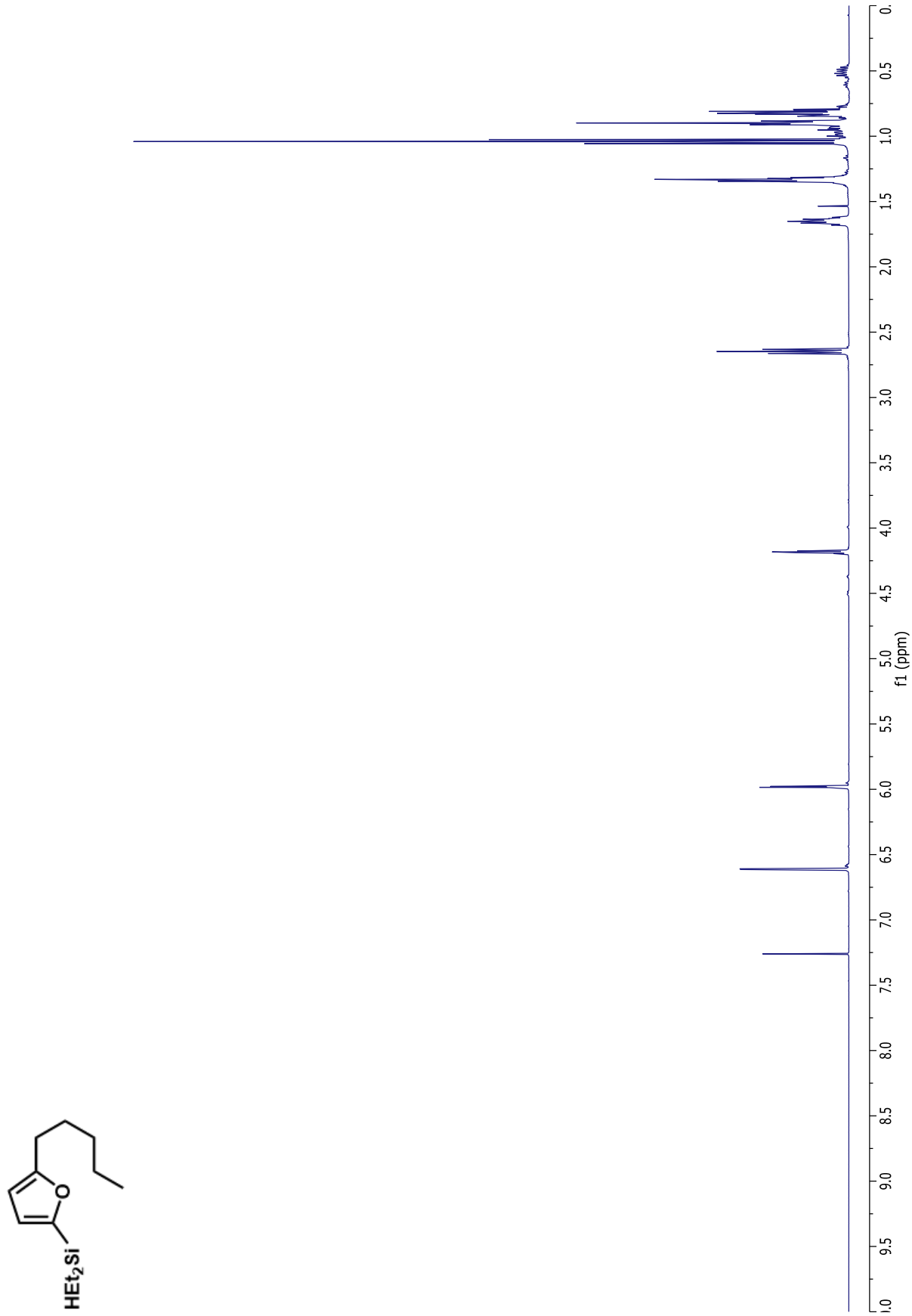
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4m**.



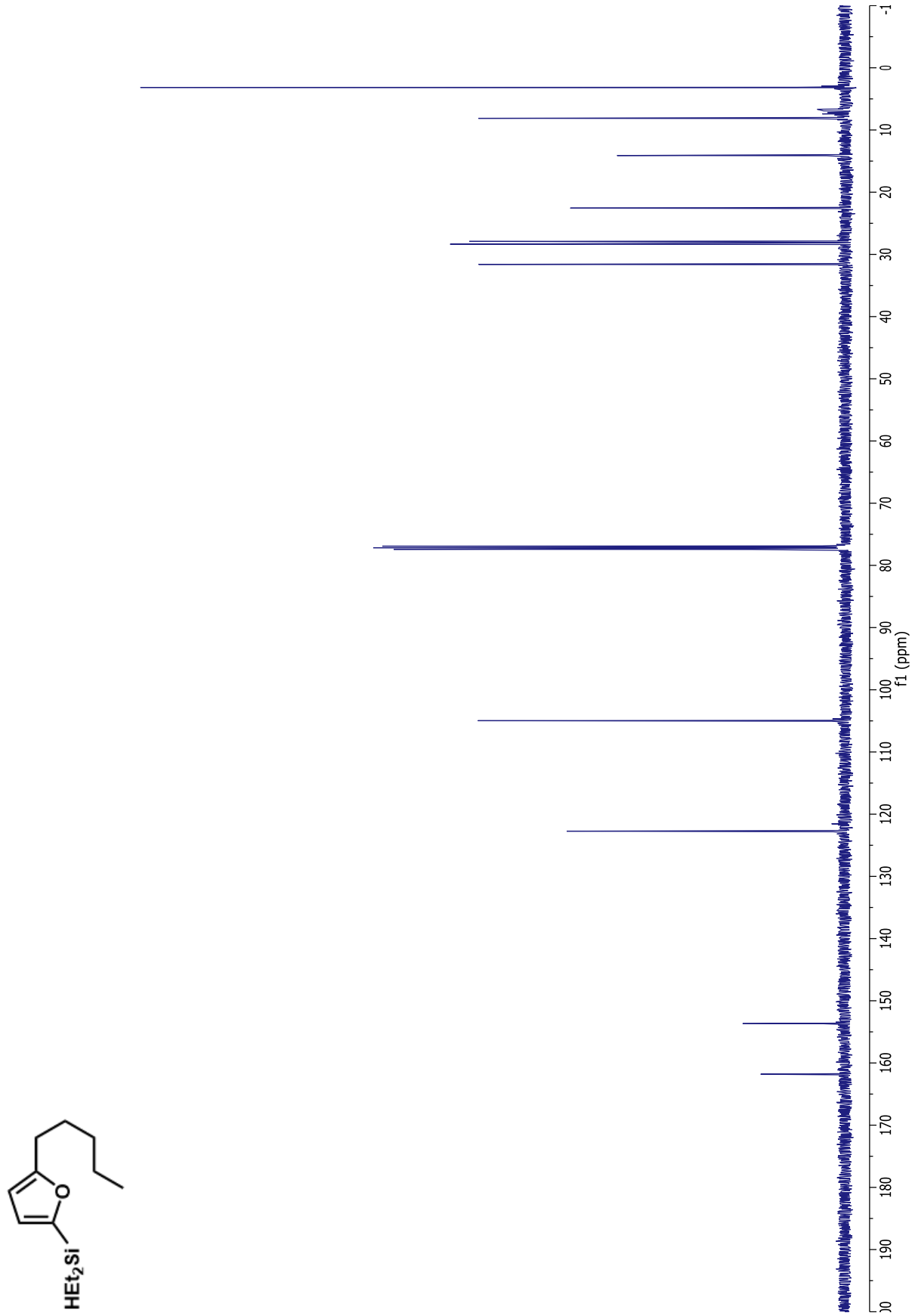
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4n**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **4n**.

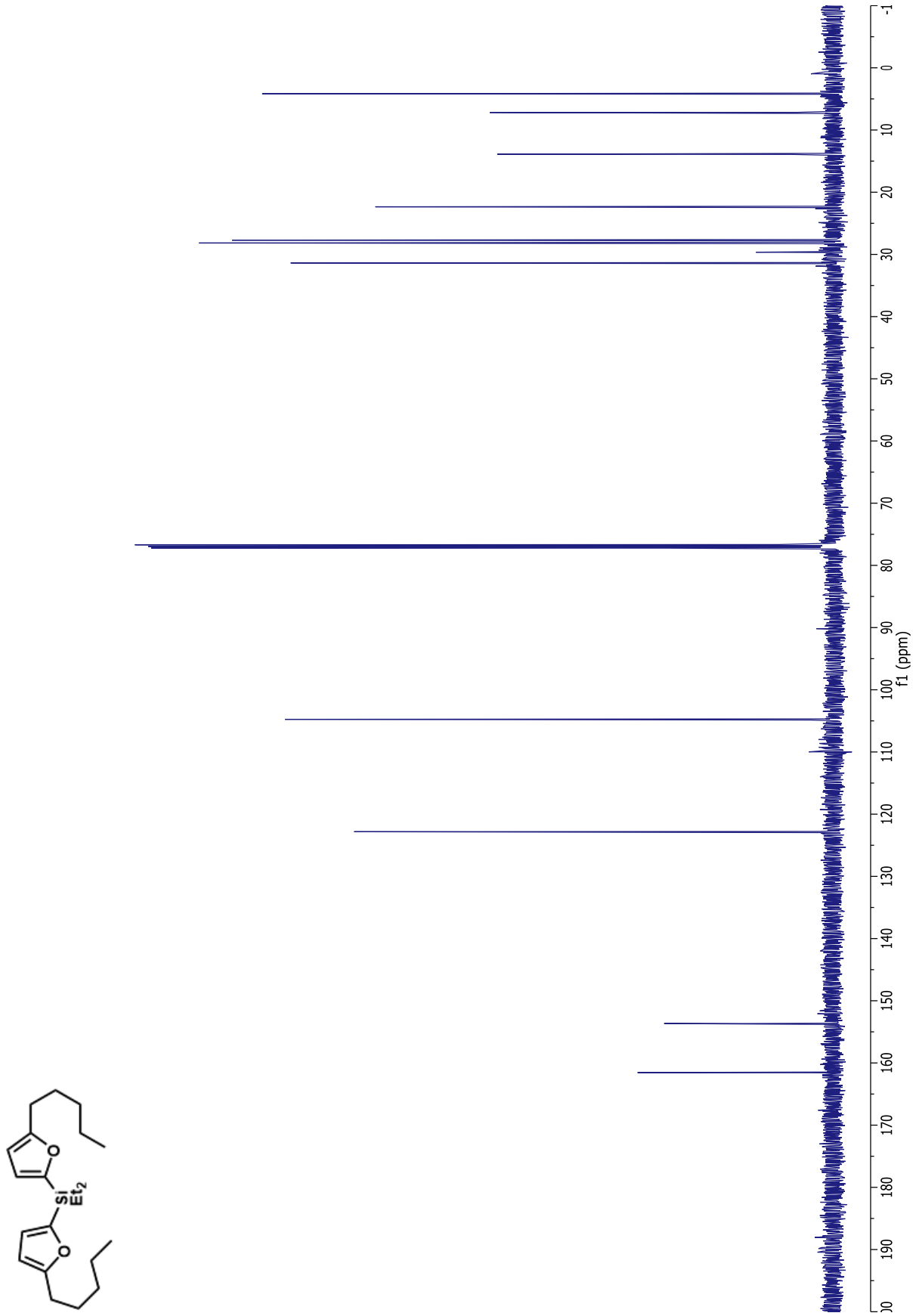


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4o**.

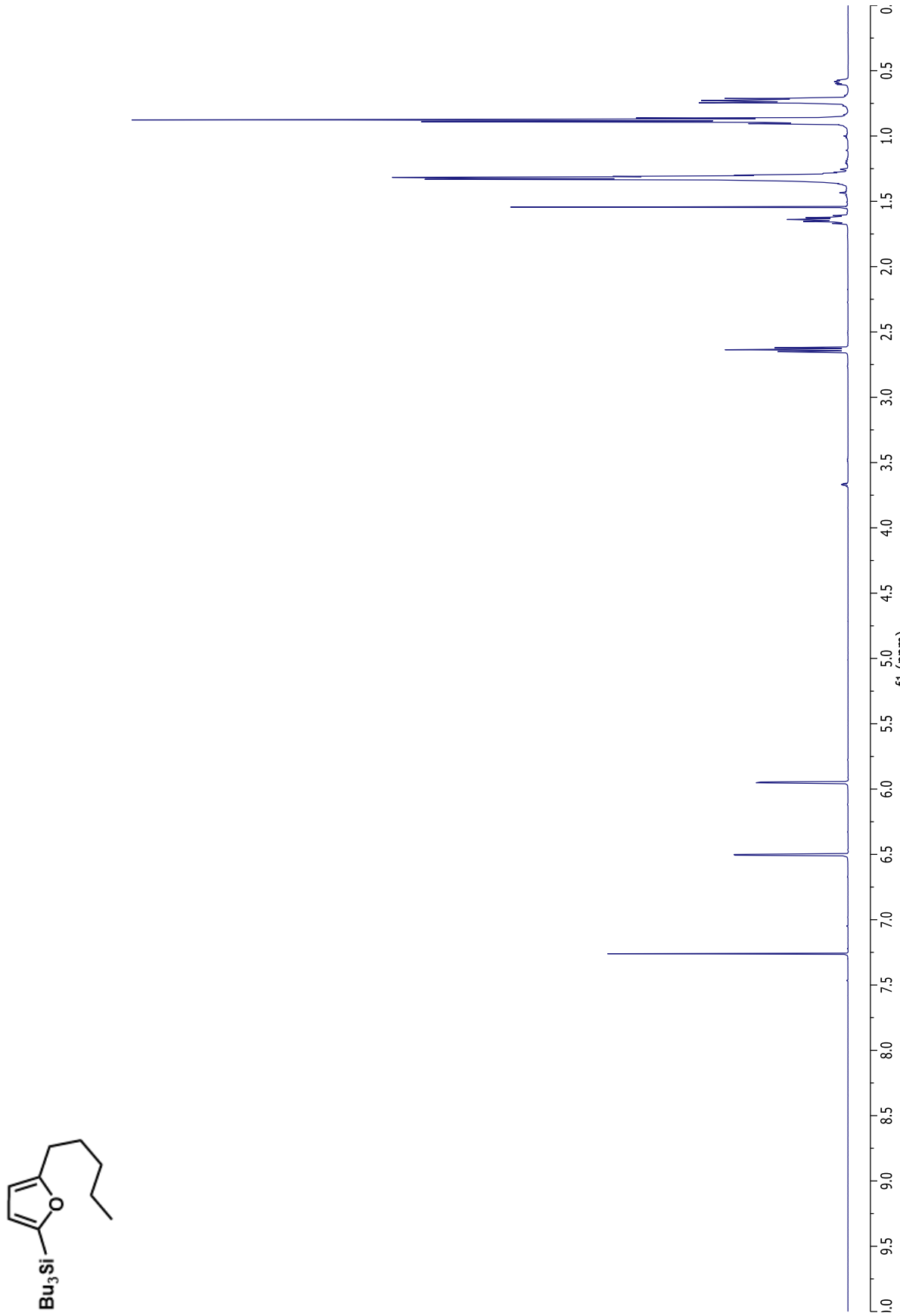


^{13}C NMR (125 MHz, $CDCl_3$) of compound **4o**.

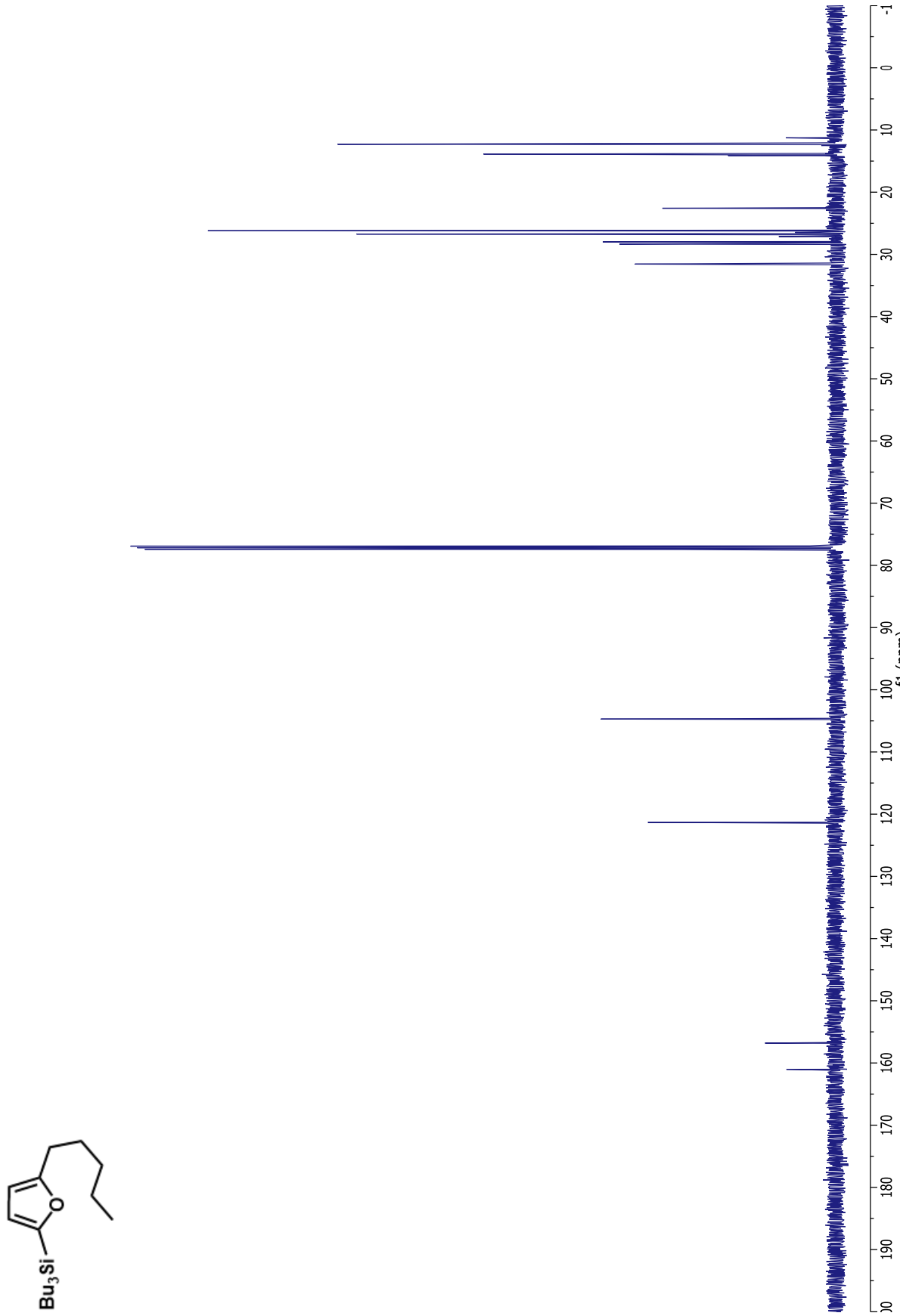
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-4o**.



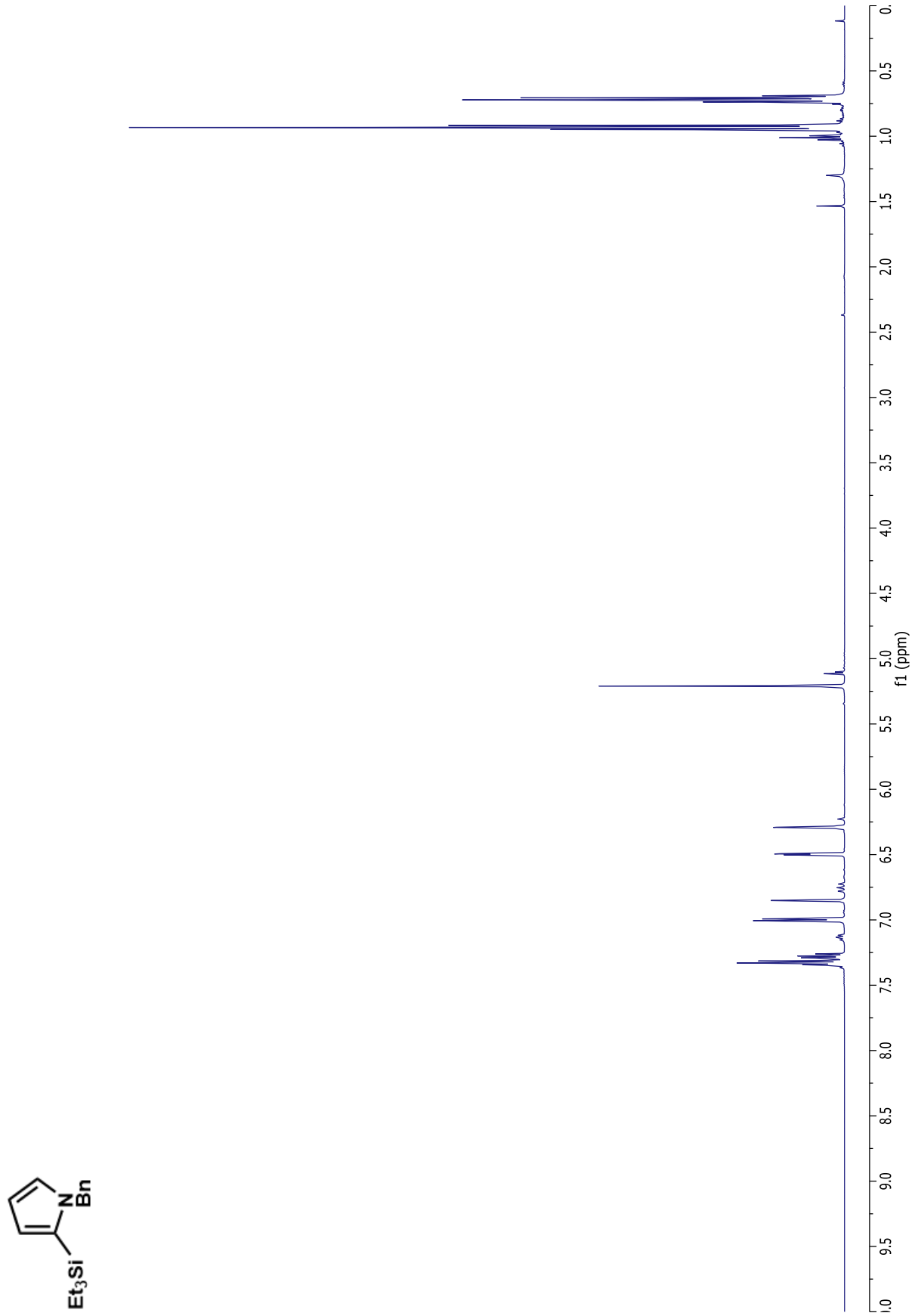
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-4o**.



