Supporting Information for

Formal Hydrotrimethylsilylation of Styrenes with Anti-Markovnikov Selectivity using Hexamethyldisilane

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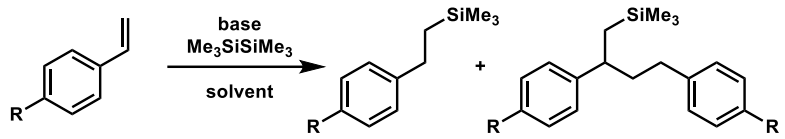
General Information and Materials

Unless otherwise stated, all reactions were carried out with oven-dried glassware under an atmosphere of dry argon using Schlenk manifolds or in a glovebox. Reactions were monitored by thin-layer chromatography (TLC) or gas chromatography mass spectrometry (GC-MS). TLC was performed using Huanghai 8 ± 0.2 μm precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, $KMnO_4$, or phosphomolybdic acid staining. Huanghai silica gel (particle size 200 – 300 mess) was used for silica gel chromatography. ^1H NMR spectra were recorded at room temperature on a Bruker ADVANCE III 400 MHz spectrometer and were reported relative to $CDCl_3$ (δ 7.26 ppm). ^{13}C NMR spectra were recorded on a Bruker ADVANCE III 400 MHz spectrometer and were reported relative to $CDCl_3$ (δ 77.16 ppm). Data for ^1H NMR were reported as chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration) using standard abbreviations for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, and br = broad signal. Data for ^{13}C NMR were reported in terms of chemical shifts (δ ppm). High resolution mass spectra (HRMS) were obtained by use of Thermo Fisher Scientific LTQ FTICR-MS spectrometer or Bruker Compact TOF mass spectrometer in an electron ionization (EI+) mode, an electrospray ionization mode (ESI+) or an atmospheric pressure chemical ionization (APCI+).

Petroleum ester (60 ~ 90 ºC) was used as eluent for silica gel chromatography. Dry solvents were purchased commercially or were dried by passage through an activated alumina column under argon. Deuterated DMSO and reagent grade hexamethyldisilane were distilled over 4Å molecular sieves and were stored under an argon atmosphere. Other reagents were purchased commercially and used without further purification unless otherwise noted.

Table S1. Reaction Condition Optimizations



1a (R = H)
1f (R = OMe)
1j (R = Ph)

2a
2f
2j

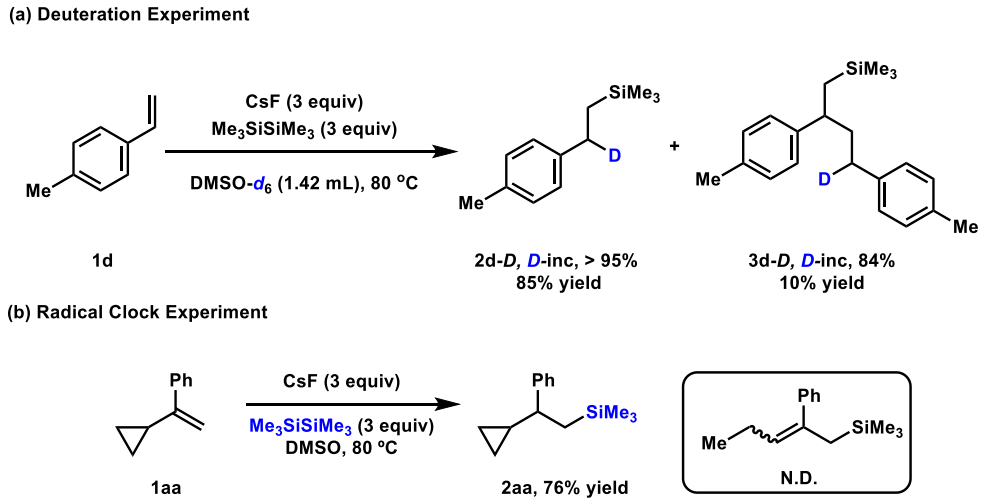
3a
3f
3j

entry[a]	alkene	base	silane	solvent	GC yield of **2** (%)[b]	GC yield of **3** (%)[b]
1	**1a**	LiF	$Me_3SiSiMe_3$	DMSO	NR	
2	**1a**	NaF	$Me_3SiSiMe_3$	DMSO	NR	
3	**1a**	TBAF	$Me_3SiSiMe_3$	DMSO	NR	
4	**1a**	KF	$Me_3SiSiMe_3$	DMSO	<5	<5
5[c]	**1a**	KF	$Me_3SiSiMe_3$	DMSO	45	18
6	**1a**	KOMe	$Me_3SiSiMe_3$	DMSO	31	15
7	**1a**	KOEt	$Me_3SiSiMe_3$	DMSO	42	18
8	**1a**	KOTMS	$Me_3SiSiMe_3$	DMSO	43	18
9	**1a**	KO^{t}Bu	$Me_3SiSiMe_3$	DMSO	16	6
10	**1a**	KHMDS	$Me_3SiSiMe_3$	DMSO	<5	<5
11	**1a**	Cs_2CO_3	$Me_3SiSiMe_3$	DMSO	6	5
12	**1a**	CsF	$Me_3SiSiMe_3$	DMSO	56	34
13[d]	**1a**	CsF	$Me_3SiSiMe_3$	DMSO	68	15
14	**1a**	–	$Me_3SiSiMe_3$	DMSO	NR	
15	**1a**	CsF	$Me_3SiSiMe_3$	DMF	6	5
16	**1a**	CsF	$Me_3SiSiMe_3$	MeCN	NR	
17	**1a**	CsF	$Me_3SiSiMe_3$	THF	NR	
18	**1a**	CsF	$Me_3SiSiMe_3$	toluene	NR	
19	**1a**	CsF	$Me_3SiSiMe_3$	benzene	NR	
20	**1a**	CsF	$Me_3SiSiMe_3$	$MeNO_2$	NR	
21	**1a**	CsF	$Me_3SiSiMe_3$	DMSO (1.0 mol/L)	30	27
22	**1a**	CsF	$Me_3SiSiMe_3$	DMSO (0.2 mol/L)	62	24
23	**1a**	CsF	$Me_3SiSiMe_3$	DMSO (0.13 mol/L)	69	20
24	**1a**	CsF	$Me_3SiSiMe_3$	DMSO (0.1 mol/L)	60	18
25	**1a**	CsF	$Me_3SiSiMe_3$	DMSO (0.08 mol/L)	58	14
26	**1a**	CsF (1 equiv)	$Me_3SiSiMe_3$ (1 equiv)	DMSO (0.13 mol/L)	51	21

27	**1a**	**CsF (3 equiv)**	**$Me_3SiSiMe_3$ (3 equiv)**	**DMSO (0.13 mol/L)**	**79 (72)[e]**	**21**
28	**1a**	CsF (4 equiv)	$Me_3SiSiMe_3$ (4 equiv)	DMSO (0.13 mol/L)	66	18
29[f]	**1f**	CsF (3 equiv)	$Me_3SiSiMe_3$ (3 equiv)	DMSO (2.8 mol/L)	75[g]	-
30[f]	**1f**	**CsF (3 equiv)**	**$Me_3SiSiMe_3$ (3 equiv)**	**DMSO (0.7 mol/L)**	**100[g]**	-
31[f]	**1f**	CsF (4 equiv)	$Me_3SiSiMe_3$ (4 equiv)	DMSO (0.35 mol/L)	65[g]	-
32	**1j**	CsF (3 equiv)	$Me_3SiSiMe_3$ (3 equiv)	DMSO (0.13 mol/L)	26[e]	
33[h]	**1j**	**CsF (3 equiv)**	**$Me_3SiSiMe_3$ (3 equiv)**	**DMSO (0.07 mol/L)**	**56[e]**	-

[a]Reactions were conducted with 0.2 mmol of **1a**, 0.4 mmol of base, and 0.4 mmol of $Me_3SiSiMe_3$ in 0.5 mL of DMSO for 12 h at room temperature. [b]Yield was determined by GC using biphenyl as an internal standard. [c]2 equiv of 18-crown-6 was added and the isolated yields were presented. [d]with CsF (20 mol%). [e]Isolated yield. [f]With **1f** at 80 °C. [g]NMR yield. [h]With **1j** (0.1 M) in DMSO added in 2 h using a syringe pump, rt. NR = no reaction.

Preliminary Mechanistic Investigations



Deuteration Experiment: Under an argon atmosphere, CsF (455.5 mg, 3.0 mmol) was added to a dry Schlenk tube equipped with a magnetic stirring bar. Then, DMSO-d_6 (20 equiv, 1.42 mL), **1d** (118.2 mg, 1.0 mmol), and $Me_3SiSiMe_3$ (0.60 mL, 3.0 mmol) were added. The mixture was heated to 80 °C with a heating mantle and stirred for 12 h, then diluted with water (3 mL). The aqueous phase was extracted with EA (3 mL × 3) and the combined organic layers were washed with water (10 mL × 2) and brine, and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure. The desired product **2d-*D*** (119.3 mg, 85% yield, colorless

oil) and the side product **3d-*D*** (15.4 mg, 10%, colorless oil) were obtained after purification by silica gel chromatography.

Radical Clock Experiment: Under an argon atmosphere, CsF (227.0 mg, 3.0 mmol) was added to a dry Schlenk tube equipped with a magnetic stirring bar. Then, DMSO (0.70 mL), **1aa** (72.0 mg, 0.5 mmol), and $Me_3SiSiMe_3$ (0.30 mL, 3.0 mmol) were added. The mixture was heated to 80 °C with a heating mantle and stirred for 12 h, then diluted with water (3 mL). The aqueous phase was extracted with EA (3 mL × 3) and the combined organic layers were washed with water (10 mL × 2) and brine, and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure. The desired product **2aa** (82.8 mg, 76% yield) was obtained as a colorless oil after purification by silica gel chromatography. No ring-opening product was detected.

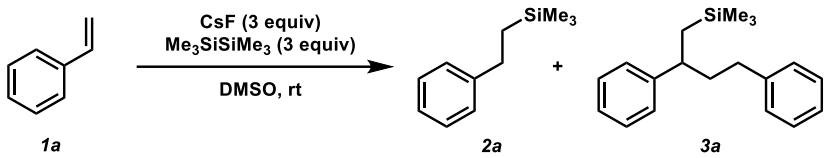
General Procedure and Spectroscopic Data for Hydrosilylation of Styrenes

General procedure A: Under an argon atmosphere, CsF (91.1 mg, 0.6 mmol) was added to a dry Schlenk tube equipped with a magnetic stirring bar. Then, DMSO (1.5 mL), substrate (0.2 mmol), and $Me_3SiSiMe_3$ (120 μL, 0.6 mmol) were added. After stirred at 25 °C for the indicated time, the mixture was diluted with water (3 mL). The mixture was separated and the aqueous phase was extracted with EA (3 mL × 3). The combined organic layers were washed with water (10 mL × 2) and brine, and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the desired product was purified by silica gel chromatography.

General procedure B: Under an argon atmosphere, CsF (91.1 mg, 0.6 mmol) was added to a dry Schlenk tube equipped with a magnetic stirring bar. Then, DMSO (20 equiv, 284 μL), substrate (0.2 mmol), and $Me_3SiSiMe_3$ (120 μL, 0.6 mmol) were added. The mixture was heated to 80 °C with a heating mantle and stirred for indicated time, then diluted with water (3 mL). The mixture was separated and the aqueous phase was extracted with EA (3 mL × 3). The combined organic layers were washed with water (10 mL × 2) and brine, and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the desired product was purified by silica gel chromatography.

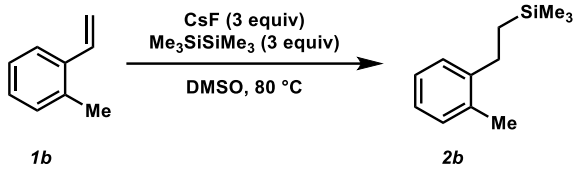
General procedure C: Under an argon atmosphere, CsF (91.1 mg, 0.6 mmol), $Me_3SiSiMe_3$ (120 μL, 0.6 mmol), and DMSO (1.0 mL) were added to a dry Schlenk tube equipped with a magnetic stirring bar. Then, a solution of substrate in DMSO (2.0 mL) was added to the mixture using a syringe pump in 2 h. After stirred at 25 °C for 2 h, the mixture was diluted with water (6 mL). The mixture was separated and the aqueous phase was extracted with EA (5 mL × 3). The combined organic layers were washed with water (10 mL × 2) and brine,

and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the desired product was purified by silica gel chromatography.

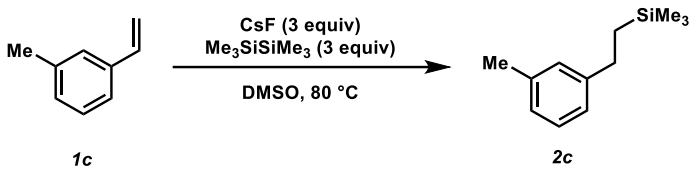


Trimethyl(phenethyl)silane (2a): The general procedure A was followed. The reaction was performed with stryene **1a** (104.2 mg, 1.0 mmol), CsF (455.7 mg, 3.0 mmol), and $Me_3SiSiMe_3$ (600 μL, 3.0 mmol) in DMSO (7.5 mL). The desired product **2a** (128.0 mg, 72% yield) as a colorless oil and side product **3a** (19.8 mg, 7%) as a colorless oil were obtained after purification by silica gel chromatography (PE). For **2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.07 (m, 5H), 2.70 – 2.58 (m, 2H), 0.92 – 0.82 (m, 2H), 0.02 (s, 9H). The spectroscopic data were consistent with those reported in the literature.[1]

For **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.06 (m, 10H), 2.71– 2.67 (m, 1H), 2.50 – 2.31 (m, 2H), 2.03 – 1.86 (m, 2H), 1.04 – 0.88 (m, 2H), -0.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 142.8, 128.51, 128.45, 128.4, 127.7, 126.1, 125.7, 42.7, 41.9, 34.1, 25.6, -1.0. HRMS (APCI+): calc'd for $C_{19}H_{27}Si$ $[M+H]^+$: 283.1877, found: 283.1869.

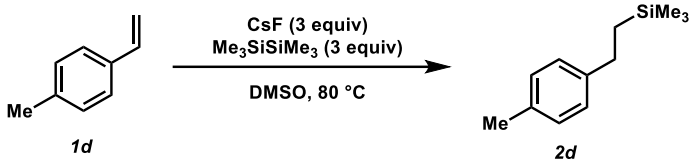


Trimethyl(2-methylphenethyl)silane (2b): The general procedure B was followed. The reaction was performed with **1b** (118.0 mg, 1.0 mmol), CsF (455.7 mg, 3.0 mmol), and $Me_3SiSiMe_3$ (600 μL, 3.0 mmol) in DMSO (1.5 mL). The desired product **2b** (155.6 mg, 81% yield) was obtained as a colorless oil after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.03 (m, 4H), 2.64 – 2.50 (m, 2H), 2.30 (s, 3H), 0.87 – 0.72 (m, 2H), 0.05 (s, 9H). The spectroscopic data were consistent with those reported in the literature.[2]



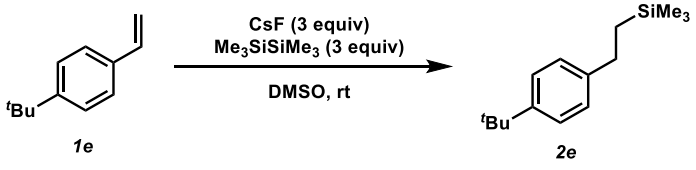
1c *2c*

Trimethyl(3-methylphenethyl)silane (2c): The general procedure B was followed. The reaction was performed with **1c** (118.0 mg, 1.0 mmol), CsF (455.7 mg, 3.0 mmol), and $Me_3SiSiMe_3$ (600 μL, 3.0 mmol) in DMSO (1.5 mL). The desired product **2c** (153.3 mg, 80% yield) was obtained as a colorless oil after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.5 Hz, 1H), 7.07 – 6.95 (m, 3H), 2.64 – 2.52 (m, 2H), 2.33 (s, 3H), 0.94 – 0.80 (m, 2H), 0.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 137.9, 128.7, 128.3, 126.3, 124.9, 30.1, 21.6, 18.9, -1.6. HRMS (EI): calc'd for $C_{12}H_{20}Si$ $[M]^{+\bullet}$: 192.1329, found: 192.1330.



1d *2d*

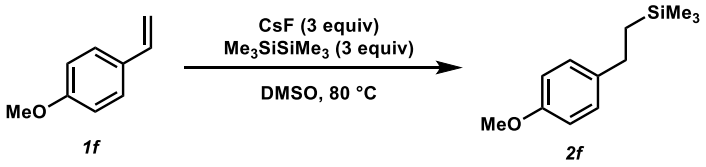
Trimethyl(4-methylphenethyl)silane (2d): The general procedure B was followed. The reaction was performed with **1d** (23.6 mg, 0.2 mmol), CsF (91.2 mg, 0.6 mmol), and $Me_3SiSiMe_3$ (120 μL, 0.6 mmol) in DMSO (0.3 mL). The desired product **2d** (36.8 mg, 96% yield) was obtained as a colorless oil after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (m, 4H), 2.83 – 2.48 (m, 2H), 2.32 (s, 3H), 0.86 (m, 2H), 0.02 (s, 9H). The spectroscopic data were consistent with those reported in the literature.[3]



1e *2e*

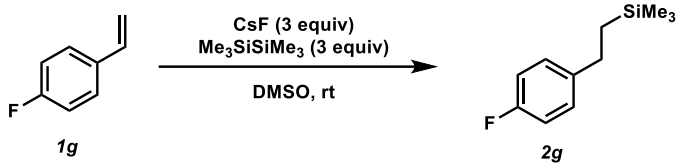
(4-(Tert-butyl)phenethyl)trimethylsilane (2e): The general procedure A was followed. The reaction was performed with **1e** (160.1 mg, 1.0 mmol), CsF (455.7 mg, 3.0 mmol), and $Me_3SiSiMe_3$ (600 μL, 3.0 mmol) in DMSO (7.5 mL). The desired product **2e** (196.9 mg, 84% yield) was obtained as a colorless oil after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.83 – 2.47 (m, 2H), 1.32 (s, 9H), 1.01 – 0.76 (m, 2H), 0.03 (s, 9H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 148.4, 142.4, 127.5, 125.3, 34.5, 31.6, 29.5, 18.7, -1.6. HRMS (EI): calc'd for $C_{15}H_{26}Si$ $[M]^{+\bullet}$: 234.1798, found: 234.1795.



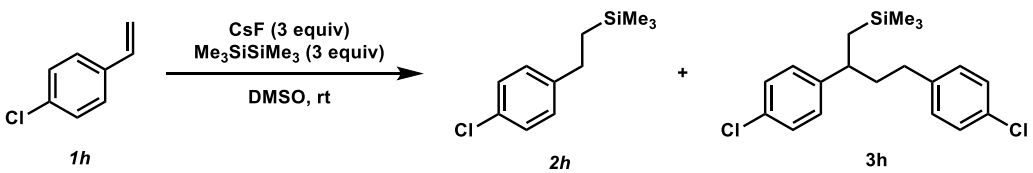
1f *2f*

(4-Methoxyphenethyl)trimethylsilane (2f): The general procedure B was followed. The reaction was performed with **1f** (26.8 mg, 0.2 mmol), CsF (91.2 mg, 0.6 mmol), and $Me_3SiSiMe_3$ (120 μL, 0.6 mmol) in DMSO (0.3 mL). The desired product **2f** (25.0 mg, 60% yield) was obtained as a yellow oil after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 2.69 – 2.49 (m, 2H), 0.99 – 0.73 (m, 2H), 0.00 (s, 9H). The spectroscopic data were consistent with those reported in the literature.[4]



1g *2g*

(4-Fluorophenethyl)trimethylsilane (2g): The general procedure A was followed. The reaction was performed with **1g** (122.1 mg, 1.0 mmol), CsF (455.7 mg, 3.0 mmol), and $Me_3SiSiMe_3$ (600 μL, 3.0 mmol) in DMSO (7.5 mL). The desired product **2g** (84.1 mg, 43% yield) was obtained as a yellow oil after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.11 (m, 2H), 7.01 – 6.91 (m, 2H), 2.66 – 2.53 (m, 2H), 0.94 – 0.80 (m, 2H), 0.01 (s, 9H). The spectroscopic data were consistent with those reported in the literature.[5]

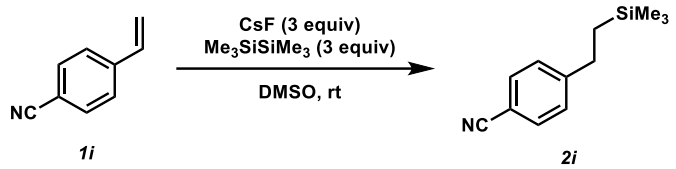


1h *2h* 3h

(4-Chlorophenethyl)trimethylsilane (2h): The general procedure C was followed. The reaction was performed with **1h** (134.0 mg, 1.0 mmol), CsF (455.7 mg, 3.0 mmol), and $Me_3SiSiMe_3$ (600 μL, 3.0 mmol) in DMSO (7.0 mL). The desired product **2h** (95.4 mg, 45% yield) as a colorless oil and side product **3h** (47.2

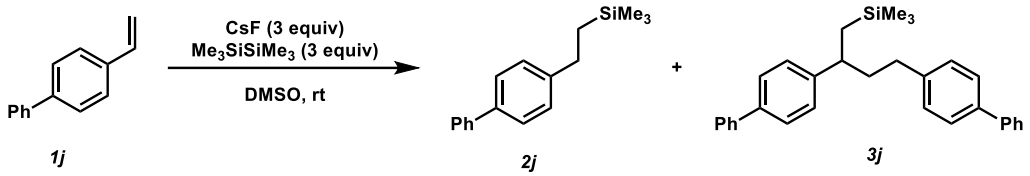
mg, 13%) as a yellow oil were obtained after purification by silica gel chromatography (PE). For **2h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 7.14 – 7.12 (m, 2H), 2.61 – 2.58 (m, 2H), 1.01 – 0.70 (m, 2H), 0.01 (s, 9H). The spectroscopic data were consistent with those reported in the literature.[5]

For **3h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 2.64 – 2.62 (m, 1H), 2.38 – 2.33 (m, 2H), 1.98 – 1.73 (m, 2H), 0.94 – 0.90 (m, 2H), -0.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 140.8, 131.8, 131.5, 129.8, 129.0, 128.6, 128.5, 42.5, 41.2, 33.3, 25.5, -0.9. HRMS (EI): calc'd for $C_{19}H_{24}Cl_2Si$ $[M]^{+\bullet}$: 350.1019, found: 350.1028.



1i *2i*

4-(2-(Trimethylsilyl)ethyl)benzonitrile (2i): The general procedure C was followed. The reaction was performed with **1i** (25.8 mg, 0.2 mmol), CsF (91.6 mg, 0.6 mmol), and $Me_3SiSiMe_3$ (120 μL, 0.6 mmol) in DMSO (3.0 mL). The desired product **2i** (26.4 mg, 65% yield) was obtained as a yellow oil after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 2.87 – 2.57 (m, 2H), 1.18 – 0.68 (m, 2H), 0.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 132.3, 128.8, 119.4, 109.5, 30.6, 18.5, -1.7. HRMS (APCI+): calc'd for $C_{12}H_{18}NSi$ $[M+H]^+$: 204.1203, found: 204.1203.

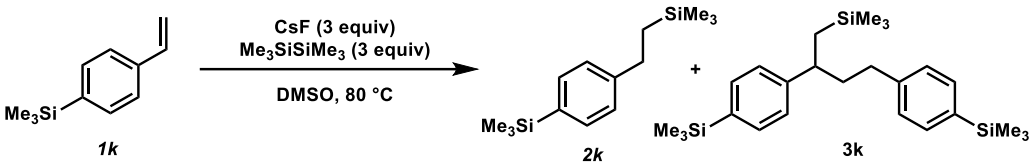


1j *2j* *3j*

(2-([1,1'-Biphenyl]-4-yl)ethyl)trimethylsilane (2j): The general procedure C was followed. The reaction was performed with **1i** (36.0 mg, 0.2 mmol), CsF (91.6 mg, 0.6 mmol), and $Me_3SiSiMe_3$ (120 μL, 0.6 mmol) in DMSO (3.0 mL). The desired product **2j** (28.4 mg, 56% yield) as a colorless oil and side product **3j** (9.6 mg, 22%) as a yellow oil were obtained after purification by silica gel chromatography (PE). For **2j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.34– 7.31 (m, 3H), 2.96 – 2.45 (m, 2H), 1.10 – 0.74 (m, 2H), 0.04 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 141.3, 138.6,

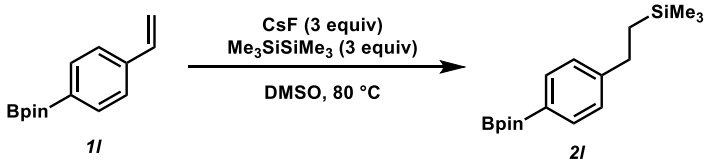
128.8, 128.3, 127.2, 127.12, 127.06, 29.8, 18.9, -1.6. HRMS (EI): calc'd for $C_{17}H_{22}Si$ $[M]^{+\bullet}$: 254.1485, found: 254.1489.

For **3j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.3 Hz, 2H), 7.57 (d, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 7.3 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.30 – 7.23 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.79 – 2.71 (m, 1H), 2.57 – 2.42 (m, 2H), 2.11 – 1.89 (m, 2H), 1.15 – 0.95 (m, 2H), -0.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 141.9, 141.3, 141.2, 138.9, 138.7, 128.93, 128.85, 128.1, 127.12, 127.08, 42.6, 41.6, 33.8, 25.6, -0.9. HRMS (ESI+): calc'd for $C_{31}H_{35}Si$ $[M+H]^{+}$: 435.2503, found: 435.2502.

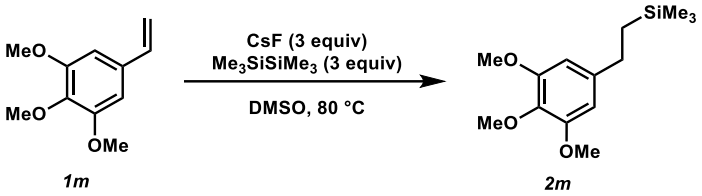


Trimethyl(4-(2-(trimethylsilyl)ethyl)phenyl)silane (2k): The general procedure B was followed. The reaction was performed with **1k** (36.5 mg, 0.2 mmol), CsF (91.2 mg, 0.6 mmol), and $Me_3SiSiMe_3$ (120 μL, 0.6 mmol) in DMSO (0.3 mL). The desired product **2k** (23.5 mg, 47% yield) as a colorless oil and side product **3k** (8.5 mg, 10% yield) as a colorless oil were obtained after purification by silica gel chromatography (PE). For **2k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.65 – 2.55 (m, 2H), 0.92 – 0.80 (m, 2H), 0.25 (s, 9H), 0.02 (s, 9H). The spectroscopic data were consistent with those reported in the literature.[5]

For **3k**: ^{1}H NMR (400 MHz, CDCl3) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 2.76 – 2.63 (m, 1H), 2.49 – 2.28 (m, 2H), 2.00 – 1.84 (m, 2H), 0.99 – 0.91 (m, 2H), 0.26 (s, 9H), 0.24 (s, 9H), -0.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 143.5, 137.8, 137.2, 133.47, 133.45, 128.0, 127.1, 42.2, 42.0, 34.1, 25.6, -0.87, -0.92. HRMS (EI): calc'd for $C_{25}H_{42}Si_3$ $[M]^{+\bullet}$: 426.2589, found: 426.2599.

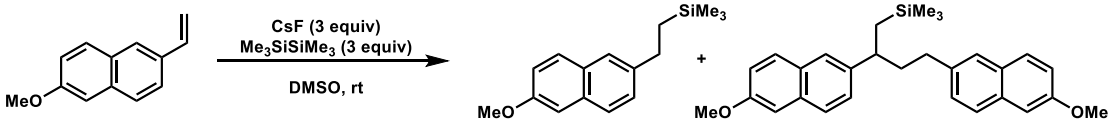


Trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenethyl)silane (2l): The general procedure B was followed. The reaction was performed with **1l** (230.0 mg, 1.0 mmol), CsF (455.0 mg, 3.0 mmol), and $Me_3SiSiMe_3$ (600 μL, 3.0 mmol) in DMSO (1.5 mL). A mixture of **2l** and **1l** (189.0 mg, **2l**:**1l** = 4:3 was determined by ^{1}H NMR) were obtained after purification by silica gel chromatography (PE). For **2l** (40% yield determined by ^{1}H NMR): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.63 (m, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 3.00 – 2.55 (m, 2H), 1.34 (s, 12H), 0.92 – 0.81 (m, 2H), 0.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 135.0, 127.4, 125.7, 83.8, 30.5, 25.0, 18.7, -1.6. HRMS (ESI+): calc'd for $C_{17}H_{30}BO_2Si$ $[M+H]^+$: 305.2103, found: 305.2092.



1m *2m*

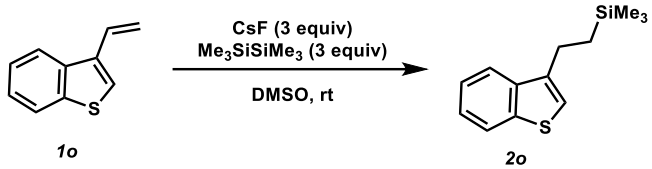
Trimethyl(3,4,5-trimethoxyphenethyl)silane (2m): The general procedure B was followed. The reaction was performed with **1m** (194.0 mg, 1.0 mmol), CsF (455.0 mg, 3.0 mmol), and $Me_3SiSiMe_3$ (600 μL, 3.0 mmol) in DMSO (1.5 mL). The desired product **2m** (197.6 mg, 74% yield) was obtained as a colorless oil after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, CDCl3) δ 6.42 (s, 2H), 3.86 (s, 6H), 3.82 (s, 3H), 2.75 – 2.38 (m, 2H), 1.20 – 0.70 (m, 2H), 0.03 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 141.3, 134.0, 104.7, 61.0, 56.2, 30.6, 18.8, -1.6. HRMS (ESI+): calc'd for $C_{14}H_{24}NaO_3Si$ $[M+Na]^+$: 291.1387, found: 291.1388.



1n *2n* *3n*

(2-(6-Methoxynaphthalen-2-yl)ethyl)trimethylsilane (2n): The general procedure C was followed. The reaction was performed with **1n** (38.0 mg, 0.2 mmol), CsF (91.2 mg, 0.6 mmol), and $Me_3SiSiMe_3$ (120 μL, 0.6 mmol) in DMSO (3.0 mL). The desired product **2n** (24.3 mg, 47% yield) as a colorless oil and byproduct **3n** (13.2 mg, 31% yield) as a colorless oil were obtained after purification by silica gel chromatography (PE). For **2n**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 2H), 7.59 – 7.53 (m, 1H), 7.32 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.16 – 7.09 (m, 2H), 3.91 (s, 3H), 2.83 – 2.71 (m, 2H), 1.07 – 0.87 (m, 2H), 0.04 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 140.7, 133.0, 129.3, 129.0, 127.7, 127.0, 125.4, 118.7, 105.8, 55.4, 30.1, 18.8, -1.6. HRMS

(ESI+): calc'd for $C_{16}H_{23}OSi$ $[M+H]^+$: 259.1513, found: 259.1519. For **3n**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 9.0, 5.8 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 1.7 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.35 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.20 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.18 – 7.06 (m, 4H), 3.93 (s, 3H), 3.90 (s, 3H), 2.92 – 2.79 (m, 1H), 2.64 – 2.44 (m, 2H), 2.14 – 1.97 (m, 2H), 1.07 (d, *J* = 7.6 Hz, 2H), -0.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 157.2, 142.5, 137.9, 133.4, 133.0, 129.21, 129,16, 129.0, 128.0, 127.1, 126.7, 126.6, 126.3, 126.2, 118.73, 118.69, 105.82, 105.76, 55.4, 42.6, 41.8, 34.1, 29.9, 25.5, -0.8. HRMS (ESI+): calc'd for $C_{29}H_{35}O_2Si$ $[M+H]^+$: 443.2401, found: 443,2426.

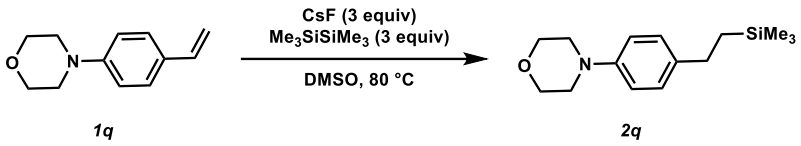


1o *2o*

(2-(Benzo[b]thiophen-3-yl)ethyl)trimethylsilane (2o): The general procedure A was followed. The reaction was performed with **1o** (160.0 mg, 1.0 mmol), CsF (455.7 mg, 3.0 mmol), and $Me_3SiSiMe_3$ (600 μL, 3.0 mmol) in DMSO (3.0 mL). The desired product **2o** (114.6 mg, 49% yield) was obtained as a yellow oil after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.30 (m, 2H), 7.10 (s, 1H), 2.94 – 2.76 (m, 2H), 1.31 – 0.81 (m, 2H), 0.08 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 139.8, 139.0, 124.2, 123.8, 123.1, 121.8, 120.3, 23.0, 16.2, -1.6. HRMS (APCI+): calc'd for $C_{13}H_{22}NSSi$ $[M+NH_4]^+$: 252.1237, found: 252.1231.

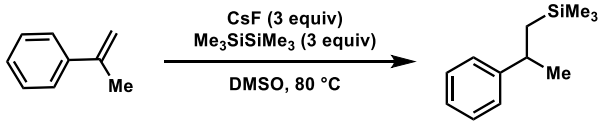
1p *2p*

9-(4-(2-(Trimethylsilyl)ethyl)phenyl)-9H-carbazole (2p): The general procedure C was followed. The reaction was performed with **1p** (56.0 mg, 0.2 mmol), CsF (91.2 mg, 0.6 mmol), and $Me_3SiSiMe_3$ (120 μL, 0.6 mmol) in DMSO (3.0 mL). The desired product **2p** (54.3 mg, 79% yield) was obtained as a colorless oil after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.8 Hz, 2H), 7.49 – 7.35 (m, 8H), 7.31 – 7.27 (m, 2H), 2.87 – 2.63 (m, 2H), 1.07 – 0.78 (m, 2H), 0.07 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 141.2, 135.1, 129.3, 127.2, 126.0, 123.3, 120.4, 119.8, 109.9, 30.0, 18.8, -1.6. HRMS (ESI+): calc'd for $C_{23}H_{26}NSi$ $[M+H]^+$: 344.1829, found: 344.1812.



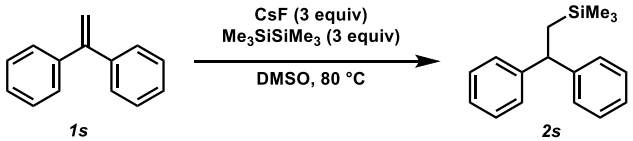
1q *2q*

4-(4-(2-(Trimethylsilyl)ethyl)phenyl)morpholine (2q): The general procedure B was followed. The reaction was performed with **1q** (33.5 mg, 0.2 mmol), CsF (91.2 mg, 0.6 mmol), and $Me_3SiSiMe_3$ (120 μL, 0.6 mmol) in DMSO (0.3 mL). The desired product **2q** (36.8 mg, 70% yield) was obtained as a yellow oil after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 3.96 – 3.74 (m, 4H), 3.22 – 3.03 (m, 4H), 2.69 – 2.47 (m, 2H), 0.94 – 0.68 (m, 2H), 0.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.6, 116.2, 67.1, 50.1, 29.2, 18.9, -1.6. HRMS (ESI+): calc'd for $C_{15}H_{26}NOSi$ $[M+H]^+$: 264.1778, found: 264.1786.



