Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Autocatalytic Carbonyl Arylation through In Situ Release of Aryl Nucleophiles from *N*-Aryl-*N*′-Silyldiazenes

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Supporting Information

Table of Contents

1. General information

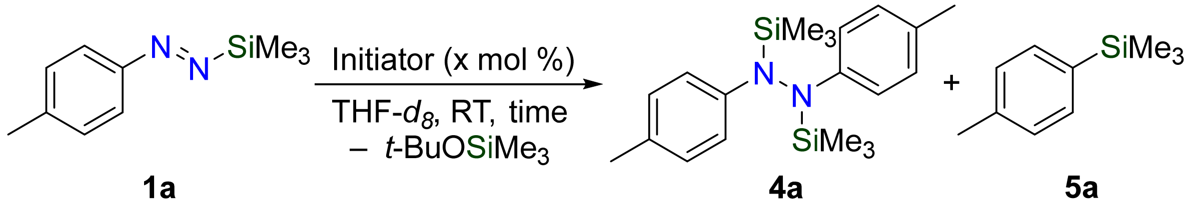
Reactions were performed in flame-dried glassware using an *MBraun* glove box (O_2 < 20 ppm, H_2O < 1.0 ppm) or conventional Schlenk techniques under a static pressure of argon (glove box) or nitrogen (fume hood) unless otherwise stated. Glassware for reactions outside a glovebox was dried under vacuum using a heat gun. Glassware for reactions performed inside a glovebox was either dried under vacuum using a heat gun or dried overnight in a 120 °C oven before being transferred into the glovebox. Liquids and solutions were transferred with syringes. All stated temperatures refer to external bath temperatures. Tetrahydrofuran (THF) was dried over sodium/benzophenone and distilled prior to use. *n*-Pentane was obtained by an *MBraun* solvent purification system (SPS-800), degassed with three freeze-pump-thaw cycles and stored in a glove box over thermally activated 4 Å molecular sieves (MS). Standard solvents and reagents were obtained from *ABCR*, *Acros*, *Alfa Aesar*, *Merck*, *Sigma-Aldrich* or *Tokyo Chemical Industry* (TCI). Benzaldehyde was distilled under vacuum prior to use. Me_3SiOM (M = Li, Na and K, all from ABCR) as well as *t*BuONa (Aldrich) and *t*BuOK (Aldrich) were sublimed under high vacuum prior to use. CsF was purchased from ABCR and used as received. Unless otherwise stated, all the *N*-aryl-*N'*-silyldiazenes were prepared according to a previously reported procedure.[1] Flash column chromatography was performed on Grace 60 (40–63 µm, 230–400 mesh, ASTM) silica gel according to the method reported by W. C. Still and co-workers.[2] Technical grade solvents were distilled prior to use. TLC analyses were performed on Macherey-Nagel Alugram® Xtra SIL G/UV_{254} silica gel 60 pre-coated aluminum-backed plates with a layer thickness of 200 µm. Product spots were visualized under UV light (λ_{max} = 254 nm) and/or by staining with a potassium permanganate solution.

^1H, ^{13}C, ^{29}Si, ^{19}F and ^{15}N NMR spectra were recorded on Bruker AV400, AV500 and AV700 instruments. $CDCl_3$, C_6D_6 and CD_2Cl_2 were degassed and stored in a glove box over 4 Å molecular sieves. THF-*d₈* was degassed and stored over activated 4 Å molecular sieves prior to use. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent signals as the internal standard ($CDCl_3$: δ = 7.26 ppm, C_6D_6: δ = 7.16 ppm, CD_2Cl_2: δ = 5.32 ppm for ^1H NMR and $CDCl_3$: δ = 77.16 ppm, C_6D_6 δ = 128.06 ppm, CD_2Cl_2 δ = 53.84 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, t = triplet, tt = triplet of triplets, q = quartet, m = multiplet, m_c = centrosymmetric multiplet), coupling constants (Hz) and integration. ^{29}Si, ^{19}F and ^{15}N NMR spectra were calibrated according to the IUPAC recommendation using a unified chemical shift scale based on the proton resonance of tetramethylsilane as primary reference.[3] Infrared (IR) spectra of aryloxysilanes and silyl hydrazines were recorded on an *Agilent Technologies Cary 630 FTIR* spectrometer equipped with an ATR unit and the bands are reported in wavenumbers (cm^{-1}). Infrared (IR) spectra of silyl aryldiazenes were recorded in a glovebox using a *Thermo Nicolet Magna-IR* 750 spectrophotometer equipped with an ATR unit and the signals are reported in wavenumbers (cm^{-1}). Melting points (**m.p.**) were determined with a *Stuart Scientific* SMP20 melting point apparatus and are not corrected. Boiling points (**b.p.**) were measured at the distillation head and are not corrected. Distillation under reduced pressure was determined directly by the connected pressure gauge (VAP 5, from *Vacuumbrand*). High resolution mass spectrometry (HRMS) analysis was performed by the Analytical Facility at the Institut für Chemie, Technische Universität Berlin. Compound names were generated by the computer program *ChemDraw* according to the guidelines specified by the International Union of Pure and Applied Chemistry (IUPAC).