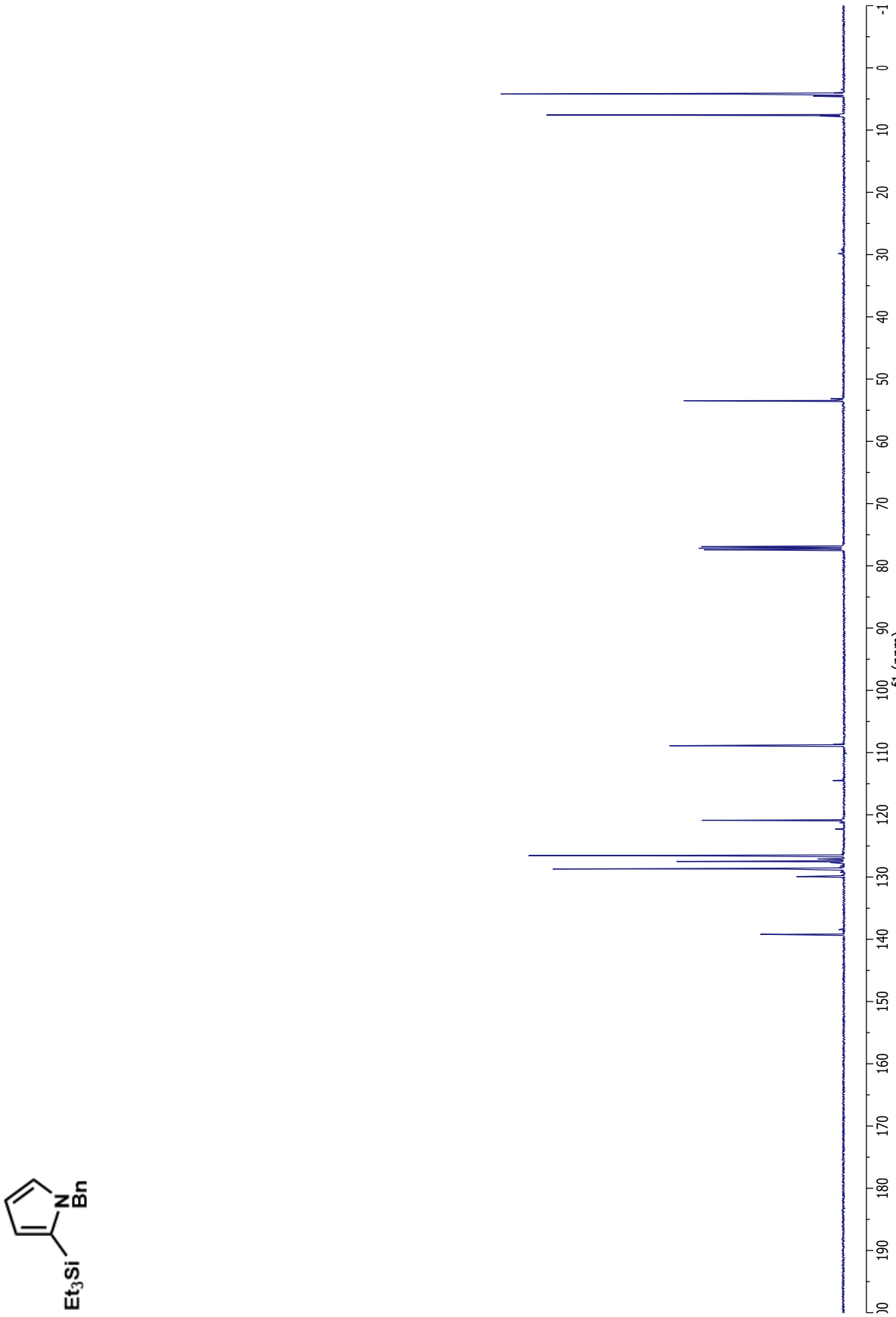
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4p**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **4p**.

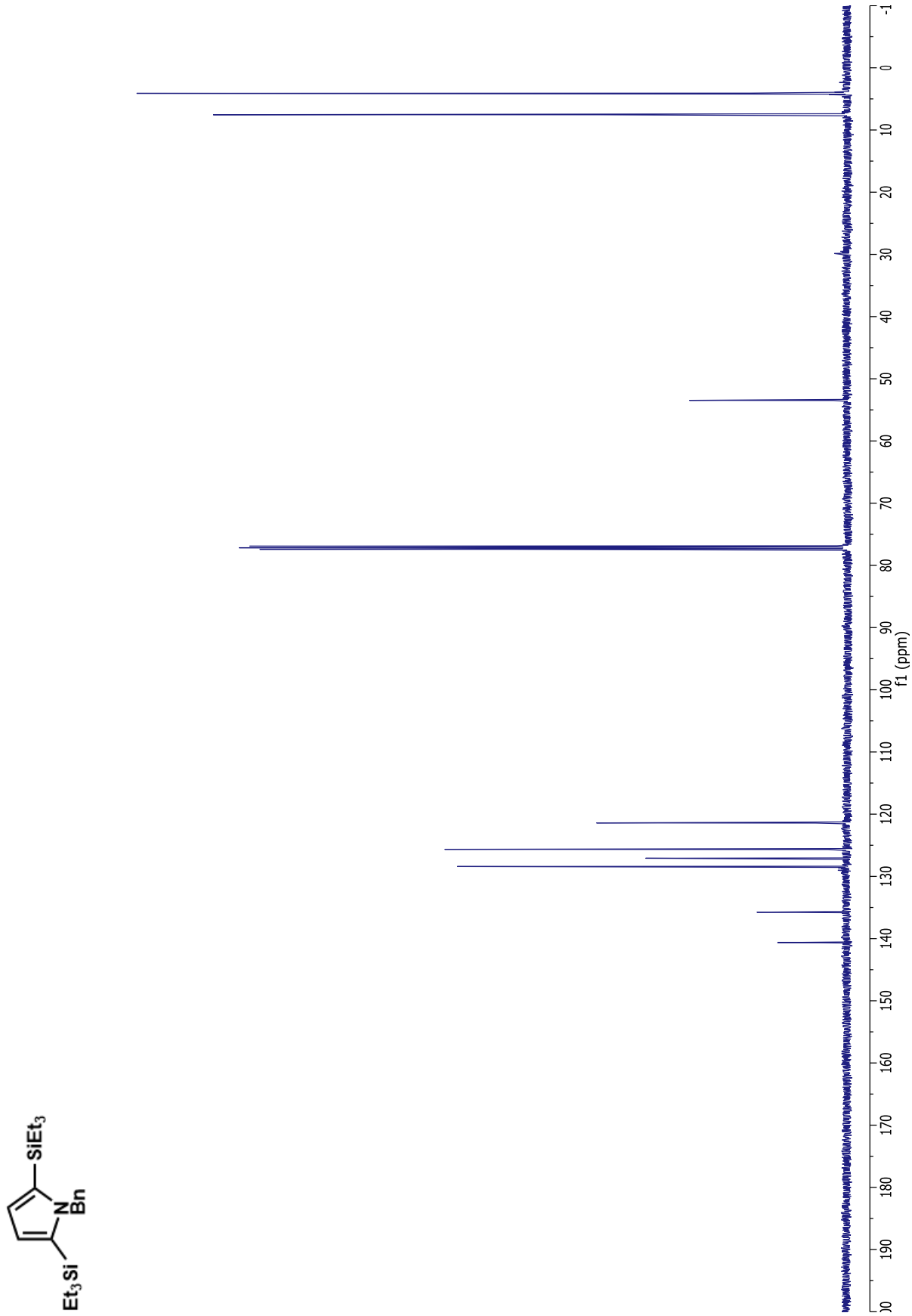


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4s**.

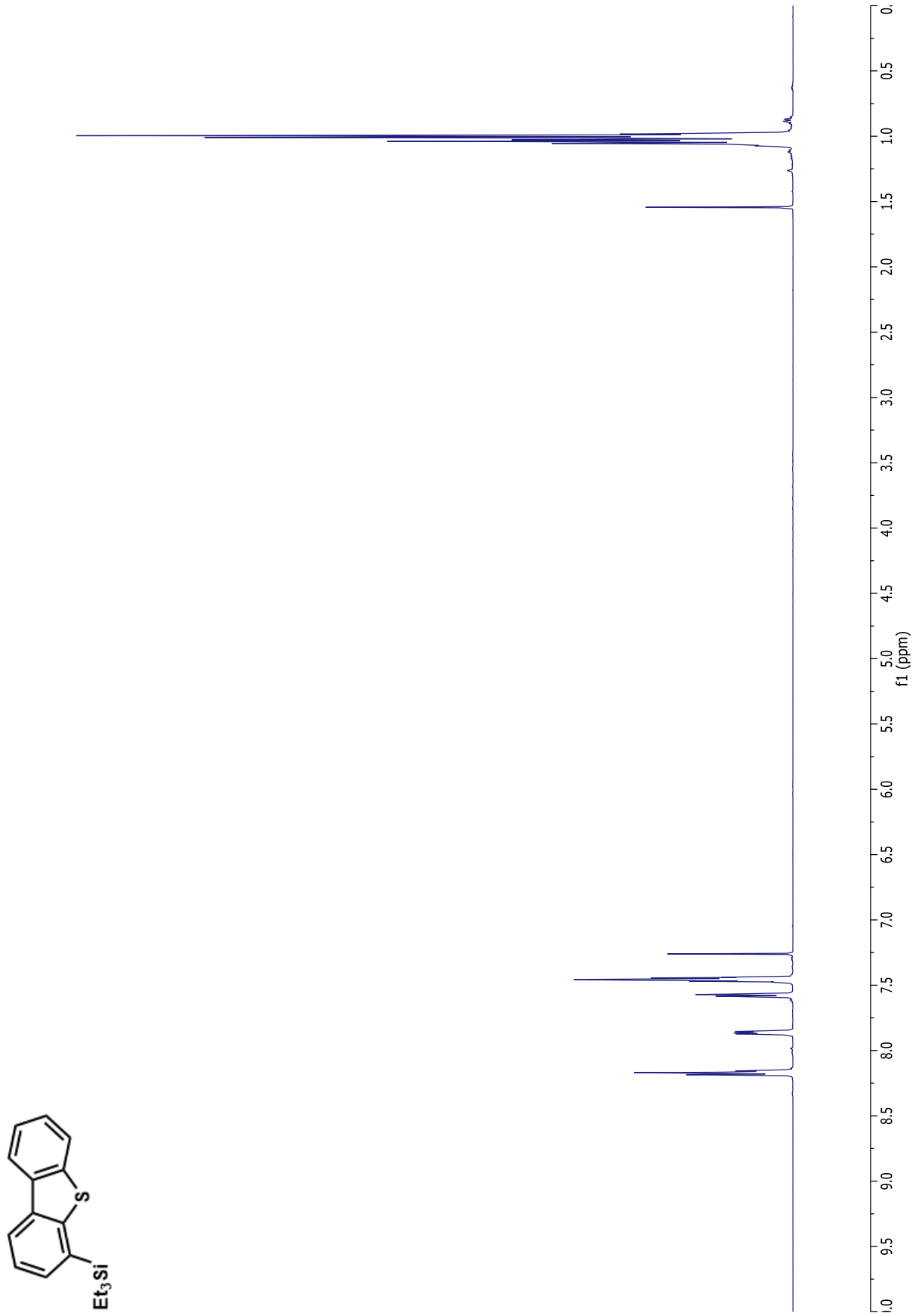


^{13}C NMR (125 MHz, $CDCl_3$) of compound **4s**.

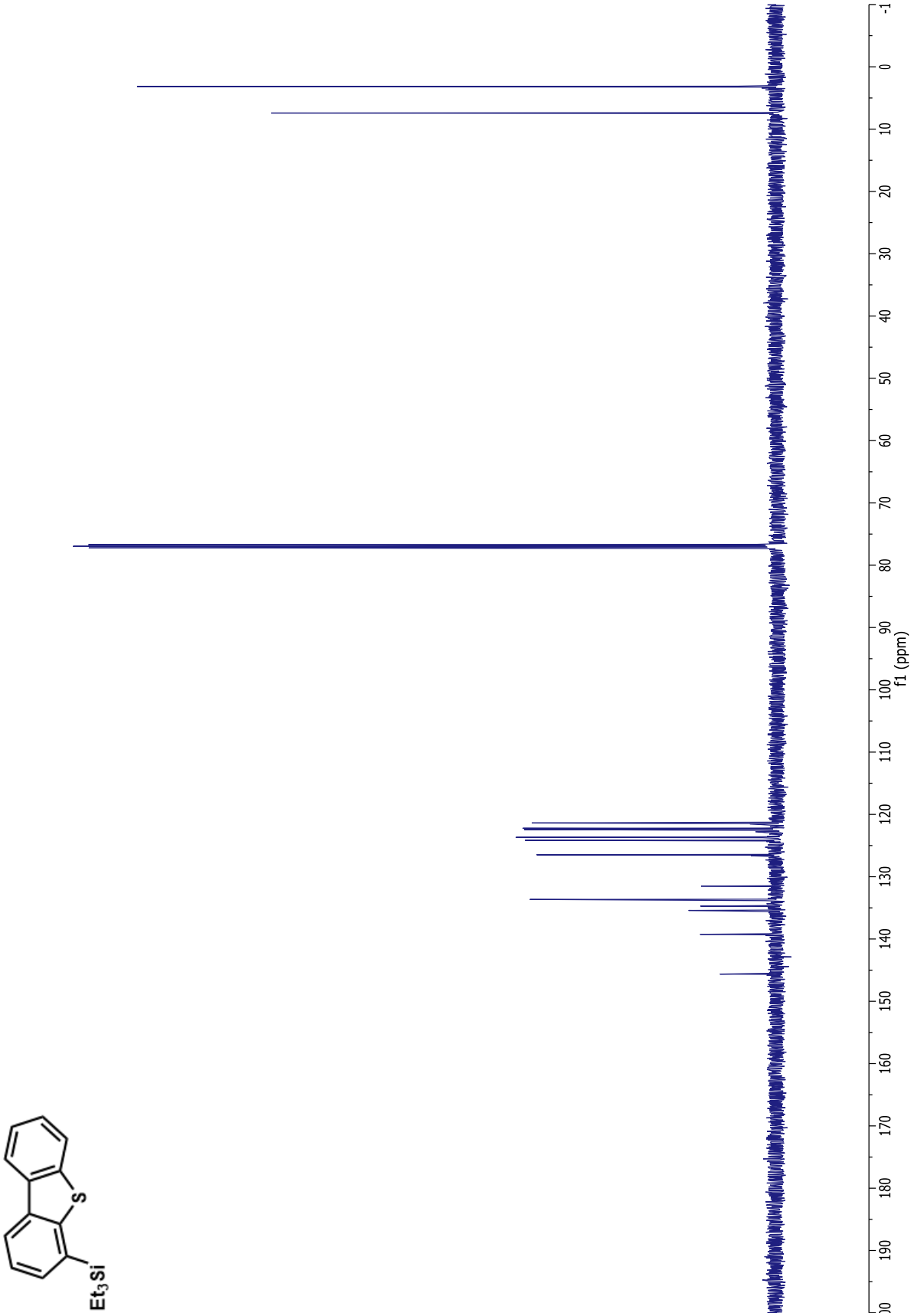
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-4s**.



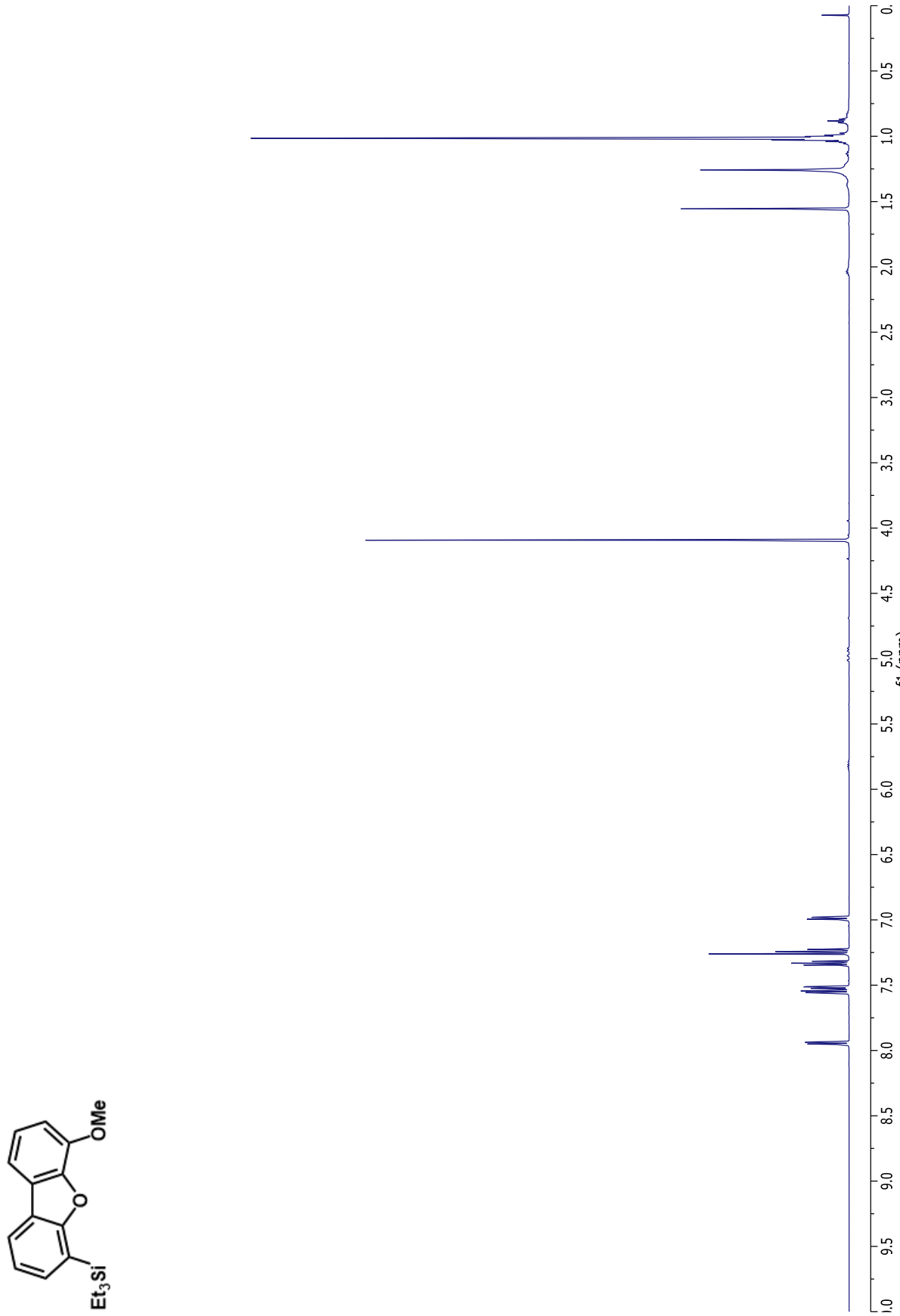
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-4s**.



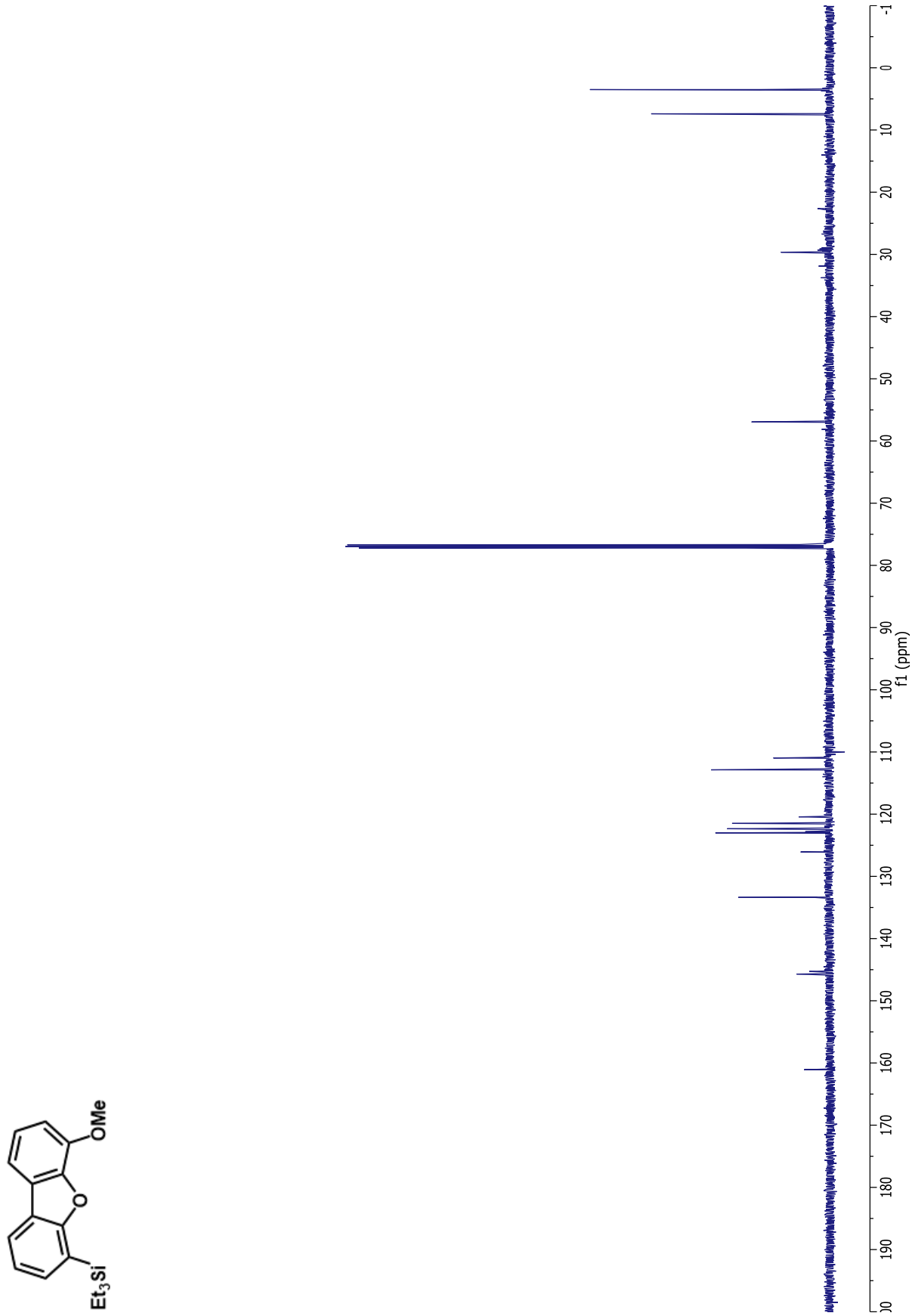
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4u**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **4u**.

