Electronic Supplementary Material (ESI) for ChemComm.

Dual Photoredox Nickel-catalyzed Silylation of Aryl/ heteroaryl Bromides using Hydrosilanes

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SUPPORTING INFORMATION

Supporting Information

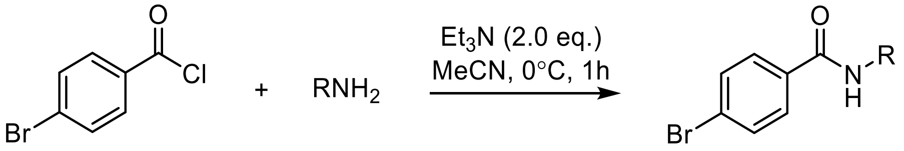
Table of contents

1. General information

All reactions were carried out under an argon atmosphere. Solvents were dried over activated alumina columns on a M-BRAUN Solvent Purification System (SPS-800) unless otherwise noted. The calculated experimental yields refer to chromatographically and spectroscopically (^{1}H-NMR) homogeneous materials unless otherwise stated. All reagent-grade chemicals were obtained from commercial suppliers and were used as received unless otherwise stated. ^{1}H NMR and ^{13}C NMR were recorded at room temperature on various spectrometers: a Bruker Avance 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) and a Bruker Avance 600 (^{1}H: 600 MHz, ^{13}C: 150 MHz) using $CDCl_3$ as internal reference unless otherwise indicated. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz respectively. The following abbreviations were used to explain the multiplicities: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, quint = quintet, hex = hex(sex)tet, hept = hep(sep)tet. Compounds were described as mixtures when it was not possible, in our hands, to separate both compounds. FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 using a KBr pellet. High-resolution mass spectra (HRMS) were recorded with a Waters Q-TOF 2 spectrometer in the electrospray ionization (ESI) or Field Ionization mode (FI). Melting points were not corrected and determined by using a Stuart Scientific SMP3 apparatus. Analytical thin layer chromatography was performed using silica gel 60 F254 pre-coated plates (Merck) with visualization by ultraviolet light. Flash chromatography was performed on silica gel (0.043-0.063 mm) with ethyl acetate (EtOAc) and Petroleum ether (PE) as eluents unless otherwise indicated.

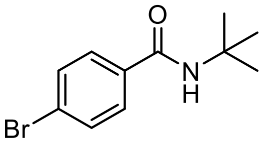
2. Synthesis of the starting Materials

General procedure A for the synthesis of amides:



To a solution of 4-bromobenzoyl chloride (1 eq.) in acetonitrile (0.67 M) were added an appropriate amine (1.5 eq.), triethylamine (2 eq.), and the reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was washed with water, and then the aqueous layer was extracted with dichloromethane. The organic layer was dried and concentrated, and the resulting residue purified by column chromatography on silica gel.

<u>4-bromo-N-(tert-butyl)benzamide (1h)</u>[1]



Based on general procedure **A**, starting from 4-bromobenzoyl chloride (1.1 g, 5.0 mmol), product **1h** has been obtained as a white solid (0.78 g, 3.05 mmol, 61% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.47 (m, 4H), 5.89 (s, 1H), 1.46 (s, 9H).

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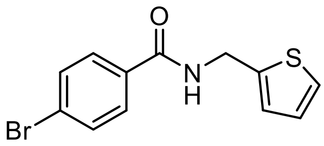
[1] Yu, J. H.; Ciancetta, A.; Dudas, S.; Duca, S.; Lottermoser, J.; Jacobson, K. A. *J. Med. Chem.* **2018**, *61*, 4860-4882.

4-bromo-N-(thiophen-2-ylmethyl)benzamide (1i)



Based on general procedure **A**, starting from 4-bromobenzoyl chloride (1.1 g, 5.0 mmol), product **1i** has been obtained as a white solid (0.79 g, 2.66 mmol, 53% yield).

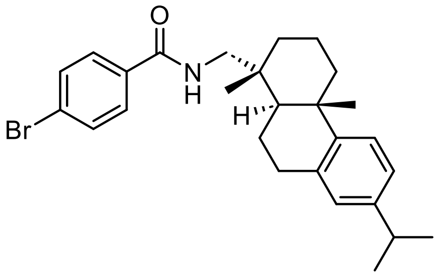
M.p. = 166 – 167 ºC (DCM)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 2H), 7.58 – 7.51 (m, 2H), 7.24 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.02 (dt, *J* = 3.1, 1.0 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.57 (s, 1H), 4.78 (dd, *J* = 5.6, 0.9 Hz, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 166.3, 140.6, 133.1, 132.0, 128.8, 127.1, 126.5, 125.6, 39.0.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 3318, 3081, 1641, 1546, 847, 696.

HRMS (ESI): calcd for $C_{12}H_{10}NOSBrNa$ $[M+Na]^+$: 317.95587, found 317.95471, delta = -3.64 ppm.

4-bromo-N-(((1R,4aS)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)benzamide (1s)



Based on general procedure **A**, starting from 4-bromobenzoyl chloride (1.1 g, 5.0 mmol) and dehydroabietylamine (2.14 g, 7.5 mmol, 1.5 eq.), product **1s** has been obtained as a white solid (1.22 g, 2.6 mmol, 52% yield).

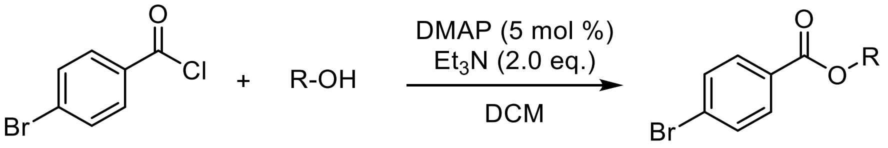
M.p. = 180 – 181 ºC (DCM)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 – 7.47 (m, 4H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.00 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.89 (d, *J* = 2.0 Hz, 1H), 6.15 (t, *J* = 6.5 Hz, 1H), 3.49 – 3.26 (m, 2H), 3.01 – 2.73 (m, 3H), 2.40 – 2.25 (m, 1H), 1.97 (ddt, *J* = 13.2, 7.1, 2.1 Hz, 1H), 1.86 – 1.67 (m, 3H), 1.56 – 1.33 (m, 4H), 1.24 (d, *J* = 1.0 Hz, 6H), 1.22 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 166.9, 147.1, 145.8, 134.8, 133.8, 131.9, 128.6, 127.1, 126.1, 124.3, 124.1, 50.5, 46.0, 38.5, 37.8, 37.7, 36.6, 33.5, 30.5, 25.6, 24.09, 24.07, 19.2, 18.9, 18.8.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 3315, 2957, 2925, 2854, 1640, 1545, 1482, 1305.

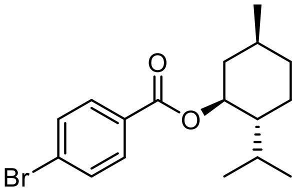
HRMS (ESI): calcd for $C_{27}H_{35}BrNO$ $[M+H]^+$: 468.18965, found 468.18799, delta = -3.56 ppm.

General procedure B for the synthesis of esters:



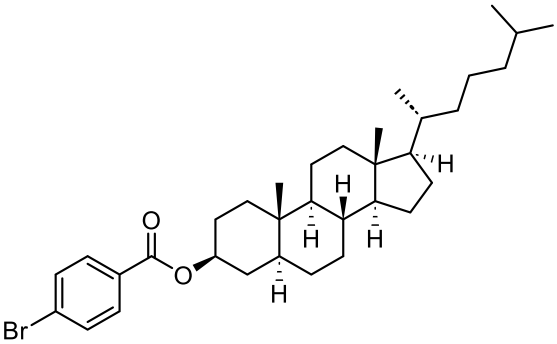
In a round bottom flask, 4-bromobenzoyl chloride (1.0 eq.), the alcohol (1.2 eq.) and 4-dimethylaminopyridine (5.0 mol%) are suspended in DCM (0.4 M). Next, triethylamine (2.0 eq.) was added dropwise to the stirred solution. The reaction was allowed to stir overnight at room temperature. Reaction was then quenched with saturated NH_4Cl and extracted with DCM. The crude material was purified by flash column chromatography to give the corresponding substituted aryl bromide.

(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-bromobenzoate (1p)[2]



Based on general procedure **B**, starting from 4-bromobenzoyl chloride (1.75 g, 8 mmol), product **1p** has been obtained as an oil (1.46 g, 4.3 mmol, 54% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 2H), 7.59 – 7.56 (m, 2H), 4.92 (td, *J* = 10.9, 4.4 Hz, 1H), 2.14 – 2.08 (m, 1H), 1.97 – 1.87 (m, 1H), 1.80 – 1.66 (m, 2H), 1.62 – 1.50 (m, 2H), 1.23 – 1.00 (m, 2H), 0.99 – 0.88 (m, 7H), 0.78 (d, *J* = 6.9 Hz, 3H).

(3S,10S,13R,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-bromobenzoate (1q)



Based on general procedure **B**, starting from 4-bromobenzoyl chloride (1.1 g, 5.0 mmol) and 5β-Coprostanol (2.91 g, 7.5 mmol, 1.5 eq.), product **1q** has been obtained as a white solid (1.8 g, 3.14 mmol, 63% yield).

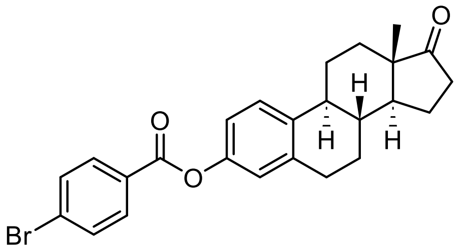
M.p. = 181 – 182 ºC (DCM)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 4.87 – 4.98 (m, 1H), 2.03 – 1.87 (m, 2H), 1.86 – 1.59 (m, 5H), 1.58 – 1.44 (m, 4H), 1.41 – 1.20 (m, 9H), 1.17 – 1.07 (m, 6H), 1.03 – 0.96 (m, 3H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.89 – 0.80 (m, 10H), 0.75 – 0.66 (m, 1H), 0.65 (s, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 165.5, 131.7, 131.2, 130.0, 127.9, 74.9, 56.6, 56.4, 54.4, 44.8, 42.7, 40.1, 39.7, 36.9, 36.3, 36.0, 35.6, 35.6, 34.2, 32.1, 28.8, 28.4, 28.2, 27.7, 24.4, 24.0, 23.0, 22.7, 21.4, 18.8, 12.4, 12.2.

FT-IR $\tilde{\upsilon}_{max}$ (cm^{-1}) = 2950, 2932, 2849, 1715, 1287, 1270, 1115.

HRMS (ESI): calcd for $C_{34}H_{51}O_2BrNa$ $[M+Na]^+$: 593.2965, found 593.2966, delta = 0 ppm.

(13S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 4-bromobenzoate (1r)[3]



para-Bromobenzoic acid (1.01 g, 5.0 mmol), 1,3,5(10)-Estratrien-3-ol-17-one (1.38 g, 5.1 mmol), DMAP (122 mg, 1.0 mmol) and dry CH_2Cl_2 (50 mL) were mixed into a 250 mL round-bottom flask. Under a nitrogen atmosphere, DCC (1.15 g, 5.5 mmol) was added into the above flask in one portion at room temperature, then reaction mixture was stirred at room temperature for 12 hours. After filtering off the solids, the reaction solution was then concentrated by rotary evaporation and the resulting crude solid was purified by column chromatography (5% EtOAc in PE) to afford 70% yield (1.6 g) of **1r** as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 – 8.00 (m, 2H), 7.70 – 7.60 (m, 2H), 7.34 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.02 – 6.90 (m, 2H), 2.92 – 2.97(m, 2H), 2.59 – 2.39 (m, 2H), 2.38 – 2.25 (m, 1H), 2.22 – 1.92 (m, 4H),

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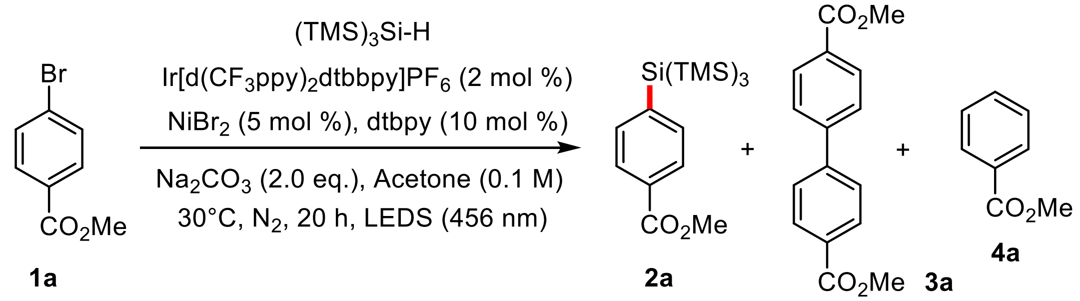
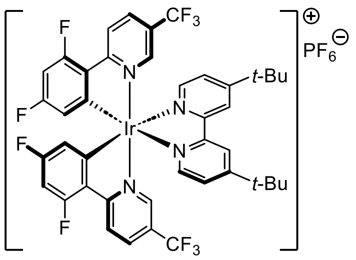
[2] Alandini, N.; Buzzetti, L.; Favi, G.; Schulte, T.; Candish, L.; Collins, K. D.; Melchiorre, P. *Angew. Chem. Int. Ed.* **2020**, *59*, 5248-5253.

[3] Guo, T.; Ding, Y.; Zhou, L.; Xu, H.; Loh, T.-P.; Wu, X. *ACS Catal.* **2020**, *10*, 7262-7268.

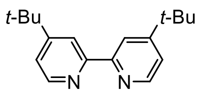
1.72 – 1.43 (m, 6H), 0.93 (s, 3H).

3. Optimization for the silylation of methyl 4-bromobenzoate

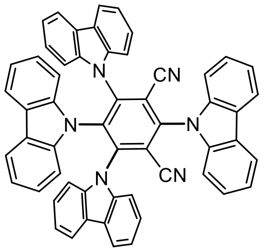




[Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$



dtbpy



4-CzIPN

Entry	Deviation from standard conditions^a	Yield (%)^c **(2a)**	Yield (%)^c **(3a)**	Yield (%)^c **(4a)**
1	none	44	5	12
2	no catalyst [Ir]	0	0	0
3	no light	0	0	0
4	no base	trace	trace	Trace
5	4-CzIPN instead of [Ir]	45	7	11
6	K_2CO_3	< 10	-	-
7	K_3PO_4	< 10	-	-
8	K_2HPO_4	< 10	-	-
9	CS_2CO_3	< 10	-	-
10	TMG	< 10	-	-
11	NaOAc	< 10	-	-
12	Li_2CO_3	21	-	-
13	Et_3N	11	-	-
14	2,6-lutidine	37	4	36
15	Na_2CO_3 (1.0 eq.)	32	4	18
15	$NiCl_2$·glyme	42	16	30
16	$NiBr_2$·glyme	44	17	20
17	$NiBr_2$	44	5	12
18	$NiBr_2$·2-methoxyethyl ether	36	13	30
19	bpy	38	24	25

20	4,4’-OMe-bpy	21	6	32
21	5,5’-CF_3-bpy	17	47	11
22	DCM	0	0	0
23	DME	39	30	19
24	MeCN	33	20	21
25	THF	27	-	-
26	DMF	0	-	-
27	DMSO	0	-	-
28	$PhCF_3$	15	7	8
39	MeOH	0	-	-
30	DME	39	30	19
31	NaBr (20 mol%) as additive	18	11	20
32	TBAB (20 mol%) as additive	< 10	-	-
33	LiBr (20 mol%) as additive	25	7	15
34[b]	$(TMS)_3SiH$ (3 eq.)	62	11	14

[a] Standard conditions: $Ir[d(CF_3ppy)_2dtbbpy]PF_6$ (2 mol %), $NiBr_2$ (5 mol %), dtbpy (10 mol %), Na_2CO_3 (2 eq.), **1a** (0.2 mmol, 1 eq.), $(TMS)_3SiH$ (0.4 mmol, 2 eq.), dry acetone (2.0 mL), Kessil 40 W LEDs (456 nm), 30°C, 20 h. [b] $(TMS)_3SiH$ (0.6 mmol, 3 eq.). [c] ^1H NMR yields of **2a**, **3a**, and **4a** using mesitylene as an internal standard.

4. General Procedure C for photoredox reactions

We used Kessil PR160L-456nm LED PhotoReaction Lighting (www.kessil.com). Kessil LED lamp had high output, precise wavelength and strong penetrating power. It could precisely control the wavelength of the light source within the required wavelength ±5nm range. The lamp emission spectrum is shown in the Fig.S1.

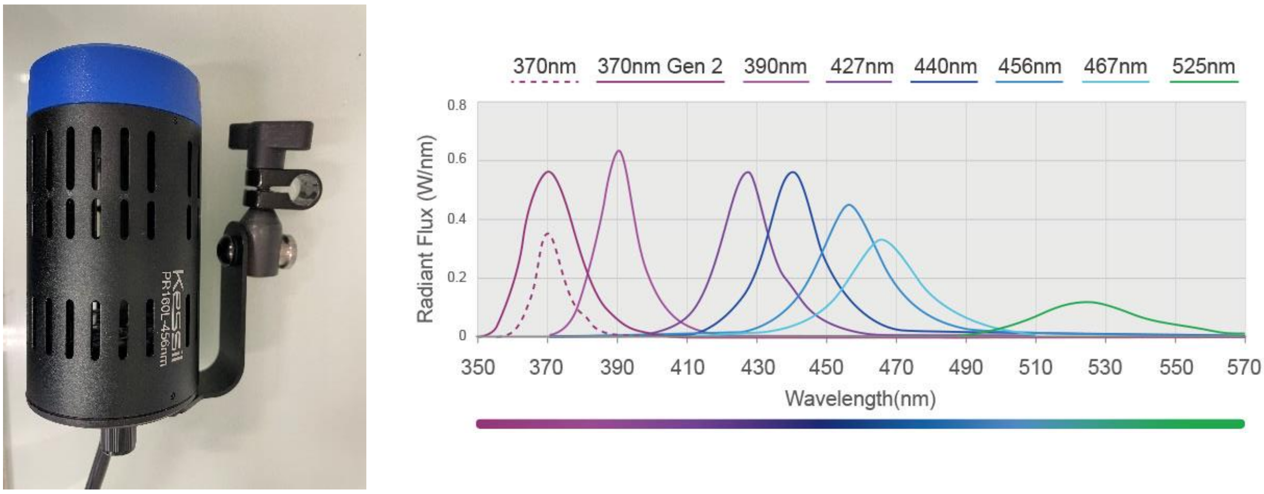
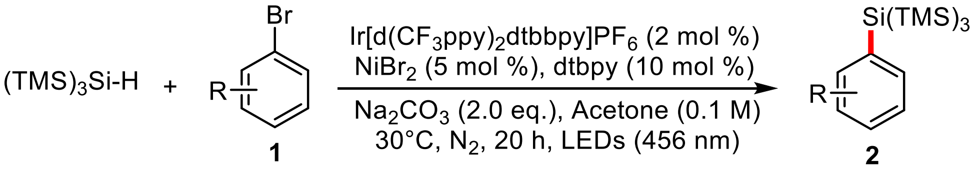


Figure S1. Kessil PR160L LED PhotoReaction Lighting and the lamp emission spectrum.



The Photo Reaction Setup was shown in Fig.S2. To a Schlenk tube with a screw-cap was added [Ir[dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 0.004 mmol, 2 mol%), NiBr$_2$ (2.2 mg, 0.01 mmol, 5 mol %), dtbpy (5.4 mg, 0.02 mmol, 10 mol %), aryl bromide **1** (0.2 mmol, 1.0 eq.) (if solid) and Na$_2$CO$_3$ (42.4 mg, 0.4 mmol, 2.0 eq.). The tube was evacuated and back-filled with nitrogen (this process was repeated three times). Aryl bromide **1** (0.2 mmol, 1.0 eq.) (if liquid), (TMS)$_3$Si-H (149 mg, 0.6 mmol, 3.0 eq.) and dry acetone (2 mL) were added consecutively using a syringe. The resulting mixture was degassed via three cycles of freeze-pump-backfill-thaw. The reaction vessel was sealed and placed ~4 cm away from a 40 W blue LED (the maximum emission peak 456 nm) and stirred for 20 h while cooling with a fan. The average temperature inside the flask was 30°C. The mixture was then concentrated under vacuum. The resulting residue was purified by silica gel chromatography to afford **2**.

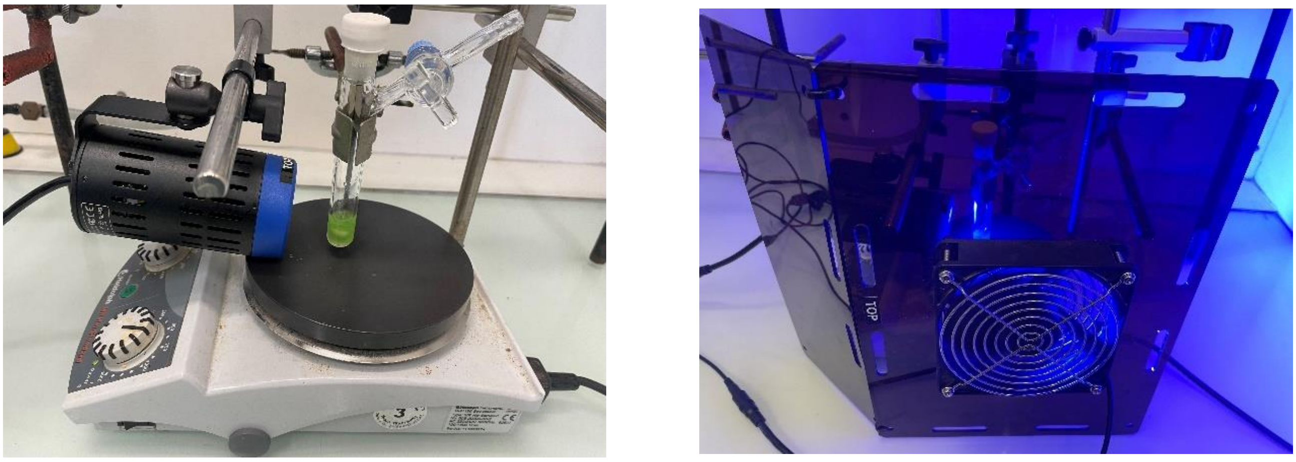
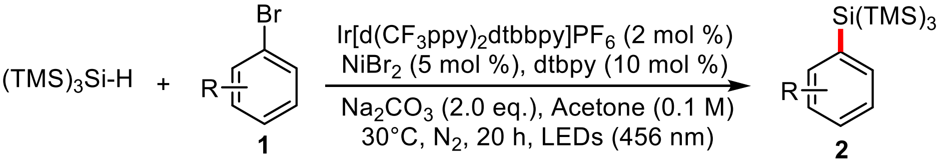
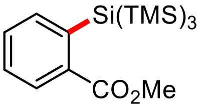


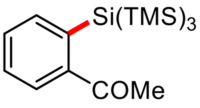
Fig.S2. The photocatalytic reaction Setup.

5. Examples of failed compounds

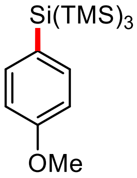




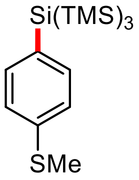
2Z, ND,



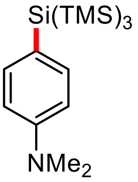
2aa, ND



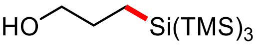
2ab, ND



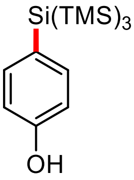
2ac, trace



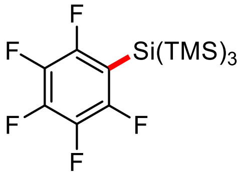
2ad, 19%



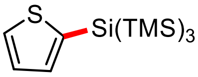
2ae, ND



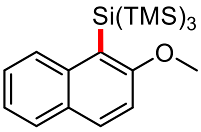
2af, ND



2ag, ND



2ah, ND



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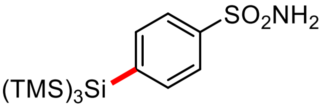
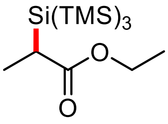
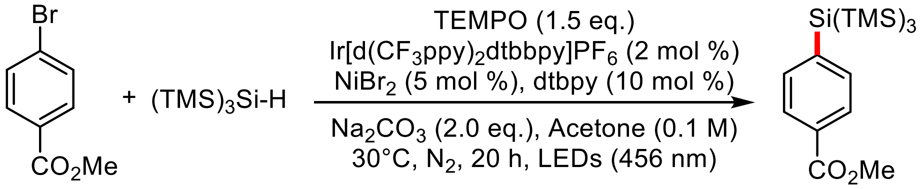


2aj, NR



2ak, ND

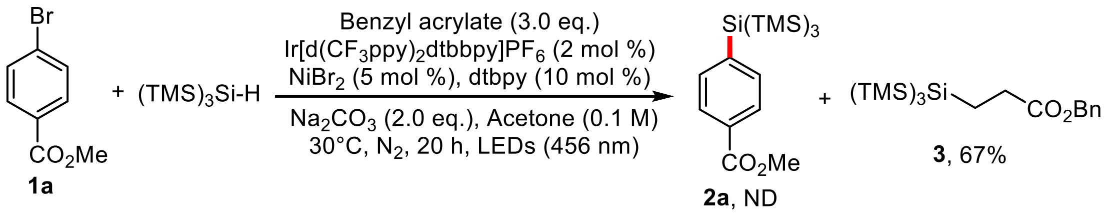
6. Mechanistic studies



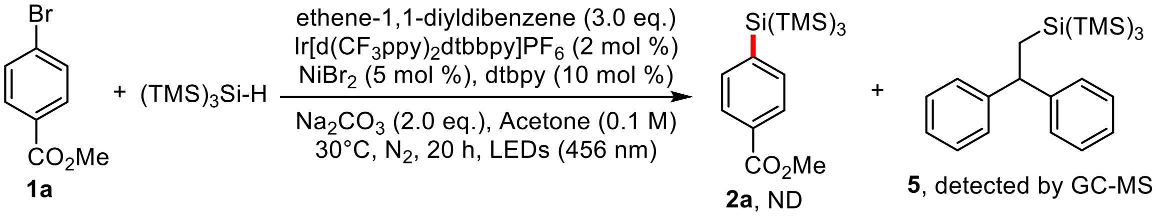
1a

2a, NR

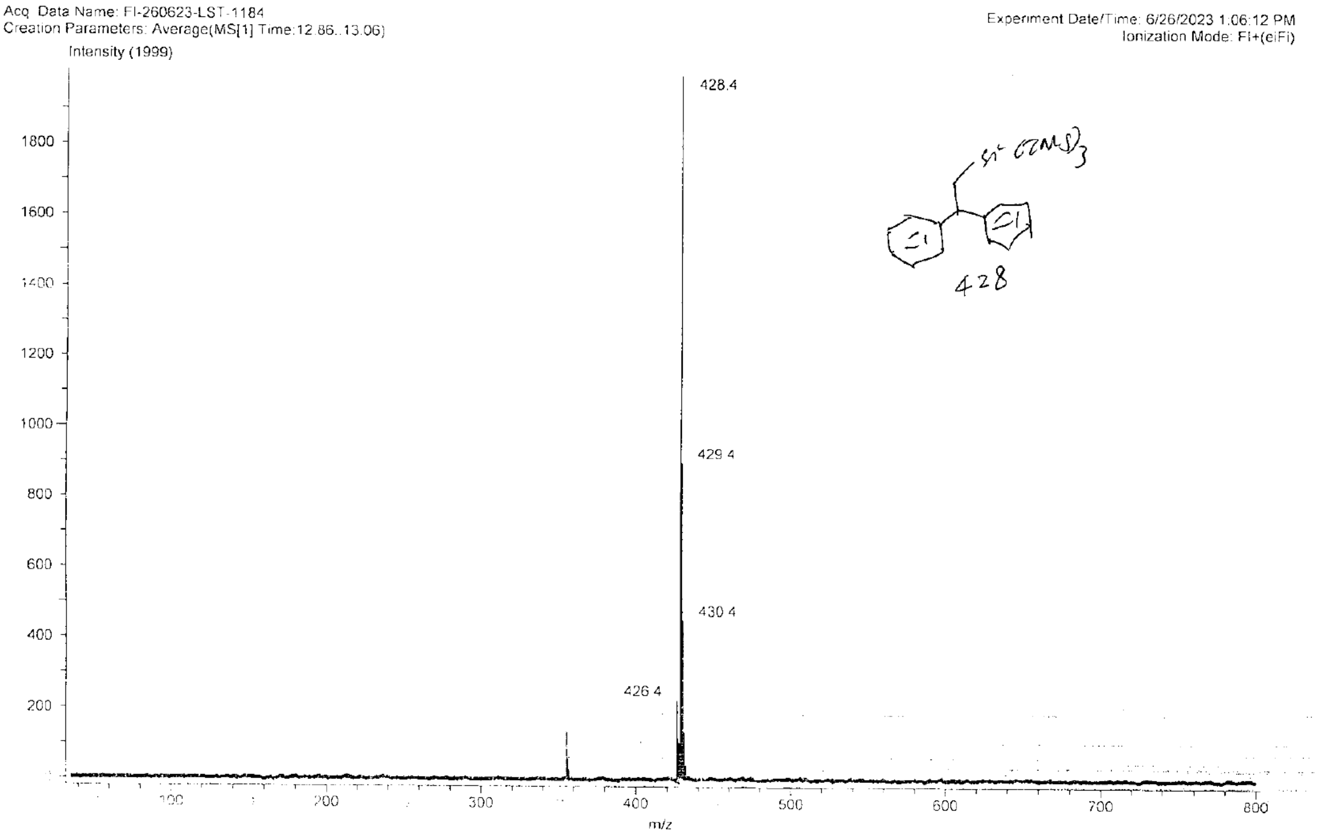
To a Schlenk tube with a screw-cap was added [Ir[dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 0.004 mmol, 2 mol%), NiBr$_2$ (2.2 mg, 0.01 mmol, 5 mol %), dtbpy (5.4 mg, 0.02 mmol, 10 mol %), methyl 4-bromobenzoate **1a** (43 mg, 0.2 mmol, 1.0 eq.), Na$_2$CO$_3$ (42.4 mg, 0.4 mmol, 2.0 eq.), and TEMPO (47 mg, 0.3 mmol, 1.5 eq.). The tube was evacuated and back-filled with nitrogen (this process was repeated three times). (TMS)$_3$Si-H (149 mg, 0.6 mmol, 3.0 eq.) and dry acetone (2 mL) were added consecutively using a syringe. The resulting mixture was degassed via three cycles of freeze-pump-backfill-thaw. The reaction vessel was sealed and placed ~4 cm away from a 40 W 456 nm blue LED and stirred for 20 h at 30°C while cooling with a fan.

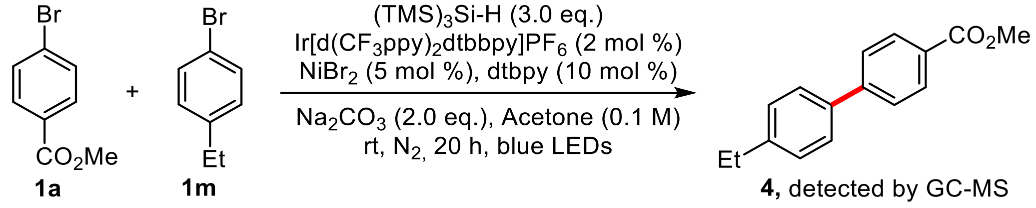


To a Schlenk tube with a screw-cap was added $[Ir[dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 0.004 mmol, 2 mol%), $NiBr_2$ (2.2 mg, 0.01 mmol, 5 mol %), dtbpy (5.4 mg, 0.02 mmol, 10 mol %), methyl 4-bromobenzoate **1a** (43 mg, 0.2 mmol, 1.0 eq.), Na_2CO_3 (42.4 mg, 0.4 mmol, 2.0 eq.), and benzyl acrylate (97 mg, 0.6 mmol, 3.0 eq.). The tube was evacuated and back-filled with nitrogen (this process was repeated three times). $(TMS)_3Si$-H (149 mg, 0.6 mmol, 3.0 eq.) and dry acetone (2 mL) were added consecutively using a syringe. The resulting mixture was degassed via three cycles of freeze-pump-backfill-thaw. The reaction vessel was sealed and placed ~4 cm away from a 40 W 456 nm blue LED and stirred at 30°C for 20 h while cooling with a fan.

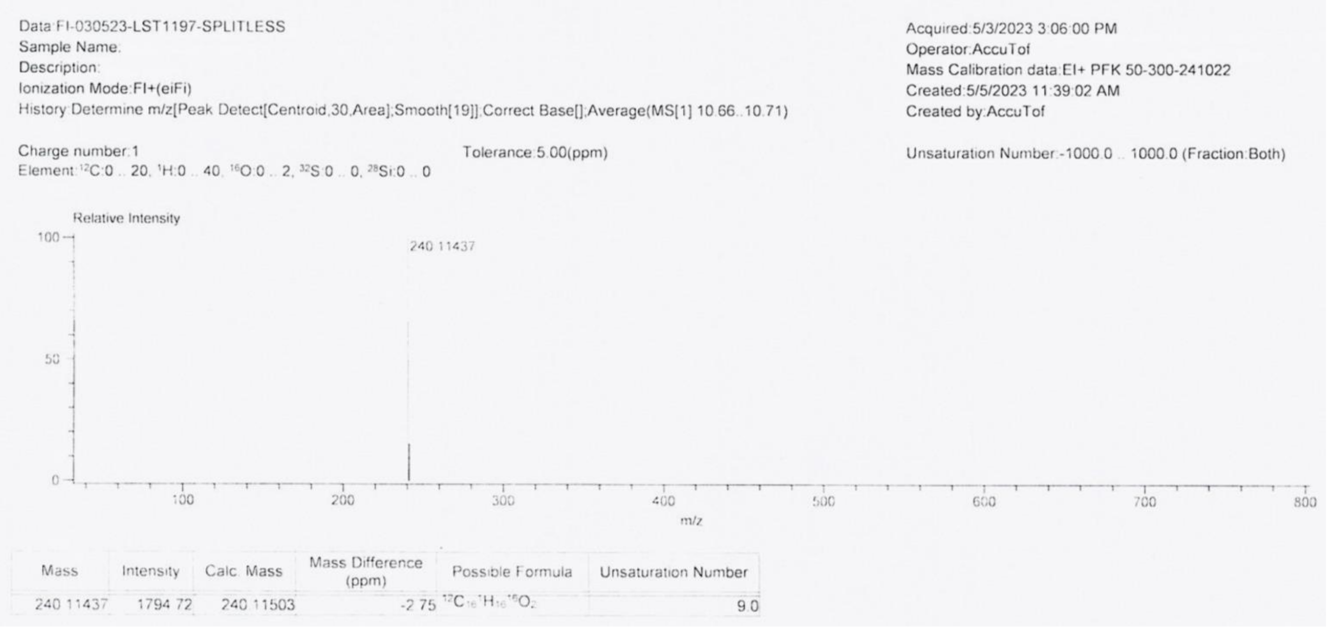


To a Schlenk tube with a screw-cap was added $[Ir[dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 0.004 mmol, 2 mol%), $NiBr_2$ (2.2 mg, 0.01 mmol, 5 mol %), dtbpy (5.4 mg, 0.02 mmol, 10 mol %), methyl 4-bromobenzoate **1a** (43 mg, 0.2 mmol, 1.0 eq.), Na_2CO_3 (42.4 mg, 0.4 mmol, 2.0 eq.), and ethene-1,1-diyldibenzene (108 mg, 0.6 mmol, 3.0 eq.). The tube was evacuated and back-filled with nitrogen (this process was repeated three times). $(TMS)_3Si$-H (149 mg, 0.6 mmol, 3.0 eq.) and dry acetone (2 mL) were added consecutively using a syringe. The resulting mixture was degassed via three cycles of freeze-pump-backfill-thaw. The reaction vessel was sealed and placed ~4 cm away from a 40 W 456 nm blue LED and stirred at 30°C for 20 h while cooling with a fan. After that, the resulting mixture was subjected to GC-MS.





To a Schlenk tube with a screw-cap was added [Ir[dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 0.004 mmol, 2 mol%), NiBr$_2$ (2.2 mg, 0.01 mmol, 5 mol %), dtbpy (5.4 mg, 0.02 mmol, 10 mol %), methyl 4-bromobenzoate **1a** (43 mg, 0.2 mmol, 1.0 eq.), and Na$_2$CO$_3$ (42.4 mg, 0.4 mmol, 2.0 eq.). The tube was evacuated and back-filled with nitrogen (this process was repeated three times). (TMS)$_3$Si-H (149 mg, 0.6 mmol, 3.0 eq.), 1-bromo-4-ethylbenzene (37 mg, 0.2 mmol, 1.0 eq.), and dry acetone (2 mL) were added consecutively using a syringe. The resulting mixture was degassed via three cycles of freeze-pump-backfill-thaw. The reaction vessel was sealed and placed ~4 cm away from a 40 W 456 nm blue LED and stirred at 30°C for 20 h while cooling with a fan. After that, the resulting mixture was subjected to GC-MS.



Data:FI-030523-LST1197-SPLITLESS
Sample Name:
Description:
Ionization Mode:FI+(eiFi)
History:Determine m/z[Peak Detect[Centroid,30,Area];Smooth[19]];Correct Base[];Average(MS[1] 10.66..10.71)

Acquired:5/3/2023 3:06:00 PM
Operator:AccuTof
Mass Calibration data:EI+ PFK 50-300-241022
Created:5/5/2023 11:39:02 AM
Created by:AccuTof

Charge number:1
Element:^{12}C:0 .. 20, ^{1}H:0 .. 40, ^{16}O:0 .. 2, ^{32}S:0 .. 0, ^{28}Si:0 .. 0

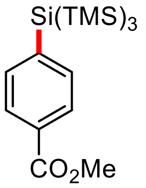
Tolerance:5.00(ppm)

Unsaturation Number:-1000.0 .. 1000.0 (Fraction:Both)

Mass	Intensity	Calc. Mass	Mass Difference (ppm)	Possible Formula	Unsaturation Number
240.11437	1794.72	240.11503	-2.75	$^{12}C_{16}{}^{1}H_{16}{}^{16}O_2$	9.0

7. Characterization Data

Methyl 4-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)benzoate (2a)



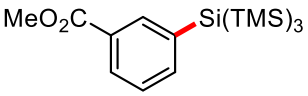
Based on general procedure **C**, starting from methyl 4-bromobenzoate (43 mg, 0.2 mmol), product **2a** has been obtained after flash column chromatography (PE: EA = 200: 1 to 100: 1) as an oil (46 mg, 0.12 mmol, 60% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.93 – 7.86 (m, 2H), 7.55 – 7.50 (m, 2H), 3.90 (s, 3H), 0.22 (s, 27H). ^{13}C NMR (76 MHz, CDCl$_3$) δ 167.6, 143.9, 136.5, 129.1, 128.4, 52.1, 1.3. ^{29}Si NMR (60 MHz, CDCl$_3$) δ -12.60, -75.72.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 2953, 2895, 1727, 1280, 1246, 835.

HRMS (FI): calcd for $C_{17}H_{34}BrO_2Si_4$ $[M]^{+\bullet}$: 382.16359, found 382.16472, delta = 2.98 ppm.

Methyl 3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)benzoate (2b)



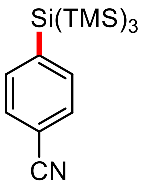
Based on general procedure **C**, starting from methyl 3-bromobenzoate (43 mg, 0.2 mmol), product **2b** has been obtained after flash column chromatography (PE: EA = 200: 1 to 100: 1) as an oil (34 mg, 0.09 mmol, 45% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.20 – 8.18 (m, 1H), 7.93 – 7.89 (m, 1H), 7.62 (dt, *J* = 7.4, 1.3 Hz, 1H), 7.30 – 7.35 (m, 1H), 3.91 (s, 3H), 0.23 (s, 27H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 167.6, 140.9, 137.7, 136.7, 129.4, 128.6, 127.8, 52.2, 1.2. ^{29}Si NMR (60 MHz, CDCl$_3$) δ -12.68, -75.94.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 2952, 2895, 1728, 1280, 1260, 1119, 835.

HRMS (FI): calcd for $C_{17}H_{34}BrO_2Si_4$ $[M]^{+\bullet}$: 382.16359, found 382.16455, delta = 2.52 ppm.

4-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)benzonitrile (2c)



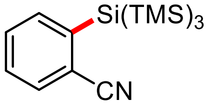
Based on general procedure **C**, starting from 4-bromobenzonitrile (36.4 mg, 0.2 mmol), product **2c** has been obtained after flash column chromatography (PE: EA = 200: 1 to 100: 1) as an oil (35 mg, 0.10 mmol, 50% yield).

^1H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 4H), 0.22 (s, 27H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.0, 136.9, 130.8, 119.4, 111.1, 1.2. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -12.52, -74.47.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 2958, 2896, 2228, 1248, 1055, 836.

HRMS (Cl^+): calcd for $C_{16}H_{32}N_1Si_4$ $[M+H]^{+\bullet}$: 350.16118, found 350.16118, delta = 0 ppm

2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)benzonitrile (2d)



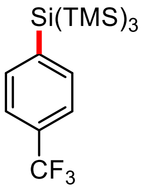
Based on general procedure **C**, starting from 2-bromobenzonitrile (36.4 mg, 0.2 mmol), product **2d** has been obtained after flash column chromatography (PE: EA = 200: 1 to 100: 1) as an oil (28 mg, 0.08 mmol, 40% yield).

^1H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.69 (m, 2H), 7.45 – 7.31 (m, 2H), 0.30 (s, 27H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 142.9, 138.2, 134.8, 131.2, 127.9, 121.6, 119.8, 2.1. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -11.44, -71.48.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 2955, 2897, 1247, 1053, 837.

HRMS (Cl^+): calcd for $C_{16}H_{32}N_1Si_4$ $[M+C_2H_5]^{+\bullet}$: 378.19248, found 378.19260, delta = 0.31 ppm.

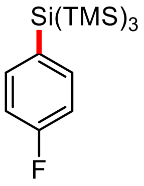
1,1,1,3,3,3-hexamethyl-2-(4-(trifluoromethyl)phenyl)-2-(trimethylsilyl)trisilane (2e)[4]



Based on general procedure **C**, starting from 1-bromo-4-(trifluoromethyl)benzene (45 mg, 0.2 mmol), product **2e** has been obtained after flash column chromatography (pentane) as an oil (33 mg, 0.084 mmol, 42% yield).

^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, J = 7.4 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 0.23 (s, 27H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.8. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -12.63, -75.75.

2-(4-fluorophenyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2f)[4]



Based on general procedure **C**, starting from 1-bromo-4-fluorobenzene (35 mg, 0.2 mmol), product **2f** has been obtained after flash column chromatography (pentane) as an oil (28 mg, 0.082 mmol, 41% yield).

^1H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 2H), 6.94 – 7.00 (m, 2H), 0.22 (s, 27H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.5 – -114.6 (m, 1F). ^{29}Si NMR (60 MHz, $CDCl_3$) δ -12.87, -76.79. ^{13}C NMR (76 MHz, $CDCl_3$) δ 163.1 (d, J = 246.5 Hz), 138.1 (d, J = 7.0 Hz), 130.7 (d, J = 4.0 Hz), 115.1 (d, J = 19.5 Hz), 1.3.

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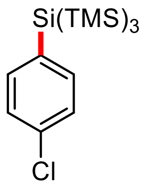
[4] Sanganee, M. J.; Steel, P. G.; Whelligan, D. K. *J. Org. Chem.* **2003**, *68*, 3337-3339.

2-(4-chlorophenyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2g)



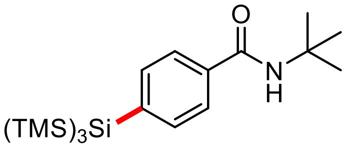
Based on general procedure **C**, starting from 1-bromo-4-chlorobenzene (38 mg, 0.2 mmol), product **2g** has been obtained after flash column chromatography (pentane) as an oil (35 mg, 0.098 mmol, 49% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.42 – 7.31 (m, 2H), 7.28 – 7.19 (m, 3H), 0.22 (s, 31H). ^{13}C NMR (76 MHz, CDCl$_3$) δ 137.8, 134.2, 133.9, 128.1, 1.3. ^{29}Si NMR (60 MHz, CDCl$_3$) δ -12.82, -76.50.

FT-IR ῡ$_{max}$ (cm^{-1}) = 2957, 2897, 1580, 1481, 1254, 1064, 845.

HRMS (FI): calcd for $C_{15}H_{31}ClSi_4$ [M]$^{+\bullet}$: 358.11913, found 358.11830, delta = -2.32 ppm.

N-(tert-butyl)-4-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)benzamide (2h)



Based on general procedure **C**, starting from 4-bromo-*N*-(*tert*-butyl)benzamide (51.2 mg, 0.2 mmol), product **2h** has been obtained after flash column chromatography (PE: EA = 100: 1 to 30: 1) as a white solid (51 mg, 0.12 mmol, 60% yield).

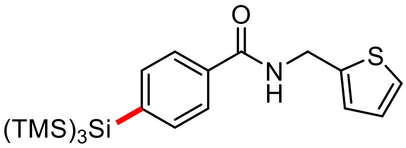
M.p. = 217 – 218 °C (DCM)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H), 5.94 (s, 1H), 1.46 (s, 9H), 0.21 (s, 27H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 167.2, 140.8, 136.7, 134.8, 125.9, 51.6, 29.0, 1.3. ^{29}Si NMR (60 MHz, CDCl$_3$) δ -12.68, -76.24.