2. Decomposition of diazene **1a** in the absence of carbonyl substrate

In the absence of a carbonyl substrate, the *N*-aryl-*N'*-silyldiazenes were found to spontaneously decompose into the corresponding arylsilane (Ar–$SiMe_3$) and bis-silylhydrazine. The results obtained for the decomposition of diazene **1a** in the presence of various initiators are presented in Table S1 below.

Table S1. Outcome of the self-decomposition of diazene **1a** in the presence of various metal salts.



Entry	Initiator [mol%]	Time	Yield of **5a** [%][a]	Ratio **5a**/**4a**
1	*t*BuOLi [100]	2 h	28	94/6
2	*t*BuOLi [10]	18 h	16	–[b]
3	*t*BuONa [100]	< 5 min	51	96/4
4	*t*BuONa [10]	< 5 min	53	85/15
5	*t*BuOK [100]	< 5 min	49	n.d.[c]
6	*t*BuOK [10]	< 5 min	57	85/15
7	Me_3SiOK [10]	< 5 min	53[d]	n.d.

Reaction conditions: Diazene **1a** (0.1 mmol), initiator (100 or 10 mol%) and THF-d_8 (0.17 M). Full conversion of **1a** was observed in all cases. [a] Yields determined by qNMR using 1,3,5-trimethoxybenzene as internal standard. [b] Not determined because of signal overlaps in the ^1H NMR spectrum. [c] Not detected. [d] Yield determined by calibrated GLC using tetracosane as an internal standard. RT = room temperature.

The aforementioned distribution of products suggests that a nucleophilic *para*-tolyl anion equivalent was formed *in situ* and was able to further react with the starting diazene **1a** by two competitive pathways namely the addition across the nitrogen–nitrogen double bond or by direct carbon–silicon bond formation. On this basis, we propose that the self-decomposition of **1a** occurs through the autocatalytic cycle presented in Figure S1 below.