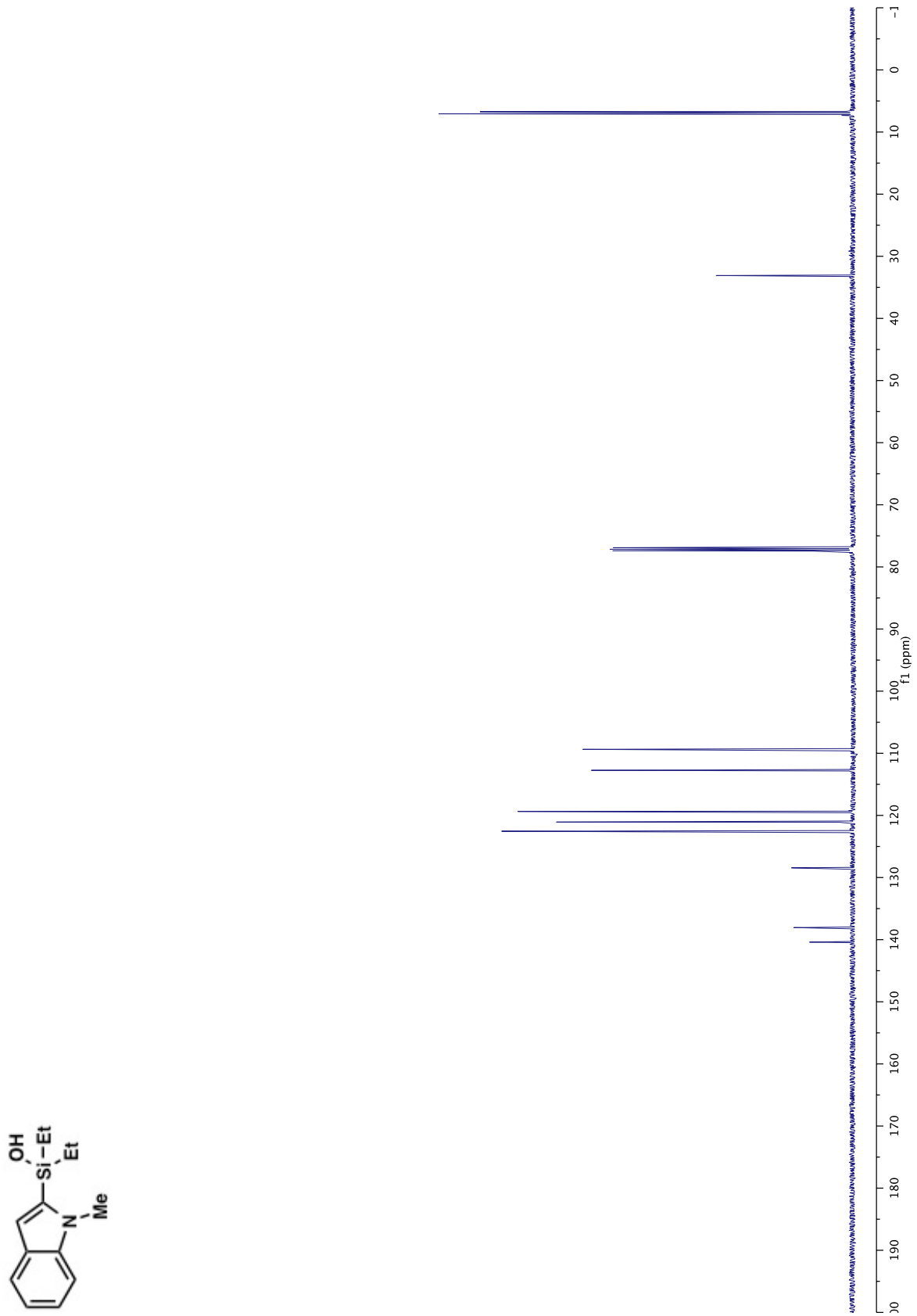


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4w**.



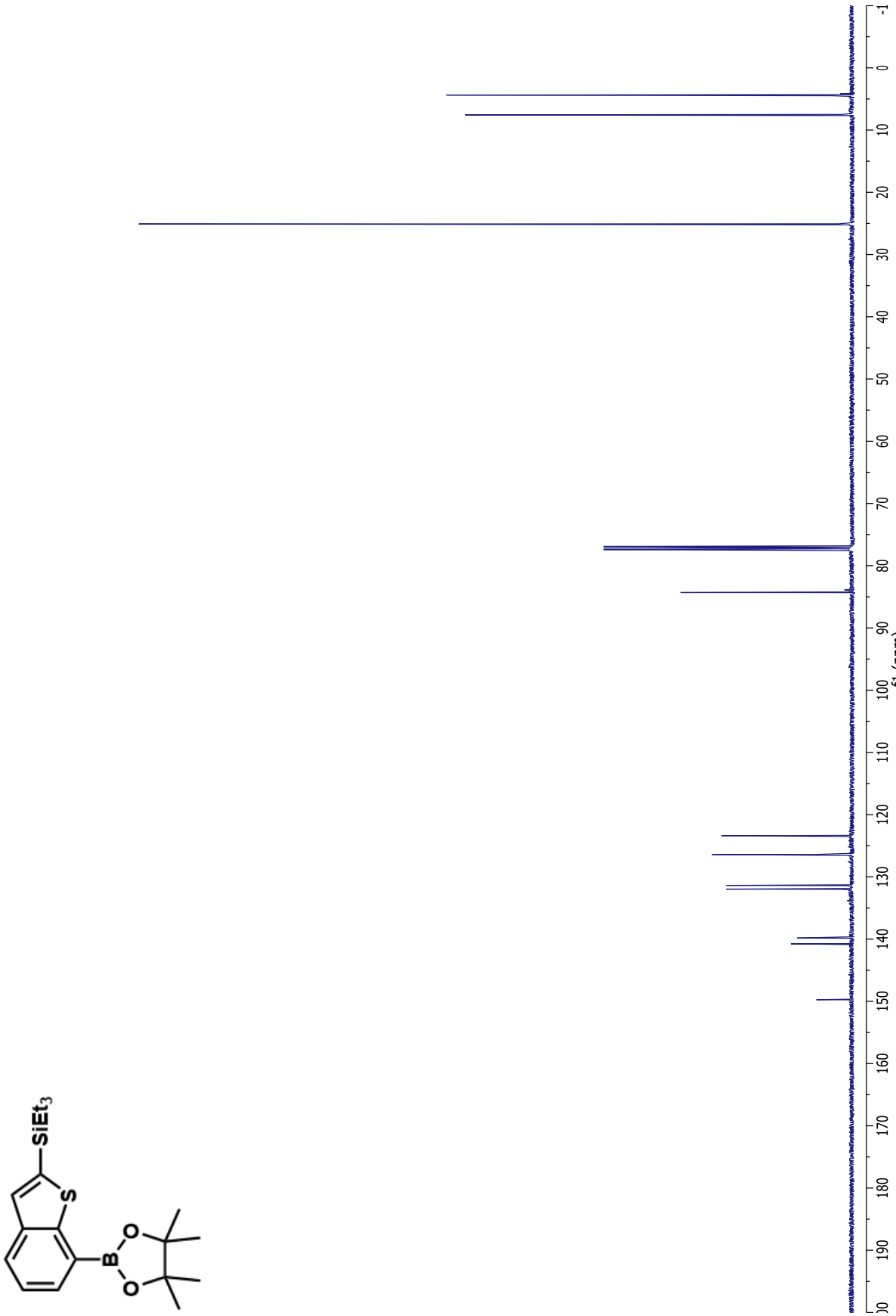
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4w**.

^{1}H NMR (500 MHz, $CDCl_3$) of compound **6**.



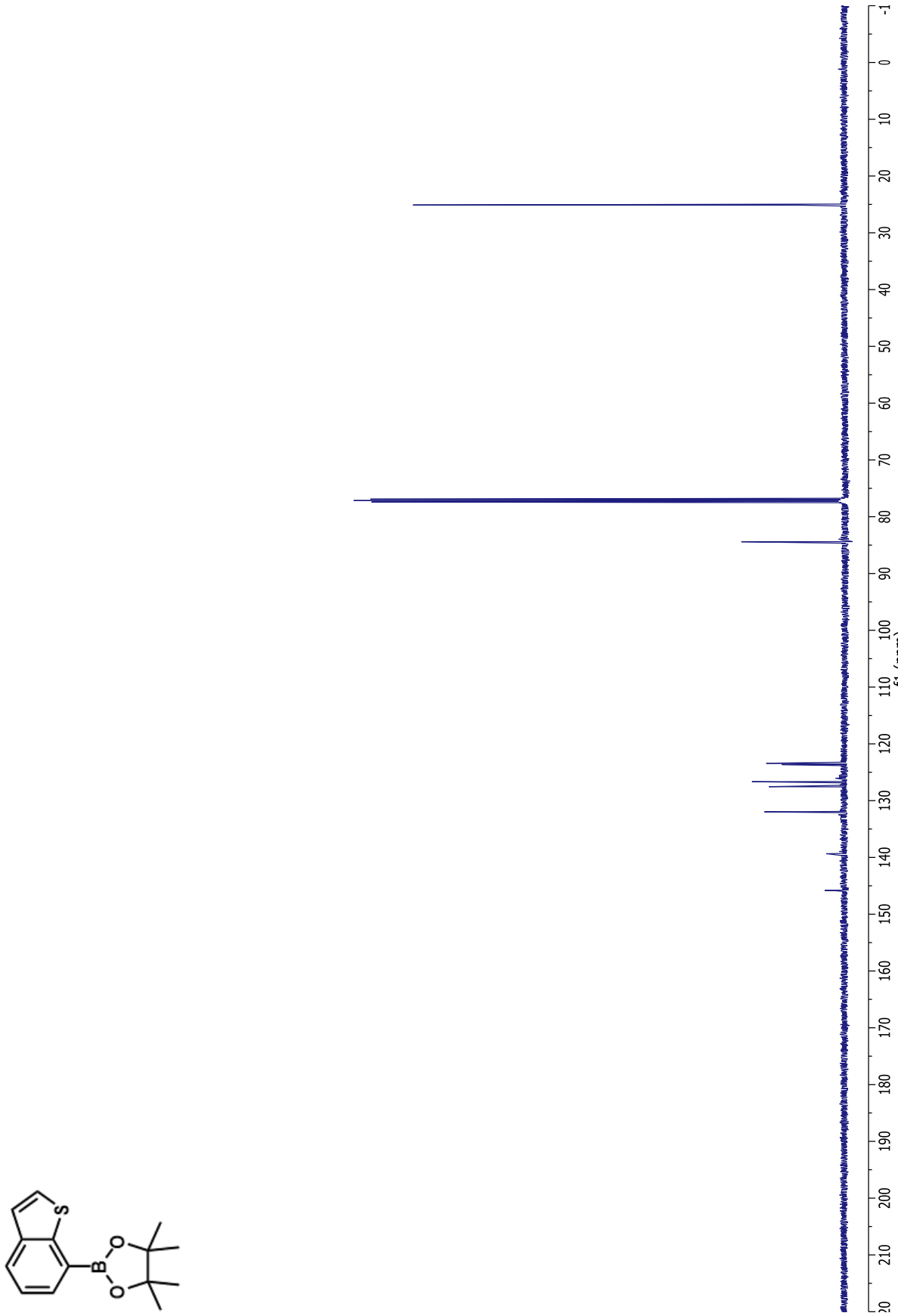
^{13}C NMR (125 MHz, $CDCl_3$) of compound **6**.

^{1}H NMR (500 MHz, $CDCl_3$) of compound **7**.

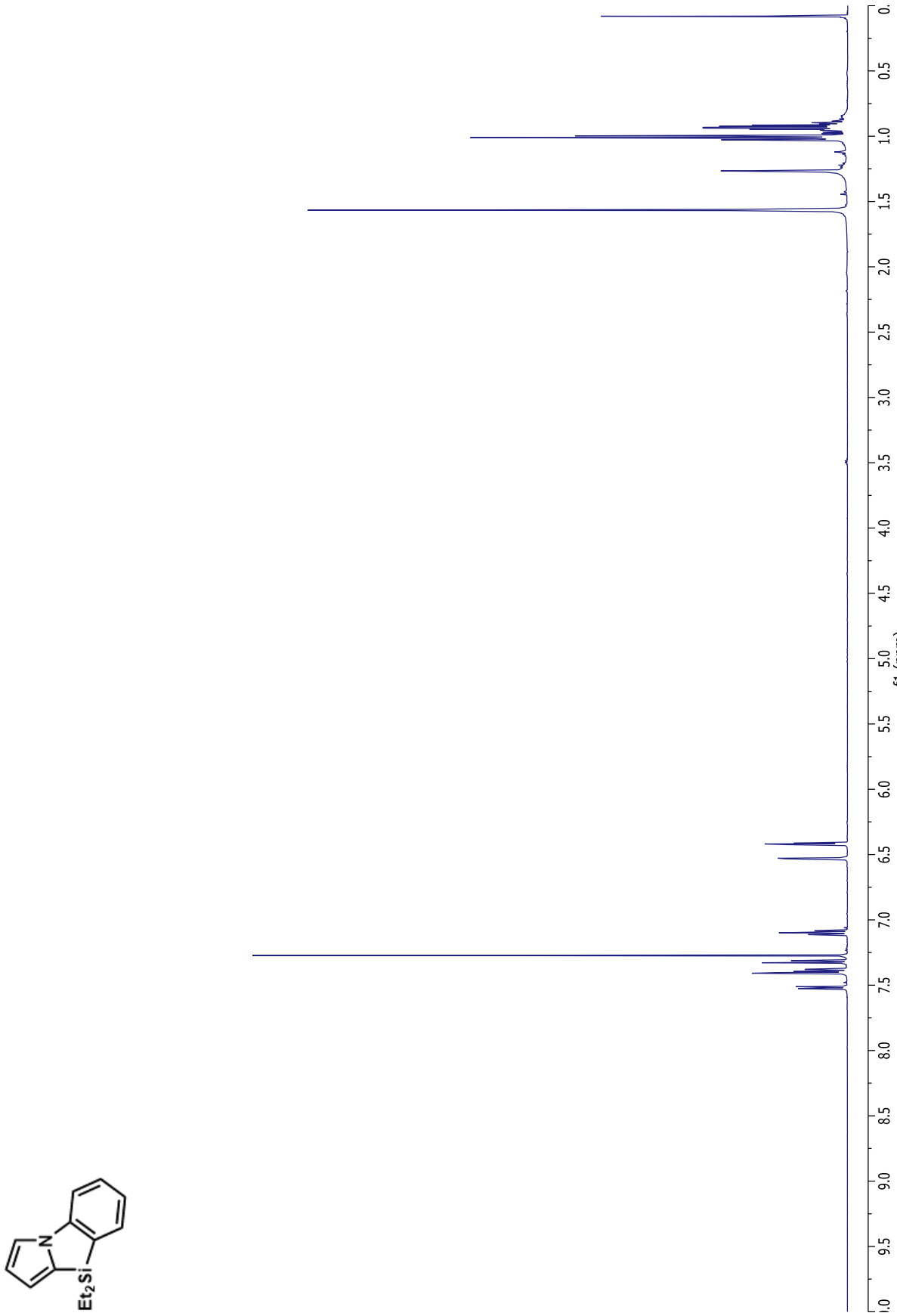


^{13}C NMR (125 MHz, $CDCl_3$) of compound **7**.

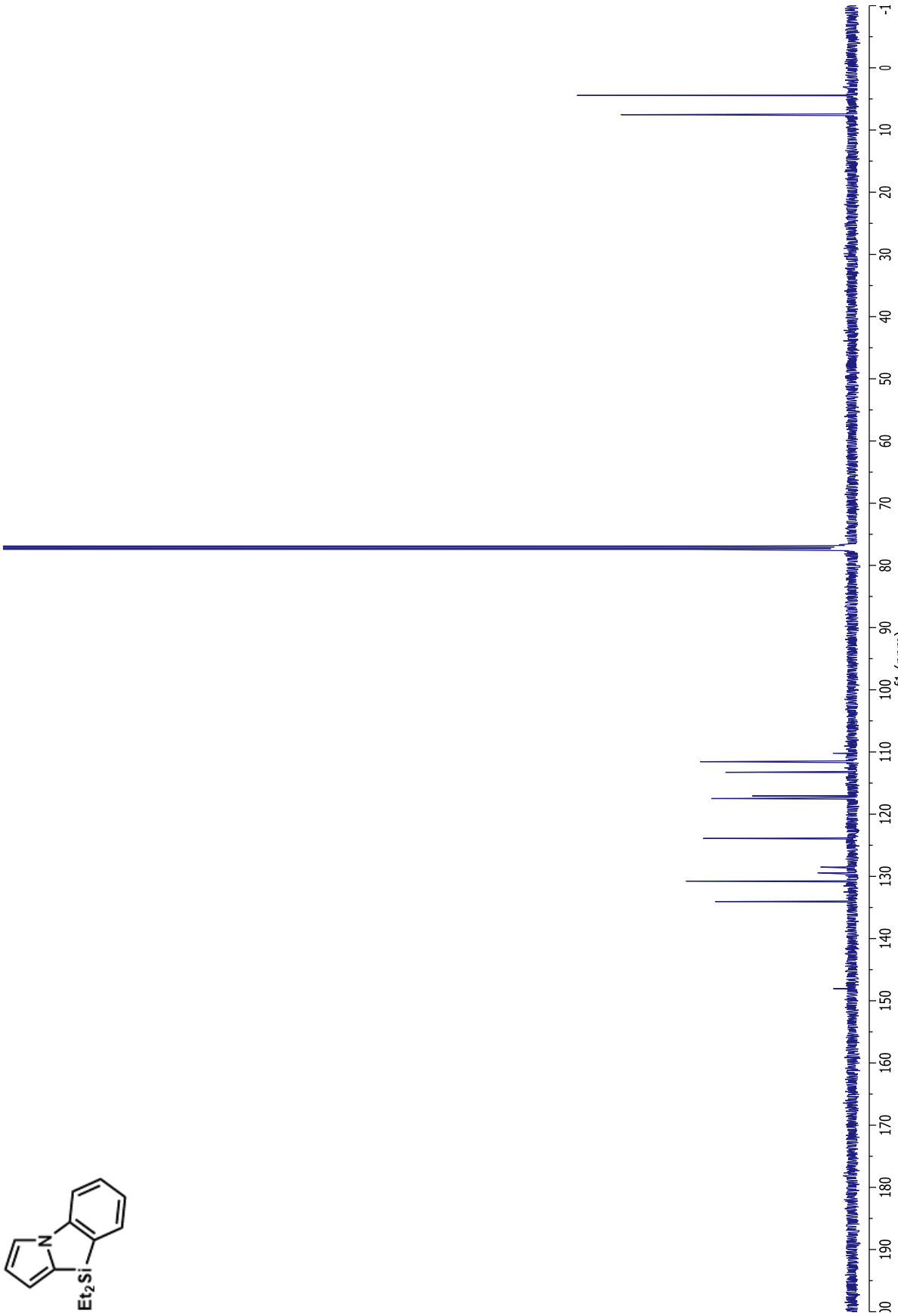
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8**.



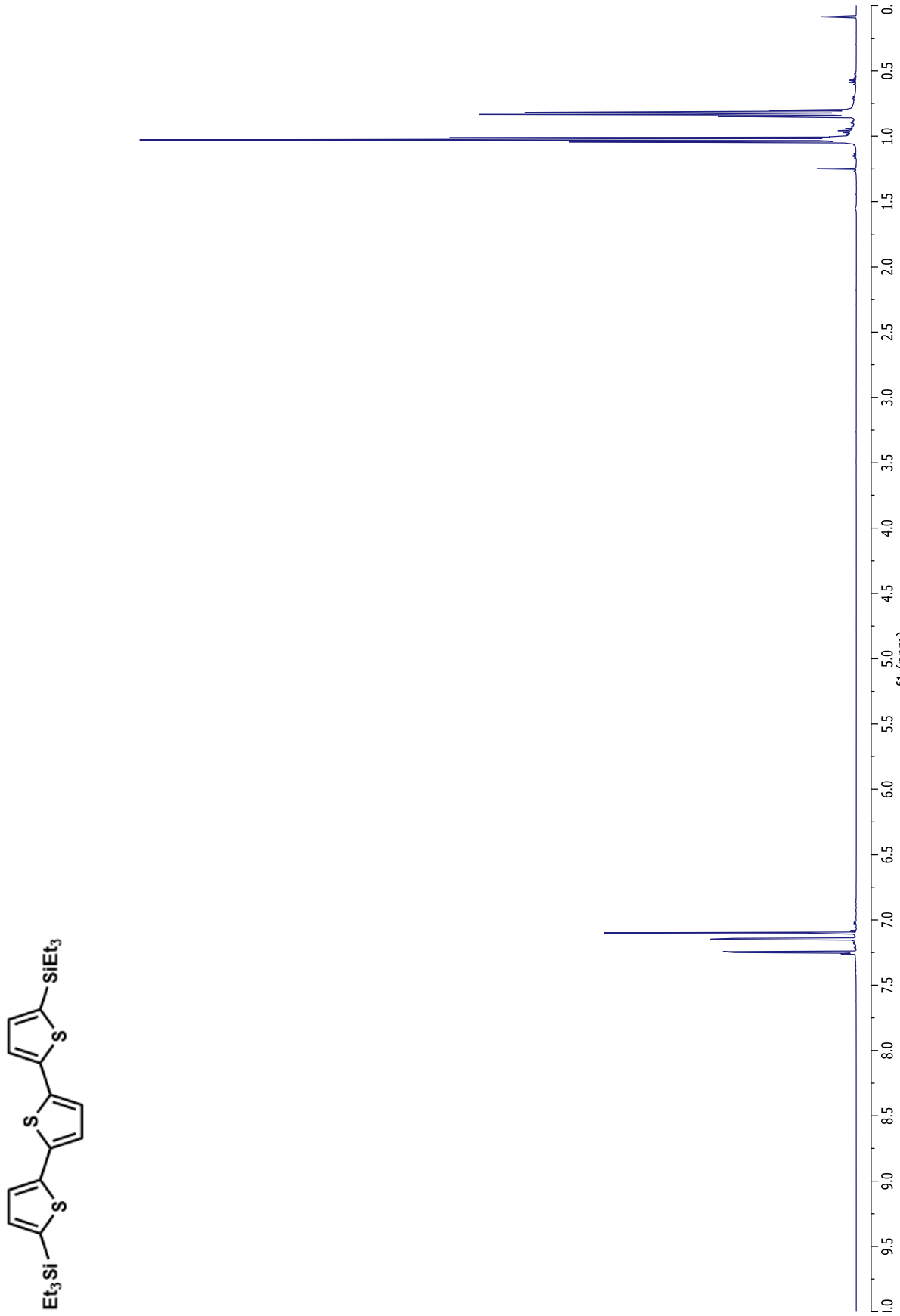
^{13}C NMR (125 MHz, $CDCl_3$) of compound **8**.