FT-IR ῡ$_{max}$ (cm^{-1}) = 3240, 3059, 2955, 2894, 1629, 1243, 834.

HRMS (ESI): calcd for $C_{20}H_{42}OSi_4$ [M+H]$^{+\bullet}$: 424.23380, found 424.23224, delta = -3.67 ppm.

4-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-N-(thiophen-2-ylmethyl)benzamide (2i)



Based on general procedure **C**, starting from 4-bromo-*N*-(thiophen-2-ylmethyl)benzamide (59.2 mg, 0.2 mmol), product **2i** has been obtained after flash column chromatography (PE: EA = 100: 1 to 10: 1) as a white solid (57 mg, 0.124 mmol, 62% yield).

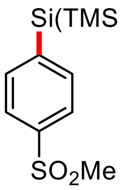
M.p. = 186 – 187 °C (DCM)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.71 – 7.62 (m, 2H), 7.56 – 7.47 (m, 2H), 7.23 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.06 – 6.99 (m, 1H), 6.95 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.53 (s, 1H), 4.80 (dd, *J* = 5.6, 0.9 Hz, 2H), 0.22 (s, 27H). ^{13}C NMR (76 MHz, CDCl$_3$) δ 167.5, 141.8, 141.0, 136.7, 133.1, 127.1, 126.3, 126.1, 125.4, 38.9, 1.3. ^{29}Si NMR (60 MHz, CDCl$_3$) δ -12.64, -76.01.

FT-IR ῡ$_{max}$ (cm^{-1}) = 3247, 3060, 2950, 2894, 1630, 1246, 835.

HRMS (ESI): calcd for $C_{21}H_{38}ONSi_4$ [M+H]$^{+\bullet}$: 464.17457, found 464.17337, delta = -2.58 ppm.

1,1,1,3,3,3-hexamethyl-2-(4-(methylsulfonyl)phenyl)-2-(trimethylsilyl)trisilane (2j)



Based on general procedure **C**, starting from 1-bromo-4-(methylsulfonyl)benzene (47 mg, 0.2 mmol), product **2j** has been obtained after flash column chromatography (PE: EA = 100: 1 to 10: 1) as a white solid (37 mg, 0.092 mmol, 46% yield).

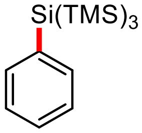
M.p. = 94 – 95 ºC (DCM)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.83 – 7.75 (m, 2H), 7.67 – 7.60 (m, 2H), 3.06 (s, 3H), 0.23 (s, 27H). ^{13}C NMR (76 MHz, CDCl$_3$) δ 146.0, 139.4, 137.1, 126.0, 44.6, 1.2. ^{29}Si NMR (60 MHz, CDCl$_3$) δ -12.47, -74.92.

FT-IR ῡ$_{max}$ (cm^{-1}) = 2953, 2895, 1577, 1315, 1247, 1155, 956, 836.

HRMS (FI): calcd for $C_{16}H_{34}O_2S_1Si_4$ [M]$^{+\bullet}$: 402.13566, found 402.13659, delta = 2.33 ppm.

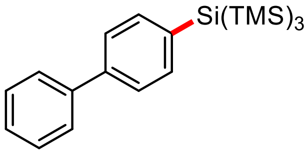
1,1,1,3,3,3-hexamethyl-2-phenyl-2-(trimethylsilyl)trisilane (2k)[4]



Based on general procedure **C**, starting from bromobenzene (31.4 mg, 0.2 mmol), product **2k** has been obtained after flash column chromatography (pentane) as an oil (43 mg, 0.132 mmol, 66% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.49 – 7.44 (m, 2H), 7.31 – 7.20 (m, 3H), 0.23 (s, 27H).

2-([1,1'-biphenyl]-4-yl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2l)



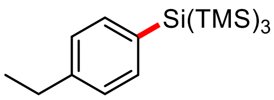
Based on general procedure **C**, starting from 4-bromo-1,1'-biphenyl (47 mg, 0.2 mmol), product **2l** has been obtained after flash column chromatography (pentane) as an oil (38 mg, 0.096 mmol, 48% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.65 – 7.59 (m, 2H), 7.52 (d, *J* = 0.6 Hz, 4H), 7.48 – 7.40 (m, 2H), 7.38 – 7.30 (m, 1H), 0.26 (s, 27H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 141.2, 140.1, 137.1, 134.6, 128.9, 127.3, 127.1, 126.5, 1.4. ^{29}Si NMR (60 MHz, CDCl$_3$) δ -12.77, -77.10.

FT-IR ῡ$_{max}$ (cm^{-1}) = 2950, 2893, 1482, 1245, 833.

HRMS (FI): calcd for $C_{21}H_{36}Si_4$ [M]$^{+\bullet}$: 400.18941, found 400.18981, delta = 1.0 ppm.

2-(4-ethylphenyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2m)



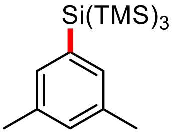
Based on general procedure **C**, starting from 1-bromo-4-ethylbenzene (37 mg, 0.2 mmol), product **2m** has been obtained after flash column chromatography (pentane) as an oil (31.9 mg, 0.09 mmol, 45% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.40 – 7.32 (m, 2H), 7.14 – 7.06 (m, 2H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H), 0.22 (s, 27H). ^{13}C NMR (76 MHz, CDCl$_3$) δ 143.4, 136.7, 131.6, 127.5, 28.8, 15.3, 1.4. ^{29}Si NMR (60 MHz, CDCl$_3$) δ -12.90, -77.56.

FT-IR ῡ$_{max}$ (cm^{-1}) = 2958, 2896, 1246, 1055, 836.

HRMS (FI): calcd for $C_{17}H_{36}Si_4$ [M]$^{+\bullet}$: 352.18941, found 352.18990, delta = 1.40 ppm.

2-(3,5-dimethylphenyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2n)



Based on general procedure **C**, starting from 1-bromo-3,5-dimethylbenzene (37 mg, 0.2 mmol), product **2n** has been obtained after flash column chromatography (pentane) as a white solid (22 mg, 0.062 mmol, 31% yield).

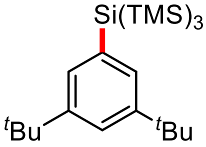
M.p.: 61 – 62 ºC (DCM)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 – 7.05 (m, 2H), 6.88 – 6.90 (m, 1H), 2.28 (s, 6H), 0.22 (s, 27H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 136.8, 135.0, 134.6, 129.3, 21.6, 1.4. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -12.93, -77.31.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 2952, 2895, 1245, 1054, 836.

HRMS (FI): calcd for $C_{17}H_{36}Si_4$ $[M]^{+\bullet}$: 352.18941, found 352.18940, delta = -0.02 ppm.

2-(3,5-di-tert-butylphenyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2o)



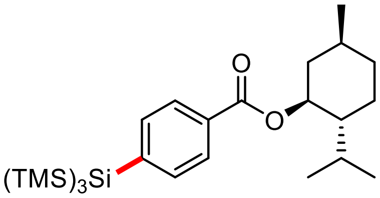
Based on general procedure **C**, starting from 1-bromo-3,5-di-tert-butylbenzene (54 mg, 0.2 mmol), product **2o** has been obtained after flash column chromatography (pentane) as an oil (21 mg, 0.048 mmol, 24% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 1.9 Hz, 2H), 7.29 – 7.27 (m, 1H), 1.32 (s, 18H), 0.23 (s, 27H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 149.5, 133.8, 131.1, 121.2, 34.9, 31.7, 1.3. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -12.86, -76.62.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 2958, 2899, 1247, 1049, 836.

HRMS (FI): calcd for $C_{23}H_{48}Si_4$ $[M]^{+\bullet}$: 436.28331, found 436.28410, delta = 1.82 ppm.

(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl-4-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)benzoate (2p)

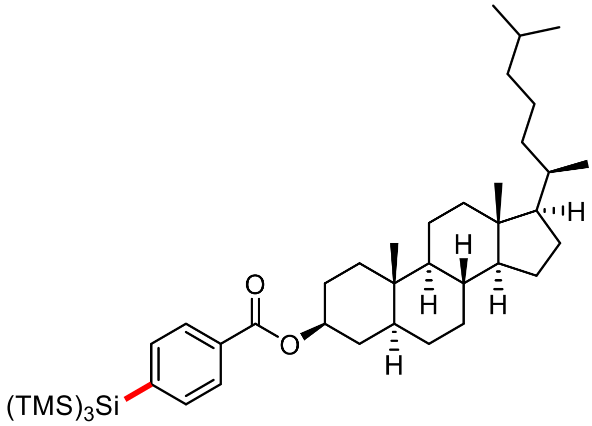


Based on general procedure **C**, starting from (1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-bromobenzoate (68 mg, 0.2 mmol), product **2p** has been obtained after flash column chromatography (PE: EA = 200: 1 to 100: 1) as an oil (53 mg, 0.104 mmol, 52% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 2H), 4.92 (td, *J* = 10.9, 4.2 Hz, 1H), 2.12 (d, *J* = 12.2 Hz, 1H), 2.05 – 1.95 (m, 1H), 1.73 (d, *J* = 12.1 Hz, 2H), 1.54 (t, *J* = 11.8 Hz, 2H), 1.23 – 0.95 (m, 3H), 0.92 (d, *J* = 7.0 Hz, 6H), 0.80 (d, *J* = 6.9 Hz, 3H), 0.23 (s, 27H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 143.4, 136.5, 129.9, 128.5, 74.8, 47.5, 41.2, 34.5, 31.6, 26.5, 23.7, 22.2, 21.0, 16.6, 1.3. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -12.60, -75.84.

HRMS (FI): calcd for $C_{26}H_{50}O_2Si_4$ $[M]^{+\bullet}$: 506.28879, found 506.28928, delta = 0.98 ppm.

(3S,10S,13R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)benzoate (2q)



Based on general procedure **C**, starting from (3S,10S,13R,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-bromobenzoate (114.3 mg, 0.2 mmol), product **2q** has been obtained after flash column chromatography (PE: EA = 200: 1 to 100: 1) as a white solid (86 mg, 0.116 mmol, 58% yield).

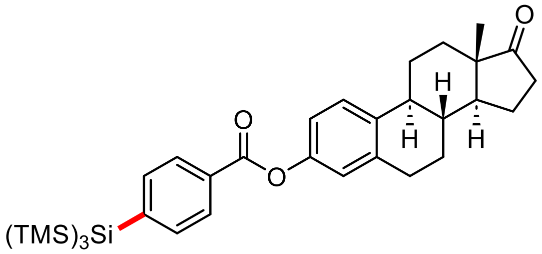
M.p. = 172 – 174 °C (DCM)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 – 7.84 (m, 2H), 7.59 – 7.45 (m, 2H), 4.93 (tt, *J* = 10.8, 4.9 Hz, 1H), 2.02 – 1.88 (m, 2H), 1.82 – 1.45 (m, 9H), 1.42 – 1.25 (m, 8H), 1.20 – 0.93 (m, 10H), 0.93 – 0.84 (m, 13H), 0.72 – 0.68 (m, 1H), 0.66 (s, 3H), 0.22 (s, 27H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 166.6, 143.4, 136.5, 129.9, 128.4, 74.3, 56.6, 56.4, 54.41, 44.9, 42.8, 40.2, 39.7, 37.0, 36.3, 36.0, 35.7, 34.3, 32.2, 28.8, 28.4, 28.2, 27.8, 24.4, 24.0, 23.0, 22.7, 21.4, 18.8, 12.4, 12.2, 1.3. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -12.61, -75.83.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 2948, 2868, 1716, 1277, 1246, 1119, 836.

HRMS (FI): calcd for $C_{43}H_{78}O_2Si_4$ $[M]^{+\bullet}$: 738.50789, found 738.50815, delta = 0.35 ppm.

(13S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 4-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)benzoate (2r)



Based on general procedure **C**, starting from (13S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 4-bromobenzoate (91 mg, 0.2 mmol), product **2r** has been obtained after flash column chromatography (PE: EA = 100: 1 to 10: 1) as a white solid (55 mg, 0.088 mmol, 44% yield).

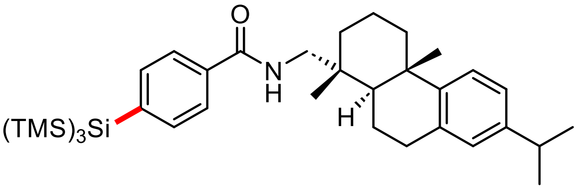
M.p. = 229 – 230 °C (DCM)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 – 8.00 (m, 2H), 7.67 – 7.54 (m, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.03 – 6.91 (m, 2H), 2.95 (dd, *J* = 9.1, 4.3 Hz, 2H), 2.59 – 2.39 (m, 2H), 2.38 – 2.26 (m, 1H), 2.22 – 1.94 (m, 4H), 1.69 – 1.43 (m, 6H), 0.93 (s, 3H), 0.25 (s, 27H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 220.9, 165.9, 149.1, 145.0, 138.2, 137.5, 136.6, 129.0, 128.5, 126.6, 121.9, 119.0, 50.6, 48.1, 44.3, 38.2, 36.0, 31.7, 29.6, 26.5, 25.1, 21.7, 14.0, 1.3. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -12.53, -75.44.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 2950, 2893, 1738, 1592, 1494, 1259, 1064, 837.

HRMS (ESI): calcd for $C_{34}H_{53}O_3Si_4$ $[M+H]^{+\bullet}$: 621.30663, found 621.30548, delta = -1.85 ppm.

4-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-N-(((1R,4aS)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)benzamide (2s)



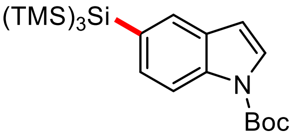
Based on general procedure **C**, starting from 4-bromo-N-(((1R,4aS)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)benzamide (94 mg, 0.2 mmol), product **2s** has been obtained after flash column chromatography (PE: EA = 100: 1 to 10: 1) as an oil (51 mg, 0.08 mmol, 40% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.63 – 7.57 (m, 2H), 7.54 – 7.48 (m, 2H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.00 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 6.12 (t, *J* = 6.3 Hz, 1H), 3.51 – 3.26 (m, 2H), 2.99 – 2.76 (m, 3H), 2.31 (d, *J* = 12.7 Hz, 1H), 2.03 – 1.96 (m, 1H), 1.85 – 1.66 (m, 3H), 1.55 – 1.49 (m, 2H), 1.46 – 1.36 (m, 2H), 1.24 (d, *J* = 1.8 Hz, 6H), 1.21 (s, 3H), 1.02 (s, 3H), 0.22 (s, 27H). ^{13}C NMR (76 MHz, CDCl$_3$) δ 168.0, 147.2, 145.8, 141.4, 136.8, 135.0, 133.8, 127.1, 125.9, 124.4, 124.0, 50.3, 45.8, 38.5, 37.8, 37.7, 36.5, 33.6, 30.6, 25.6, 24.1, 19.2, 19.0, 18.8, 1.3. ^{29}Si NMR (60 MHz, CDCl$_3$) δ -12.64, -76.10.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 3329, 2955, 2895, 1643, 1538, 1246, 836.

HRMS (ESI): calcd for $C_{36}H_{62}OSi_4$ [M+H]$^{+\bullet}$: 636.39030, found 636.38861, delta = -2.65 ppm.

tert-butyl 5-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-1H-indole-1-carboxylate (2t)



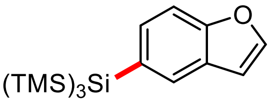
Based on general procedure **C**, starting from tert-butyl 5-bromo-1H-indole-1-carboxylate (94 mg, 0.2 mmol), product **2t** has been obtained after flash column chromatography (PE: EA = 200: 1) as an oil (51 mg, 0.8 mmol, 40% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.65 (t, *J* = 1.1 Hz, 1H), 7.56 (d, *J* = 3.7 Hz, 1H), 7.37 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.52 (dd, *J* = 3.8, 0.8 Hz, 1H), 1.67 (s, 9H), 0.24 (s, 27H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 150.0, 135.0, 132.6, 130.8, 129.3, 128.2, 125.6, 114.7, 107.3, 83.7, 28.4, 1.4. ^{29}Si NMR (60 MHz, CDCl$_3$) δ -12.88, -76.36.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 2956, 2927, 1738, 1370, 1250, 1160, 837.

HRMS (ESI): calcd for $C_{22}H_{42}NO_2Si_4$ [M+H]$^+$: 464.2287, found 464.2289.

2-(benzofuran-5-yl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2u)



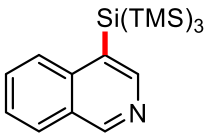
Based on general procedure **C**, starting from 5-bromobenzofuran (39.4 mg, 0.2 mmol), product **2u** has been obtained after flash column chromatography (pentane) as an oil (28 mg, 0.076 mmol, 38% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.71 – 7.66 (m, 1H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.43 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.35 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.73 (dd, *J* = 2.2, 0.9 Hz, 1H), 0.24 (s, 27H). ^{13}C NMR (76 MHz, CDCl$_3$) δ 155.1, 144.6, 132.5, 129.3, 128.3, 127.6, 111.1, 106.4, 1.4. ^{29}Si NMR (60 MHz, CDCl$_3$) δ -12.89, -75.90.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 2955, 2896, 1815, 1247, 1055, 835.

HRMS (FI): calcd for $C_{17}H_{32}O_1Si_4$ $[M]^{+\bullet}$: 364.15302, found 364.15320, delta = 0.48 ppm.

4-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)isoquinoline (2v)



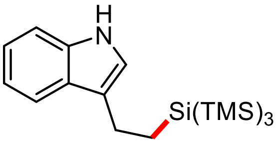
Based on general procedure **C**, starting from 4-bromoisoquinoline (41.6 mg, 0.2 mmol), product **2v** has been obtained after flash column chromatography (PE: EA = 100: 1 to 10: 1) as an oil (15 mg, 0.04 mmol, 20% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.69 (s, 1H), 8.03 – 7.92 (m, 2H), 7.70 – 7.56 (m, 2H), 0.26 (s, 27H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 152.9, 150.8, 140.7, 129.5, 129.3, 128.7, 128.5, 128.3, 127.1, 2.2. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -11.69, -81.08.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 2957, 2922, 1251, 1058, 842.

HRMS (Cl^+): calcd for $C_{18}H_{34}N_1Si_4$ $[M+H]^{+\bullet}$: 376.17683, found 376.17690, delta = 0.18 ppm.

3-(2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)ethyl)-1H-indole (2w)



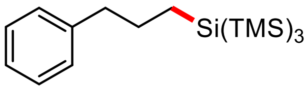
Based on general procedure **C**, starting from 3-(2-bromoethyl)-1H-indole (45 mg, 0.2 mmol), product **2w** has been obtained after flash column chromatography (PE: EA = 100: 1 to 30: 1) as an oil (16 mg, 0.04 mmol, 20% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.63 – 7.57 (m, 1H), 7.36 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.23 – 7.10 (m, 2H), 7.00 (dd, *J* = 2.2, 1.1 Hz, 1H), 2.91 – 2.78 (m, 2H), 1.28 – 1.21 (m, 2H), 0.23 (s, 27H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 136.6, 127.2, 122.1, 120.6, 120.5, 119.3, 119.0, 111.3, 24.9, 9.1, 1.4. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -12.71, -81.71.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 3419, 3059, 2954, 2896, 1245, 1051, 835.

HRMS (ESI): calcd for $C_{19}H_{36}N_1Si_4$ $[M-H]^-$: 390.19303, found 390.19330, delta = 0.69.

1,1,1,3,3,3-hexamethyl-2-(3-phenylpropyl)-2-(trimethylsilyl)trisilane (2x)



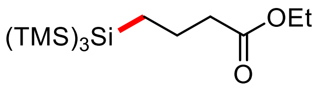
Based on general procedure **C**, starting from (3-bromopropyl)benzene (40 mg, 0.2 mmol), product **2x** has been obtained after flash column chromatography (pentane) as an oil (19 mg, 0.052 mmol, 26% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.22 – 7.12 (m, 3H), 2.64 (t, *J* = 7.5 Hz, 2H), 1.77 – 1.65 (m, 2H), 0.86 – 0.78 (m, 2H), 0.15 (s, 27H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 128.6, 128.4, 125.8, 40.7, 31.1, 7.6, 1.3. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -12.81, -81.99.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 2953, 2895, 1245, 1056, 835.

HRMS (Cl^+): calcd for $C_{18}H_{38}Si_4$ $[M]^{+\bullet}$: 366.20506, found 366.20510, delta = 0.11 ppm.

ethyl 4-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)butanoate (2y)



Based on general procedure **C**, starting from ethyl 4-bromobutanoate (39 mg, 0.2 mmol), product **2y** has been obtained after flash column chromatography (PE: EA = 200: 1 to 100: 1) as an oil (36 mg, 0.082 mmol, 41% yield).

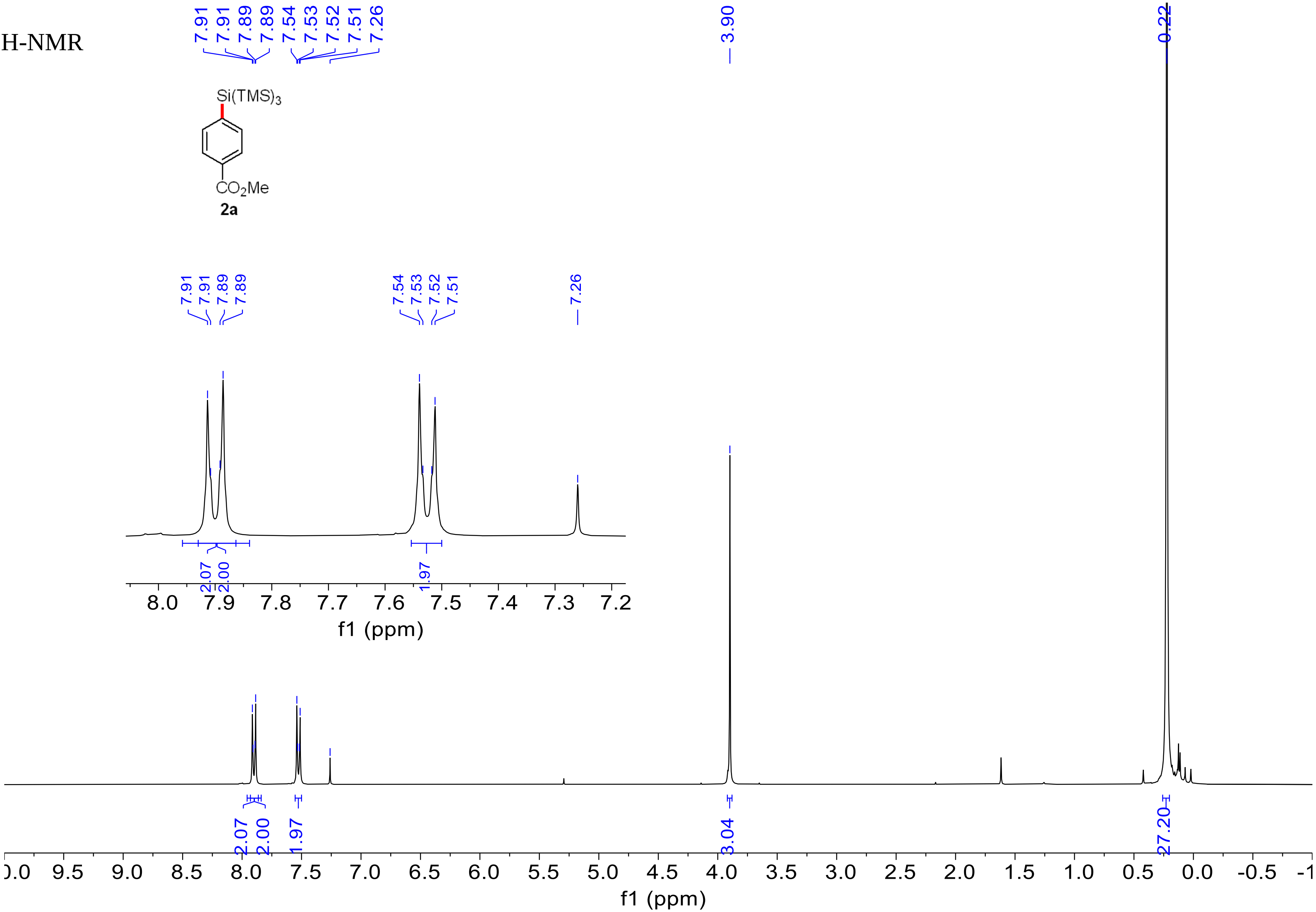
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.13 (q, *J* = 7.1 Hz, 2H), 2.33 (t, *J* = 7.0 Hz, 2H), 1.77 – 1.64 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.84 – 0.72 (m, 2H), 0.16 (s, 27H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 173.5, 60.3, 38.7, 24.9, 14.4, 7.7, 1.3. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -12.79, -81.93.

FT-IR $\bar{\upsilon}_{max}$ (cm^{-1}) = 2955, 2896, 1739, 1245, 1049, 838.

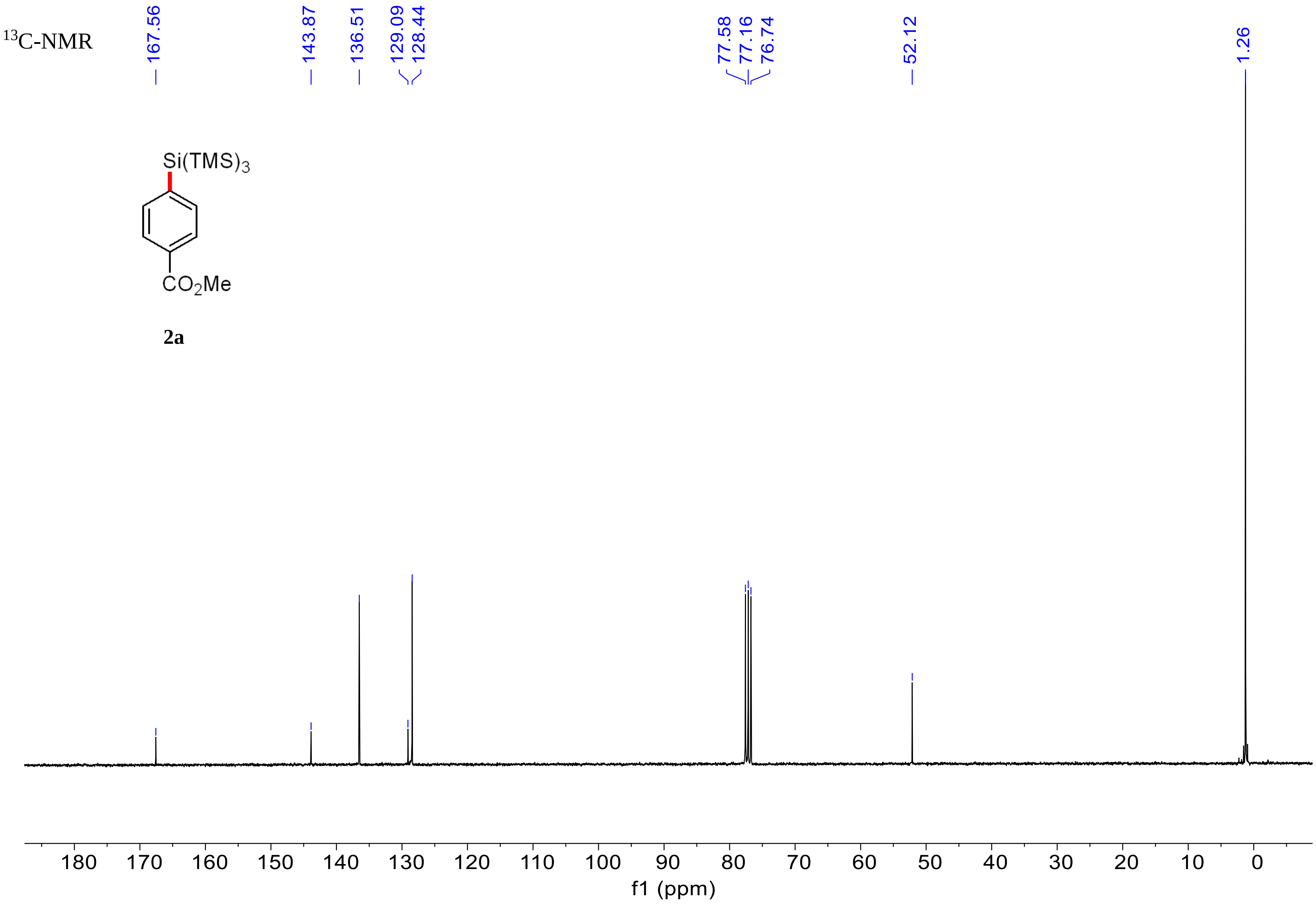
HRMS (ESI): calcd for $C_{15}H_{38}O_2Si_4$ $[M+Na]^+$: 385.18411, found 385.18362, delta = -1.25 ppm.

8. NMR data

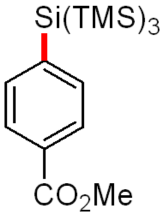
^{1}H-NMR



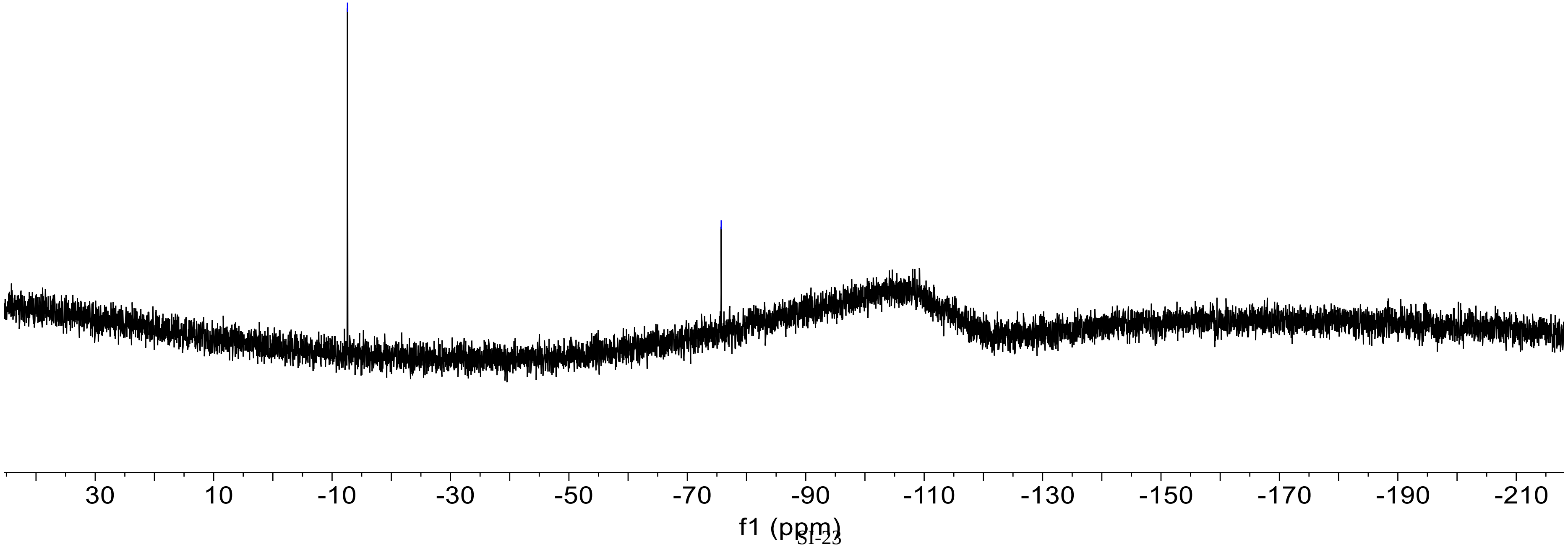
2a

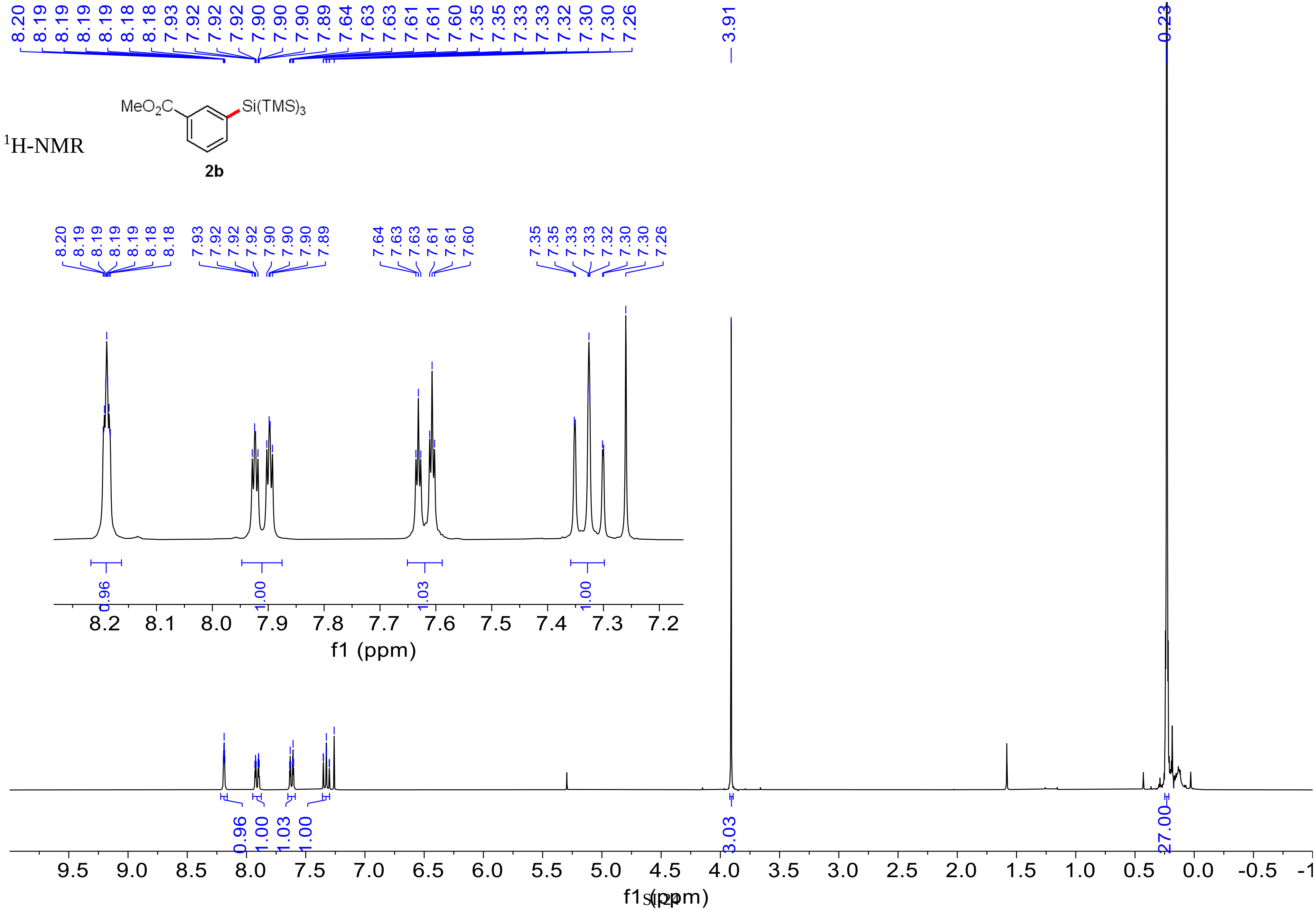

^{13}C-NMR
167.56
143.87
136.51
129.09
128.44
77.58
77.16
76.74
52.12
1.26
Si(TMS)$_3$
CO$_2$Me
2a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{29}Si-NMR

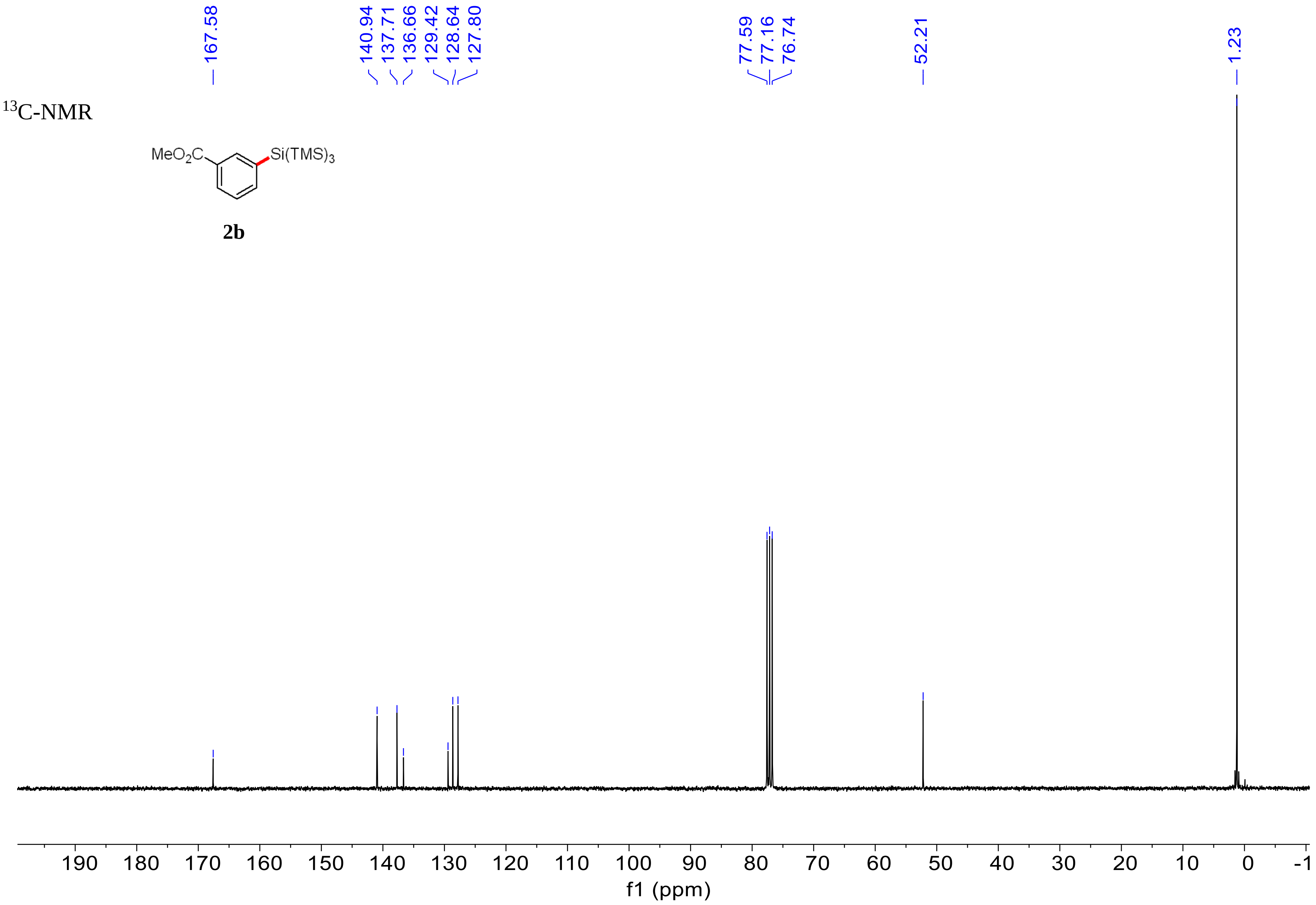

Si(TMS)3
CO2Me

2a


-12.60
-75.72
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


8.20
8.19
8.19
8.19
8.19
8.18
8.18
7.93
7.92
7.92
7.92
7.90
7.90
7.90
7.89
7.64
7.63
7.63
7.61
7.61
7.60
7.35
7.35
7.33
7.33
7.32
7.30
7.30
7.26
3.91
0.23
^{1}H-NMR
MeO$_2$C
Si(TMS)$_3$
0.96
1.00
1.03
1.00
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
3.03
27.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

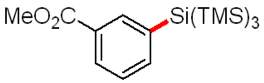
2b


167.58
140.94
137.71
136.66
129.42
128.64
127.80
77.59
77.16
76.74
52.21
1.23
MeO2C
Si(TMS)3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