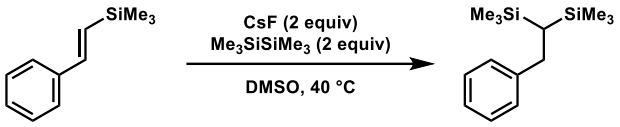
1r *2r*

Trimethyl(2-phenylpropyl)silane (2r): The general procedure B was followed. The reaction was performed with **1r** (118.2 mg, 1.0 mmol), CsF (445.0 mg, 3.0 mmol), and $Me_3SiSiMe_3$ (600 μL, 3.0 mmol) in DMSO (1.5 mL). The desired product **2r** (163.0 mg, 85% yield) was obtained as a colorless oil after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.13 (m, 2H), 7.12–7.03 (m, 3H), 2.78 (m, 1H), 1.23 (d, J = 6.9, 3H), 0.92 (dd, J = 14.6, 8.6, 1H), 0.78 (dd, J = 14.7, 6.6, 1H), -0.11 (s, 9H). The spectroscopic data were consistent with those reported in the literature.[1]



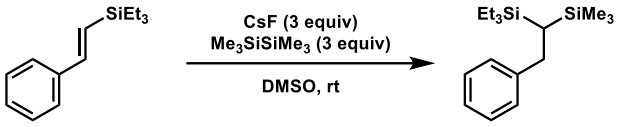
1s *2s*

(2,2-Diphenylethyl)trimethylsilane (2s): The general procedure B was followed. The reaction was performed with **1s** (180.1 mg, 1.0 mmol), CsF (445.0 mg, 3.0 mmol), and $Me_3SiSiMe_3$ (600 μL, 3.0 mmol) in DMSO (1.5 mL). The desired product **2s** (159.4 mg, 63% yield) was obtained as a colorless oil after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 8H), 7.18 – 7.10 (m, 2H), 4.08 (t, *J* = 8.0 Hz, 1H), 1.41 (d, *J* = 8.1 Hz, 2H), -0.17 (s, 9H). The spectroscopic data were consistent with those reported in the literature.[1]



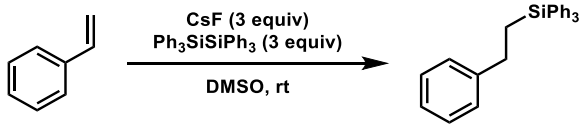
1t *2t*

(2-Phenylethane-1,1-diyl)bis(trimethylsilane) (2t): The modified procedure B was followed. The reaction was performed with **1t** (35.2 mg, 0.2 mmol), CsF (60.8 mg, 0.4 mmol), and $Me_3SiSiMe_3$ (80 μL, 0.4 mmol) in DMSO (0.5 mL). The desired product **2t** (41.0 mg, 80% yield) was obtained as a colorless oil after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.14 (m, 5H), 2.82 (d, *J* = 7.0 Hz, 2H), 0.35 (t, *J* = 7.0 Hz, 1H), 0.00 (s, 18H). The spectroscopic data were consistent with those reported in the literature.[7]



1u *2u*

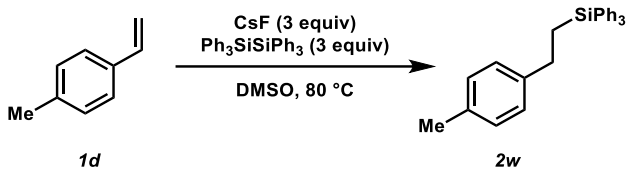
Triethyl(2-phenyl-1-(trimethylsilyl)ethyl)silane (2u): The general procedure A was followed. The reaction was performed with **1u** (21.8 mg, 0.1 mmol), CsF (45.0 mg, 0.3 mmol), and $Me_3SiSiMe_3$ (60 μL, 0.3 mmol) in DMSO (0.75 mL). A mixture of **2u** and **1u** (27.5 mg, **2u**:**1u** = 4:1 was determined by ^{1}H NMR) were obtained after purification by silica gel chromatography (PE). For **2u** (79% yield determined by ^{1}H NMR): ^{1}H NMR (400 MHz, CDCl3) δ 7.24 (d, *J* = 7.0 Hz, 2H), 7.20 (d, *J* = 6.8 Hz, 2H), 7.19 – 7.11 (m, 1H), 2.91 (dd, *J* = 14.8, 5.3 Hz, 1H), 2.72 (dd, *J* = 14.8, 8.5 Hz, 1H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.63 – 0.53 (m, 6H), 0.47 (dd, *J* = 8.5, 5.3 Hz, 1H), -0.07 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 128.5, 128.3, 125.7, 32.1, 11.8, 7.6, 3.7, 0.7. HRMS (EI): calc'd for $C_{15}H_{27}Si_2$ $[M–C_2H_5]^{+\bullet}$: 263.1651, found: 263.1642.



1a *2v*

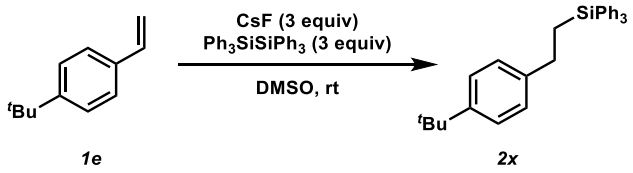
Phenethyltriphenylsilane (2v): The general procedure A was followed. The reaction was performed with **1a** (20.8 mg, 0.2 mmol), CsF (91.2 mg, 0.6 mmol), and $Ph_3SiSiPh_3$ (311.3 mg, 0.6 mmol) in DMSO (1.5 mL). The desired product **2v** (36.4 mg, 50% yield) was obtained as a white solid after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 6H), 7.47 – 7.38 (m, 9H), 7.31 – 7.26

(m, 2H), 7.24 – 7.13 (m, 3H), 2.93 – 2.66 (m, 2H), 1.89 – 1.71 (m, 2H). The spectroscopic data were consistent with those reported in the literature.[8]



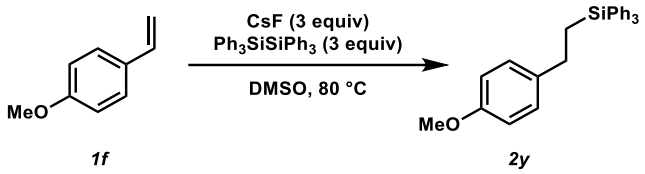
1d *2w*

(4-Methylphenethyl)triphenylsilane (2w): The general procedure B was followed. The reaction was performed with **1d** (11.8 mg, 0.1 mmol), CsF (45.1 mg, 0.3 mmol), and $Ph_3SiSiPh_3$ (155.6 mg, 0.3 mmol) in DMSO (145 μL). The desired product **2w** (30.8 mg, 81% yield) was obtained as a white solid after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 6H), 7.50 – 7.35 (m, 9H), 7.14 – 7.10 (m, 4H), 2.90 – 2.66 (m, 2H), 2.35 (s, 3H), 1.83 – 1.70 (m, 2H). The spectroscopic data were consistent with those reported in the literature.[3]



1e *2x*

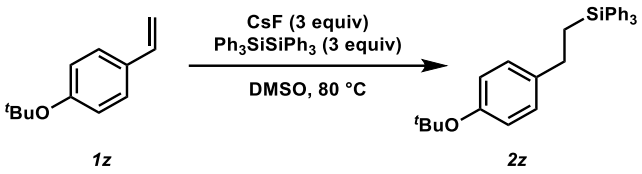
(4-(Tert-butyl)phenethyl)triphenylsilane (2x): The general procedure A was followed. The reaction was performed with **1e** (32.0 mg, 0.2 mmol), CsF (91.2 mg, 0.6 mmol), and $Ph_3SiSiPh_3$ (311.3 mg, 0.6 mmol) in DMSO (1.5 mL). The desired product **2x** (50.1 mg, 60% yield) was obtained as a white solid after purification by silica gel chromatography (PE). ^{1}H NMR (400 MHz, CDCl3) δ 7.59 – 7.57 (m, 6H), 7.49 – 7.36 (m, 9H), 7.34 – 7.28 (m, 2H), 7.18 – 7.12 (m, 2H), 2.85 – 2.73 (m, 2H), 1.86 – 1.71 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 141.9, 135.8, 135.1, 129.6, 128.1, 127.5, 125.4, 34.5, 31.6, 29.5, 15.4. HRMS (EI): calc'd for $C_{30}H_{32}Si$ $[M]^{+\bullet}$: 420.2268, found: 420.2259.



1f *2y*

(4-Methoxyphenethyl)triphenylsilane (2y): The general procedure B was followed. The reaction was performed with **1f** (26.8 mg, 0.2 mmol), CsF (91.2 mg, 0.6 mmol), and $Ph_3SiSiPh_3$ (311.3 mg, 0.6 mmol) in

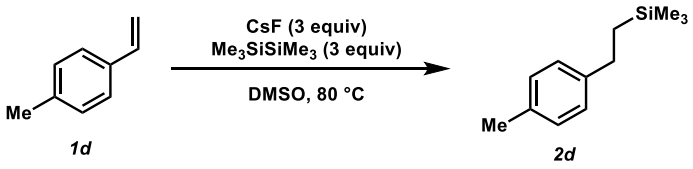
DMSO (300 μL). A mixture of **2y** and **Ph_3SiF** (104.0 mg, **2y**: **Ph_3SiF** = 1:1 was determined by ^1H NMR) were obtained after purification by silica gel chromatography (PE). For **2y** (75% yield determined by ^1H NMR): ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (m, 6H), 7.49 – 7.39 (m, 9H), 7.19 – 7.16 (m, 2H), 6.89 – 6.87 (m, 2H), 3.83 (s, 3H), 2.86 – 2.74 (m, 2H), 1.82 – 1.77 (m, 2H). The spectroscopic data were consistent with those reported in the literature.[9]



1z *2z*

(4-(Tert-butoxy)phenethyl)triphenylsilane (2z): The general procedure B was followed. The reaction was performed with **1z** (35.3 mg, 0.2 mmol), CsF (91.2 mg, 0.6 mmol), and $Ph_3SiSiPh_3$ (311.3 mg, 0.6 mmol) in DMSO (300 μL). A mixture of **2z** and **Ph_3SiF** (44.2 mg, **2z**: **Ph_3SiF** = 10:1 was determined by ^1H NMR) were obtained after purification by silica gel chromatography (PE). For **2z** (50% yield determined by ^1H NMR): ^1H NMR (400 MHz, CDCl3) δ 7.51 – 7.42 (m, 6H), 7.30 – 7.25 (m, 9H), 6.99 – 6.97 (m, 2H), 6.80 – 6.78 (m, 2H), 2.76 – 2.59 (m, 2H), 1.72 – 1.59 (m, 2H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 139.8, 135.8, 135.1, 129.6, 128.12, 128.07, 124.3, 78.2, 29.4, 29.9, 15.5. HRMS (EI): calc'd for $C_{30}H_{32}OSi$ $[M]^{+\bullet}$: 436.2217, found: 436.2220.

Procedure of Gram-scale Reaction

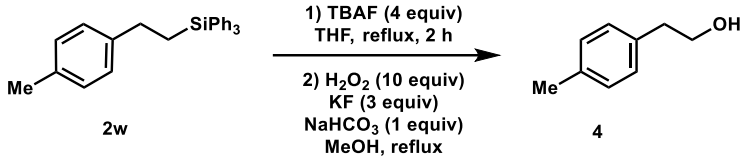


1d *2d*

Under an argon atmosphere, CsF (4.55 g, 30 mmol) was added to a dry Schlenk flask equipped with a magnetic stirring bar. Then, DMSO (20 equiv, 15 mL), **1d** (1.18 g, 10 mmol), and $Me_3SiSiMe_3$ (6 mL, 30 mmol) were added. The mixture was heated to 80 °C with a heating mantle and stirred for 12 h, then diluted with water (30 mL). The mixture was separated and the aqueous phase was extracted with EA (15 mL × 3). The combined organic layers were washed with water (30 mL × 2) and brine, and dried over anhydrous Na_2SO_4. The solvents

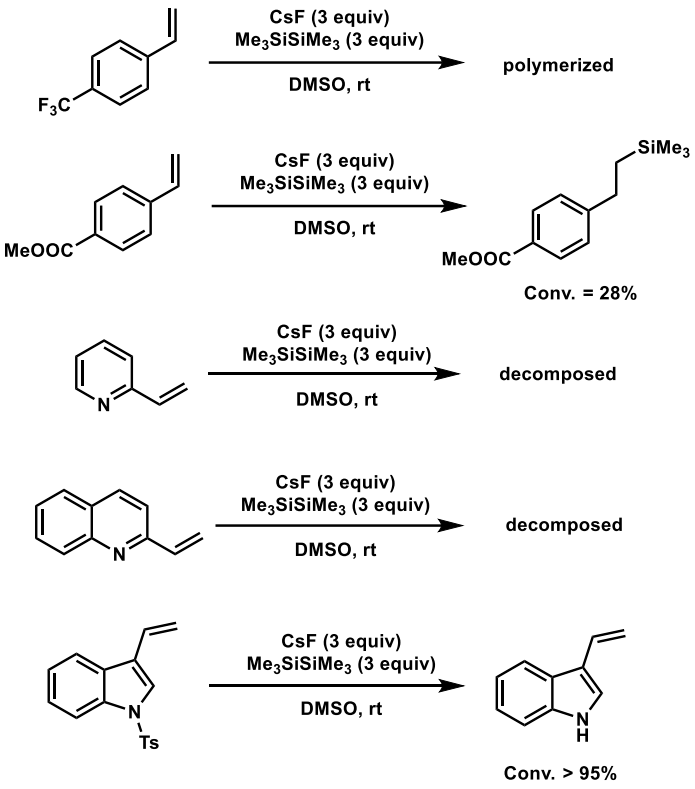
were removed under reduced pressure and the desired product **2d** (1.88 g, 98% yield) was obtained as a colorless oil after purification by silica gel chromatography (PE).

Procedure for the Oxidation of the Silylated Product to Alcohol



Under an argon atmosphere, **2w** (76.8 mg, 0.2 mmol), tetrabutylammonium fluoride (1 m in THF, 0.88 mL) and 0.5 mL of THF were added to a 10 mL Schlenk tube. The mixture was heated to reflux with an oil bath for 2 h. After the tube was brought back to room temperature, potassium fluoride (35.8 mg, 0.6 mmol), sodium bicarbonate (20.3 mg, 0.2 mmol), hydrogen peroxide (30% in water, 0.1 mL), and 0.5 mL of methanol were added. The resultant mixture was stirred at 70 ° C for another 3 hours. The reaction mixture was quenched by $NaHCO_3$, extracted with EA (5 mL × 3) and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. The desired product **4** (22.3 mg, 82%) was obtained as a yellow oil after purification by silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.10 (m, 4H), 3.84 (t, J = 6.6 Hz, 2H), 2.84 (t, J = 6.6 Hz, 2H), 2.33 (s, 3H). The spectroscopic data were consistent with those reported in the literature.[10]

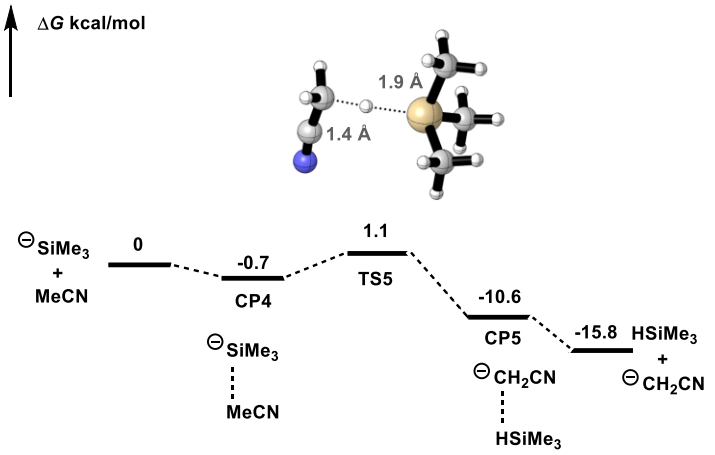
Scheme S1. Failed Substrates



DFT Study on the Mechanism of Formal Hydrosilylation of Styrenes

DFT calculations were performed with Gaussian 09.[11] The functional M06-2X[12] and a basis set 6-31+G(d,p)[13] for all atoms were employed for optimizing the geometries of minima and transition states under the SMD[14] implicit solvation model to account for solvation effects of DMSO or MeCN. Unscaled harmonic frequency calculations at the same level were performed to validate each structure as either a minimum or a transition state and to evaluate the zero-point energy and thermal corrections at 298 K. On the basis of the optimized structures, single-point energies were computed under the SMD(DMSO/MeCN) solvation model with the functional M06-2X using 6-311+G(d,p)[15] for all atoms. All of the 3D structures were prepared with CYLview.[16] All discussed energy differences were based on the Gibbs energies in DMSO/MeCN at 298 K. Standard states for solutes in DMSO solution are the hypothetical states at 1 mol/L, while pure DMSO concentration is 14.1 mol/L. Standard states for solutes in MeCN solution are the hypothetical states at 1 mol/L, while pure MeCN concentration is 19.1 mol/L. The final free energy was calculated by adding TCGs (low level) to SPEs (high level).

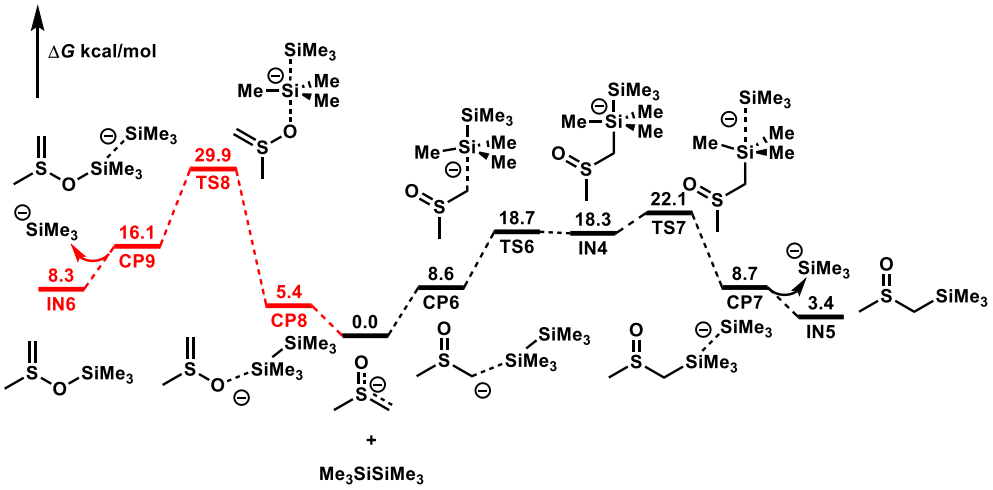
Figure S1: The Reaction Pathway in MeCN



The free energy barriers of Me_3Si^- reaction with MeCN and all free energy profiles calculated at SMD(MeCN)/M06-2X/6-311+G(d,p)//SMD(MeCN)/M06-2X/6-31+G(d,p).

Notably, the hydrosilylation reaction does not occur when MeCN is used as the solvent, whereas the previous dehalogenation reaction could be carried out both in MeCN and DMSO.[17] To answer this question, we carried out DFT calculations to study the solvent effect. The activation free energies of Me_3Si^- reaction with MeCN are shown in Figure S1. The activation free energy of abstracting a proton from MeCN by Me_3Si^- is 1.1 kcal/mol, which is much lower than silyl anion adding onto an alkene (13.0 kcal/mol), suggesting that, in MeCN, the silyl anion is quenched by the solvent.

Figure S2: The Reaction of $MeS(O)CH_2^-$ with $Me_3SiSiMe_3$



The free energy barriers of generating Me_3Si^- from reaction of $MeS(O)CH_2^-$ and $Me_3SiSiMe_3$. All free energy profiles calculated at SMD(DMSO)/M06-2X/6-311+G(d,p)//SMD(DMSO)/M06-2X/6-31+G(d,p).

The reaction between disilane and the deprotonated DMSO anion ($MeSOCH_2^-$) was also considered. The reaction map of Gibbs free energy was shown in Figure S2. From the $MeSOCH_2^-$ anion and $Me_3SiSiMe_3$ which were set as the energy reference point, two pathways were proposed. The nucleophilic attack to disilane may occur both on carbon and oxygen atom in $MeSOCH_2^-$. The C-attack process requires an activation Gibbs free energy of 22.1 kcal/mol (**TS7**) while the O-attack one demands a much higher 29.9 kcal/mol. The former barrier is compatible with the fluorine anion activation process mentioned in the main text (Figure 1). Thus, the presented C-attack process may act as a minor pathway of generating the trimethylsilyl anion, since $MeSOCH_2^-$ is gradually generated during the reaction process, compared to the exogenously added fluoride anion. These results are consistent with our experiment (Table S1, entry 13) that a moderate yield of the hydrosilylation reaction was achieved even with 20 mol% of CsF.

Table S2. Computed Energies of All of the Stationary Points:

Thermal corrections to Gibbs energies (TCGs), single-point energies (SPEs) at high/low level

	Imaginary Frequencies (cm^{-1})	Solvent	TCGs[a] (hartree)	SPEs[a] (hartree)	SPEs[b] (hartree)
F^-	None	DMSO	-0.014159	-99.951691	-99.984027
$Me_3SiSiMe_3$	None	DMSO	0.179683	-818.334752	-818.436416
DMSO	None	DMSO	0.052226	-553.097231	-553.163966
Styrene	None	DMSO	0.102962	-309.527629	-309.589730
CP1	None	DMSO	0.179783	-918.275889	-918.409400
TS1	-92.29	DMSO	0.179470	-918.262434	-918.395498
Me_3SiF	None	DMSO	0.081745	-509.048451	-509.128945
IN1	None	DMSO	0.078060	-409.215461	-409.267295
TS2	-216.15	DMSO	0.200014	-718.737380	-718.852287
IN2	None	DMSO	0.198044	-718.790425	-718.906696
CP2	None	DMSO	0.269454	-1271.896522	-1272.080420
TS3	-1390.93	DMSO	0.268432	-1271.871903	-1272.054010
$MeSOCH_2^-$	None	DMSO	0.038365	-552.563643	-552.632743
$PhCH_2CH_2SiMe_3$	None	DMSO	0.214031	-719.331572	-719.445270
CP3	None	DMSO	0.146076	-962.317089	-962.436376
TS2'	-1487.83	DMSO	0.140559	-962.281173	-962.400090

$HSiMe_3$	None	DMSO	0.088585	-409.755607	-409.806914
TS4	-296.43	DMSO	0.324150	-1028.317951	-1028.496168
IN3	None	DMSO	0.328196	-1028.356888	-1028.534495
MeCN	None	MeCN	0.021572	-132.711305	-132.743361
IN1	None	MeCN	0.077700	-409.216979	-409.268814
CP4	None	MeCN	0.110333	-541.929304	-542.013279
TS5	-1505.87	MeCN	0.107274	-541.906295	-541.990000
CP5	None	MeCN	0.110250	-541.953871	-542.039872
$HSiMe_3$	None	MeCN	0.088198	-409.757895	-409.809185
$NCCH_2^-$	None	MeCN	0.007242	-132.192699	-132.227079
CP6	None	DMSO	0.238626	-1370.902188	-1371.073752
TS6	-92.16	DMSO	0.238650	-1370.886244	-1371.057807
IN4	None	DMSO	0.239995	-1370.888122	-1371.058917
TS7	-81.45	DMSO	0.241850	-1370.884030	-1371.055136
CP7	None	DMSO	0.236296	-1370.899823	-1371.070645
IN5	None	DMSO	0.142568	-961.6801366	-961.7987593
CP8	None	DMSO	0.232078	-1370.900813	-1371.072294
TS8	-97.13	DMSO	0.242577	-1370.872201	-1371.044769
CP9	None	DMSO	0.237100	-1370.888845	-1371.061319
IN6	None	DMSO	0.139992	-961.669638	-961.789538

[a]Calculated at SMD(Solvent)/M06-2X/6-31+G(d,p).

[b]Calculated at SMD(Solvent)/M06-2X/6-311+G(d,p)//SMD(Solvent)/M06-2X/6-31+G(d,p).

Cartesian Coordinates for the Stationary Points

F^-

F	0.000000	0.000000	0.000000

$Me_3SiSiMe_3$

Si	1.16967500	-0.02286700	-0.00651400
Si	-1.17257000	0.01026300	0.00921400
C	1.79033000	-1.78298800	-0.30948100
C	1.82006000	1.10320900	-1.37914800
C	1.83014600	0.58865800	1.65696200
C	-1.79203100	1.70290500	-0.56273600
C	-1.81061600	-0.31878100	1.75853800
C	-1.84347600	-1.32196500	-1.15302800
H	2.88623600	-1.81991200	-0.28242200
H	1.41021900	-2.47324000	0.45250700
H	1.46446500	-2.15200500	-1.28886400

H	2.91529400	1.06728800	-1.42613200
H	1.52288700	2.14436900	-1.20781200
H	1.43022300	0.79840100	-2.35731100
H	1.46297800	1.59756600	1.87865900
H	1.51263000	-0.07128500	2.47251600
H	2.92643800	0.62027300	1.65485200
H	-2.88726600	1.75001400	-0.52920500
H	-1.47545500	1.90972700	-1.59159200
H	-1.39963000	2.50187400	0.07712200
H	-2.90719400	-0.33479100	1.77699700
H	-1.45265600	-1.28325800	2.13697200
H	-1.47243500	0.46018700	2.45166800
H	-1.47800100	-1.17461500	-2.17597800
H	-1.53105400	-2.32022400	-0.82517700
H	-2.93973600	-1.30212000	-1.17899700

DMSO

S	0.00000000	0.21557800	-0.44745600
C	1.35236000	-0.79525500	0.18975500
C	-1.35236000	-0.79525500	0.18975500
O	0.00000000	1.49960600	0.37919600
H	2.28584900	-0.28328000	-0.05227400
H	1.32993200	-1.77420800	-0.29635600
H	1.24134000	-0.89402800	1.27296500
H	-2.28584900	-0.28328000	-0.05227400
H	-1.32993200	-1.77420700	-0.29635600
H	-1.24134000	-0.89402800	1.27296500

Styrene

C	1.35310700	1.33088200	-0.00000200
C	2.25923600	0.26687900	0.00000300
C	1.78136100	-1.04235600	0.00000300
C	0.40769900	-1.28355100	0.00000000
C	-0.51143100	-0.22529600	-0.00000300
C	-0.01724800	1.08889100	-0.00000400
C	-1.95501300	-0.53850800	-0.00000500
C	-2.96231800	0.34116200	0.00000700
H	1.71765200	2.35407600	-0.00000300
H	3.32791800	0.46002600	0.00000600
H	2.47557600	-1.87771500	0.00000500
H	0.03785500	-2.30621200	0.00000000
H	-0.70516400	1.92958800	-0.00000800
H	-2.19039100	-1.60252100	-0.00001600
H	-3.99228900	-0.00239600	0.00000500

H	-2.80351900	1.41653300	0.00001900

CP1

Si	-1.18143200	0.00077500	0.00109800
Si	1.30128400	0.00023900	-0.00159800
C	-1.22846900	-1.76698400	-0.74039300
C	-1.21589300	0.23505100	1.90491100
C	-1.21818500	1.52619300	-1.16117400
C	2.10402400	1.31742800	1.14263400
C	2.12124900	0.33280200	-1.70677100
C	2.11923800	-1.64036000	0.56919200
H	-0.59637100	-1.82786100	-1.63602700
H	-0.81173200	-2.47736100	-0.01360900
H	-2.23438800	-2.11014900	-1.00673900
H	-2.21347400	0.12281900	2.34388900
H	-0.85120800	1.24137600	2.15307900
H	-0.54032200	-0.47507900	2.39898800
H	-0.55400300	2.31664900	-0.78850100
H	-0.83505700	1.23396400	-2.14864200
H	-2.21767300	1.95249300	-1.30105100
H	3.19766700	1.32925800	1.03503900
H	1.87765300	1.11673900	2.19765000
H	1.73810500	2.32746400	0.91614800
H	3.21400000	0.22702900	-1.65415500
H	1.75773200	-0.36634400	-2.47122600
H	1.90395800	1.34815200	-2.06258400
H	1.73876700	-1.96388600	1.54667600
H	1.92124700	-2.45077500	-0.14388800
H	3.20964100	-1.53423400	0.65603900
F	-3.03941500	0.01185600	0.00636300

TS1

Si	1.56842300	0.11038800	0.06398100
Si	-1.75107100	-0.35718100	0.11583500
C	1.10585900	1.28030300	1.46246500
C	1.78333700	-1.70901200	0.49268200
C	0.99593900	0.55431000	-1.67303900
C	-3.21487400	-1.15156400	1.13498000
C	-2.47985600	-0.65182100	-1.67094300
C	-2.27671000	1.51100500	0.31434700
H	0.38497800	2.03213700	1.12655000
H	0.65723900	0.74297500	2.30259300
H	2.00199100	1.80186800	1.82093000
H	2.85128100	-1.95090200	0.56130600

H	1.33235800	-2.35339700	-0.26778900
H	1.31135500	-1.94932800	1.44956200
H	0.71719700	-0.34290800	-2.23528600
H	0.12661300	1.21805500	-1.65800600
H	1.80692900	1.05991400	-2.21201700
H	-4.19623900	-0.76401400	0.81619700
H	-3.11398700	-0.94834600	2.21014400
H	-3.23970000	-2.24392600	1.01938600
H	-3.53311000	-0.33327900	-1.73303300
H	-1.92390100	-0.09422000	-2.43700100
H	-2.44034200	-1.71236800	-1.95624700
H	-2.17021300	1.85187000	1.35368400
H	-1.66808800	2.18246500	-0.30740300
H	-3.32934400	1.66206100	0.02474900
F	3.21065000	0.52886800	-0.09705100

Me_3SiF

Si	-0.00071700	-0.00000200	0.00148500
F	0.02626800	0.00004100	1.65592000
C	0.89129300	1.54775600	-0.52463700
C	0.89130800	-1.54777100	-0.52458400
C	-1.80399000	-0.00001800	-0.49819500
H	0.92017300	1.61400000	-1.61834100
H	0.38352700	2.44223600	-0.14779500
H	1.92320200	1.55581700	-0.15797000
H	0.92034500	-1.61394900	-1.61828800
H	0.38346100	-2.44226200	-0.14787400
H	1.92316300	-1.55588700	-0.15776900
H	-2.44482300	-0.00095000	0.39023500
H	-2.05376500	0.88658000	-1.09011500
H	-2.05331700	-0.88572400	-1.09164200

IN1

Si	0.00043500	0.00059900	-0.67063000
C	1.61975700	0.51553100	0.28223200
C	-1.25729600	1.14348100	0.28204800
C	-0.36304500	-1.65987000	0.28147700
H	1.92748000	1.54044600	0.03413100
H	1.47759300	0.46771700	1.37427900
H	2.46398400	-0.14064600	0.03043800
H	-1.10834100	2.20339400	0.03482800
H	-2.29807900	0.90000900	0.02891500
H	-1.14908400	1.03993900	1.37413200
H	0.36744500	-2.44081800	0.03012700

H	-0.32788300	-1.51335500	1.37343400
H	-1.35569500	-2.05991800	0.03398300

TS2

C	2.76511100	-1.27655400	0.84243300
C	3.71955400	-1.03129400	-0.14624200
C	3.56848600	0.09389500	-0.96602800
C	2.49017400	0.95363700	-0.79406000
C	1.51995600	0.73199600	0.21122400
C	1.68253600	-0.41673900	1.01994600
C	0.38329900	1.62183800	0.35554800
C	-0.57892400	1.47707800	1.32256300
Si	-2.30795600	-0.26902300	0.21471600
C	-3.73034900	-1.60183100	0.17576200
C	-1.22605600	-0.91632700	-1.25212700
C	-3.23243600	1.19434600	-0.65405700
H	2.85902600	-2.15201100	1.48042800
H	4.56120600	-1.70392100	-0.28128800
H	4.29726600	0.29743500	-1.74664400
H	2.38271600	1.81975700	-1.44450200
H	0.95053000	-0.64074900	1.79063300
H	0.23224900	2.34675900	-0.44338500
H	-0.38671100	0.90882200	2.22467900
H	-1.38451200	2.20135600	1.39823100
H	-4.55172300	-1.33311400	0.85289800
H	-4.15503000	-1.70959700	-0.83532400
H	-3.36436300	-2.58847200	0.48889400
H	-0.36990400	-0.26017400	-1.45267400
H	-1.82040500	-0.97504300	-2.17718100
H	-0.83284700	-1.92069400	-1.04673300
H	-3.72560000	0.86427600	-1.58121400
H	-4.00653000	1.62476100	-0.00426000
H	-2.54209000	2.00665500	-0.91836000

IN2

C	3.55552200	1.33316500	-0.00006100
C	4.47426300	0.27355600	-0.00005900
C	3.94380000	-1.03512000	0.00003000
C	2.58413400	-1.27262500	0.00009600
C	1.60237200	-0.20408200	0.00005000
C	2.18181400	1.12488700	0.00001200
C	0.23232700	-0.43970800	0.00004900
C	-0.79417500	0.66570800	0.00004200
Si	-2.56980100	0.03819200	-0.00005600

C	-3.76000600	1.50112600	0.00011300
C	-2.89128000	-1.00807700	1.53580000
C	-2.89116700	-1.00798100	-1.53598400
H	3.92396500	2.35891100	-0.00009500
H	5.54490400	0.45024300	-0.00009400
H	4.62239600	-1.88754200	0.00006300
H	2.22265900	-2.30077600	0.00017600
H	1.51887800	1.98683700	0.00002800
H	-0.10448600	-1.47755200	0.00010500
H	-0.69481700	1.34060200	0.87381500
H	-0.69464800	1.34071600	-0.87361300
H	-3.61204200	2.12954000	-0.88608900
H	-4.80200100	1.16039500	0.00026400
H	-3.61176200	2.12951600	0.88628300
H	-2.27337800	-1.91292800	1.54081700
H	-3.94155800	-1.31973300	1.58359000
H	-2.66611400	-0.44278800	2.44800100
H	-3.94138800	-1.31978200	-1.58394100
H	-2.66589400	-0.44270100	-2.44816200
H	-2.27313900	-1.91275200	-1.54087900

CP2

C	-3.84139200	-0.45520700	1.30838200
C	-4.75130300	-0.39704900	0.24350700
C	-4.22670200	-0.54752300	-1.05894300
C	-2.87995300	-0.75154700	-1.28364200
C	-1.91012200	-0.82784700	-0.20887500
C	-2.47980300	-0.65399200	1.11149900
C	-0.55177900	-1.03037400	-0.43277000
C	0.46136900	-1.13677900	0.67791000
Si	2.15682000	-1.71472600	0.09230800
C	3.38053400	-1.63693900	1.52480800
C	2.81191500	-0.63745300	-1.31165600
C	2.03887700	-3.49333100	-0.52507800
H	-4.20606500	-0.33574900	2.32844800
H	-5.81147500	-0.23796500	0.41154000
H	-4.89888200	-0.50419600	-1.91520900
H	-2.52055400	-0.86476900	-2.30627700
H	-1.82086100	-0.68046600	1.97634900
H	-0.21569800	-1.12925900	-1.46608200
H	0.60213800	-0.19048700	1.24058000
H	0.14897900	-1.86198100	1.45471400
H	3.05095000	-2.26214500	2.36294500
H	4.37290700	-1.98552000	1.21550900

H	3.48526400	-0.60947400	1.89366500
H	2.11261000	-0.59341800	-2.15427200
H	3.75984600	-1.04273900	-1.68661800
H	3.00246400	0.38672700	-0.97122900
H	3.02266700	-3.86826600	-0.83134800
H	1.65423400	-4.15641100	0.25885000
H	1.36731000	-3.56943800	-1.38786900
C	-0.52097400	2.38956600	0.68955100
H	-1.10413800	3.19701800	0.23706000
H	-0.87086700	1.40976800	0.34730900
H	-0.56515800	2.45294900	1.77884800
S	1.20266900	2.57971100	0.19477900
O	1.57700700	4.03838800	0.45939800
C	0.92665300	2.44580800	-1.58366800
H	0.49403000	1.46506400	-1.80391200
H	0.25001000	3.24871400	-1.89034800
H	1.89211600	2.55173200	-2.08276900

TS3

C	-3.39213900	-1.38903300	1.29351400
C	-4.22866000	-1.74594100	0.23388700
C	-3.66377200	-1.87122800	-1.04337000
C	-2.30915500	-1.64486300	-1.24811900
C	-1.43344000	-1.28071800	-0.18859100
C	-2.03050700	-1.16103100	1.09307000
C	-0.04944300	-0.94332700	-0.45410200
C	0.94405800	-0.87529600	0.69446900
Si	2.73169400	-1.02427500	0.11593000
C	3.90404200	-0.72315600	1.56119300
C	3.08388200	0.24293000	-1.23507600
C	3.04057700	-2.75255900	-0.57232700
H	-3.80397300	-1.28776400	2.29553100
H	-5.28733600	-1.92500600	0.39498600
H	-4.29028600	-2.15210700	-1.88716300
H	-1.89497300	-1.75191700	-2.24980100
H	-1.41067400	-0.88789300	1.94381500
H	0.32652500	-1.42944000	-1.36285400
H	0.86077500	0.08958100	1.23236000
H	0.77967000	-1.64999200	1.46527000
H	3.73896500	-1.45243200	2.36289700
H	4.94971400	-0.80622500	1.24219600
H	3.76067000	0.27855000	1.98300100
H	2.43578500	0.08665300	-2.10526500
H	4.12434700	0.16953500	-1.57356000

H	2.92055200	1.26418500	-0.87020600
H	4.08220600	-2.86164100	-0.89686000
H	2.84304100	-3.51804600	0.18729600
H	2.39827000	-2.96105500	-1.43544300
C	-1.26280200	2.42862600	1.17669400
H	-2.20691700	2.33479500	0.62978800
H	-0.97075700	1.46742700	1.60299200
H	-1.35940400	3.17547500	1.96794500
S	0.01471900	3.00626300	0.03368400
O	-0.49689000	4.40158500	-0.39403800
C	-0.21875500	1.80000700	-1.22203200
H	-0.12368700	0.44652000	-0.82562500
H	-1.22206600	1.92683200	-1.65363200
H	0.54213500	1.96445700	-1.99260600

$MeSOCH_2^-$

S	0.11465200	0.14686900	0.41446800
C	1.32129800	-0.92661500	-0.18668600
C	-1.36433200	-0.74331000	-0.13552300
O	-0.02470800	1.49539800	-0.35336500
H	2.30026400	-0.57900700	0.16048800
H	1.28603100	-0.98770700	-1.28411200
H	-1.45659700	-1.68734100	0.40442700
H	-2.23340500	-0.11118300	0.05945500
H	-1.27485200	-0.92830200	-1.21157000

$PhCH_2CH_2SiMe_3$

C	3.99640100	-0.98386200	-0.03454400
C	4.44451100	0.33980700	-0.03315100
C	3.51303400	1.37425000	-0.00003300
C	2.14365900	1.09253500	0.03143900
C	1.68211700	-0.22655300	0.03235500
C	2.63179300	-1.25881400	-0.00225000
C	0.20683800	-0.58438800	0.07655300
C	-0.77686600	0.58365200	-0.01578800
Si	-2.59092900	0.05091300	-0.01091100
C	-3.66970800	1.59043000	-0.10898700
C	-2.97536000	-0.89016500	1.57469900
C	-2.93580100	-1.05655100	-1.49491800
H	4.71151500	-1.80150900	-0.06273000
H	5.50806100	0.55852700	-0.05876500
H	3.84755600	2.40803400	0.00033400
H	1.43600100	1.91577300	0.05488200
H	2.28995700	-2.29216400	-0.00483400