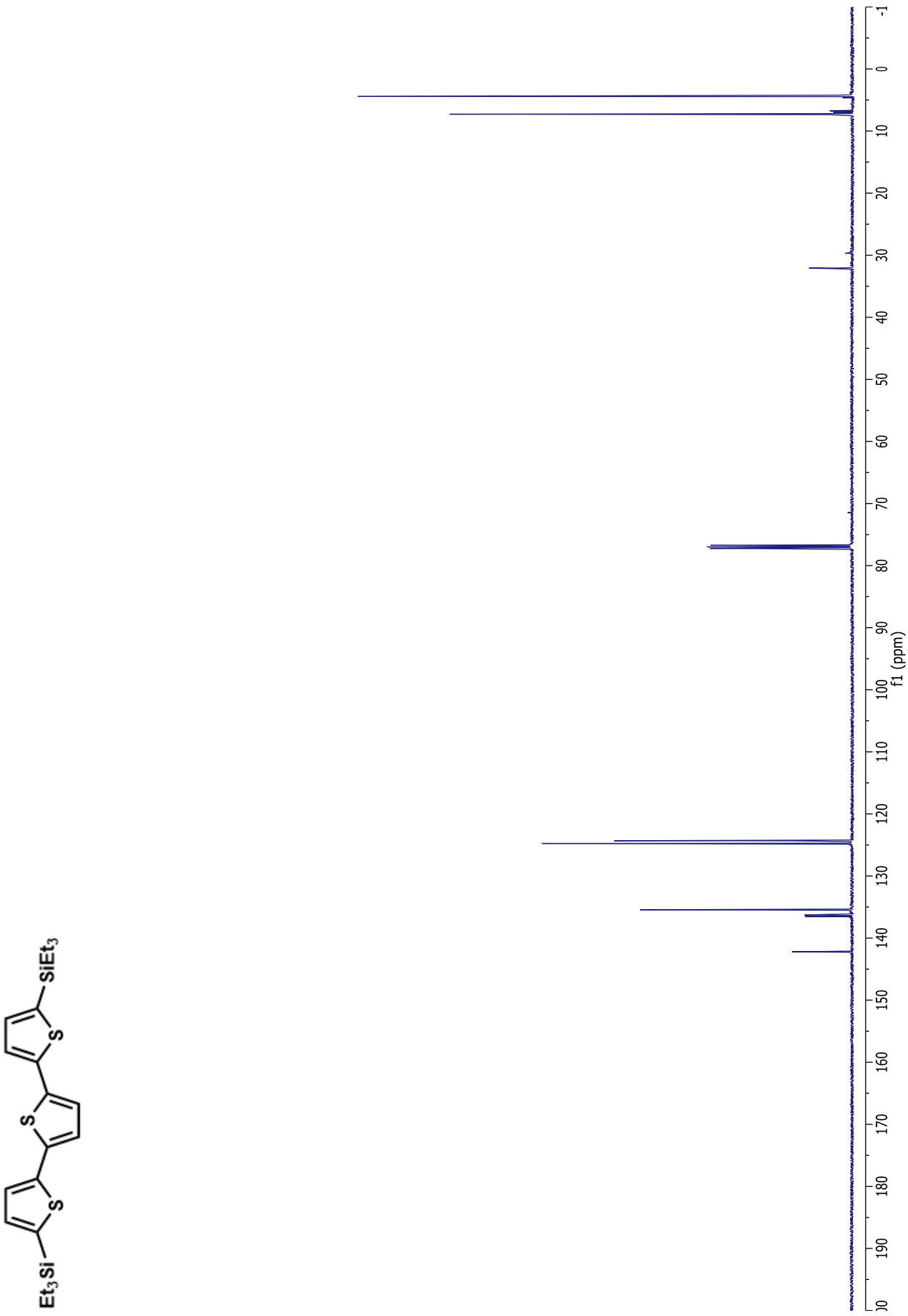
^{1}H NMR (500 MHz, $CDCl_3$) of compound **9**.



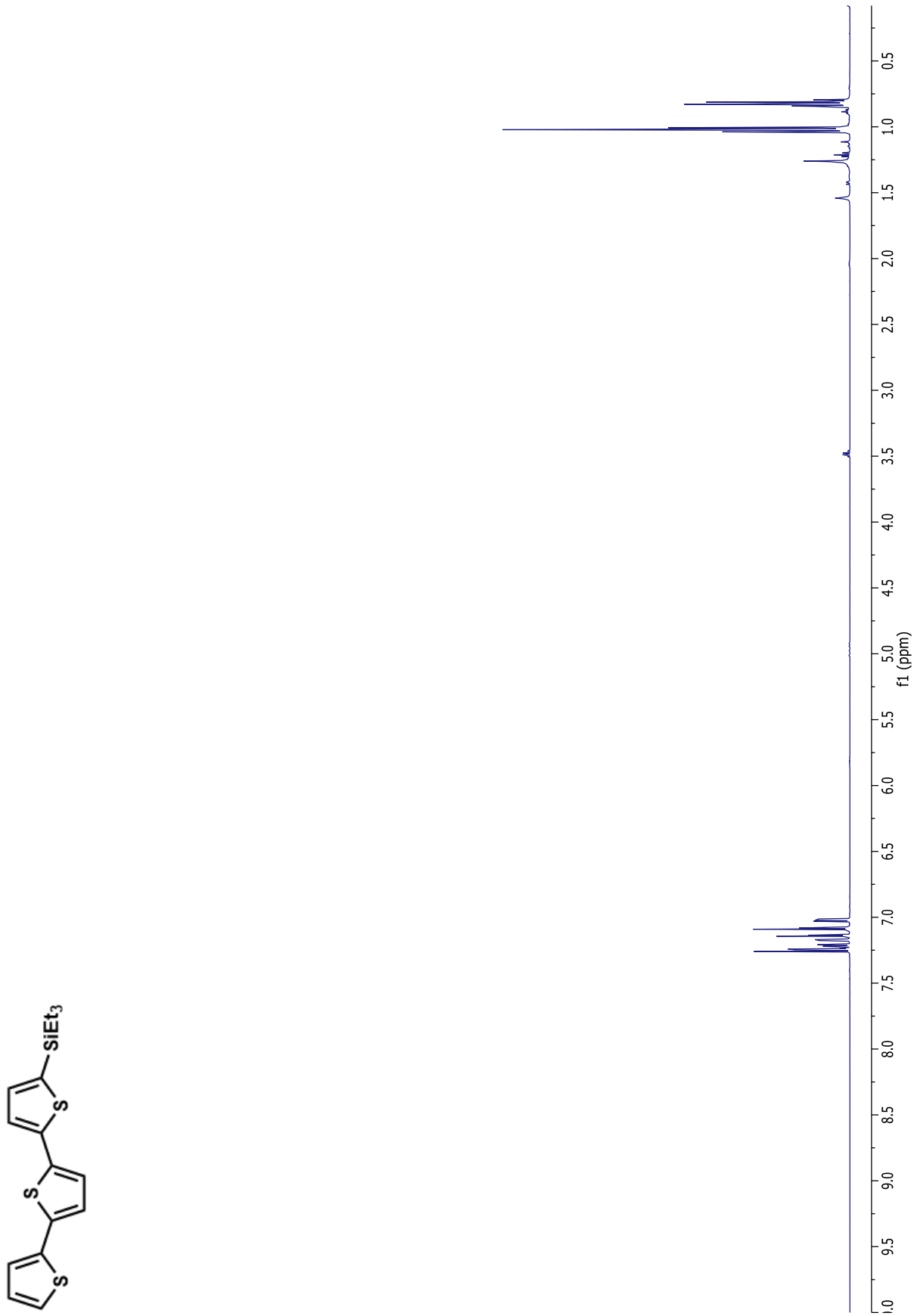
^{13}C NMR (125 MHz, $CDCl_3$) of compound **9**.



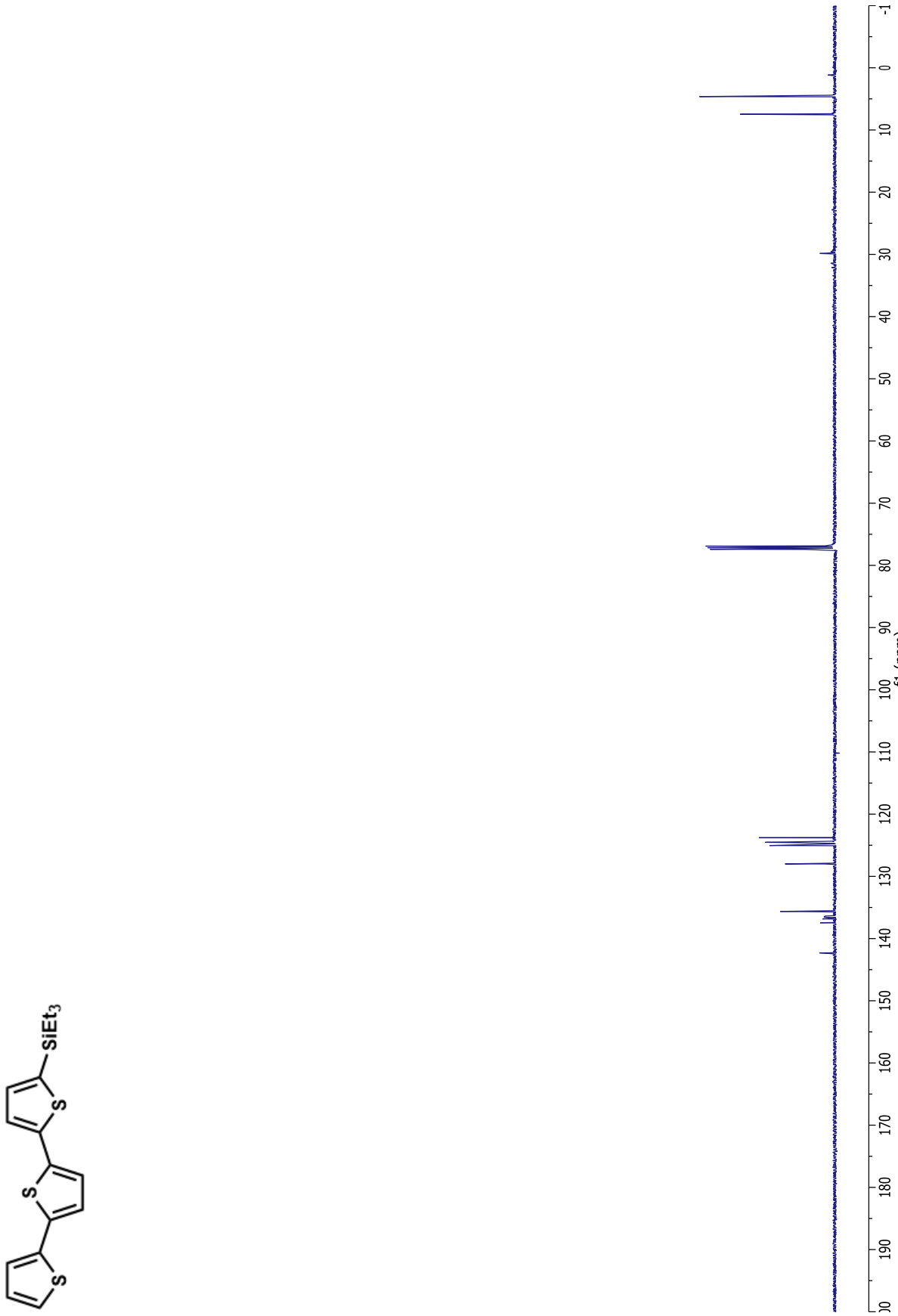
^{1}H NMR (500 MHz, $CDCl_3$) of compound **10**.



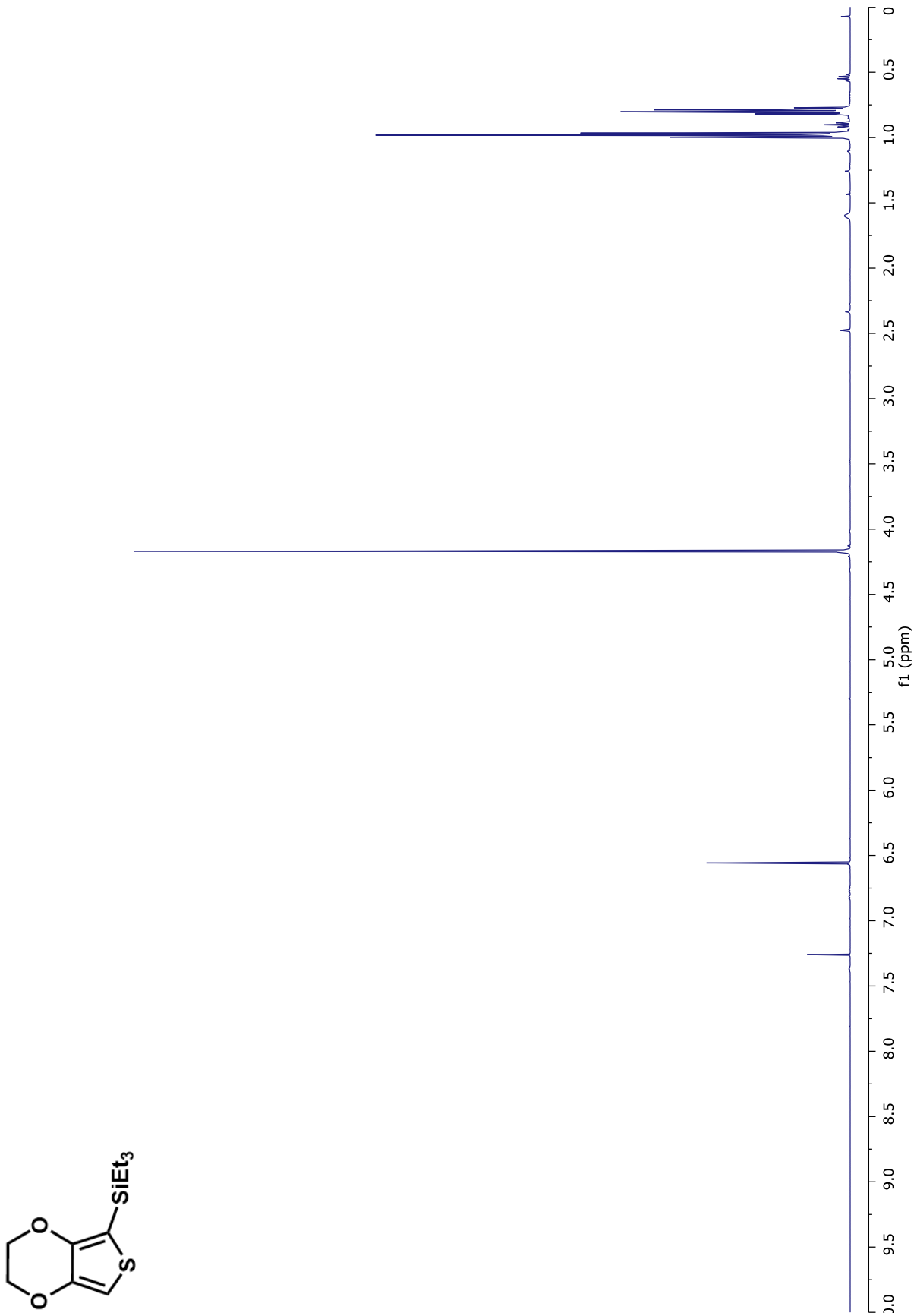
^{13}C NMR (125 MHz, $CDCl_3$) of compound **10**.



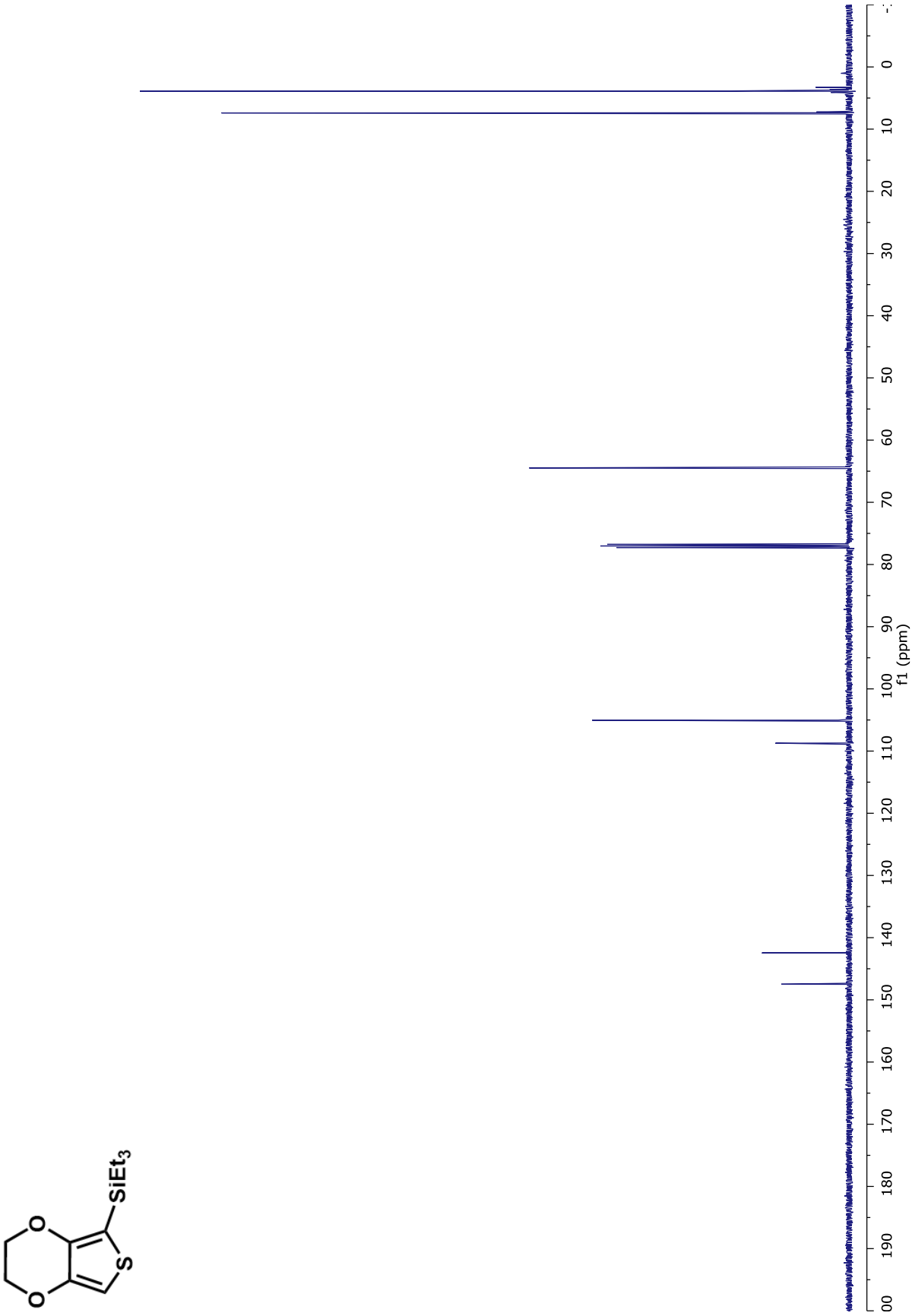
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-10**.



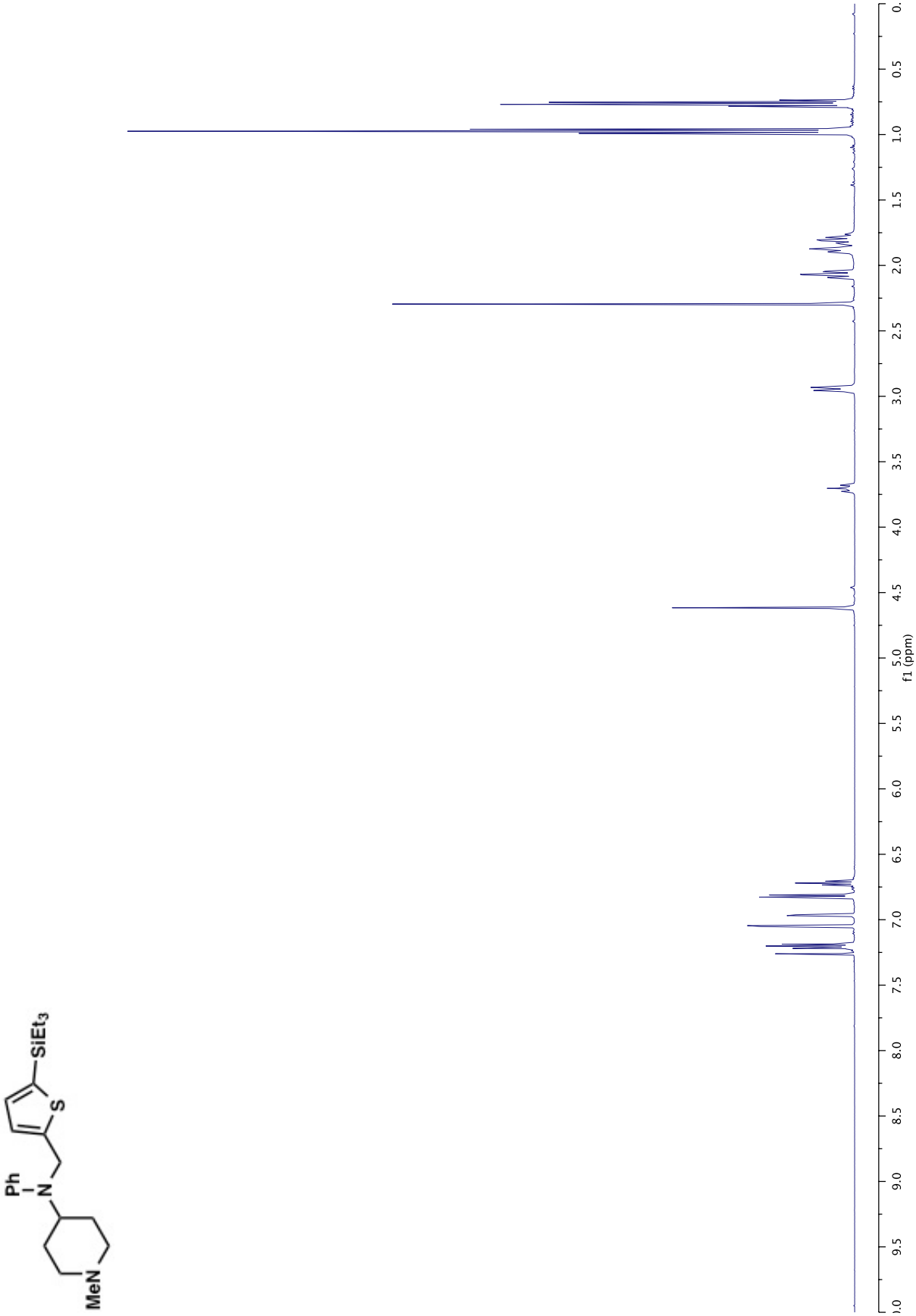
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-10**.



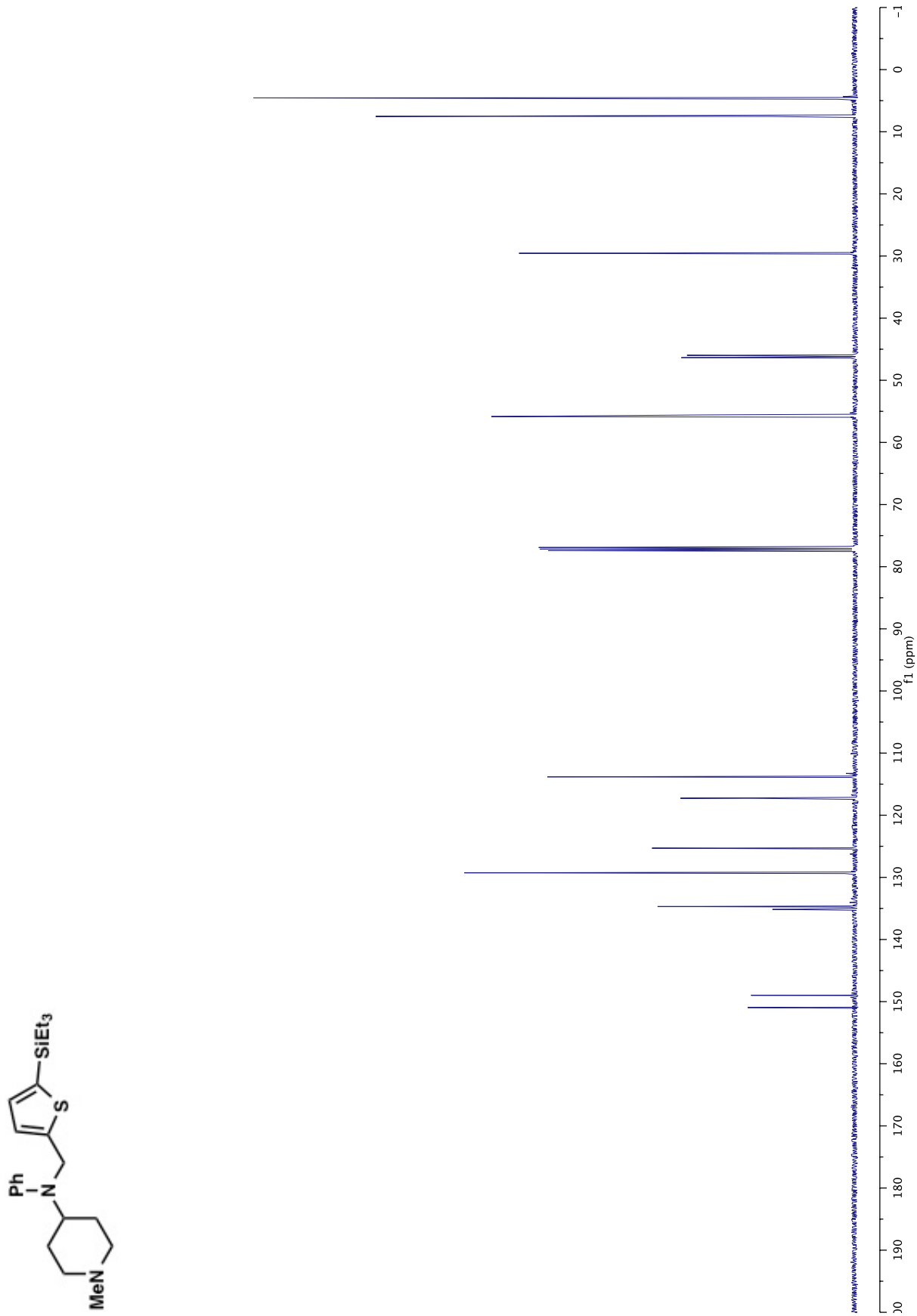
^{1}H NMR (500 MHz, $CDCl_3$) of compound **11**.