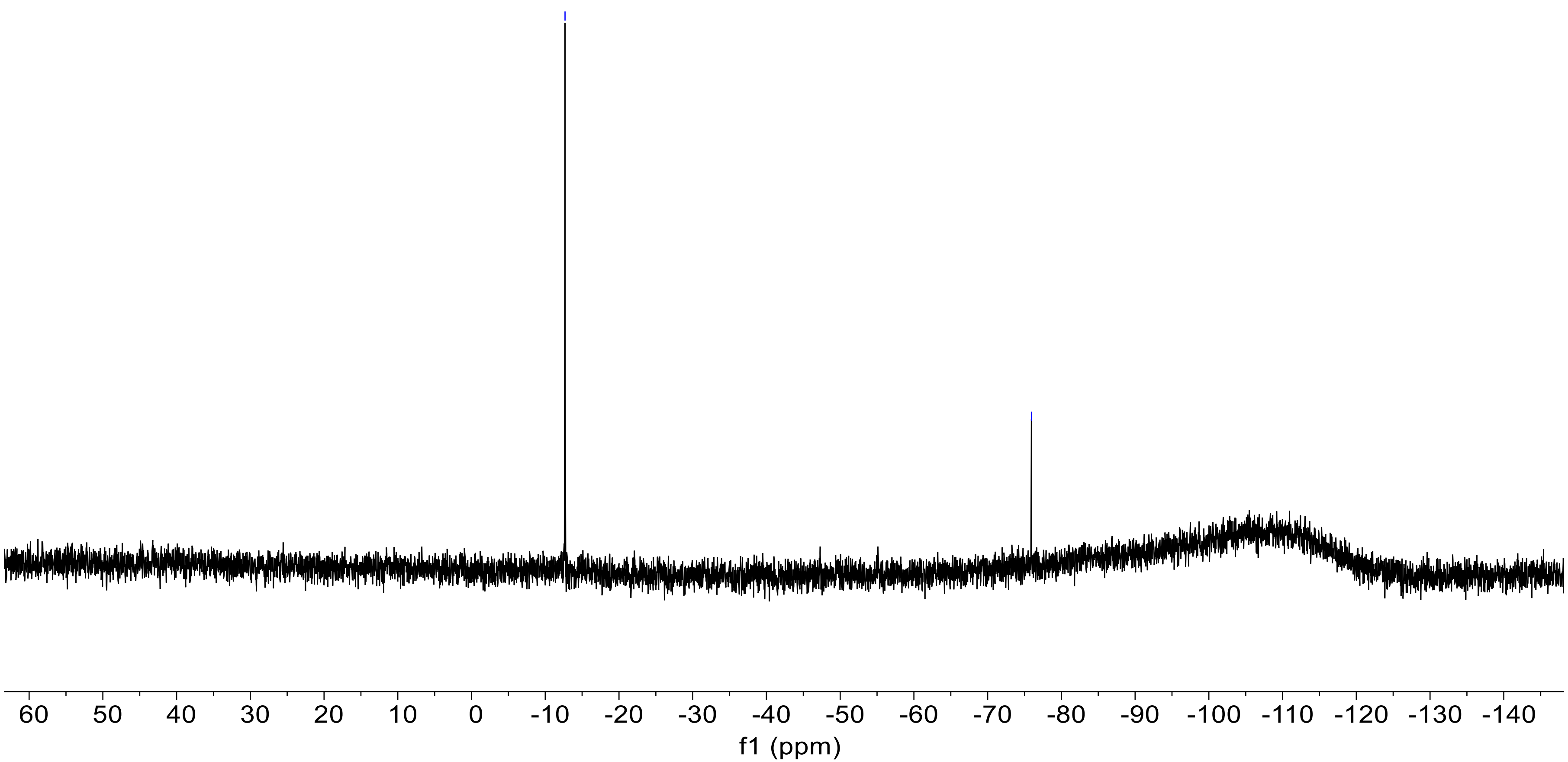
^{13}C-NMR

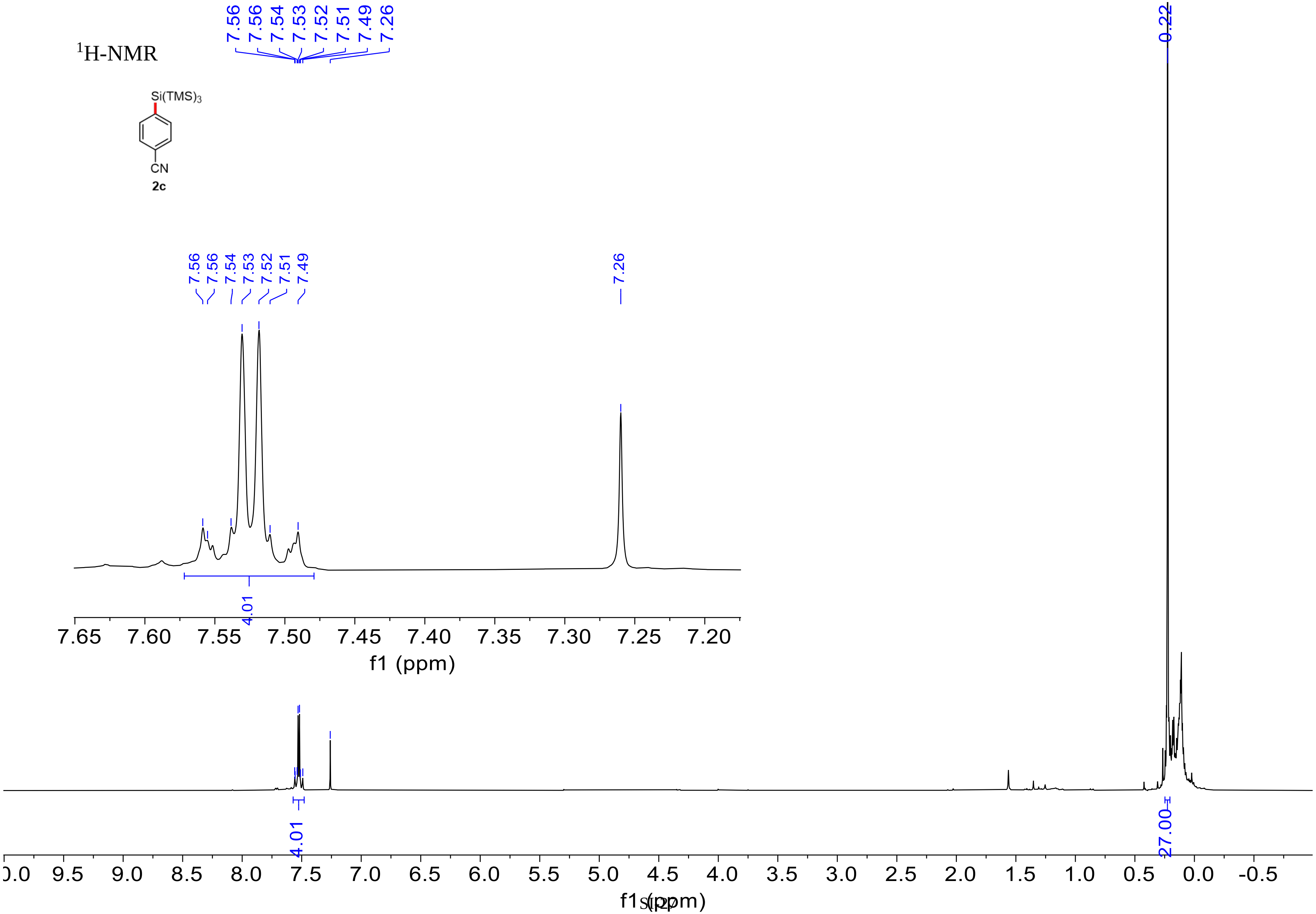
2b

^{29}Si-NMR

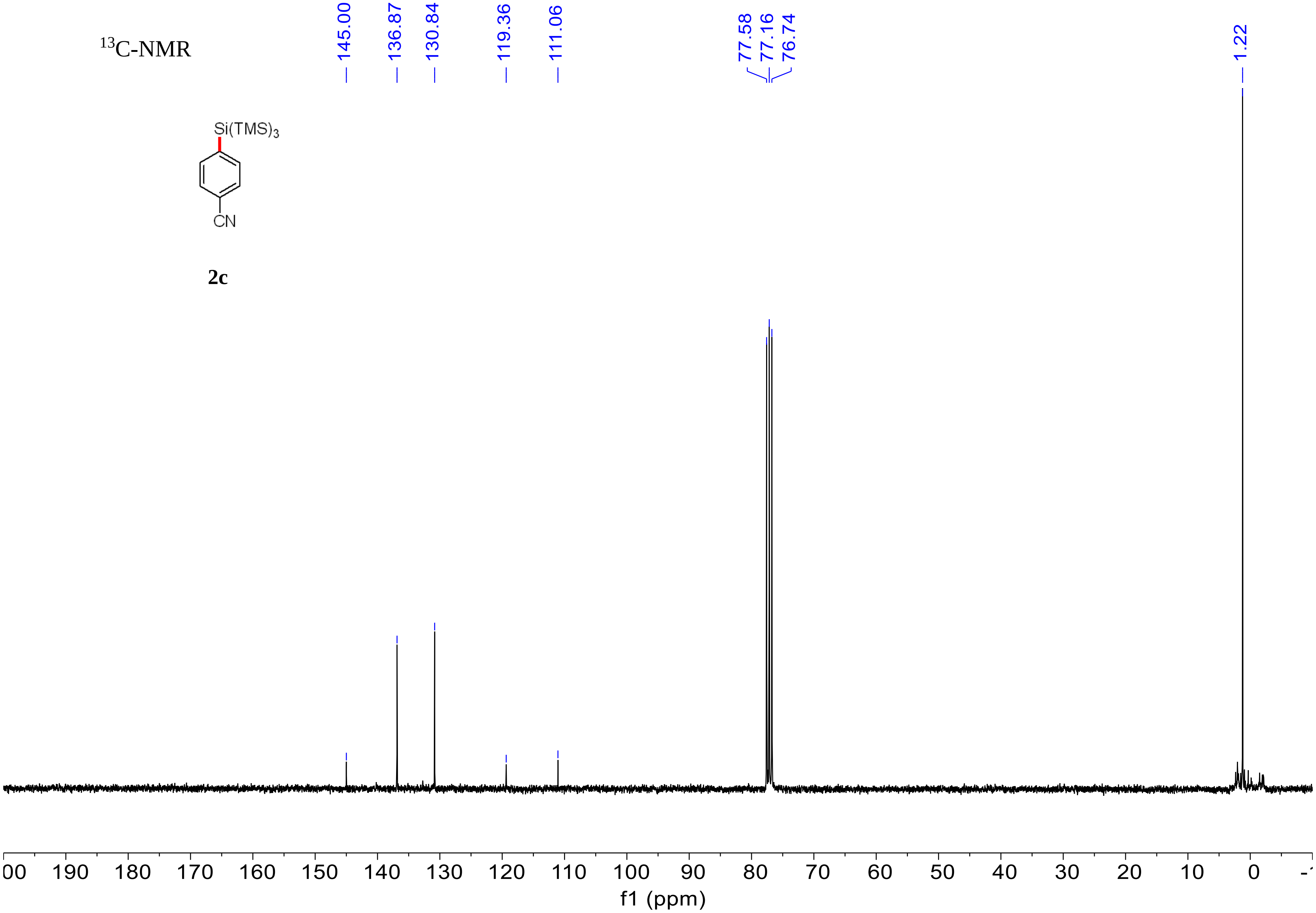

MeO2C
Si(TMS)3

2b


-12.68
-75.94
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)

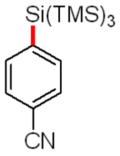

1H-NMR
Si(TMS)3
CN
2c
7.56
7.56
7.54
7.53
7.52
7.51
7.49
7.26
0.22
7.56
7.56
7.54
7.53
7.52
7.51
7.49
7.26
4.01
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
f1 (ppm)
4.01
27.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

^{13}C-NMR

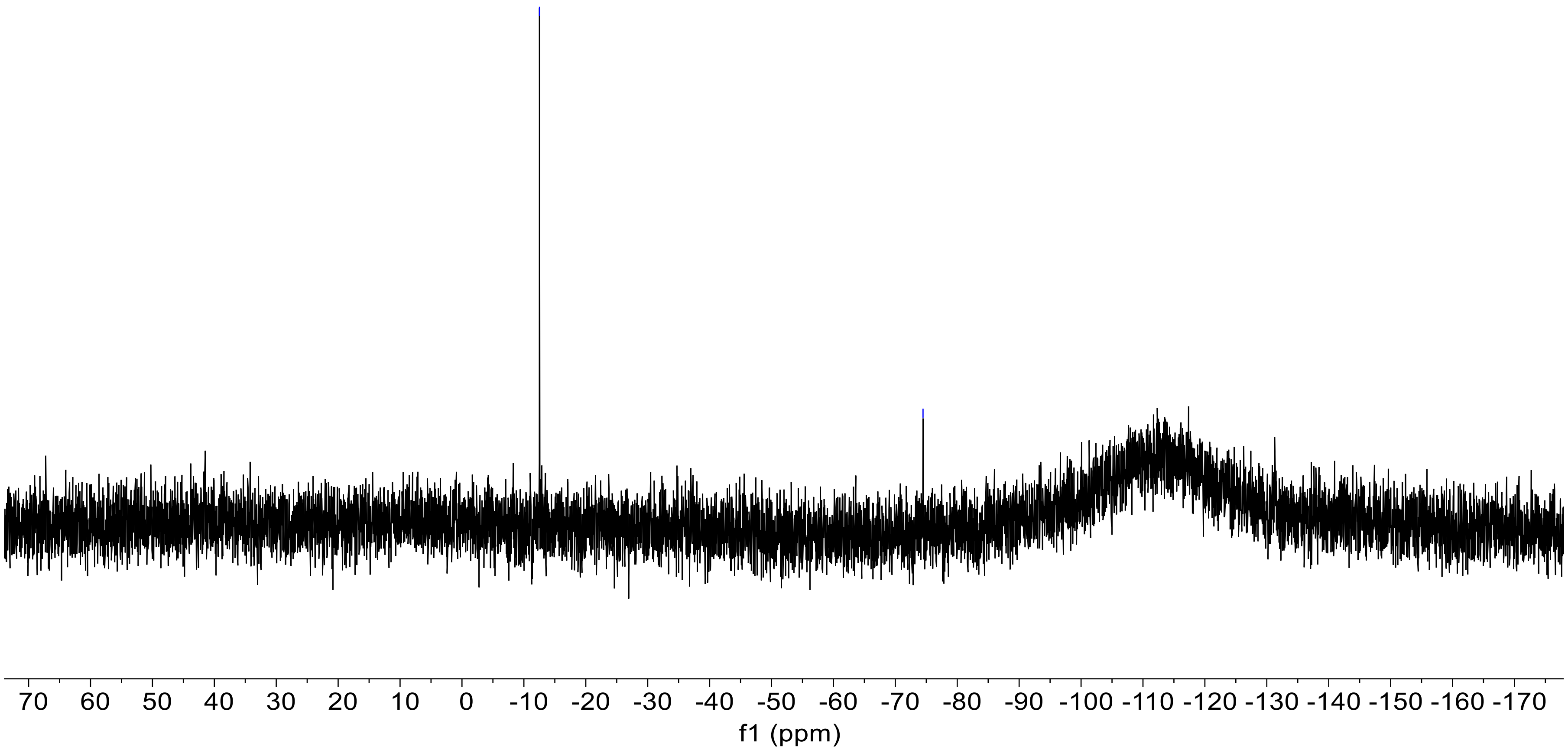

Si(TMS)3
CN
145.00
136.87
130.84
119.36
111.06
77.58
77.16
76.74
1.22
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

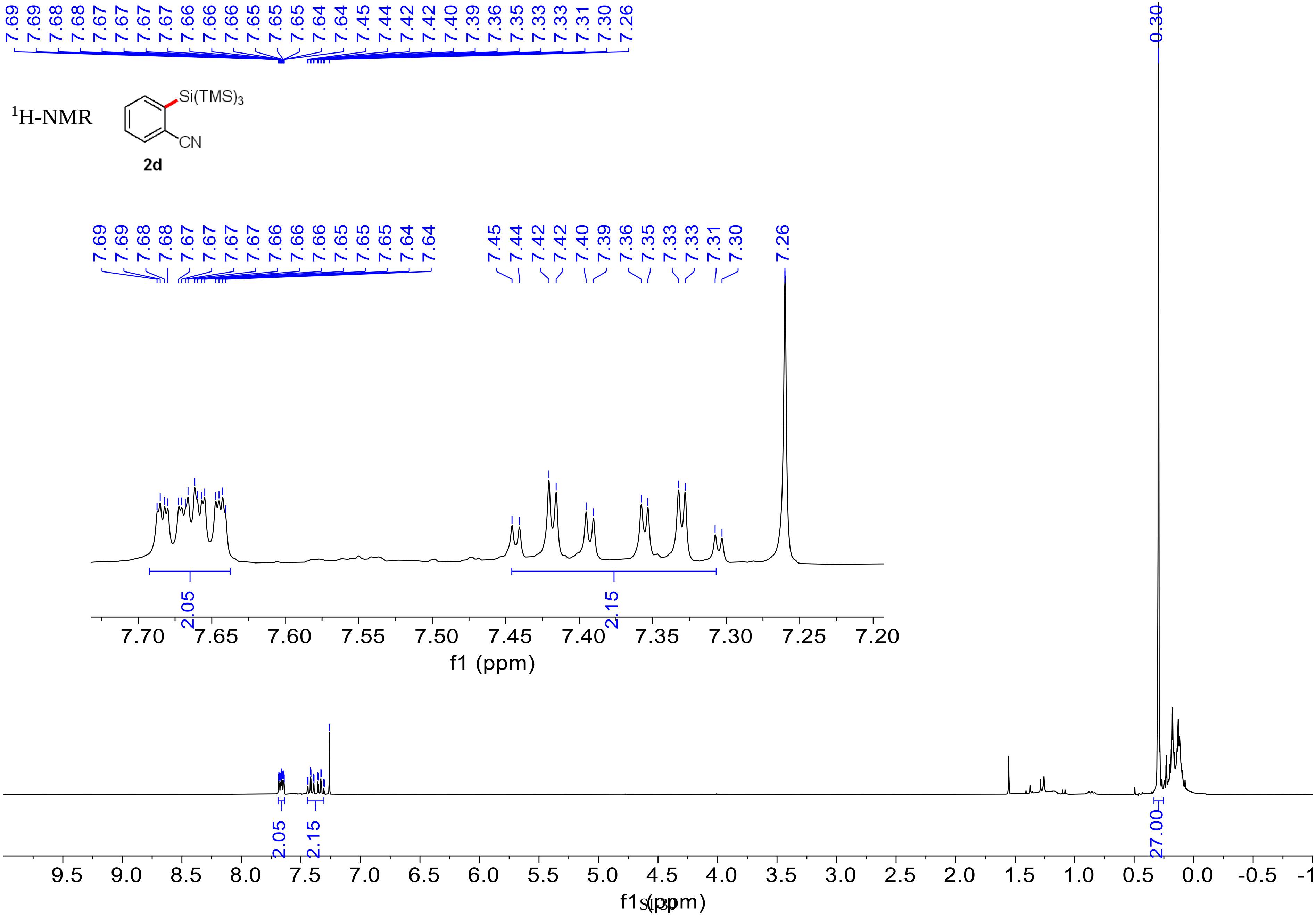
2c

^{29}Si-NMR

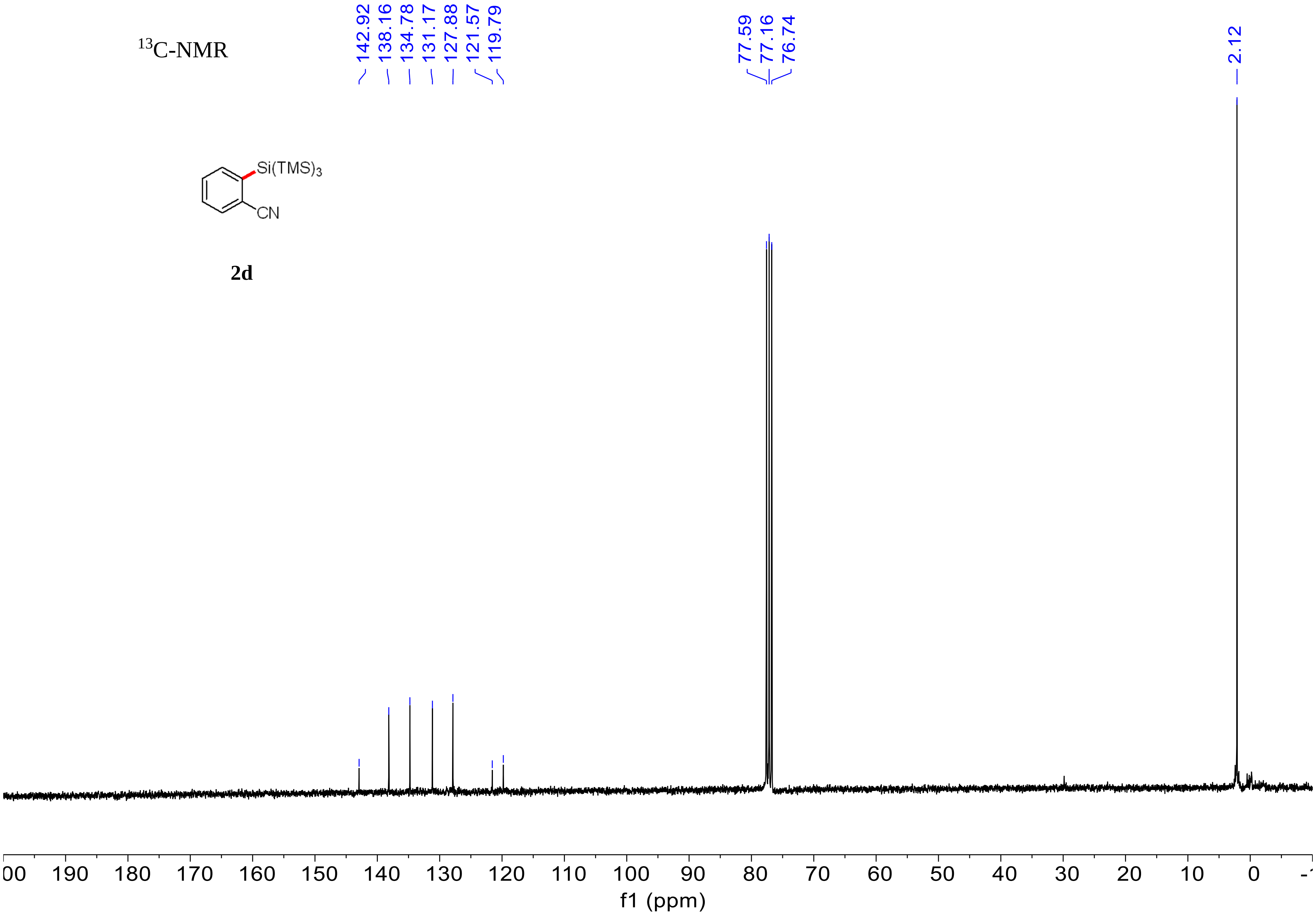

Si(TMS)3
CN

2c


-12.52
-74.47
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

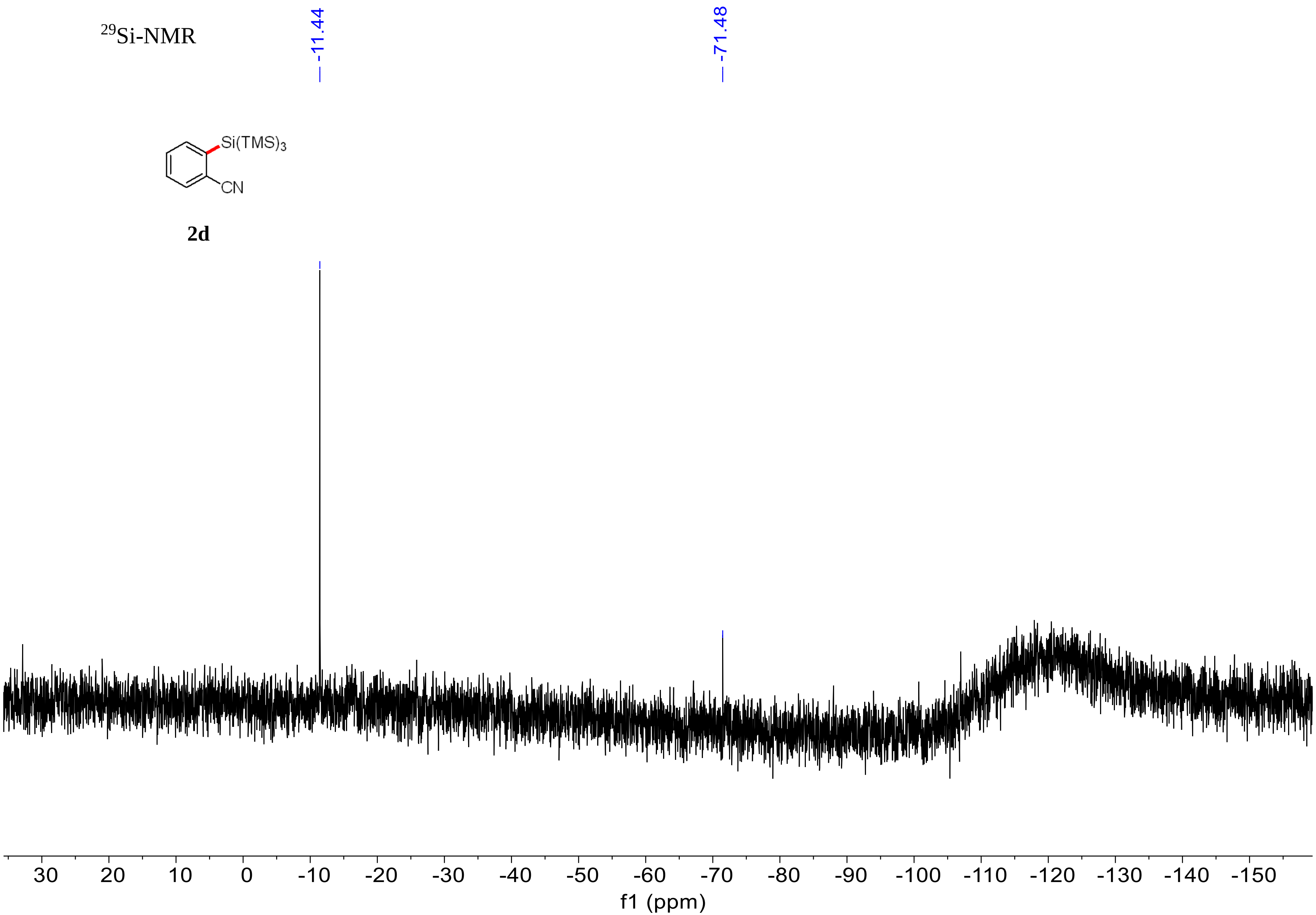

7.69
7.69
7.68
7.68
7.67
7.67
7.67
7.67
7.66
7.66
7.66
7.65
7.65
7.65
7.64
7.64
7.45
7.44
7.42
7.42
7.40
7.39
7.36
7.35
7.33
7.33
7.31
7.30
7.26
0.30
^{1}H-NMR
Si(TMS)$_3$
CN
2d
2.05
2.15
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
f1 (ppm)
27.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

^{13}C-NMR


142.92
138.16
134.78
131.17
127.88
121.57
119.79
77.59
77.16
76.74
2.12
Si(TMS)3
CN
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

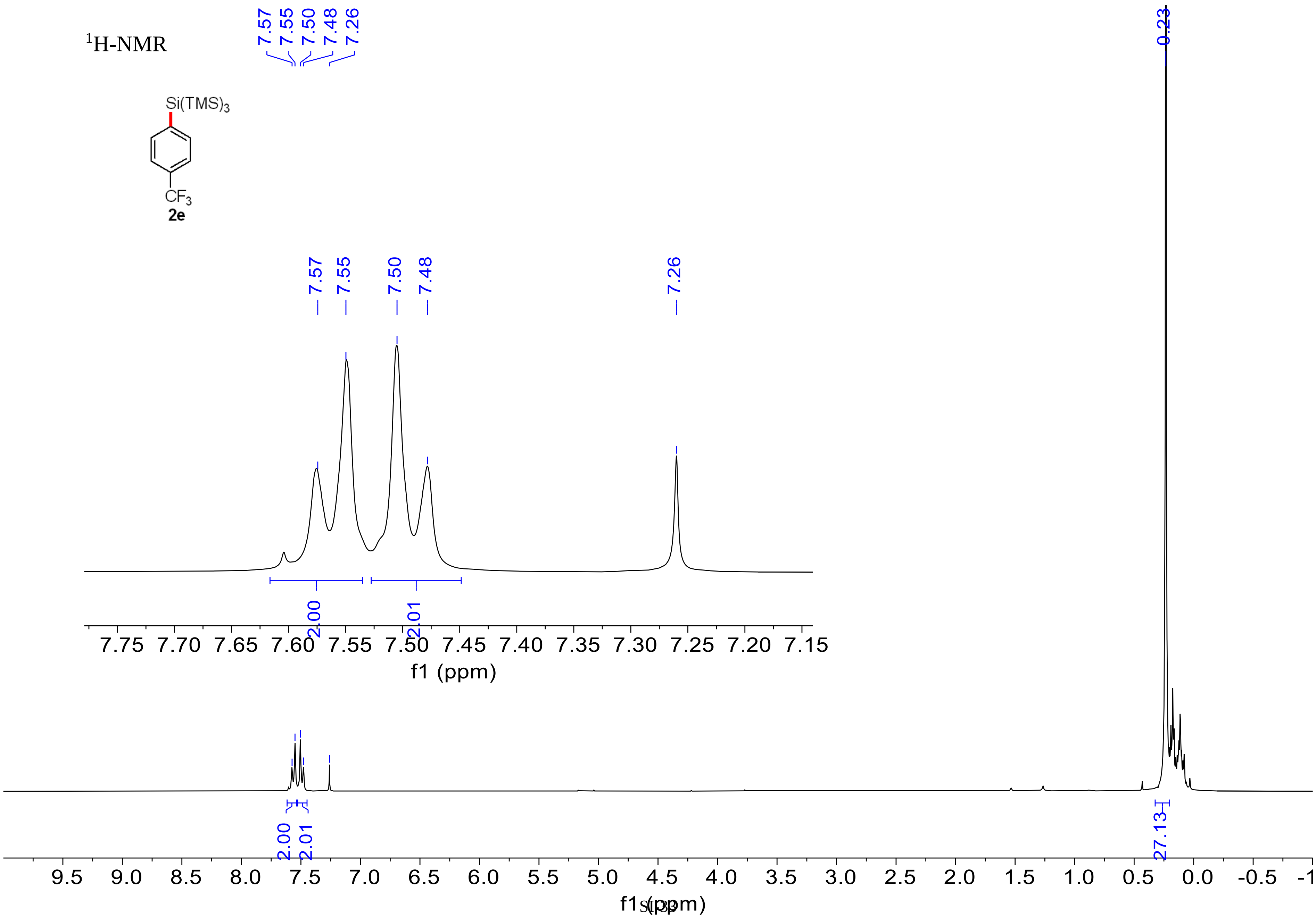
2d

^{29}Si-NMR

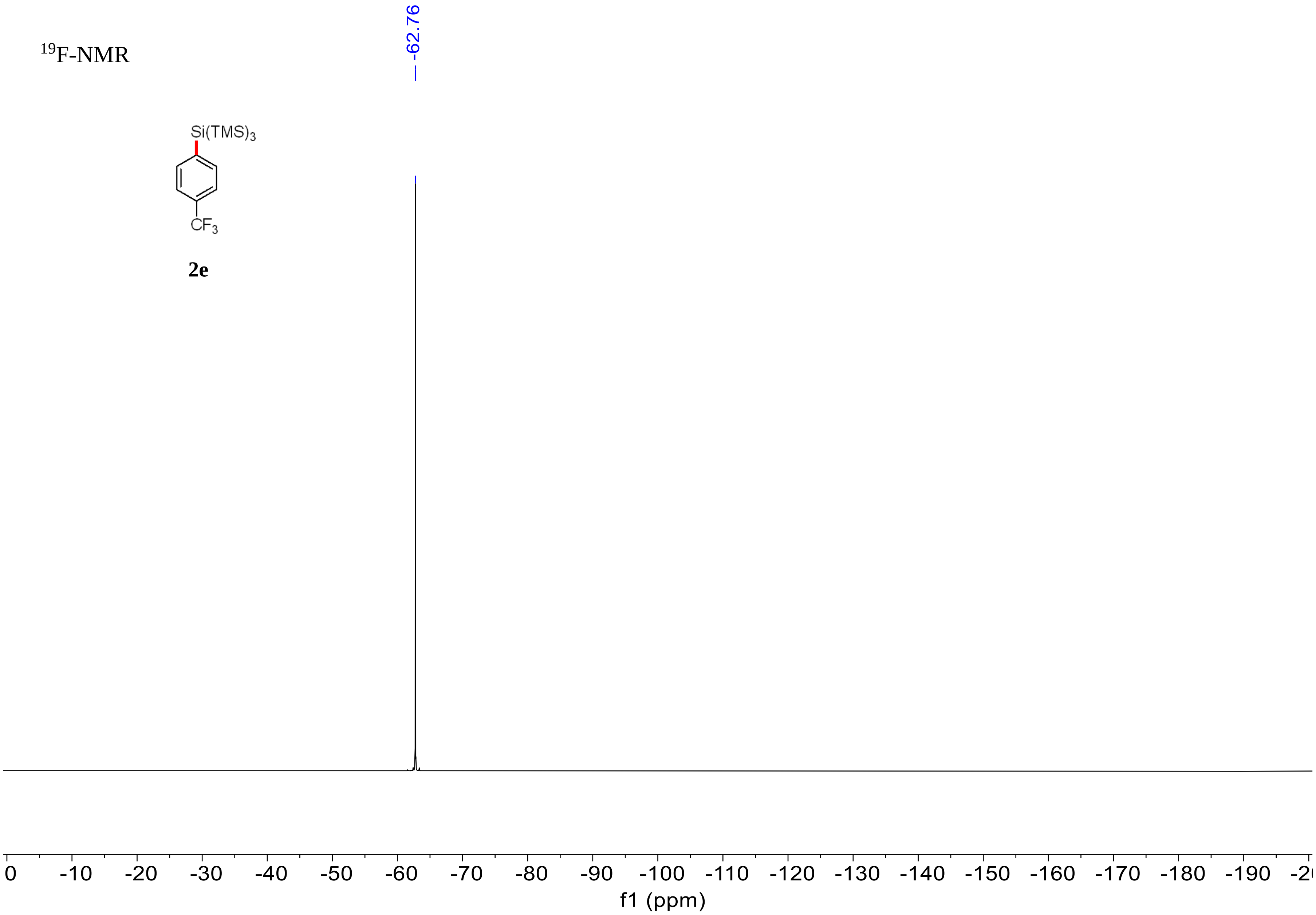


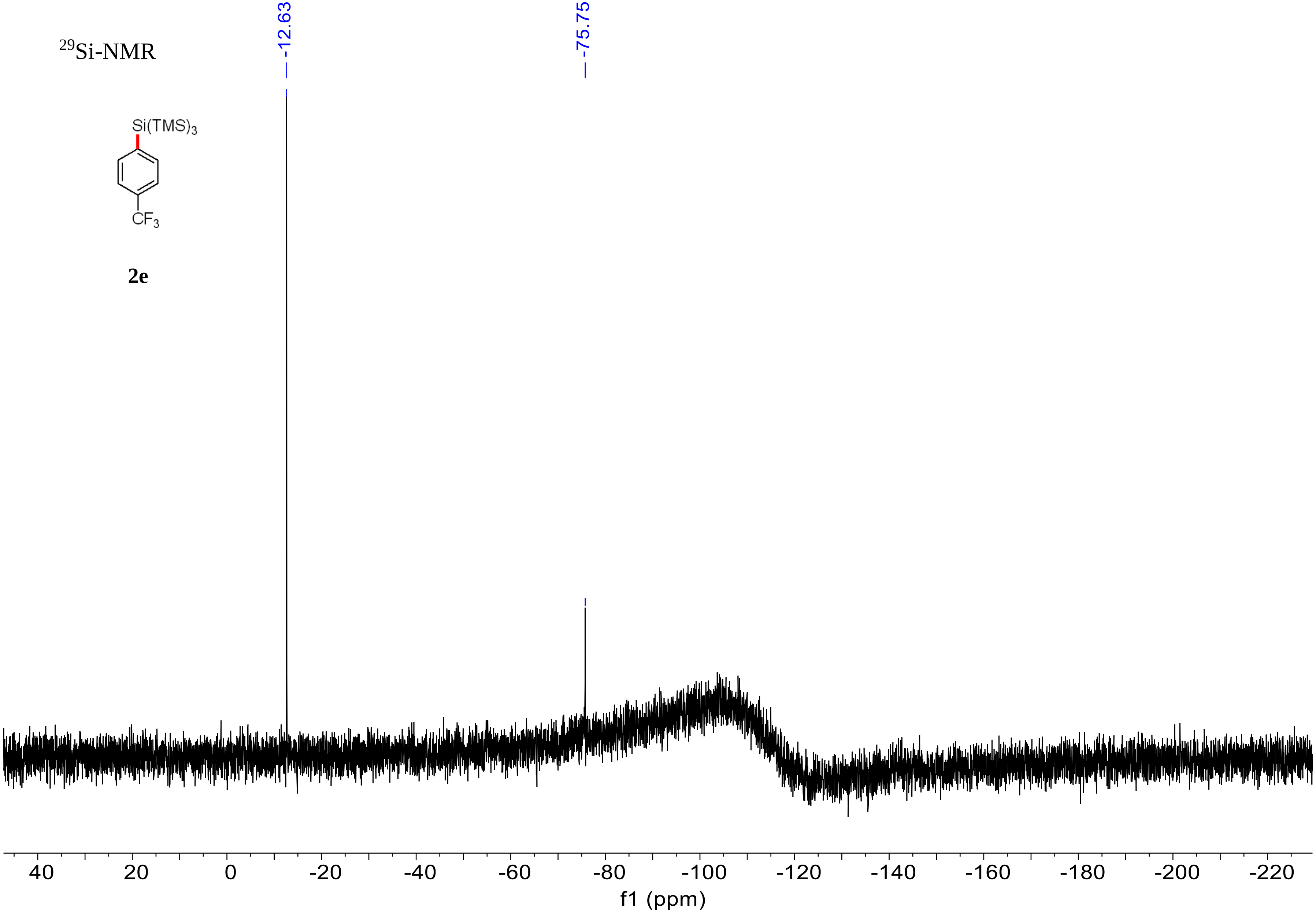
-11.44
-71.48
Si(TMS)3
CN
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

2d

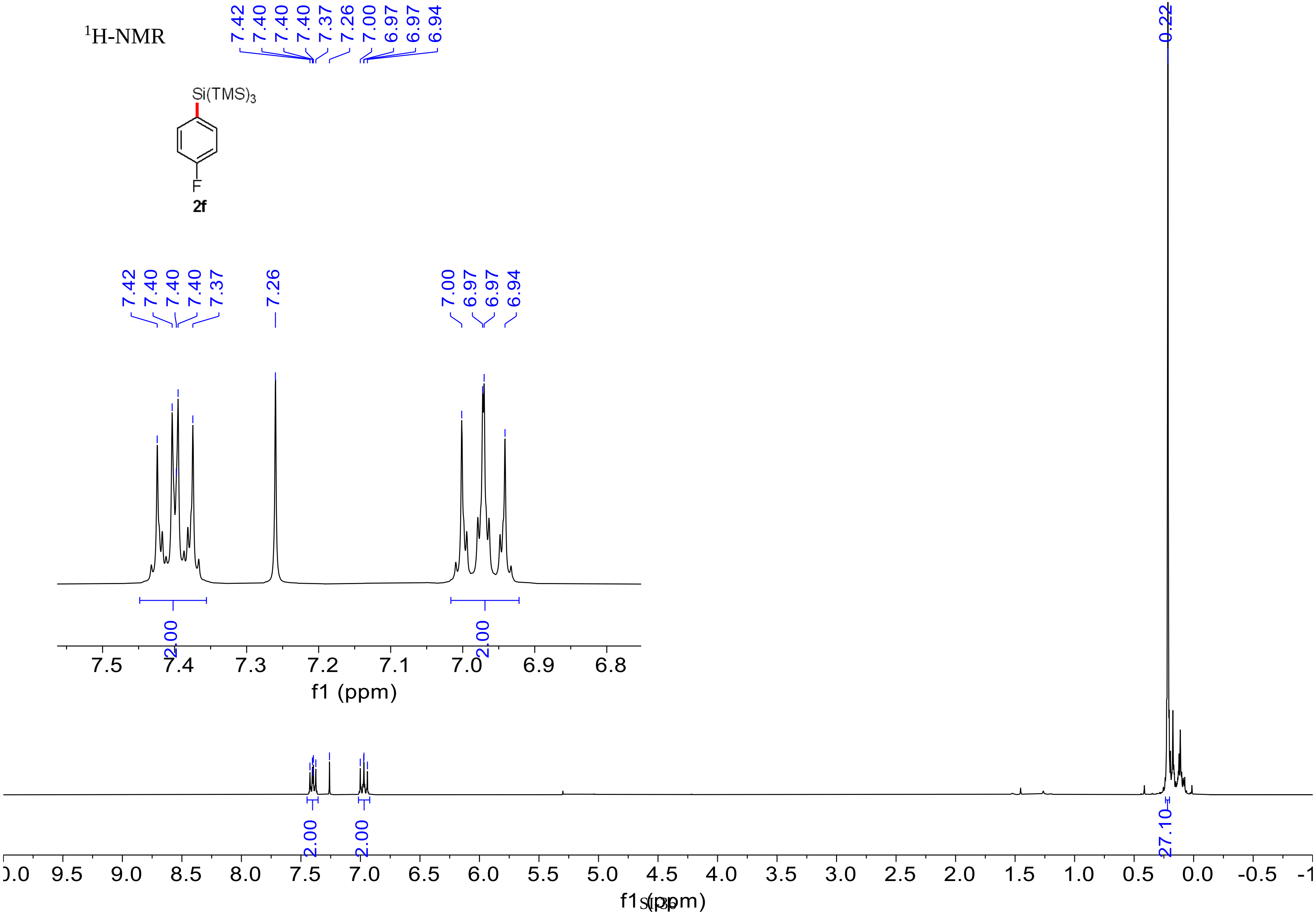

^{1}H-NMR
Si(TMS)$_3$
CF$_3$
2e
7.57
7.55
7.50
7.48
7.26
0.23
2.00
2.01
27.13
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

^{19}F-NMR

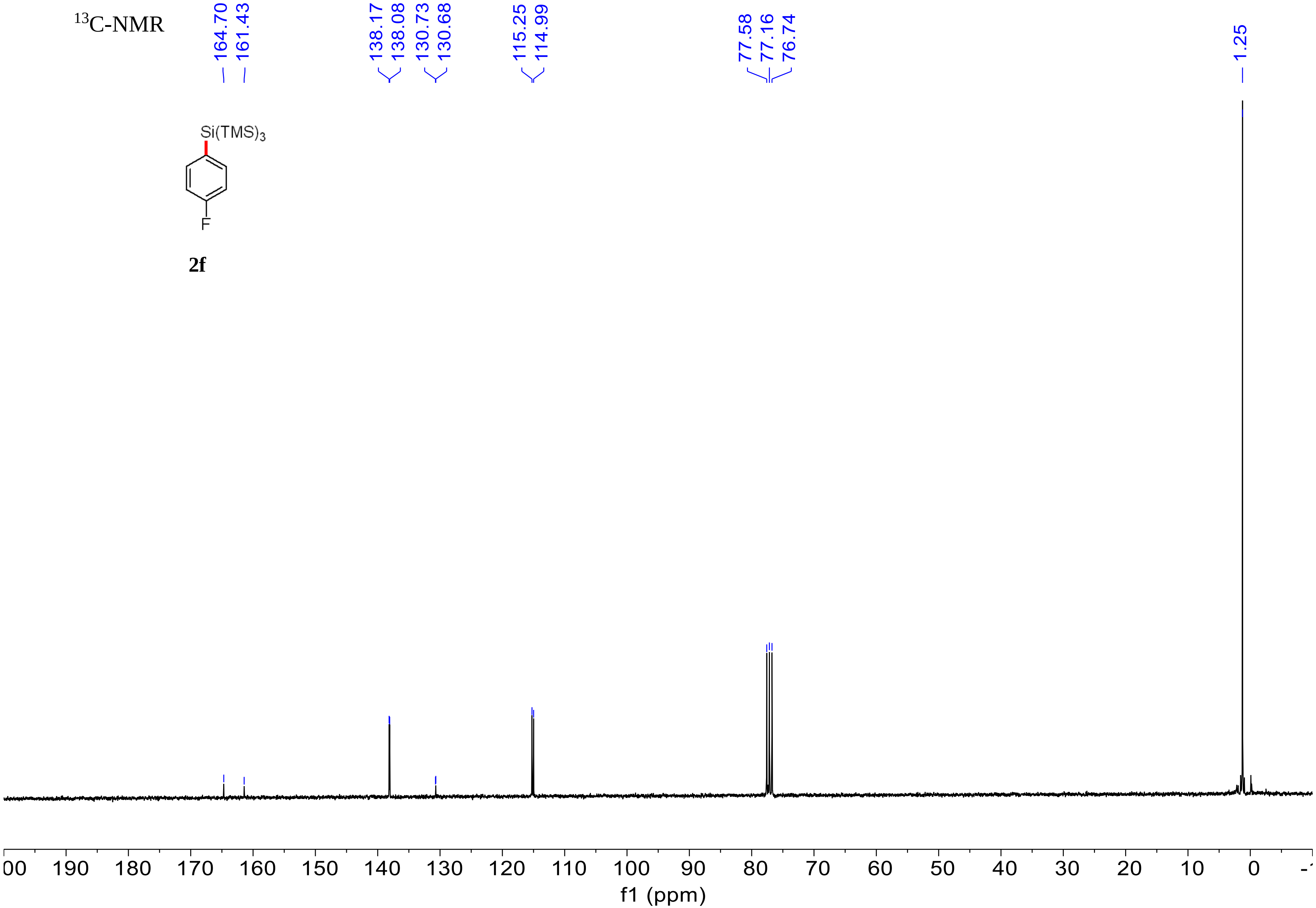

-62.76
Si(TMS)3
CF3
2e
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)


^{29}Si-NMR
Si(TMS)$_3$
CF$_3$
2e
-12.63
-75.75
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)

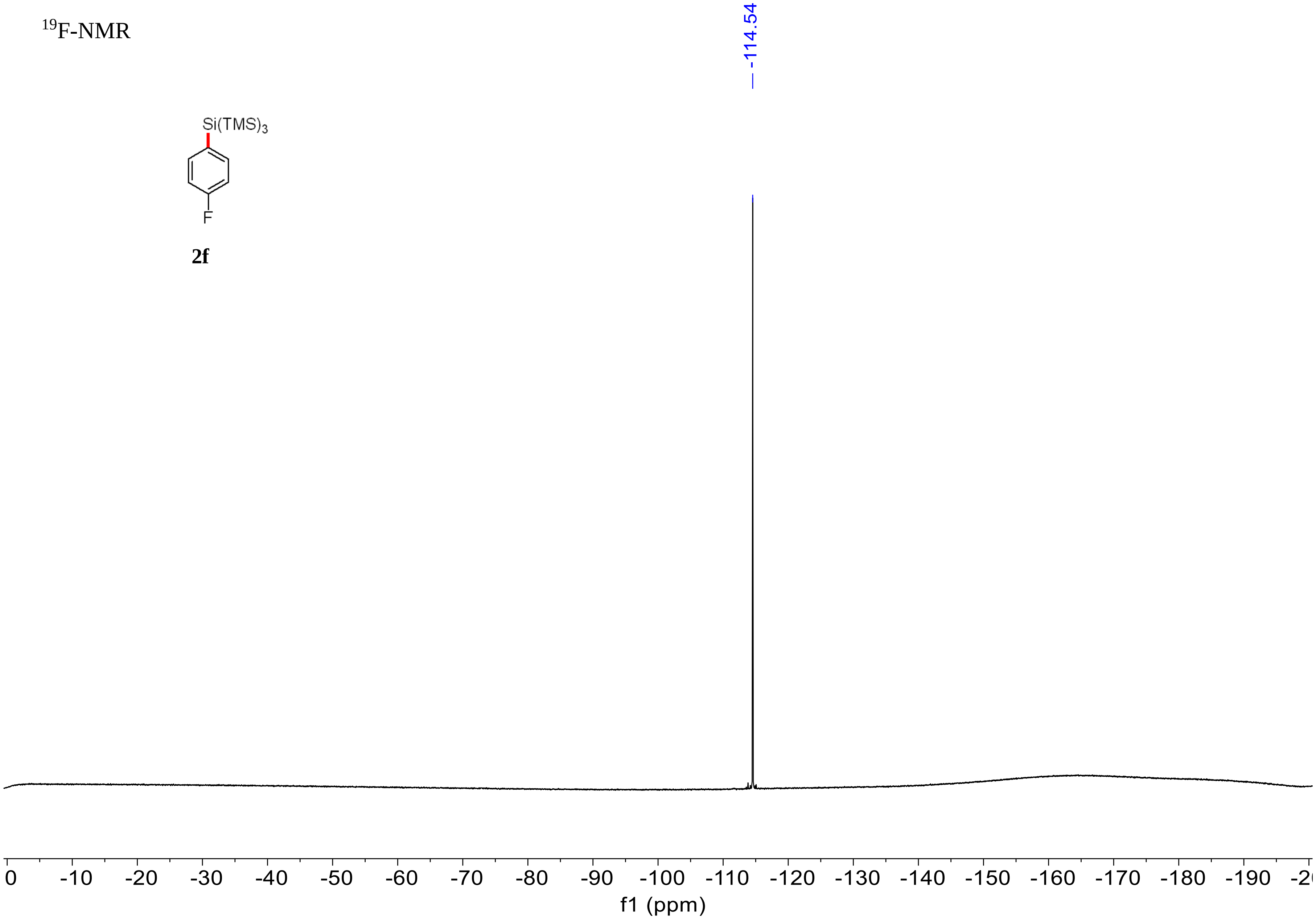
^{1}H-NMR

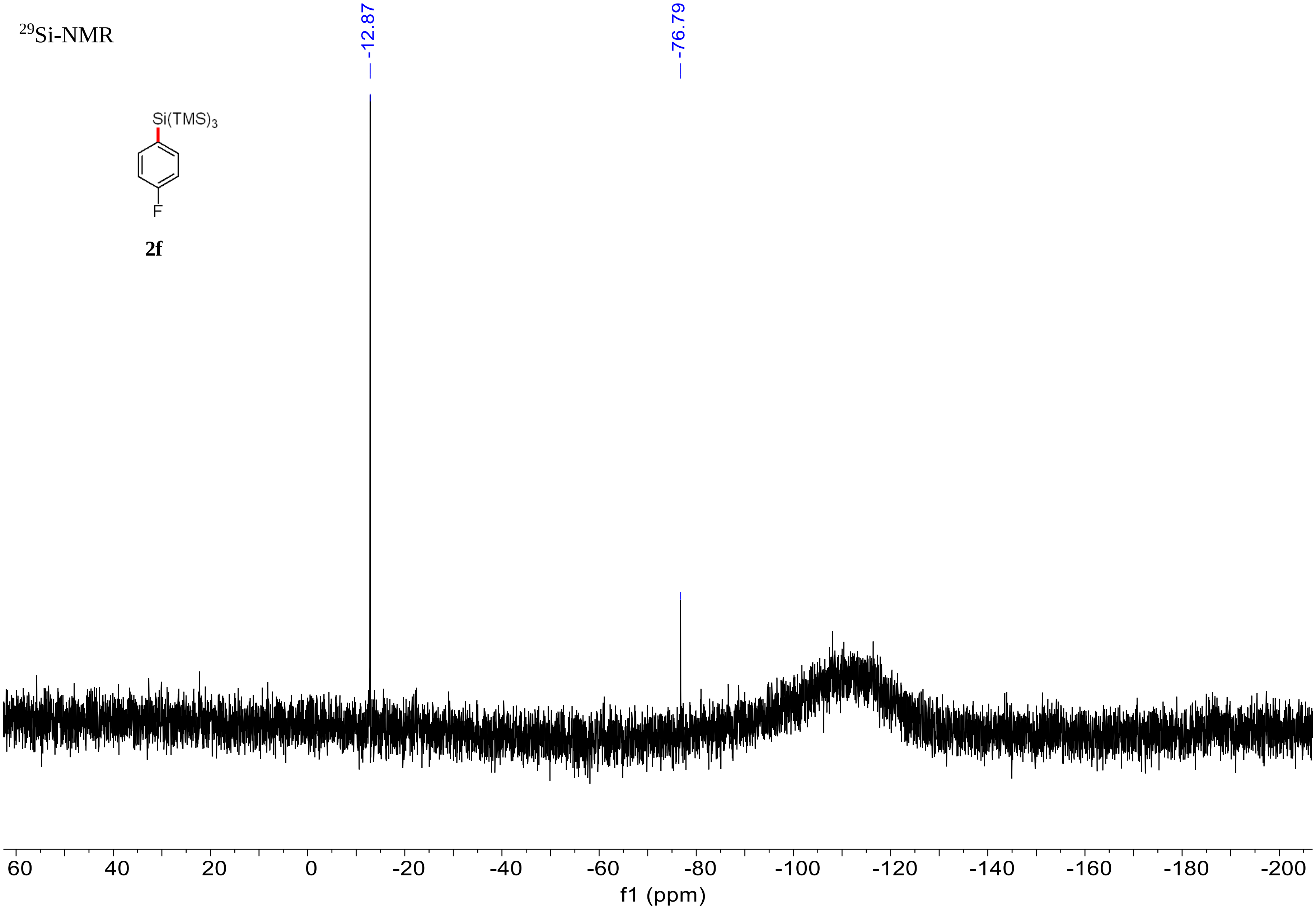

7.42
7.40
7.40
7.40
7.37
7.26
7.00
6.97
6.97
6.94
0.22
Si(TMS)3
F
2f
2.00
2.00
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
2.00
2.00
27.10
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