H	0.01240400	-1.29648100	-0.73676300
H	0.02478000	-1.14262500	1.00526300
H	-0.62582300	1.27803500	0.82271200
H	-0.59284400	1.16156800	-0.93283900
H	-3.46117900	2.15921500	-1.02249100
H	-4.73320900	1.32524500	-0.11292500
H	-3.49018600	2.25103800	0.74723000
H	-2.42625100	-1.83740500	1.62264300
H	-4.04519600	-1.12184700	1.63559200
H	-2.70856400	-0.29902500	2.45849100
H	-4.00305500	-1.30051900	-1.55368600
H	-2.65251500	-0.56066200	-2.43071900
H	-2.38213800	-2.00002900	-1.43090200

CP3

Si	-2.14998600	0.01913800	-0.45800100
C	-3.16668400	-1.57537000	0.00752700
C	-3.52510100	1.35105400	-0.09841200
C	-1.15373700	0.19430400	1.20900400
H	-2.52301800	-2.46481800	0.04919800
H	-3.95121100	-1.78442100	-0.73233500
H	-3.65565700	-1.47414500	0.99001600
H	-3.11694700	2.37069400	-0.12245800
H	-4.32763900	1.31224200	-0.84759500
H	-3.98769100	1.20335700	0.89086100
H	-0.59568000	1.13929900	1.26885400
H	-0.42608100	-0.61851500	1.34312700
H	-1.83466300	0.16276600	2.07510000
S	2.40732300	0.01736300	0.37414700
C	1.79602200	-1.36161800	-0.61612700
H	2.25513100	-1.30825300	-1.60742900
H	2.08225200	-2.28722800	-0.11254200
C	1.79664500	1.33225000	-0.69843700
H	0.70790600	1.24657600	-0.78291700
H	2.06823500	2.28782200	-0.24504600
H	2.26893200	1.22681600	-1.67931400
O	3.92878800	0.01134200	0.22619900
H	0.70560300	-1.29237400	-0.69278400

TS2’

Si	-1.79474500	-0.07980600	-0.18928900
C	-3.24033900	-1.34083900	-0.30316100
C	-2.66354800	1.60177100	-0.52913800
C	-1.43005900	-0.00282300	1.69630100

H	-2.91627300	-2.34991100	-0.01918900
H	-3.63998600	-1.40208000	-1.32309700
H	-4.06846200	-1.05808300	0.36253900
H	-1.97971500	2.44620300	-0.37594200
H	-3.03396000	1.66454600	-1.55981000
H	-3.52251700	1.74433900	0.14292300
H	-0.71090000	0.79329300	1.93223800
H	-0.99509900	-0.94593000	2.05346700
H	-2.33965400	0.18771900	2.28315400
S	2.26443300	-0.20098400	0.29639900
C	1.27998000	-1.11681100	-0.81151500
H	1.58746000	-0.94705900	-1.85233000
H	1.31515700	-2.17850200	-0.54821500
C	1.74640900	1.43958200	-0.25719700
H	0.66712000	1.55253700	-0.10801700
H	2.28797100	2.18829800	0.32446700
H	1.99094600	1.54180600	-1.31947800
O	3.78173900	-0.22231700	-0.01553600
H	-0.15516200	-0.61088900	-0.73251000

$HSiMe_3$

Si	0.00013900	0.00014900	0.38179400
C	-1.11106600	-1.39057900	-0.22342600
C	1.76001800	-0.26670200	-0.22359200
C	-0.64916900	1.65710600	-0.22355400
H	0.00032100	-0.00019200	1.87380300
H	-2.14066100	-1.25837600	0.12631400
H	-0.75593700	-2.36540700	0.12799700
H	-1.12761300	-1.41304300	-1.31923100
H	2.42636300	0.52847000	0.12798700
H	2.16027700	-1.22451100	0.12608400
H	1.78761400	-0.26980100	-1.31939800
H	-0.02158800	2.48293200	0.12863200
H	-1.67189400	1.83547300	0.12557300
H	-0.65752100	1.68342000	-1.31944200

TS4

C	-3.13361200	-2.67785000	0.66190500
C	-4.48984100	-2.34910300	0.72631500
C	-4.92820900	-1.17978800	0.09606500
C	-4.03082100	-0.36414200	-0.58491100
C	-2.65609300	-0.68171000	-0.66989700
C	-2.23186000	-1.86119500	-0.01605500
C	-1.74144000	0.18940400	-1.39338000

C	-0.40831000	-0.06338100	-1.58569800
H	-2.77072600	-3.57828500	1.15177600
H	-5.18901100	-2.98631100	1.25935400
H	-5.97861400	-0.90237600	0.13651600
H	-4.38914200	0.54276200	-1.06838400
H	-1.18118900	-2.13867200	-0.03629600
H	-2.15111300	1.14390700	-1.72156700
H	0.00330400	-1.06398500	-1.46775300
H	0.17901900	0.60554200	-2.21082200
C	0.73318900	4.25354800	-0.36374800
C	-0.39669100	4.55321200	0.41111400
C	-1.02316800	3.49762800	1.09214200
C	-0.53523300	2.20052600	1.01746600
C	0.63480100	1.86807900	0.25838900
C	1.23388600	2.95971100	-0.45109100
C	1.06744400	0.53207200	0.13507300
C	2.36291200	0.14291300	-0.52892900
Si	3.07090500	-1.48749800	0.10211900
C	4.53741700	-1.99561200	-0.96916800
C	1.77078900	-2.85149300	0.05040700
C	3.64884700	-1.27886200	1.88423400
H	1.23394800	5.04967300	-0.91215000
H	-0.77975000	5.56682200	0.47567300
H	-1.90896700	3.69623400	1.69315400
H	-1.03771600	1.40561200	1.56738100
H	2.10963700	2.77237500	-1.06829400
H	0.61792300	-0.17620900	0.83358300
H	2.26356700	0.06205700	-1.63190000
H	3.15108100	0.90011700	-0.37513300
H	5.31401700	-1.22159300	-0.96726200
H	4.98881400	-2.92537500	-0.60352200
H	4.22817500	-2.15851200	-2.00826500
H	0.93563600	-2.62923700	0.72439900
H	2.20833600	-3.80523000	0.37000700
H	1.36775400	-2.99032400	-0.95974500
H	4.05630600	-2.21812600	2.27636800
H	4.43148100	-0.51463800	1.95720700
H	2.82052300	-0.97499300	2.53460600

IN3

C	-3.65429000	-1.29098800	0.63744200
C	-4.83628000	-0.53484300	0.67619900
C	-4.80364900	0.73484200	0.06136300
C	-3.67104000	1.21596200	-0.56546500

C	-2.44085300	0.45243200	-0.65561200
C	-2.50048200	-0.83115000	0.01697600
C	-1.31988800	0.91274100	-1.33856700
C	-0.02915900	0.14653000	-1.40235200
H	-3.62974500	-2.27089800	1.11438000
H	-5.73036600	-0.90293600	1.16868600
H	-5.69534300	1.36065600	0.07909300
H	-3.69731300	2.20145800	-1.02990600
H	-1.61479300	-1.46247400	0.02630200
H	-1.35195400	1.91298400	-1.76958300
H	-0.21847000	-0.91919700	-1.60549500
H	0.58688600	0.50134400	-2.24203200
C	2.69205700	3.54718600	-0.53125100
C	2.12284000	4.31246300	0.48945200
C	1.15712400	3.73941600	1.31556300
C	0.76503700	2.41308800	1.11976000
C	1.32857600	1.63316000	0.10404500
C	2.29823700	2.22322500	-0.71895900
C	0.86774000	0.20938600	-0.13072000
C	2.04525000	-0.78067400	-0.22835000
Si	1.67512700	-2.60481200	0.12549600
C	3.33715800	-3.48868000	0.22914400
C	0.64673400	-3.46242300	-1.20280000
C	0.79194200	-2.75156400	1.78396400
H	3.44469300	3.98330400	-1.18267800
H	2.43008900	5.34374900	0.63768800
H	0.70473400	4.32346100	2.11257900
H	0.00775300	1.97317300	1.76592400
H	2.75082000	1.63968800	-1.51801900
H	0.23824800	-0.06484300	0.72829300
H	2.52263400	-0.69856300	-1.21657800
H	2.82176300	-0.50718000	0.50221800
H	3.96574900	-3.05951200	1.01794400
H	3.20164300	-4.55429100	0.44755800
H	3.88461100	-3.40803500	-0.71753300
H	-0.40218200	-3.14770900	-1.18827700
H	0.67109500	-4.54687300	-1.03837100
H	1.04663500	-3.26713600	-2.20472800
H	0.69796800	-3.80459400	2.07506700
H	1.34841100	-2.23304600	2.57381000
H	-0.21766000	-2.32581100	1.74772400

MeCN

C	1.18050600	0.00011300	0.00003500

C	-0.27810700	-0.00047900	-0.00028600
N	-1.43493300	0.00018800	0.00013400
H	1.54338000	-0.23954300	1.00136200
H	1.54399400	-0.74712200	-0.70803000
H	1.54276700	0.98754600	-0.29276300

IN1 (in MeCN)

Si	0.00005500	-0.00027900	-0.67000500
C	-0.16170300	1.69271200	0.28170900
C	-1.38569000	-0.98616400	0.28190800
C	1.54734400	-0.70629500	0.28189500
H	-1.09787800	2.20986200	0.03116700
H	-0.14704200	1.54347300	1.37367900
H	0.65897600	2.37823800	0.03049500
H	-2.38930400	-0.61722000	0.03044400
H	-1.36662300	-2.05550800	0.03132200
H	-1.26406500	-0.89907600	1.37392600
H	2.46278400	-0.15315400	0.03152100
H	1.41087300	-0.64467200	1.37389700
H	1.73179800	-1.75954900	0.03054000

CP4

Si	1.63417500	0.25612200	-0.31158300
C	2.28860800	-1.47499000	-0.92136700
C	1.03458800	-0.28011800	1.46294300
C	3.34412200	1.04560500	0.18965400
H	2.83111100	-1.39047100	-1.87256600
H	1.46556400	-2.18330000	-1.08585100
H	2.97468400	-1.92880100	-0.18756500
H	0.77842200	0.58965800	2.08295200
H	0.13532500	-0.90929600	1.41087100
H	1.80986600	-0.85210100	1.99829200
H	3.20960300	1.98760300	0.73830500
H	3.95588800	1.27694000	-0.69303000
H	3.93125700	0.36853100	0.83200000
C	-3.23824400	1.04762200	-0.68073100
H	-3.48824300	1.99489100	-0.19849100
H	-2.16281600	0.87289300	-0.59910700
H	-3.51941400	1.08660400	-1.73502500
C	-3.95545000	-0.03735200	-0.02307000
N	-4.52020500	-0.90049600	0.50097200

TS5

Si	0.91551700	0.00083800	-0.00665900

C	1.57852800	-1.17158600	-1.38405200
C	1.59229100	-0.82943700	1.59447500
C	2.07632500	1.52828900	-0.18517800
H	1.37927300	-0.77037600	-2.38569500
H	1.10745100	-2.16094800	-1.32888700
H	2.66572400	-1.31326700	-1.29209200
H	1.39059800	-0.21672400	2.48215400
H	1.13041700	-1.81015800	1.76396400
H	2.68044100	-0.97895700	1.53280800
H	1.91372300	2.25297900	0.62291900
H	1.90583300	2.05518500	-1.13277300
H	3.13461300	1.23001700	-0.15671400
C	-2.19946200	1.18952200	-0.01325800
H	-2.28776800	1.78950900	0.89376900
H	-0.87376500	0.62839100	-0.01796500
H	-2.29586000	1.78393200	-0.92312300
C	-3.02196300	0.04161500	-0.00595800
N	-3.54603200	-1.00739000	-0.00018800

CP5

Si	1.10692200	0.02981400	0.16911800
C	2.71969500	0.81650900	0.73872400
C	0.42470700	0.97203100	-1.30819800
C	1.40534200	-1.77034100	-0.28892900
H	0.12803700	0.09468900	1.29212800
H	3.12829600	0.29891100	1.61347300
H	2.57473000	1.86936800	1.00433900
H	3.46791800	0.77006800	-0.06113000
H	-0.48767700	0.49852900	-1.68672700
H	0.18918200	2.00940500	-1.04722900
H	1.16299600	0.98578300	-2.11894400
H	0.49474300	-2.23091700	-0.68662200
H	1.73308800	-2.35353600	0.57855500
H	2.18409000	-1.84120700	-1.05741700
C	-2.54542600	-1.20939900	0.12815400
C	-2.75811000	0.14708300	0.24664600
N	-2.91855900	1.32054400	0.31240000
H	-1.75288300	-1.66013300	0.71568700
H	-3.36676900	-1.83746900	-0.19893800

$HSiMe_3$ (in MeCN)

Si	0.00015500	0.00029700	0.38231600
C	-1.56449900	0.84982400	-0.22369400
C	0.04549500	-1.77903600	-0.22360200

C	1.51875800	0.92884400	-0.22377500
H	0.00024000	0.00077600	1.87451800
H	-1.61516500	1.88718000	0.12429900
H	-2.46152900	0.32920700	0.12848500
H	-1.58871300	0.86031800	-1.31955500
H	0.94430700	-2.29646500	0.12873300
H	-0.82817900	-2.34046000	0.12446800
H	0.04884800	-1.80485000	-1.31957700
H	2.44134100	0.45341800	0.12649100
H	1.51691100	1.96685500	0.12578100
H	1.54124600	0.94206900	-1.31963400

$NCCH_2^-$

C	0.00000000	0.00000000	-1.19416700
C	0.00000000	0.00000000	0.17855600
N	0.00000000	0.00000000	1.36657300
H	0.00000000	0.93722400	-1.73617200
H	0.00000000	-0.93722400	-1.73617200

CP6

Si	-0.87922000	-0.28754600	0.19776000
C	3.41538500	-0.67392700	0.44643000
C	-0.13617200	-0.89077300	-1.43162400
S	3.45200900	0.42814100	-0.87998300
H	3.10445700	-0.12943300	1.34529800
H	4.40193400	-1.13884900	0.59211100
C	0.03144800	1.25623000	0.79854100
C	-0.67892100	-1.65255700	1.49095400
Si	-3.14858400	0.22598300	-0.09655100
H	-0.70879400	-1.73421700	-1.83518800
H	0.89510000	-1.22260500	-1.26539400
H	-0.12197800	-0.09632100	-2.18711500
C	3.84501400	-0.74119900	-2.20657800
O	4.68481300	1.38106700	-0.92209500
H	-0.42556700	1.64582600	1.71614400
H	0.00288500	2.05042200	0.04341600
H	1.08259300	1.02929900	1.01059700
H	-1.20948600	-2.56539800	1.19587300
H	-1.06908700	-1.33573100	2.46518200
H	0.38268300	-1.90260400	1.61435200
C	-3.35258400	2.07186900	-0.45721600
C	-4.11686400	-0.20006500	1.47187100
C	-3.86965000	-0.75762700	-1.54310700
H	3.01916600	-1.43932600	-2.35580200

H	4.02314400	-0.16958700	-3.12013000
H	4.75516500	-1.28290600	-1.92719100
H	-4.40764900	2.32251100	-0.62157700
H	-2.98733000	2.67924900	0.37890100
H	-2.79266700	2.36362600	-1.35330800
H	-3.72805900	0.34682500	2.33866700
H	-5.17691800	0.05800200	1.35777300
H	-4.05226600	-1.27140600	1.69462900
H	-3.76744400	-1.83686700	-1.38087800
H	-4.93628000	-0.53482400	-1.66908300
H	-3.36037200	-0.50868200	-2.48150600

TS6

Si	0.37898500	0.47310400	-0.23234000
C	-2.12853600	1.24782500	-0.34255200
C	0.16927400	-0.06967700	-2.04537600
S	-3.44247600	0.14376900	-0.08201700
H	-2.16039700	1.97309400	0.48104500
H	-2.26384900	1.76434300	-1.30603600
C	-0.31857800	-0.60611600	1.18059100
C	0.57265500	2.35012400	0.05266100
Si	2.67944700	-0.16259800	0.01222800
H	-0.76493700	0.26316300	-2.50329900
H	0.21901300	-1.16410300	-2.11701700
H	1.00743000	0.32593800	-2.63395800
C	-3.13395600	-1.00404100	-1.44568200
O	-4.85490300	0.69725000	-0.43720500
H	0.46279100	-1.11097000	1.76278100
H	-0.98171300	-1.37490100	0.76699700
H	-0.92049500	0.00368200	1.86261000
H	1.59810500	2.69068600	-0.13685500
H	0.33435900	2.58612100	1.09774700
H	-0.10494300	2.93333900	-0.57908400
C	2.95430800	-2.04686600	-0.10689700
C	3.37087700	0.36046700	1.71209500
C	3.85962400	0.59580800	-1.28019200
H	-2.17710700	-1.51176400	-1.30690200
H	-3.94707800	-1.73341800	-1.45806700
H	-3.13364100	-0.43772300	-2.38303200
H	4.00960400	-2.30543200	0.05184100
H	2.36261400	-2.58882600	0.64079900
H	2.66416500	-2.42475900	-1.09516400
H	2.80157600	-0.09477500	2.53197400
H	4.42003200	0.05763200	1.82629200

H	3.32204800	1.44899000	1.84084900
H	3.80330800	1.69105400	-1.28947700
H	4.90103800	0.31788000	-1.07052100
H	3.61967700	0.24348000	-2.29088600

IN4

Si	0.14021700	-0.36810200	0.14382600
C	-1.97013300	-0.86570100	0.26846300
C	0.04121600	0.79495100	1.67075600
S	-3.21976400	0.17107600	-0.45124700
H	-2.08151400	-1.81580000	-0.27393500
H	-2.26250800	-1.03786900	1.31619800
C	-0.13909100	0.19400600	-1.67993700
C	0.51822800	-2.20986500	0.53867300
Si	2.58940300	0.14840100	-0.08840100
H	-0.92597700	0.80816100	2.18423300
H	0.29808500	1.82614200	1.39333500
H	0.80434800	0.46420000	2.38796000
C	-2.92205000	1.70166700	0.45896100
O	-4.63098800	-0.25813500	0.01217700
H	0.76705100	0.13307000	-2.29447300
H	-0.45722500	1.24759000	-1.67876600
H	-0.93202300	-0.38103100	-2.17318300
H	1.41220800	-2.30067100	1.16775000
H	0.72715800	-2.74288600	-0.39925300
H	-0.30708600	-2.73151300	1.03778200
C	2.98535400	1.84345800	-0.90619900
C	3.53158300	-1.10758100	-1.19921000
C	3.64819600	0.18282200	1.51653000
H	-1.92219700	2.08242400	0.23744400
H	-3.67480500	2.42234600	0.13162500
H	-3.03454500	1.50652200	1.52942000
H	4.06862100	2.02042100	-0.96718100
H	2.58228300	1.89821200	-1.92561000
H	2.54627100	2.67371900	-0.33769800
H	3.05278100	-1.22215300	-2.18038400
H	4.57071500	-0.79370200	-1.37310500
H	3.56053500	-2.10095200	-0.73260700
H	3.53159200	-0.74104500	2.09857600
H	4.71782900	0.29907700	1.29072100
H	3.35579500	1.01732500	2.16681100

TS7

Si	-0.23263100	0.62201000	-0.04664600

C	-2.12798700	1.22882400	-0.18374500
C	0.10766700	0.16505100	-1.86006400
S	-3.47267000	0.04193900	-0.13533400
H	-2.34057100	1.89252800	0.66483500
H	-2.26985100	1.81587600	-1.10229300
C	-0.44154900	-0.76893100	1.23477100
C	0.44498500	2.31436400	0.48985500
Si	2.76123700	-0.15659500	0.06936600
H	-0.70713500	0.48192600	-2.52179700
H	0.24410600	-0.91585700	-1.97748000
H	1.02960400	0.64871000	-2.19974100
C	-2.95009200	-1.07389800	-1.45490400
O	-4.73971300	0.72249500	-0.67558900
H	-0.04153300	-1.70834100	0.83886200
H	-1.48555600	-0.93192500	1.53467400
H	0.13819300	-0.52781900	2.13138200
H	1.37290400	2.54733100	-0.03959100
H	0.67310700	2.29703700	1.56244700
H	-0.27604700	3.12233100	0.30955900
C	3.20273300	-1.62472500	-1.13717400
C	4.02407100	-0.57534900	1.49600000
C	3.78656100	1.25265500	-0.80540300
H	-2.03192600	-1.59151500	-1.16369000
H	-3.75329100	-1.80228300	-1.58694900
H	-2.80512100	-0.50373100	-2.37620000
H	4.29204700	-1.76322400	-1.22938300
H	2.77833300	-2.57836300	-0.79279500
H	2.80988100	-1.44714400	-2.14787800
H	3.74116200	-1.49789900	2.02205200
H	5.04798800	-0.71491200	1.11302700
H	4.06015500	0.22237000	2.25074300
H	3.91505800	2.12088500	-0.14382500
H	4.79352700	0.90533500	-1.08737800
H	3.29950500	1.61774900	-1.72065700

CP7

Si	-0.80427400	1.03644000	-0.16892700
C	-2.70896800	0.91122400	-0.05723800
C	-0.22823800	-0.02615300	-1.60659100
S	-3.29821800	-0.77873100	-0.27271200
H	-3.07074100	1.28240300	0.91025500
H	-3.16513200	1.51028000	-0.85619600
C	-0.04330800	0.48648500	1.45322200
C	-0.42040700	2.84608100	-0.49381500

Si	3.83773200	0.06809700	-0.06021500
H	-0.76398400	0.23995200	-2.52575700
H	-0.38828900	-1.09317100	-1.41442300
H	0.84304900	0.12715300	-1.78190300
C	-5.01086800	-0.53584100	0.24435900
O	-2.64674900	-1.61602500	0.82936500
H	1.04540200	0.61554700	1.42750800
H	-0.27607500	-0.56560200	1.64644700
H	-0.43710700	1.08255800	2.28509000
H	-0.83745200	3.17236700	-1.45312300
H	0.66350200	3.00828700	-0.52133900
H	-0.83726500	3.48389800	0.29395100
C	2.80216100	-1.56797100	-0.28000500
C	4.24424400	-0.11419500	1.83601400
C	5.53010500	-0.57825600	-0.77666700
H	-5.49502900	0.16870100	-0.43686700
H	-5.51319400	-1.50462600	0.19698900
H	-5.01619600	-0.15333400	1.26854300
H	3.34114100	-2.43406200	0.13766800
H	1.82953600	-1.51176000	0.22819100
H	2.59962900	-1.78547200	-1.33770100
H	3.34967200	0.02366400	2.45883400
H	4.65637800	-1.11003700	2.06695900
H	4.98008200	0.63237400	2.16433300
H	6.34249500	0.14113900	-0.60607200
H	5.82909300	-1.53243300	-0.31322800
H	5.47200800	-0.74154700	-1.86145300

IN5

Si	1.35561500	0.01586900	0.01639800
C	-0.30762200	0.92488500	0.24845800
C	1.41649700	-0.69850200	-1.71992000
S	-1.70747600	-0.02168300	-0.38143800
H	-0.48796500	1.14056600	1.30933400
H	-0.28962800	1.87338800	-0.30407400
C	1.52796600	-1.33919800	1.29988600
C	2.69575600	1.31205600	0.24471400
H	1.23052200	0.07359100	-2.47519200
H	0.67509800	-1.49416900	-1.85482300
H	2.40556100	-1.12906600	-1.91503200
C	-3.04032300	0.97312800	0.32101600
O	-1.72191700	-1.34379800	0.38720500
H	2.49188700	-1.85017700	1.19361300
H	0.72419200	-2.07282000	1.18479900

H	1.47249400	-0.92695000	2.31386000
H	2.61825800	2.09849500	-0.51424500
H	3.68933100	0.85692700	0.16169800
H	2.62169100	1.78276200	1.23153300
H	-2.99361900	1.98130600	-0.09894300
H	-3.98652500	0.50006700	0.04895300
H	-2.92407800	0.99721500	1.40780700

CP8

Si	0.91395200	-0.00914000	-0.27146500
C	-4.74912800	-1.58393800	-0.27039700
C	0.68083600	0.22407400	-2.13071100
S	-3.38365400	-0.55861100	-0.03465600
H	-5.27166900	-1.32953500	-1.20369100
H	-4.40387300	-2.62339800	-0.28107800
C	0.29098300	-1.72378300	0.21578400
C	-0.07734700	1.31219400	0.64653400
Si	3.17893400	0.20930900	0.28844100
H	-0.38459500	0.08380300	-2.35126600
H	1.26515300	-0.50368500	-2.70635500
H	0.98188800	1.22872300	-2.45049000
C	-4.23719400	1.03017000	0.13384700
O	-2.50908200	-0.31153100	-1.30094800
H	-0.76258100	-1.80862600	-0.07552000
H	0.37461900	-1.89336500	1.29569700
H	0.85941700	-2.51017200	-0.29486400
H	-0.04445500	1.15606800	1.73123100
H	-1.12146700	1.26449500	0.31712900
H	0.30662900	2.31818500	0.43852200
C	4.07092100	-1.45264200	0.12669100
C	3.35904600	0.82513100	2.06916400
C	4.00873000	1.45793800	-0.86696200
H	-3.48467400	1.82130900	0.16806400
H	-4.87875300	1.16864100	-0.74315100
H	-4.83551700	1.03933400	1.04660600
H	3.65380500	-2.19205300	0.82026900
H	3.97536300	-1.85475200	-0.88881300
H	5.14000300	-1.34762800	0.34882600
H	2.88167500	0.13760400	2.77715100
H	4.41609900	0.91615500	2.34749600
H	2.89217800	1.80941200	2.19126000
H	3.98503200	1.10711400	-1.90534800
H	3.49910900	2.42806800	-0.82933600
H	5.05748800	1.61606200	-0.58719200

TS8

Si	0.36933000	-0.28336400	-0.22619500
C	4.20448400	-0.52651500	1.20950400
C	0.10067400	1.10826100	-1.48146500
S	3.56702300	-0.18008100	-0.27130000
H	3.74477900	-0.14566200	2.11753500
H	4.74151100	-1.46876100	1.25593900
C	0.55693600	0.13121400	1.61218400
C	-0.40665100	-1.94644300	-0.67181800
Si	-2.74285300	0.24298000	0.31348400
H	0.90214500	1.11470800	-2.23100200
H	0.07632600	2.08731700	-0.98947400
H	-0.85472800	0.97826500	-1.99727600
C	3.17143000	1.57553900	-0.12812800
O	2.03016600	-0.75349500	-0.63857700
H	-0.16532600	-0.44770600	2.19459700
H	0.34718000	1.18946700	1.79898700
H	1.56344300	-0.10221800	1.97864400
H	-1.32100900	-1.83521300	-1.26181900
H	-0.66161400	-2.50175600	0.23836100
H	0.31070600	-2.54470300	-1.24525500
C	-3.92007200	1.53079100	1.18984500
C	-3.57143800	-1.38945000	0.99146600
C	-3.57670900	0.26954700	-1.44964600
H	4.11357300	2.11779100	-0.04298100
H	2.63702500	1.89109300	-1.02427800
H	2.56246900	1.74389800	0.76429800
H	-4.98491800	1.29631100	1.02936000
H	-3.74937400	1.55559900	2.27510900
H	-3.74816200	2.55052800	0.81843100
H	-3.32287800	-1.56642300	2.04744000
H	-4.67006400	-1.34935600	0.91446000
H	-3.23759900	-2.27407700	0.43221300
H	-3.12943600	-0.46460400	-2.13463500
H	-4.65456400	0.04828700	-1.39109000
H	-3.47133100	1.25520800	-1.92480200

CP9

Si	0.92421200	0.14701900	-0.60575600
C	3.64884800	-1.13756200	1.73203400
C	1.11121200	1.83721100	-1.40109700
S	3.79112600	-0.87311700	0.13051900
H	3.23309000	-0.38458500	2.39461400

H	3.65031100	-2.17837500	2.03652000
C	0.53470400	0.37759000	1.21564800
C	-0.43287400	-0.79829500	-1.47911100
Si	-3.85869200	0.56390000	0.15180600
H	1.46138800	1.75173500	-2.43614900
H	1.81129600	2.47666500	-0.85305200
H	0.13737900	2.34294600	-1.41657300
C	4.17381200	0.88663100	0.03645600
O	2.32592600	-0.76605700	-0.83279600
H	-0.41970800	0.91301600	1.30324000
H	1.29761700	0.98177300	1.72014100
H	0.44191800	-0.57543500	1.74745100
H	-1.37270900	-0.23509700	-1.42529500
H	-0.59411500	-1.78445000	-1.03034600
H	-0.18196200	-0.94060400	-2.53676700
C	-5.55990200	0.77170800	1.07796400
C	-3.02973400	-0.71239600	1.36959800
C	-4.44045600	-0.70013100	-1.21226600
H	5.20372600	1.01950300	0.37055000
H	4.06404300	1.20874500	-0.99942200
H	3.49475100	1.44028500	0.69021800
H	-6.01069900	-0.20416200	1.32136600
H	-5.44435600	1.32588000	2.01930800
H	-6.28487300	1.32763700	0.46787600
H	-2.72980800	-0.24486700	2.31747000
H	-3.72352700	-1.53431700	1.61110900
H	-2.12787500	-1.16407400	0.93450600
H	-3.59434200	-1.11083000	-1.78011600
H	-4.98075000	-1.55056900	-0.76539300
H	-5.11458800	-0.22632200	-1.93879900

IN6

Si	1.40846000	0.13601800	-0.18729500
C	-1.96059100	-1.08853600	0.52178200
C	2.67774100	1.22609700	-1.02246100
S	-1.48319100	0.46772000	0.54182900
H	-2.31046700	-1.55373200	-0.39571400
H	-1.59689600	-1.70581700	1.33572300
C	1.42634700	-1.58245300	-0.93730700
C	1.73146200	0.02156600	1.65805300
H	2.67592000	2.23440900	-0.59478800
H	2.47432500	1.31003700	-2.09576800
H	3.68338100	0.80659200	-0.90130600
C	-2.57564100	1.27479000	-0.63820000

O	-0.08316300	0.87674400	-0.45851900
H	2.42588300	-2.02661900	-0.85725400
H	1.15519900	-1.55068800	-1.99863100
H	0.71862400	-2.24437900	-0.42577300
H	1.03935400	-0.66911500	2.15360700
H	1.63754700	1.00184900	2.13911700
H	2.74849500	-0.34620700	1.83932500
H	-2.20828500	2.28512000	-0.81440900
H	-2.56919700	0.69815200	-1.56550500
H	-3.57467600	1.29707300	-0.20187400

References

(1) A. Simonneau, M. Oestreich, 3-Silylated Cyclohexa-1,4-dienes as Precursors for Gaseous Hydrosilanes: The $B(C_6F_5)_3$-Catalyzed Transfer Hydrosilylation of Alkenes. *Angew. Chem. Int. Ed.* **2013**, *52*, 11905.

(2) M. L. Kwan, C. W. Yeung, K. L. Breno, K. M. Doxsee, Stereoselective One-pot Synthesis of Vinylsilanes from Aromatic Aldehydes. *Tetrahedron Lett.* **2001**, *42*, 1411.

(3) L. F. Cason, H. G. Brooks, The Addition of Organolithium Compounds to Vinyltriphenyl- and Vinyltrimethyl-Silanes. *J. Org. Chem.* **1954**, *19*, 1278.

(4) T. Beppu, K. Sakamoto, Y. Nakajima, K. Matsumoto, K. Sato, S. Shimada, Hydrosilane Synthesis via Catalytic Hydrogenolysis of Halosilanes Using a Metal-ligand Bifunctional Iridium Catalyst. *J. Organomet. Chem.* **2018**, *869*, 75.

(5) C. Wang, L. Yan, Z. Zheng, D. Yang, Y. Pan, Synthesis of (E)-alkenes via Hydroindation of C≡C in $InCl_3$–$NaBH_4$ System. *Tetrahedron.* **2006**, *62*, 7712.

(6) D. R. Weyenberg, L. H. Toporcer, A. E. Bey, The Disilylation of Styrene and α-Methylstyrene. The Trapping of Short-Lived Intermediates from Alkali Metals and Aryl Olefins. *J. Org. Chem.* **1965**, *30*, 4096.

(7) C. A. Laskowski, D. J. Bungum, S. M Baldwin, S. A. Del Ciello, V. M. lluc, G. L. Hillhouse, Synthesis and Reactivity of Two-Coordinate Ni(I) Alkyl and Aryl Complexes. *J. Am. Chem. Soc.* **2013**, *135*, 18272.

(8) M. Rubin, T. Schwier, V. Gevorgyan, Highly Efficient $B(C_6F_5)_3$-Catalyzed Hydrosilylation of Olefins. *J. Org. Chem.* **2002**, *67*, 1936.

(9) J. A. Bailey, H. A. Sparkes, P. G. Pringle, Single Oxygen-Atom Insertion into P–B Bonds: On- and Off-Metal Transformation of a Borylphosphine into a Borylphosphinite. *Chem. Eur. J.* **2015**, *21*, 5360.

(10) W.-Z. Weng, H. Liang, B. Zhang. Visible-Light-Mediated Aerobic Oxidation of Organoboron Compounds Using in Situ Generated Hydrogen Peroxide. *Org. Lett.* **2018**, *20*, 4979.

(11) J.-Z. Zhang, Y. Tang, Iron-Catalyzed Regioselective Oxo- and Hydroxy-Phthalimidation of Styrenes: Access to α-Hydroxyphthalimide Ketones. *Adv. Synth. Catal*. **2016**, *358*, 752.

(12) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.

(13) W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, **1986**.

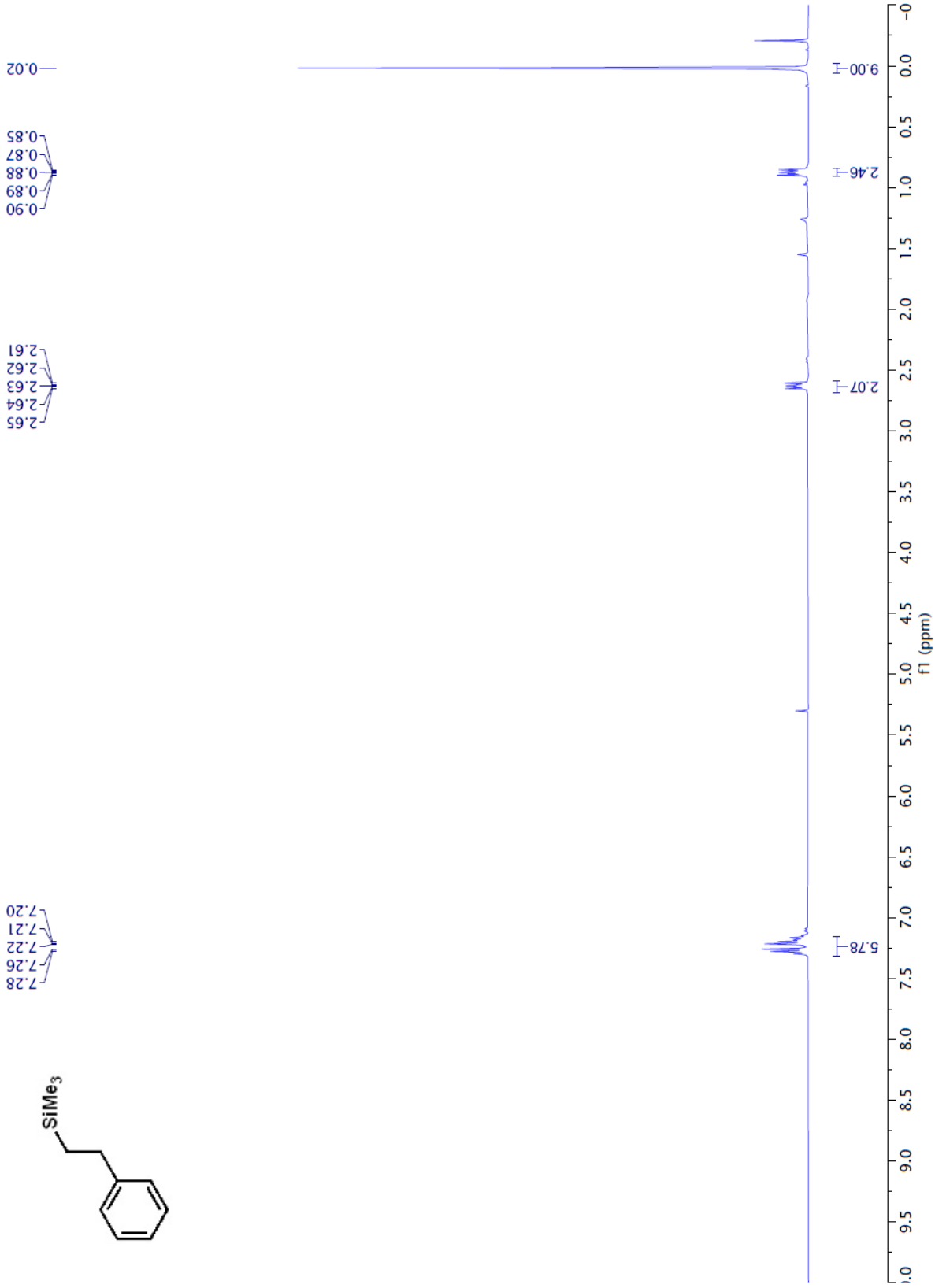
(14) A. V. Marenich, C. J. Cramer, D. G. Truhlar. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem., B.* **2009**, *113*, 6378.

(15) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople. Self-Consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions. *J. Chem. Phys.* **1980**, *72*, 650.

(16) Legault, C. Y. CYLview, 1.0b; Université de Sherbrooke, **2009**. http://www.cylview.org.