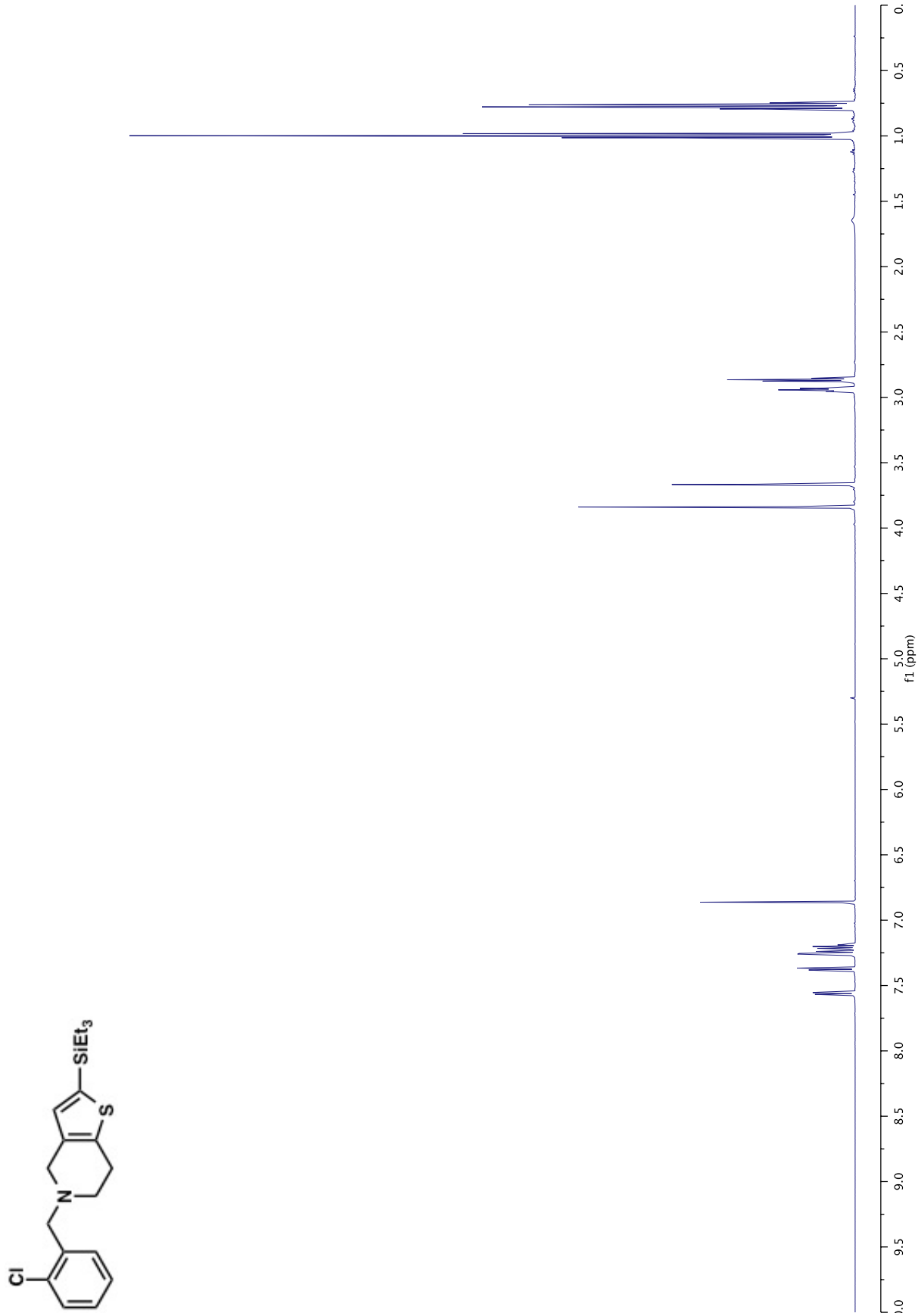
^{13}C NMR (125 MHz, $CDCl_3$) of compound **11**.



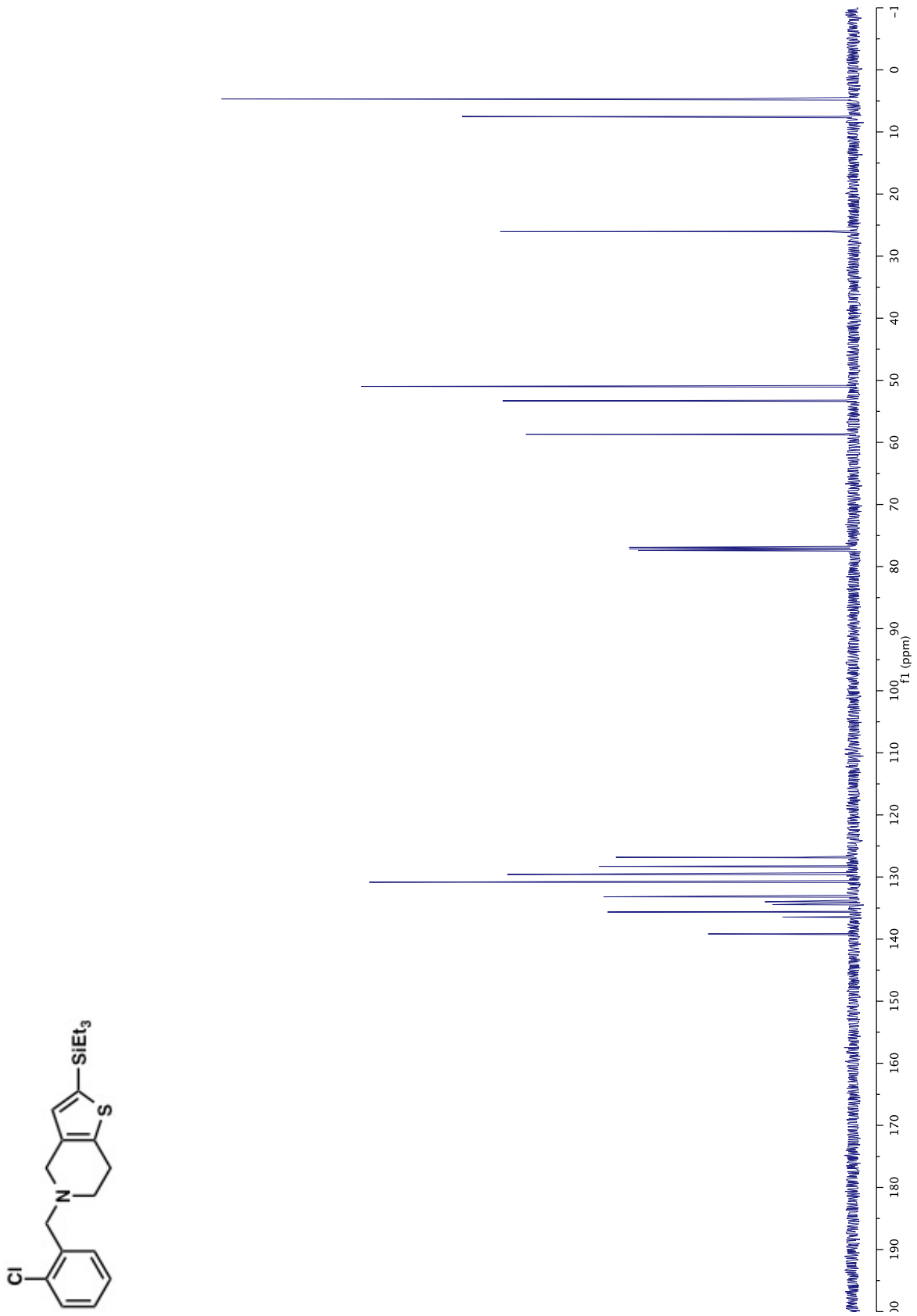
^{1}H NMR (500 MHz, $CDCl_3$) of compound **12**.



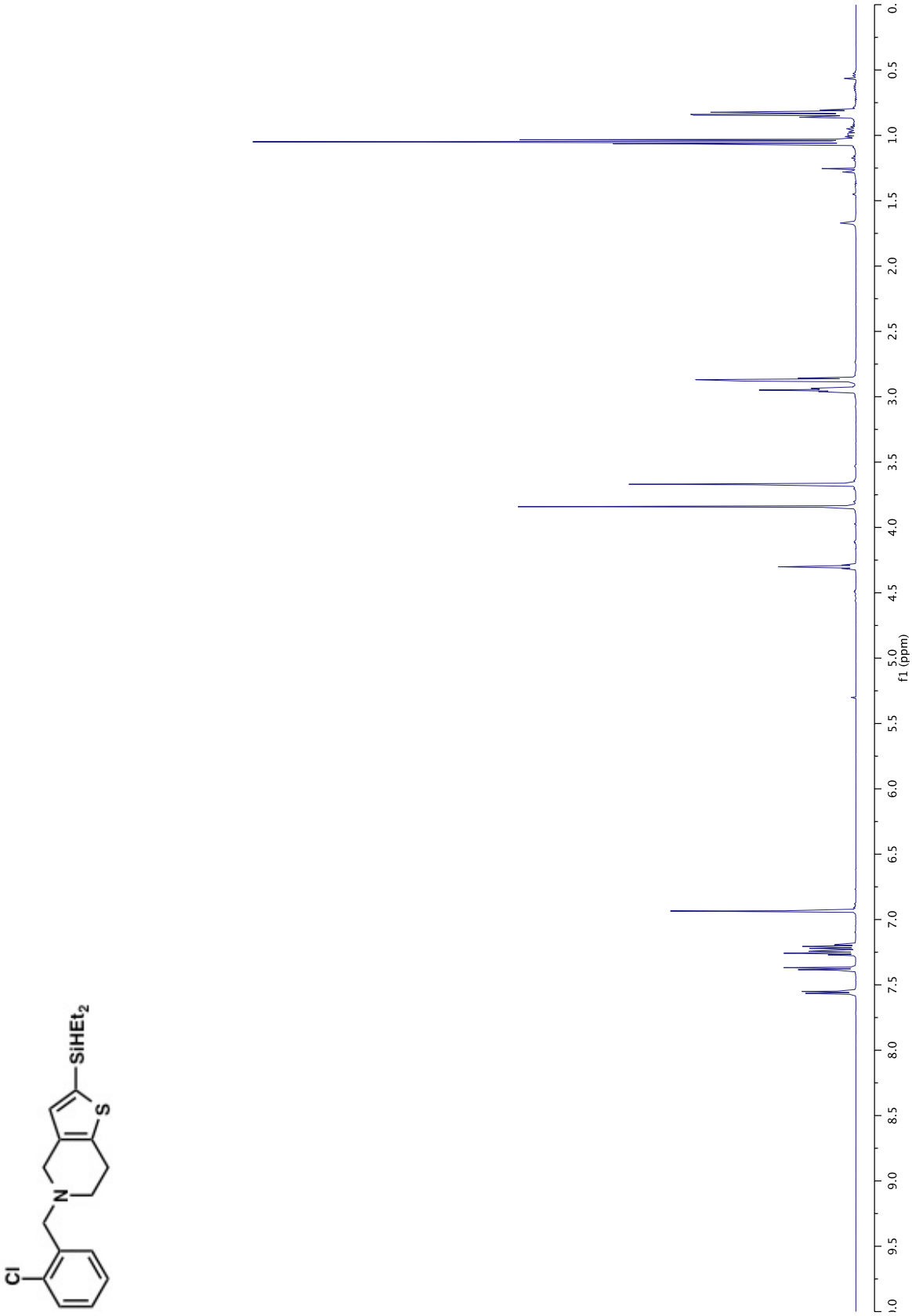
^{13}C NMR (125 MHz, $CDCl_3$) of compound **12**.



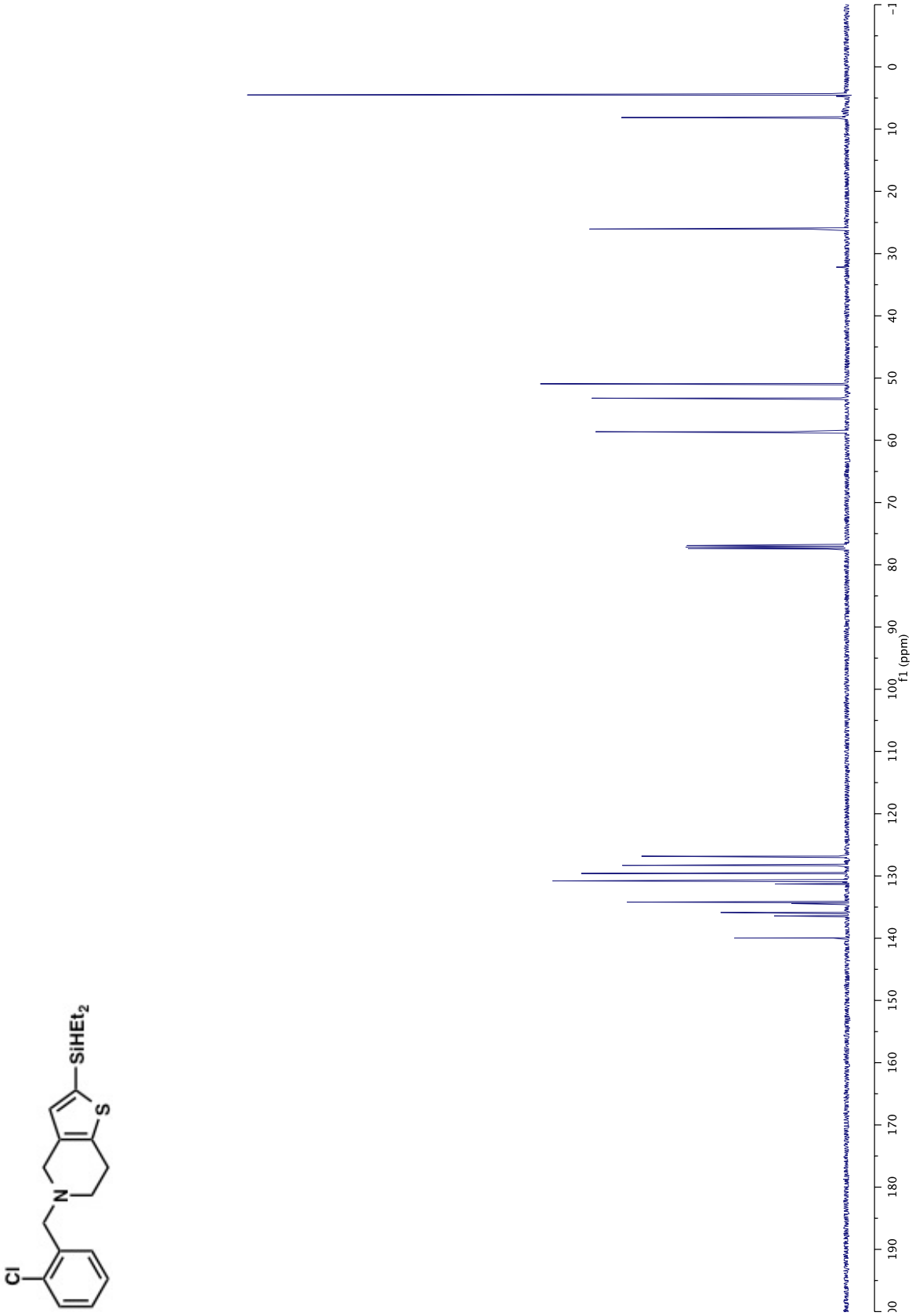
^{1}H NMR (500 MHz, $CDCl_3$) of compound **13a**.



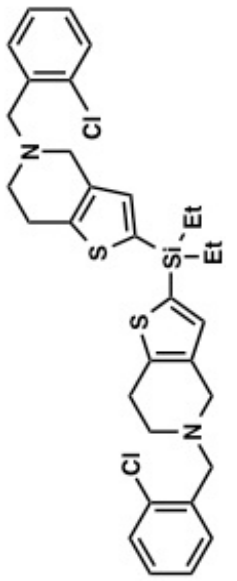
^{13}C NMR (125 MHz, $CDCl_3$) of compound **13a**.

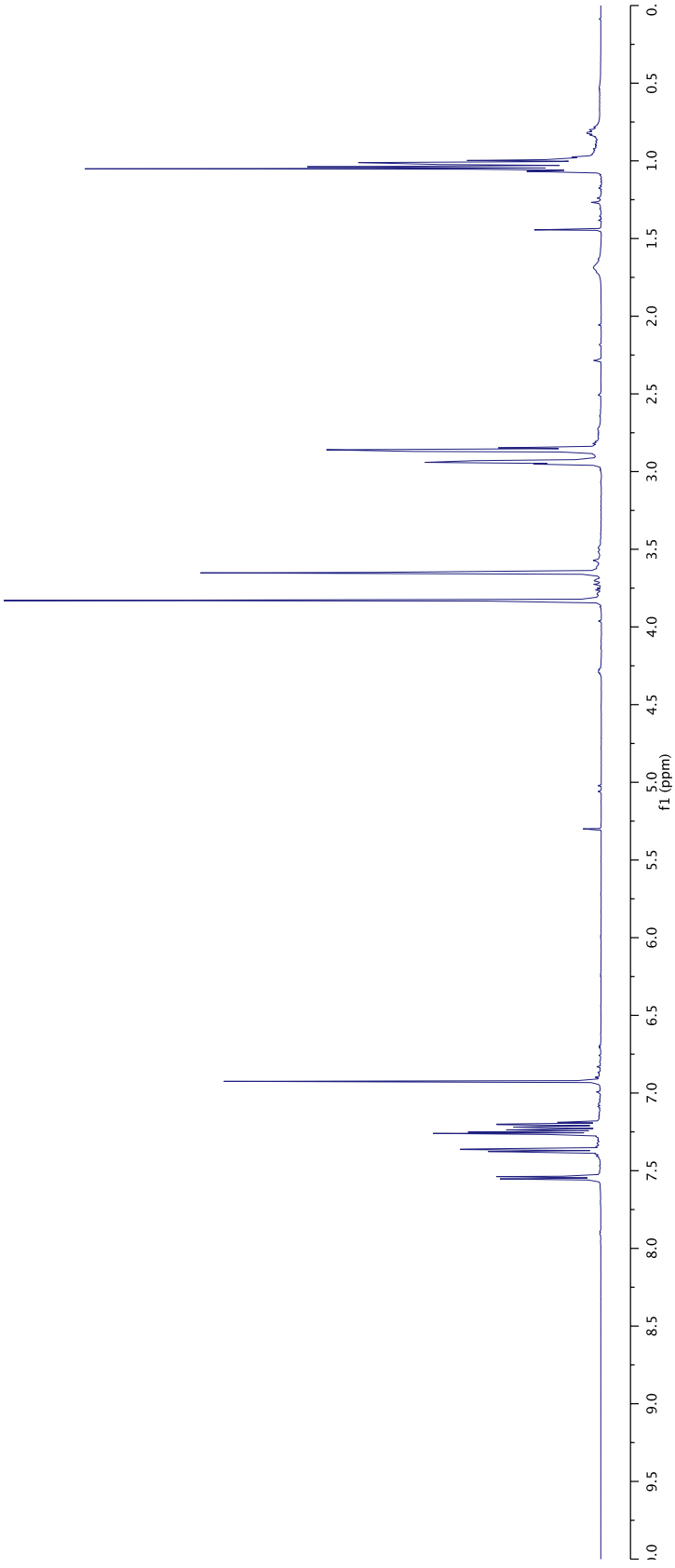


^{1}H NMR (500 MHz, $CDCl_3$) of compound **13b**.

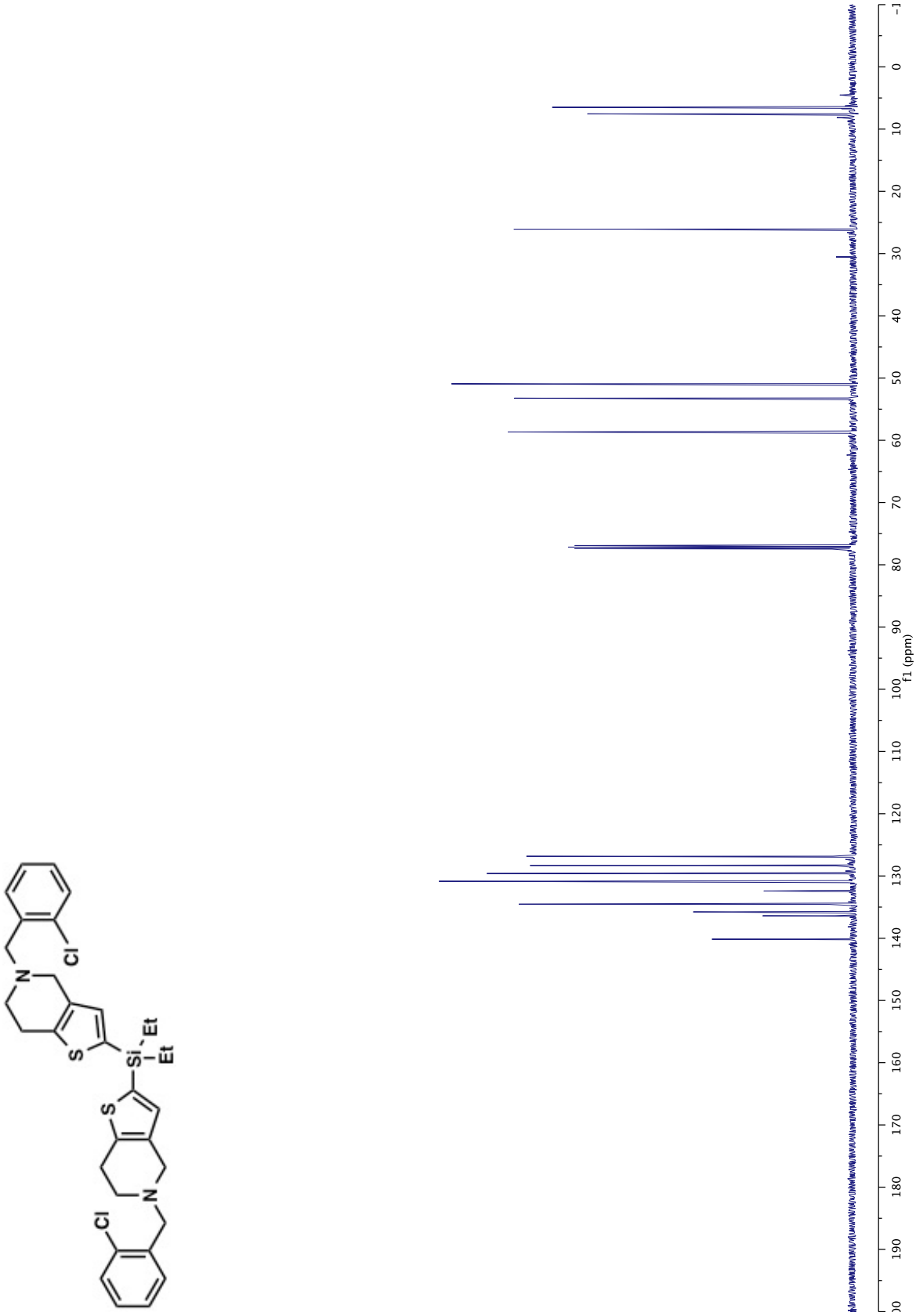


^{13}C NMR (125 MHz, $CDCl_3$) of compound **13b**.