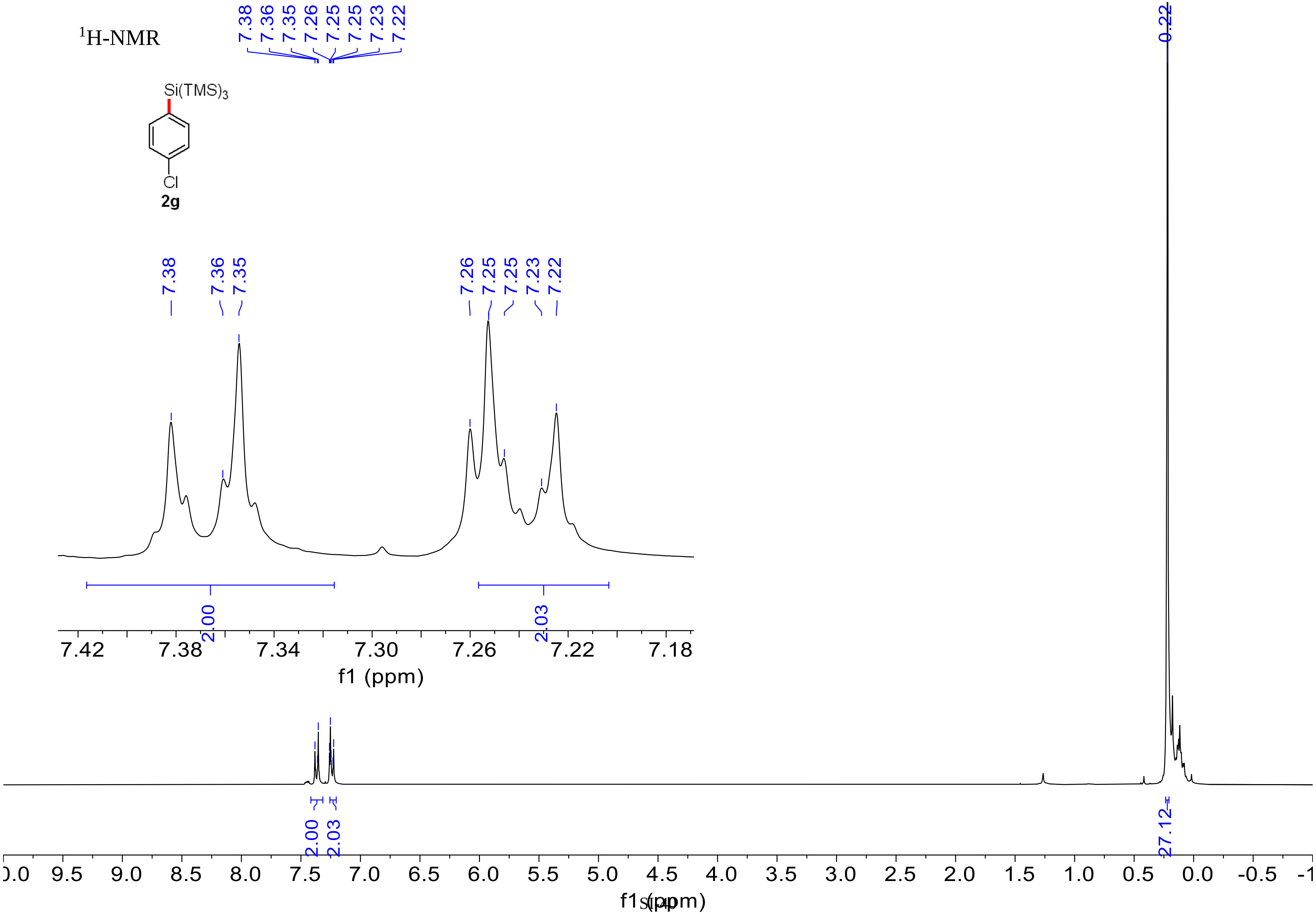
^{13}C-NMR


164.70
161.43
138.17
138.08
130.73
130.68
115.25
114.99
77.58
77.16
76.74
1.25
Si(TMS)3
F
2f
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{19}F-NMR


-114.54
Si(TMS)3
F
2f
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

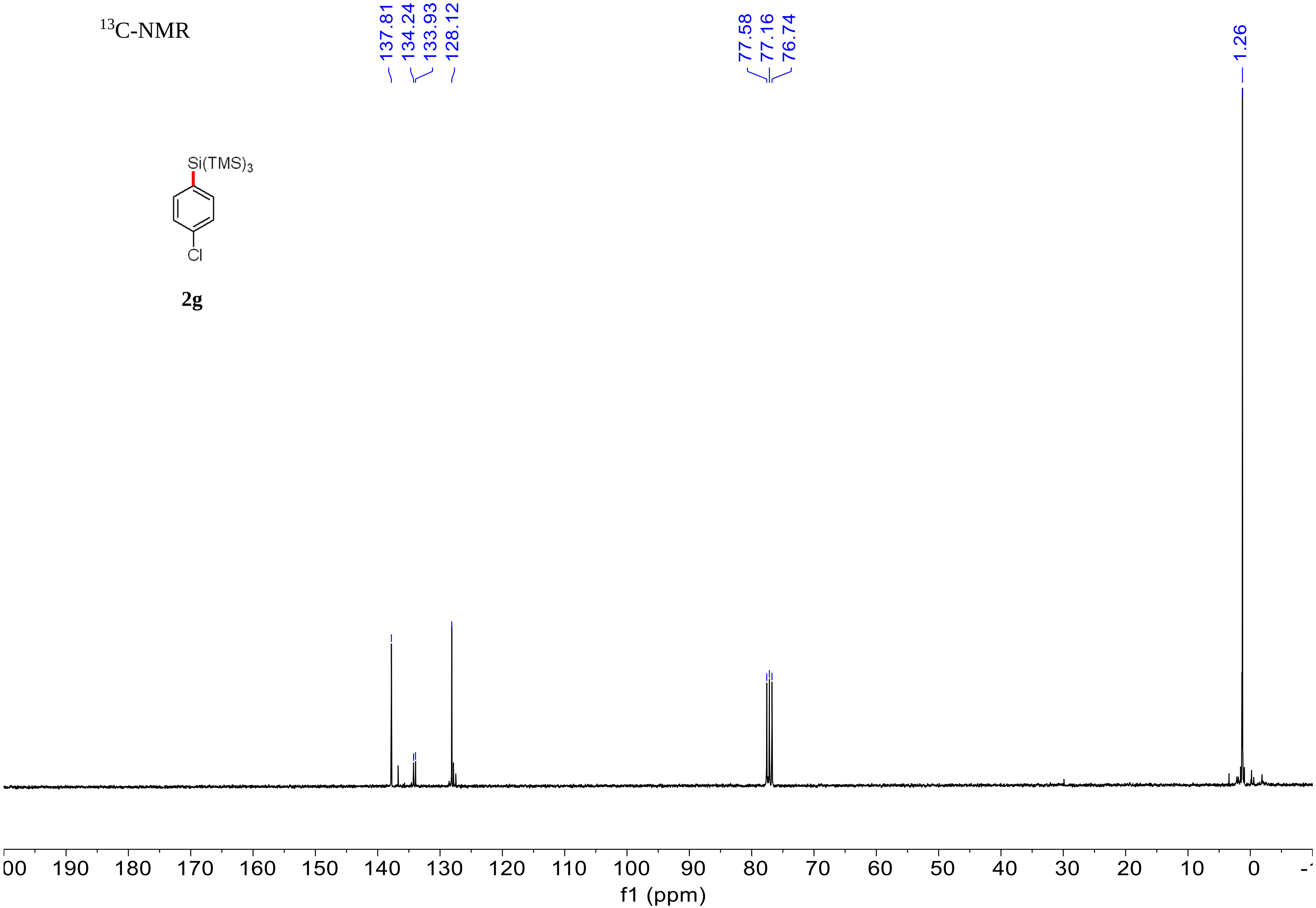

^{29}Si-NMR
Si(TMS)$_3$
F
2f
-12.87
-76.79
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)


^{1}H-NMR
7.38
7.36
7.35
7.26
7.25
7.25
7.23
7.22
0.22
Si(TMS)$_3$
Cl
2g
7.38
7.36
7.35
7.26
7.25
7.25
7.23
7.22
2.00
2.03
7.42
7.38
7.34
7.30
7.26
7.22
7.18
f1 (ppm)
2.00
2.03
27.12
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

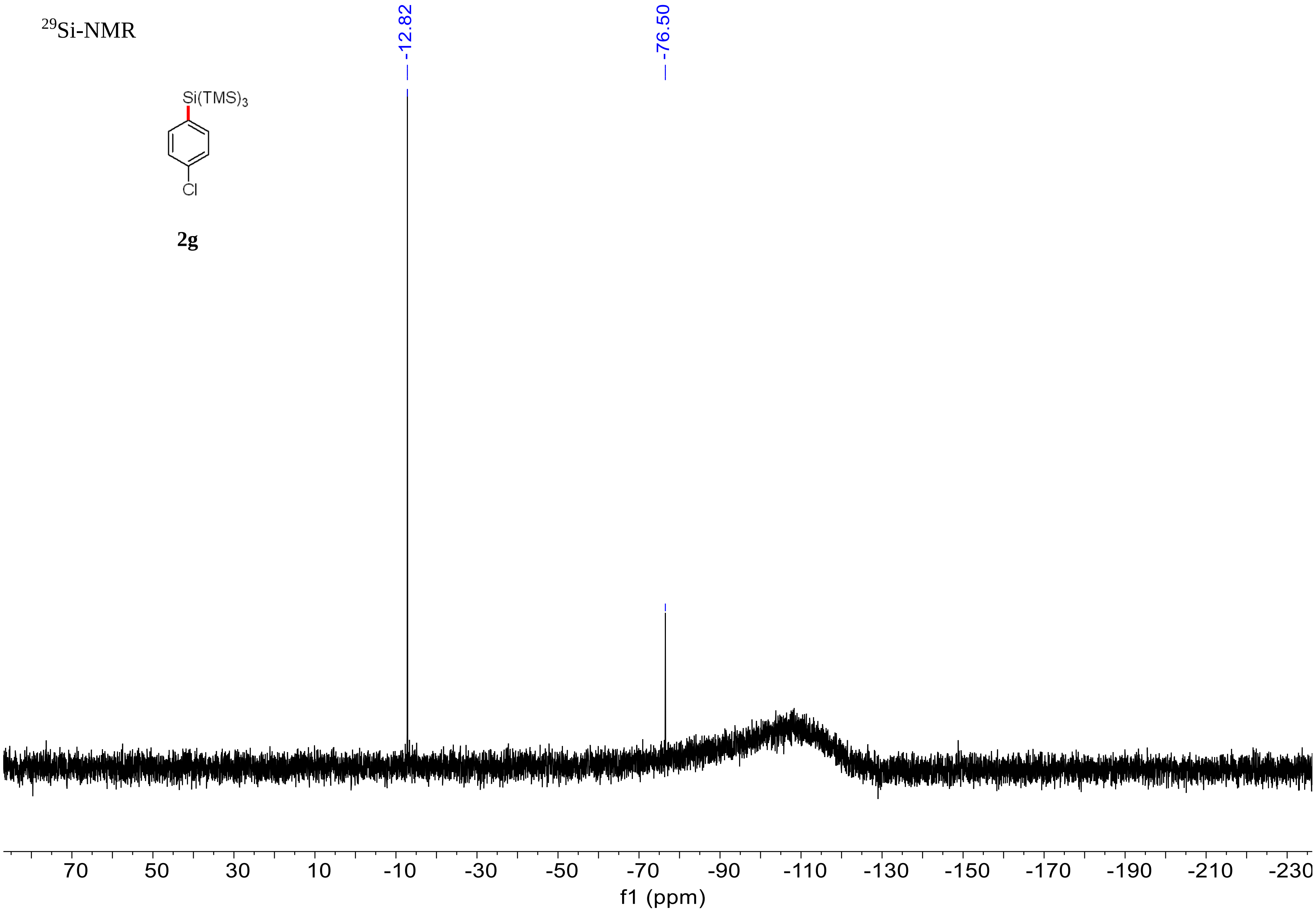
^{13}C-NMR

Si(TMS)3
Cl

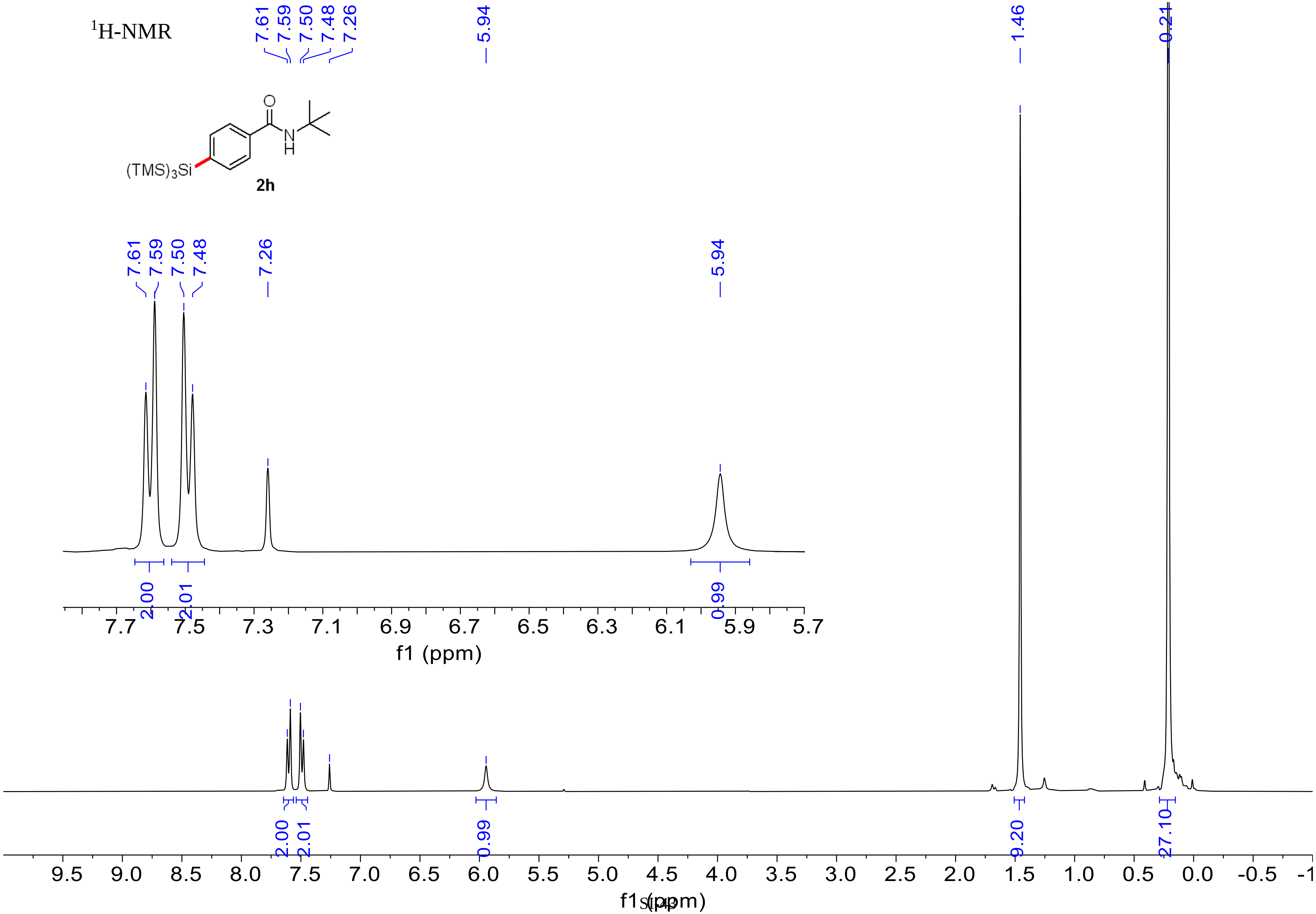
2g


137.81
134.24
133.93
128.12
77.58
77.16
76.74
1.26
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{29}Si-NMR

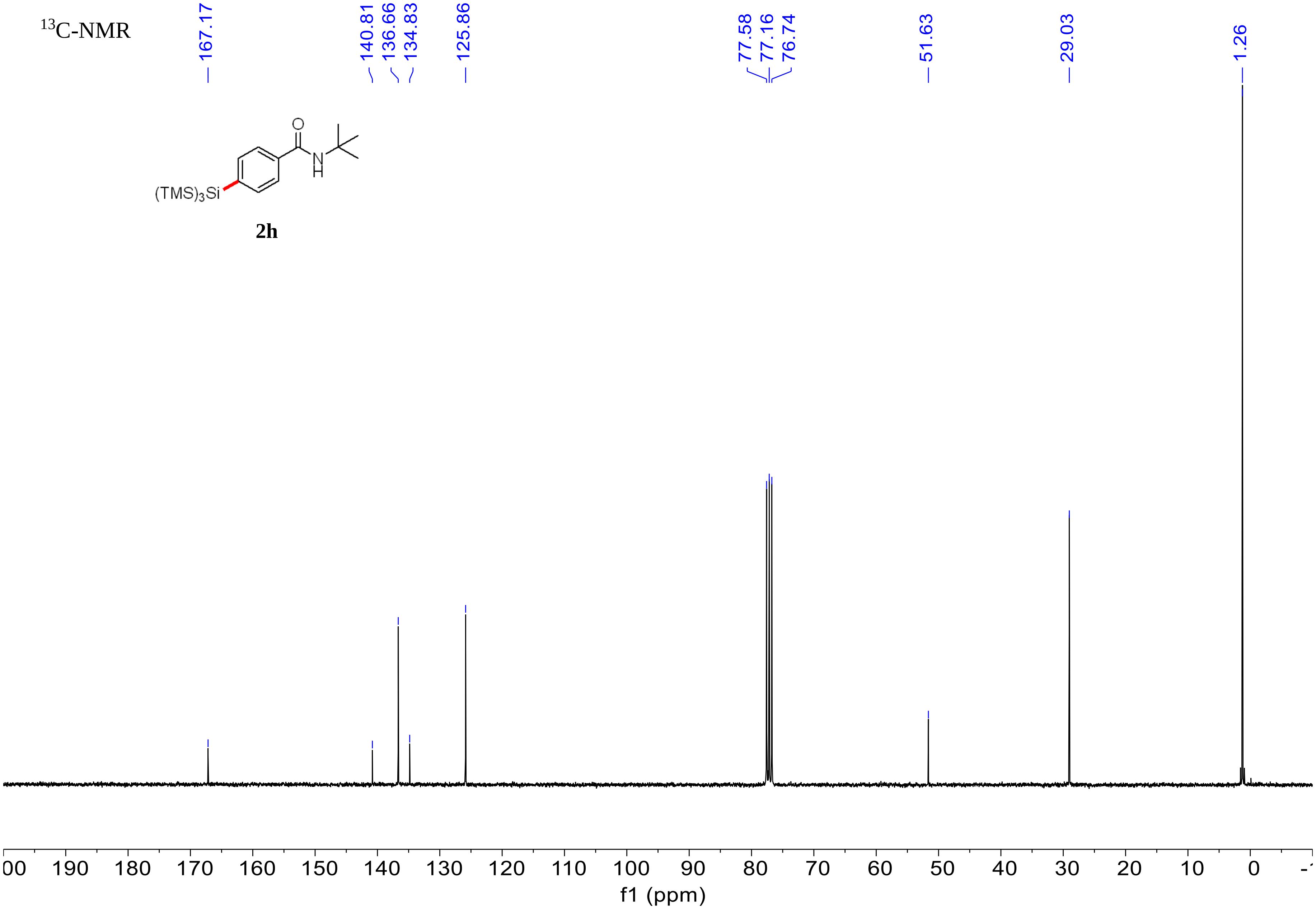

-12.82
-76.50
Si(TMS)3
Cl
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

2g



1H-NMR
7.61
7.59
7.50
7.48
7.26
5.94
1.46
0.21
O
N
H
(TMS)3Si
2h
2.00
2.01
0.99
7.7
7.5
7.3
7.1
6.9
6.7
6.5
6.3
6.1
5.9
5.7
f1 (ppm)
9.20
27.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

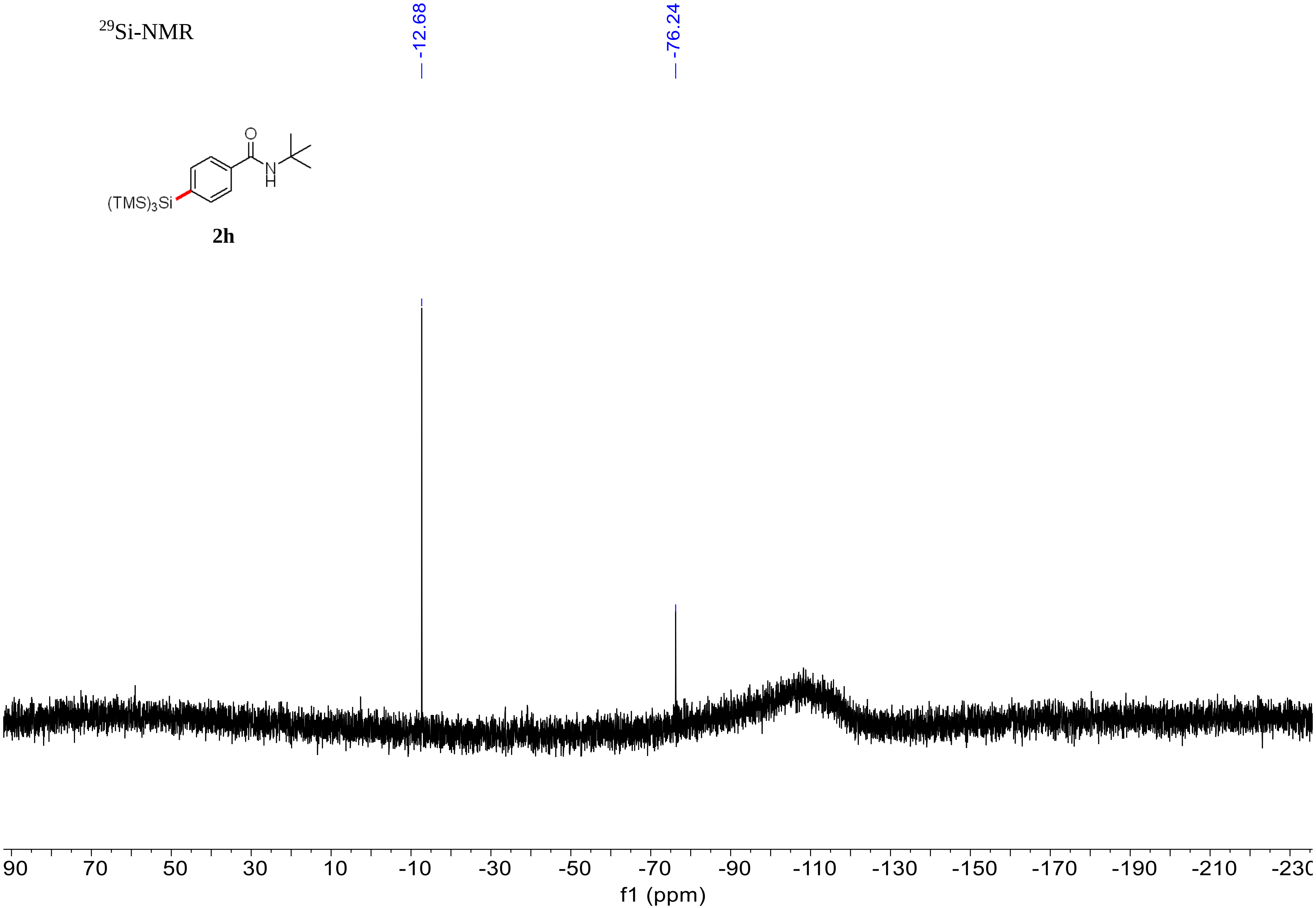
^{13}C-NMR



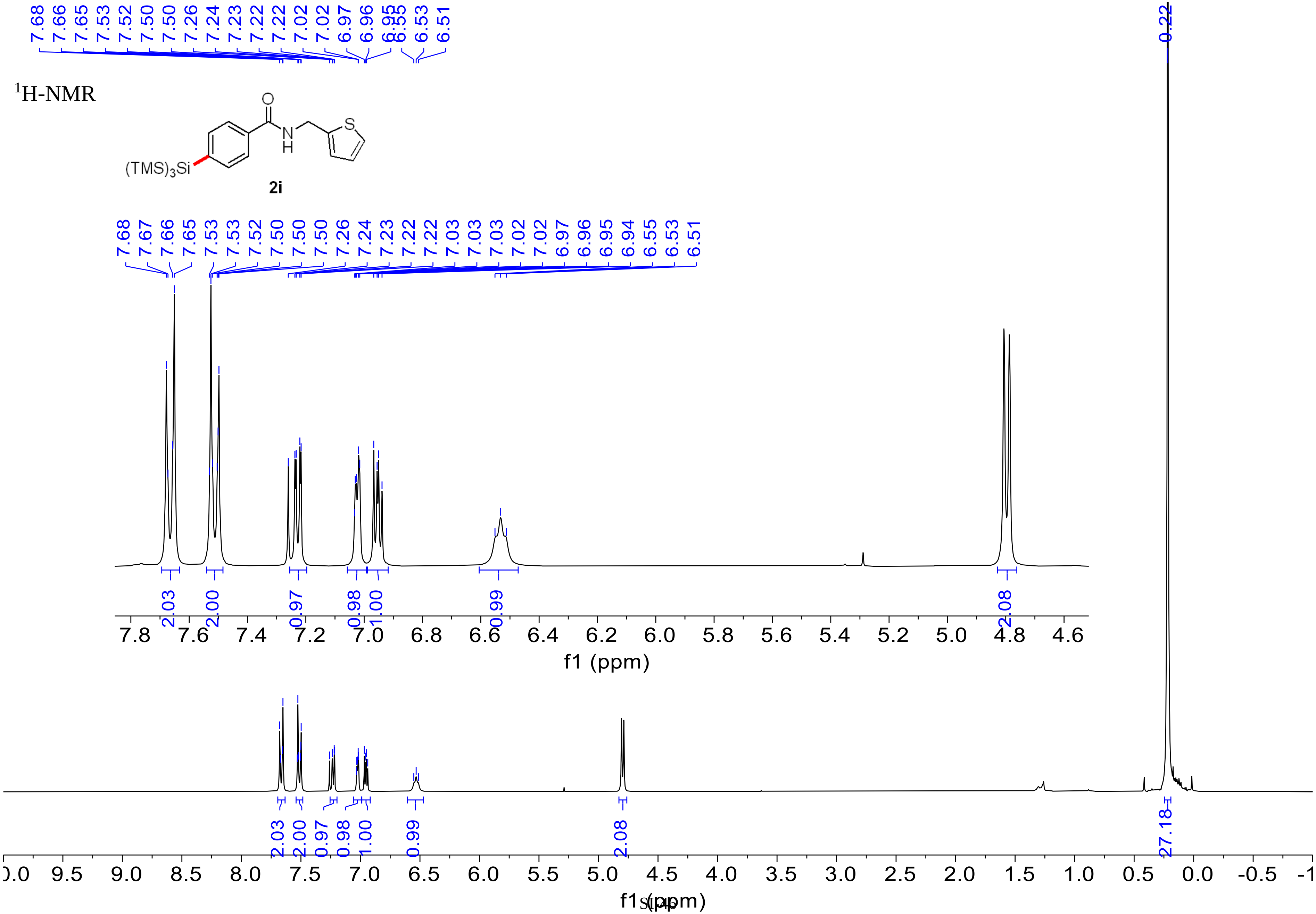
2h

167.17
140.81
136.66
134.83
125.86
77.58
77.16
76.74
51.63
29.03
1.26
(TMS)3Si
O
N
H
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

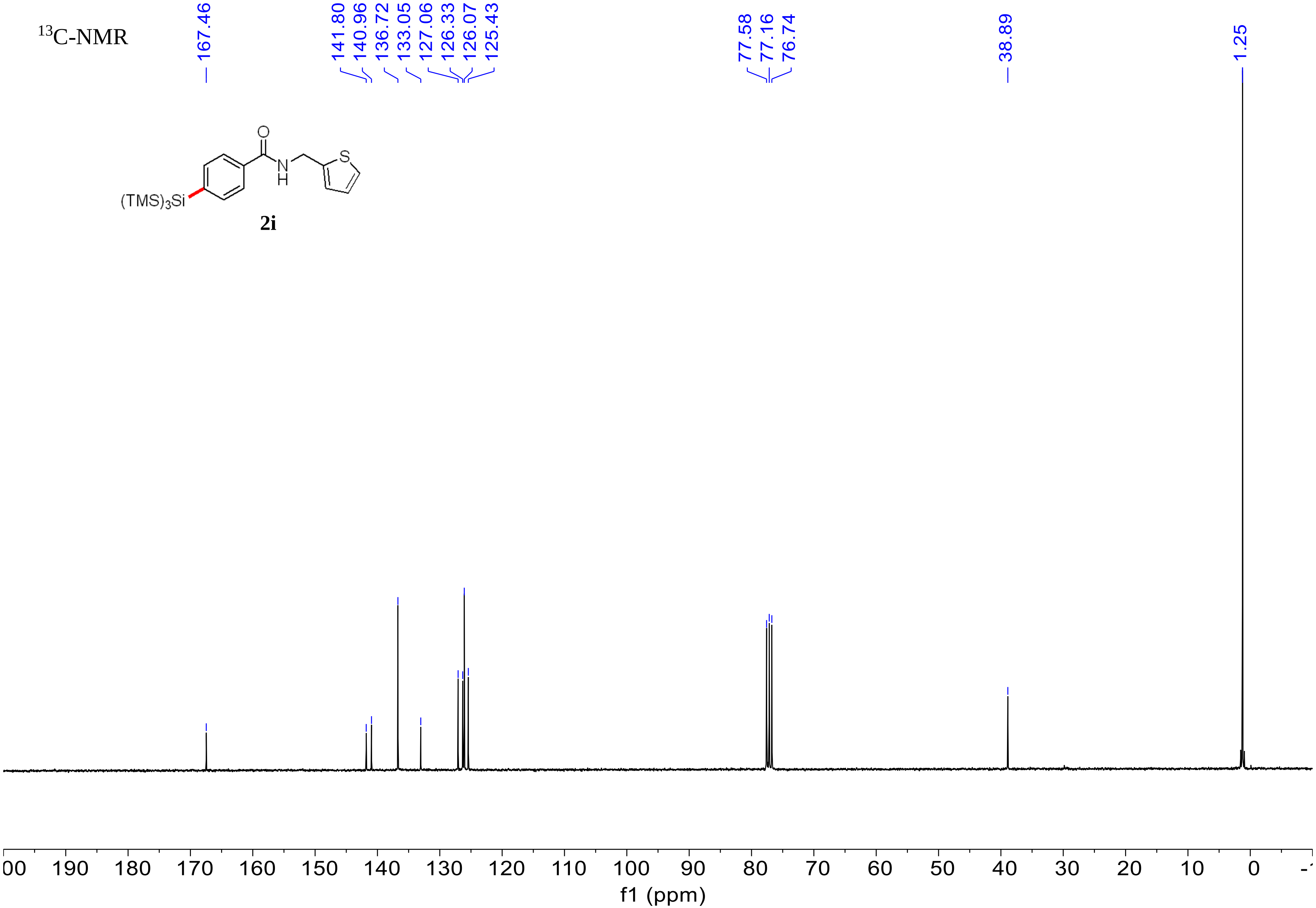
^{29}Si-NMR


-12.68
-76.24
(TMS)$_3$Si
O
N
H
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-23
f1 (ppm)

2h


^{1}H-NMR
O
N
H
S
(TMS)$_3$Si
7.68 7.66 7.65 7.53 7.52 7.50 7.50 7.26 7.24 7.23 7.22 7.22 7.02 7.02 6.97 6.96 6.95 6.55 6.53 6.51
0.22
7.68 7.67 7.66 7.65 7.53 7.53 7.52 7.50 7.50 7.50 7.26 7.24 7.23 7.22 7.22 7.03 7.03 7.03 7.02 7.02 6.97 6.96 6.95 6.94 6.55 6.53 6.51
2.03 2.00 0.97 0.98 1.00 0.99 2.08
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6
f1 (ppm)
2.03 2.00 0.97 0.98 1.00 0.99 2.08 27.18
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

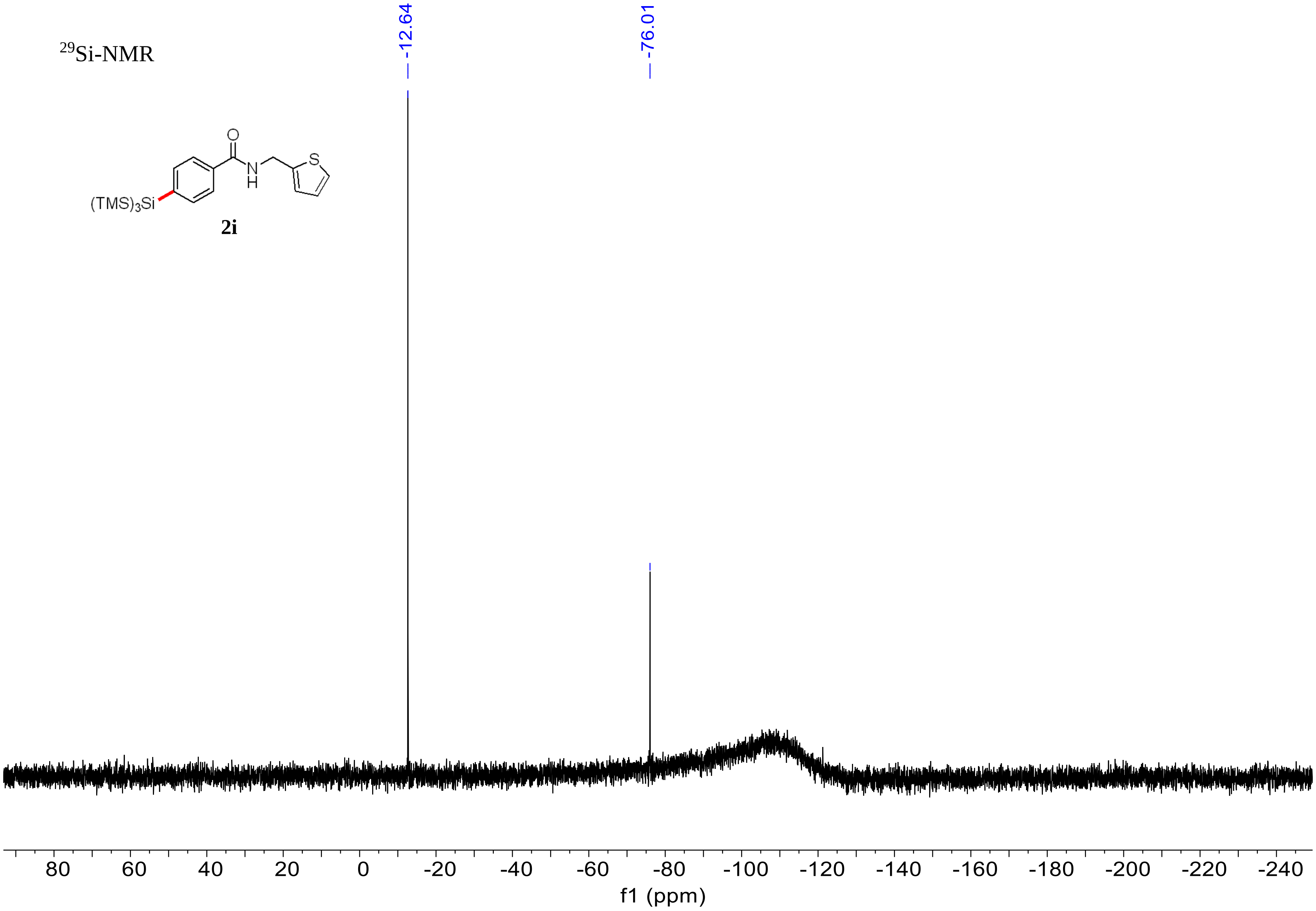
2i


167.46
141.80
140.96
136.72
133.05
127.06
126.33
126.07
125.43
77.58
77.16
76.74
38.89
1.25
O
N
H
S
(TMS)$_3$Si
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)

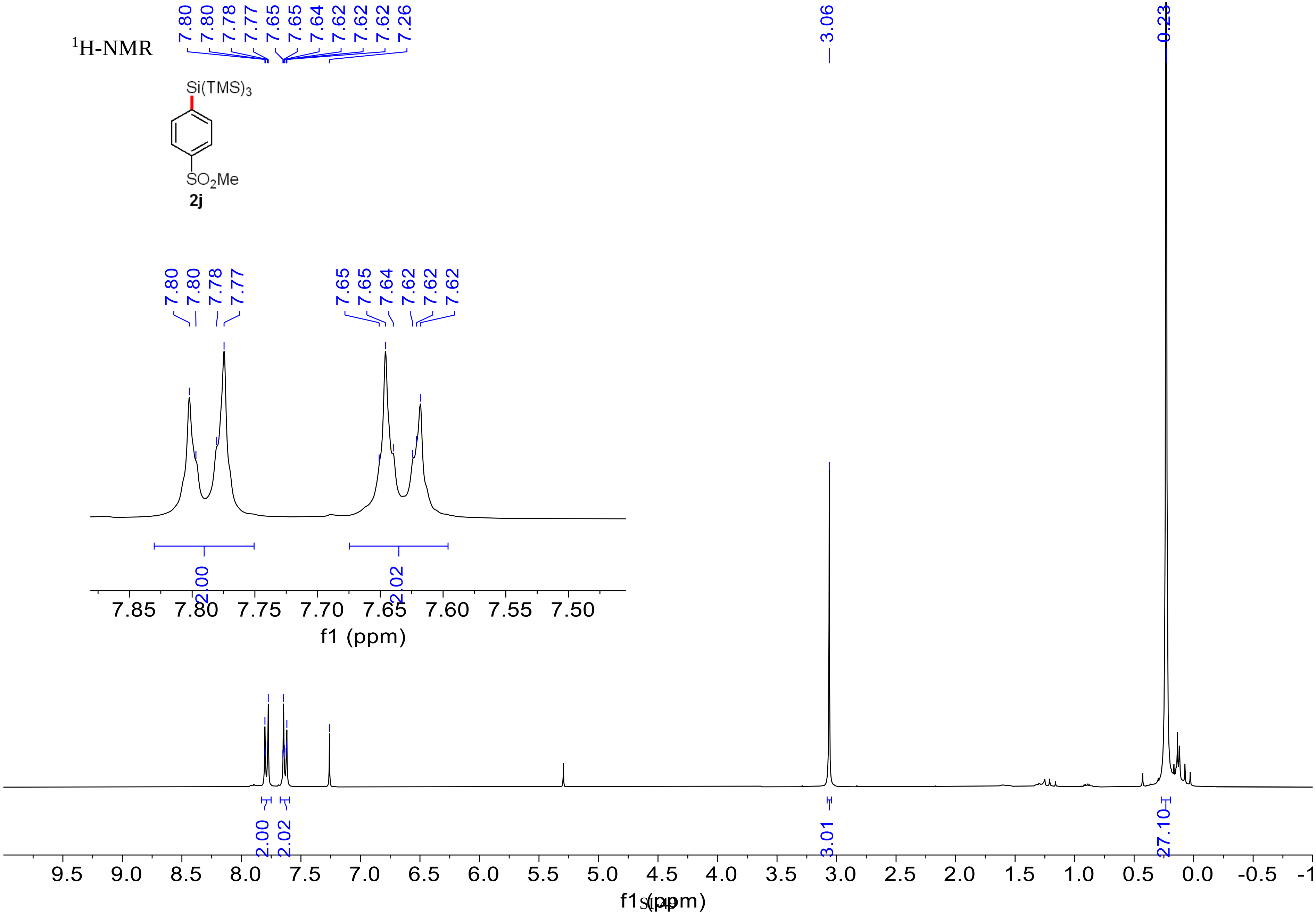
^{13}C-NMR

2i

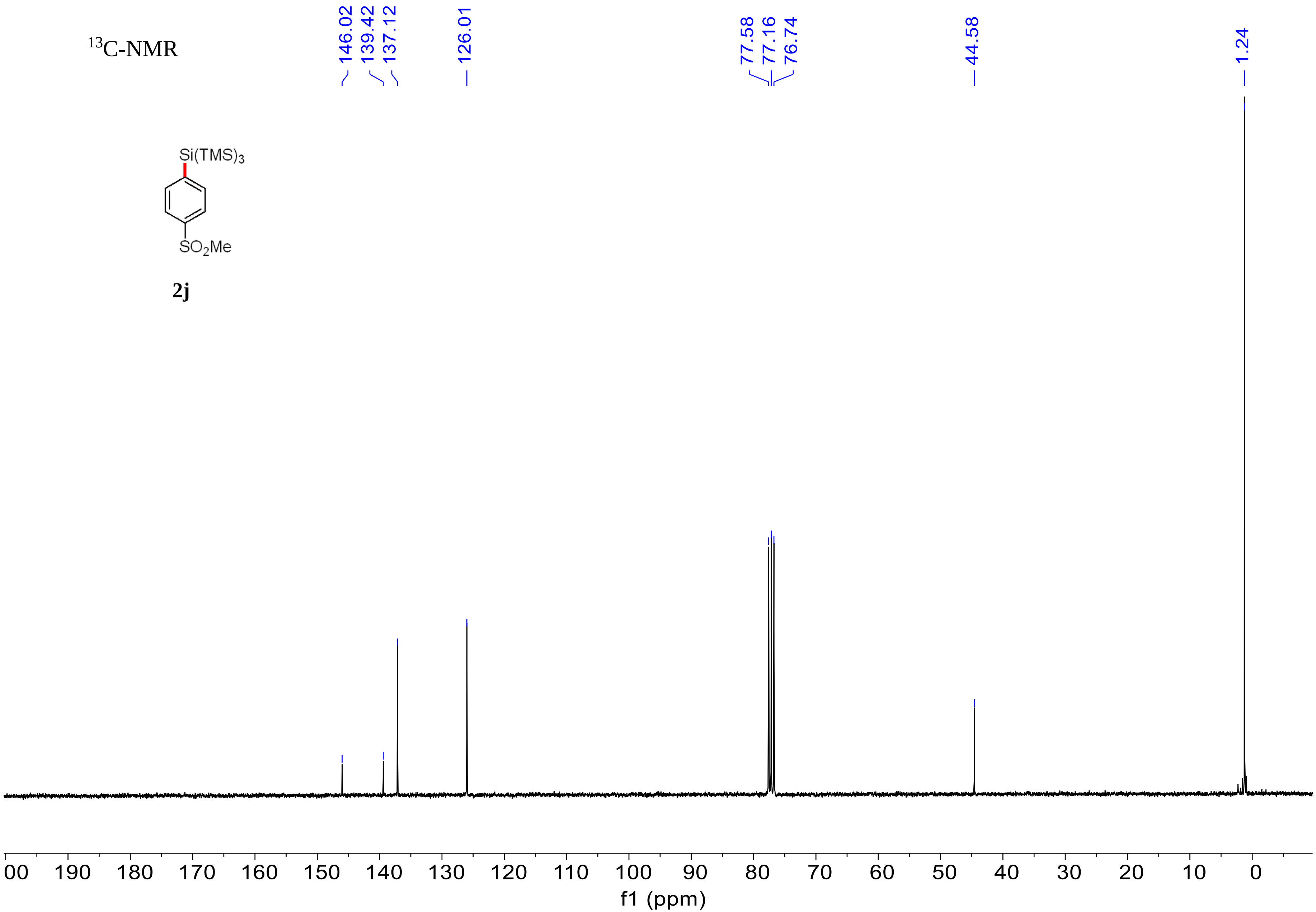
^{29}Si-NMR


-12.64
-76.01
O
N
H
S
(TMS)3Si
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