(17) X. Wang, M.-H. Zhu, D. P. Schuman, D. Zhong, W.-Y. Wang, L.-Y. Wu, W. Liu, B. M. Stoltz, W.-B. Liu, General and Practical Potassium Methoxide/Disilane-Mediated Dehalogenative Deuteration of (Hetero)Arylhalides. *J. Am. Chem. Soc.* **2018**, *140*, 10970.

NMR Spectra



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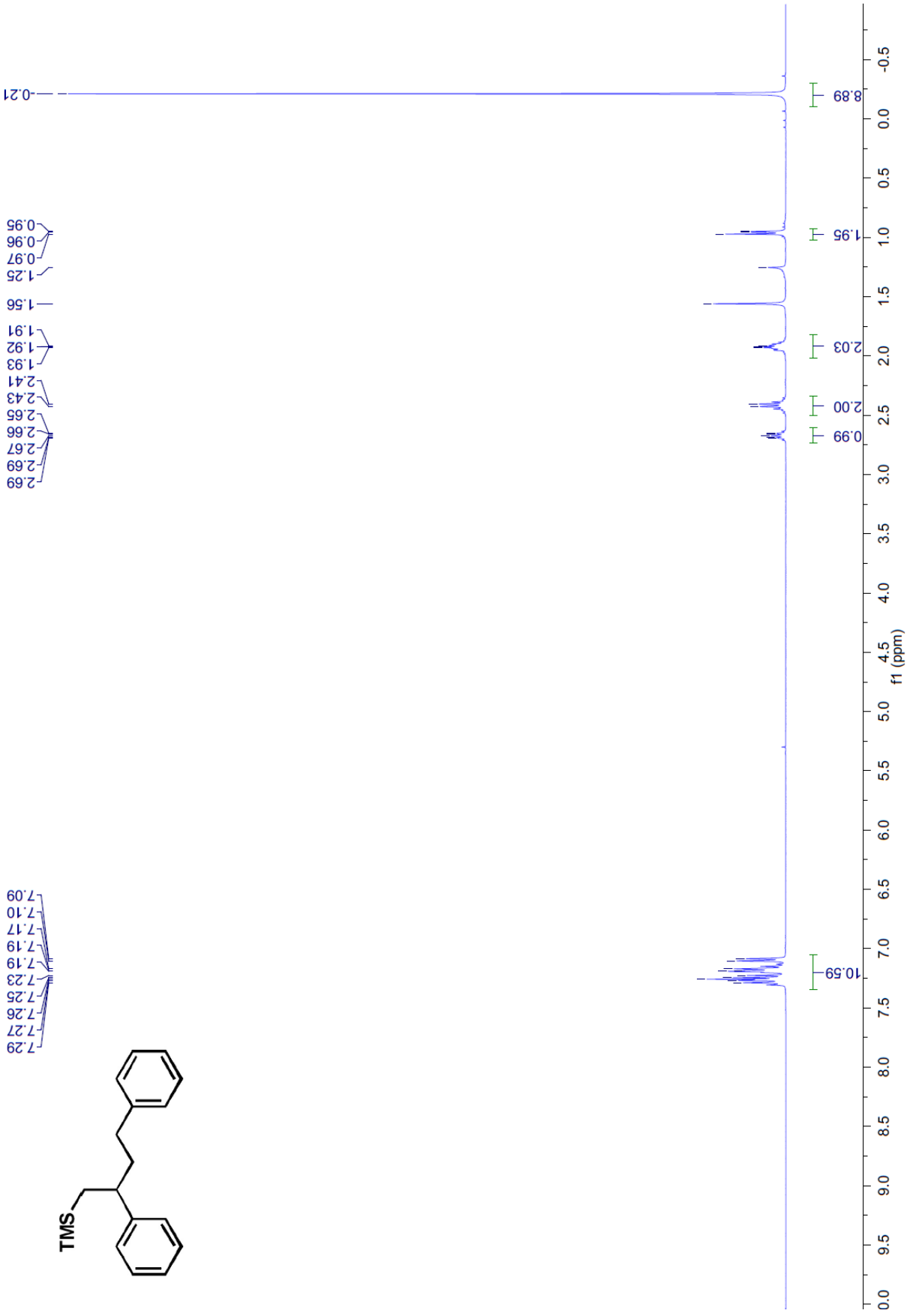

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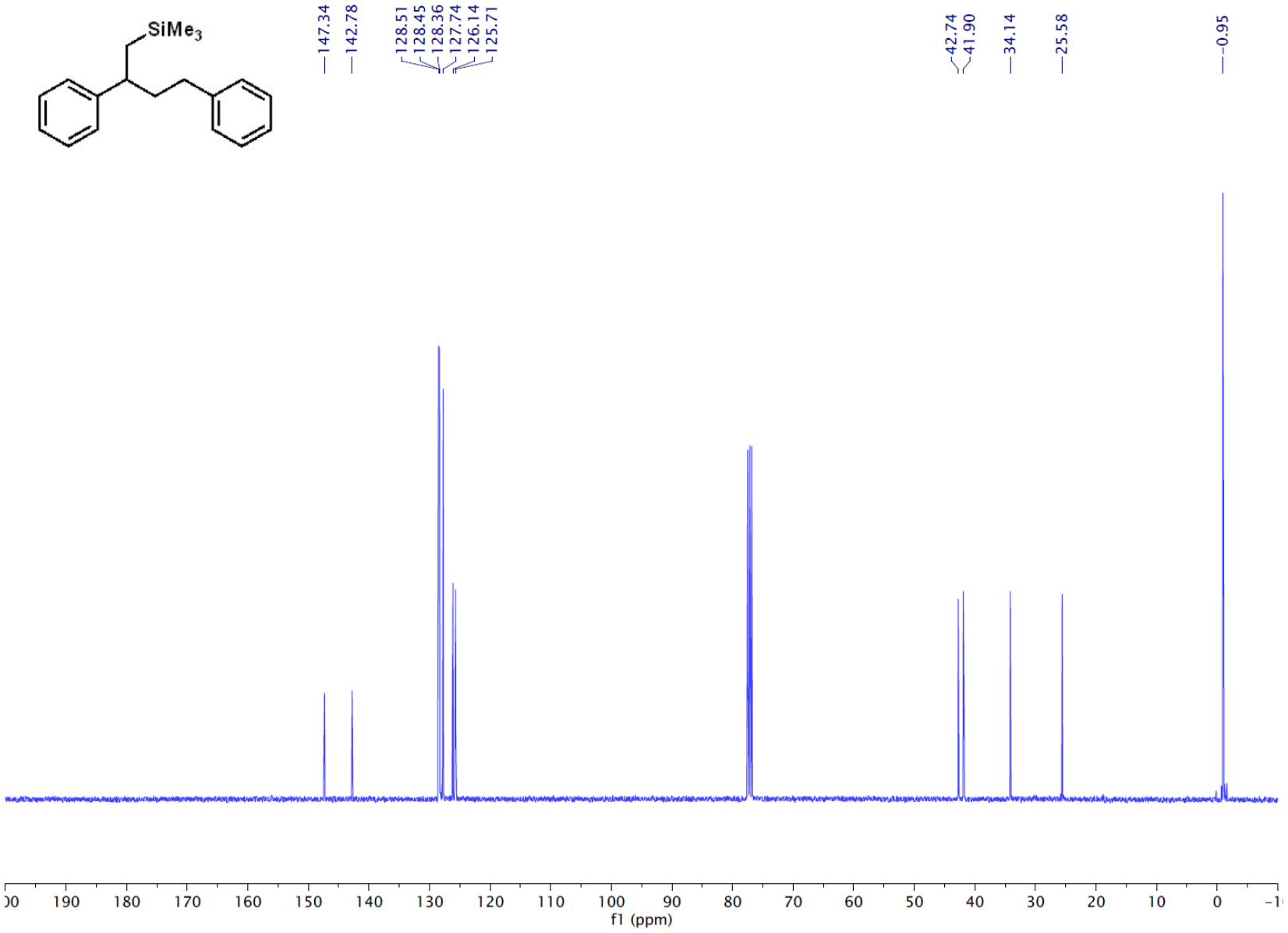

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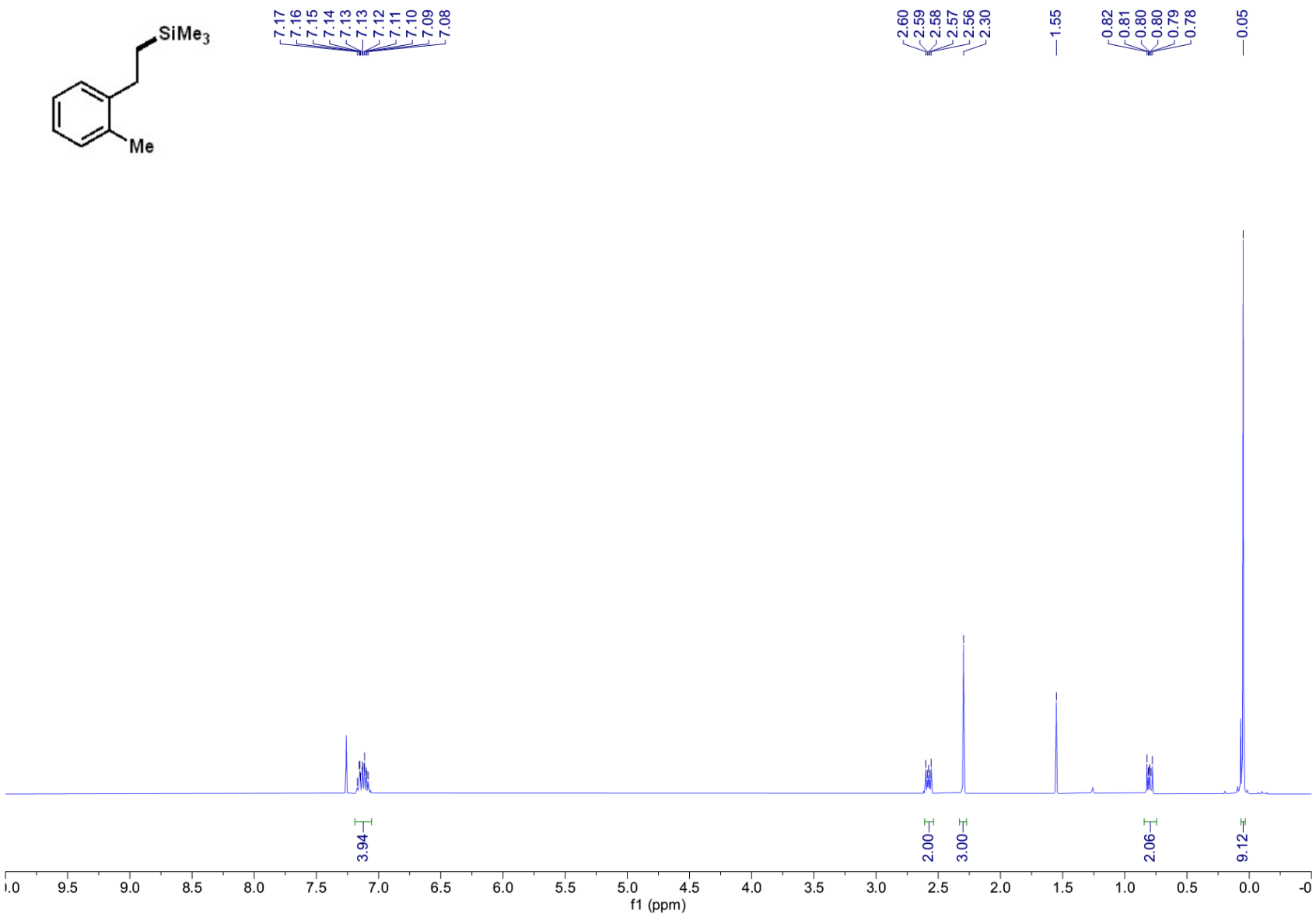

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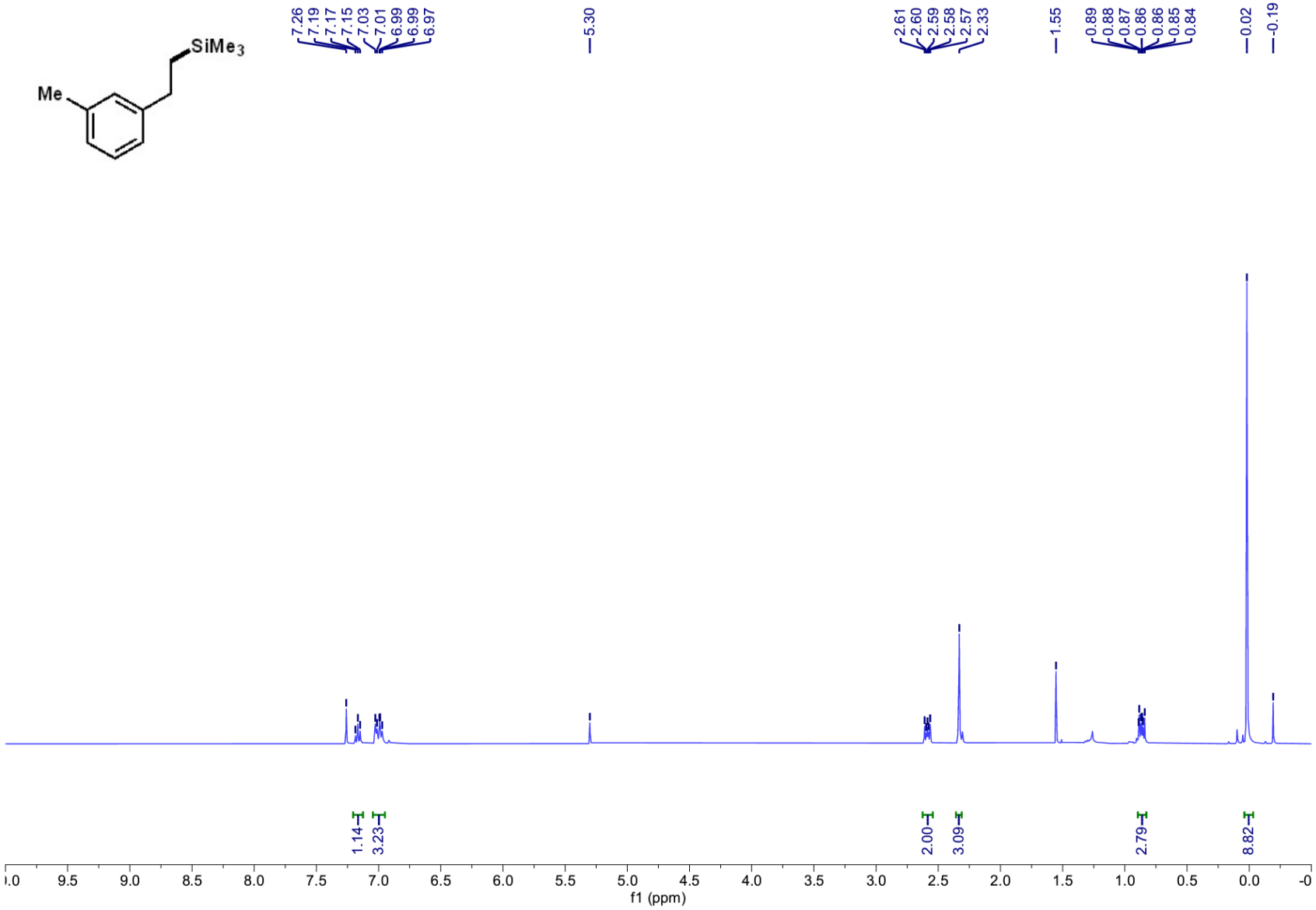

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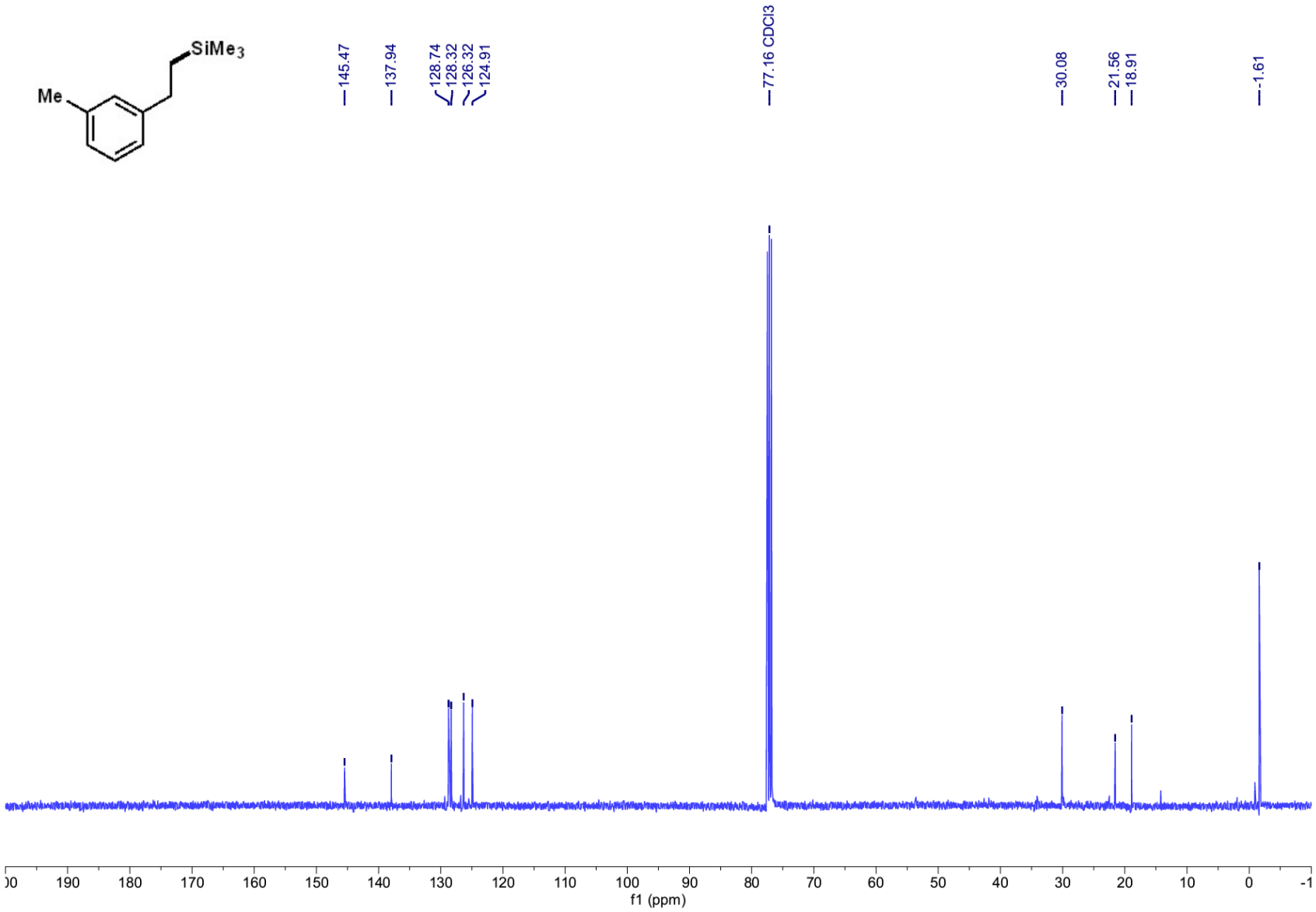

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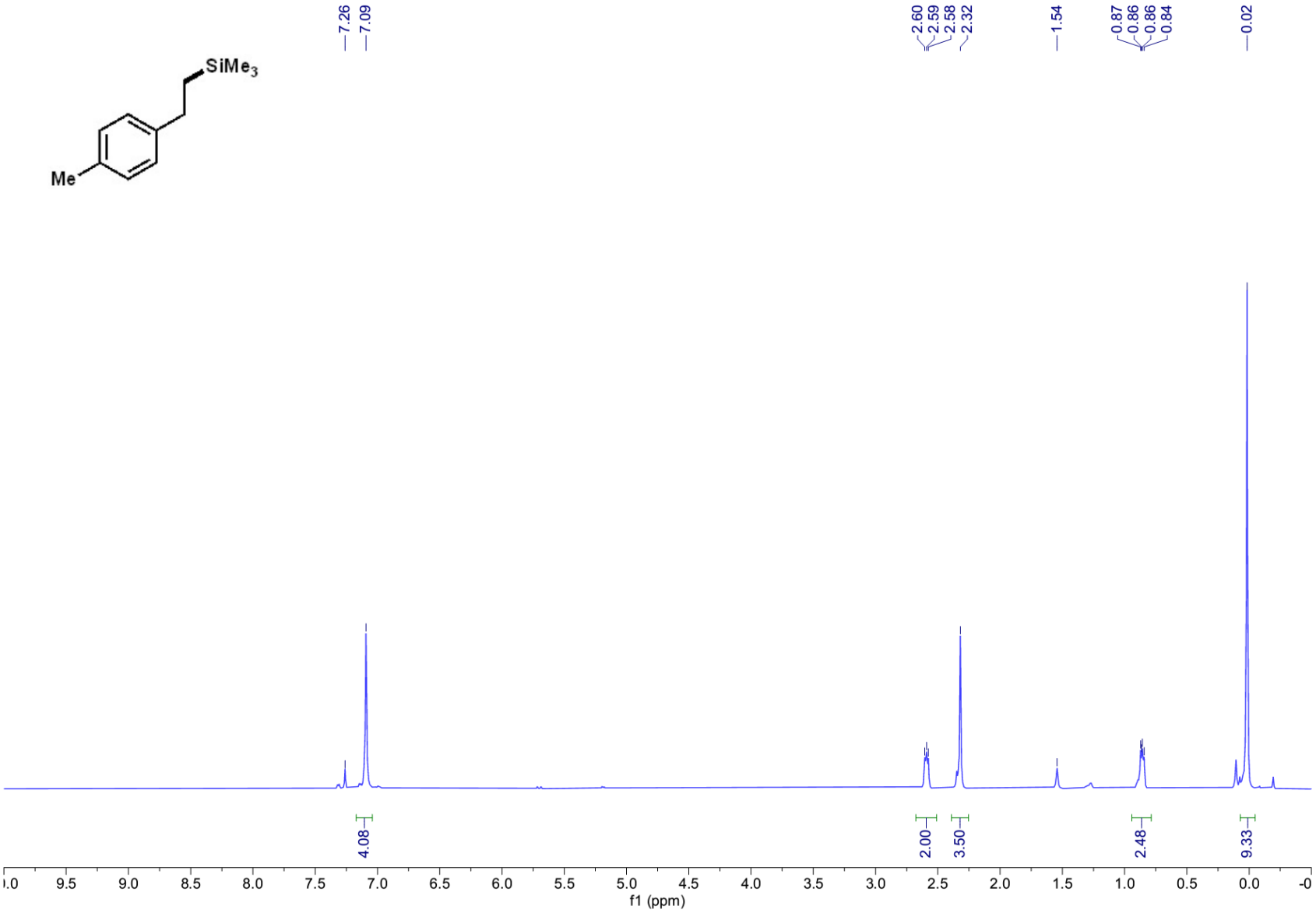

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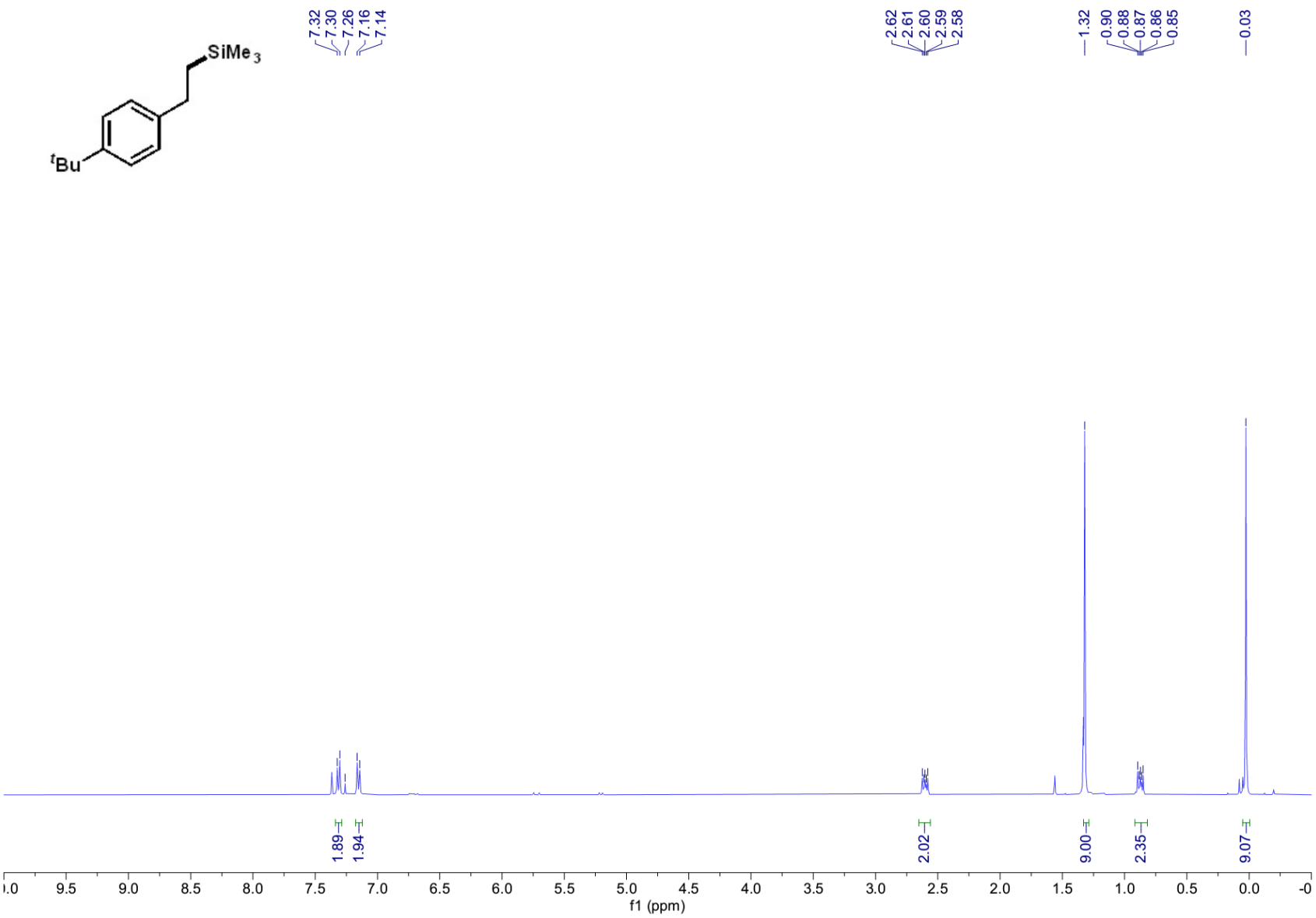

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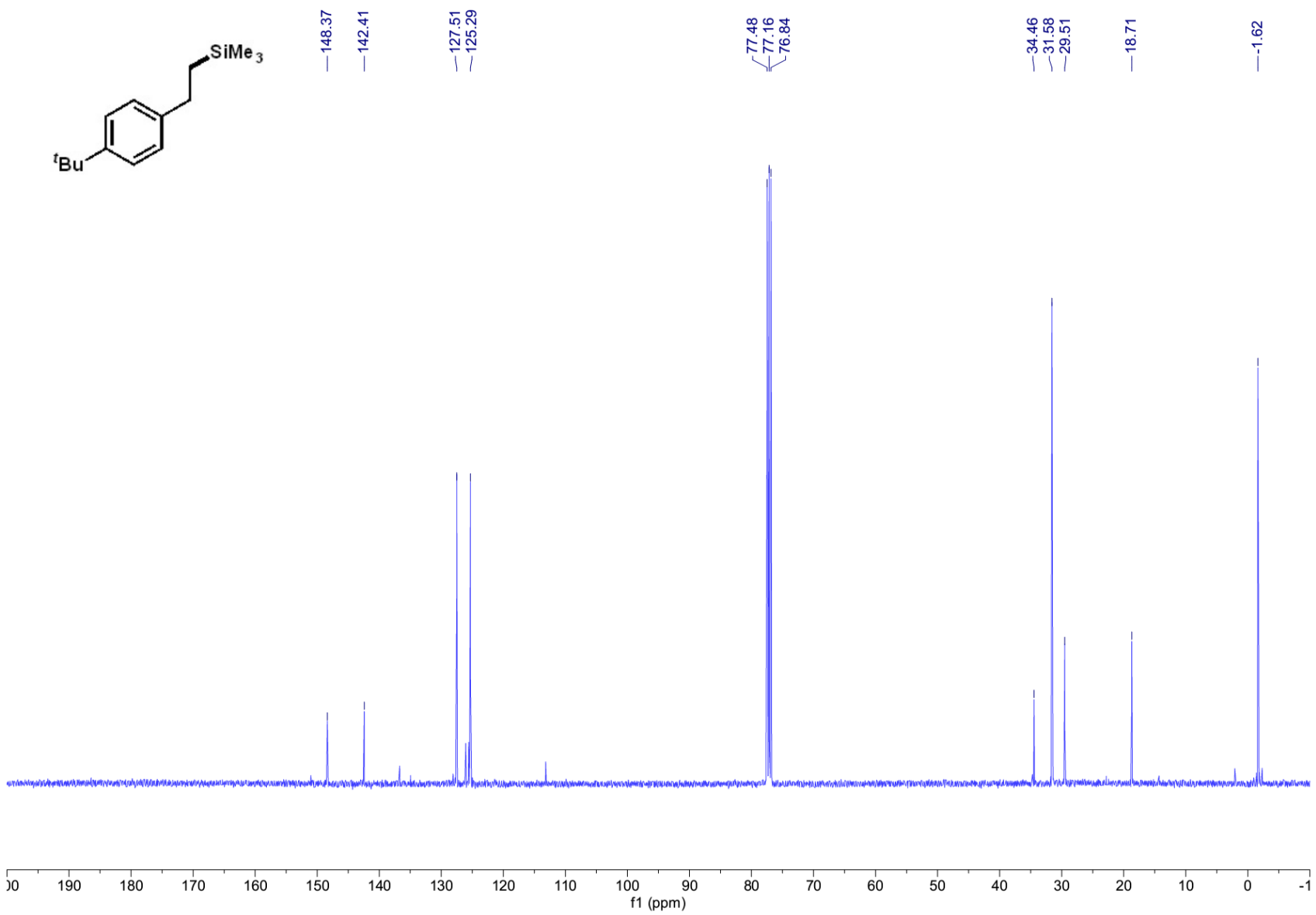

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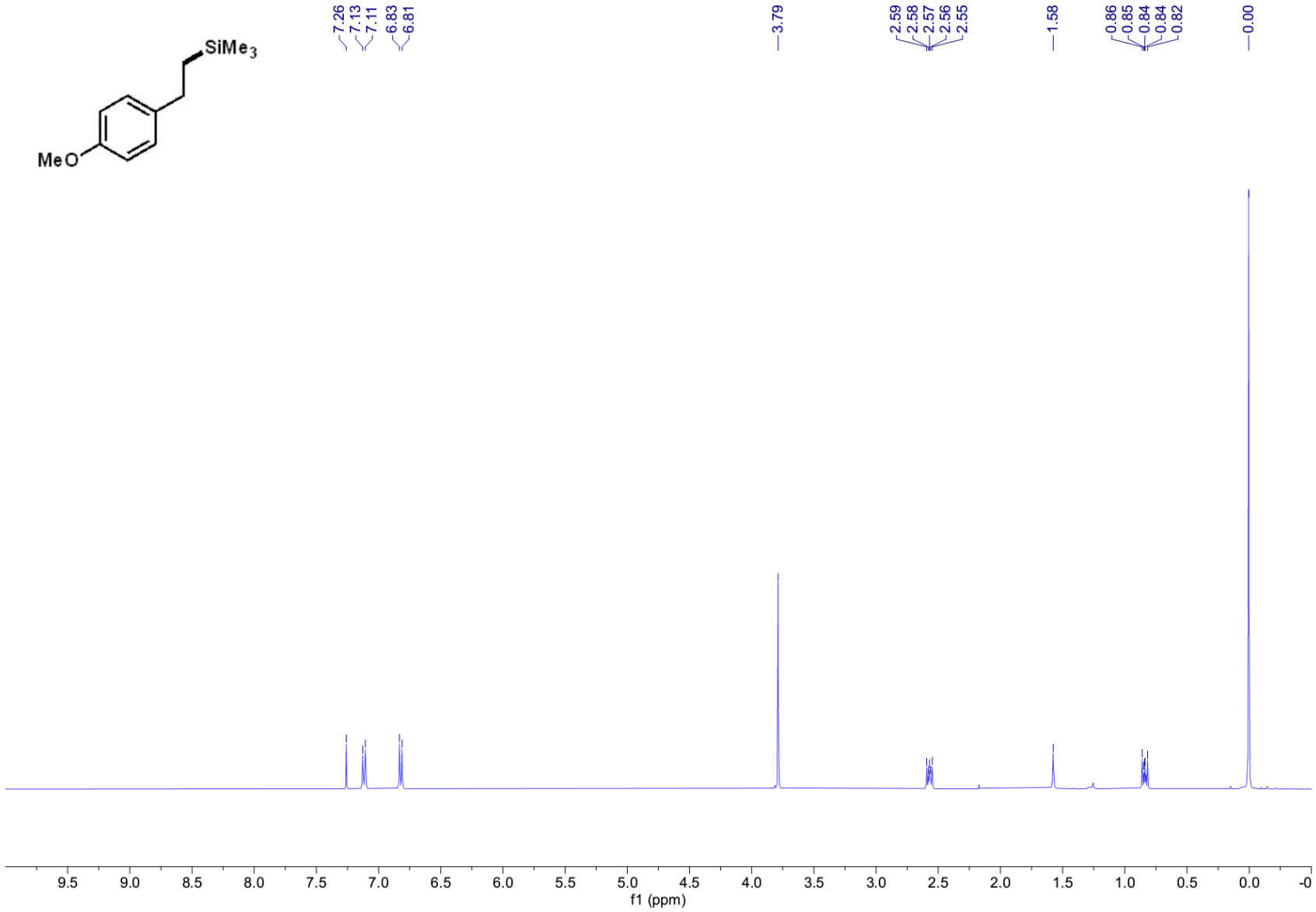

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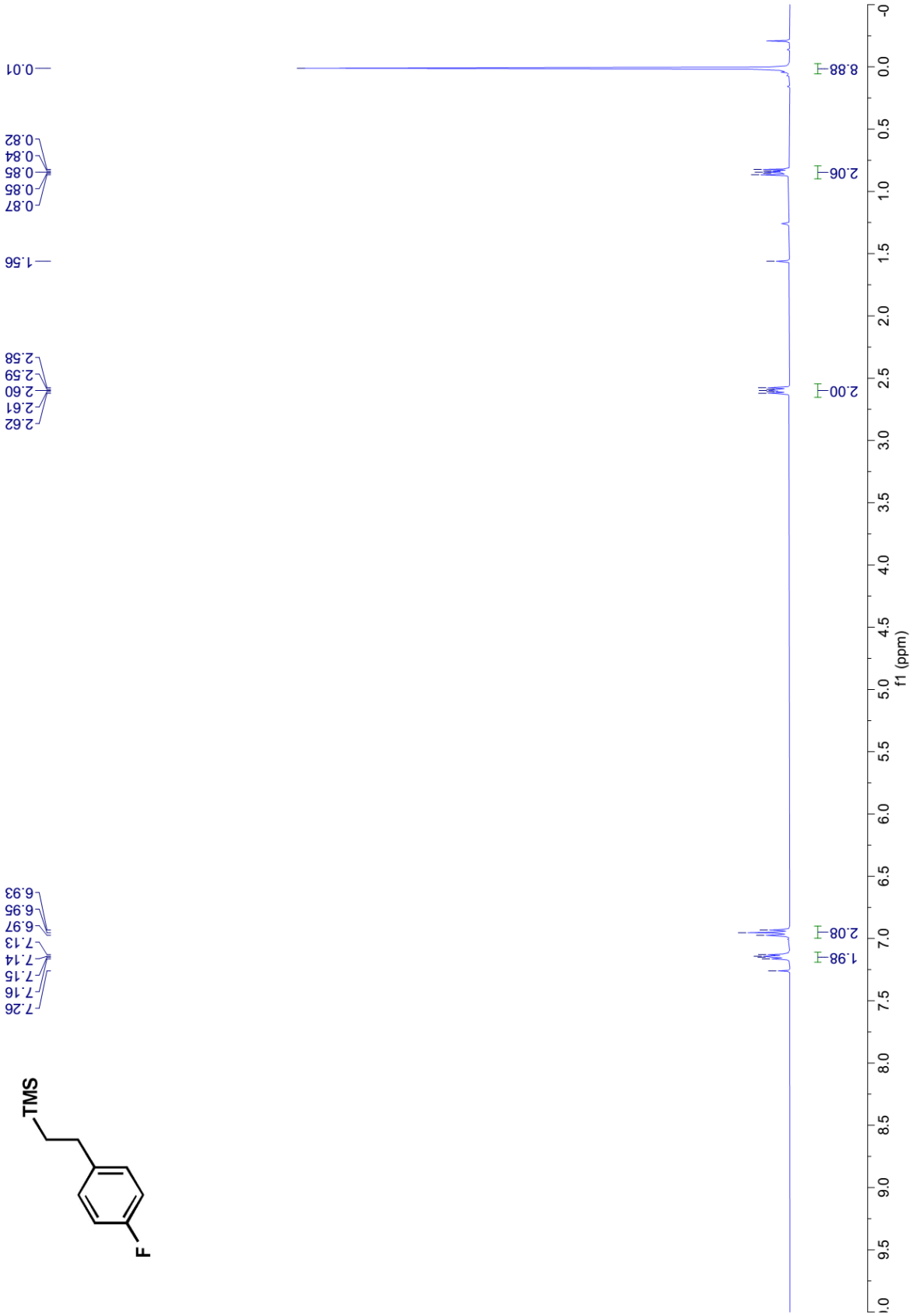