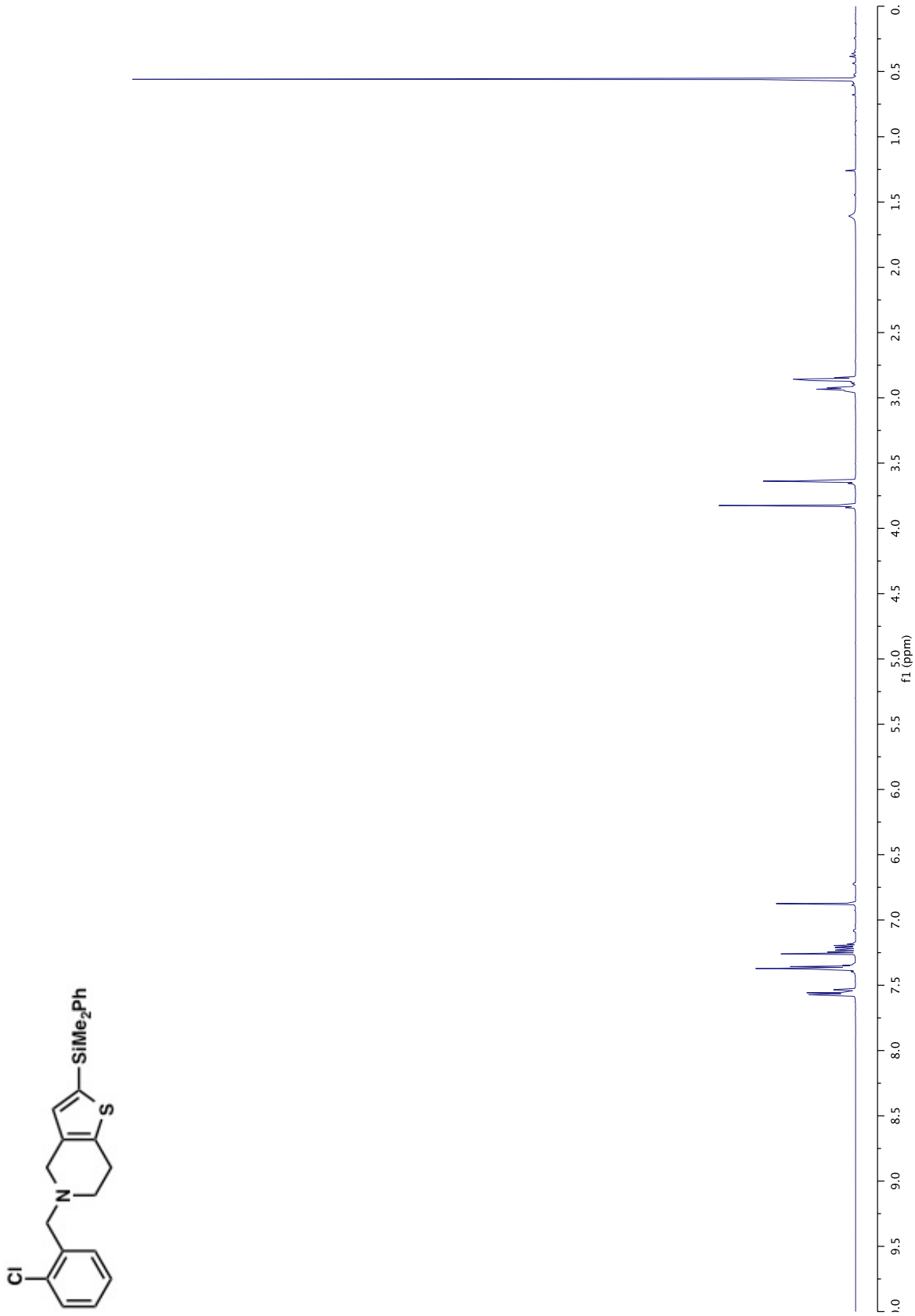




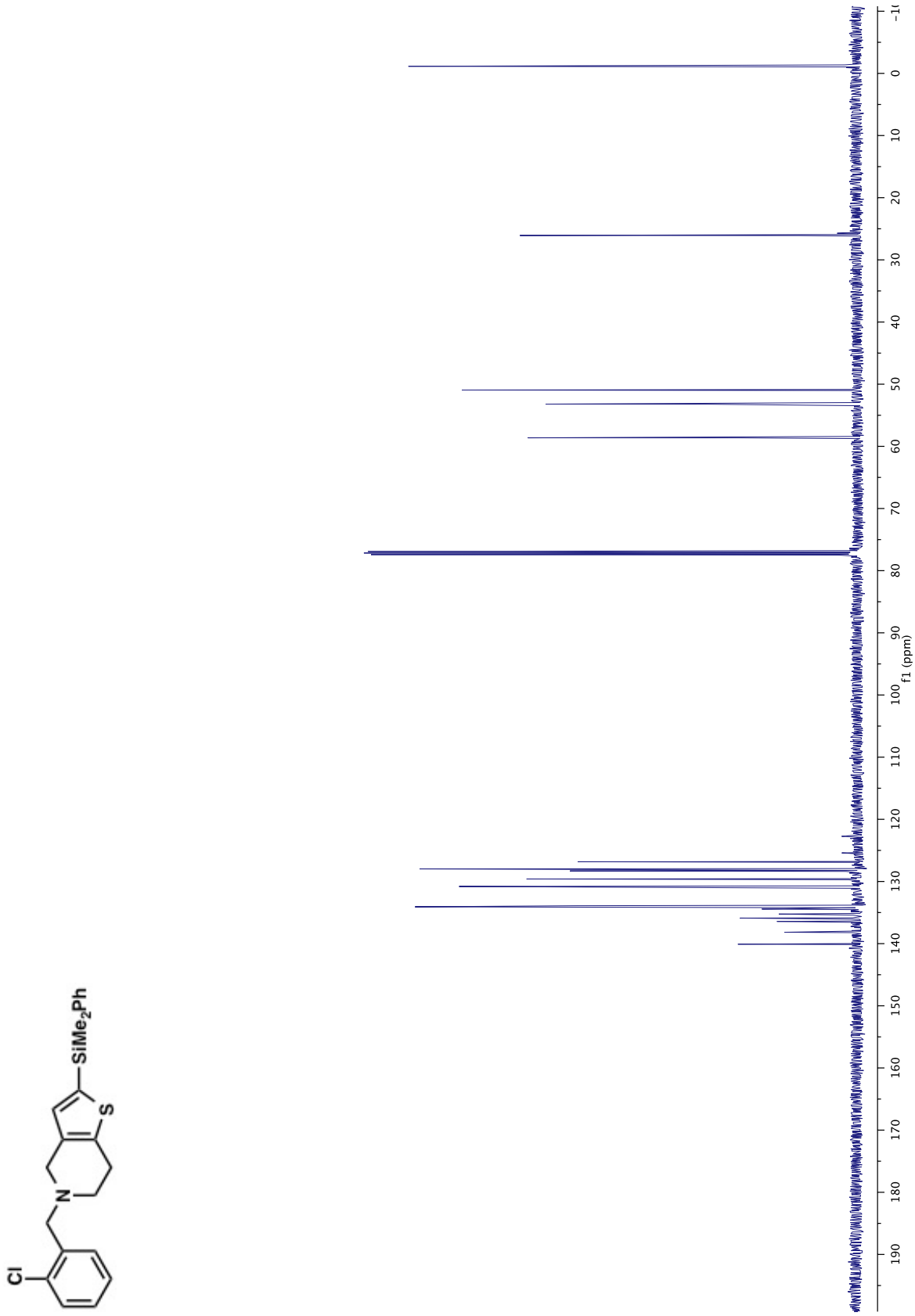
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-13b**.



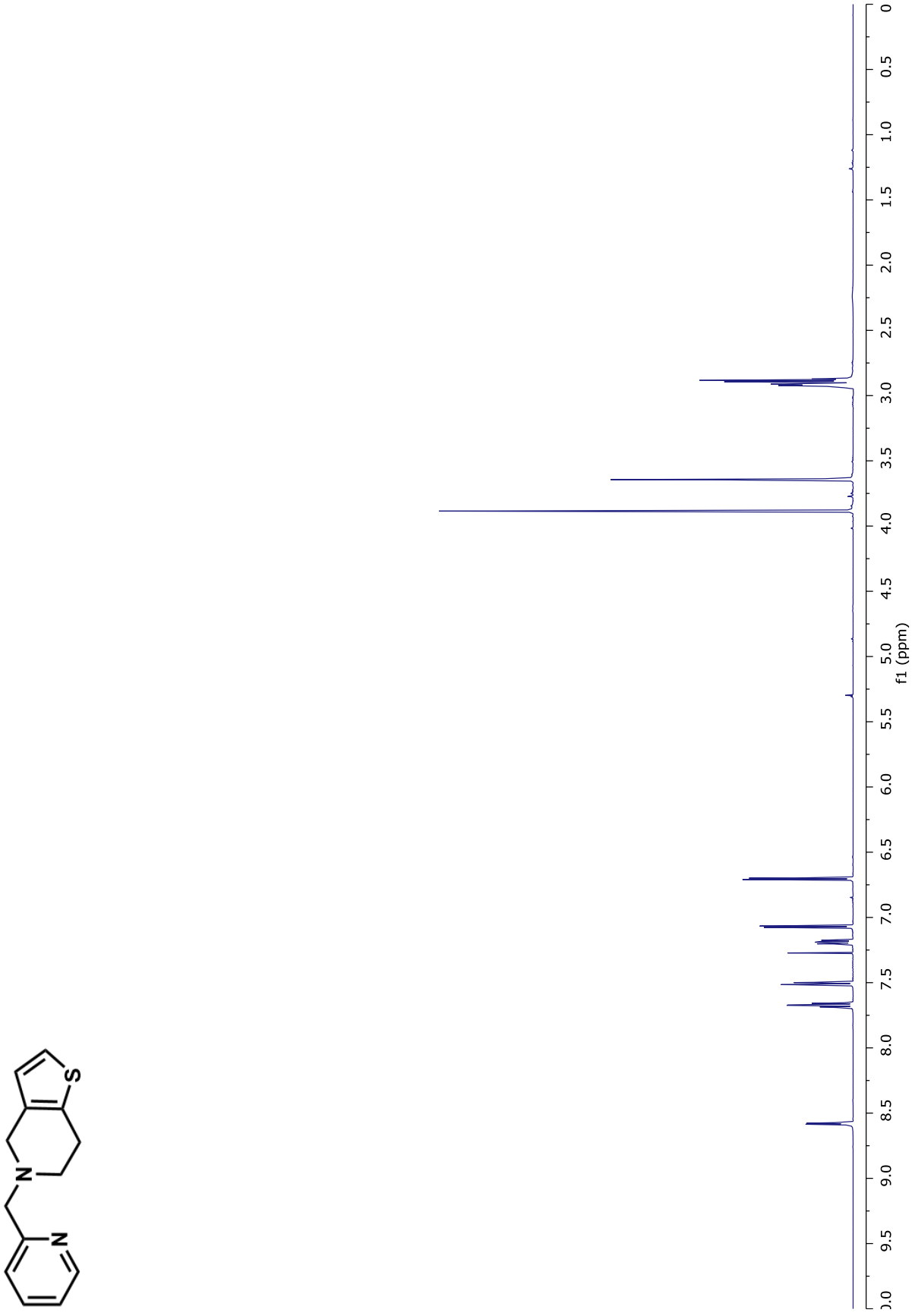
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-13b**.



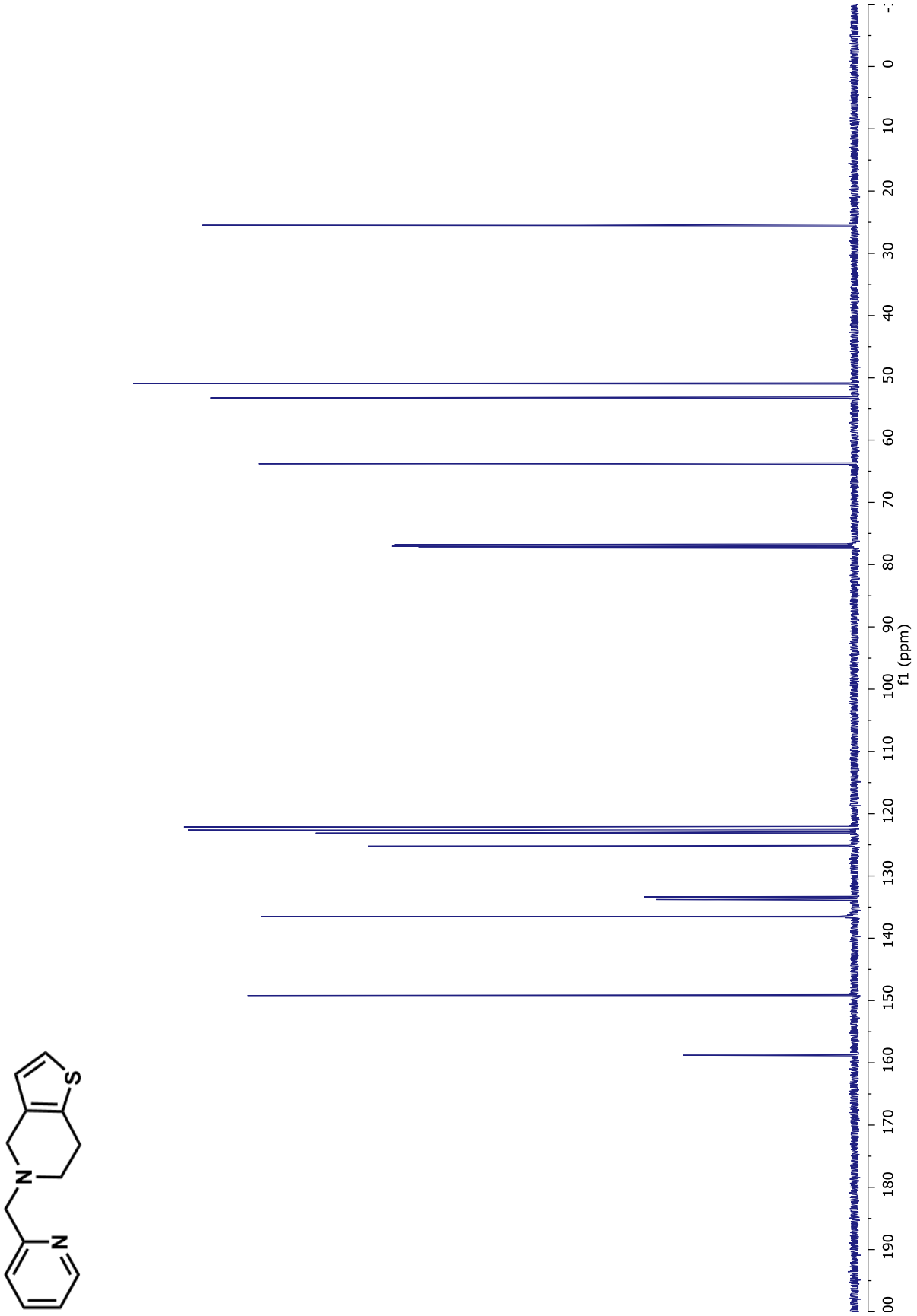
^{1}H NMR (500 MHz, $CDCl_3$) of compound **13c**.



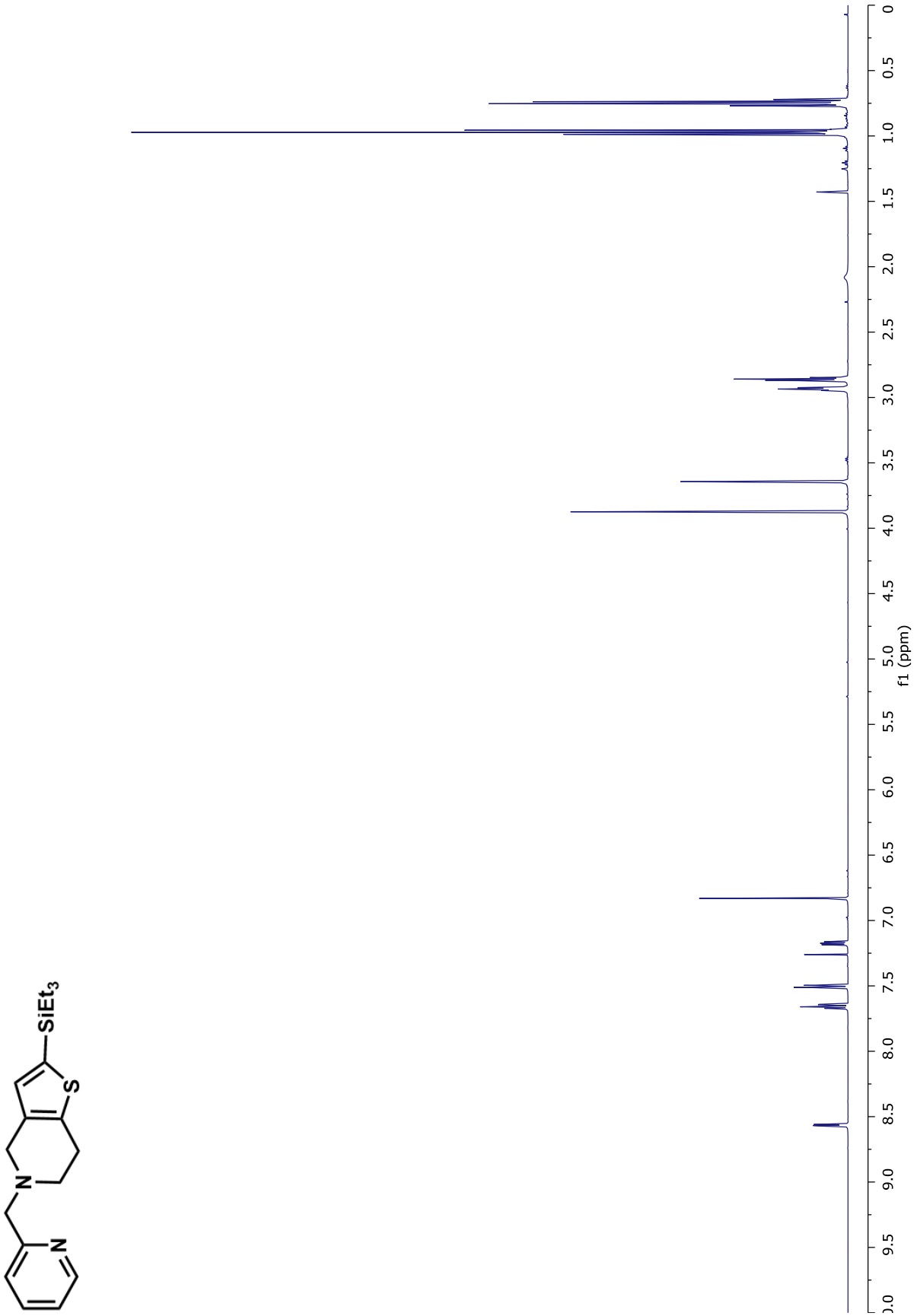
^{13}C NMR (125 MHz, $CDCl_3$) of compound **13c**.



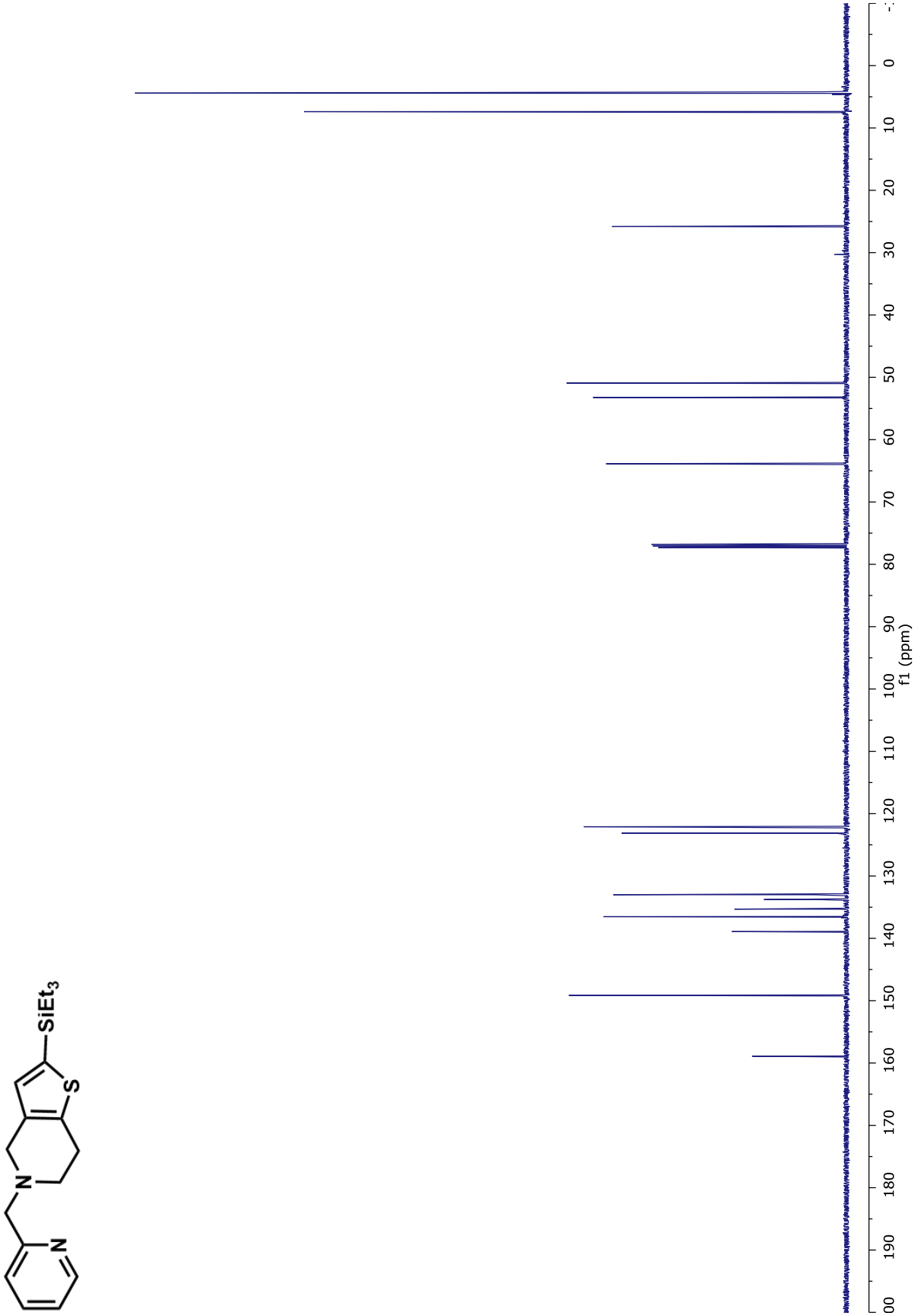
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SM-14**.