2i


^{1}H-NMR
7.80 7.80 7.78 7.77 7.65 7.65 7.64 7.62 7.62 7.62 7.26
3.06
0.23
Si(TMS)$_3$
SO$_2$Me
2j
7.80 7.80 7.78 7.77
7.65 7.65 7.64 7.62 7.62 7.62
2.00
2.02
7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50
f1 (ppm)
2.00
2.02
3.01
27.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

^{13}C-NMR

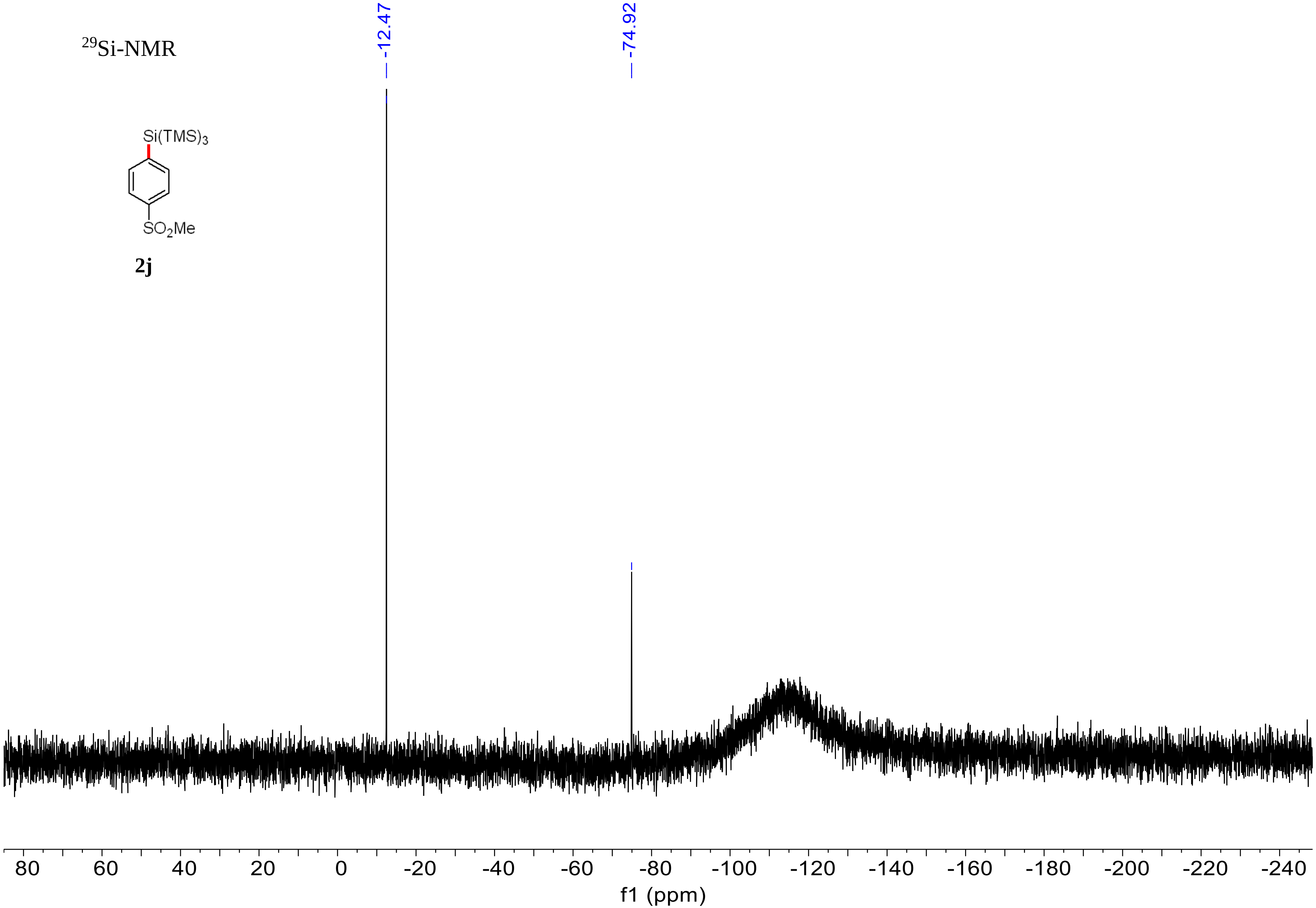

146.02
139.42
137.12
126.01
77.58
77.16
76.74
44.58
1.24
Si(TMS)$_3$
SO$_2$Me
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

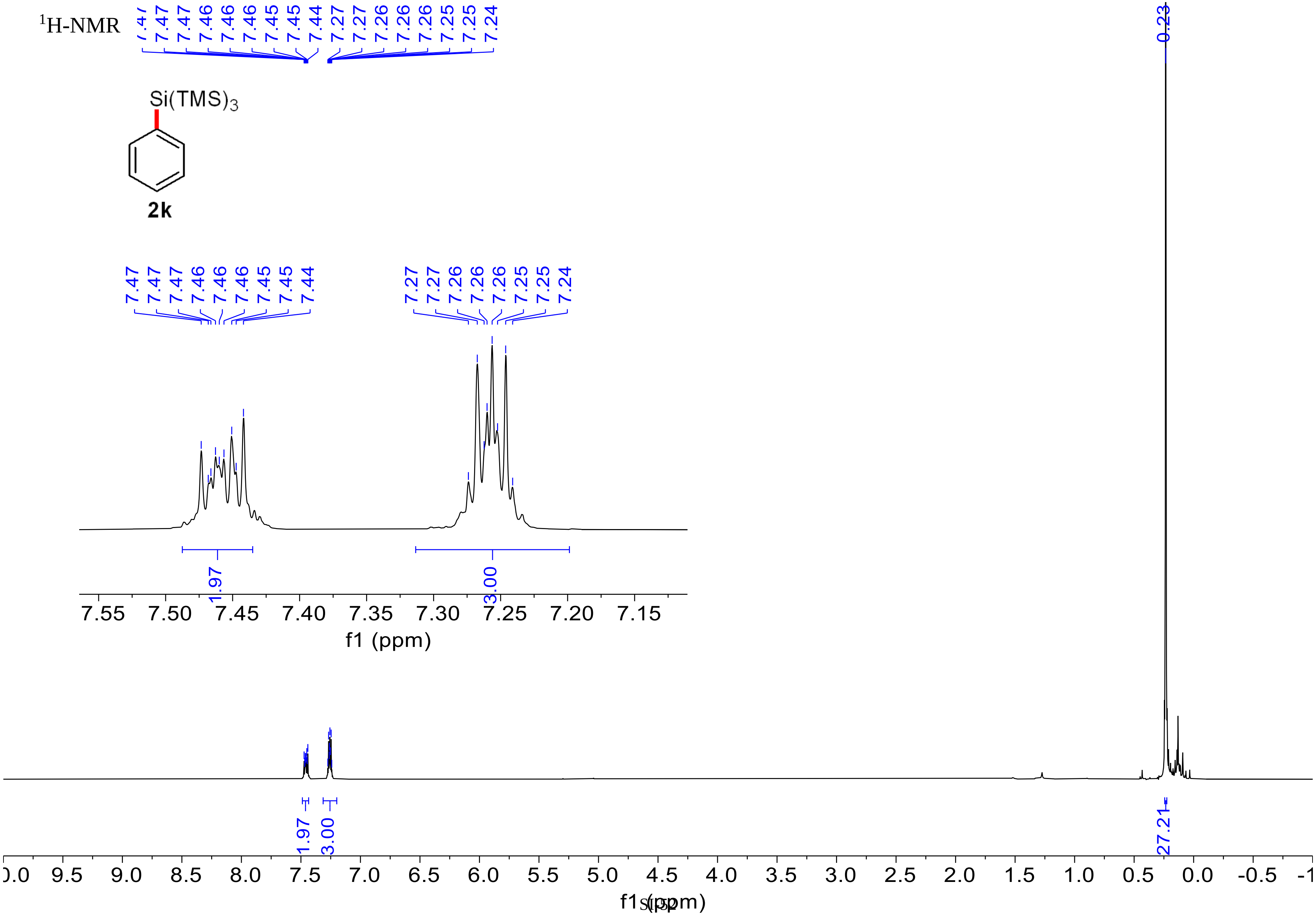
2j

^{29}Si-NMR

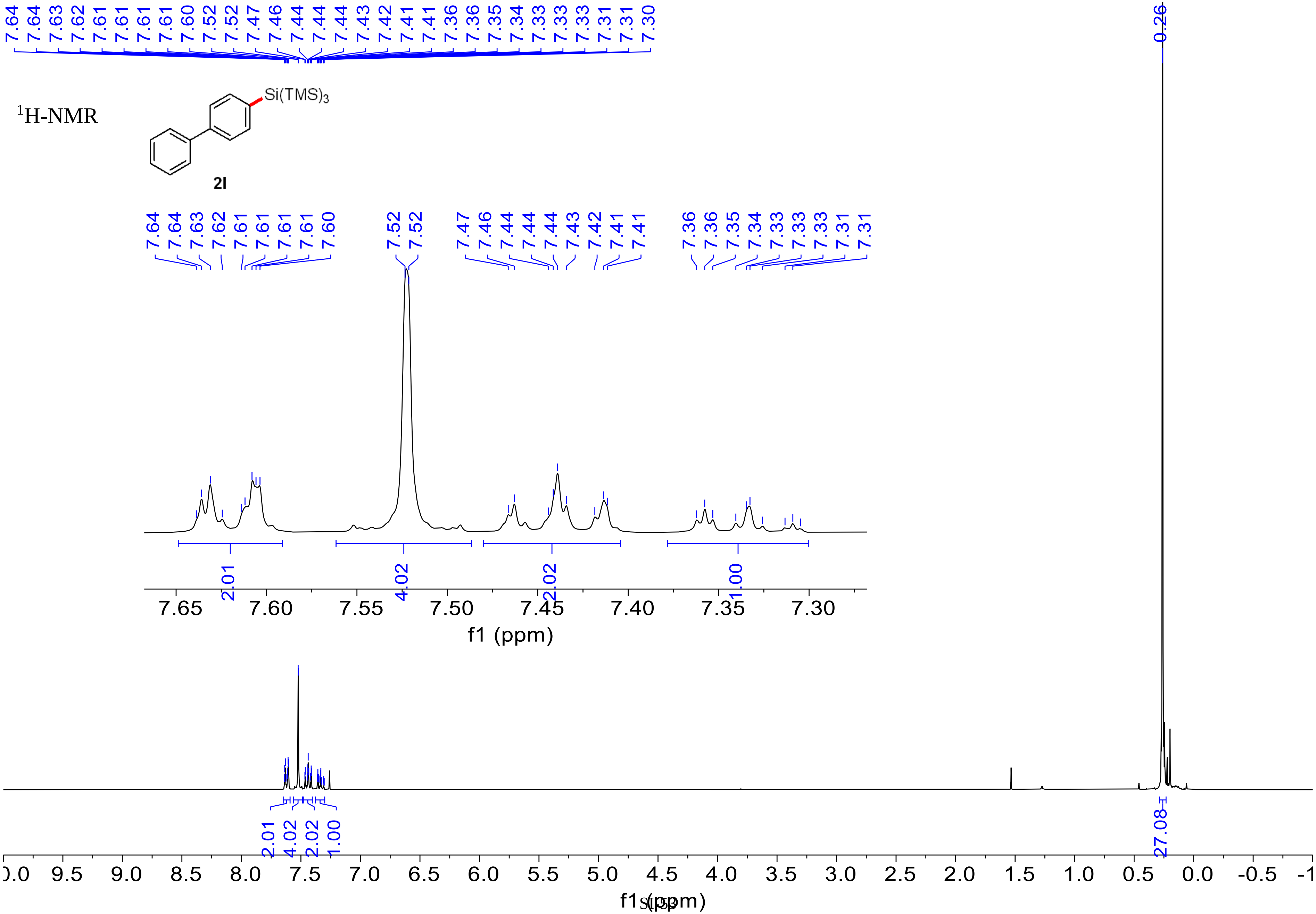
Si(TMS)3
SO2Me

2j

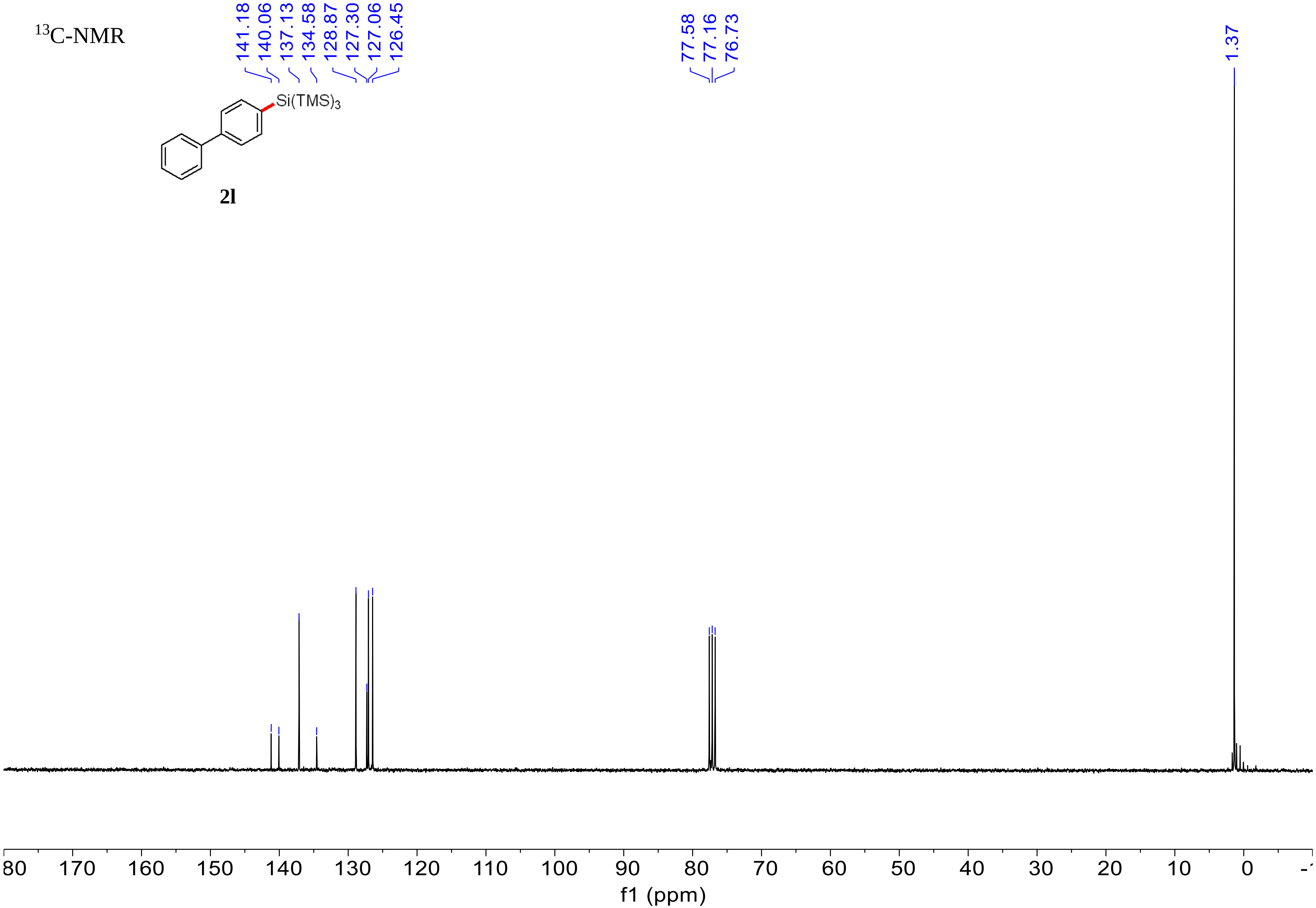

-12.47
-74.92
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)



^{1}H-NMR
7.47 7.47 7.47 7.46 7.46 7.46 7.45 7.45 7.44 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.24
0.23
Si(TMS)$_3$
2k
7.47 7.47 7.47 7.46 7.46 7.46 7.45 7.45 7.44
7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.24
1.97
3.00
7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
1.97
3.00
27.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

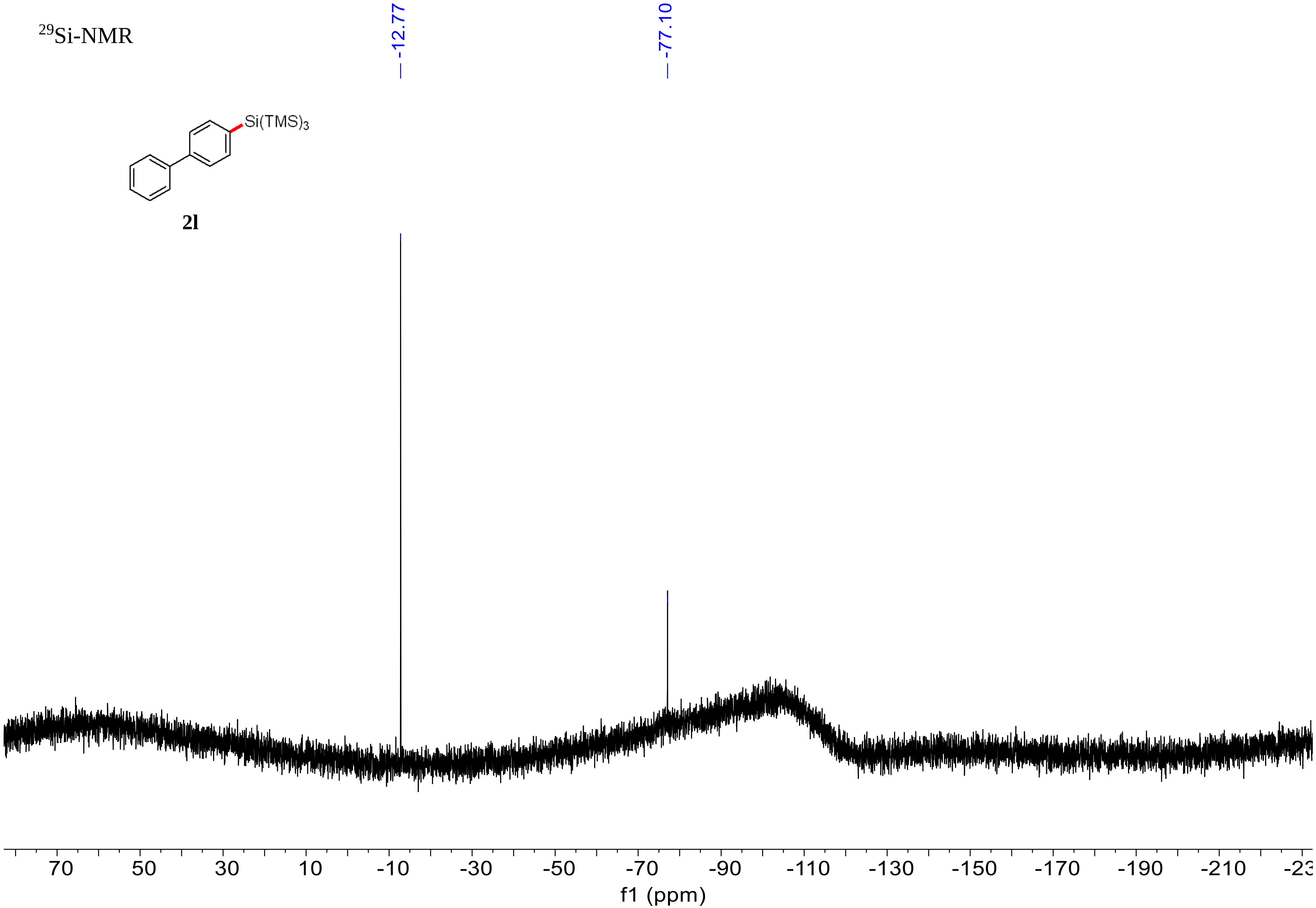

7.64 7.64 7.63 7.62 7.61 7.61 7.61 7.61 7.60 7.52 7.52 7.47 7.46 7.44 7.44 7.44 7.43 7.42 7.41 7.41 7.36 7.36 7.35 7.34 7.33 7.33 7.33 7.31 7.31 7.30
0.26
^{1}H-NMR
Si(TMS)$_3$
2l
7.64 7.64 7.63 7.62 7.61 7.61 7.61 7.61 7.60
7.52 7.52
7.47 7.46 7.44 7.44 7.44 7.43 7.42 7.41 7.41
7.36 7.36 7.35 7.34 7.33 7.33 7.33 7.31 7.31
2.01
4.02
2.02
1.00
7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30
f1 (ppm)
2.01 4.02 2.02 1.00
27.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

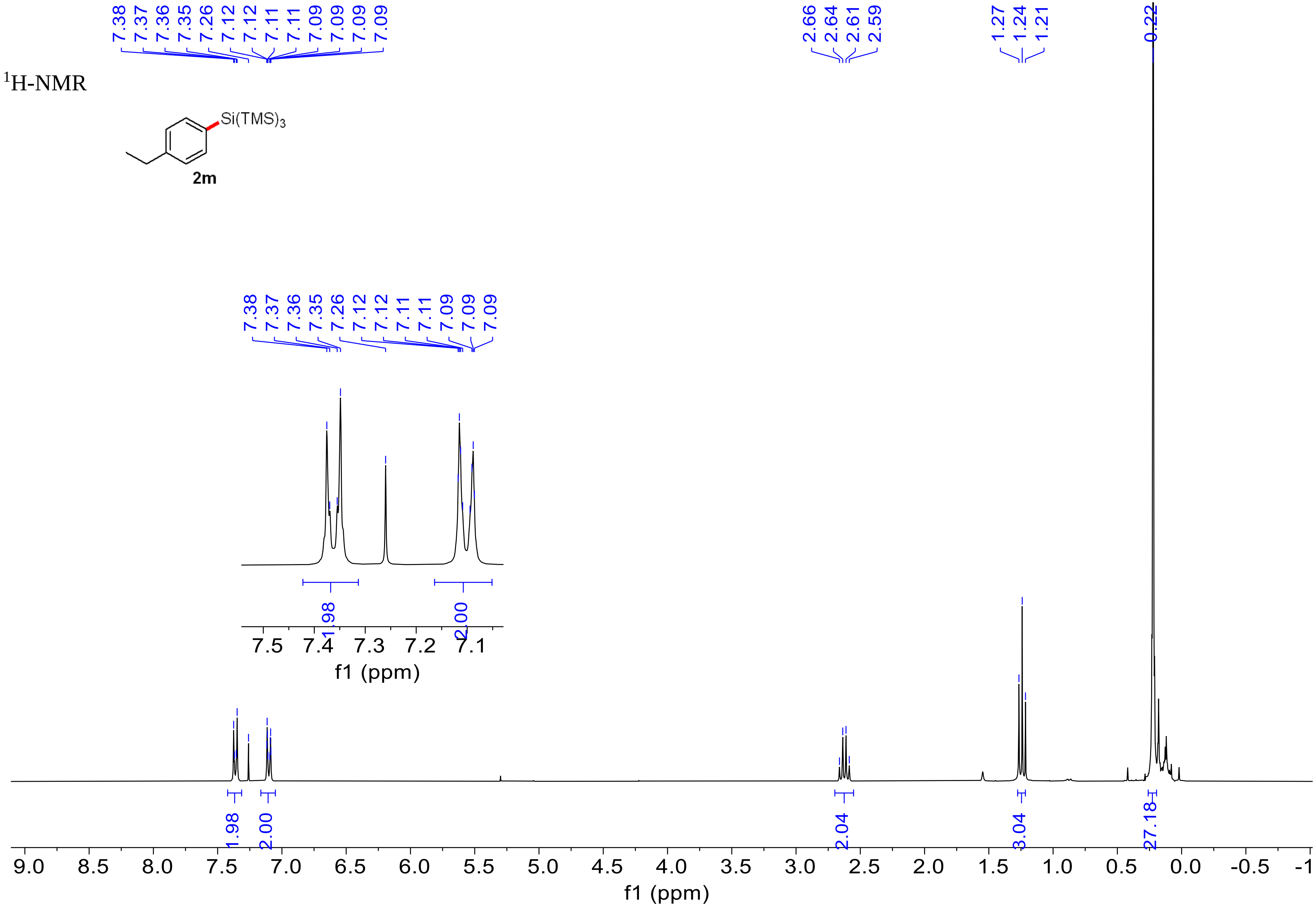
^{13}C-NMR


141.18
140.06
137.13
134.58
128.87
127.30
127.06
126.45
77.58
77.16
76.73
1.37
Si(TMS)$_3$
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)

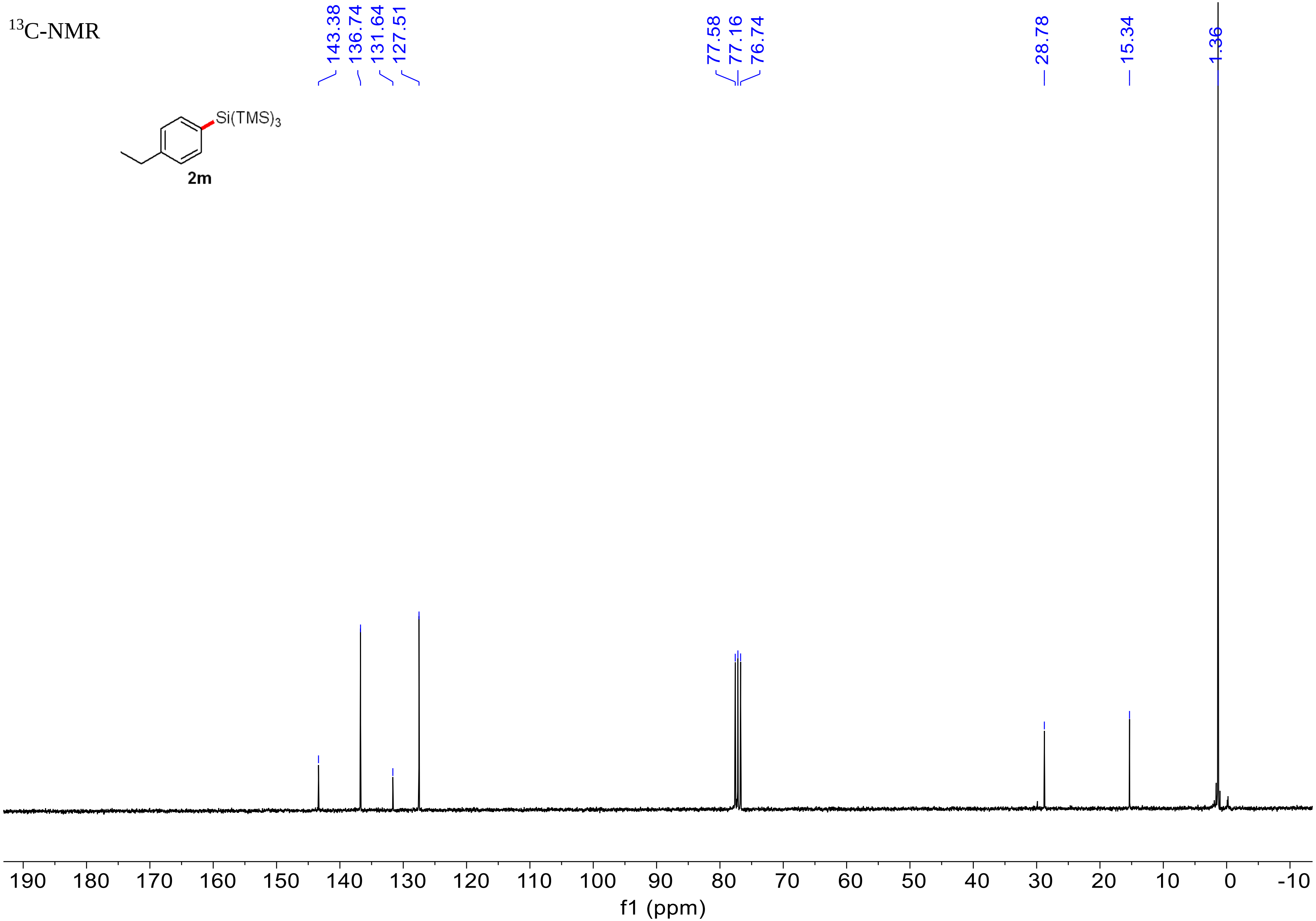
2l

^{29}Si-NMR

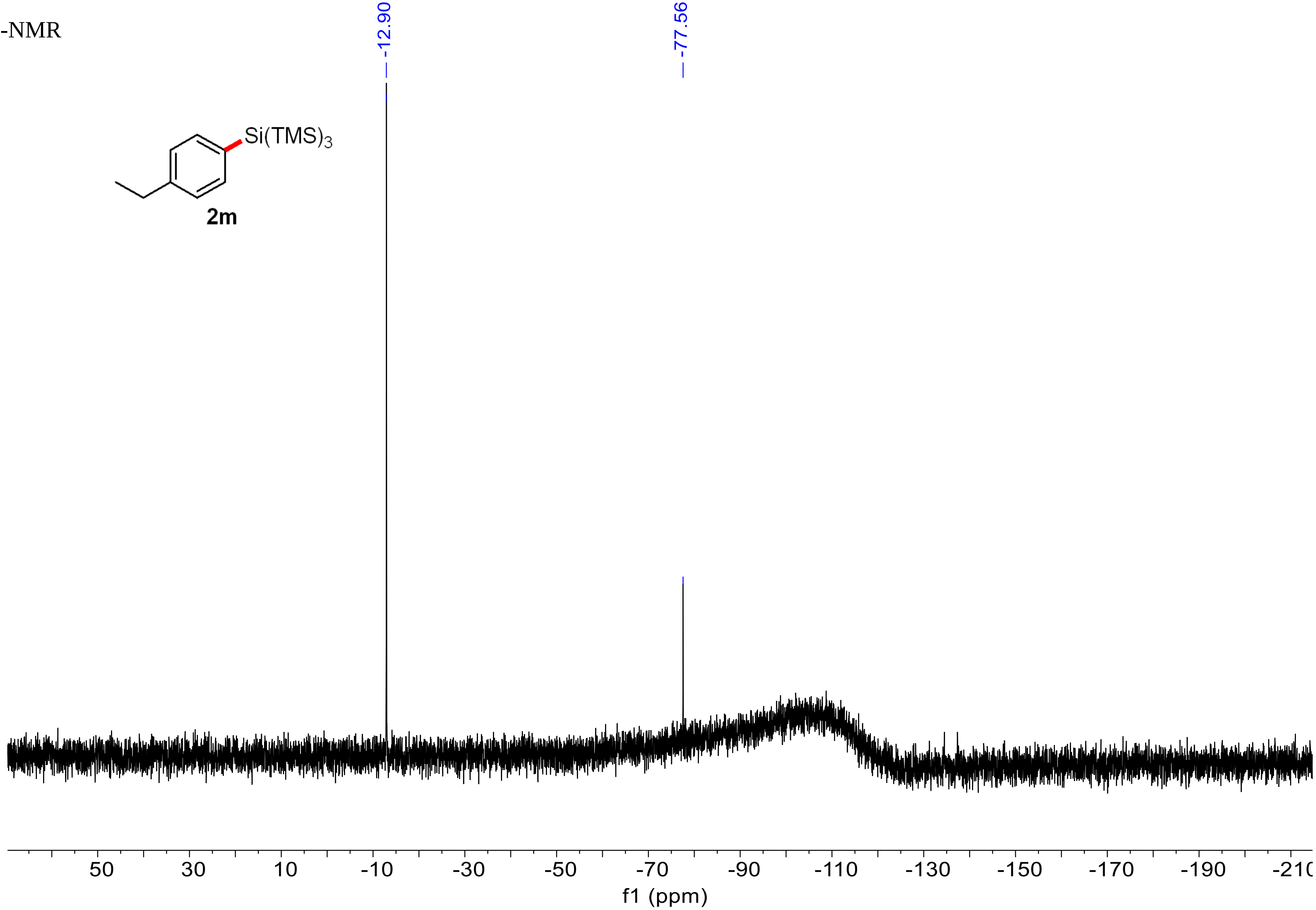

2l
-12.77
-77.10
Si(TMS)$_3$
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-23
f1 (ppm)


^{1}H-NMR
Si(TMS)$_3$
2m
7.38 7.37 7.36 7.35 7.26 7.12 7.12 7.11 7.11 7.09 7.09 7.09 7.09
2.66 2.64 2.61 2.59
1.27 1.24 1.21
0.22
1.98
2.00
2.04
3.04
27.18
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)
7.38 7.37 7.36 7.35 7.26 7.12 7.12 7.11 7.11 7.09 7.09 7.09
1.98
2.00
7.5 7.4 7.3 7.2 7.1
f1 (ppm)

^{13}C-NMR


143.38
136.74
131.64
127.51
77.58
77.16
76.74
28.78
15.34
1.36
Si(TMS)3
2m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

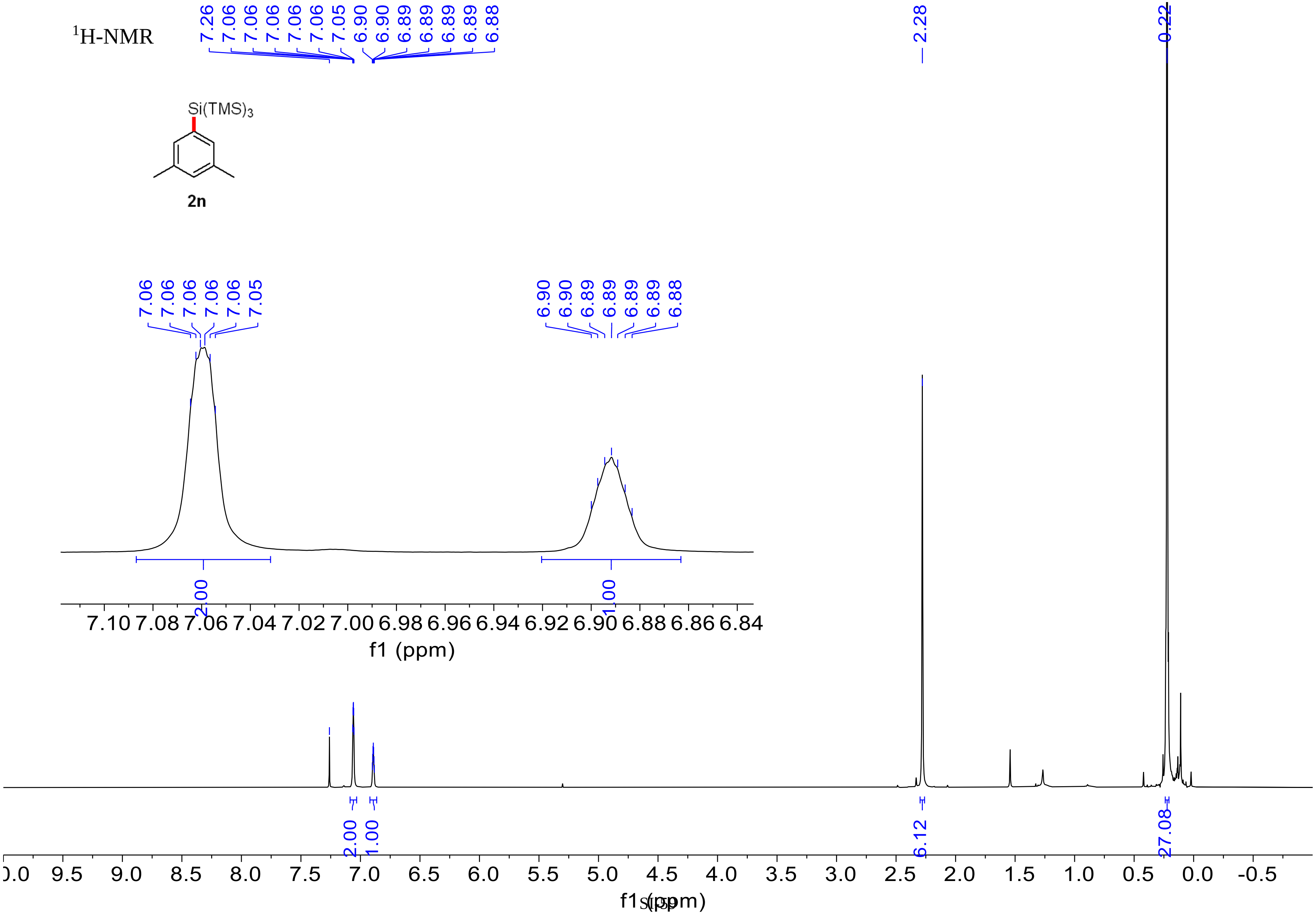
^{29}Si-NMR



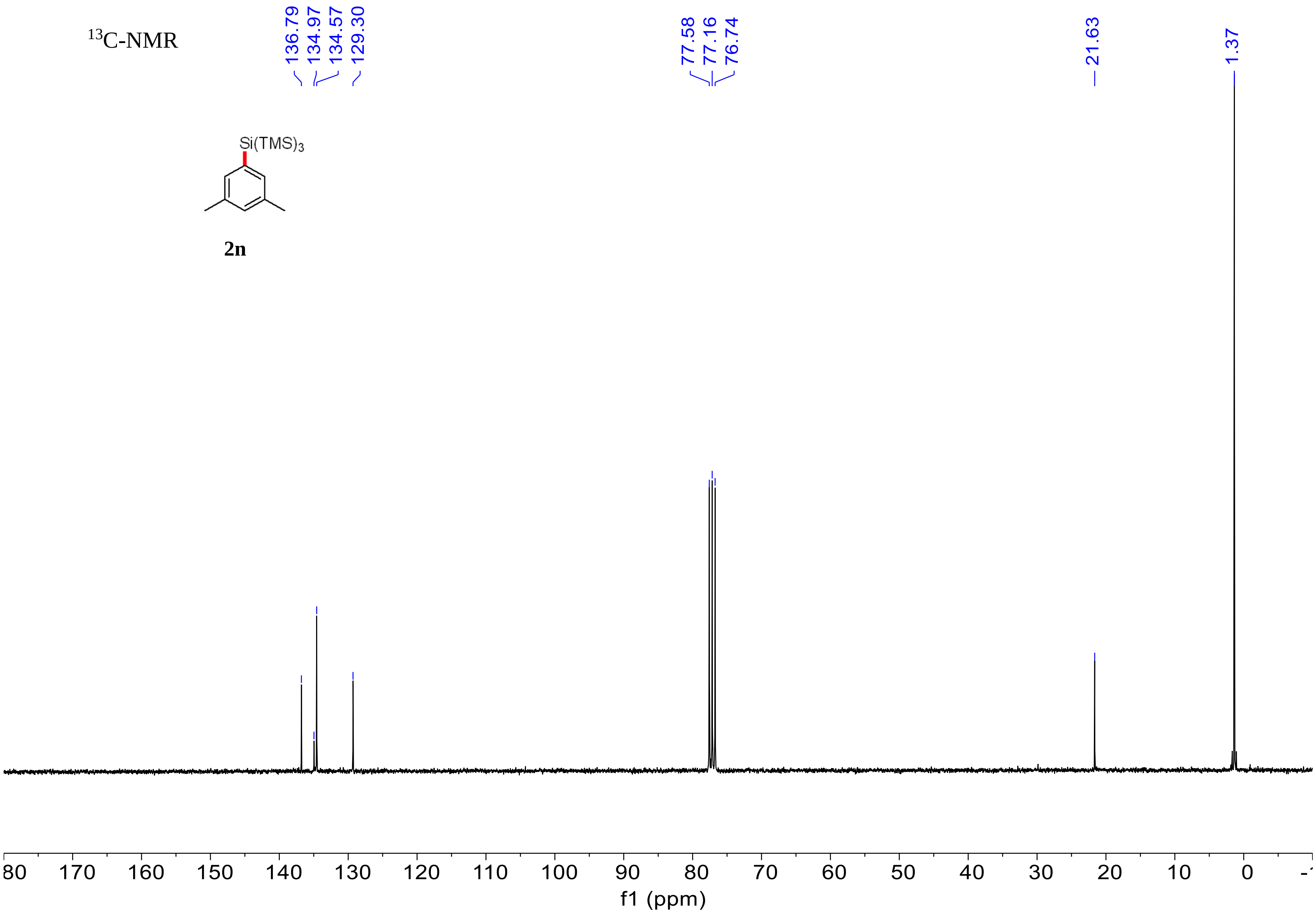
2m

Si(TMS)$_3$
-12.90
-77.56
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

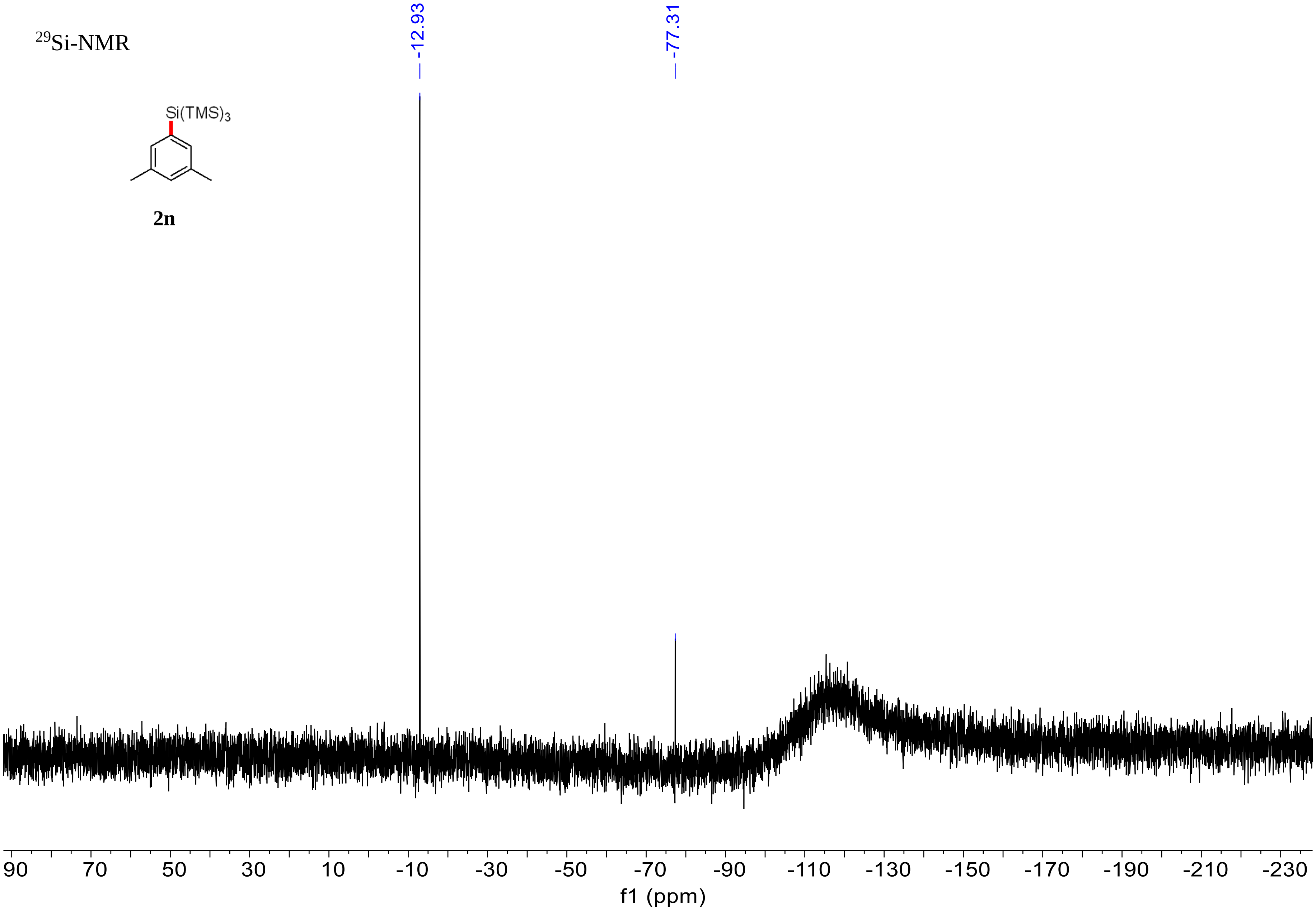
^{1}H-NMR


7.26
7.06
7.06
7.06
7.06
7.06
7.05
6.90
6.90
6.89
6.89
6.89
6.89
6.88
2.28
0.22
Si(TMS)3
2.00
1.00
7.10 7.08 7.06 7.04 7.02 7.00 6.98 6.96 6.94 6.92 6.90 6.88 6.86 6.84
f1 (ppm)
2.00
1.00
6.12
27.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