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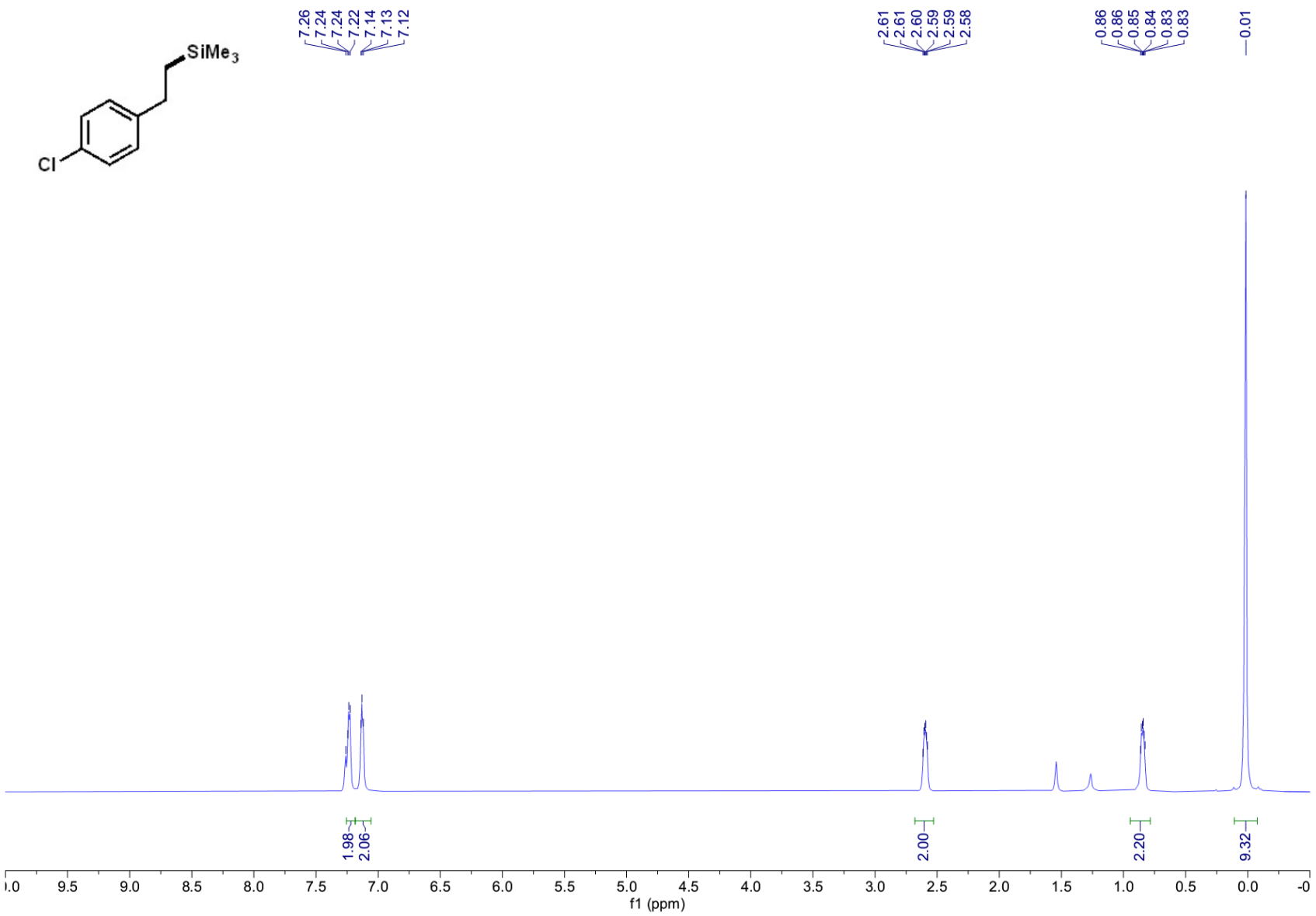

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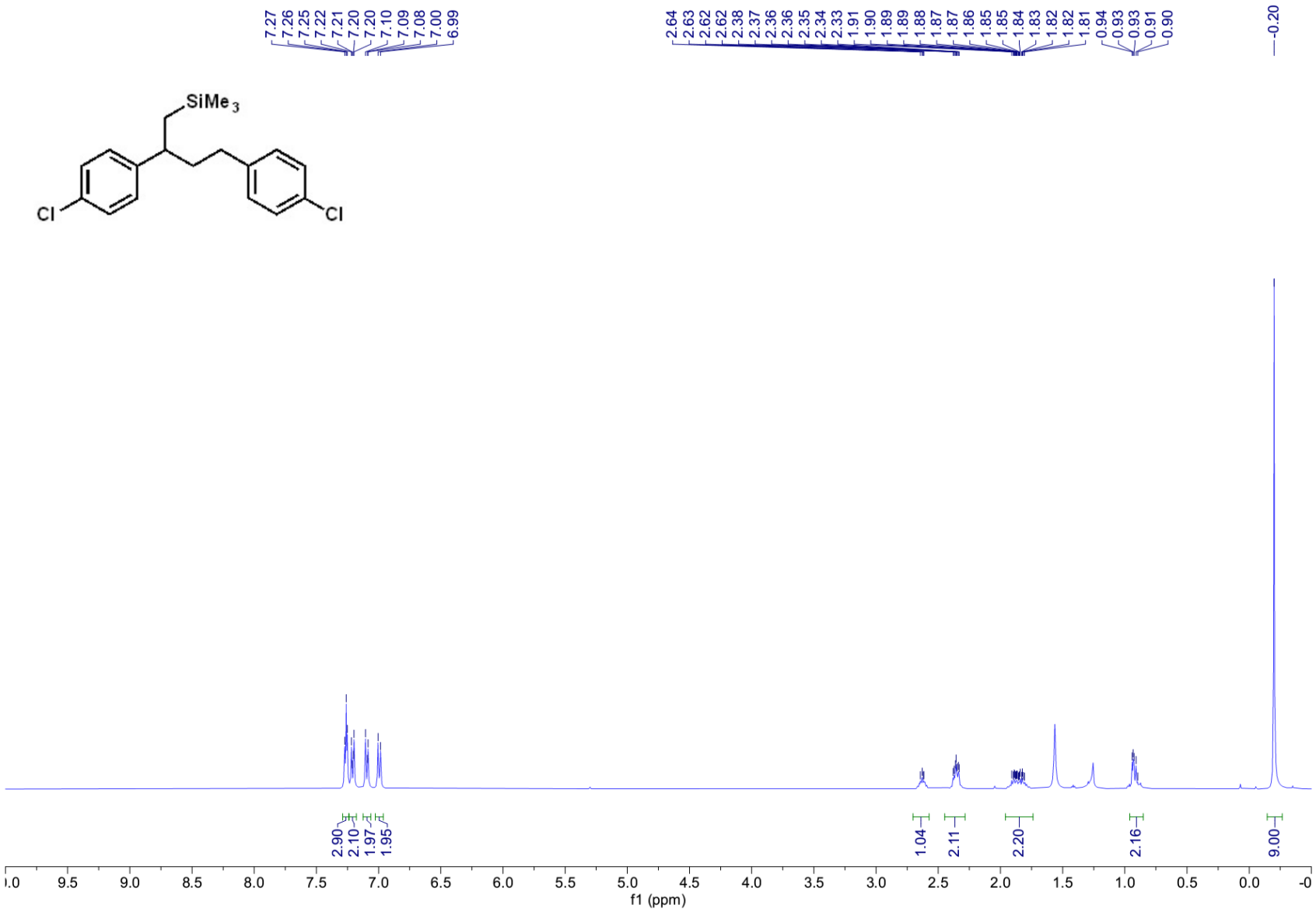

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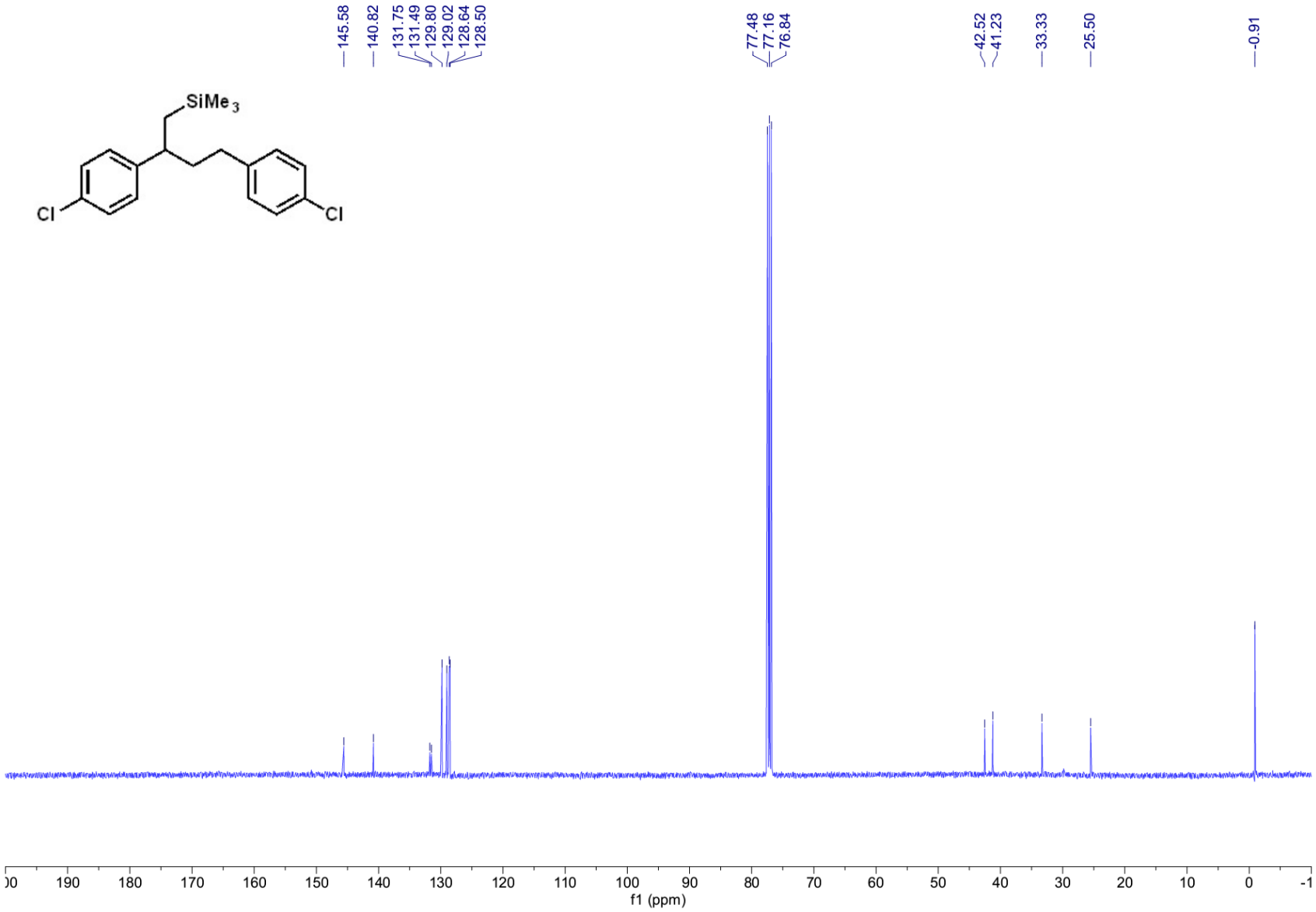

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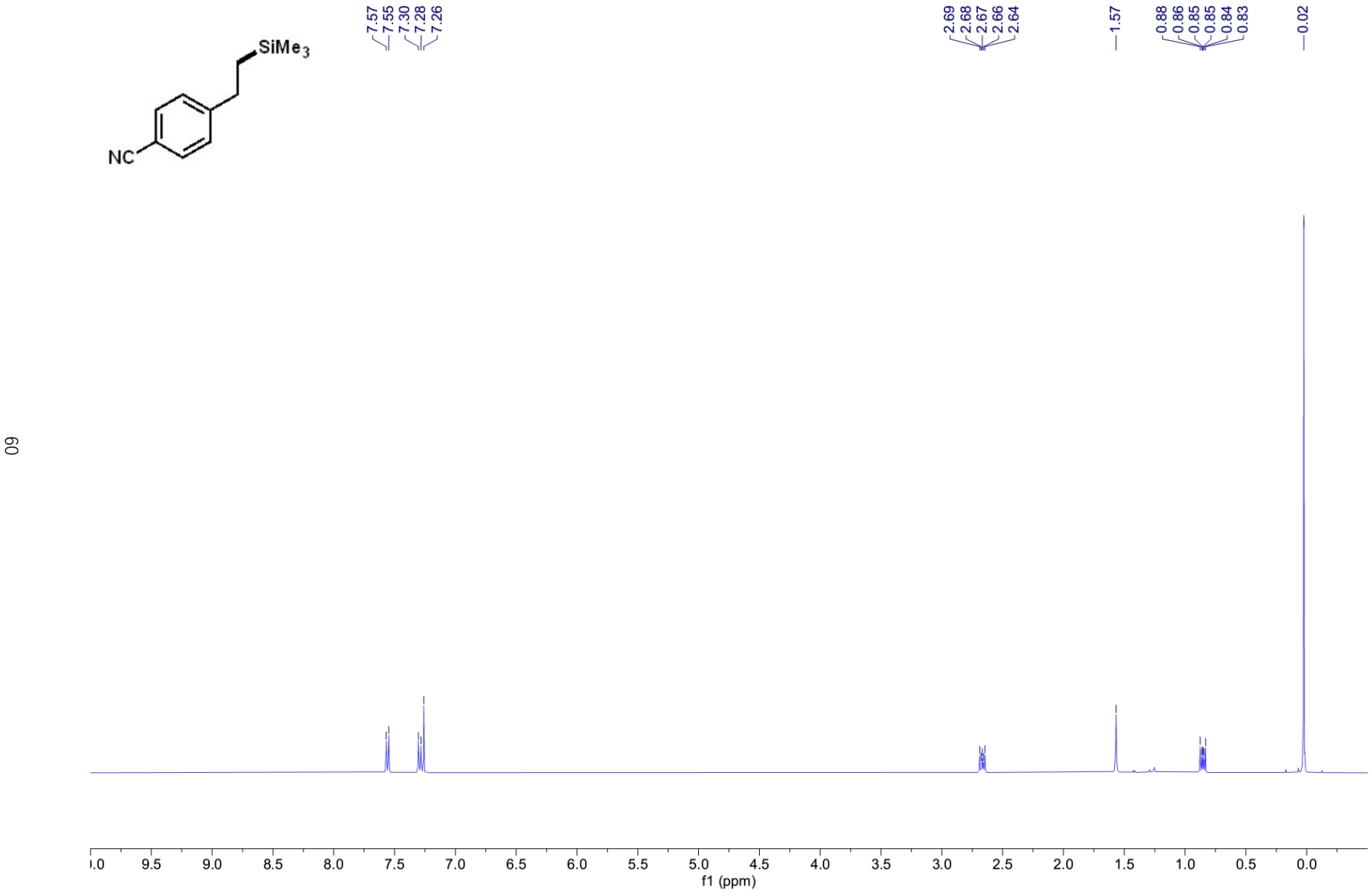

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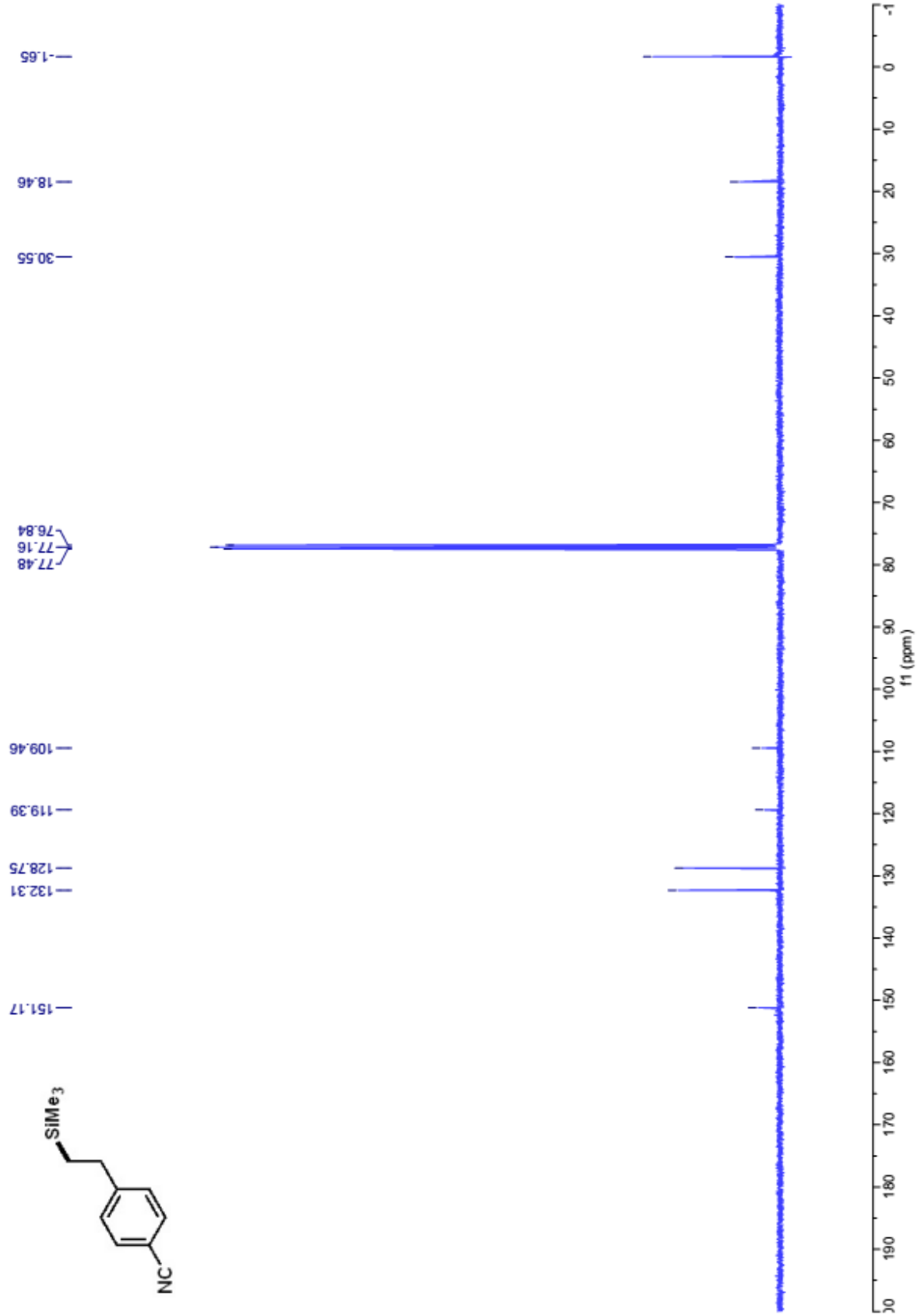

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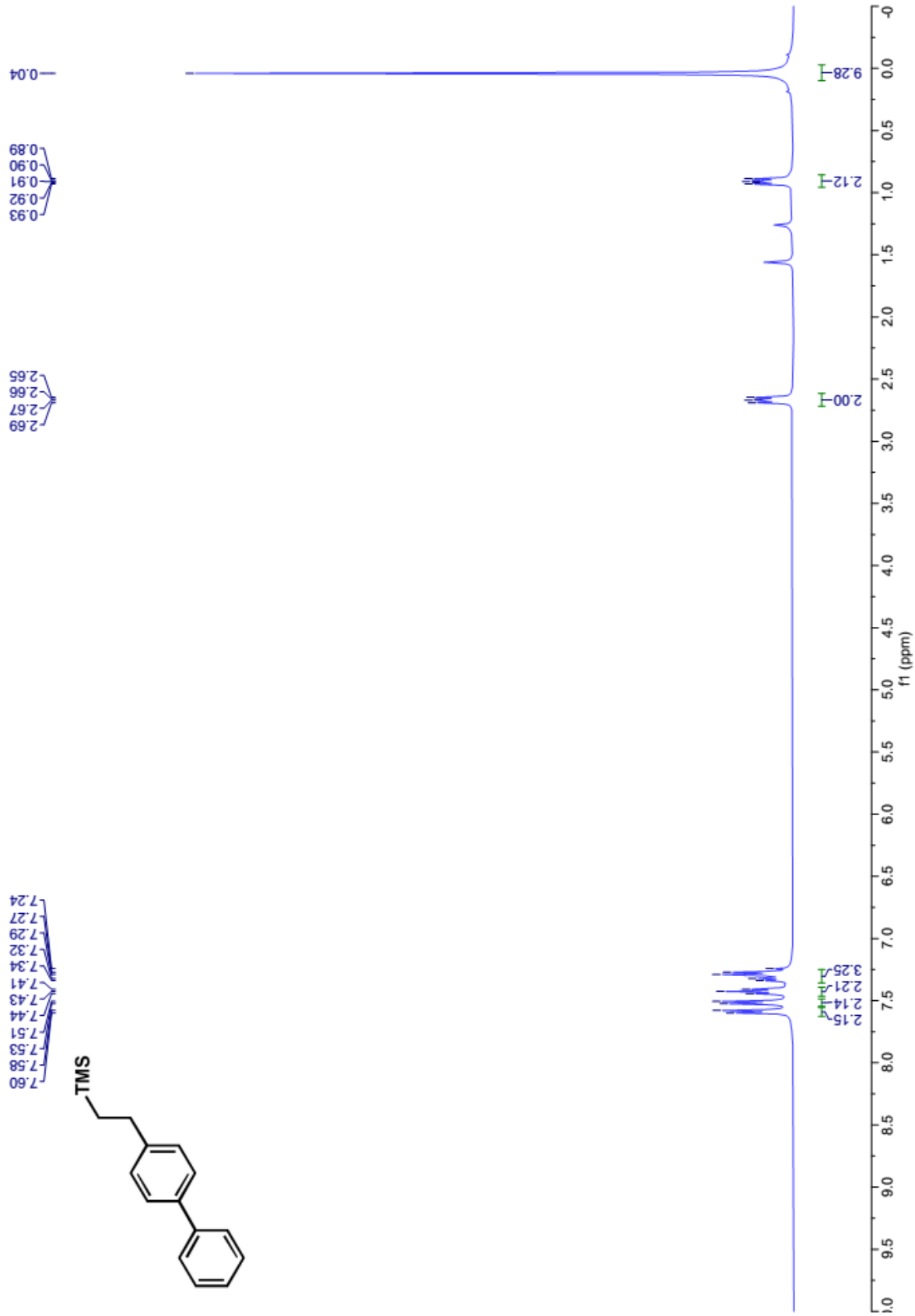

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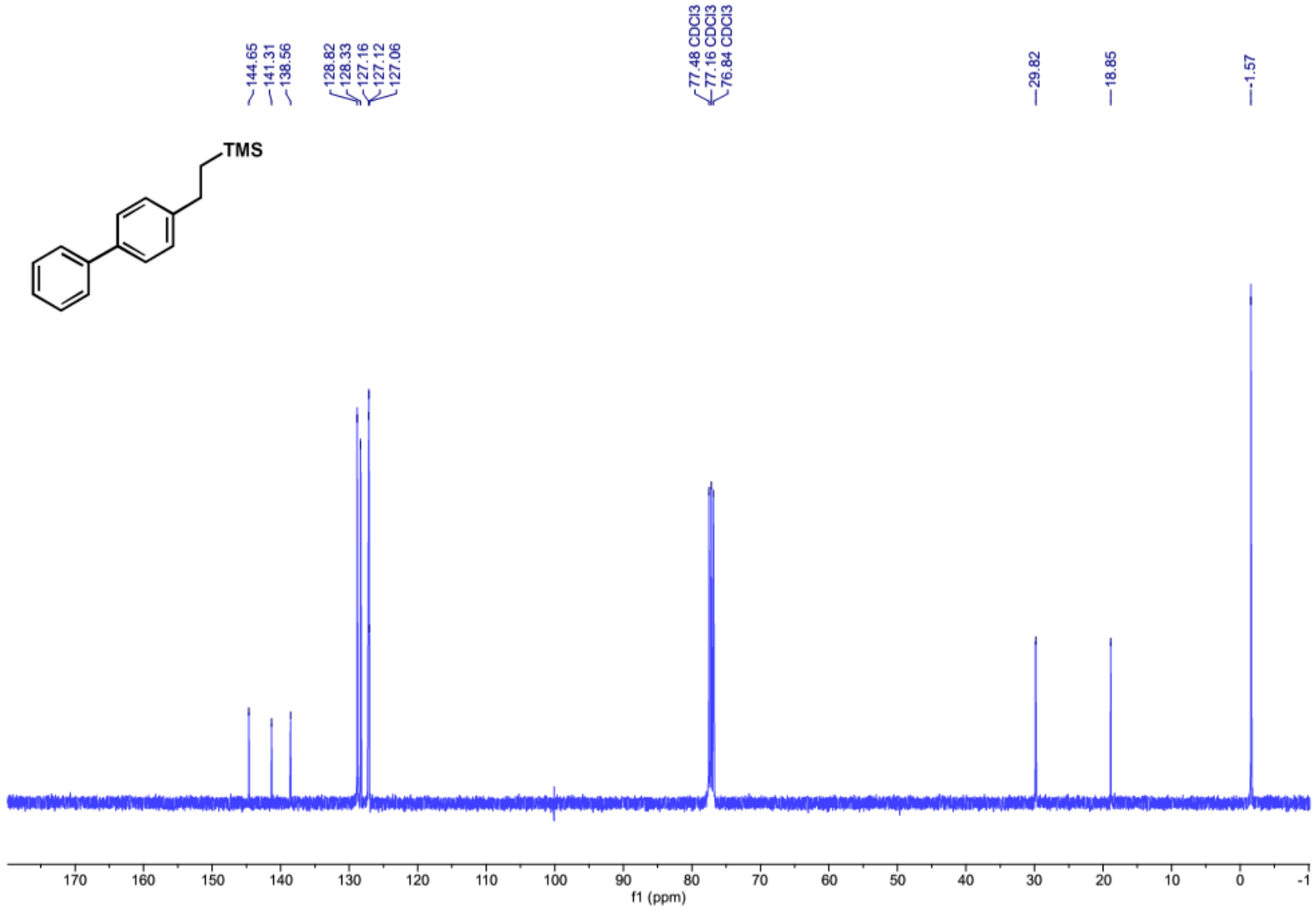

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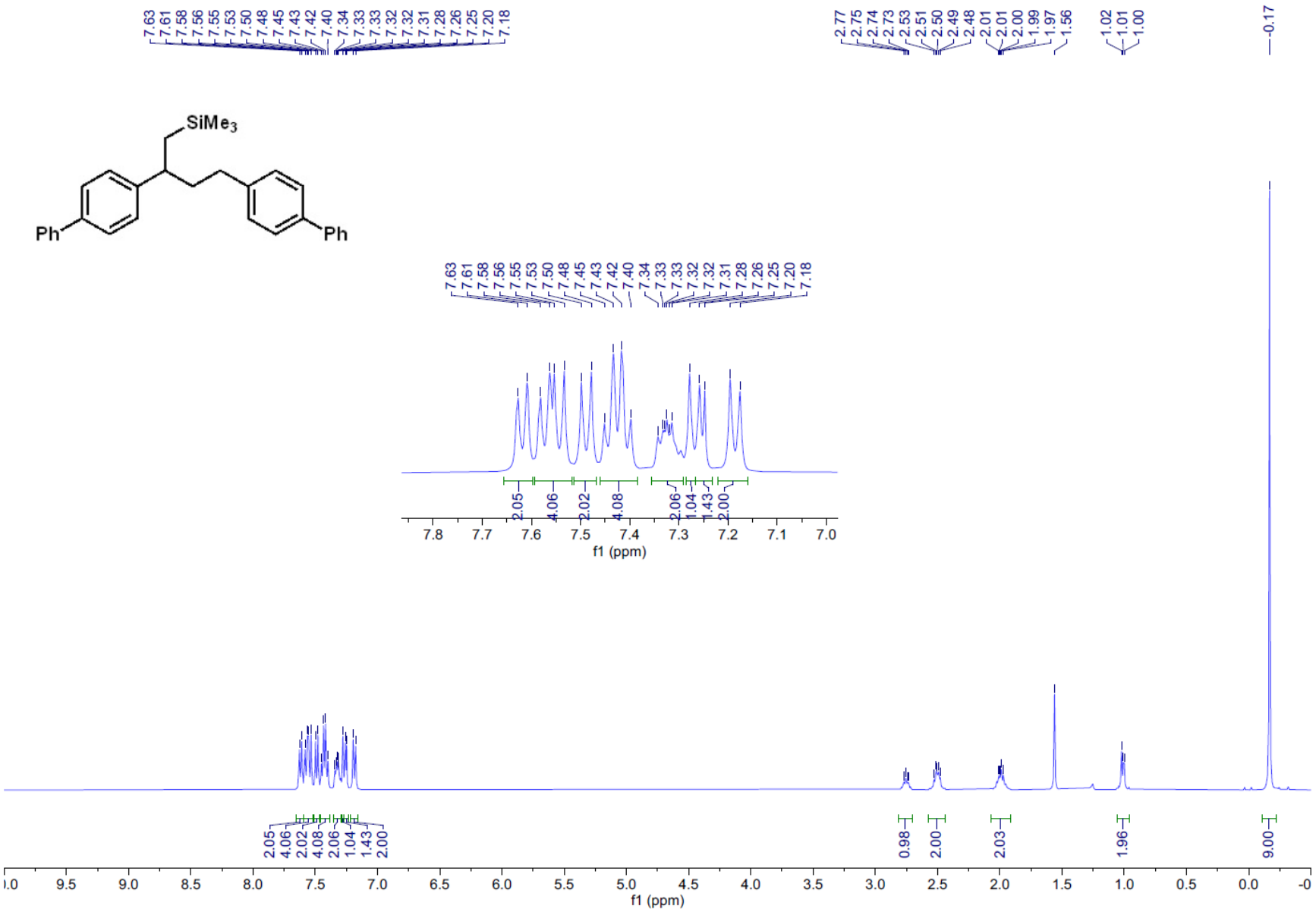

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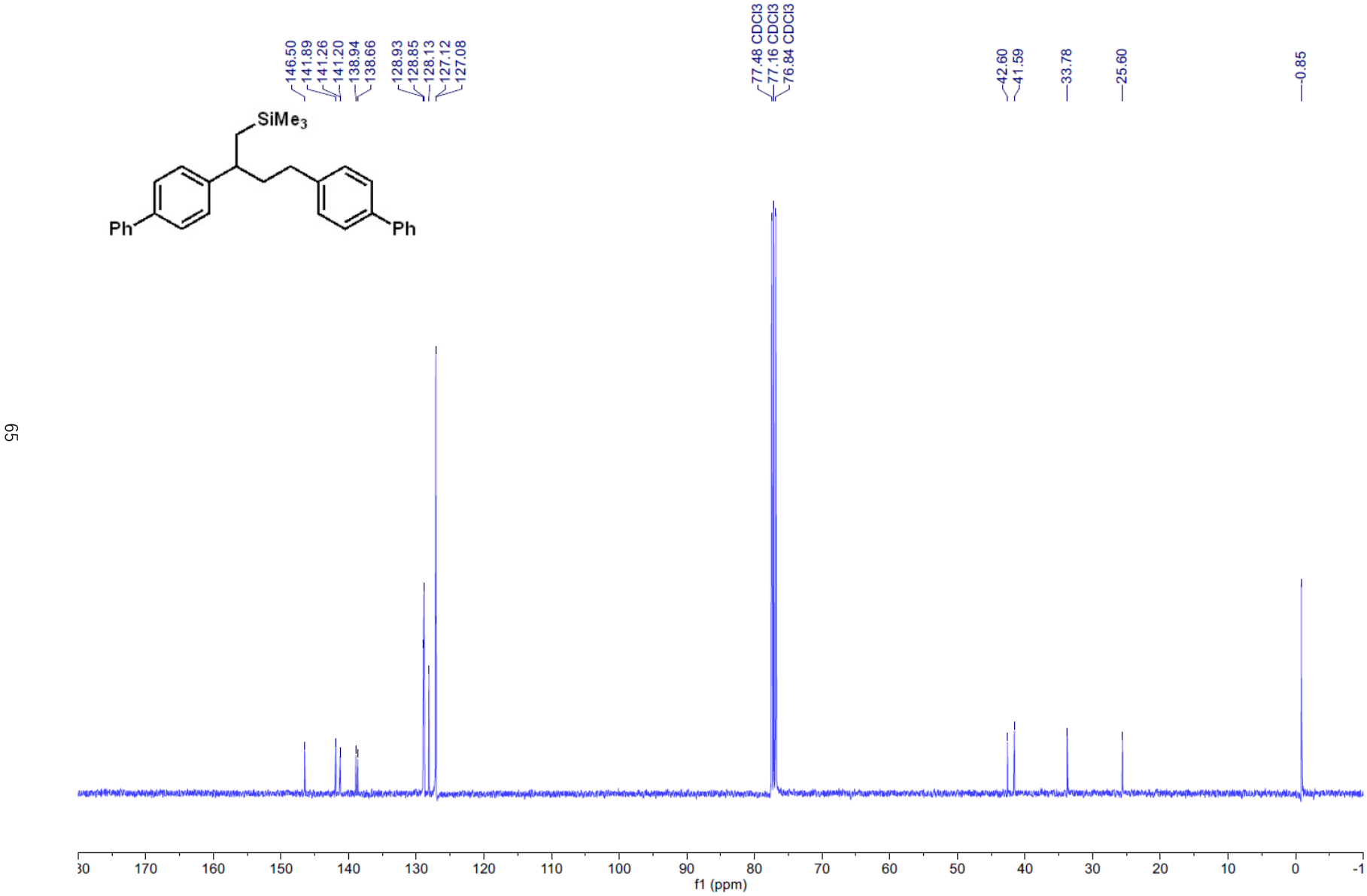

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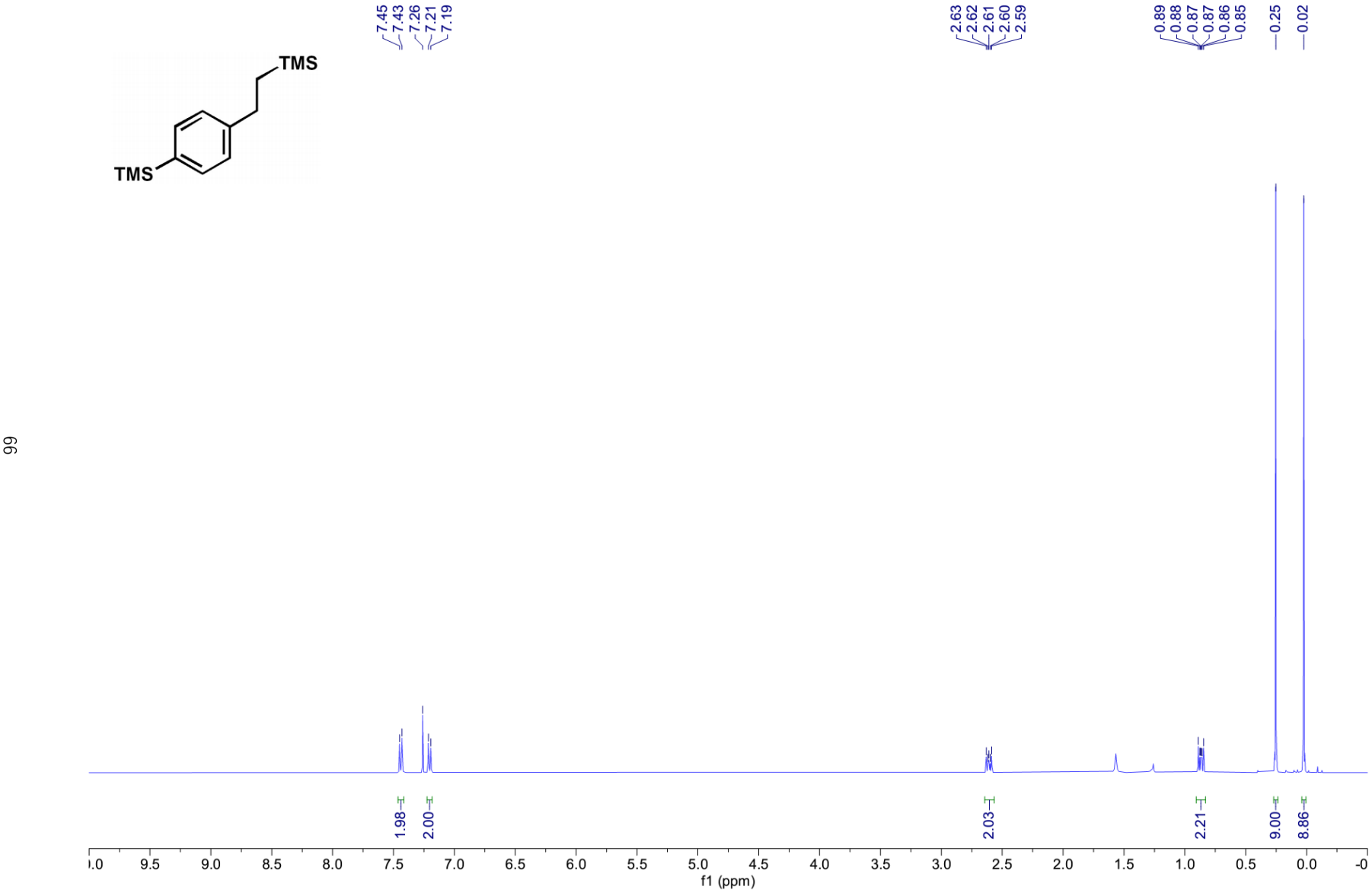