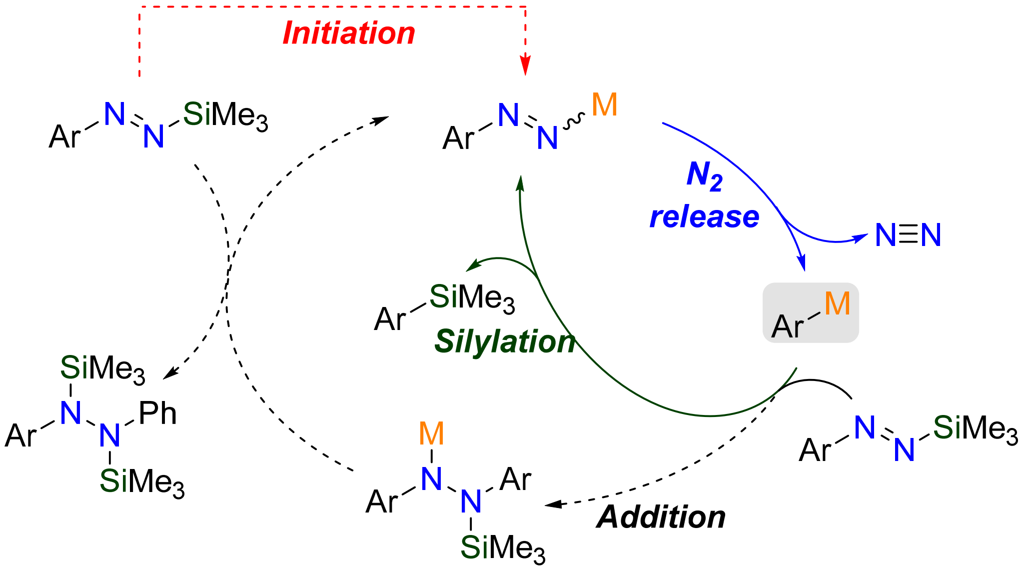


Figure S1. Proposed mechanism for the autocatalytic decomposition of *N*-aryl-*N'*-silyldiazenes in the absence of a carbonyl electrophile. Ar = aryl, M = Li, Na or K.

2.1. Representative procedure for the decomposition of **1a** with *tert*-butoxide salts

A 1.3-mL GLC vial equipped with a stirring bar was charged with the *tert*-butoxide salt (1.05 equiv or 10 mol%) followed by THF-d_8 (0.4 mL) and vigorously stirred. Into a separate vial was weighed the diazene **1a** (19 mg, 0.10 mmol, 1.0 equiv) and THF-d_8 (0.3 mL) was then added. The diazene solution was then rapidly added to the *tert*-butoxide solution and the resulting solution vigorously stirred at room temperature for the indicated time. Irrespective of the loading, the reactions are complete within 5 min with *t*BuONa and *t*BuOK and within 2 h with *t*BuOLi (1.05 equiv) or 16 h (10 mol%). The internal standard (1,3,5-trimethoxybenzene) was then added to the crude reaction mixture, that was subsequently transferred into a J-Young NMR tube for NMR analysis.

Note: The results obtained from these experiments were found to dramatically depend on the quality of the *tert*-butoxide salt. The use of unsublimed *t*BuOK and *t*BuONa leads to reduced yields of *p*-tolylSiMe$_3$ (**5a**) and large amount of toluene was produced as indicated by ^{1}H NMR, presumably because of the presence of protic impurities in these non-purified salts. As an illustration, the decomposition of **1a** with unsublimed *t*BuOK (1.05 equiv) affords **5a** in 19% yield compared to 49% with sublimed *t*BuOK (and minor amount of toluene).