2n

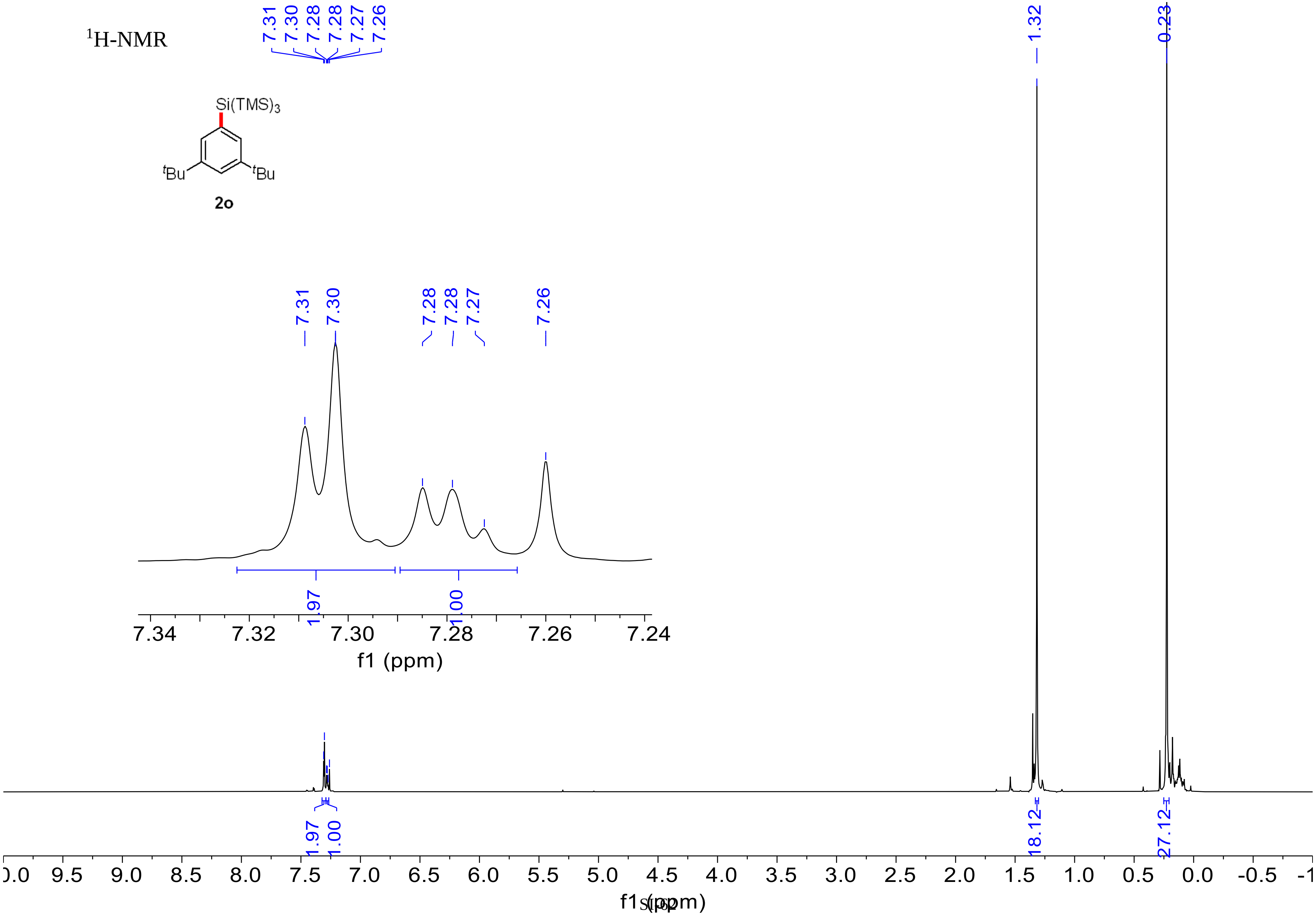

^{13}C-NMR
136.79
134.97
134.57
129.30
77.58
77.16
76.74
21.63
1.37
Si(TMS)$_3$
2n
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)

^{29}Si-NMR

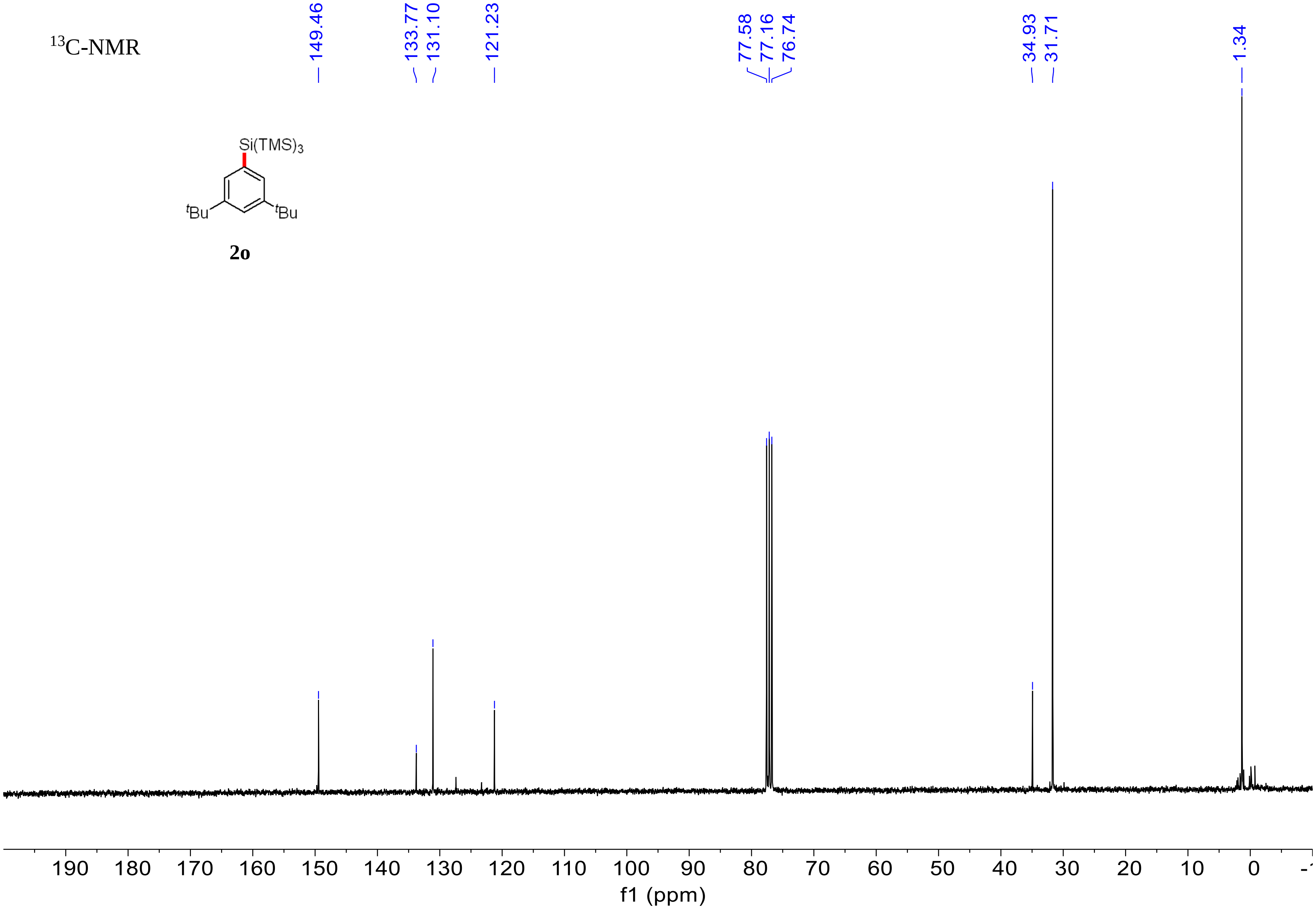

Si(TMS)$_3$

2n

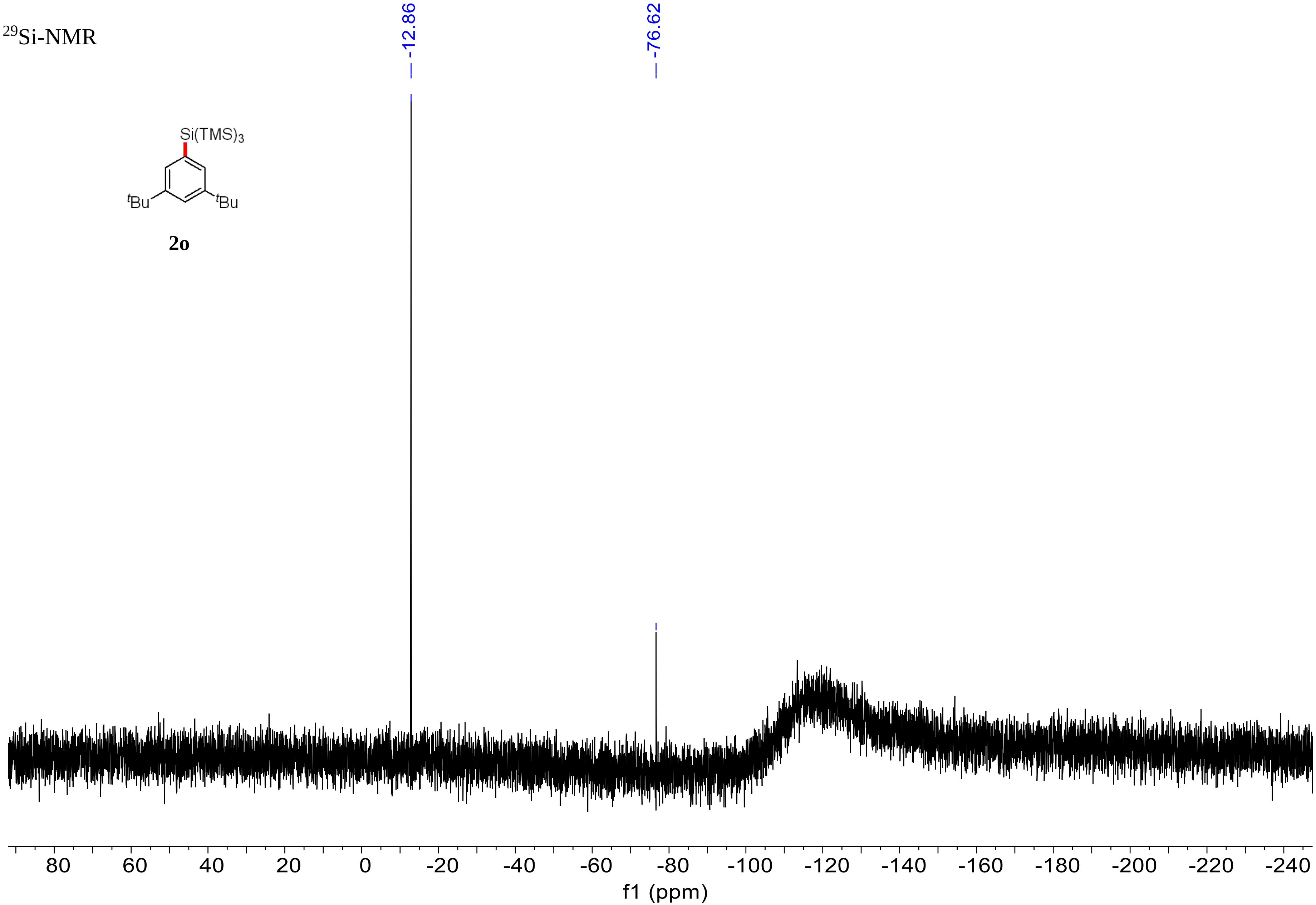
-12.93
-77.31
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)



^{1}H-NMR
7.31
7.30
7.28
7.28
7.27
7.26
1.32
0.23
Si(TMS)$_3$
^{t}Bu
^{t}Bu
2o
1.97
1.00
7.34
7.32
7.30
7.28
7.26
7.24
f1 (ppm)
1.97
1.00
18.12
27.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

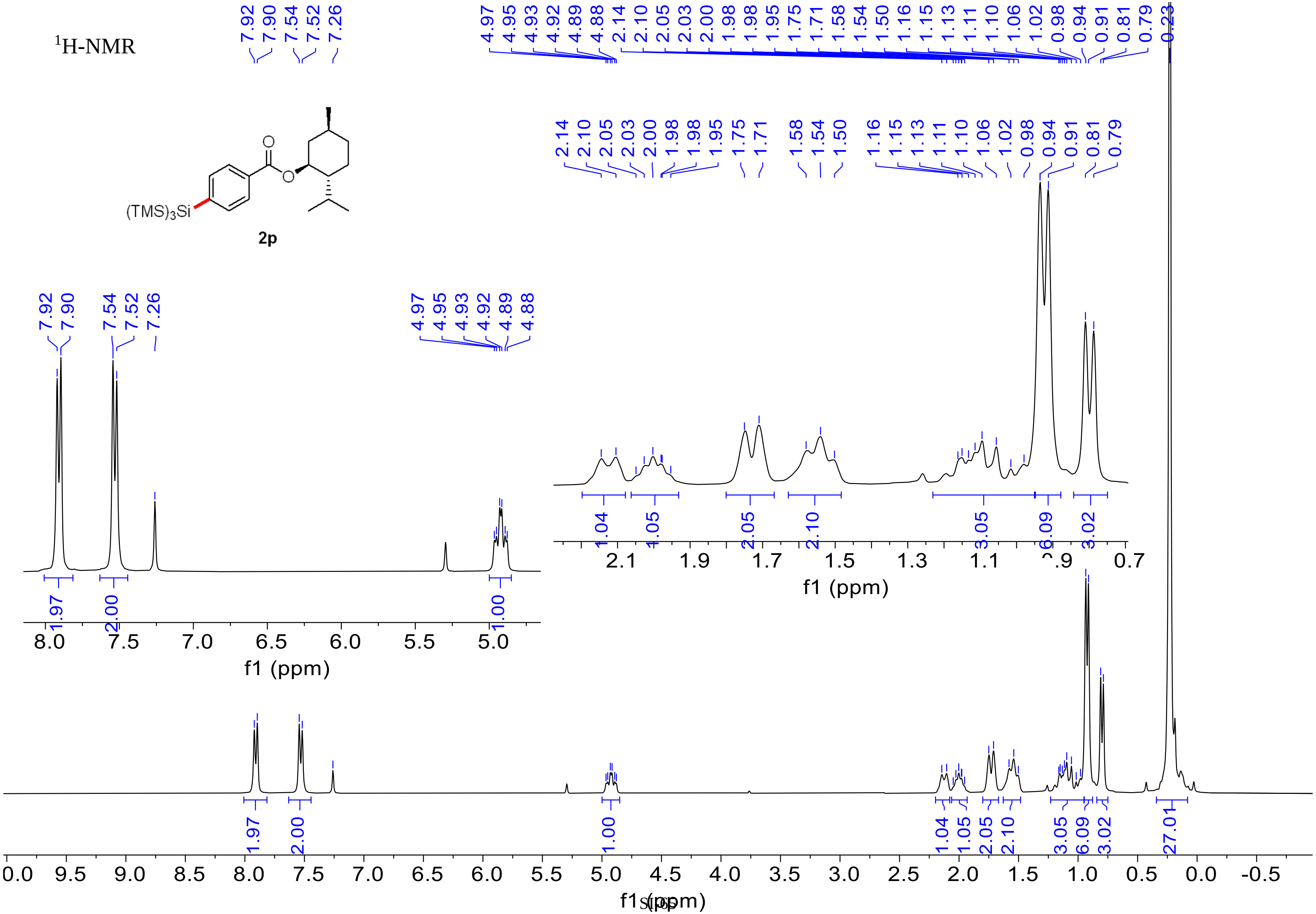

^{13}C-NMR
149.46
133.77
131.10
121.23
77.58
77.16
76.74
34.93
31.71
1.34
Si(TMS)$_3$
^{t}Bu
^{t}Bu
2o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{29}Si-NMR


-12.86
-76.62
Si(TMS)3
tBu
tBu
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

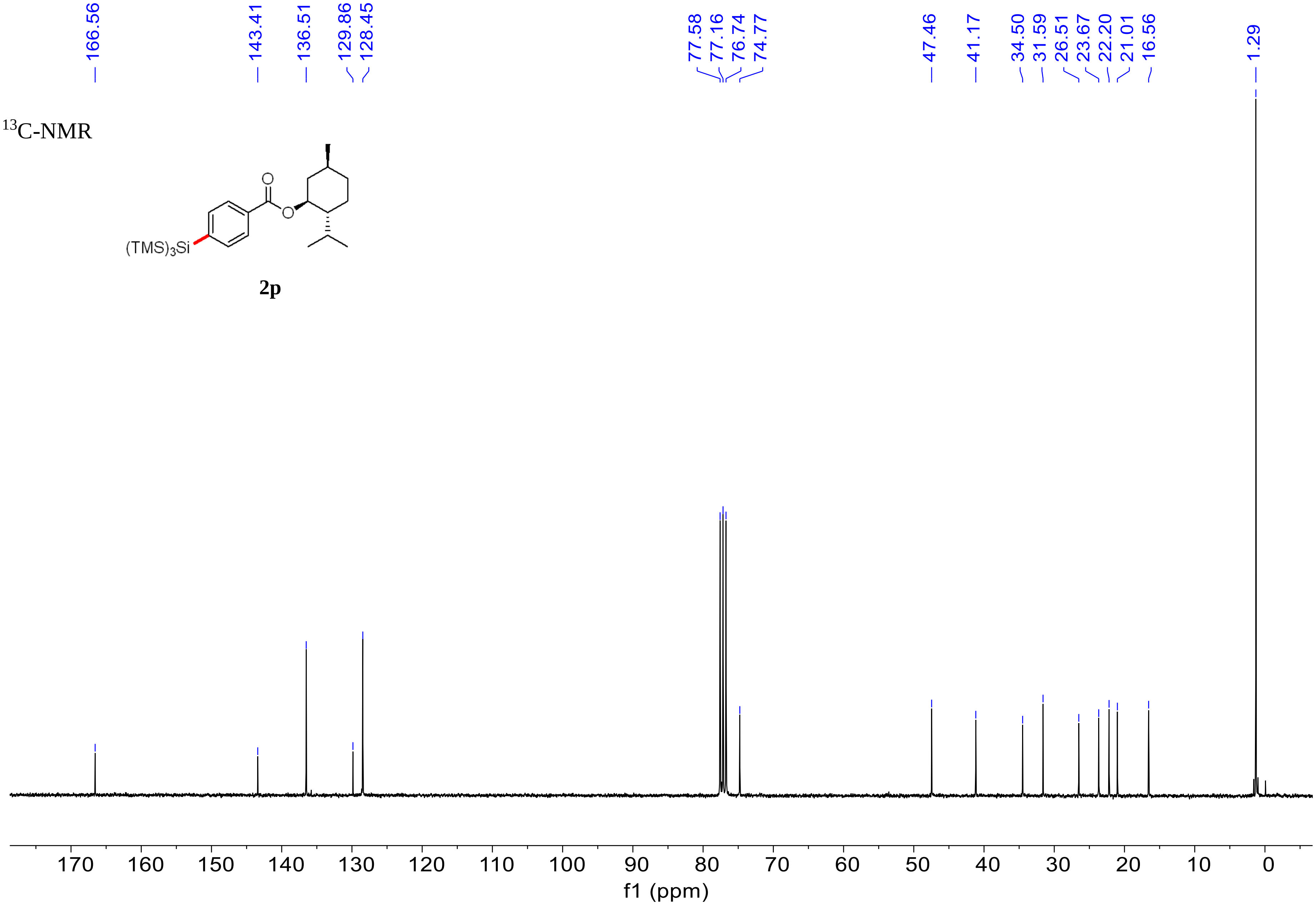
2o

^{1}H-NMR



(TMS)3Si
O
O
7.92 7.90 7.54 7.52 7.26
4.97 4.95 4.93 4.92 4.89 4.88 2.14 2.10 2.05 2.03 2.00 1.98 1.98 1.95 1.75 1.71 1.58 1.54 1.50 1.16 1.15 1.13 1.11 1.10 1.06 1.02 0.98 0.94 0.91 0.81 0.79 0.23
1.04 1.05 2.05 2.10 3.05 6.09 3.02
2.1 1.9 1.7 1.5 1.3 1.1 0.9 0.7
f1 (ppm)
1.97 2.00 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0
f1 (ppm)
1.97 2.00 1.00 1.04 1.05 2.05 2.10 3.05 6.09 3.02 27.01
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

2p

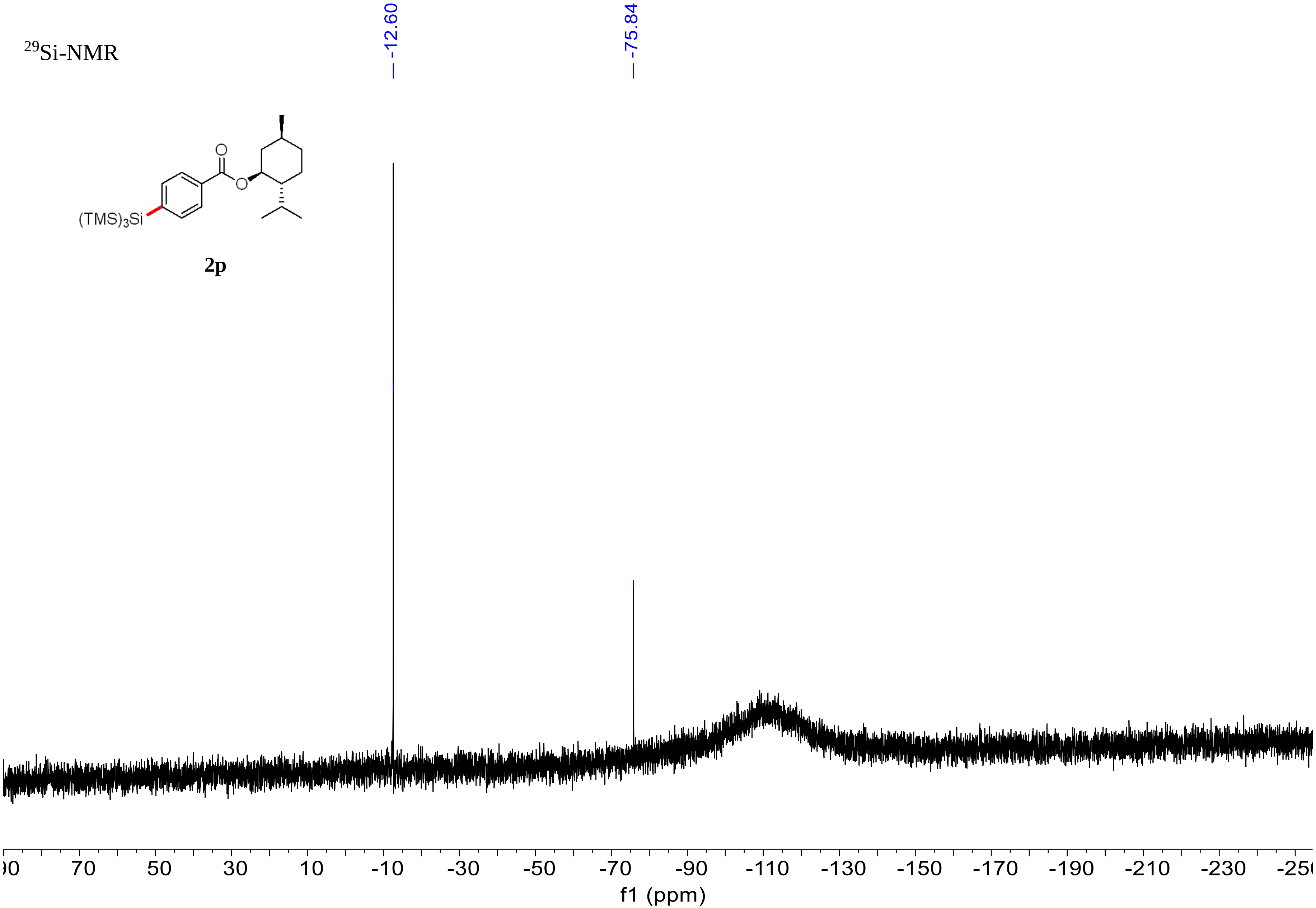


^{13}C-NMR

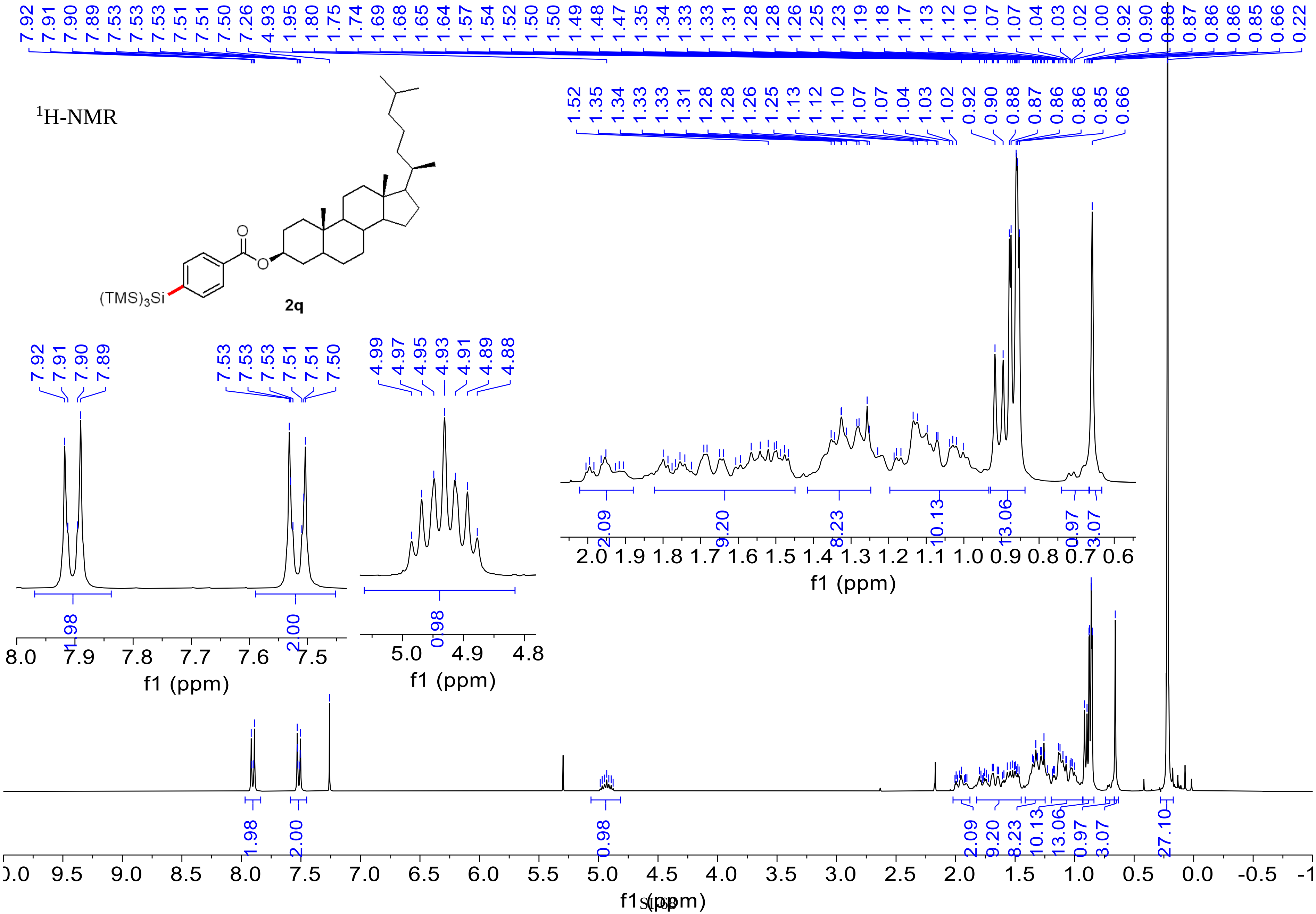
2p

166.56
143.41
136.51
129.86
128.45
77.58
77.16
76.74
74.77
47.46
41.17
34.50
31.59
26.51
23.67
22.20
21.01
16.56
1.29
(TMS)3Si
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{29}Si-NMR

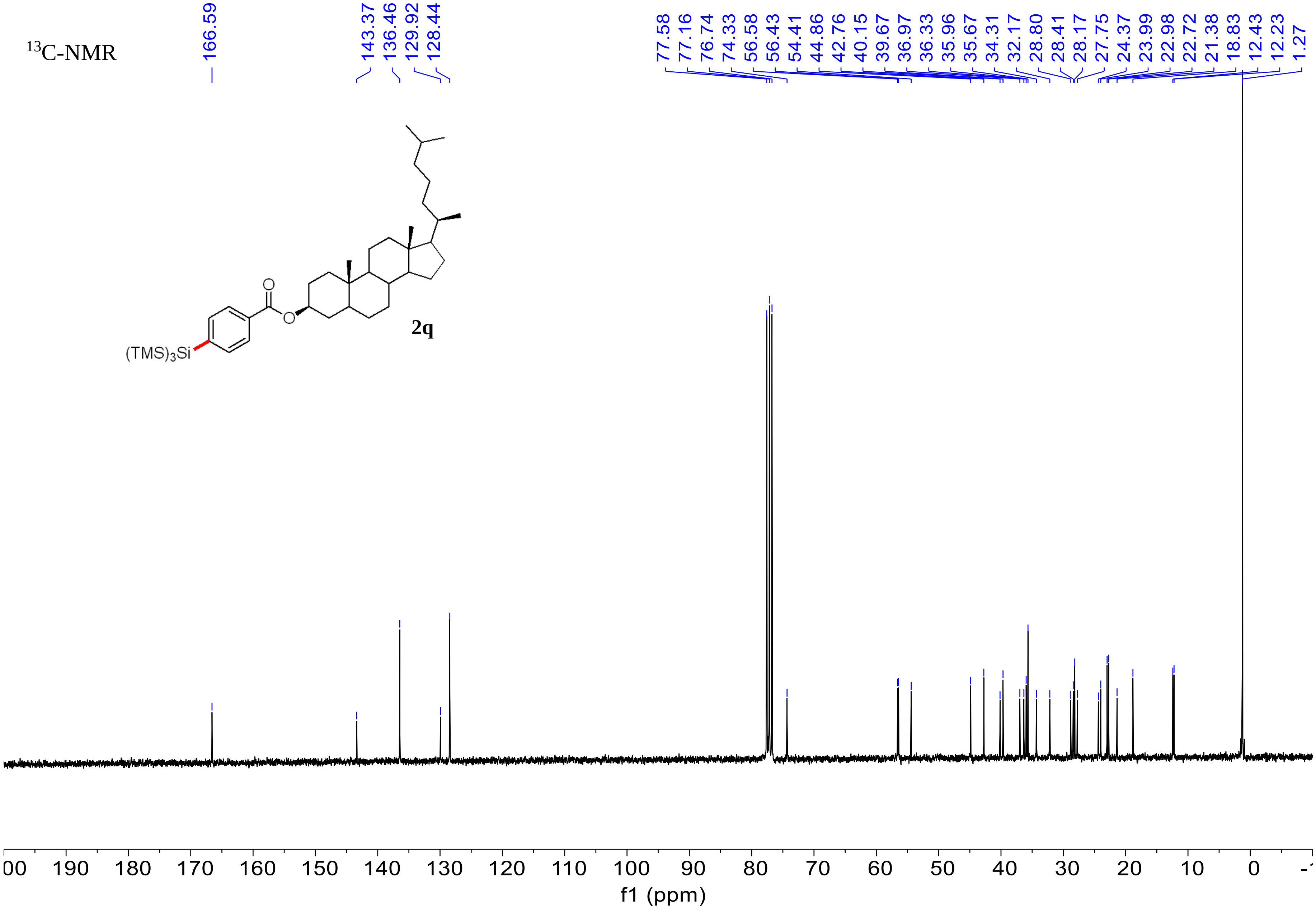

-12.60
-75.84
(TMS)3Si
O
O
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

2p

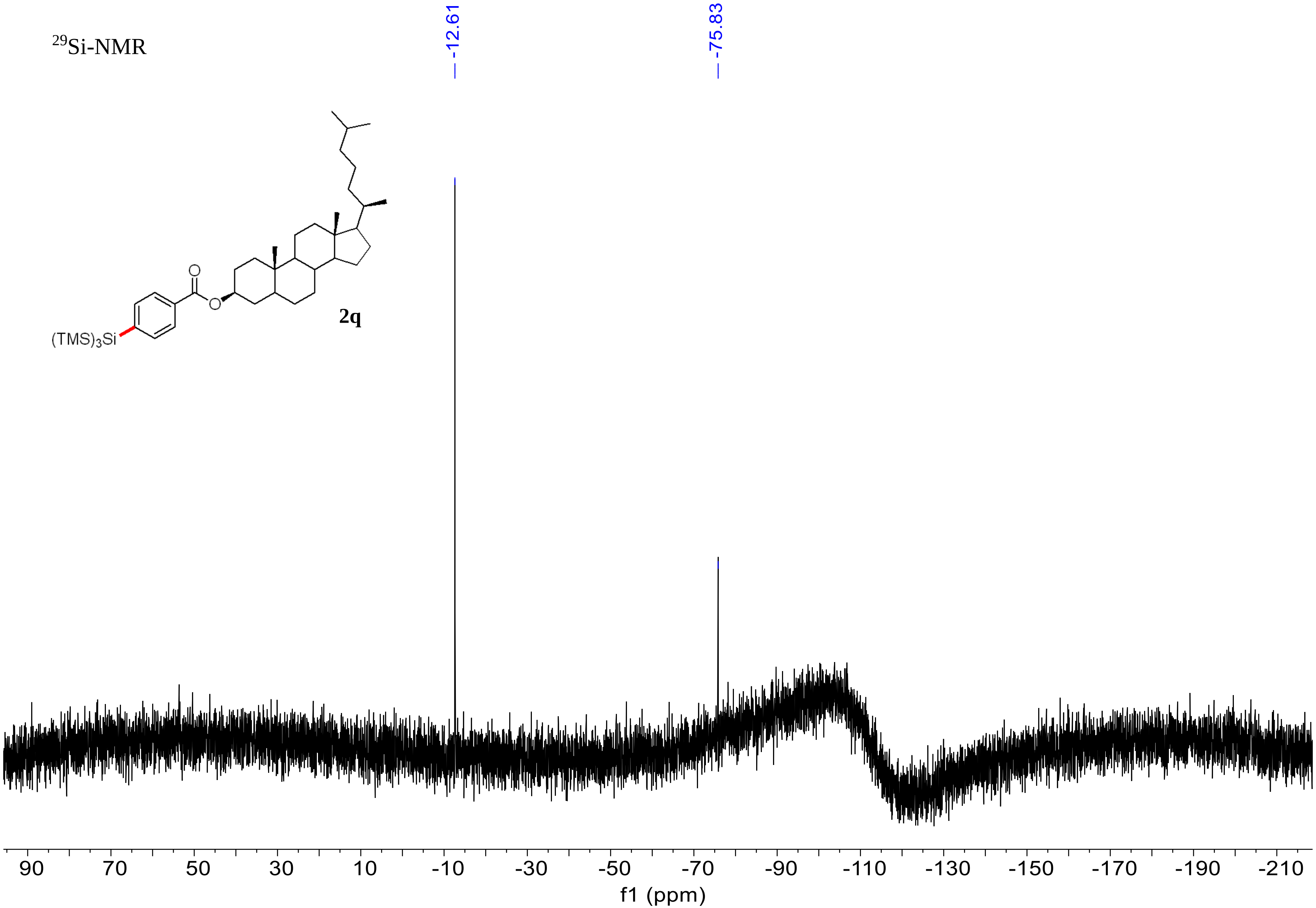


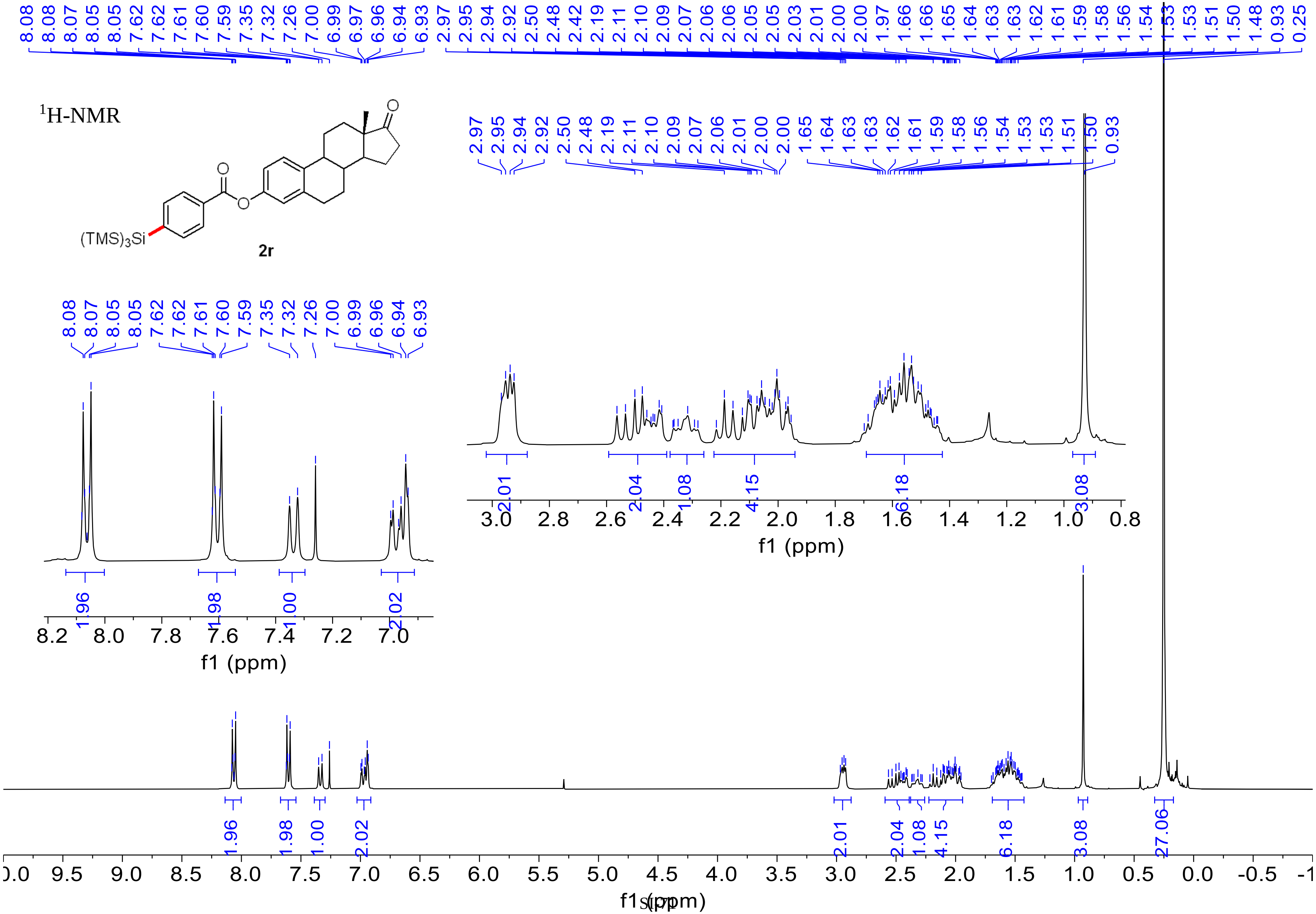
1H-NMR
(TMS)3Si
2q
7.92 7.91 7.90 7.89 7.53 7.53 7.53 7.51 7.51 7.50 7.26 4.93 1.95 1.80 1.75 1.74 1.69 1.68 1.65 1.64 1.57 1.54 1.52 1.50 1.50 1.49 1.48 1.47 1.35 1.34 1.33 1.33 1.31 1.28 1.28 1.26 1.25 1.23 1.19 1.18 1.17 1.13 1.12 1.10 1.07 1.07 1.04 1.03 1.02 1.00 0.92 0.90 0.88 0.87 0.86 0.86 0.85 0.66 0.22
1.52 1.35 1.34 1.33 1.33 1.31 1.28 1.28 1.26 1.25 1.13 1.12 1.10 1.07 1.07 1.04 1.03 1.02 0.92 0.90 0.88 0.87 0.86 0.86 0.85 0.66
2.09 9.20 8.23 10.13 13.06 0.97 3.07
2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6
f1 (ppm)
7.92 7.91 7.90 7.89 7.53 7.53 7.53 7.51 7.51 7.50
1.98 2.00
8.0 7.9 7.8 7.7 7.6 7.5
f1 (ppm)
4.99 4.97 4.95 4.93 4.91 4.89 4.88
0.98
5.0 4.9 4.8
f1 (ppm)
1.98 2.00 0.98 2.09 9.20 8.23 10.13 13.06 0.97 3.07 27.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

^{13}C-NMR


166.59
143.37
136.46
129.92
128.44
77.58
77.16
76.74
74.33
56.58
56.43
54.41
44.86
42.76
40.15
39.67
36.97
36.33
35.96
35.67
34.31
32.17
28.80
28.41
28.17
27.75
24.37
23.99
22.98
22.72
21.38
18.83
12.43
12.23
1.27
O
O
(TMS)$_3$Si
2q
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