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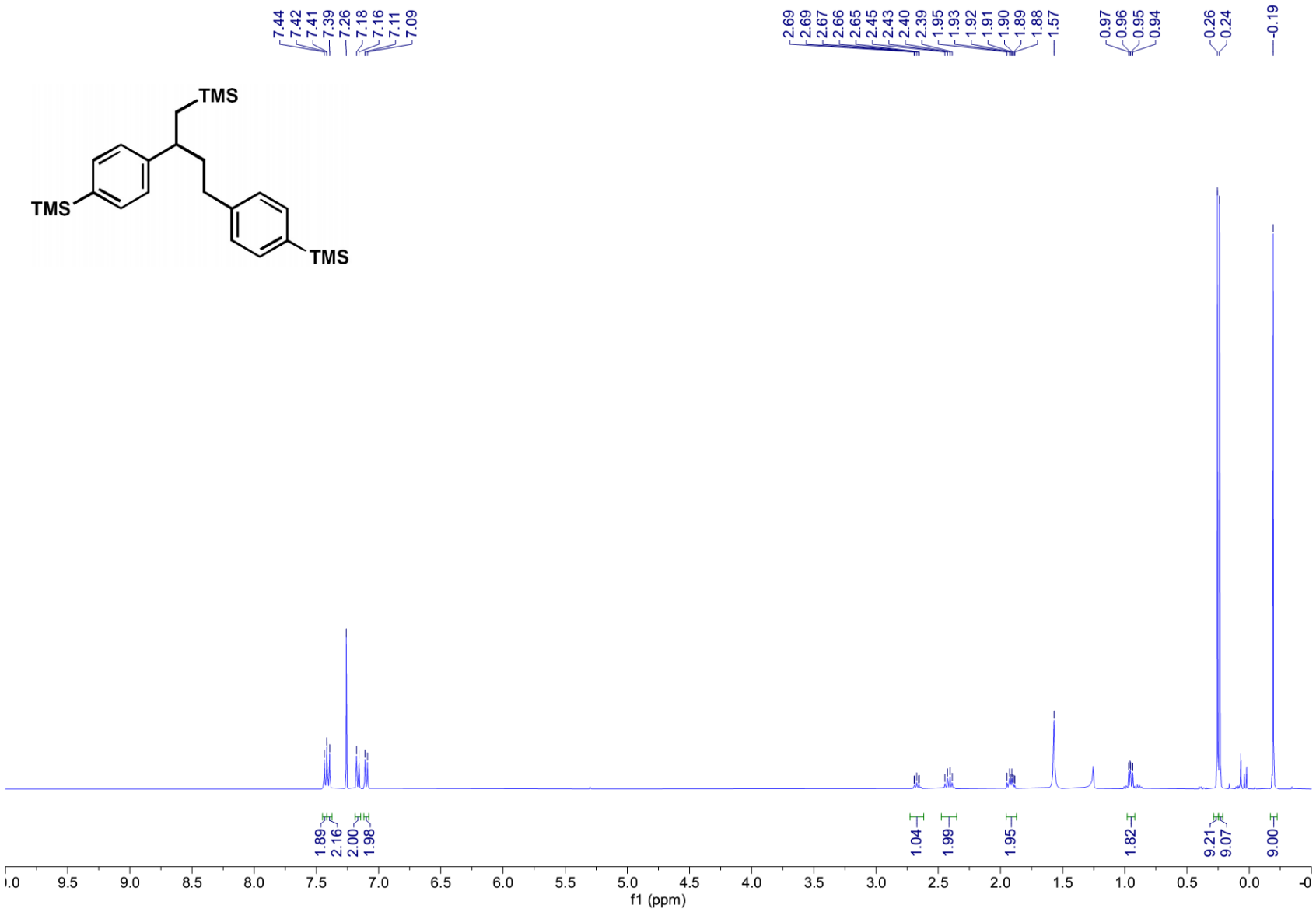

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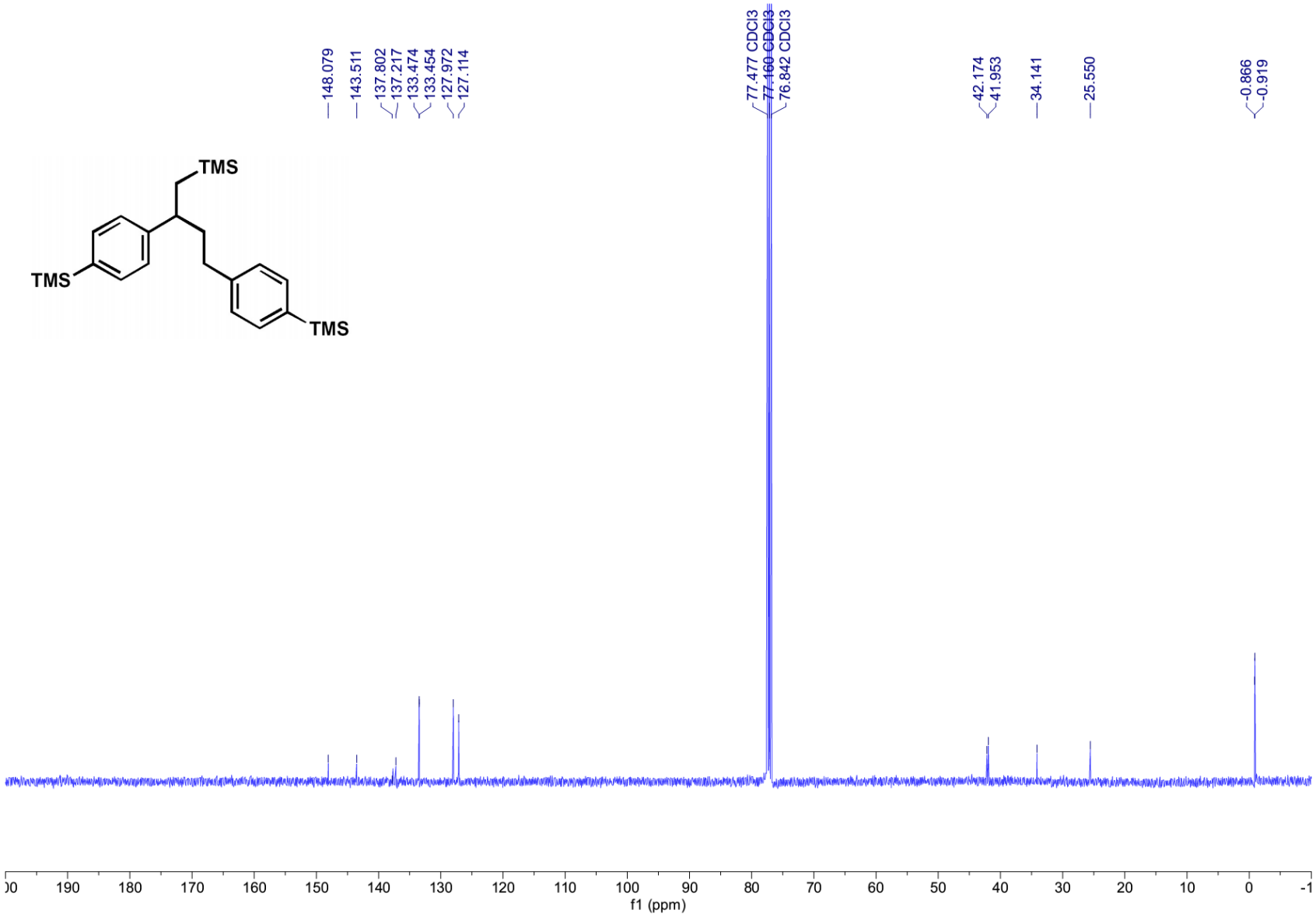

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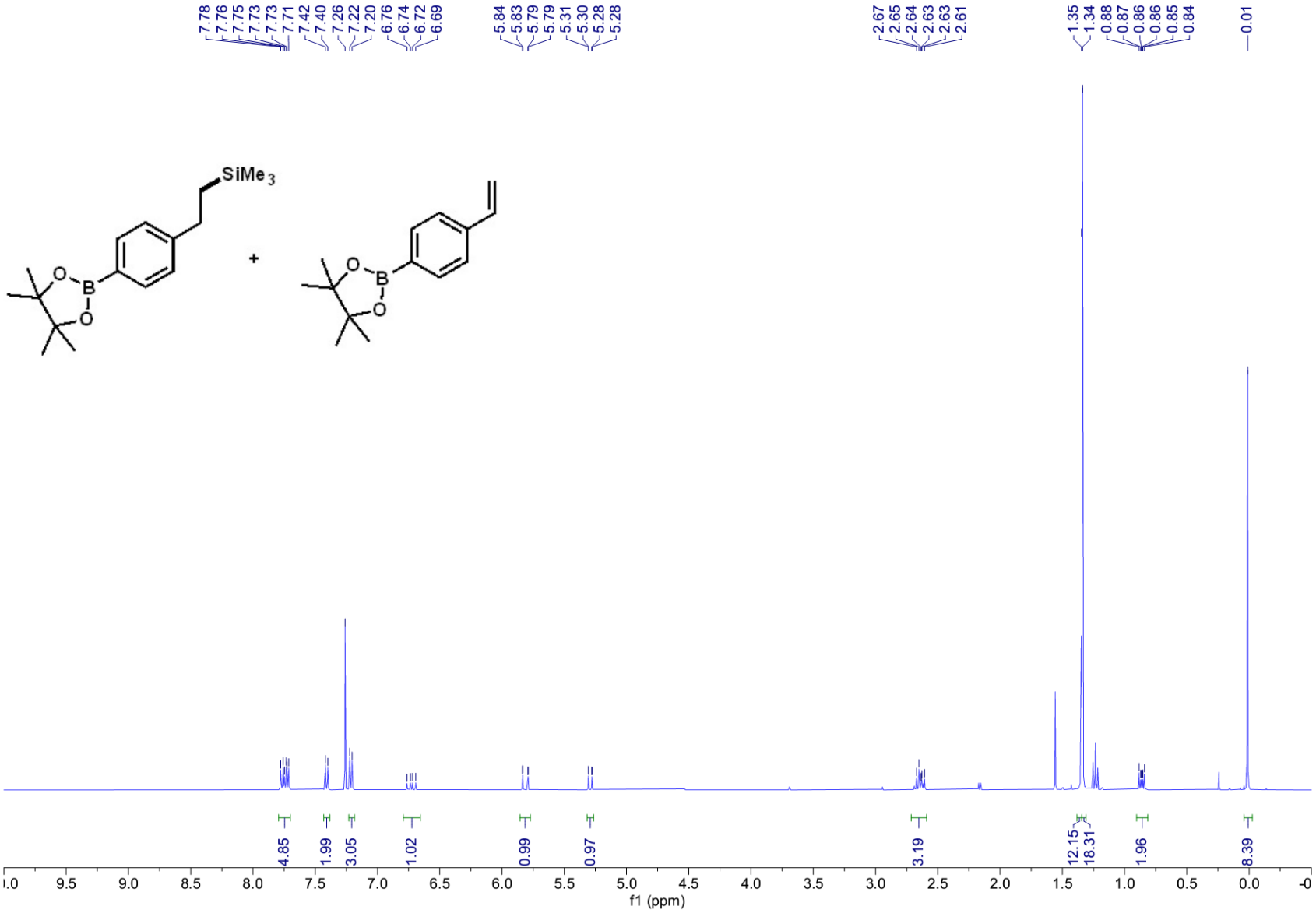

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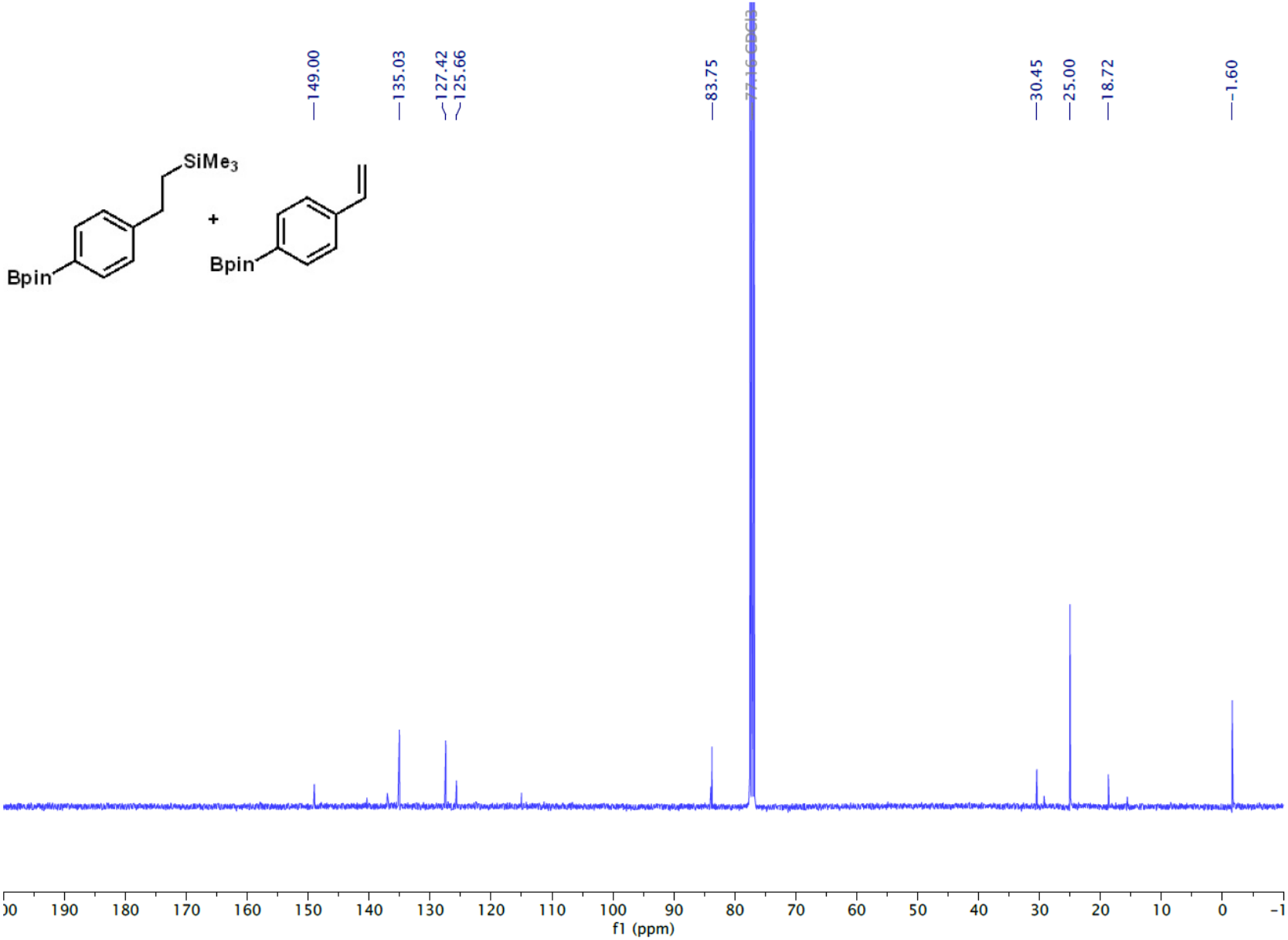

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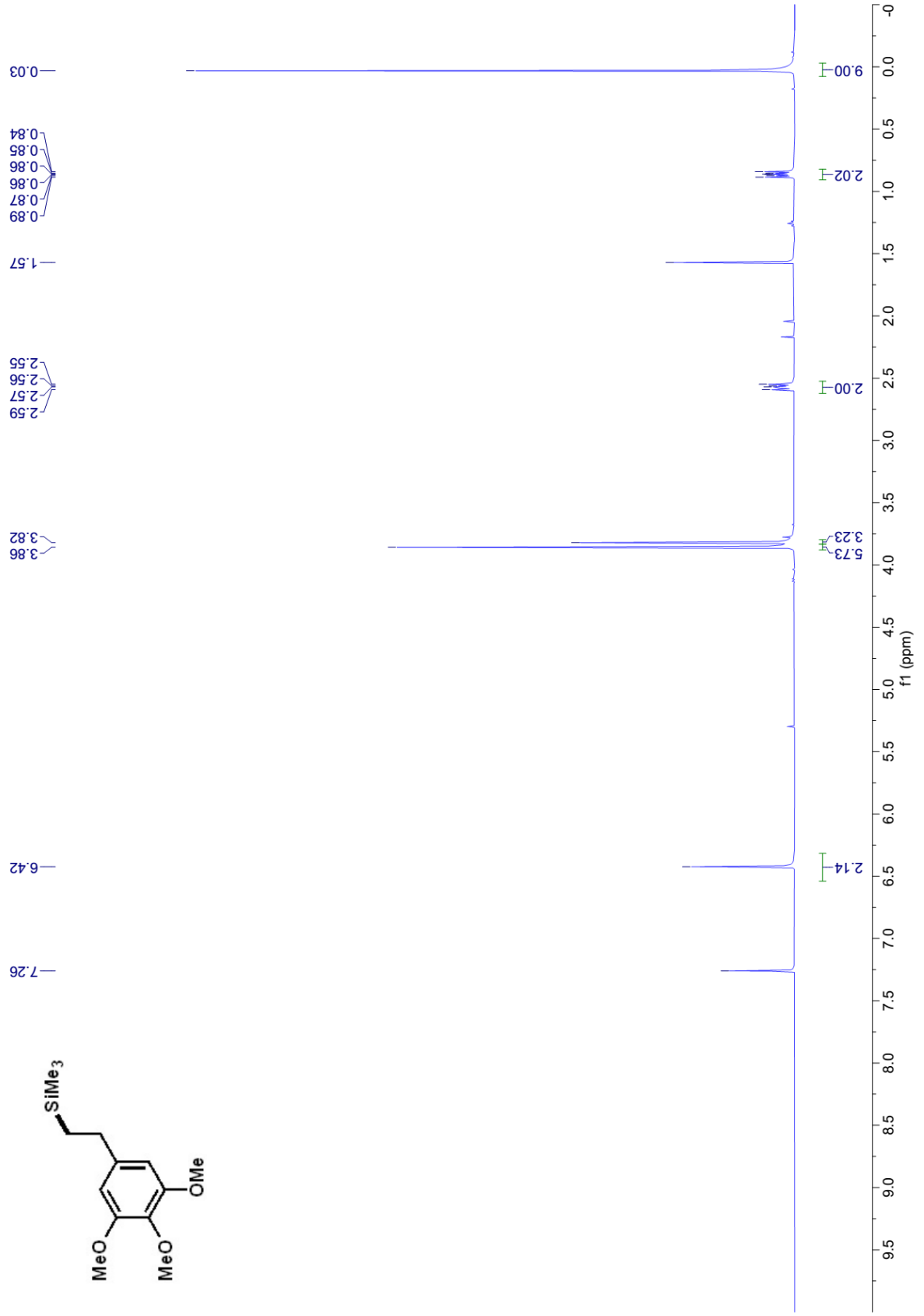

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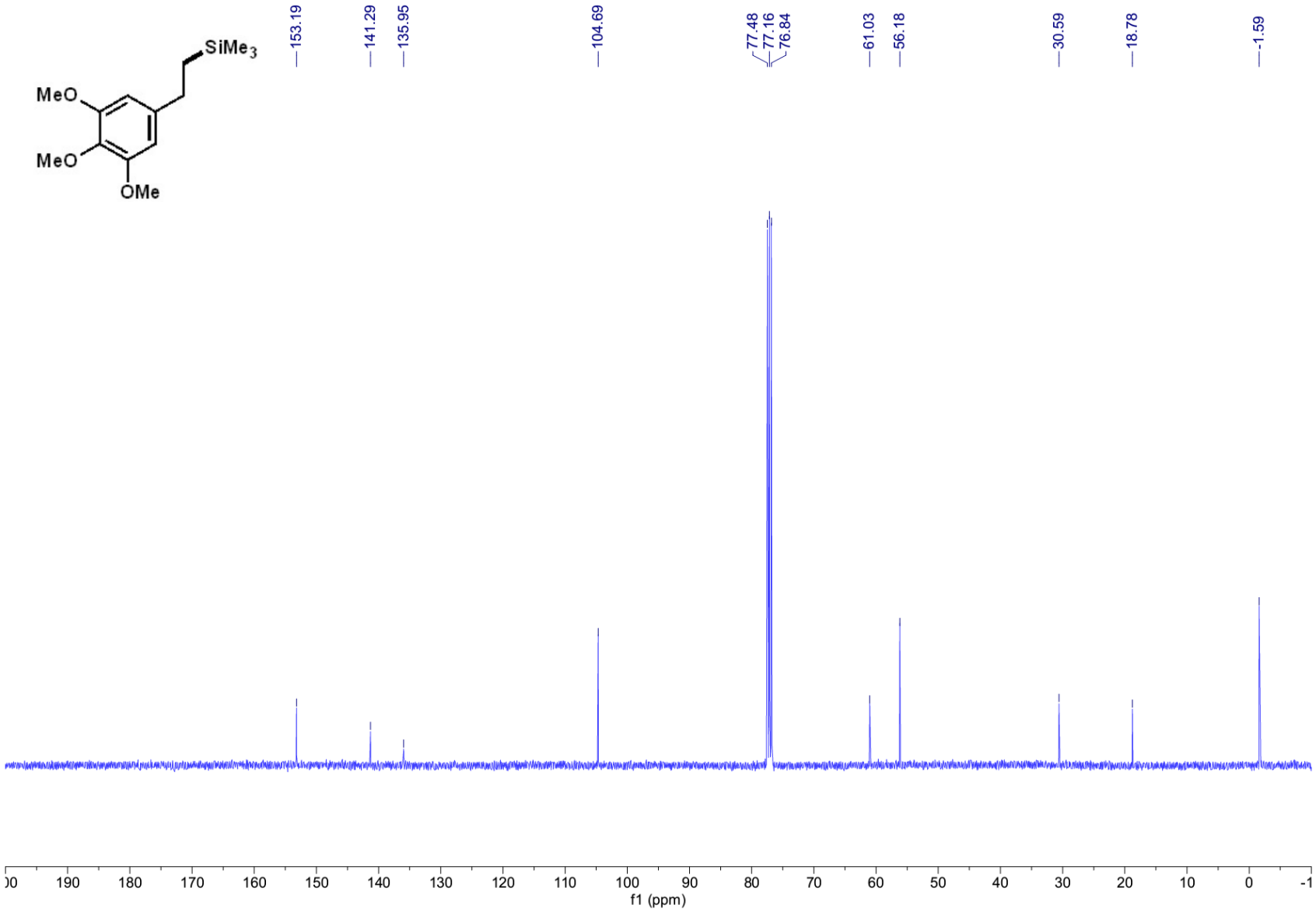

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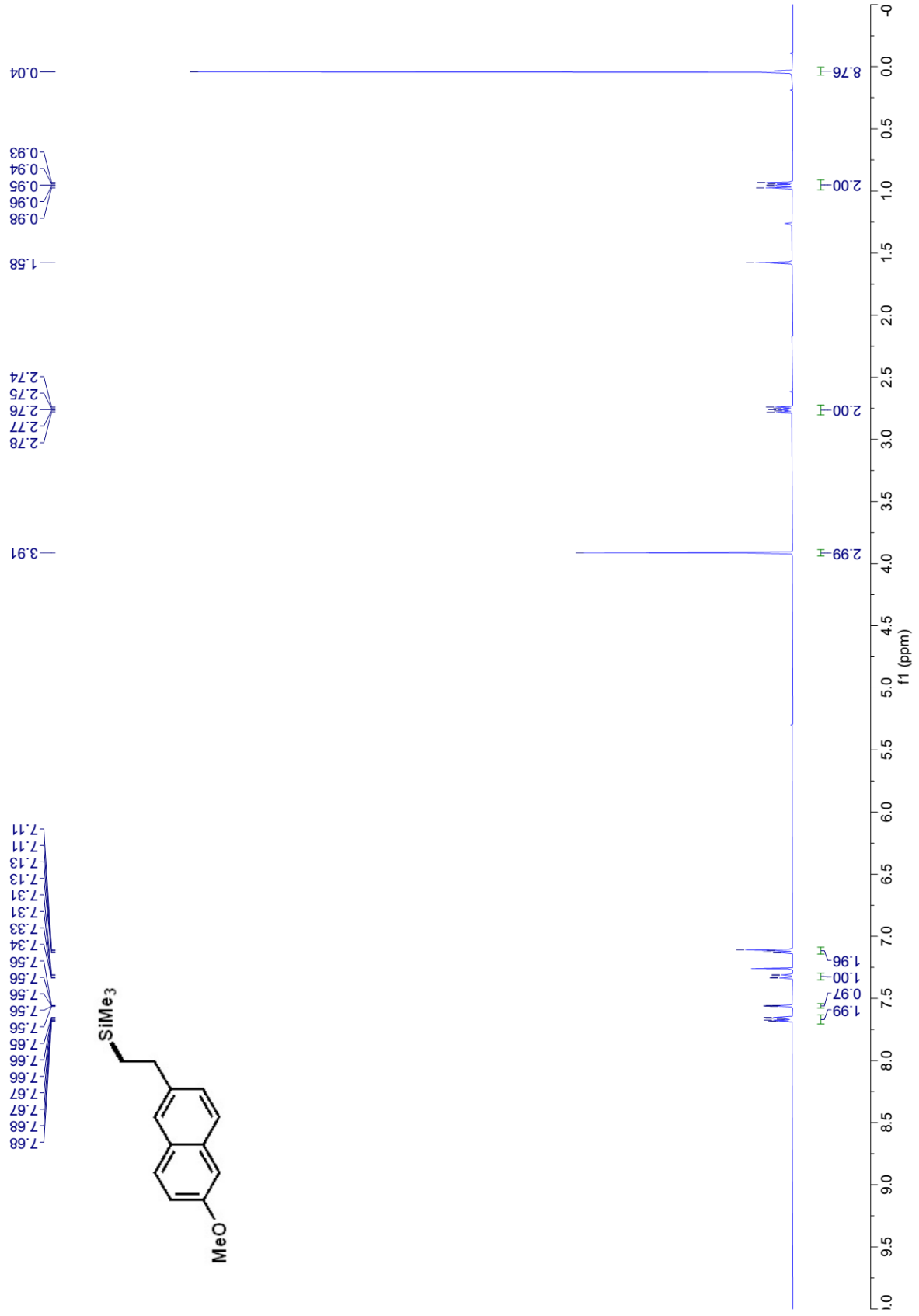

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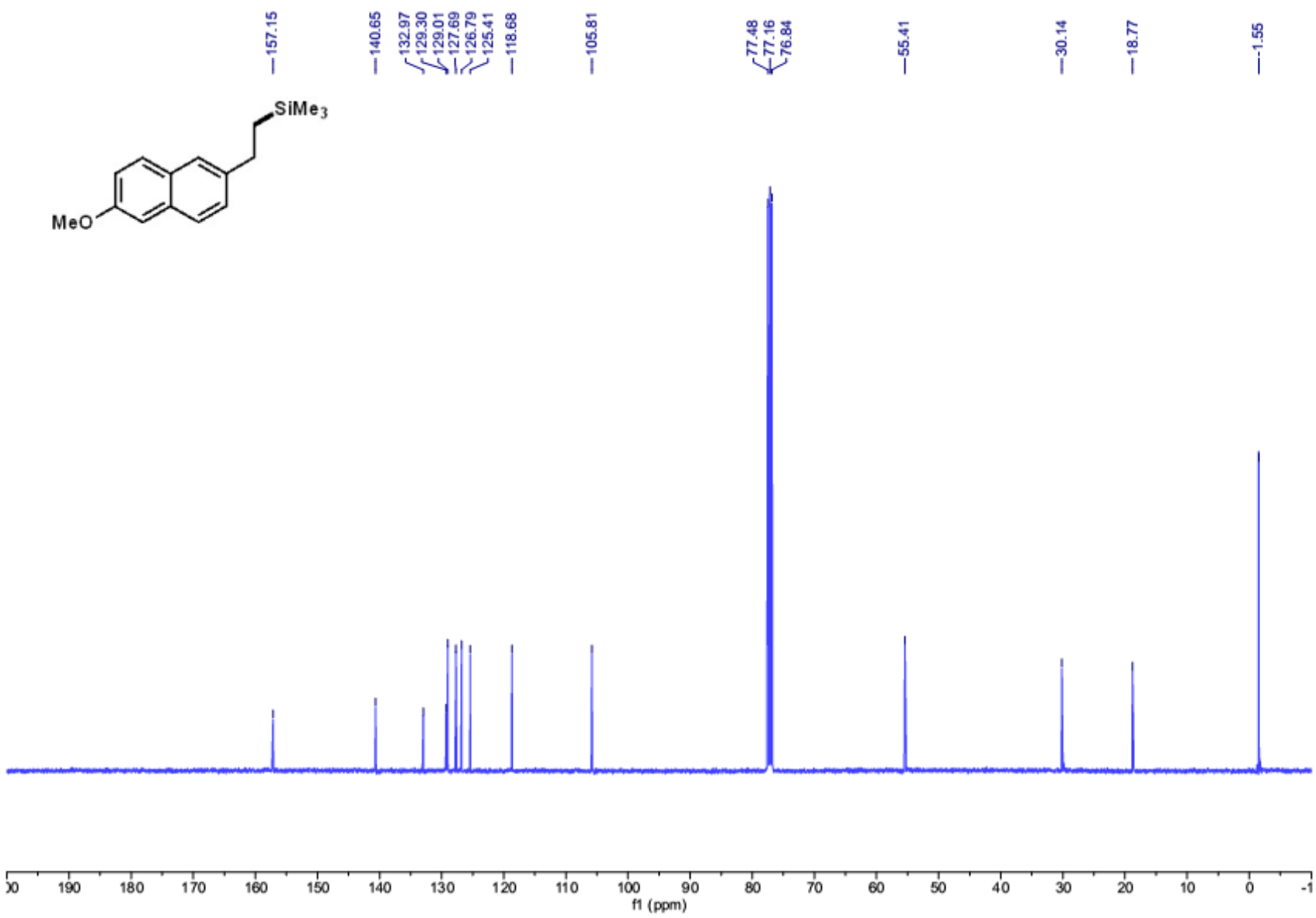

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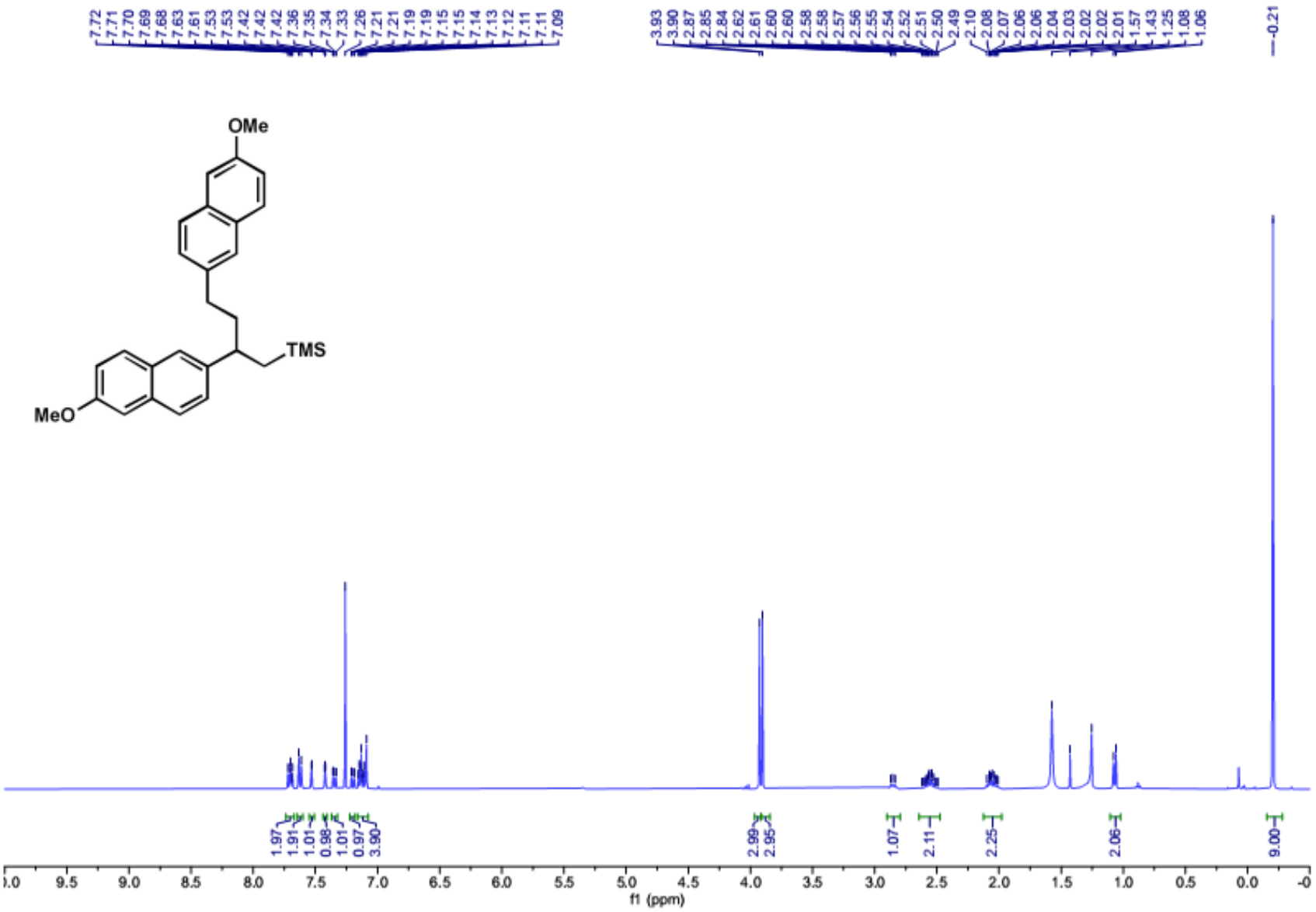

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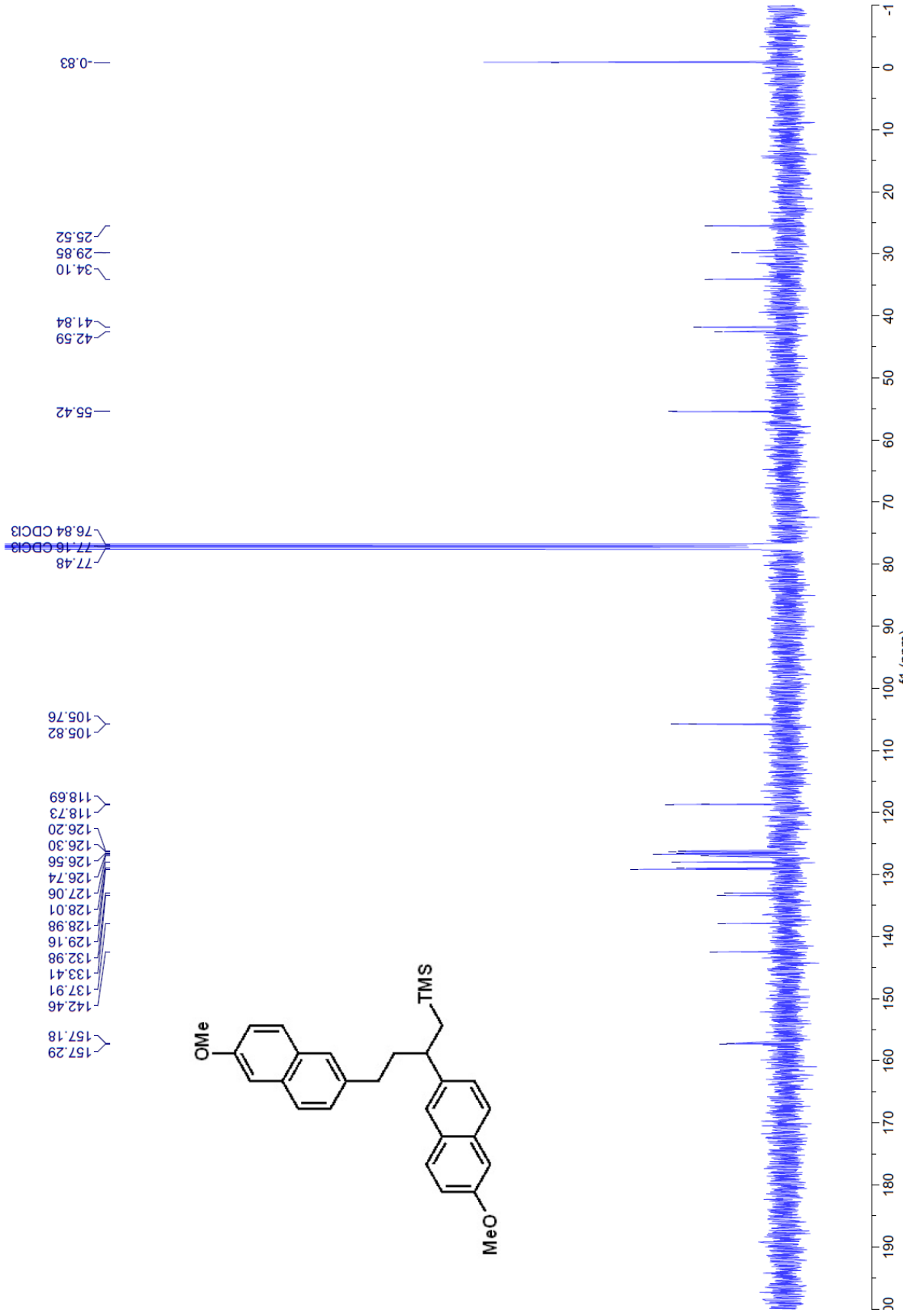