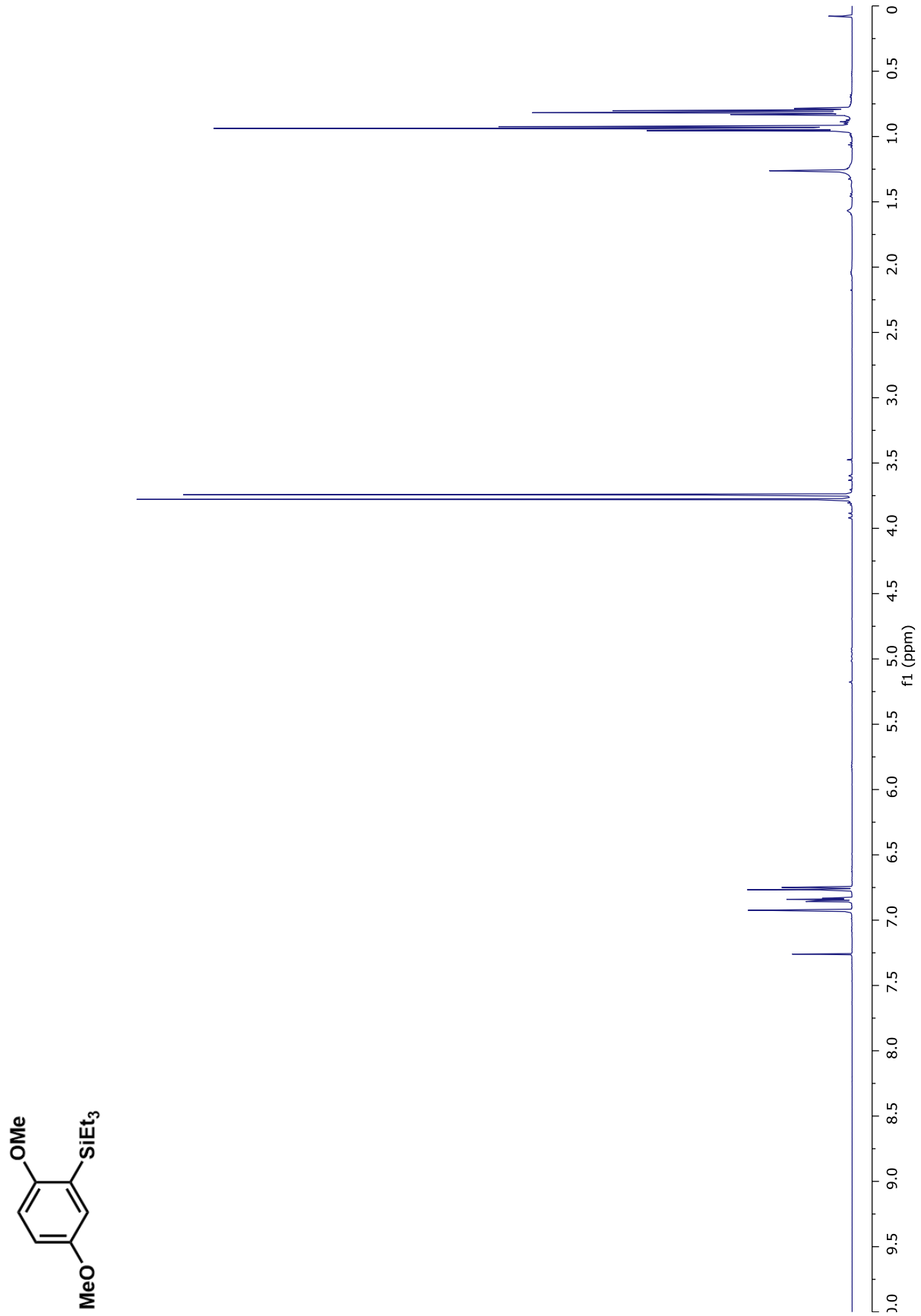
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SM-14.**



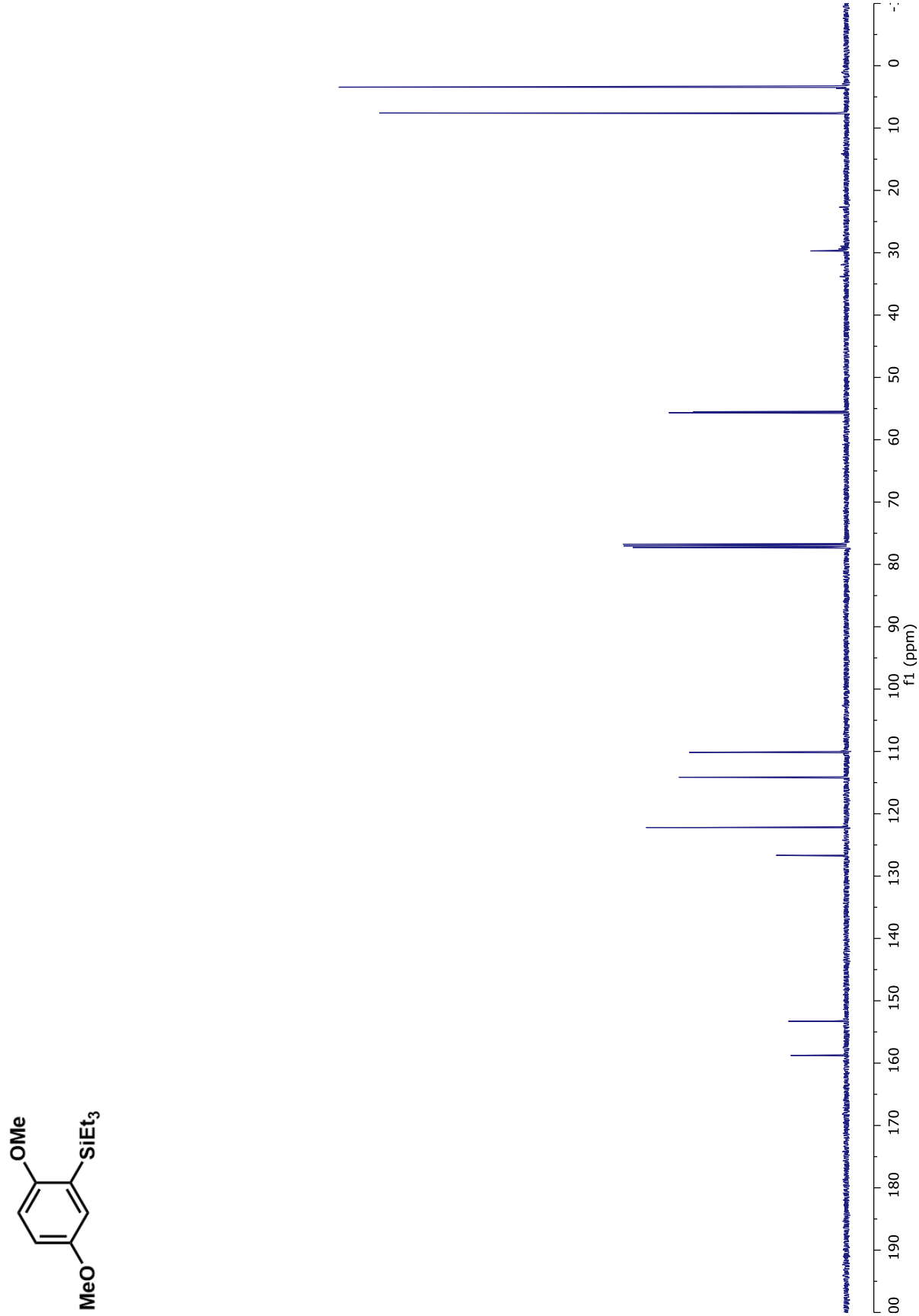
^{1}H NMR (500 MHz, $CDCl_3$) of compound **14**.



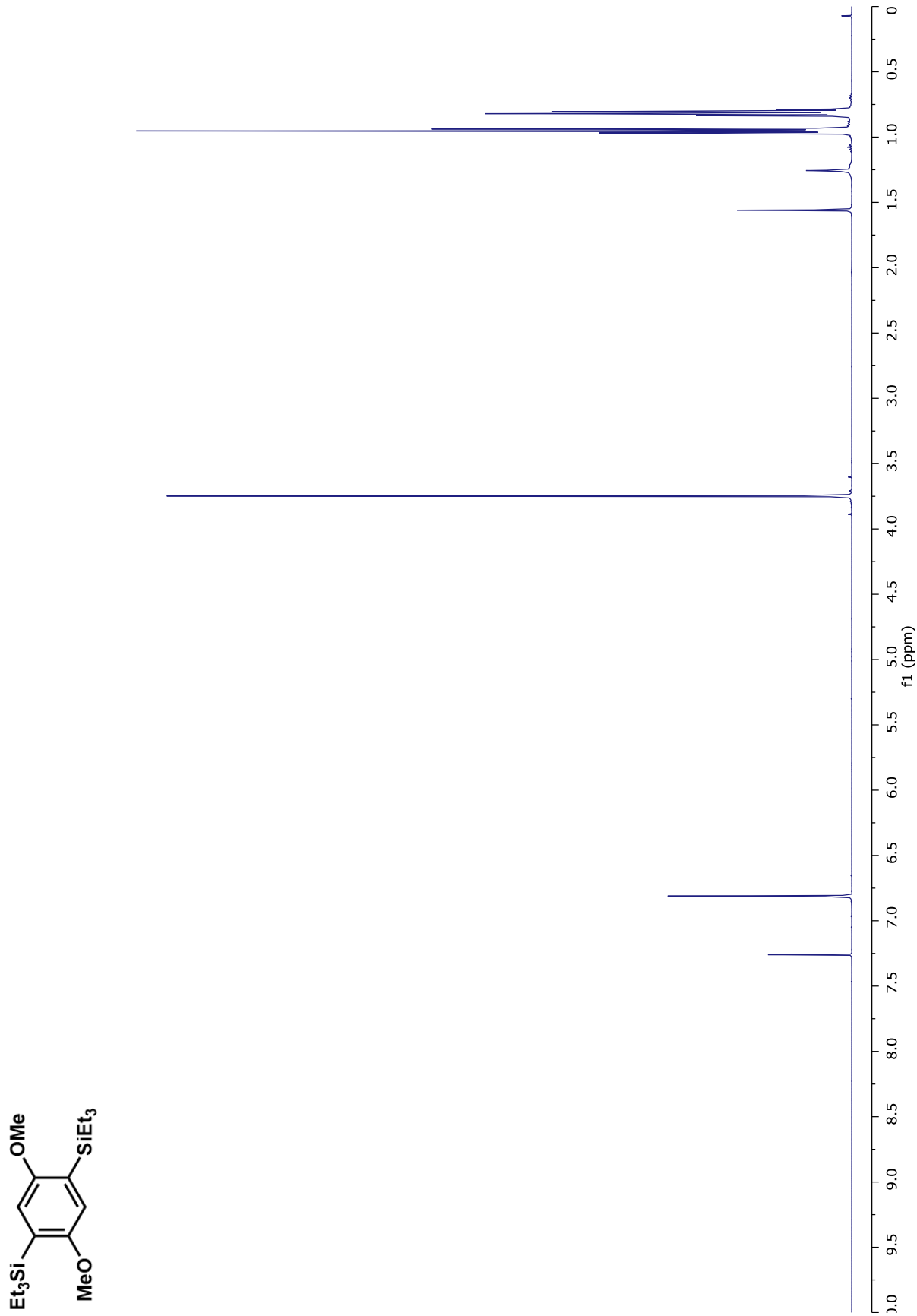
^{13}C NMR (125 MHz, $CDCl_3$) of compound **14**.



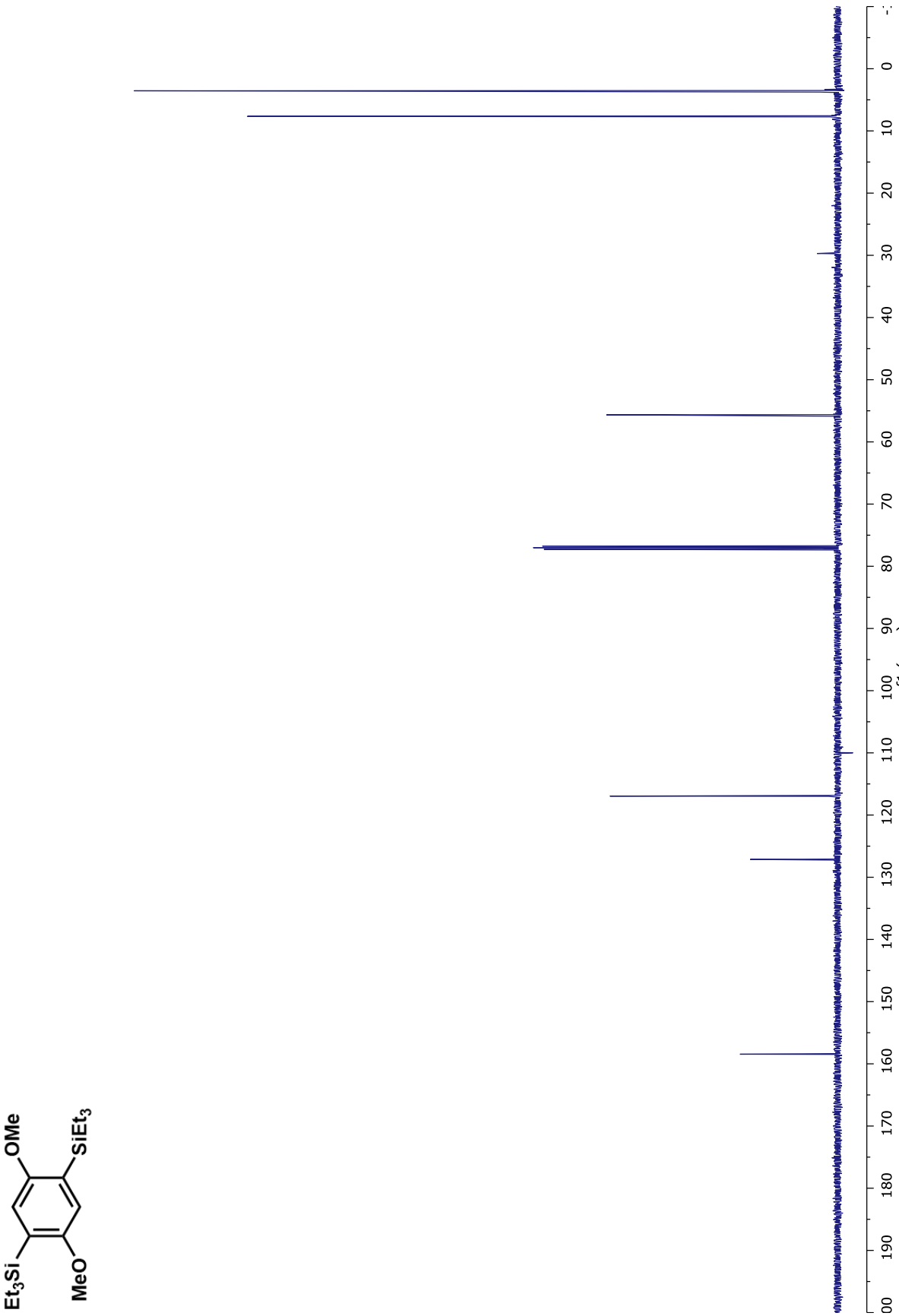
^{1}H NMR (500 MHz, $CDCl_3$) of compound **17c**.



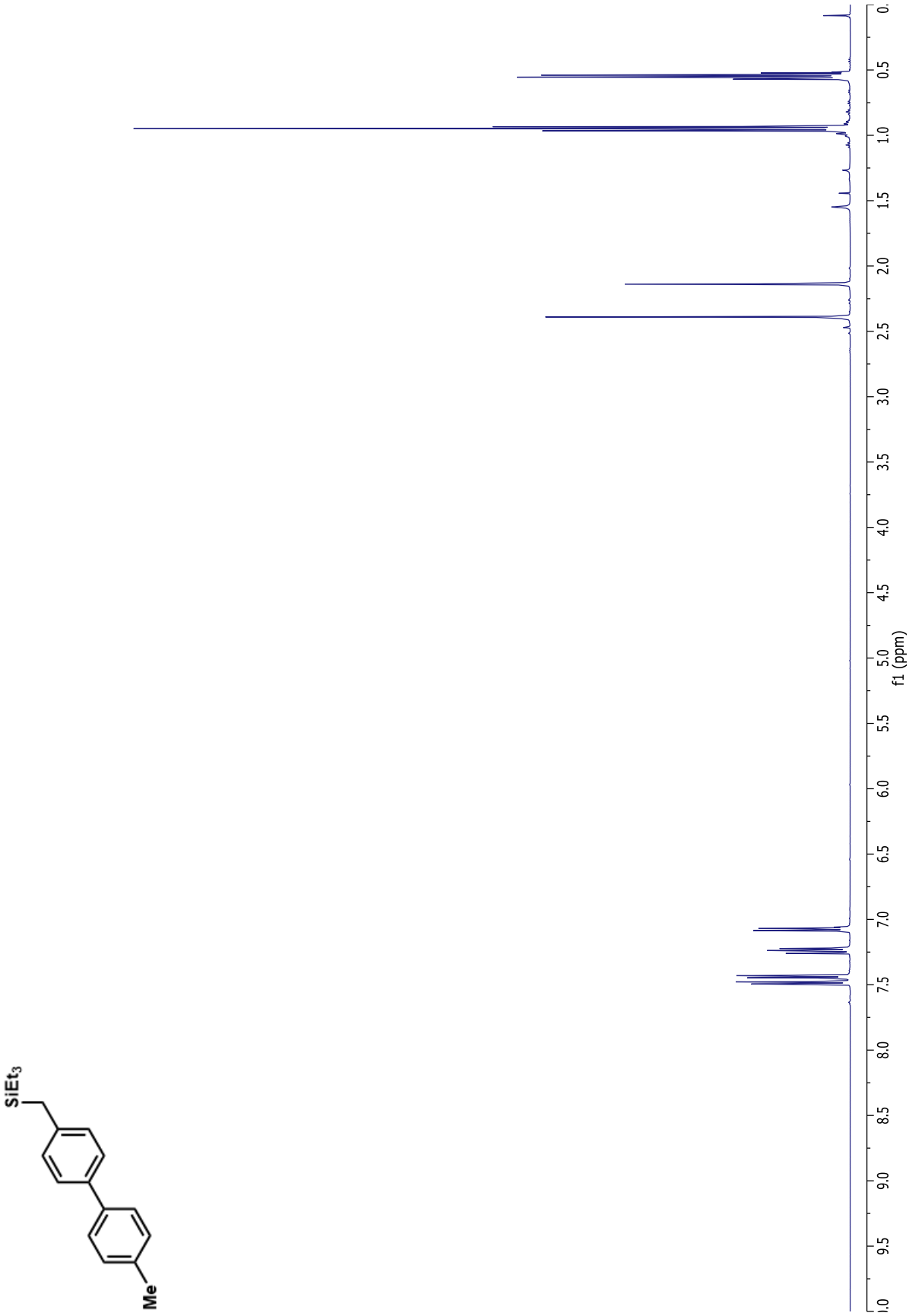
^{13}C NMR (125 MHz, $CDCl_3$) of compound **17c**.



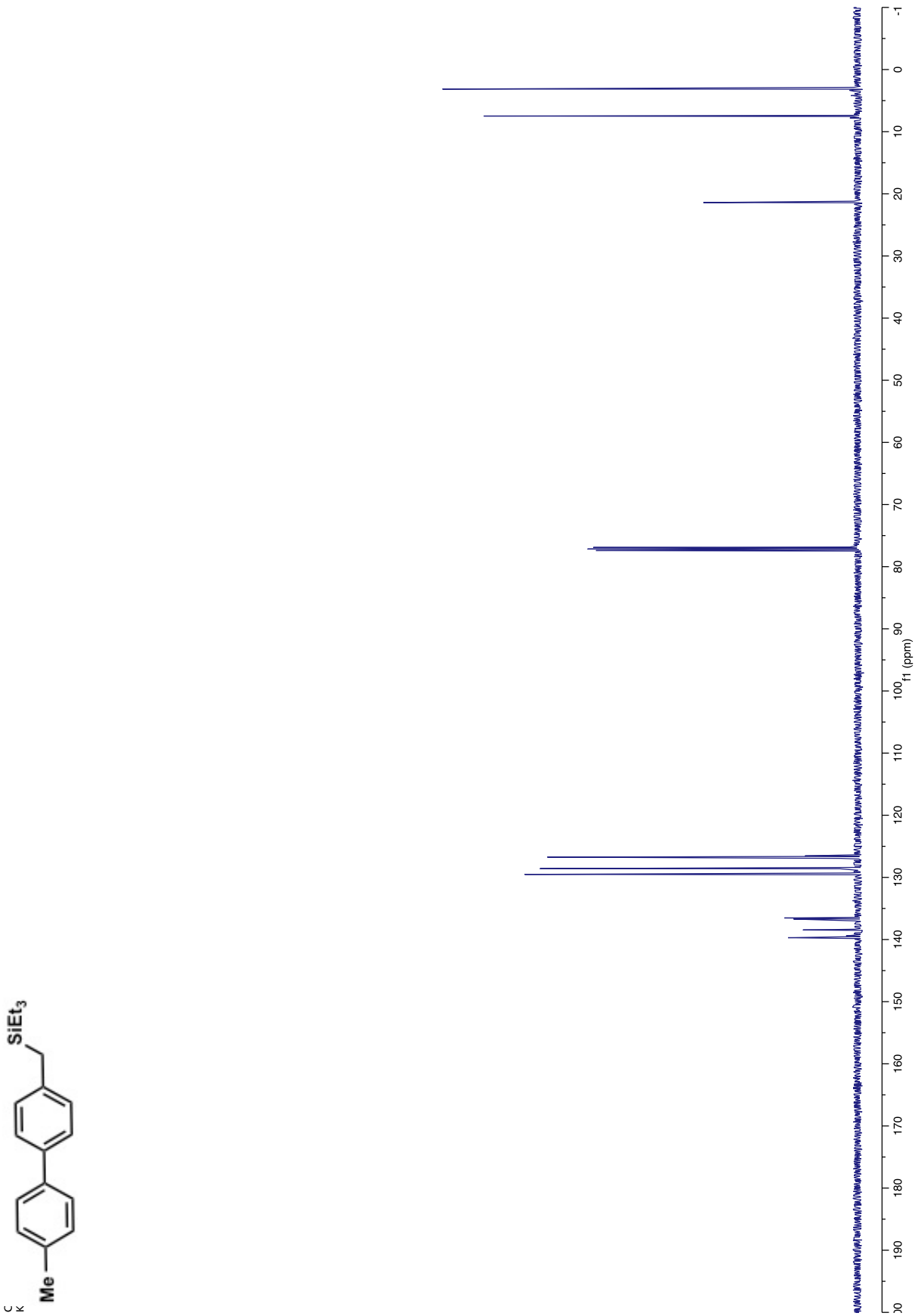
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-17c**.