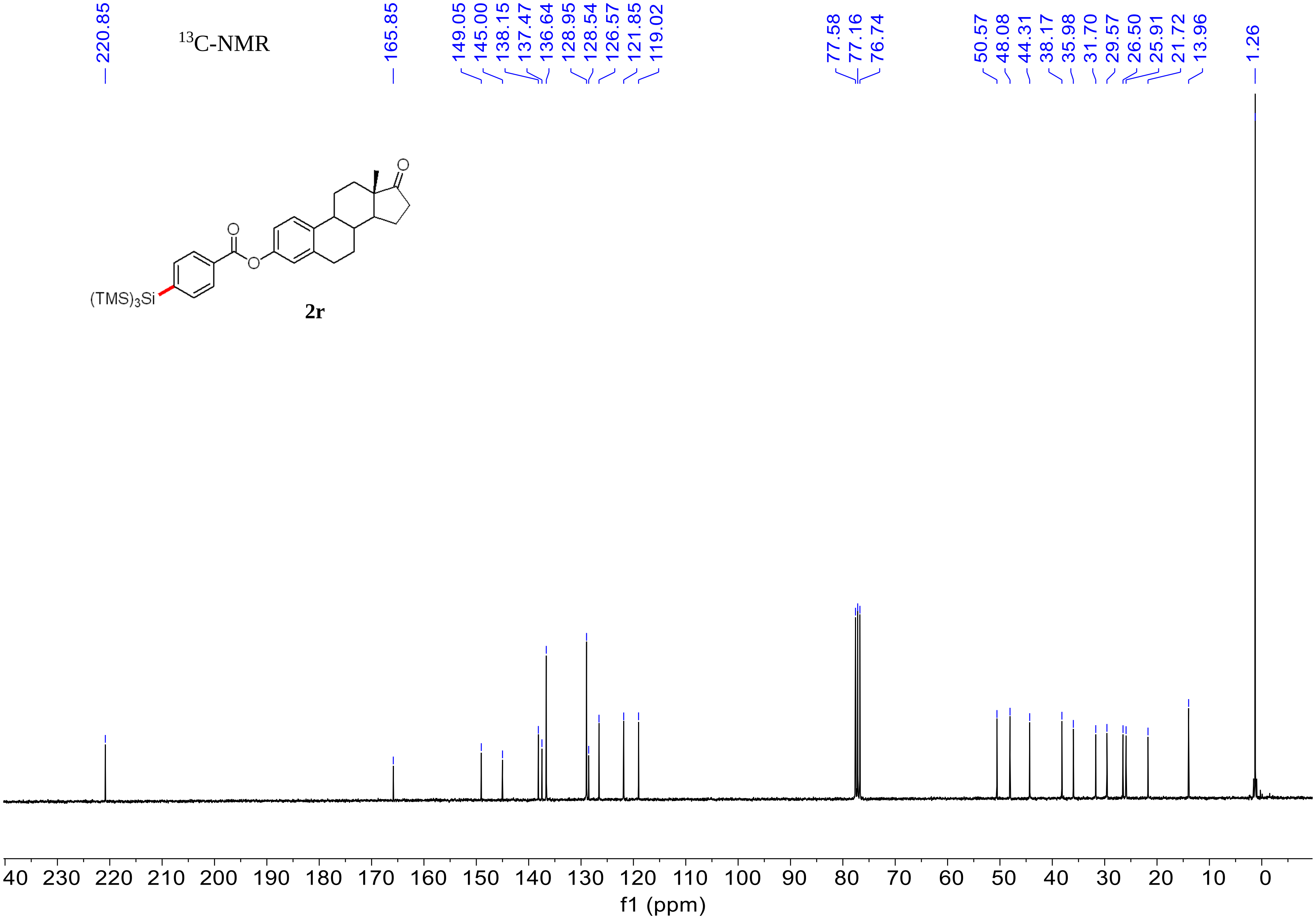
^{29}Si-NMR

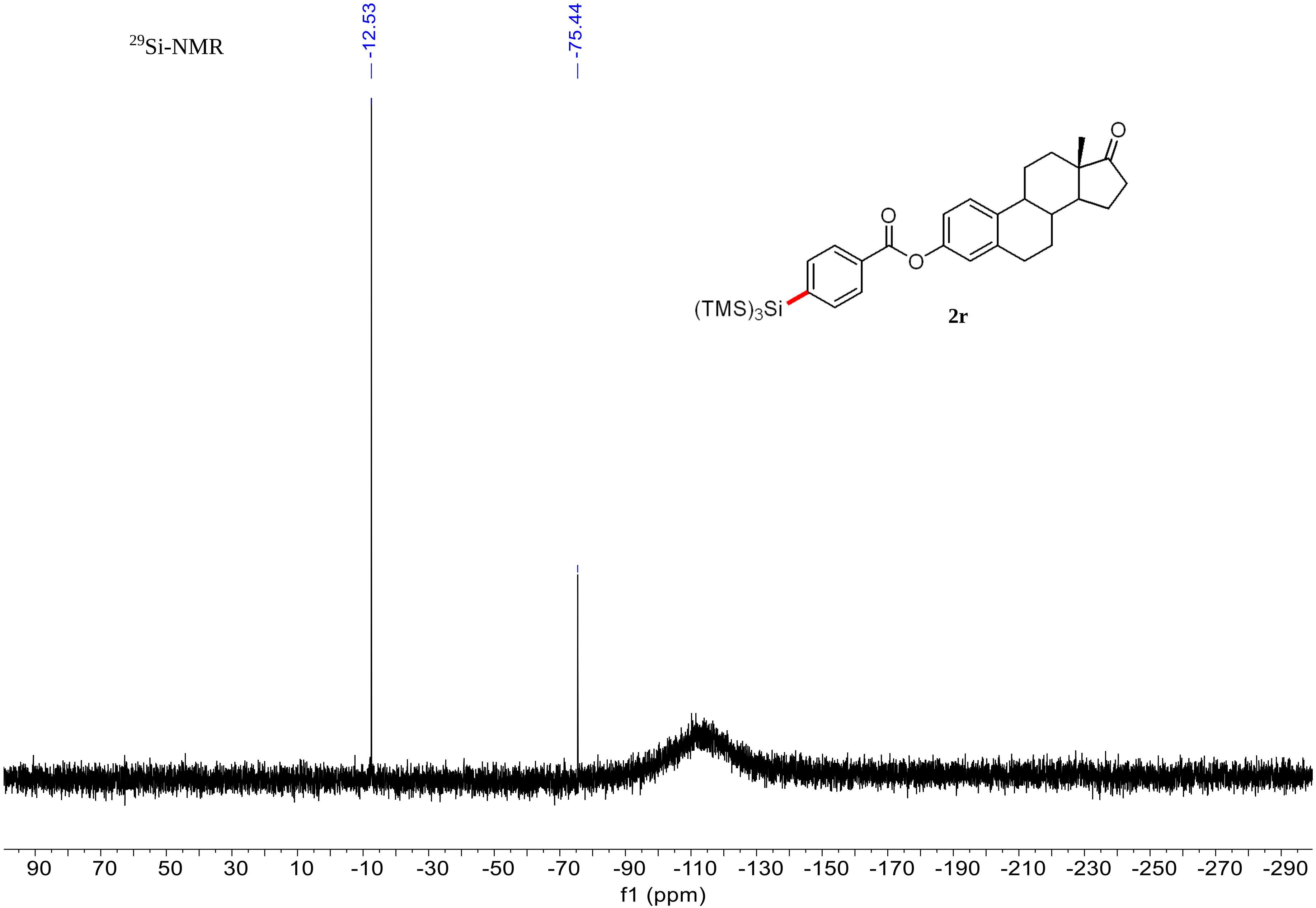

-12.61
-75.83
(TMS)$_3$Si
O
O
2q
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)



^{1}H-NMR
(TMS)$_3$Si
8.08 8.08 8.07 8.05 8.05 7.62 7.62 7.61 7.60 7.59 7.35 7.32 7.26 7.00 6.99 6.97 6.96 6.94 6.93 2.97 2.95 2.94 2.92 2.50 2.48 2.42 2.19 2.11 2.10 2.09 2.07 2.06 2.06 2.05 2.05 2.03 2.01 2.00 2.00 1.97 1.66 1.66 1.65 1.64 1.63 1.63 1.62 1.61 1.59 1.58 1.56 1.54 1.53 1.53 1.51 1.50 1.48 0.93 0.25
1.96
1.98
1.00
2.02
2.01
2.04
1.08
4.15
6.18
3.08
27.06
f1 (ppm)

2r

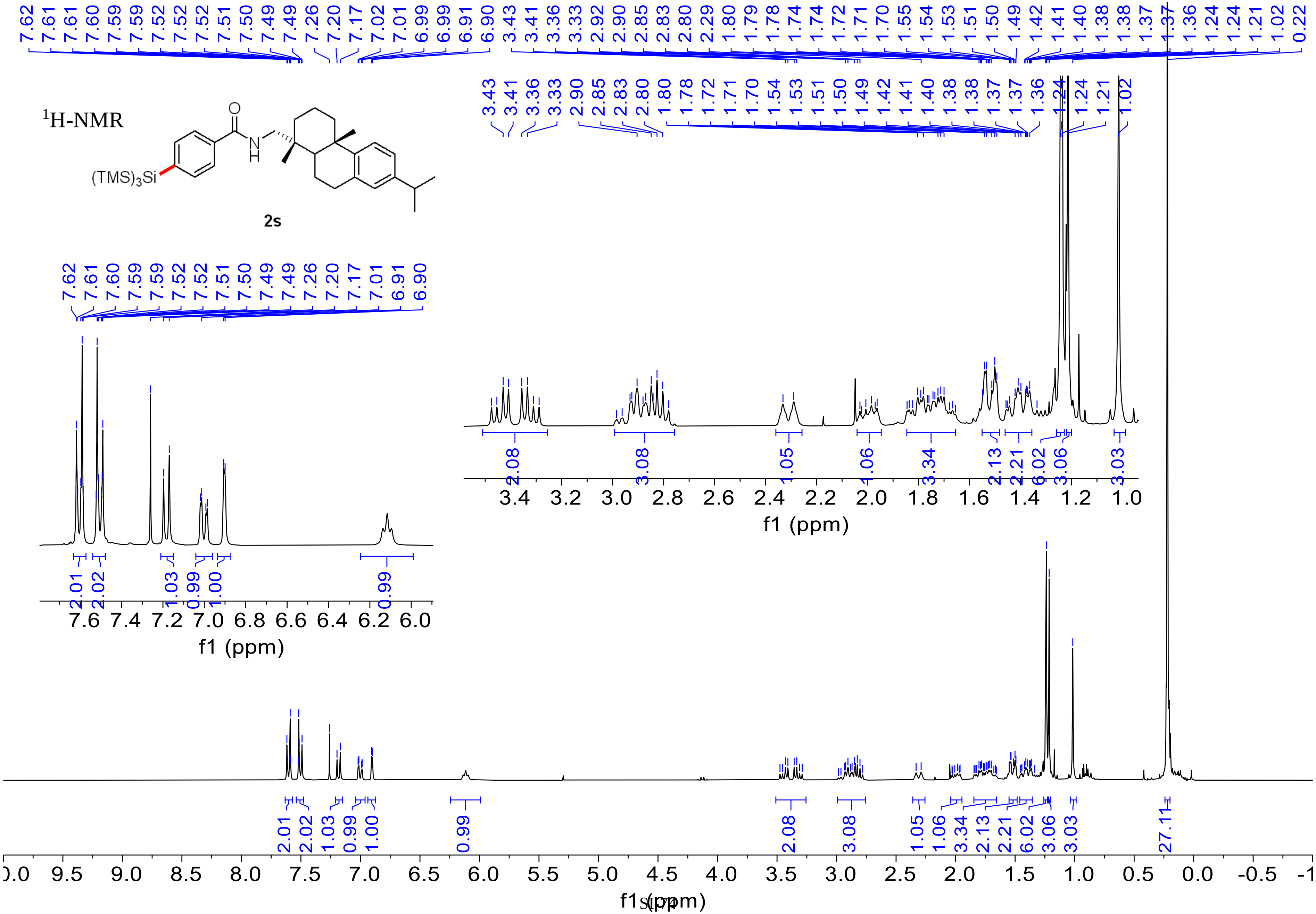

220.85
^{13}C-NMR
165.85
149.05
145.00
138.15
137.47
136.64
128.95
128.54
126.57
121.85
119.02
77.58
77.16
76.74
50.57
48.08
44.31
38.17
35.98
31.70
29.57
26.50
25.91
21.72
13.96
1.26
(TMS)3Si
O
O
O
2r
40
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



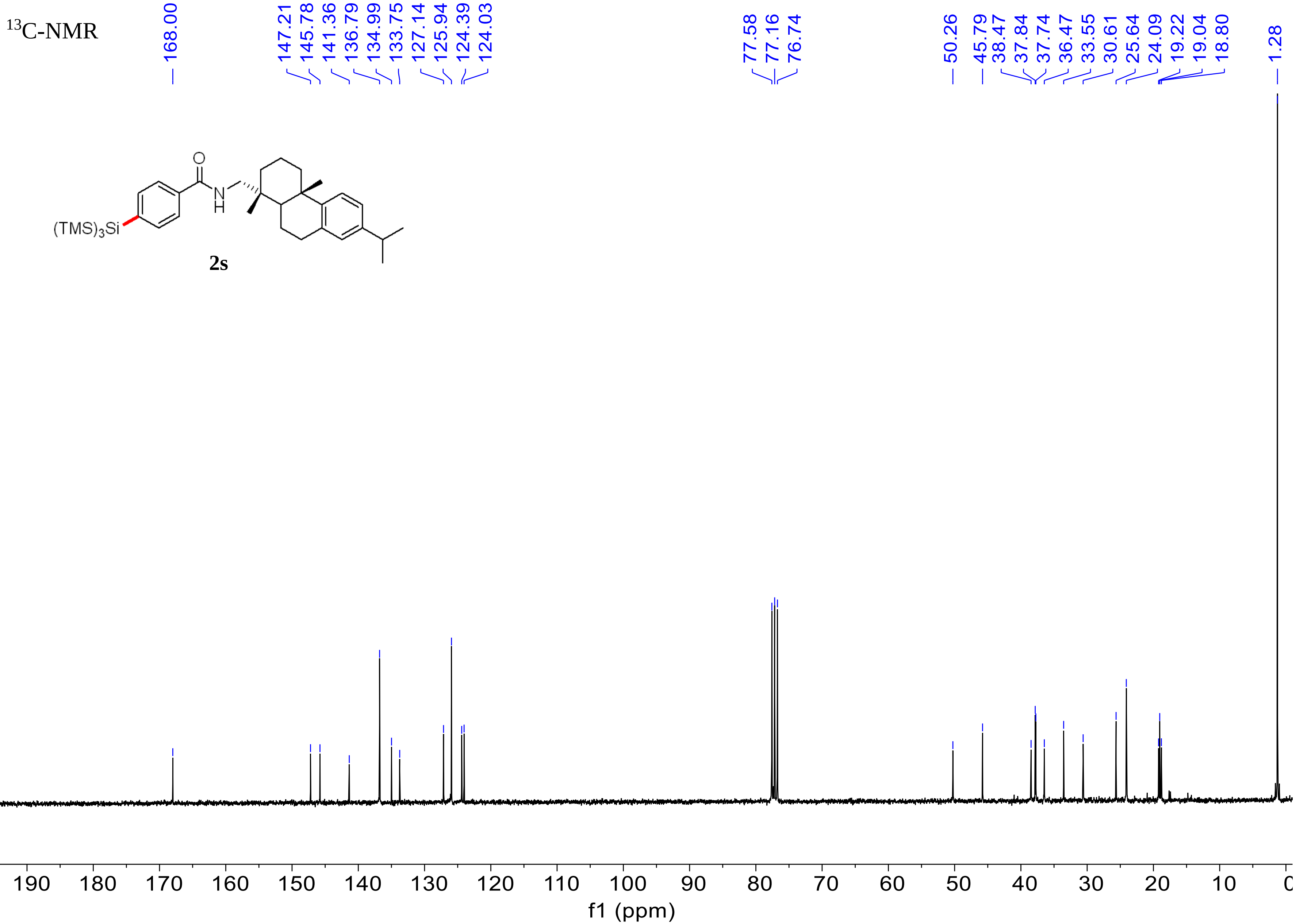
^{29}Si-NMR

-12.53
-75.44
(TMS)3Si
O
O
O
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

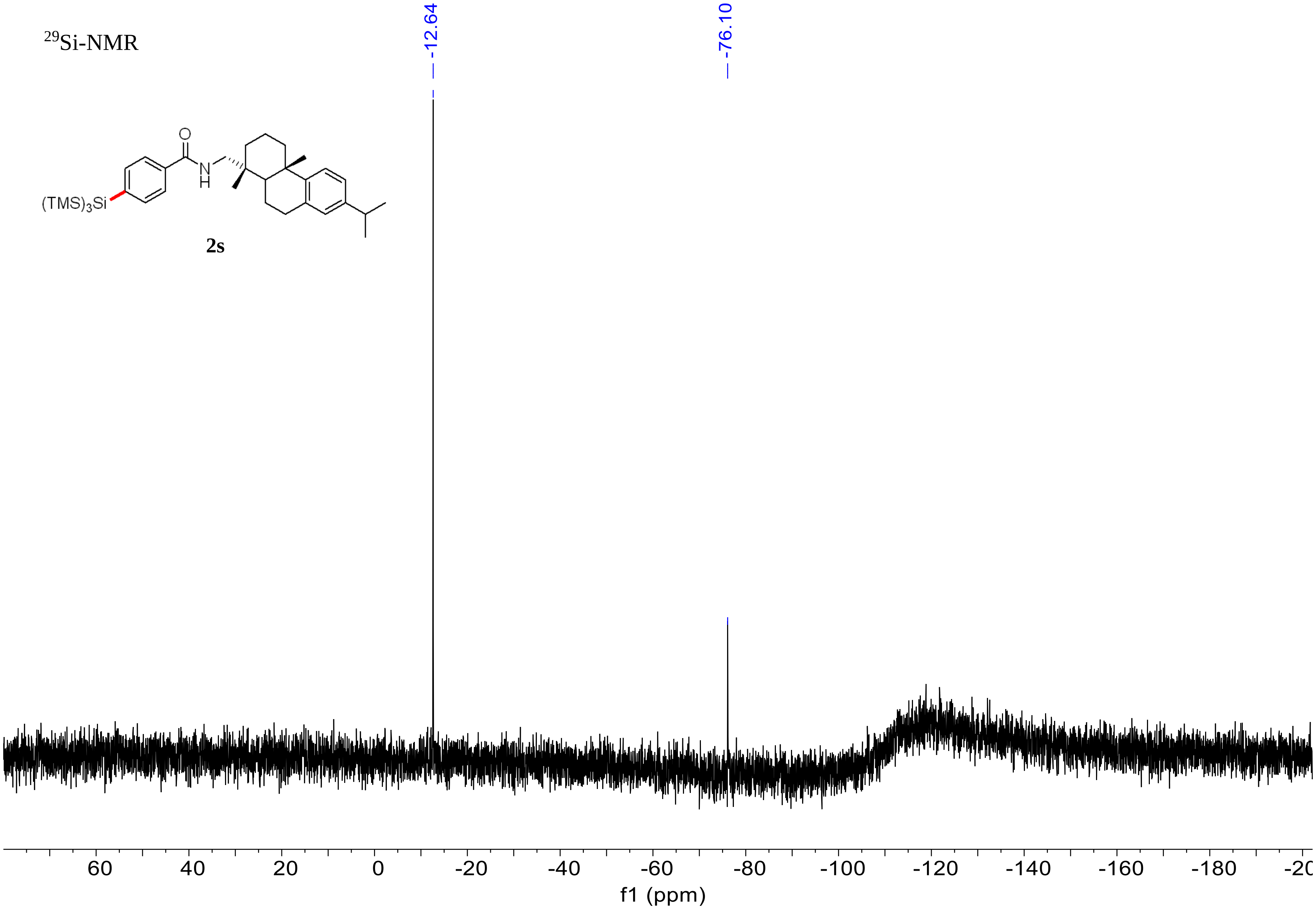
2r

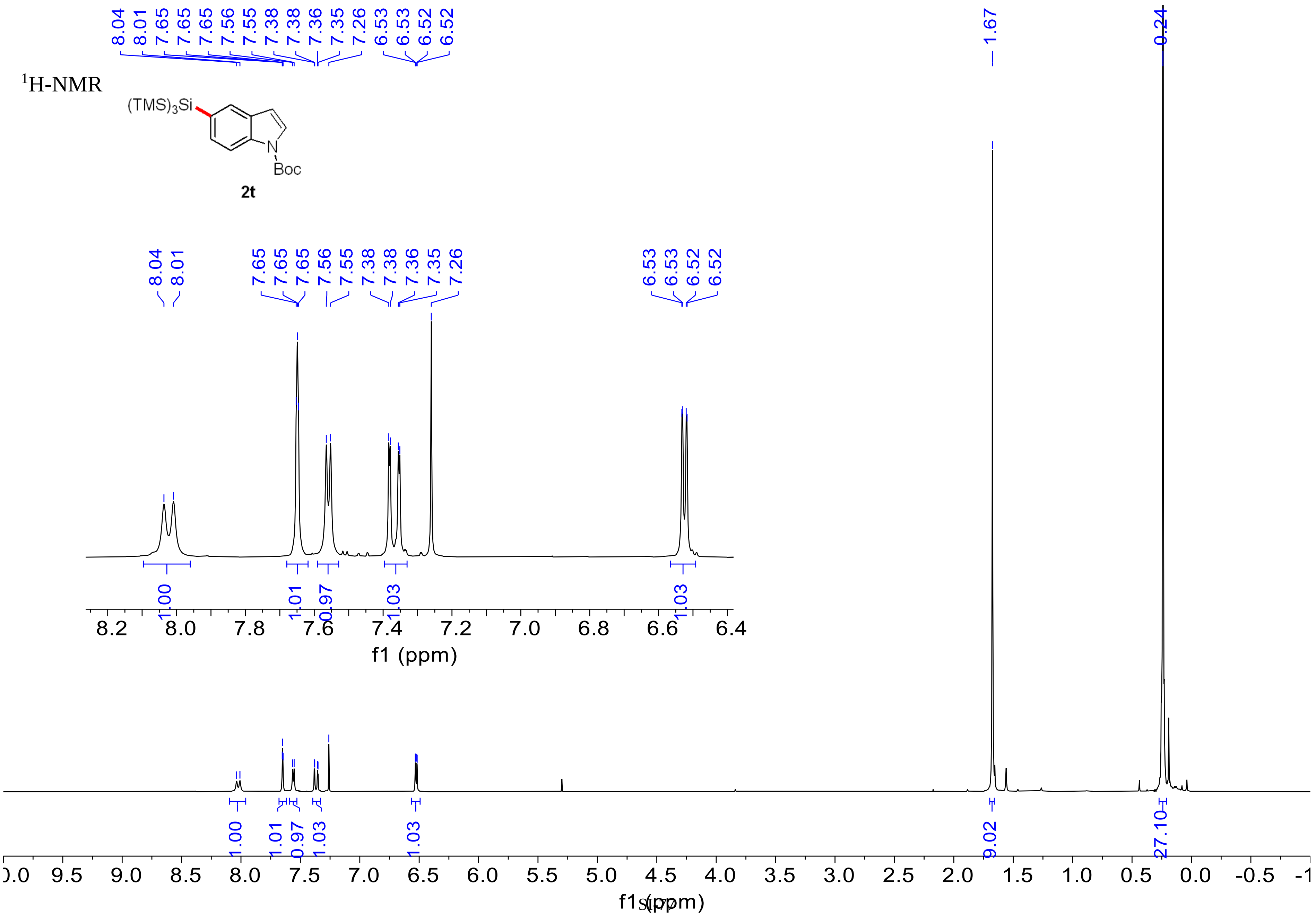


7.62 7.61 7.61 7.60 7.59 7.59 7.52 7.52 7.52 7.51 7.50 7.49 7.49 7.26 7.20 7.17 7.02 7.01 6.99 6.99 6.91 6.90 3.43 3.41 3.36 3.33 2.92 2.90 2.85 2.83 2.80 2.29 1.80 1.79 1.78 1.74 1.74 1.72 1.71 1.70 1.55 1.54 1.53 1.51 1.50 1.49 1.42 1.41 1.40 1.38 1.38 1.37 1.37 1.36 1.24 1.24 1.21 1.02 0.22
^{1}H-NMR
(TMS)$_3$Si
O
N
H
2s
3.43 3.41 3.36 3.33 2.90 2.85 2.83 2.80 1.80 1.78 1.72 1.71 1.70 1.54 1.53 1.51 1.50 1.49 1.42 1.41 1.40 1.38 1.38 1.37 1.37 1.36 1.24 1.24 1.21 1.02
2.08 3.08 1.05 1.06 3.34 2.13 2.21 6.02 3.06 3.03
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
f1 (ppm)
7.62 7.61 7.60 7.59 7.59 7.52 7.52 7.51 7.50 7.49 7.49 7.26 7.20 7.17 7.01 6.91 6.90
2.01 2.02 1.03 0.99 1.00 0.99
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0
f1 (ppm)
2.01 2.02 1.03 0.99 1.00 0.99 2.08 3.08 1.05 1.06 3.34 2.13 2.21 6.02 3.06 3.03 27.11
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

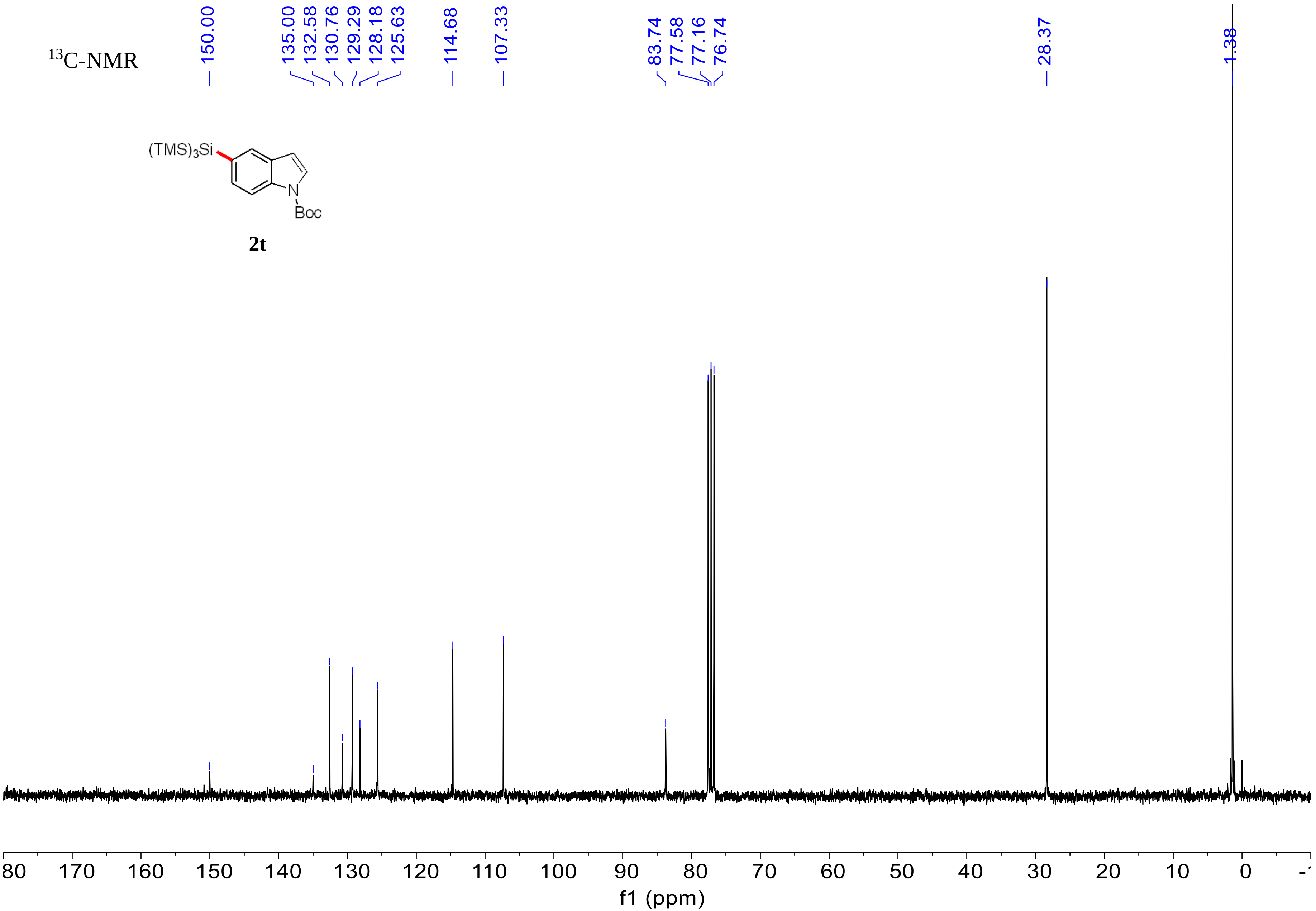

^{13}C-NMR
168.00
147.21
145.78
141.36
136.79
134.99
133.75
127.14
125.94
124.39
124.03
77.58
77.16
76.74
50.26
45.79
38.47
37.84
37.74
36.47
33.55
30.61
25.64
24.09
19.22
19.04
18.80
1.28
O
N
H
(TMS)$_3$Si
2s
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{29}Si-NMR


-12.64
-76.10
(TMS)3Si
O
N
H
2s
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-20
f1 (ppm)

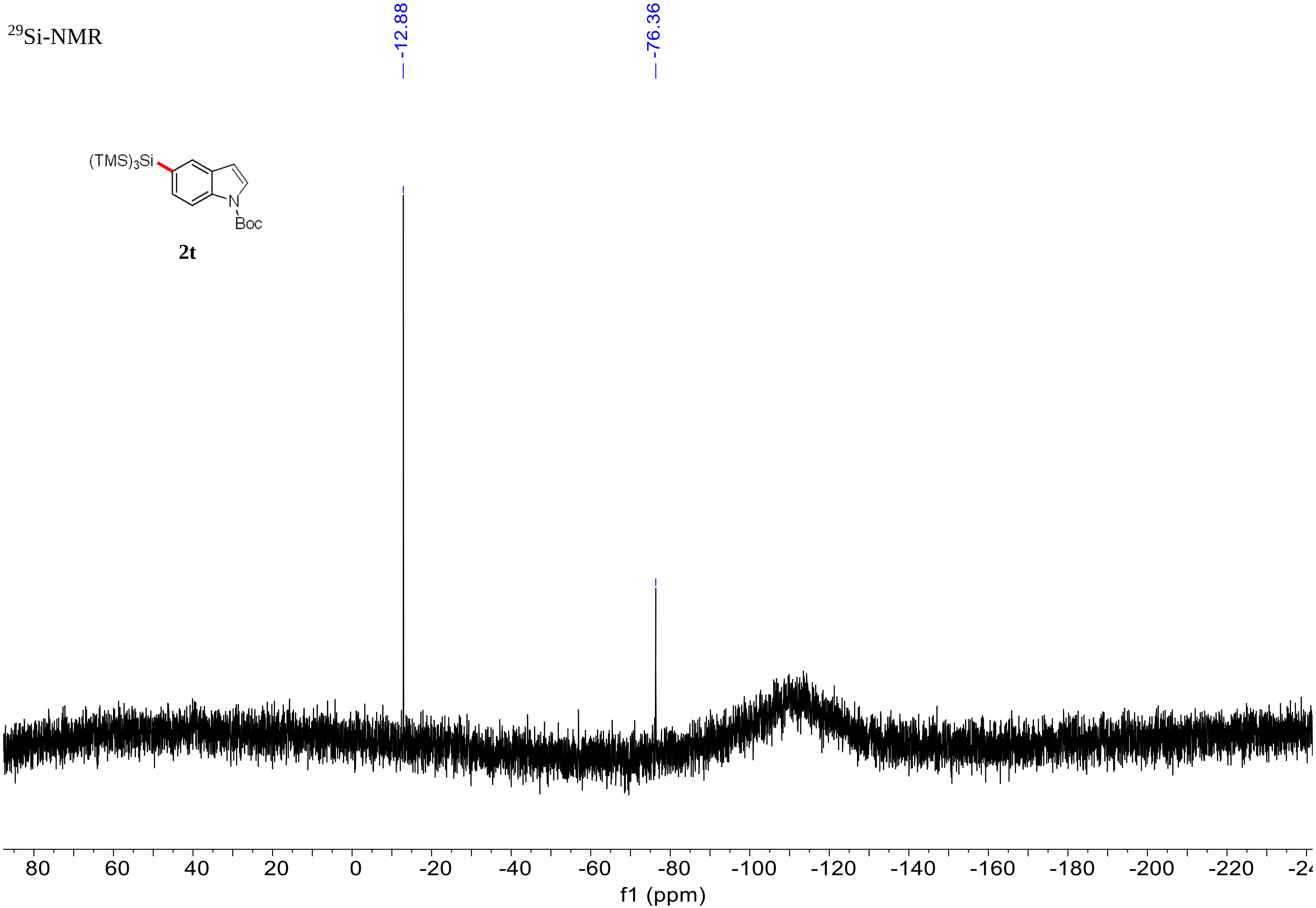

¹H-NMR
(TMS)₃Si
N
Boc
2t
8.04 8.01 7.65 7.65 7.65 7.56 7.55 7.38 7.38 7.36 7.35 7.26 6.53 6.53 6.52 6.52
1.67
0.24
1.00
1.01
0.97
1.03
1.03
9.02
27.10
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

^{13}C-NMR

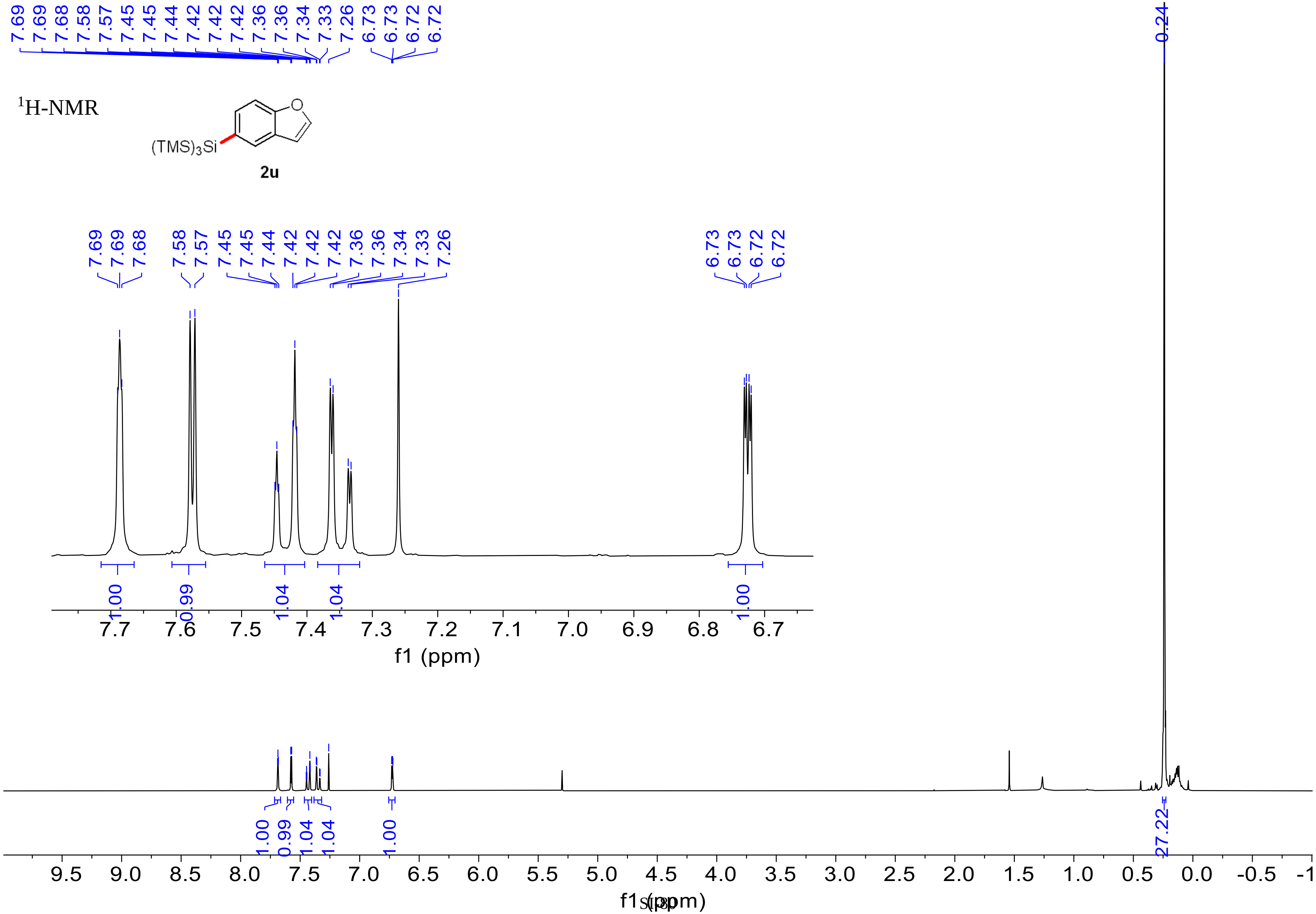

150.00
135.00
132.58
130.76
129.29
128.18
125.63
114.68
107.33
83.74
77.58
77.16
76.74
28.37
1.38
(TMS)3Si
N
Boc
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

2t

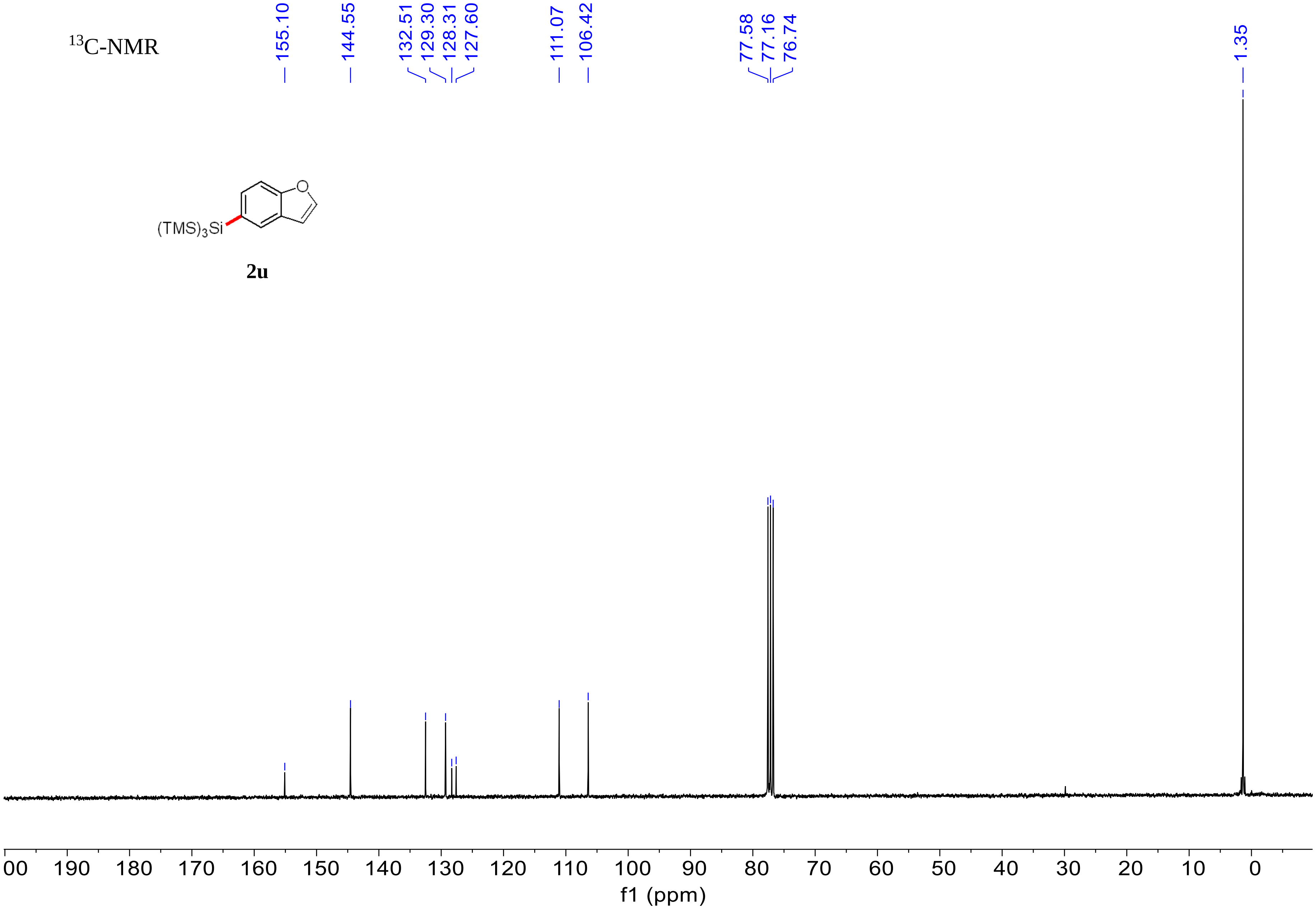
^{29}Si-NMR


-12.88
-76.36
(TMS)3Si
N
Boc
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)

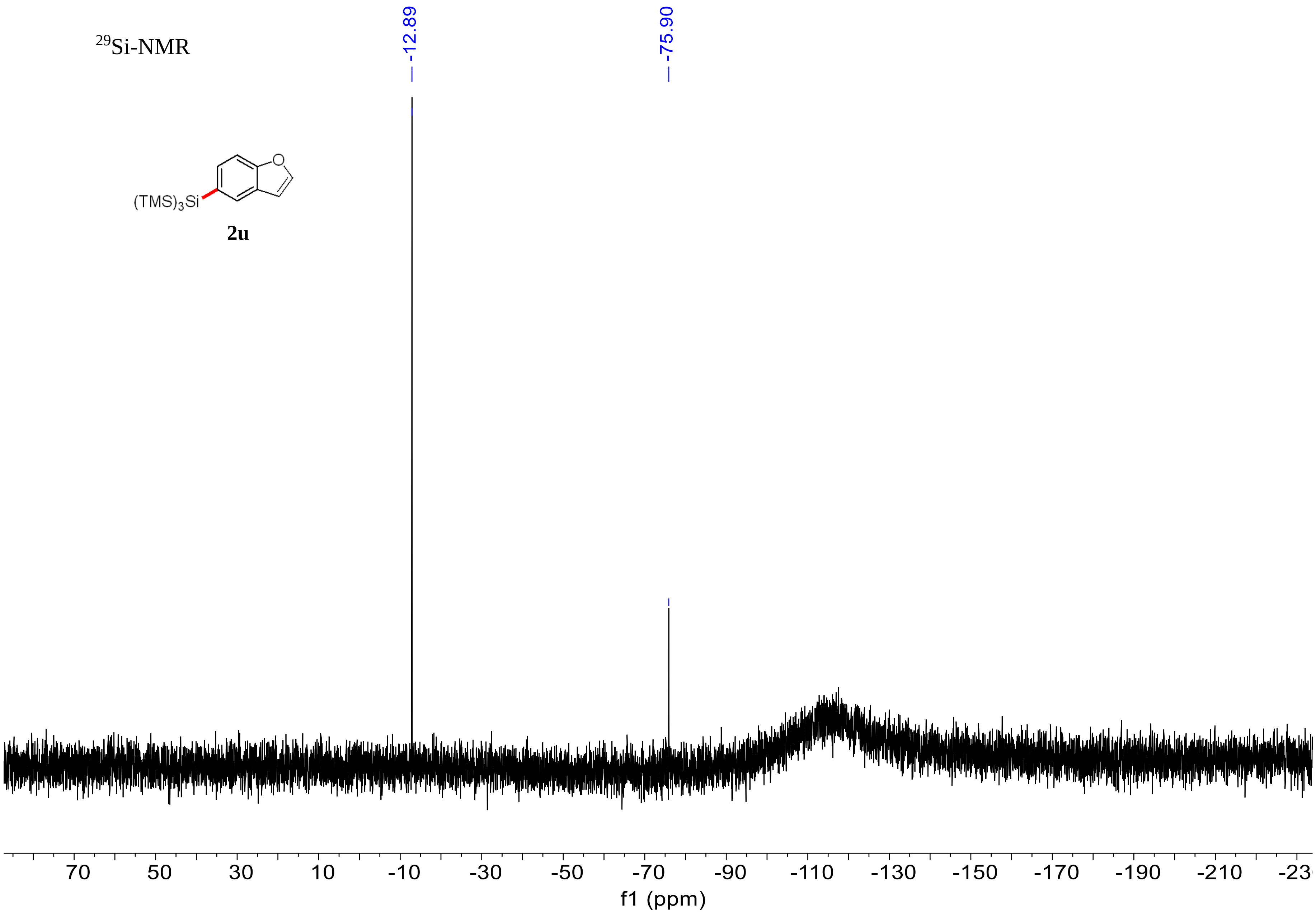
2t


7.69 7.69 7.68 7.58 7.57 7.45 7.45 7.44 7.42 7.42 7.42 7.36 7.36 7.34 7.33 7.26 6.73 6.73 6.72 6.72
0.24
1H-NMR
(TMS)3Si
O
2u
1.00
0.99
1.04
1.04
1.00
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
27.22
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

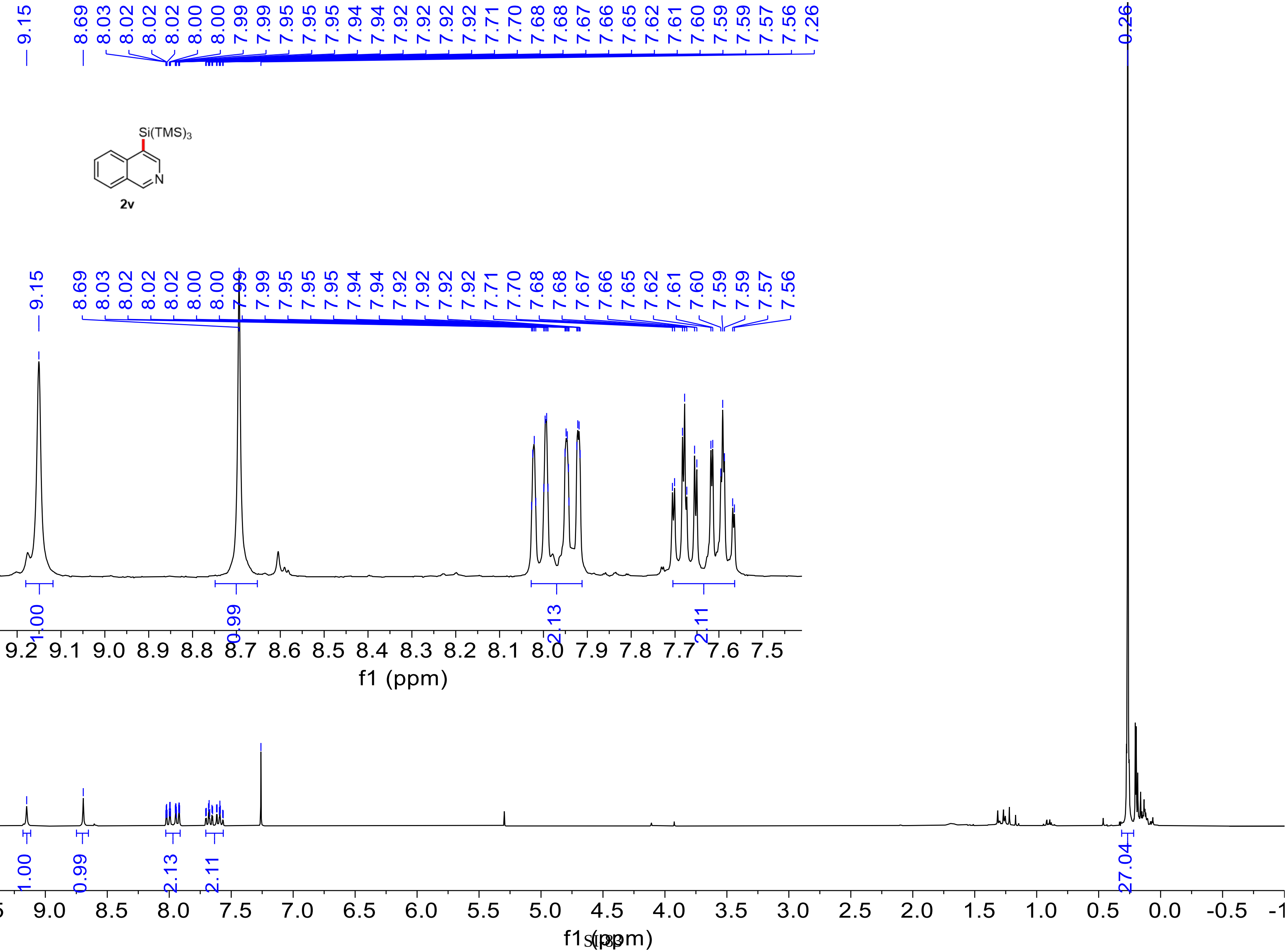
^{13}C-NMR


155.10
144.55
132.51
129.30
128.31
127.60
111.07
106.42
77.58
77.16
76.74
1.35
(TMS)$_3$Si
O
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