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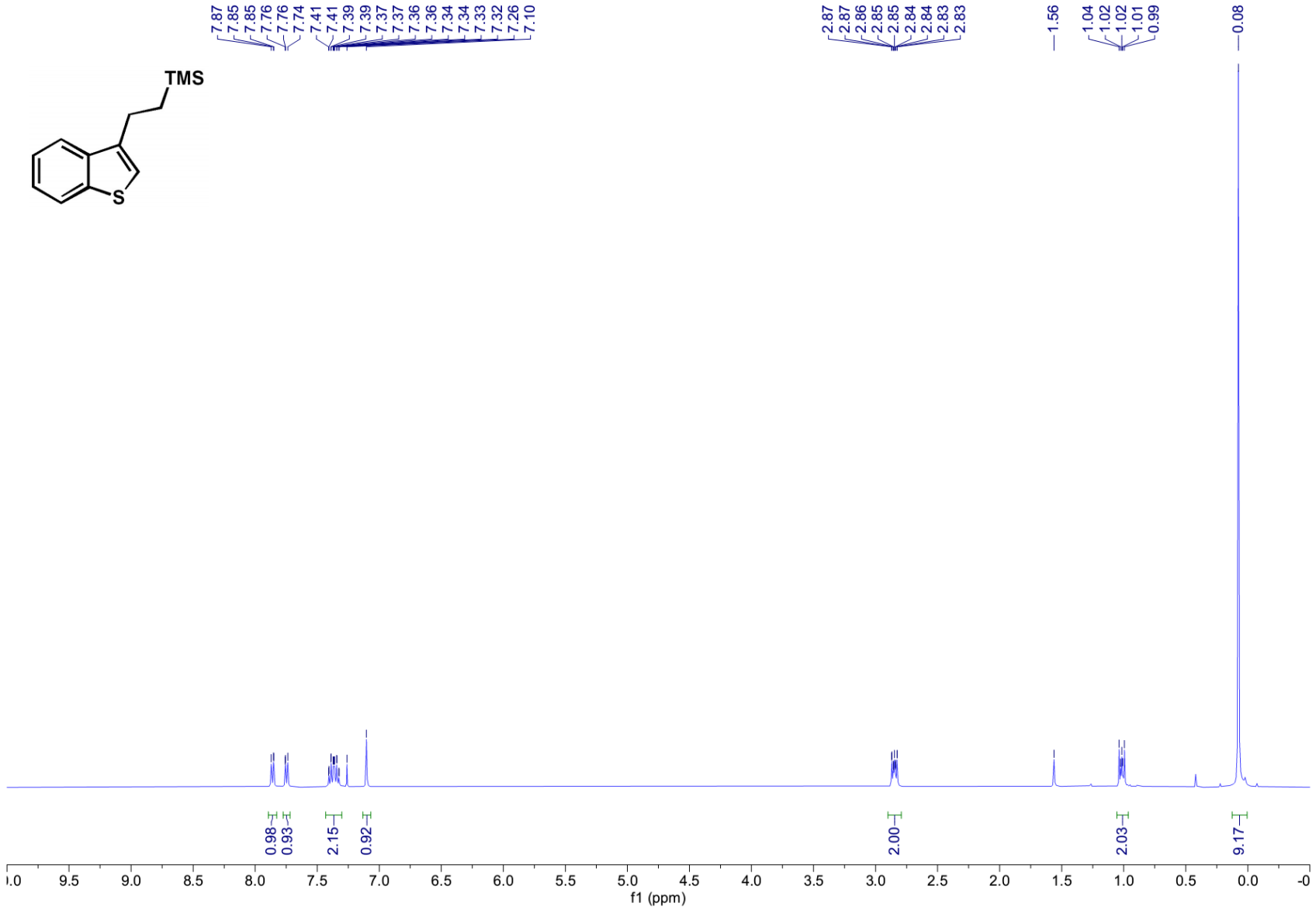

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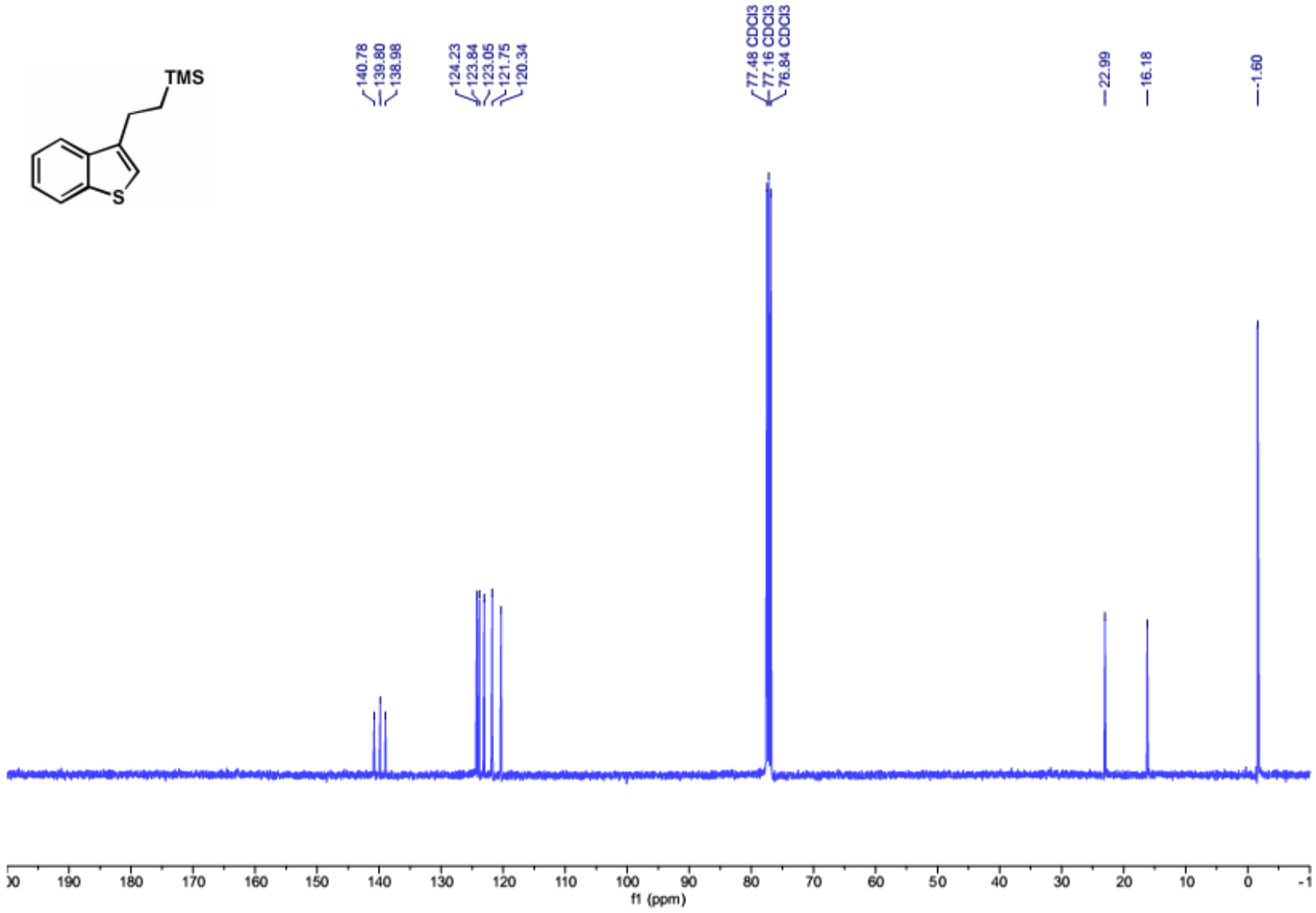

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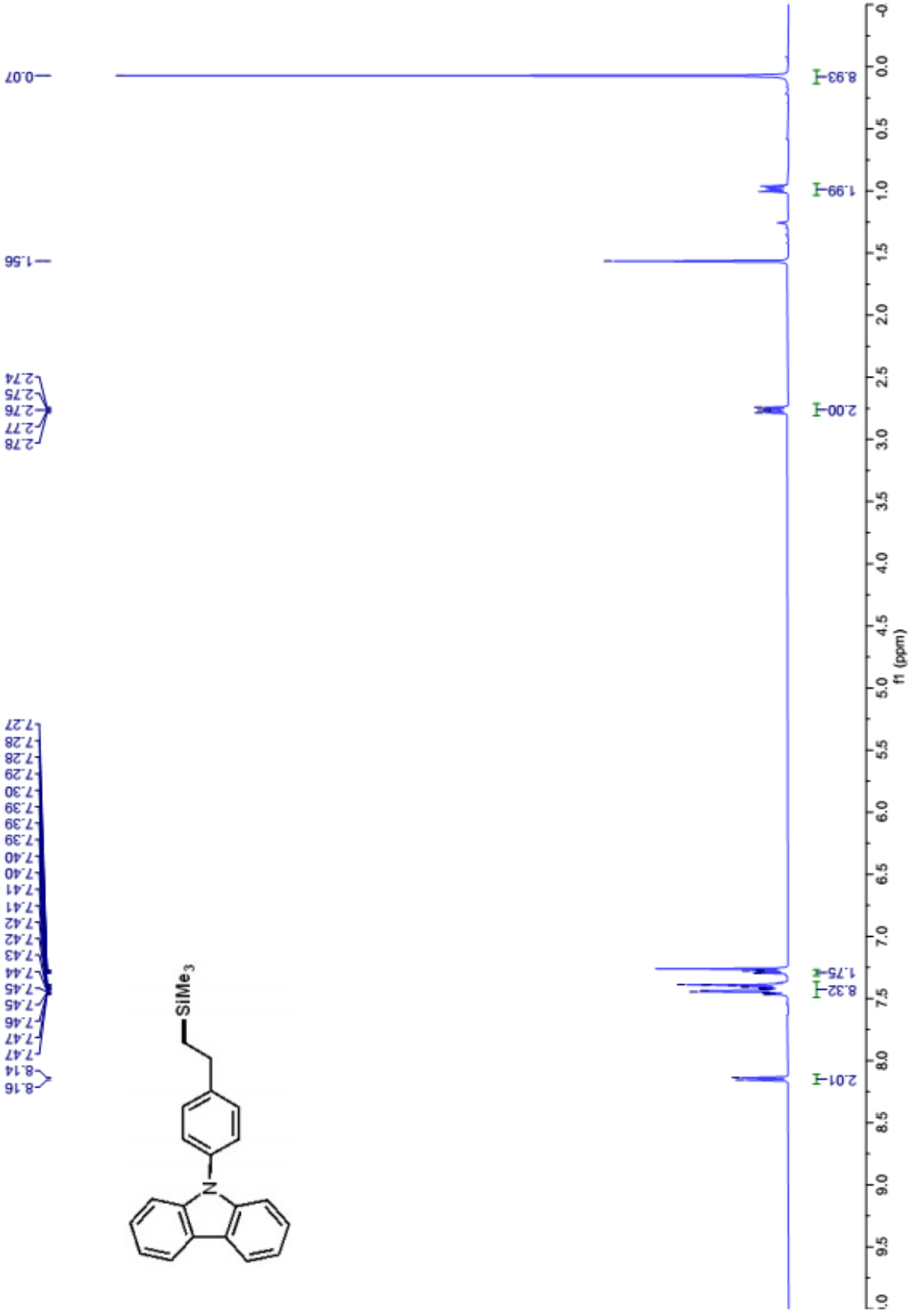

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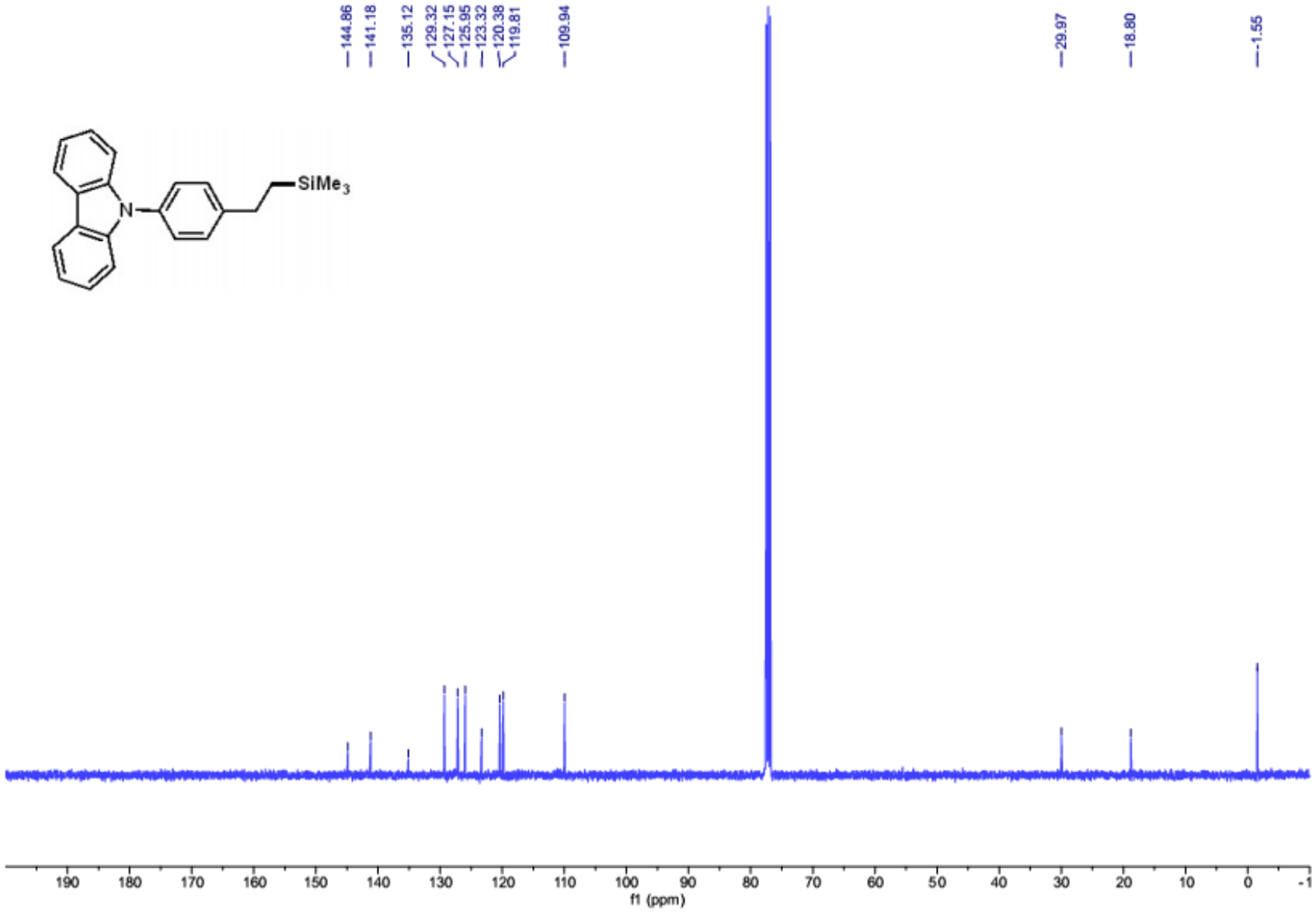

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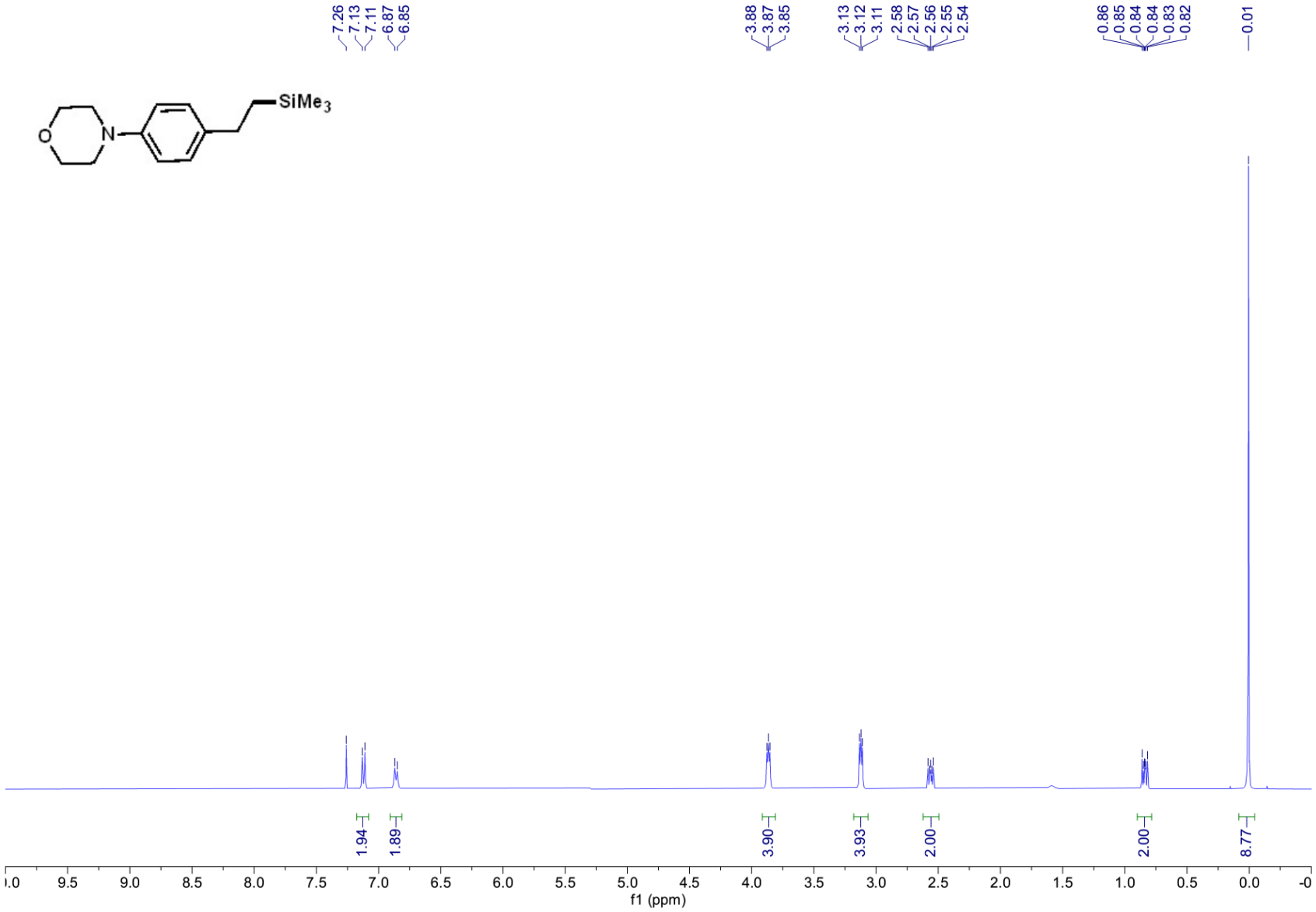

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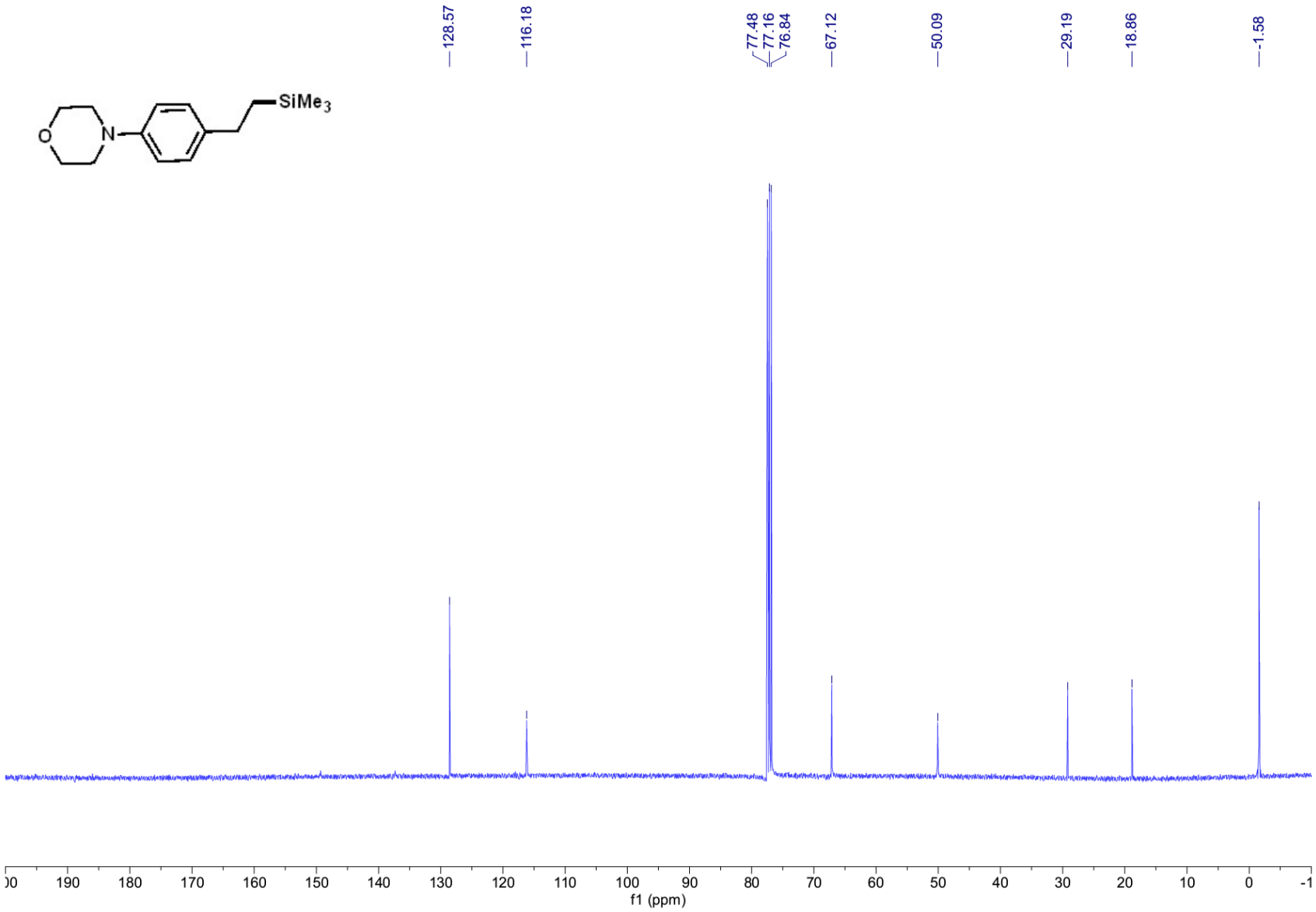

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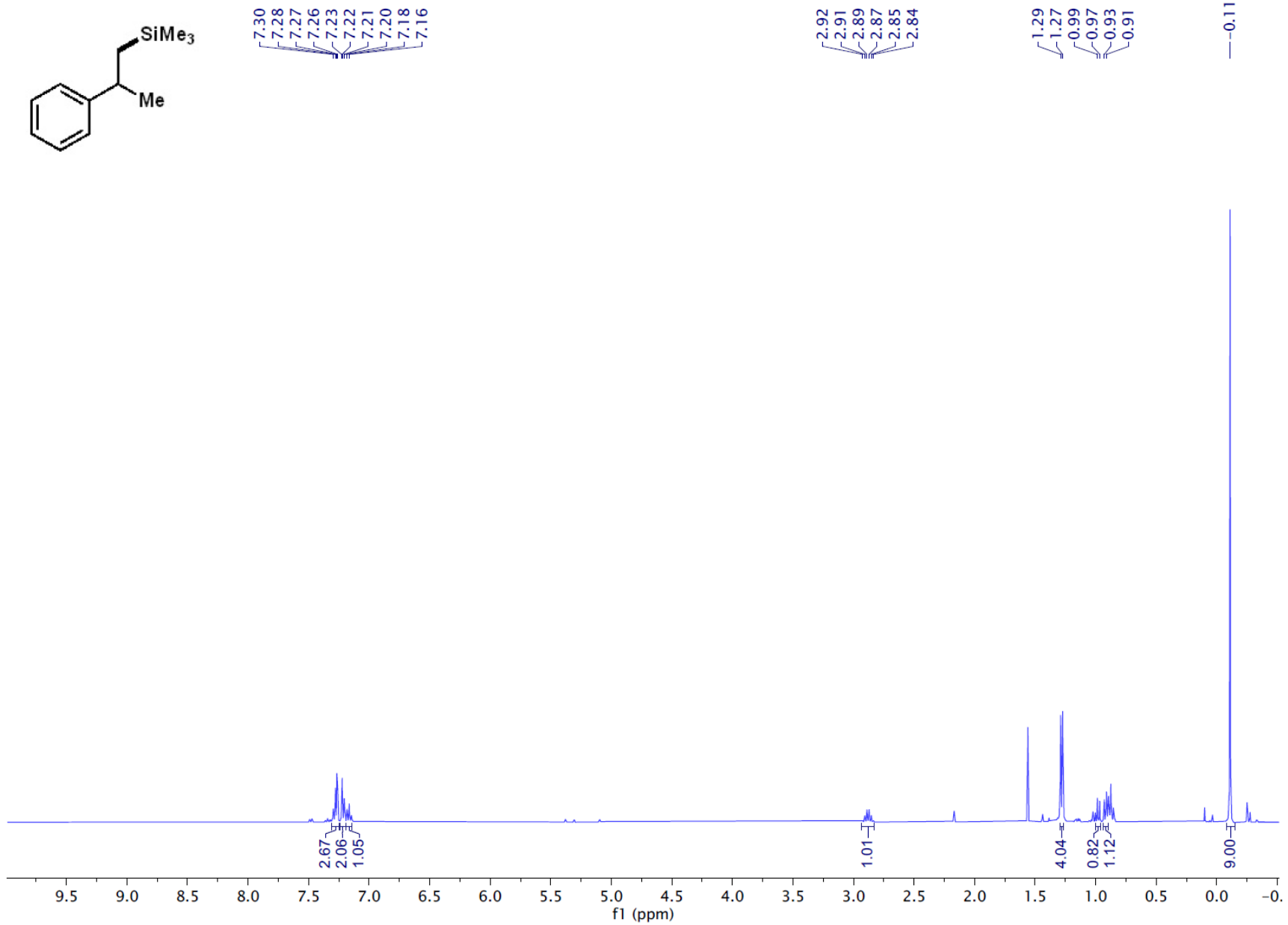

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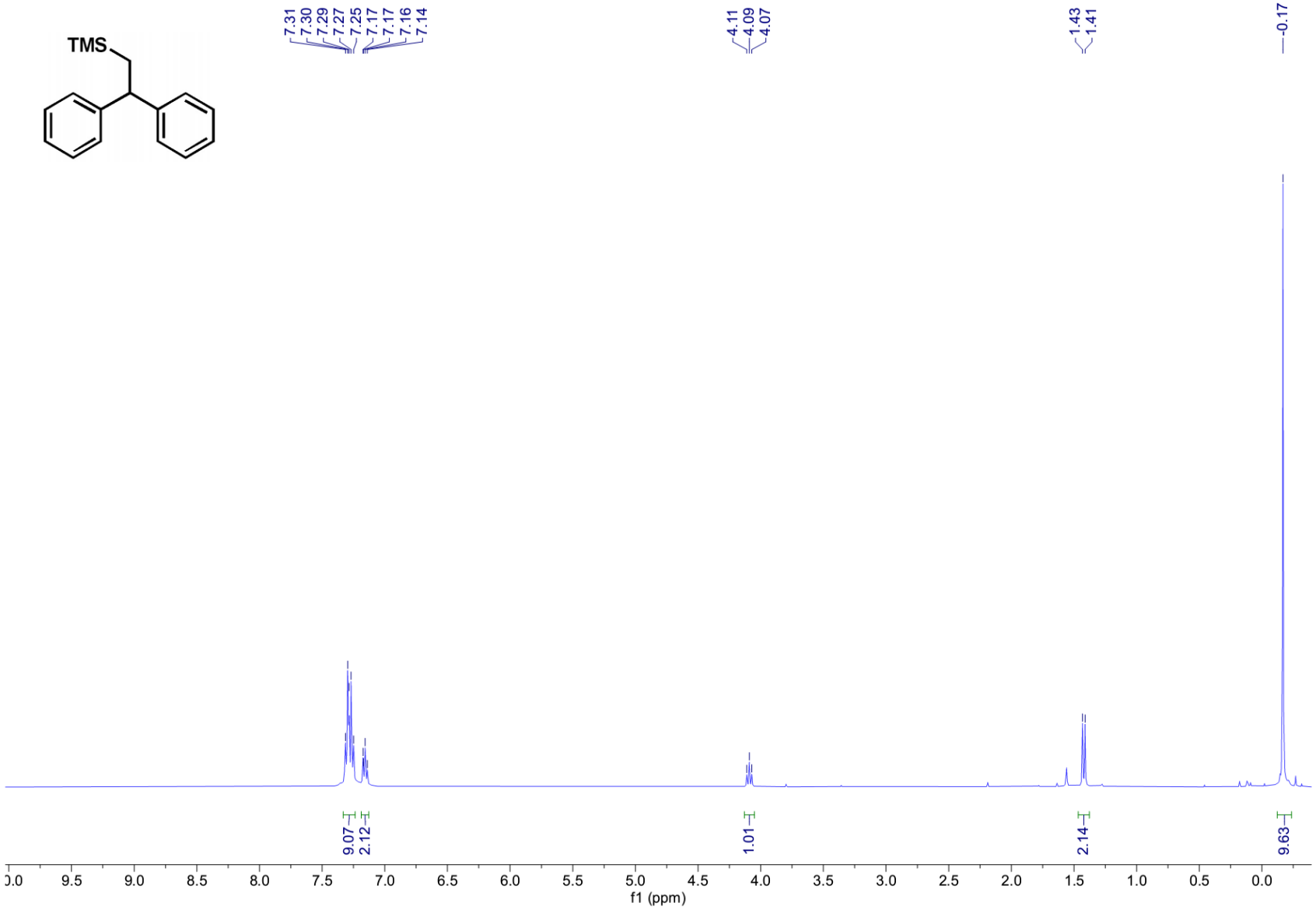

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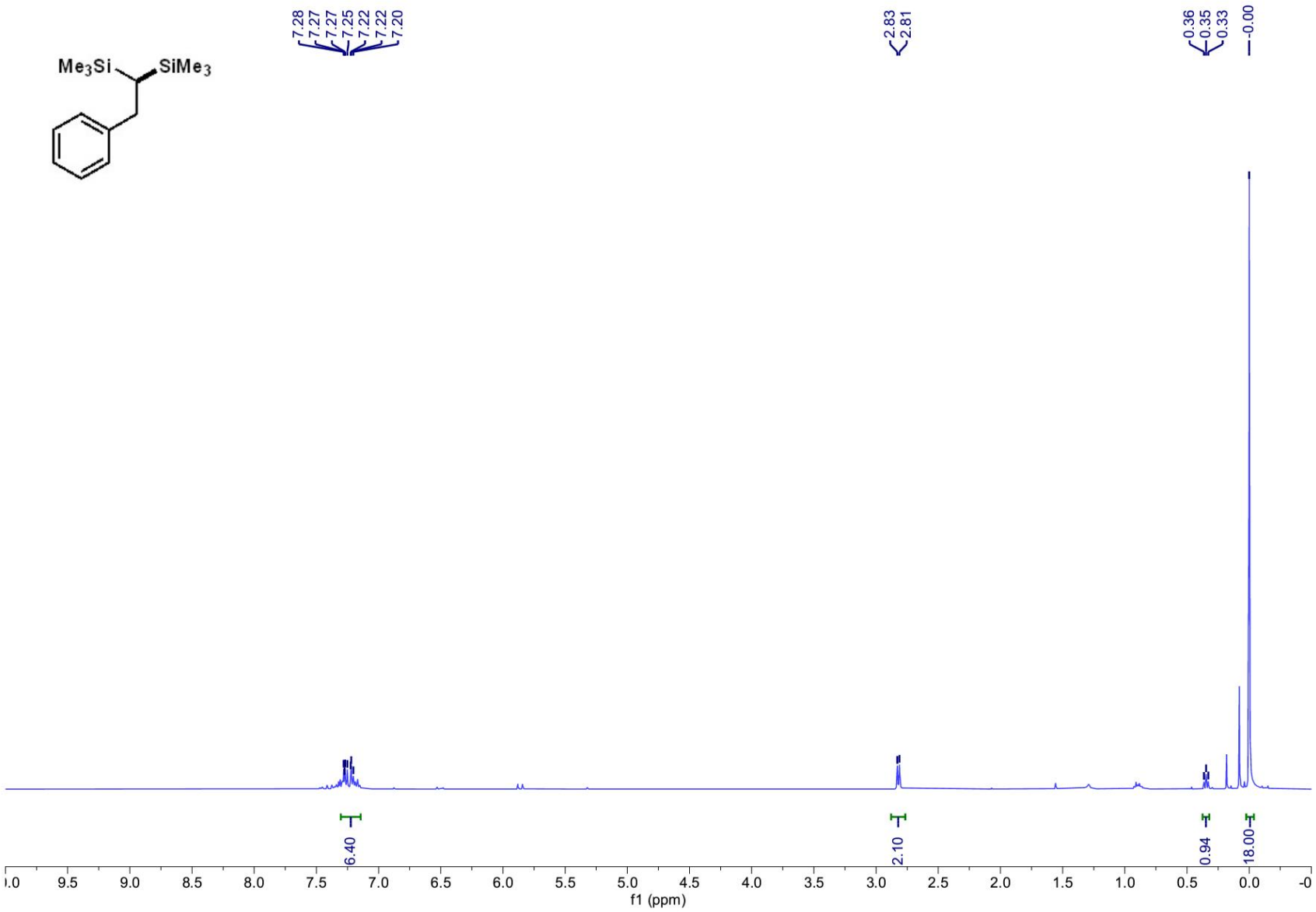

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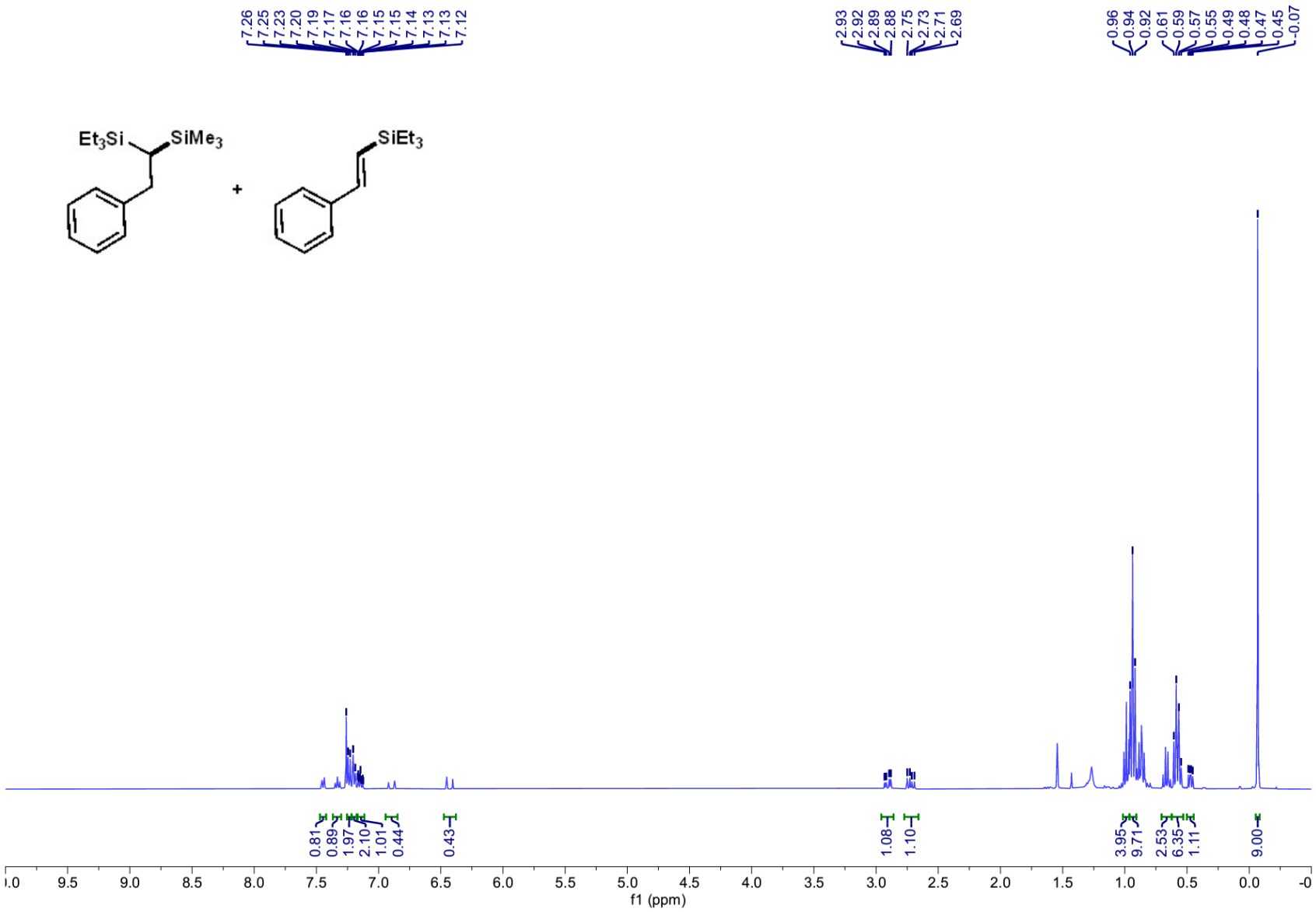