2.2. Representative ^{1}H NMR spectrum obtained for the decomposition of **1a** with 10 mol% *t*BuONa

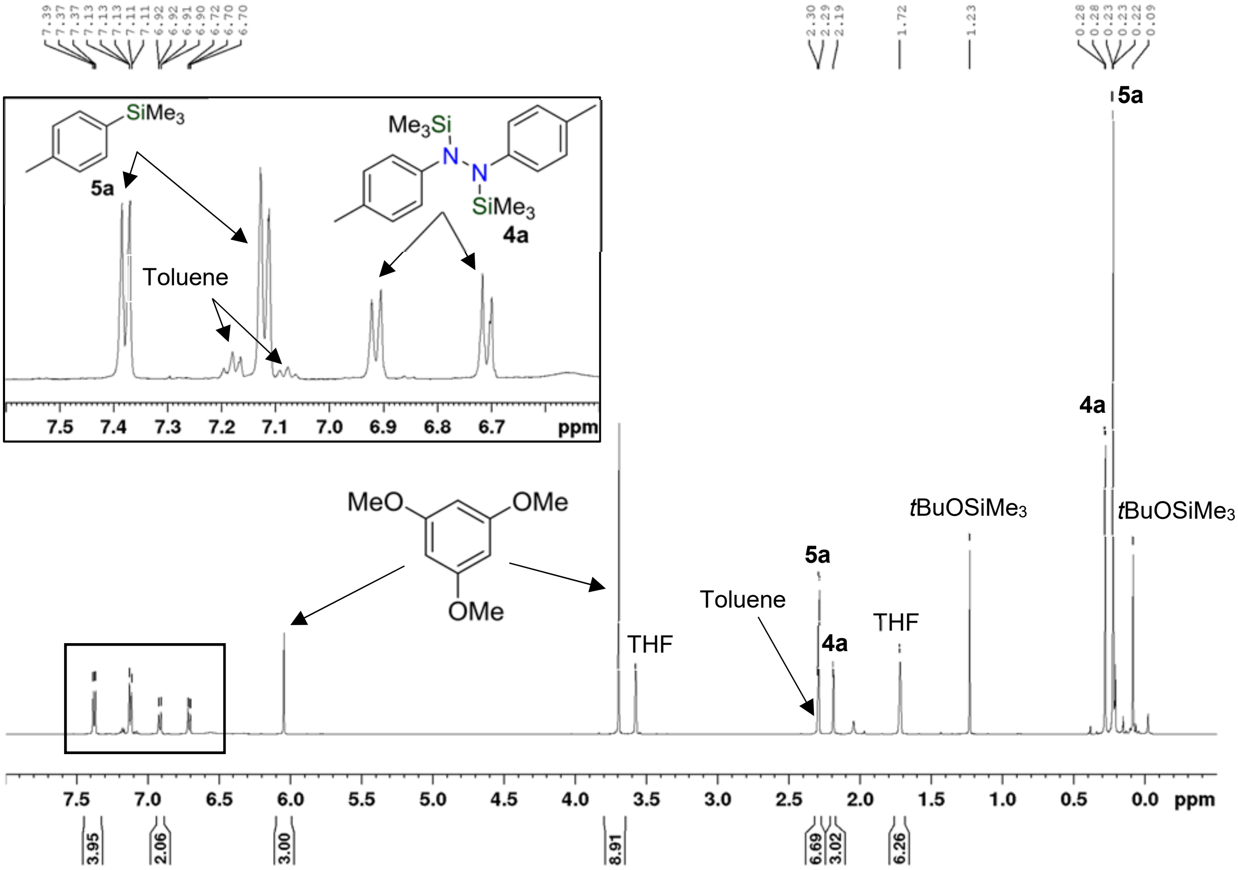
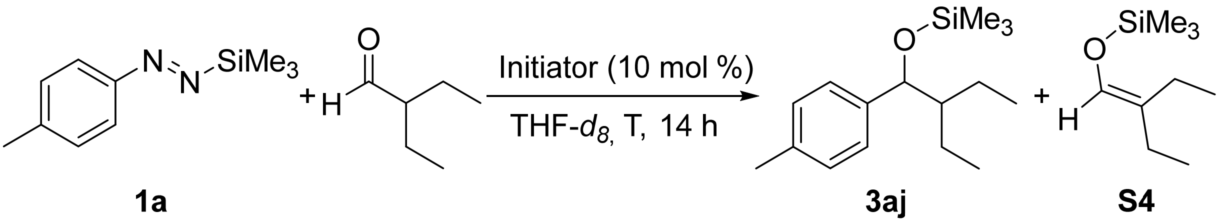


Figure S2. ^{1}H NMR spectra obtained for the decomposition of **1a** with 10 mol% *t*BuONa in THF-d_8. Full conversion of **1a** was reached in less than 5 min.

3. Additional optimization data

3.1. Reaction of **1a** with enolizable *α*-branched aldehydes

Table S2. Competing arylation and deprotonation reactions of enolizable 2-ethylbutyraldehyde (**2j**).

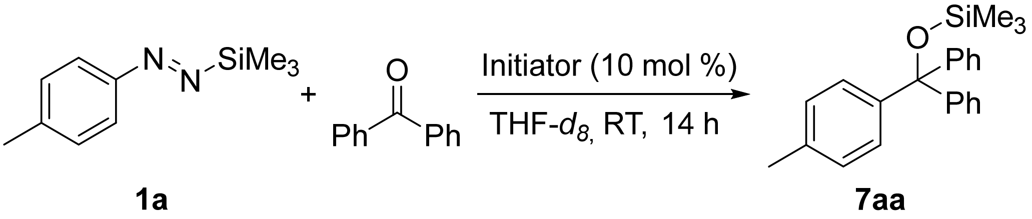


Entry	Initiator	Temperature [°C]	Yield of **3aj** [%][a]	Yield of **S4** [%][a]
1	Me_3SiOK	RT	70	30
2	Me_3SiONa	RT	56	44
3	Me_3SiOLi + 18-C-6	RT	44	41
4	Me_3SiOK	0	66	32