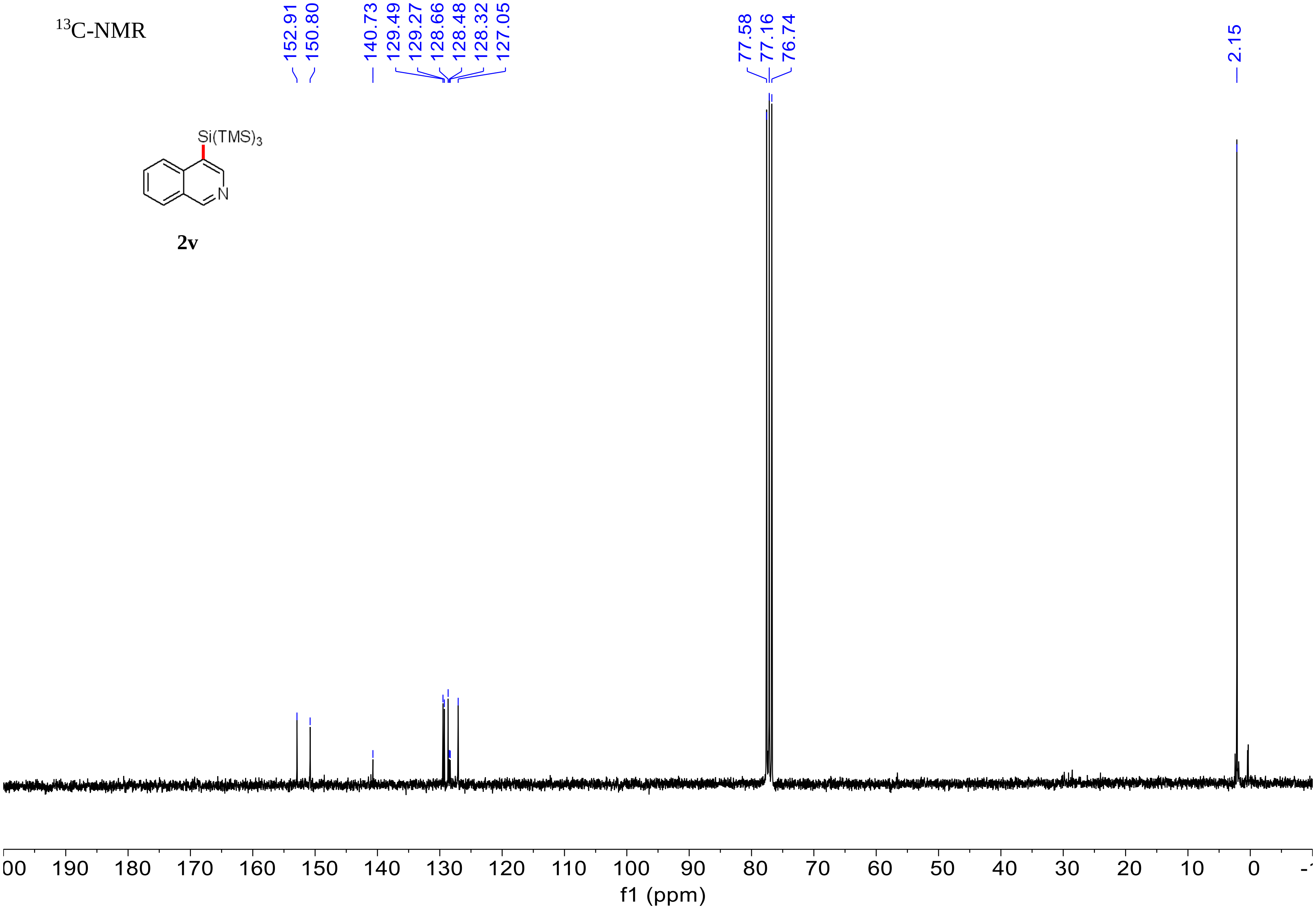
2u


29Si-NMR
(TMS)3Si
O
2u
-12.89
-75.90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-23
f1 (ppm)

^{1}H-NMR

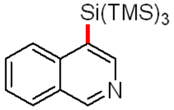

9.15
8.69
8.03 8.02 8.02 8.02 8.00 8.00 7.99 7.99 7.95 7.95 7.95 7.94 7.94 7.92 7.92 7.92 7.92 7.71 7.70 7.68 7.68 7.67 7.66 7.65 7.62 7.61 7.60 7.59 7.59 7.57 7.56 7.26
0.26
Si(TMS)3
N
2v
1.00
0.99
2.13
2.11
27.04
9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

^{13}C-NMR

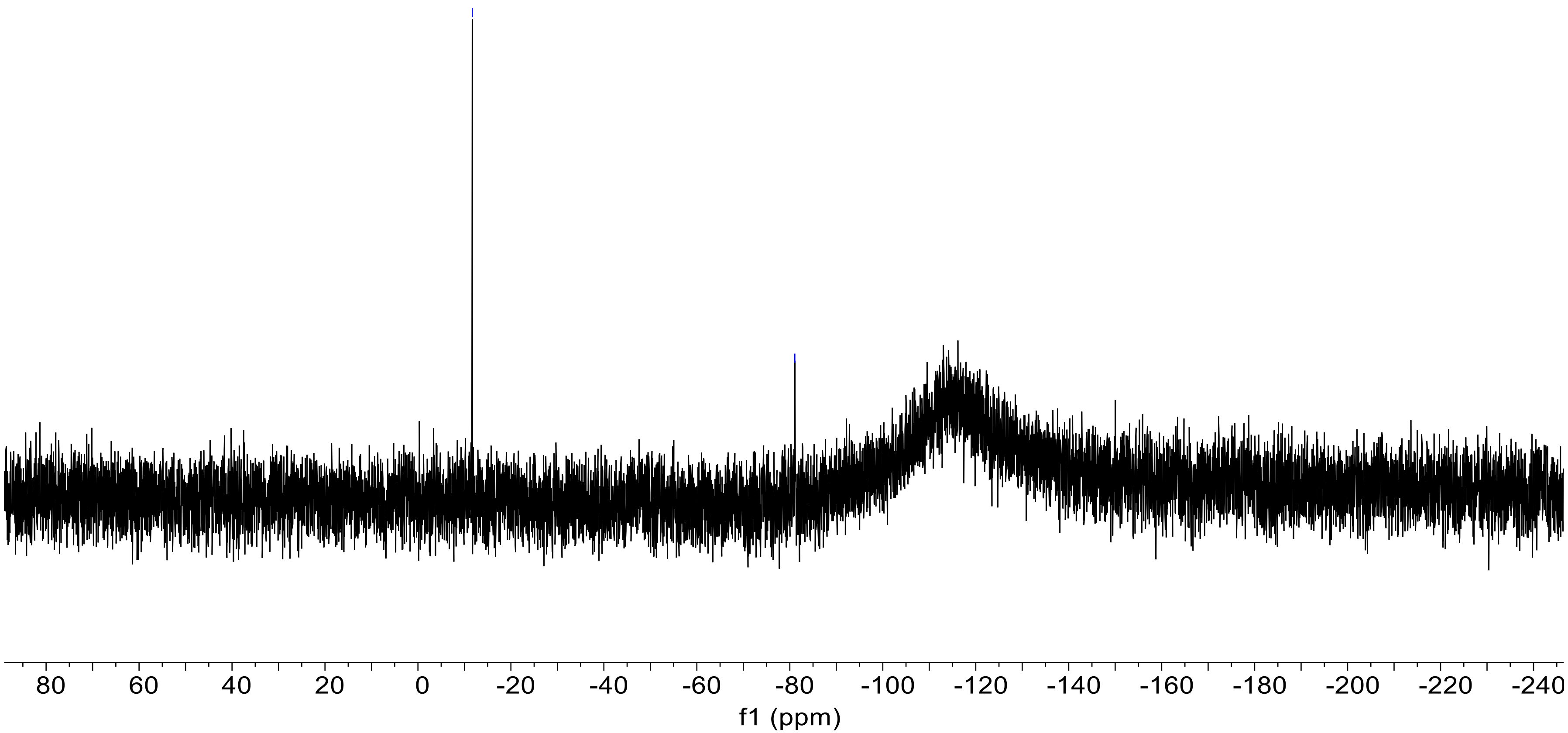

152.91
150.80
140.73
129.49
129.27
128.66
128.48
128.32
127.05
77.58
77.16
76.74
2.15
Si(TMS)3
N
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

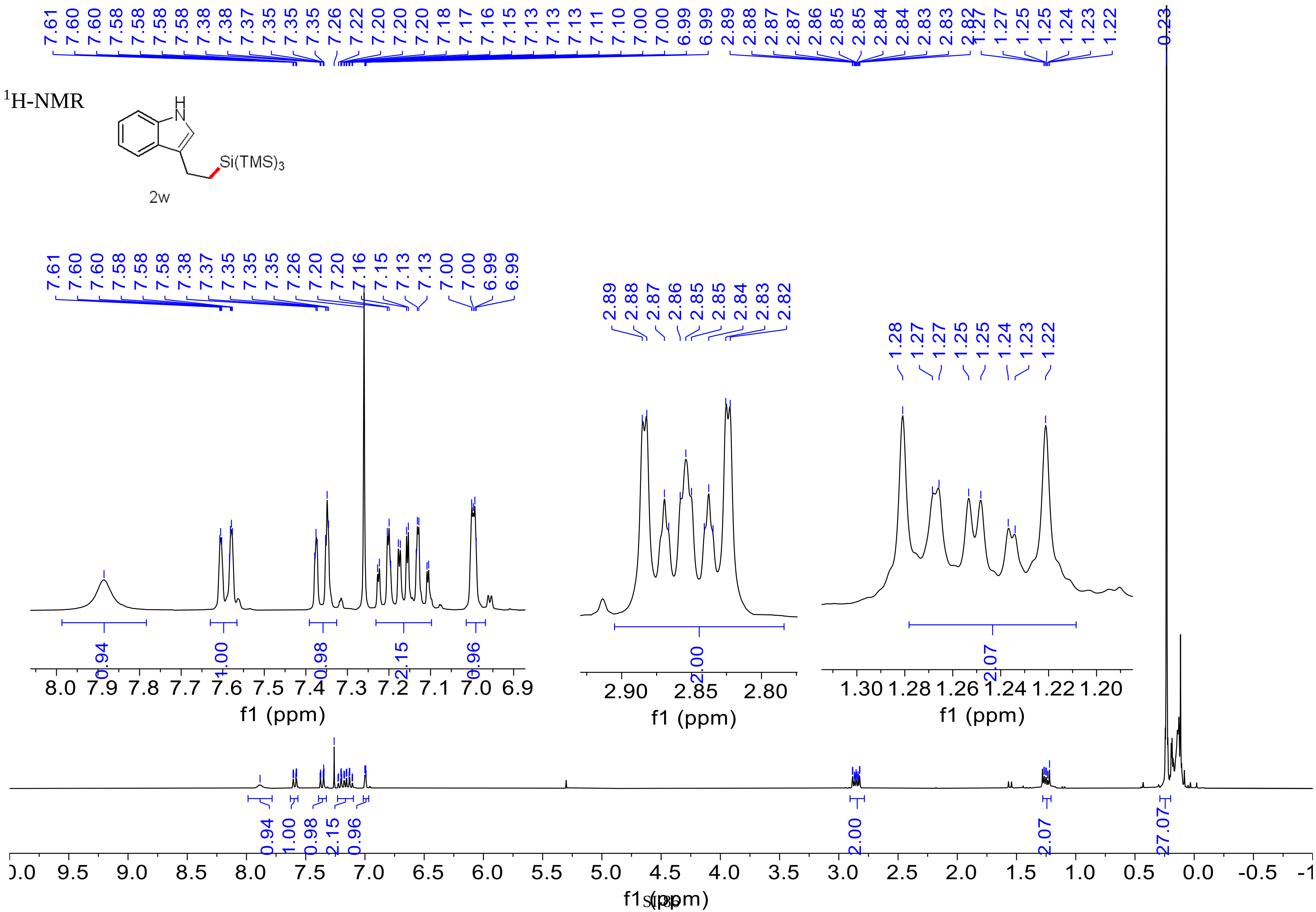
2v

^{29}Si-NMR

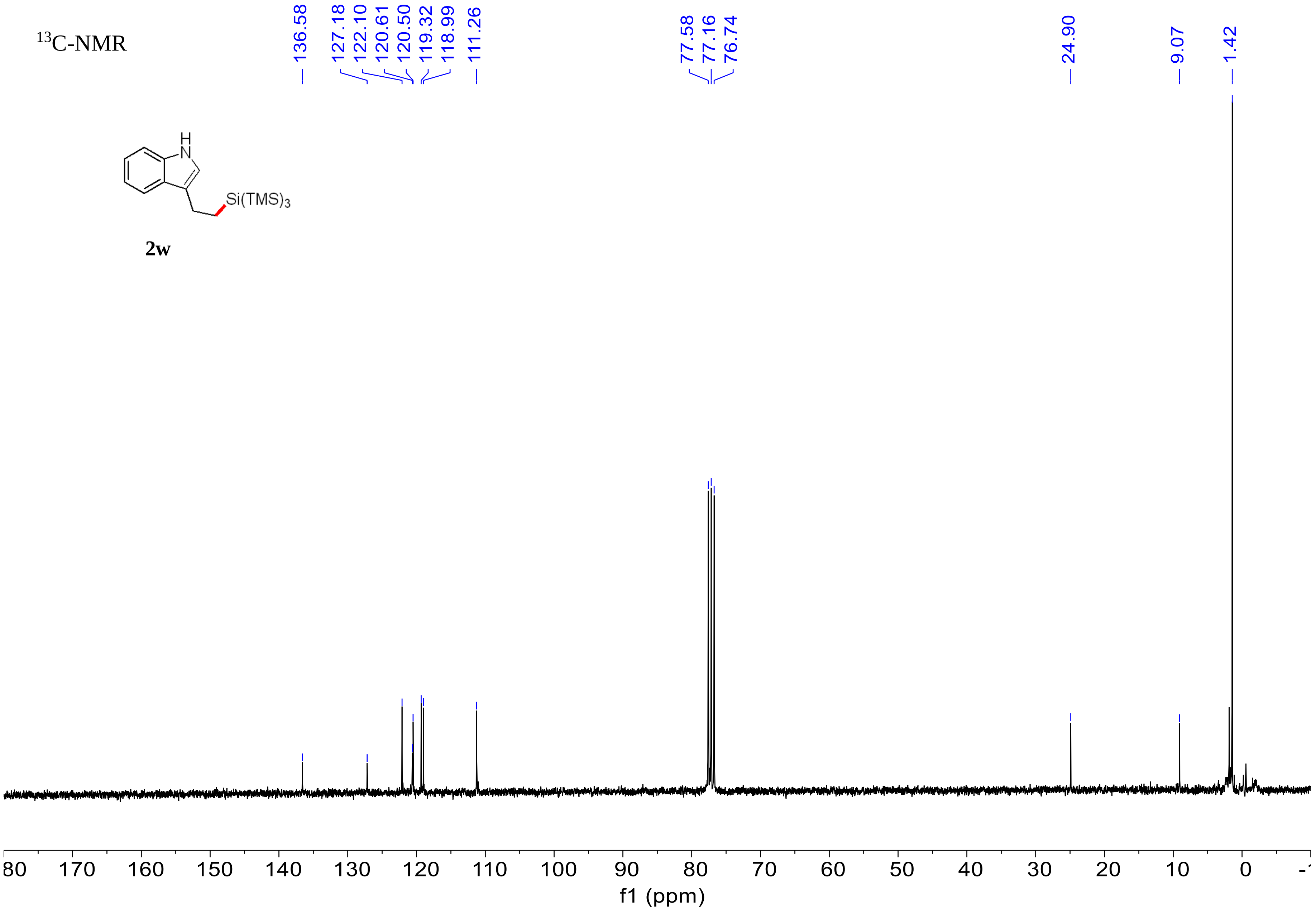

Si(TMS)$_3$
N

2v


-11.69
-81.08
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

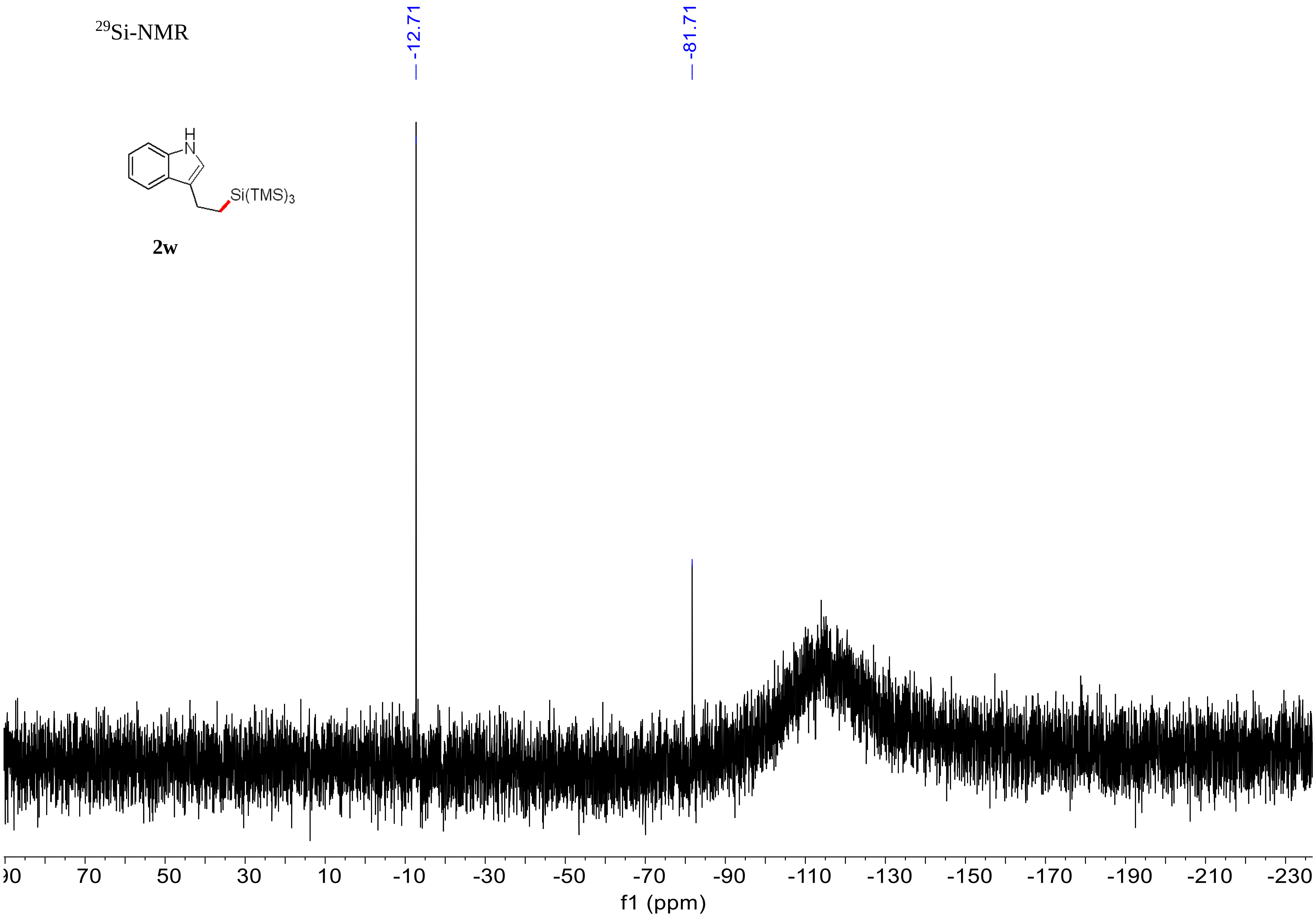

^{1}H-NMR
2w
Si(TMS)$_3$
7.61 7.60 7.60 7.58 7.58 7.58 7.58 7.38 7.38 7.37 7.35 7.35 7.35 7.26 7.22 7.20 7.20 7.20 7.18 7.17 7.16 7.15 7.13 7.13 7.13 7.11 7.10 7.00 7.00 6.99 6.99
2.89 2.88 2.87 2.87 2.86 2.85 2.85 2.84 2.84 2.83 2.83 2.82
1.27 1.27 1.25 1.25 1.24 1.23 1.22
0.23
0.94 1.00 0.98 2.15 0.96
2.00
2.07
27.07
f1 (ppm)

^{13}C-NMR


136.58
127.18
122.10
120.61
120.50
119.32
118.99
111.26
77.58
77.16
76.74
24.90
9.07
1.42
H
N
Si(TMS)3
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)

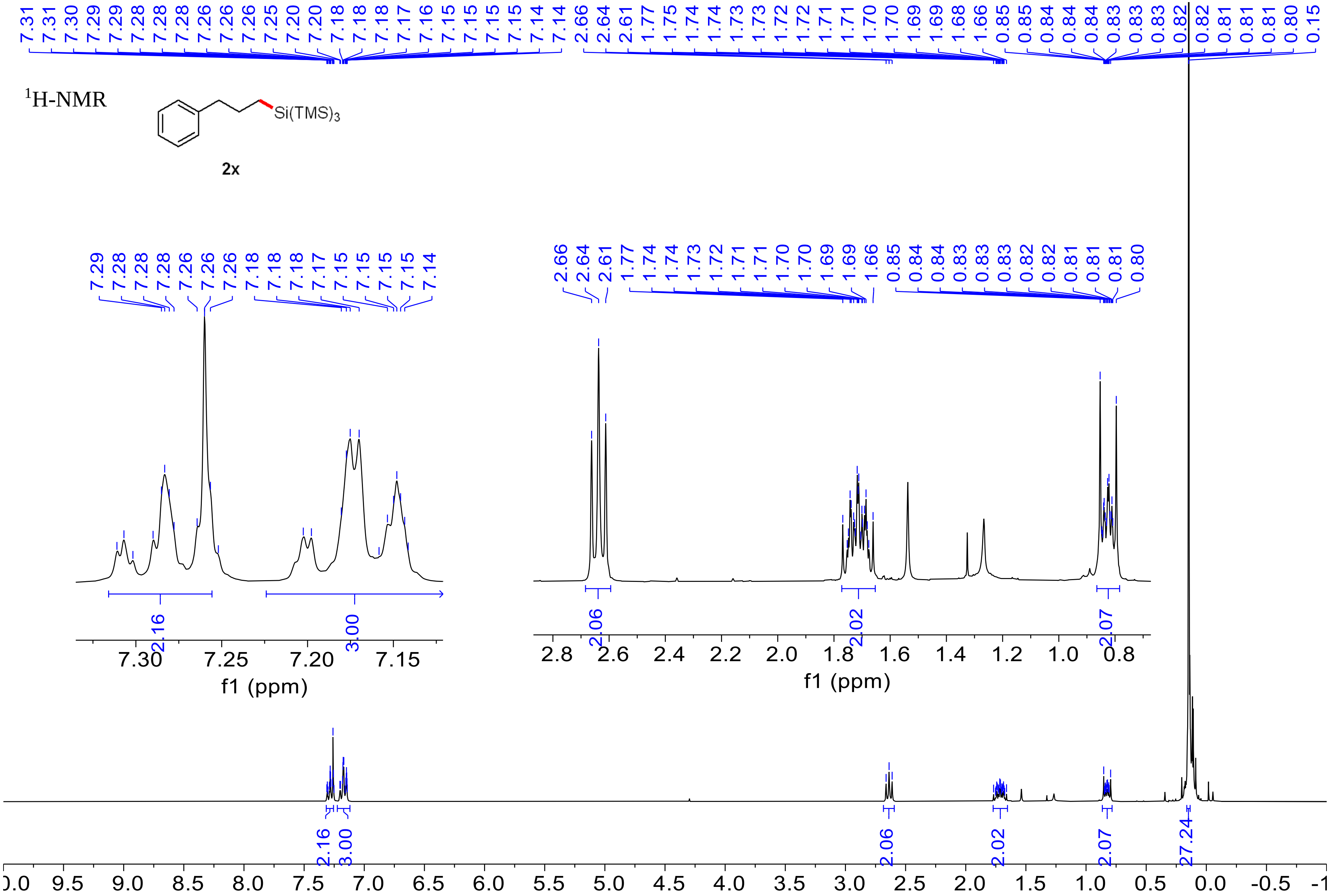
2w

^{29}Si-NMR

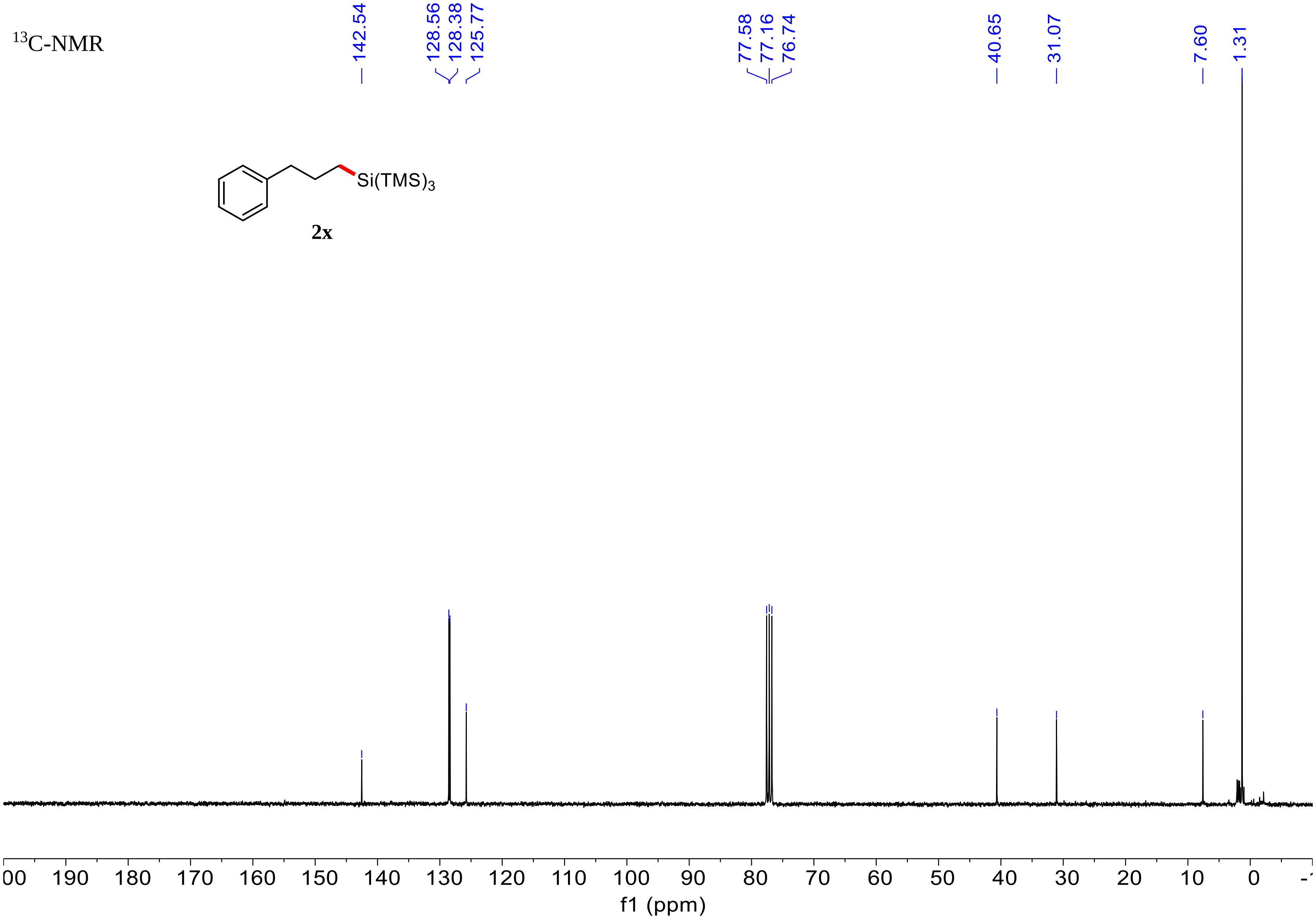


2w

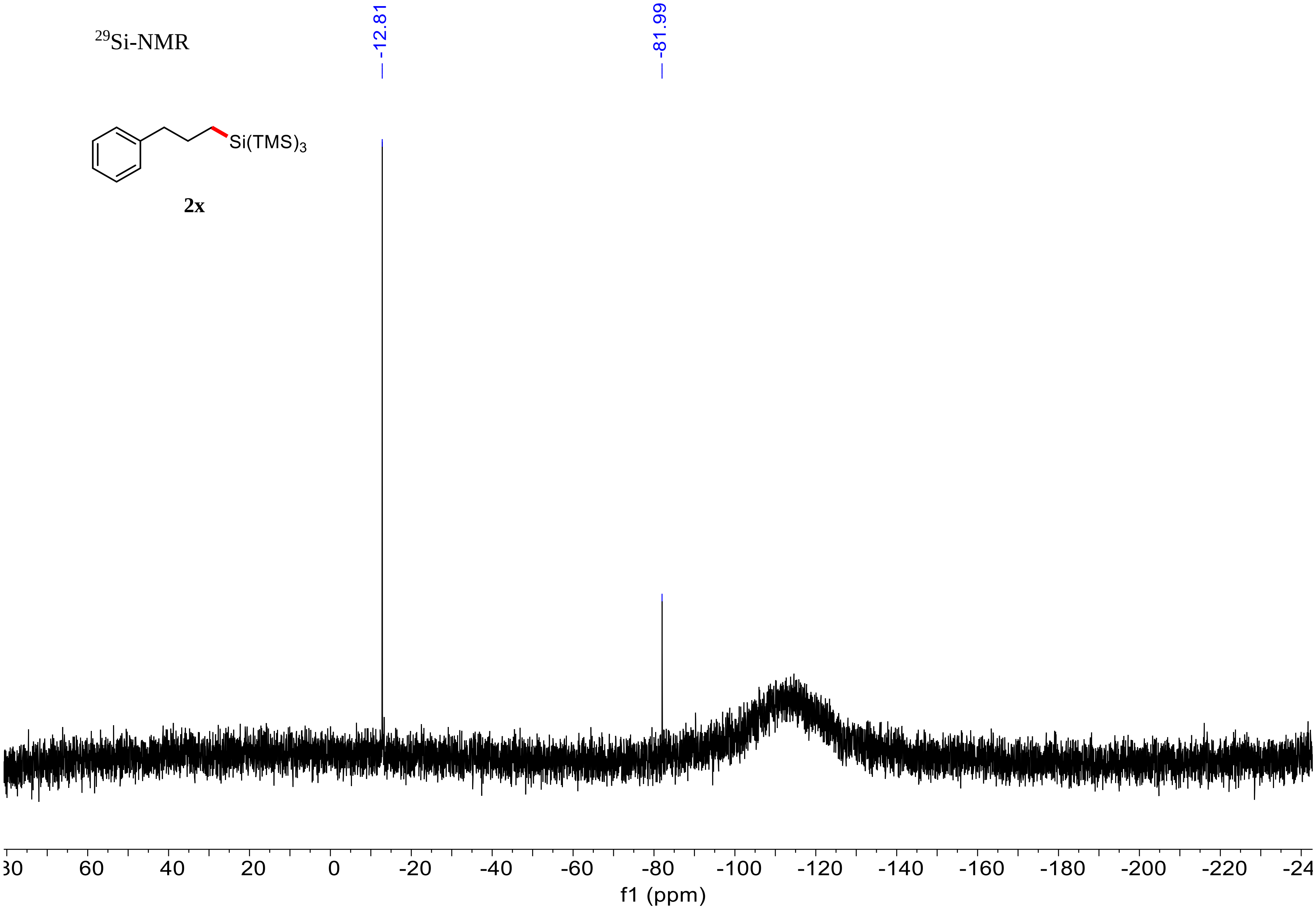
-12.71
-81.71
H
N
Si(TMS)3
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

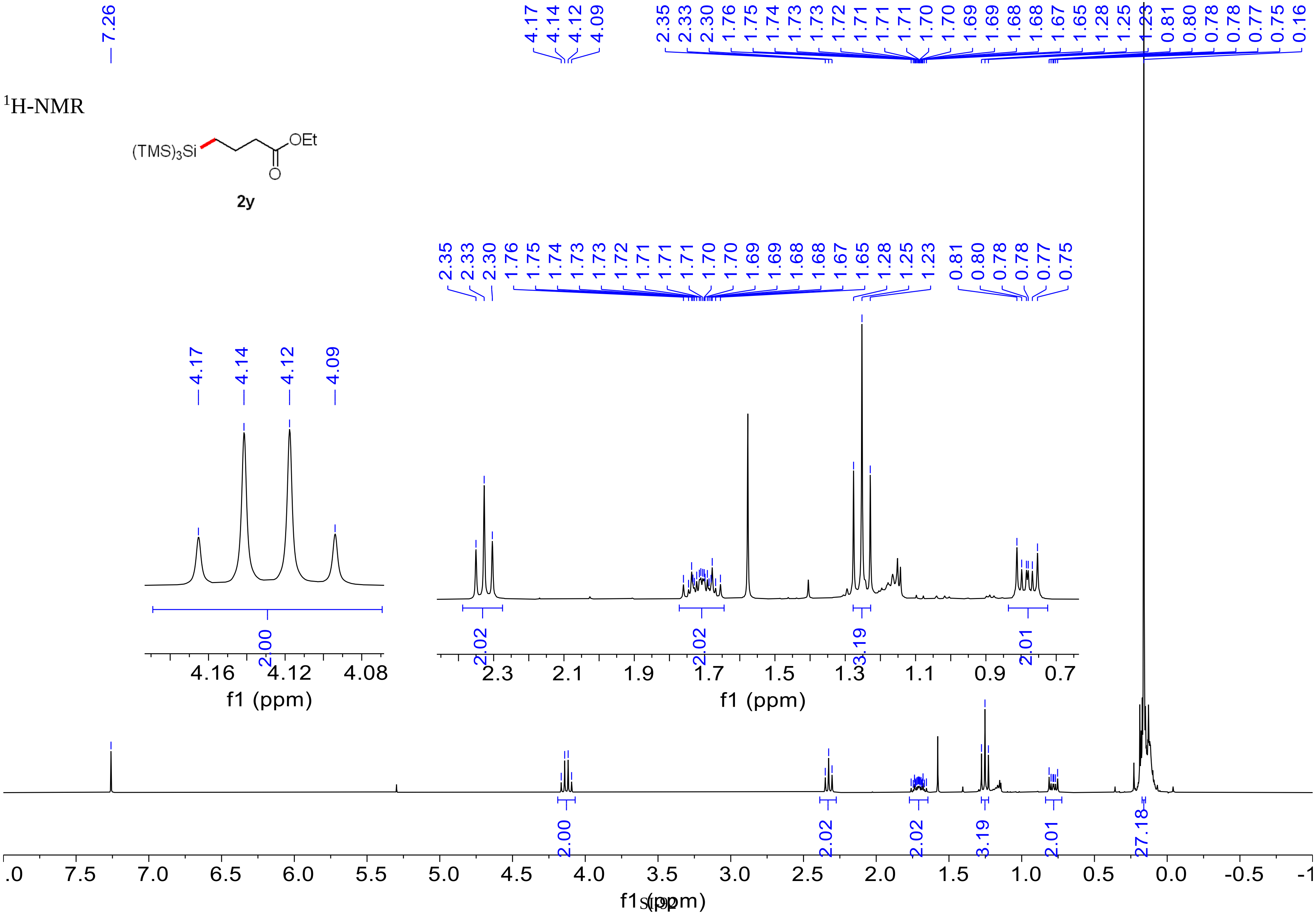

7.31 7.31 7.30 7.29 7.29 7.28 7.28 7.28 7.26 7.26 7.26 7.25 7.20 7.20 7.18 7.18 7.18 7.17 7.16 7.15 7.15 7.15 7.15 7.14 7.14 2.66 2.64 2.61 1.77 1.75 1.74 1.74 1.73 1.73 1.72 1.72 1.71 1.71 1.70 1.70 1.69 1.69 1.68 1.66 0.85 0.85 0.84 0.84 0.84 0.83 0.83 0.83 0.82 0.82 0.81 0.81 0.81 0.80 0.15
¹H-NMR
Si(TMS)3
2x
7.29 7.28 7.28 7.28 7.26 7.26 7.26 7.18 7.18 7.18 7.17 7.15 7.15 7.15 7.15 7.14
2.16
3.00
7.30 7.25 7.20 7.15
f1 (ppm)
2.66 2.64 2.61 1.77 1.74 1.74 1.73 1.72 1.71 1.71 1.70 1.70 1.69 1.69 1.66 0.85 0.84 0.84 0.83 0.83 0.83 0.82 0.82 0.81 0.81 0.81 0.80
2.06
2.02
2.07
2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f1 (ppm)
2.16 3.00 2.06 2.02 2.07 27.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

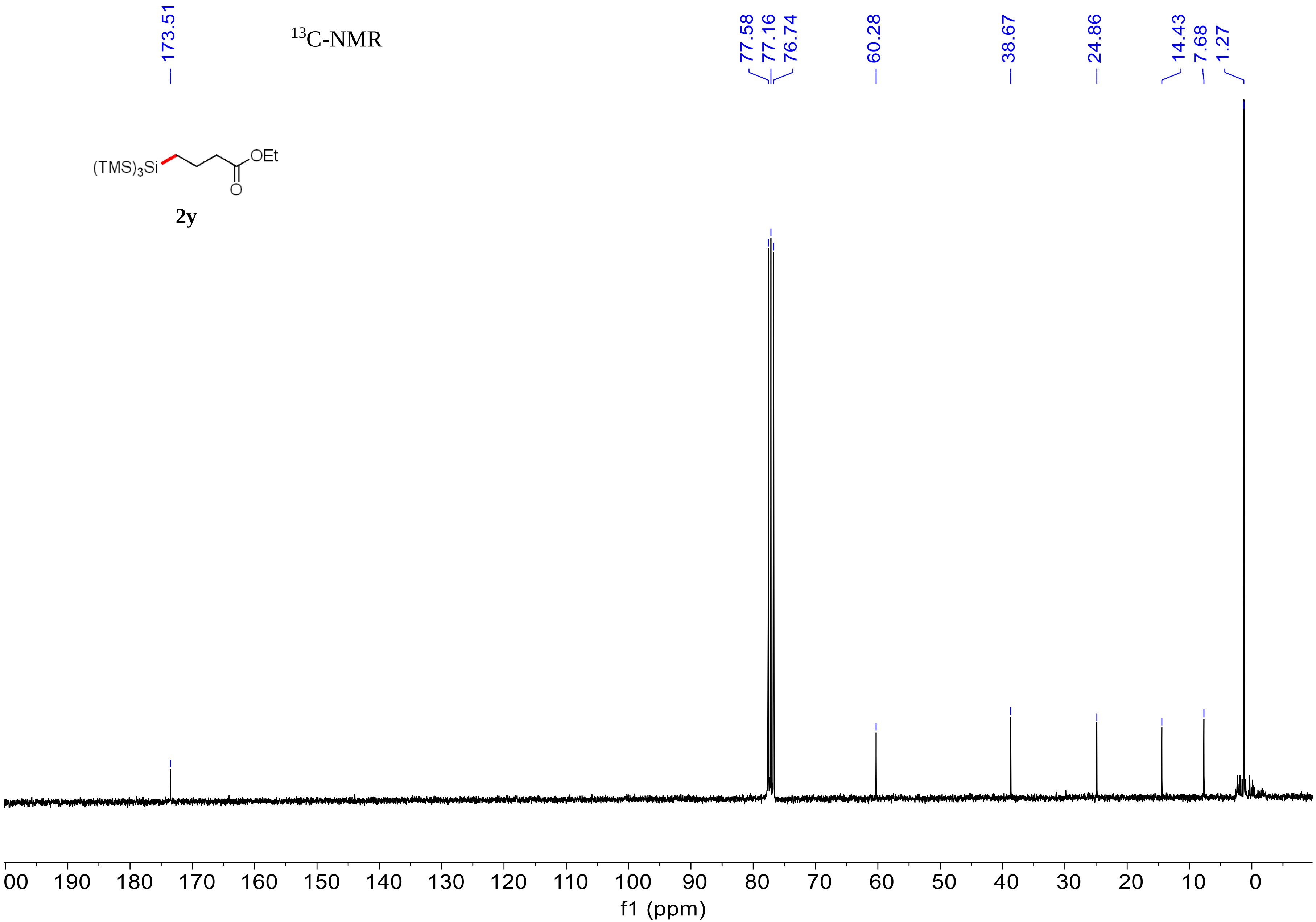
^{13}C-NMR


142.54
128.56
128.38
125.77
77.58
77.16
76.74
40.65
31.07
7.60
1.31
Si(TMS)$_3$
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

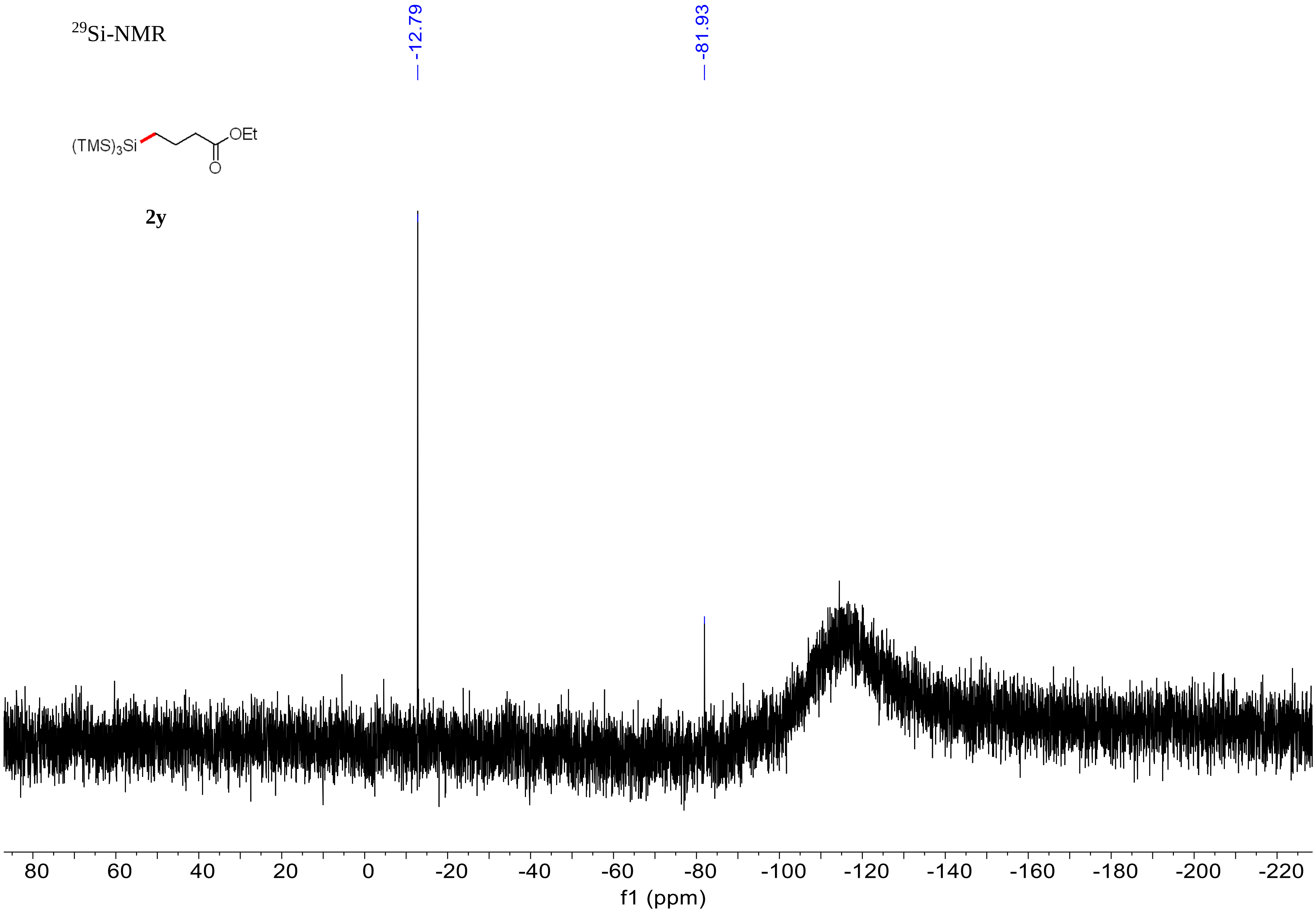
2x


^{29}Si-NMR
-12.81
-81.99
Si(TMS)$_3$
2x
30
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-24
f1 (ppm)


^{1}H-NMR
(TMS)$_3$Si
OEt
O
2y
7.26
4.17 4.14 4.12 4.09
2.35 2.33 2.30 1.76 1.75 1.74 1.73 1.73 1.72 1.71 1.71 1.71 1.70 1.70 1.69 1.69 1.68 1.68 1.67 1.65 1.28 1.25 1.23 0.81 0.80 0.78 0.78 0.77 0.75 0.16
2.00
2.02
2.02
3.19
2.01
27.18
4.16 4.12 4.08
2.3 2.1 1.9 1.7 1.5 1.3 1.1 0.9 0.7
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1


173.51
^{13}C-NMR
77.58
77.16
76.74
60.28
38.67
24.86
14.43
7.68
1.27
(TMS)$_3$Si
OEt
O
2y
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{29}Si-NMR



-12.79
-81.93
(TMS)3Si
OEt
O
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)

2y