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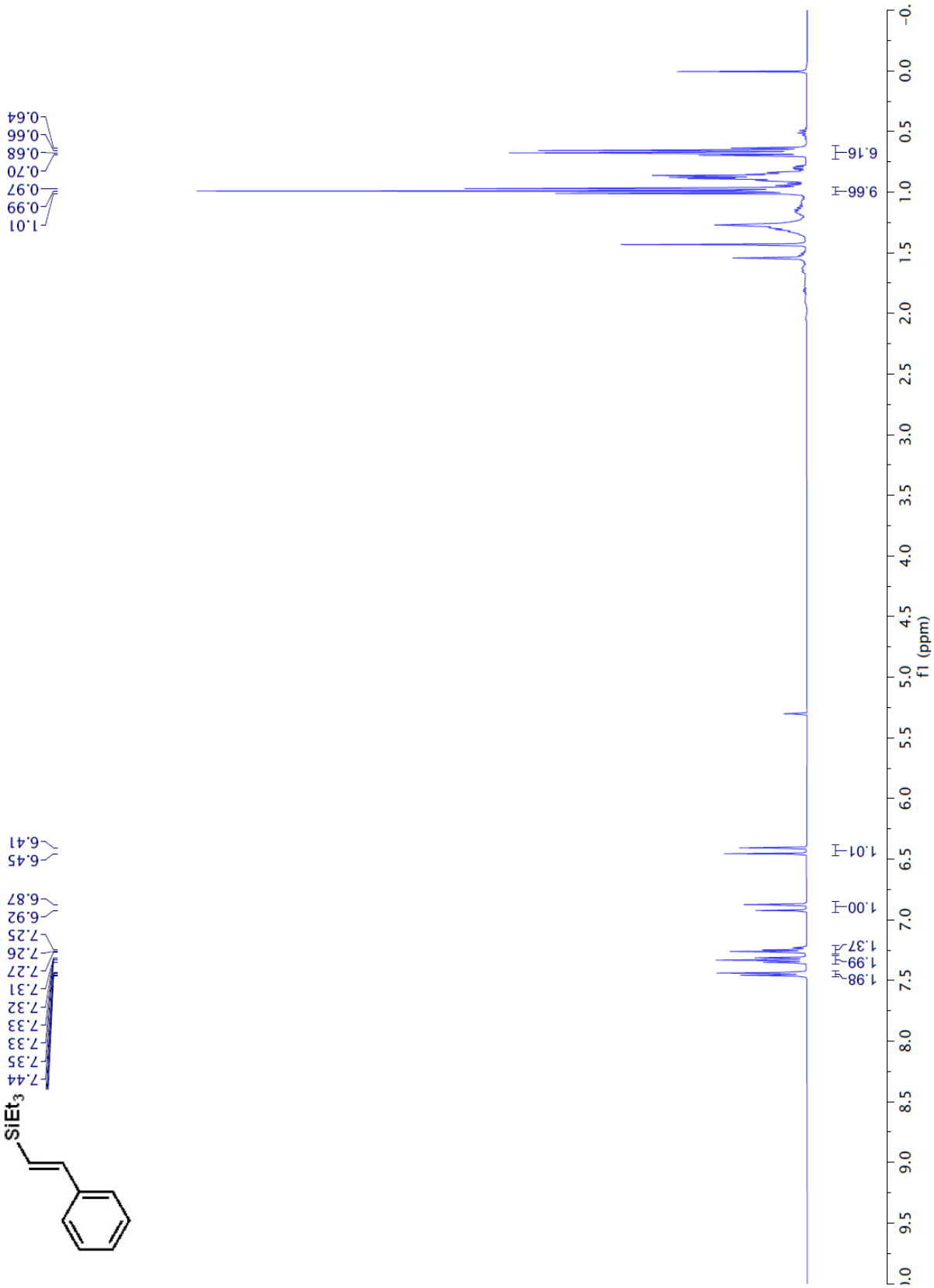

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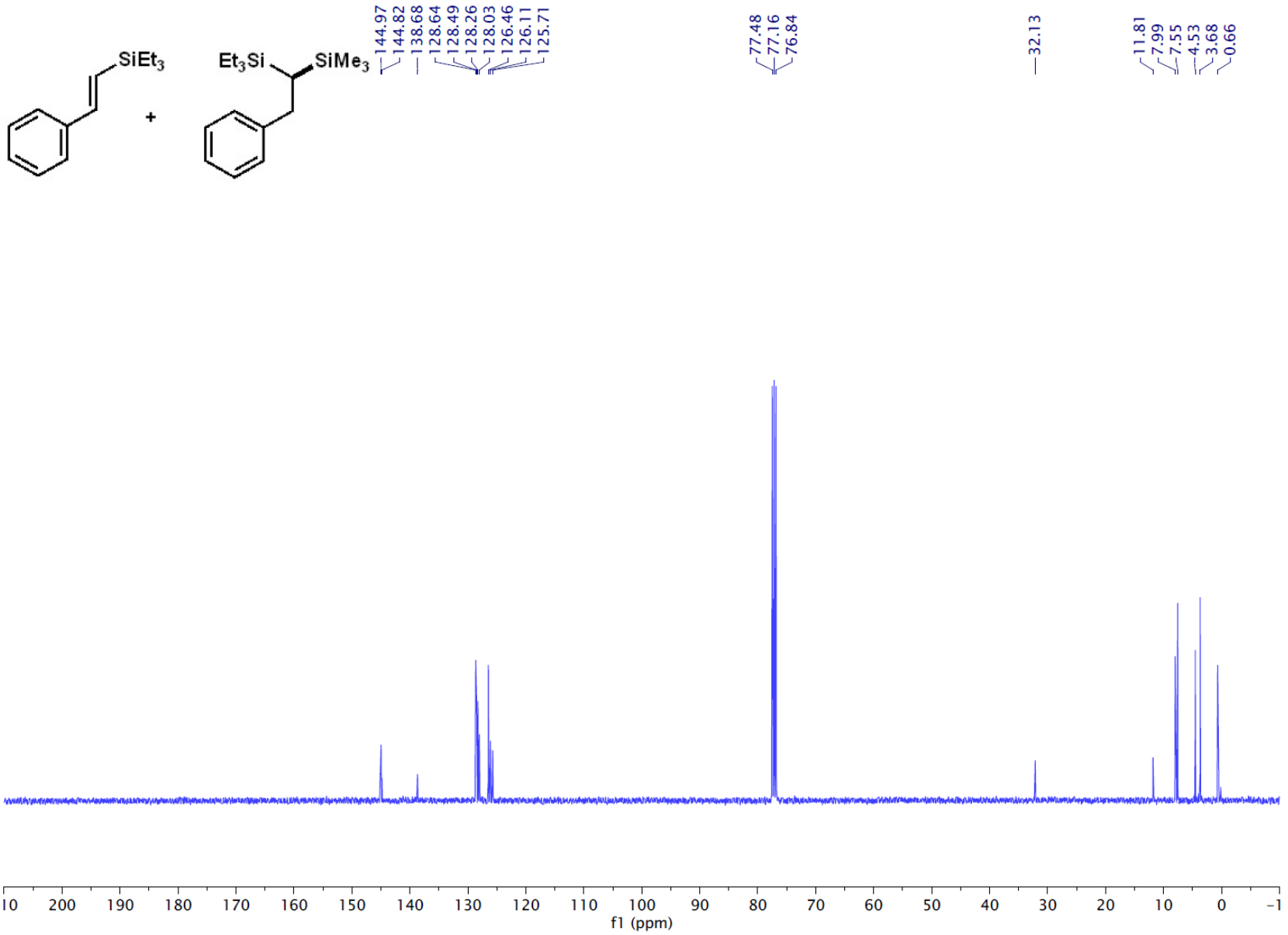
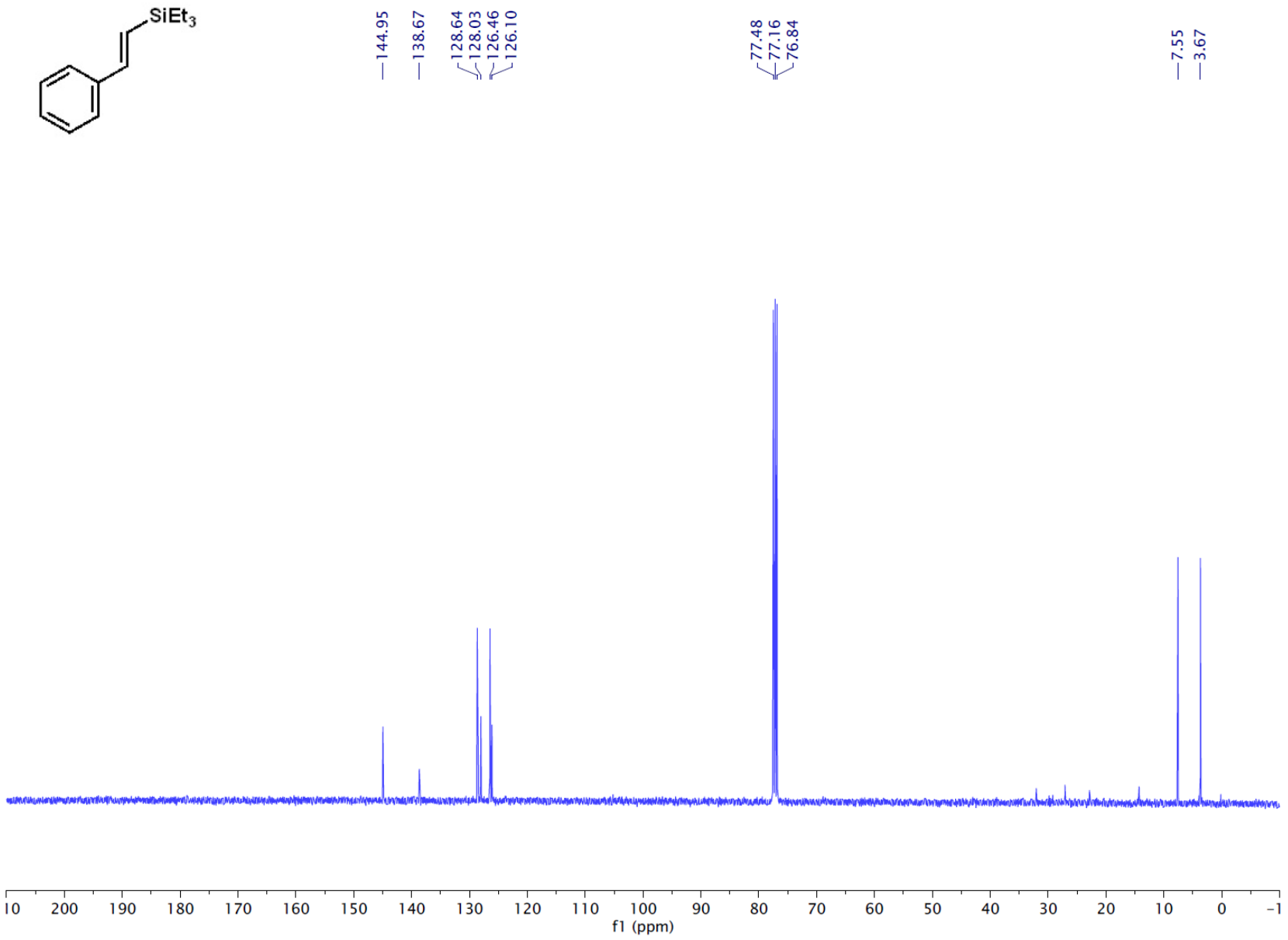
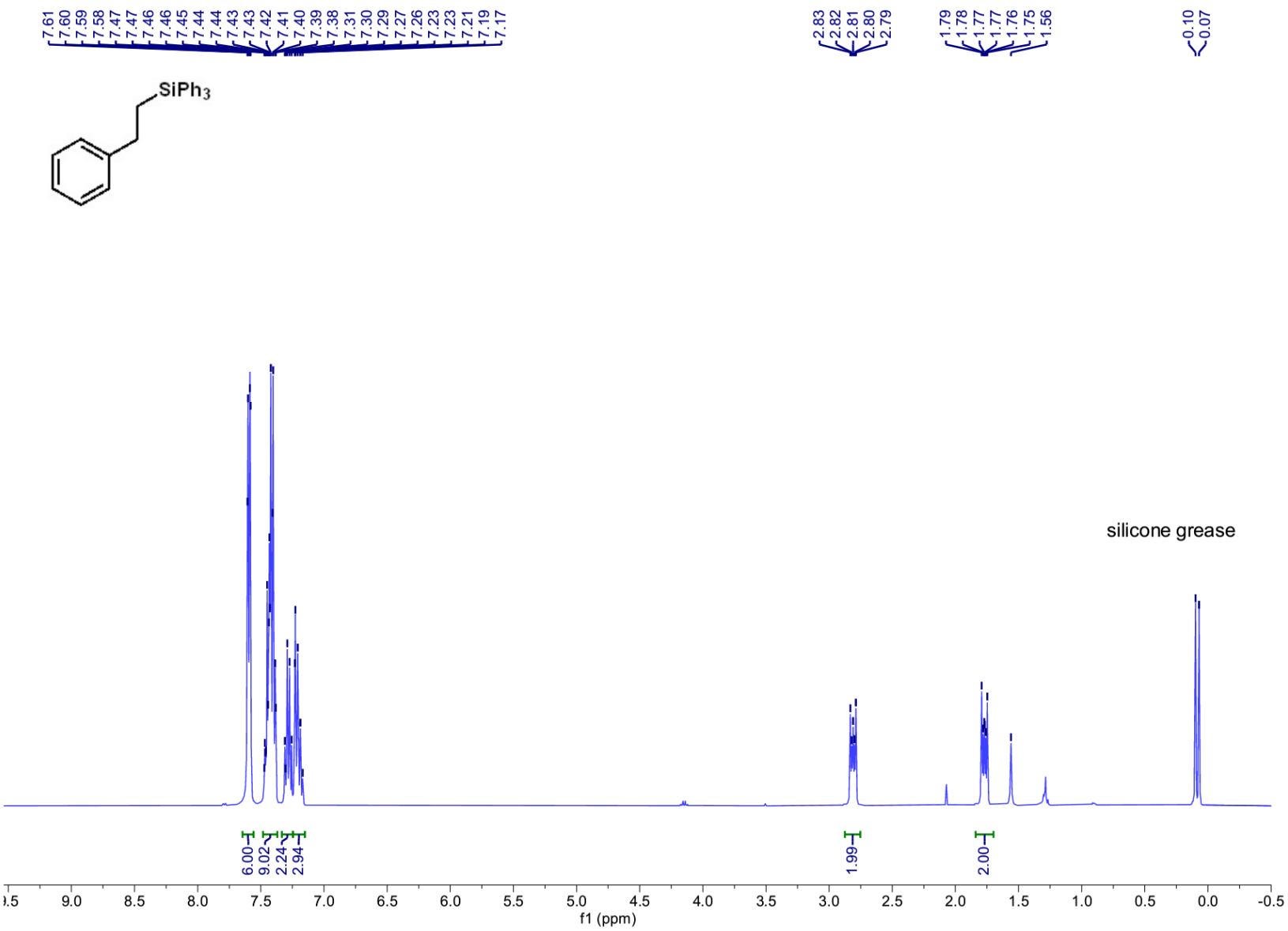


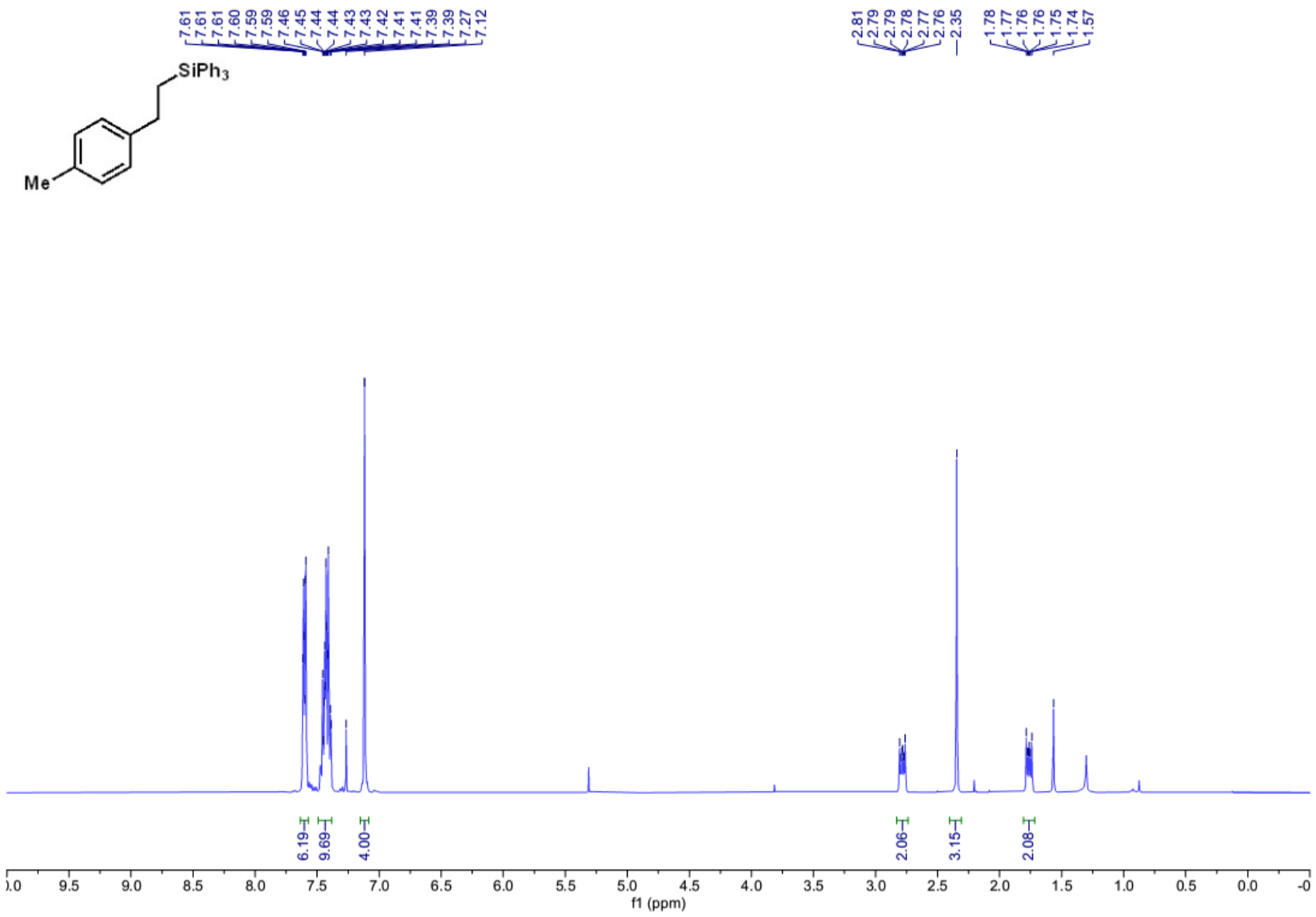
^{13}C NMR (100 MHz, $CDCl_3$) of ***2u***



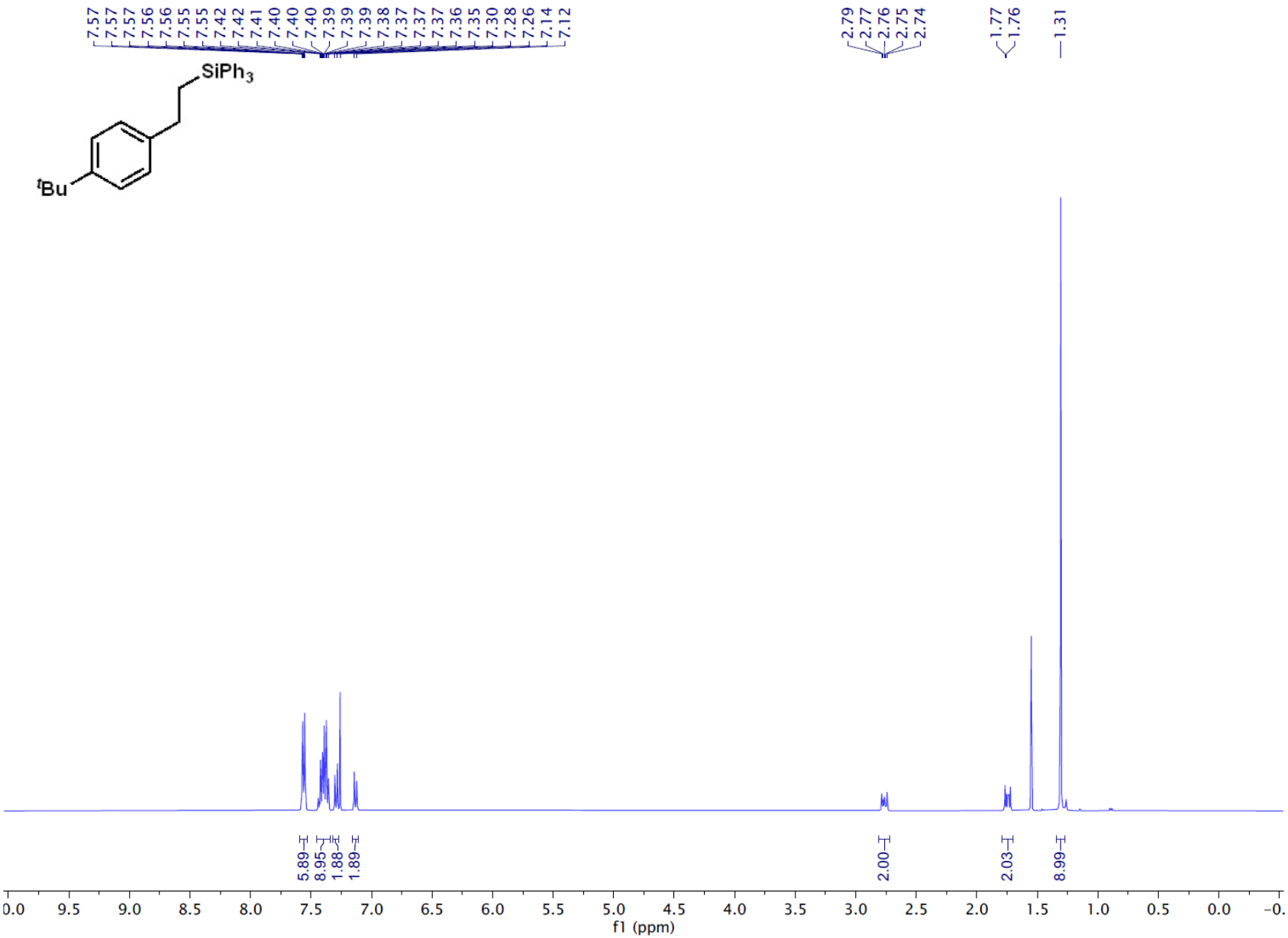
^{13}C NMR (100 MHz, $CDCl_3$) of ***1u***



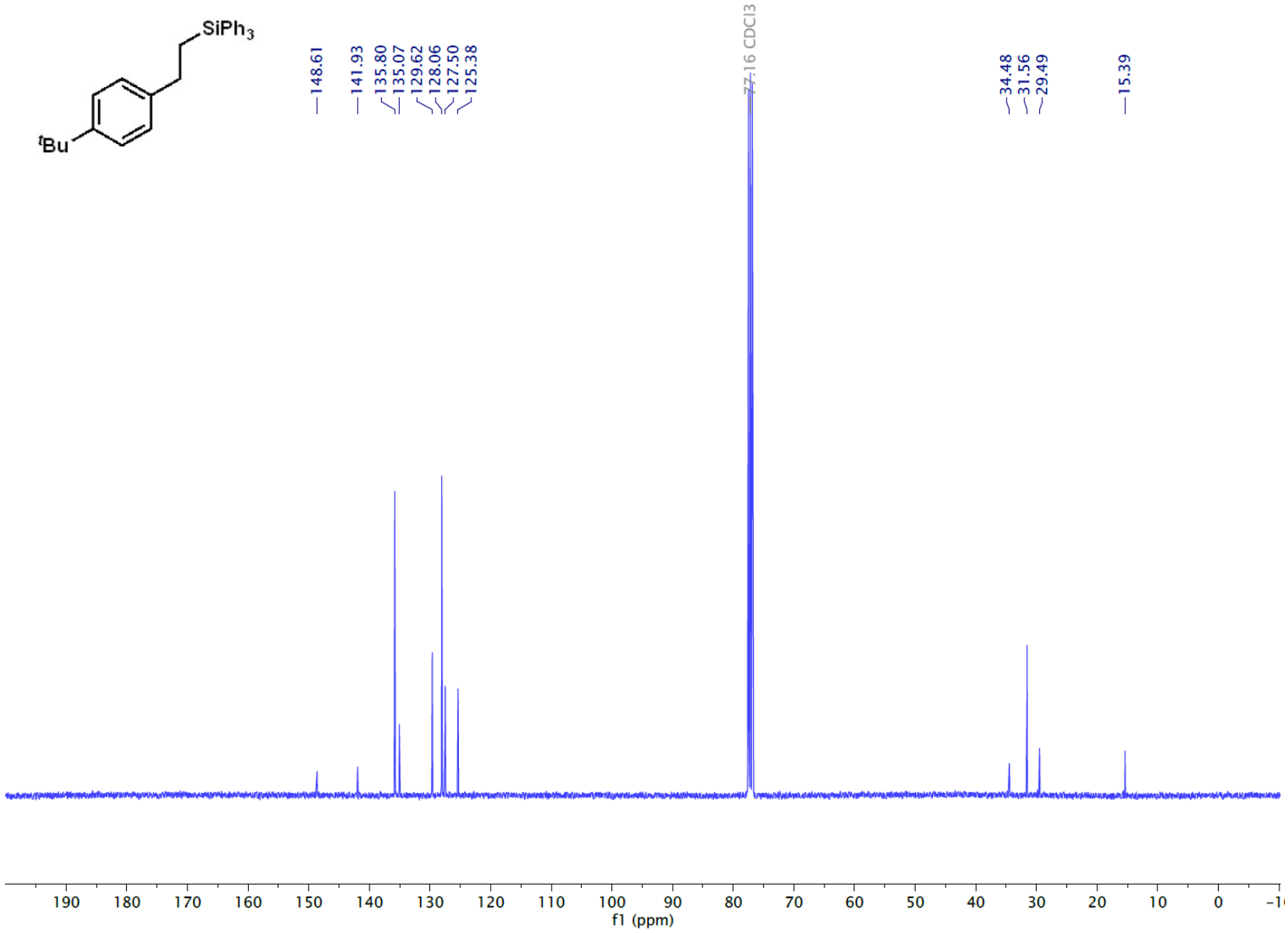
^{1}H NMR (400 MHz, $CDCl_3$) of ***2v***



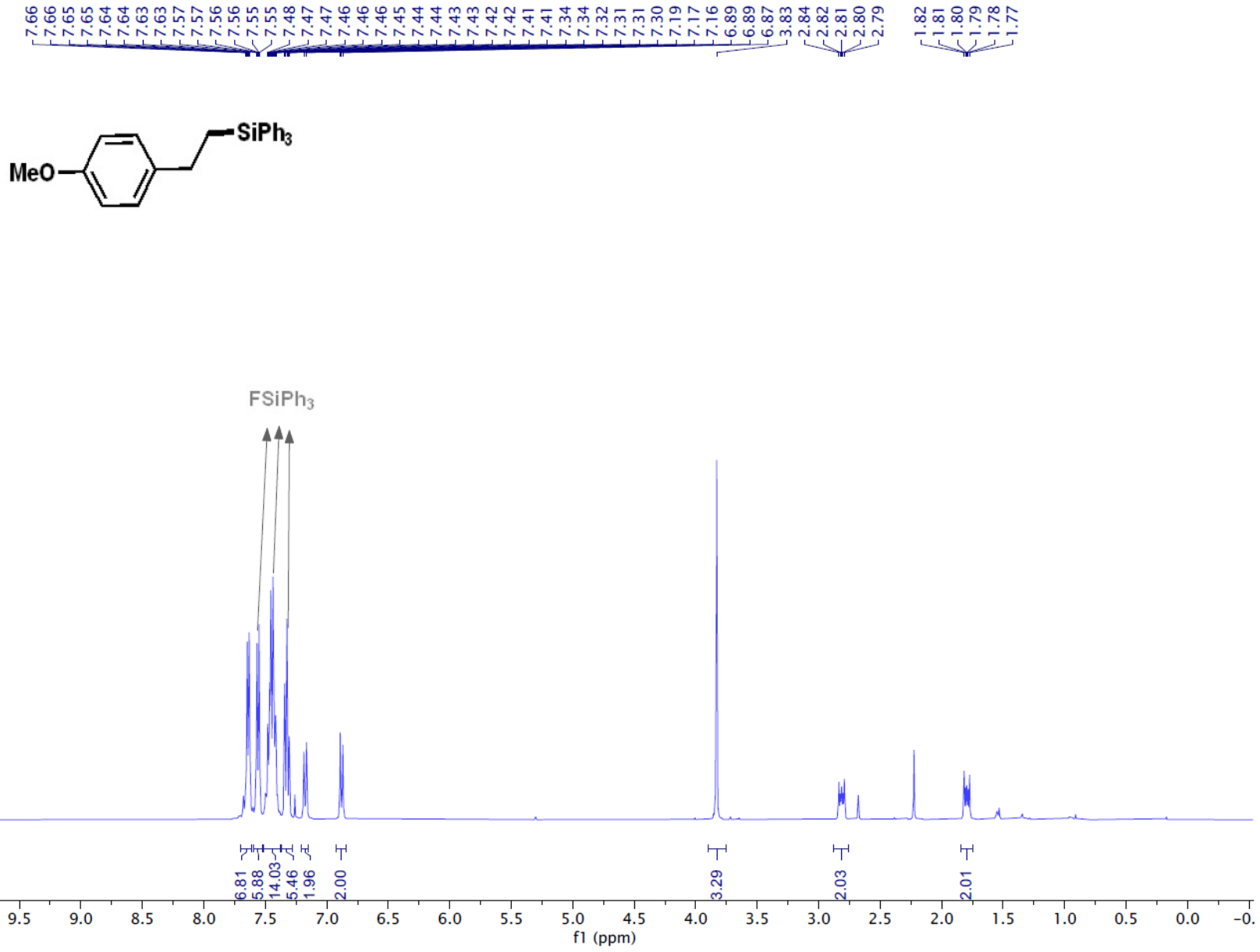
^{1}H NMR (400 MHz, $CDCl_3$) of ***2w***



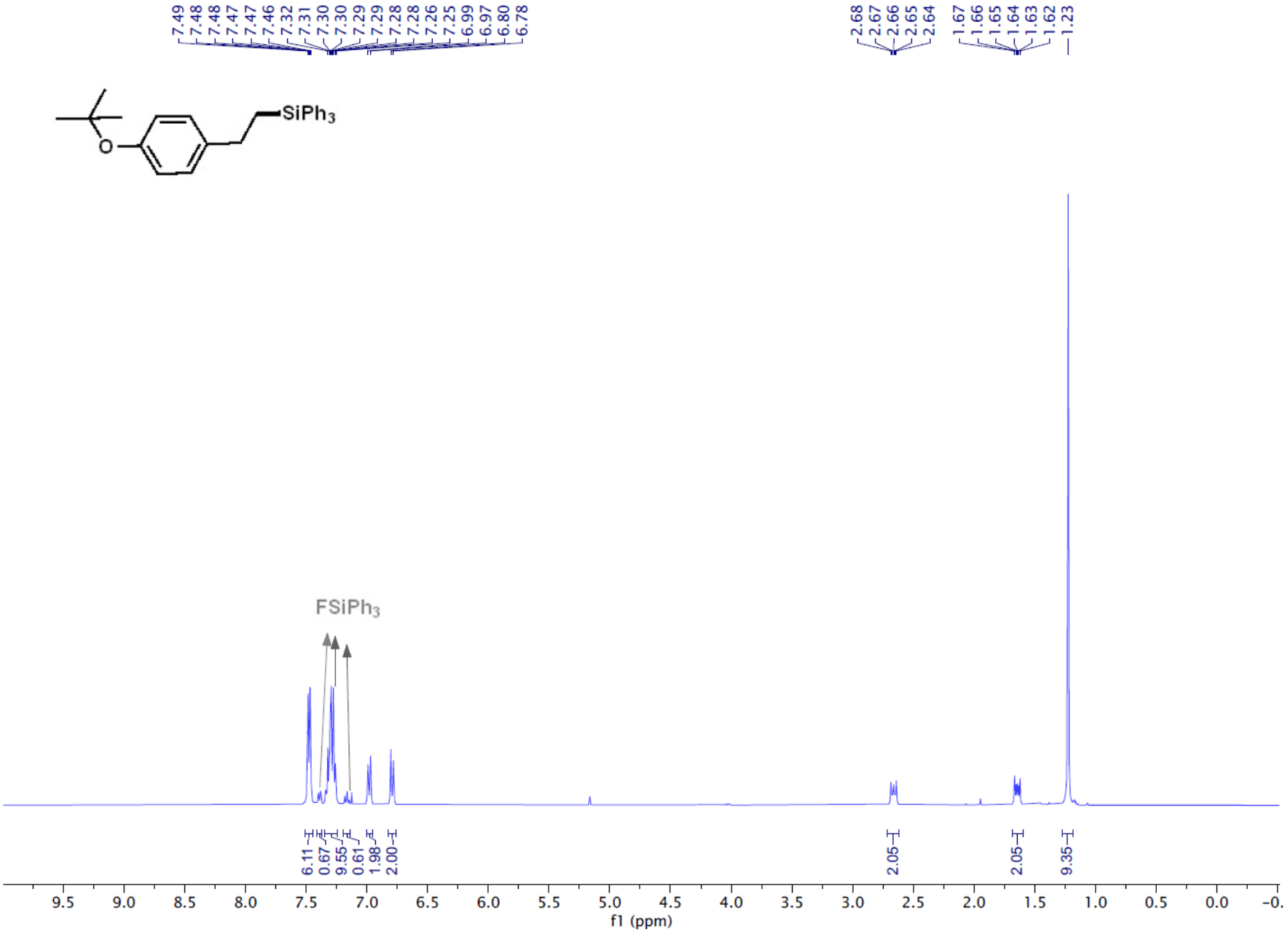
^{1}H NMR (400 MHz, $CDCl_3$) of ***2x***



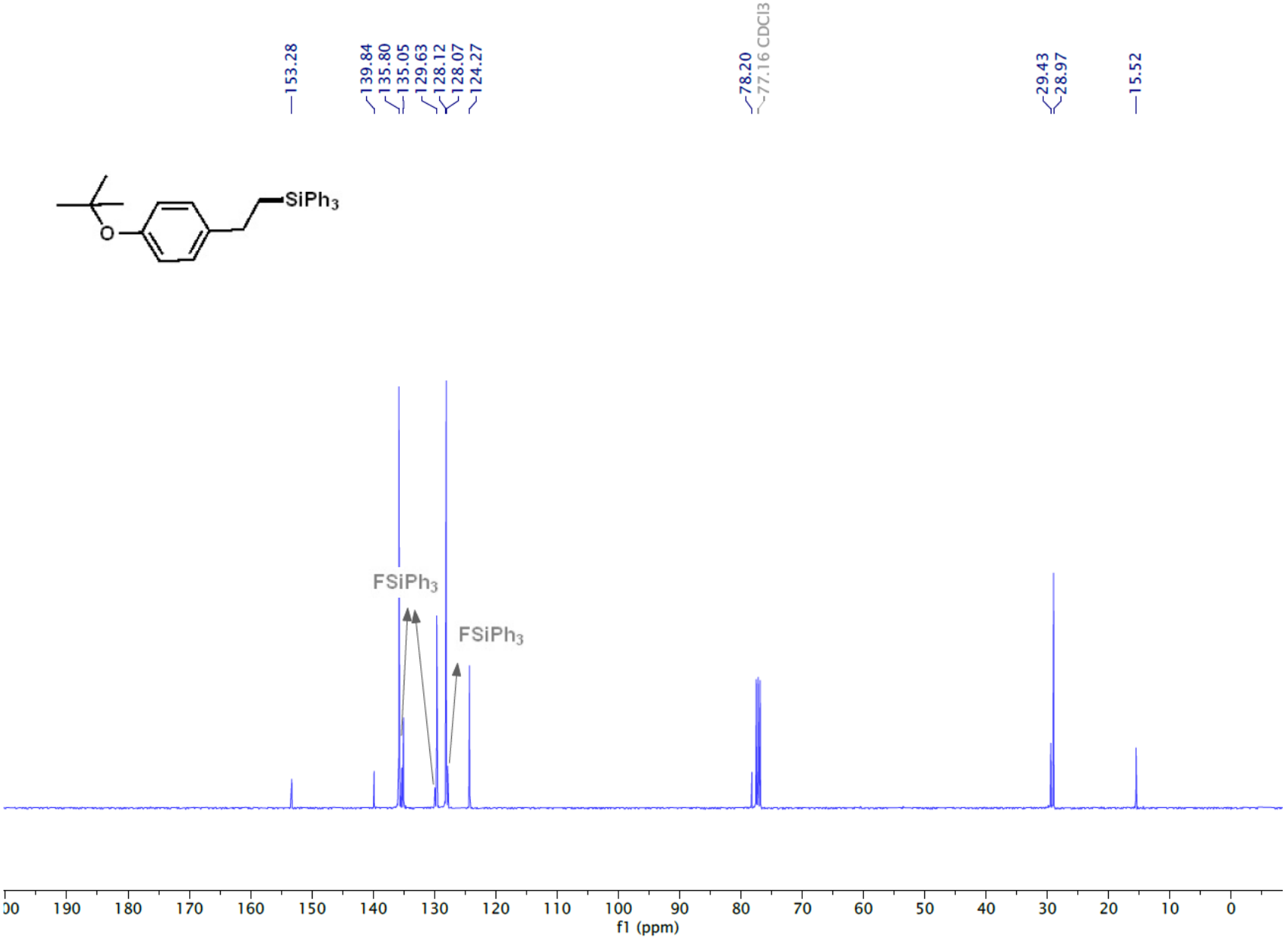
^{13}C NMR (100 MHz, $CDCl_3$) of ***2x***



^{1}H NMR (400 MHz, $CDCl_3$) of ***2y***



^{1}H NMR (400 MHz, $CDCl_3$) of ***2z***



^{13}C NMR (100 MHz, $CDCl_3$) of ***2z***