Reaction conditions: Diazene **1a** (0.12 mmol), 2-ethylbutyraldehyde (**2j**) (0.10 mmol) and THF-d_8 (0.14 M). Full conversion of **2j** was observed in all cases. [a] Yields determined by qNMR using dibromomethane as internal standard. RT = room temperature.

3.2. Reaction of **1a** with benzophenone

Table S3. Screening of various initiators for the silylarylation of benzophenone.

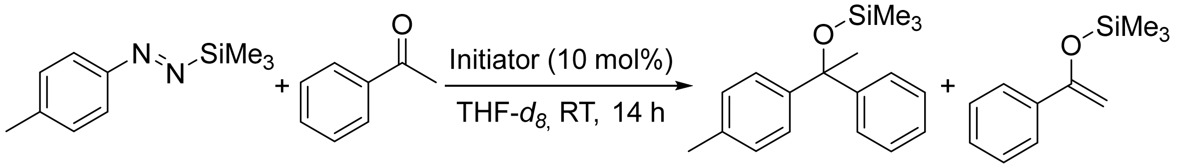


Entry	Initiator	Yield of **7aa** [%][a]
1	Me_3SiOK	72
2	Me_3SiOK + 18-C-6	61
3	Me_3SiONa + 18-C-6	23
4	Me_3SiONa	trace

Reaction conditions: Diazene **1a** (0.12 mmol), benzophenone (0.10 mmol) and THF (0.14 M). Full conversion of benzophenone was observed in all cases. [a] Yields determined by calibrated GLC using tetracosane as an internal standard. RT = room temperature.

3.3. Reaction of **1a** with enolizable acetophenone

Table S4. Competing arylation and deprotonation reactions of enolizable acetophenone.



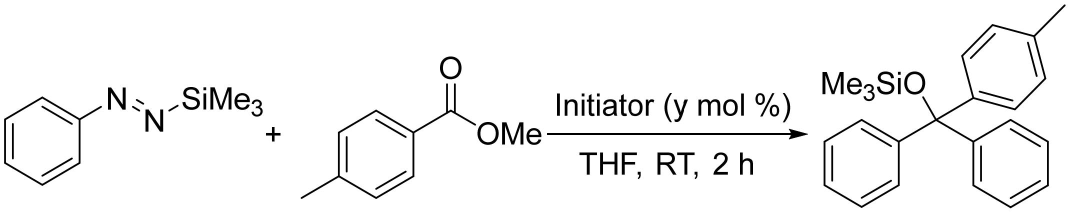
1a **S5** **S6**

Entry	Initiator	Yield of **S5** [%][a]	Yield of **S6** [%][a]
1	Me_3SiOK	38	60
2	Me_3SiONa	22	54
3	Me_3SiOLi	trace	trace
4	Me_3SiOLi + 18-C-6	trace	trace

Reaction conditions: Diazene 1a (0.12 mmol), acetophenone (0.10 mmol) and THF-d_8 (0.14 M). Full conversion of acetophenone was observed in all cases. [a] Yields determined by qNMR using dibromomethane as internal standard. RT = room temperature.

3.4. Reaction of **1e** with methyl 4-tolylbenzoate

Table S5. Screening of various reaction conditions for the silylarylation of esters.