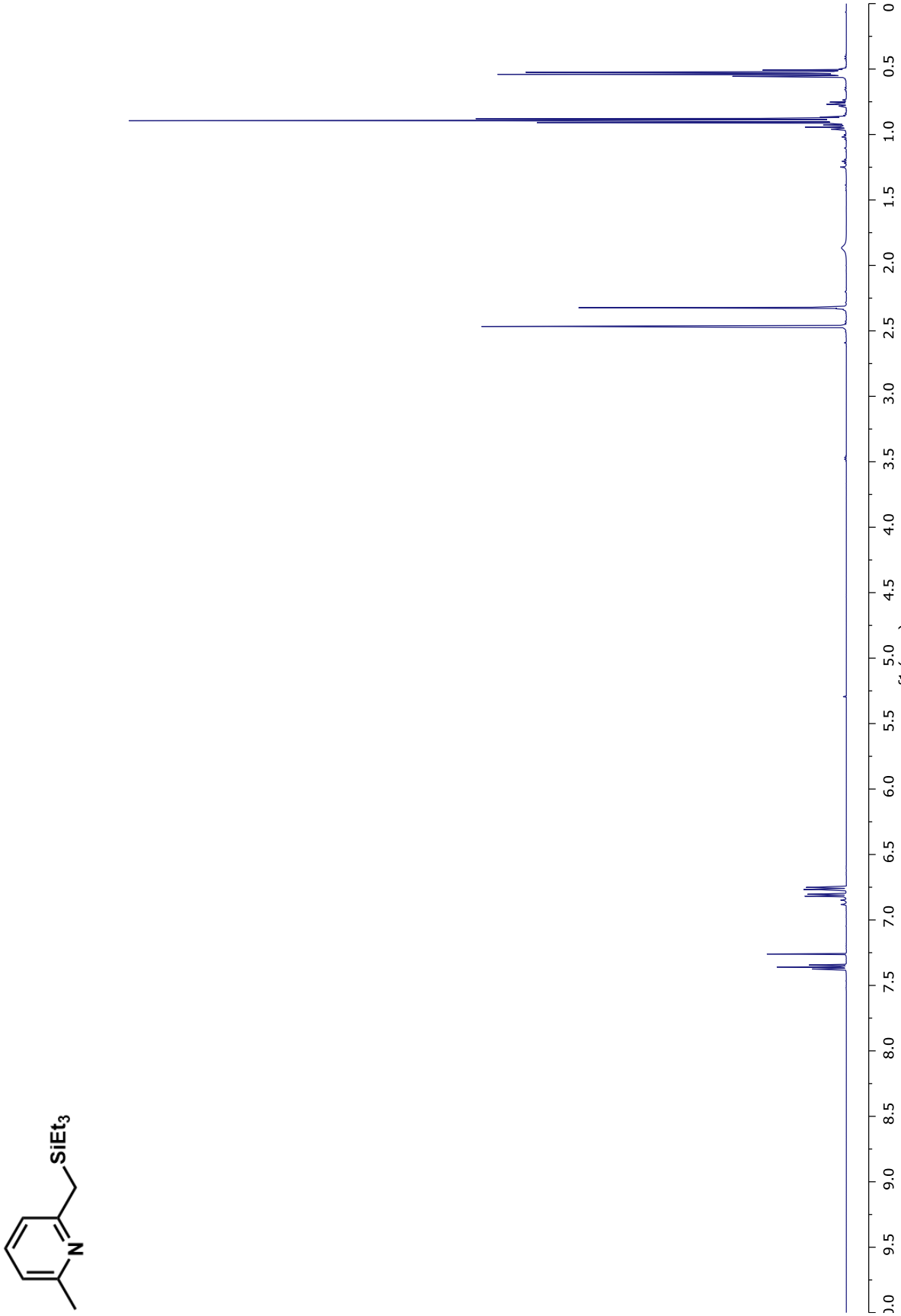
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-17c**.



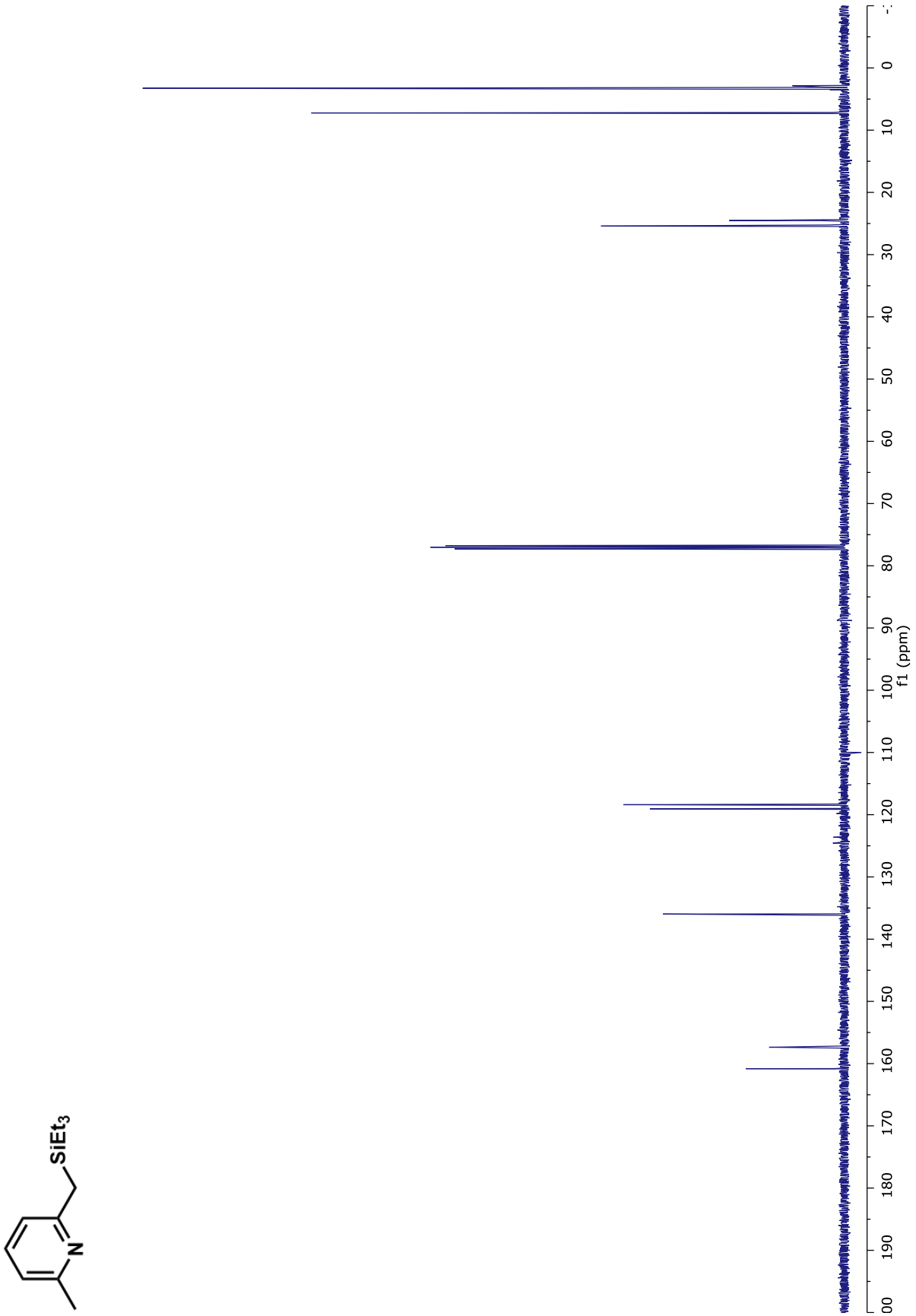
^{1}H NMR (500 MHz, $CDCl_3$) of compound **18b**.



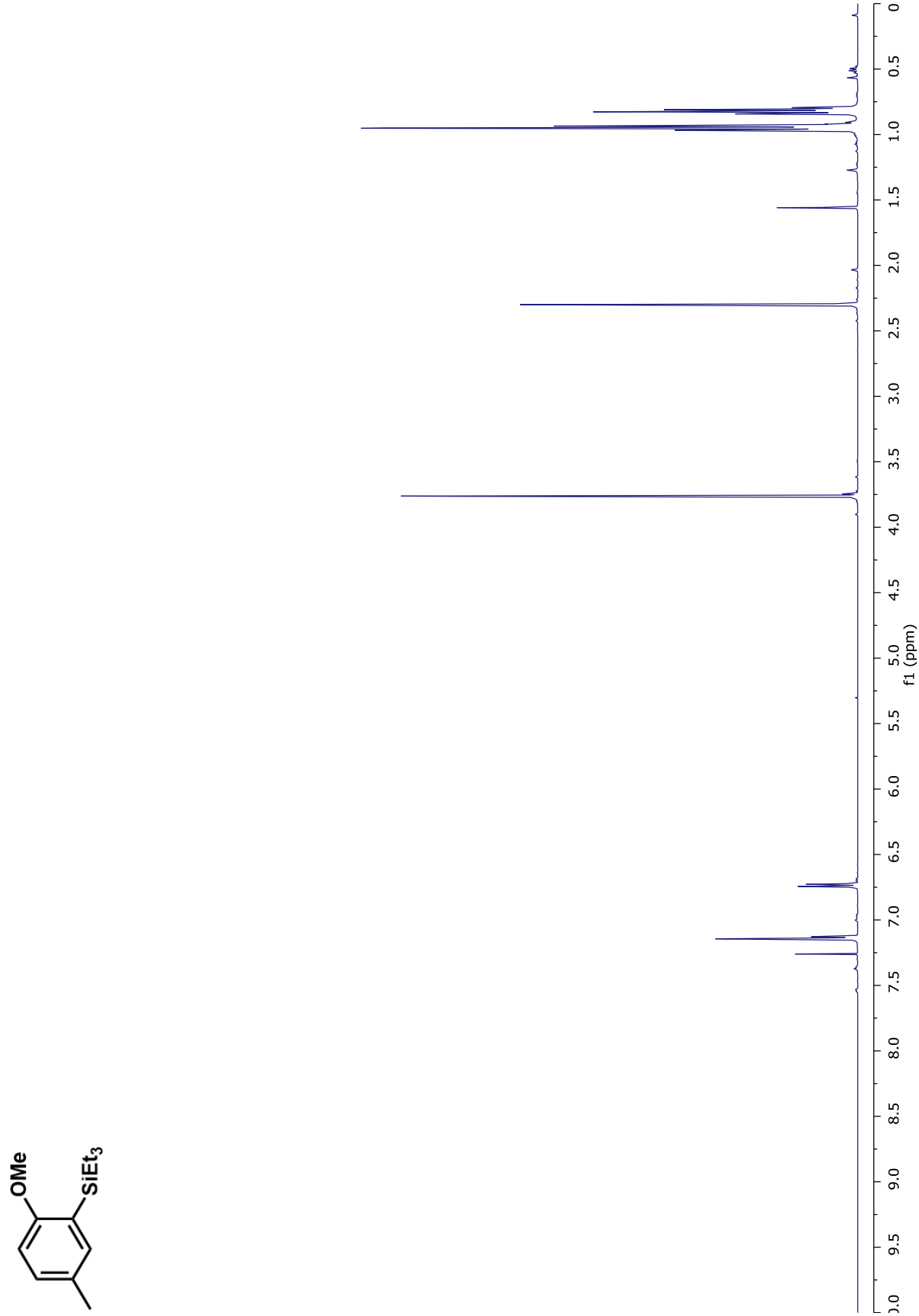
^{13}C NMR (125 MHz, $CDCl_3$) of compound **18b**.



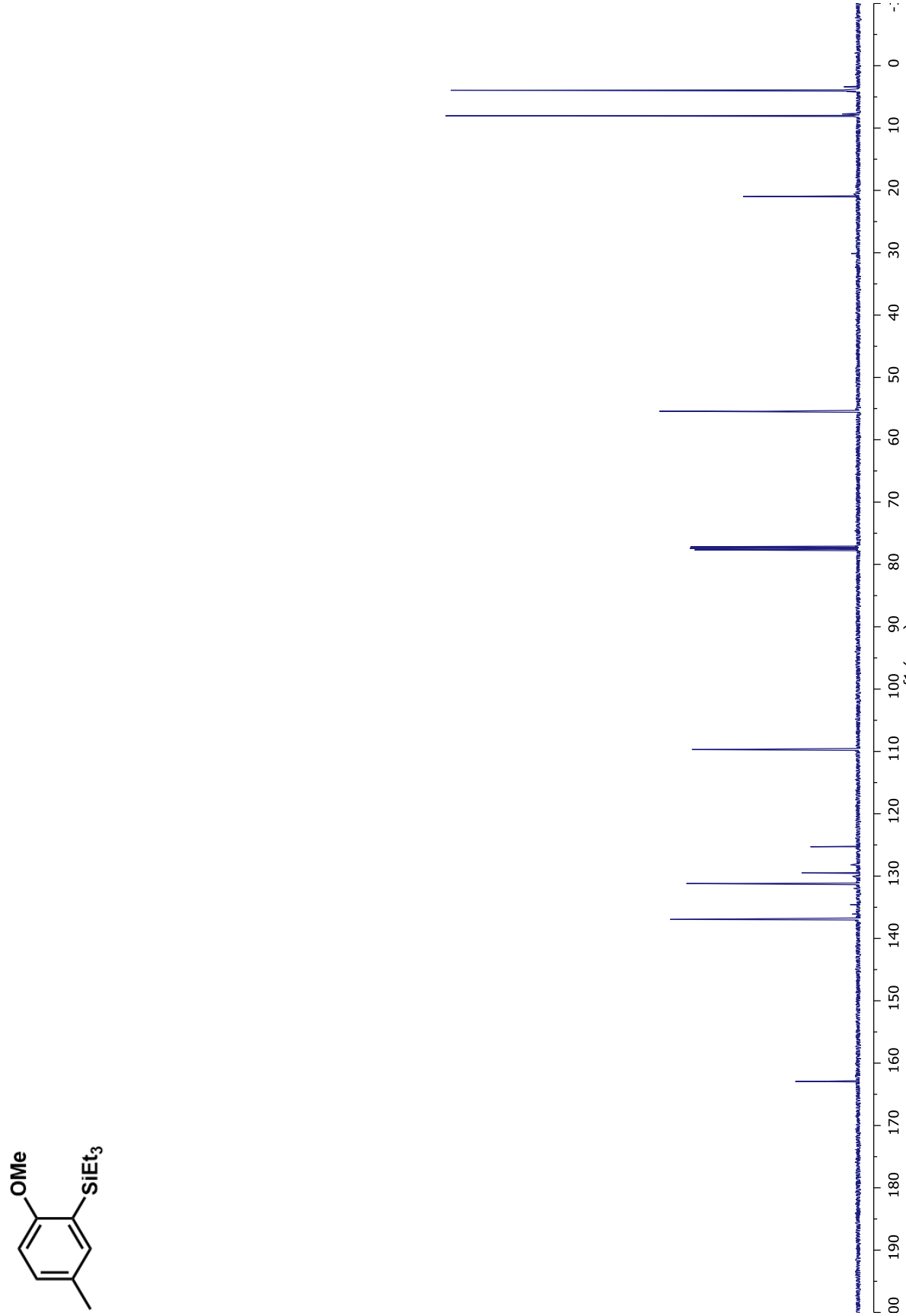
^{1}H NMR (500 MHz, $CDCl_3$) of compound **18c**.



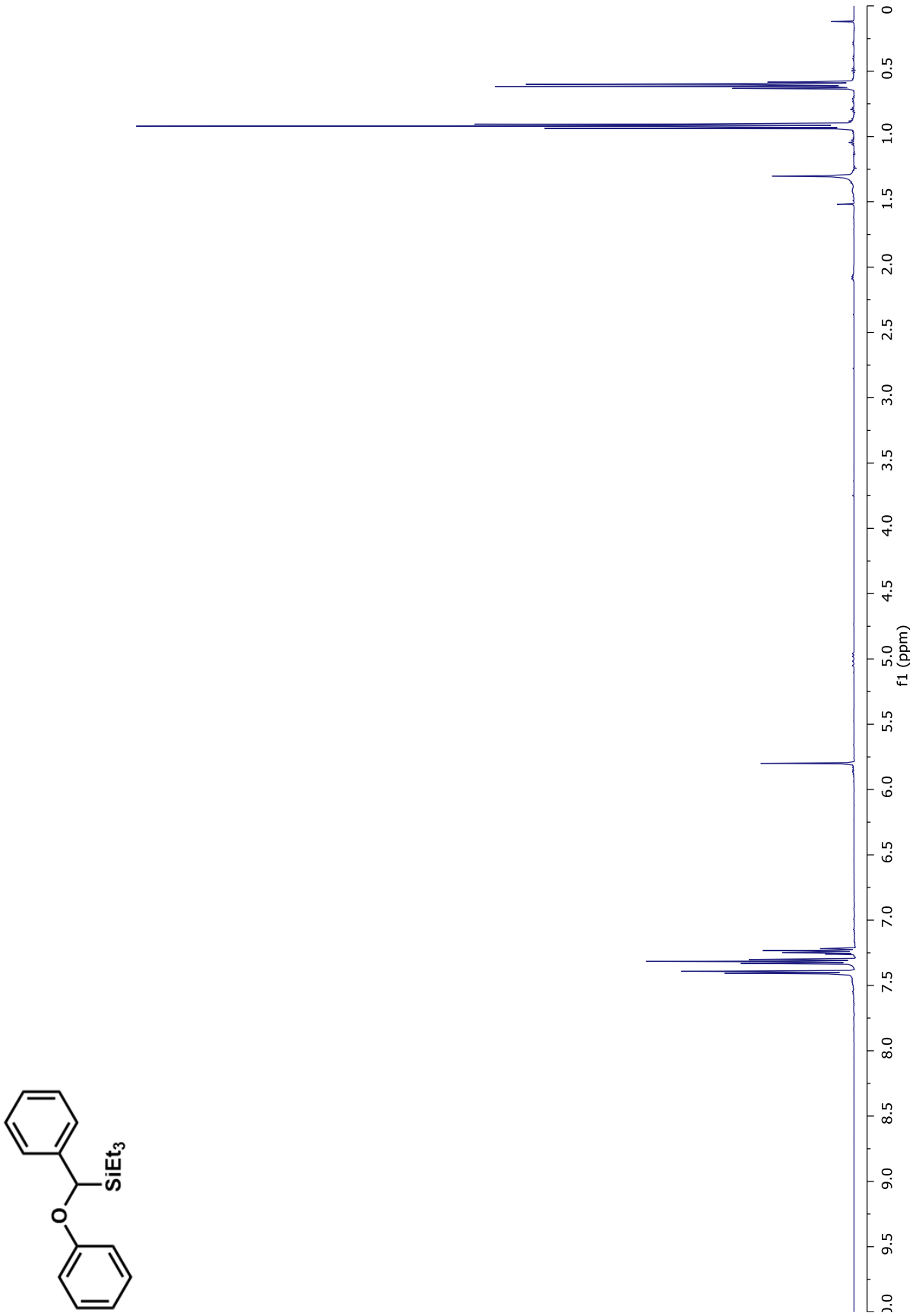
^{13}C NMR (125 MHz, $CDCl_3$) of compound **18c**.



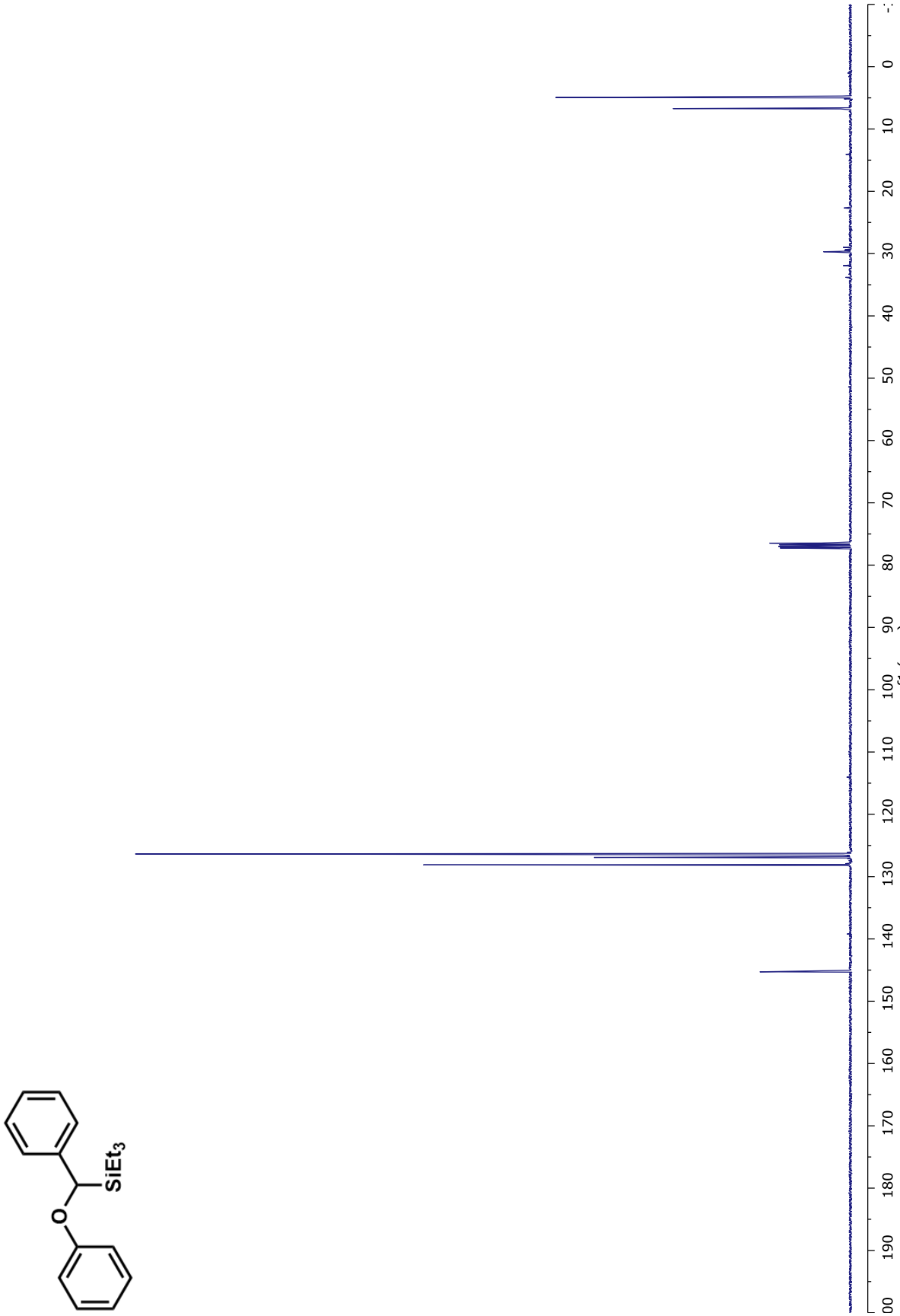
^{1}H NMR (500 MHz, $CDCl_3$) of compound **20**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **20**.



^{1}H NMR (500 MHz, $CDCl_3$) of compound **22**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **22**.