1e
(x equiv)

9ba

Entry	Initiator [mol %]	Equivalents of **1e**	Yield of **9ba** [%][a]
1	Me_3SiOK [10]	2.4	45
2	Me_3SiOK [20]	2.4	61
3	^{t}BuOK [20]	2.4	33
4	Me_3SiOK [20] 18-C-6 [20]	2.4	19
5	Me_3SiOK [20]	3.0	19
6	Me_3SiOK [20]	2.4	36[b]
7	Me_3SiOK |20]	3.0	19[c]
8	Me_3SiOK |20]	3.0	**93**[c,d]

Reaction conditions: A solution of diazene **1e** in THF was added dropwise to a vigorously stirred solution of the initiator and methyl *p*-toluate (0.10 mmol) in THF (0.2 M). Full conversion of diazene **1e** was observed in all cases. [a] Yields determined by calibrated GLC using tetracosane as an internal standard. [b] A solution of the initiator in THF was added dropwise to a vigorously stirred solution of diazene **1e** and methyl *p*-toluate (0.10 mmol) in THF

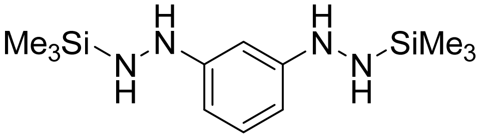
(0.2 M). [c] Higher dilution (0.1 M). [d] Diazene **1e** in solution was added *via* a syringe pump (GPS3). RT = room temperature.

For entries 1–7, the low-to-moderate yields of desired product **9ba** are due to the rapid decomposition of diazene **1e** in the corresponding arylsilane ($PhSiMe_3$) as is observed with the **1a** (*vide supra)*.

4. Synthesis of the 1,3-dimetallobenzene equivalent **1p**

4.1. Synthesis of 1,3-bis((*E*)-(trimethylsilyl)diazenyl)benzene (**1p**)

1,3-Bis(2-(trimethylsilyl)hydrazineyl)benzene (S2)



S2

$C_{12}H_{26}N_4Si_2$

282.54 g/mol

The 1,3-bis(2-(trimethylsilyl)hydrazineyl)benzene **(S2)** was prepared *via* diazotization of *m*-phenylenediamine (Aldrich, 99%), tin-mediated reduction of the resulting bis-diazonium salt with $SnCl_2$ and silylation of the isolated *m*-phenylenedihydrazinonium dichloride salt **(S1)**.

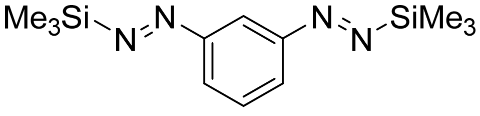
Preparation of *m*-phenylenedihydrazinonium dichloride salt (S1). In accordance with a modified literature procedure,[5] a 500-mL three-necked flask equipped with an overhead mechanical stirrer and a dropping funnel, was charged with anhydrous tin chloride $SnCl_2$ (21.8 g, 115 mmol, 4.60 equiv), metallic Sn (119 mg, 1.00 mmol, 0.04 equiv) and concentrated hydrochloric acid (50 mL). Tin powder was dissolved by gentle heating with a heat gun and the resulting solution was cooled to –15 °C. In parallel, a 250-mL three-necked flask equipped with a large olive-shaped magnetic stirring bar, a dropping funnel and an internal thermometer, was charged with the solid *m*-phenylenediamine (2.70 g, 25.0 mmol, 1.00 equiv) followed by concentrated hydrochloric acid (90 mL) at room temperature. The resulting suspension was vigorously stirred and cooled to –5 °C. A solution of sodium nitrite $NaNO_2$ (3.62 g, 52.5 mmol, 2.10 equiv) in water (30 mL) was then added dropwise to the reaction mixture over 30 min (keeping internal reaction temperature below –5 °C). The resulting orange suspension was stirred for another 30 min at –5 °C, transferred to the dropping funnel and was added dropwise to the $SnCl_2$/Sn solution with vigorous stirring. To the resulting pinkish suspension was added concentrated hydrochloric acid (55 mL) and the mixture was stirred for another 30 min at –5 °C. The crude reaction mixture was then filtered over a fritted funnel, the pale pink solid filtered off was washed with isopropanol followed by diethylether and was further dried under high vacuum (10^{-2} mbar) for 15 h. The *m*-phenylenedihydrazine salt (6.30 g) was obtained as a pale pink solid and was engaged in the subsequent silylation step without any further purification. Identity was verified by NMR analysis:
^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ/ppm = 6.53 (t, *J* = 1.9 Hz, 1H), 6.60 (dd, *J* = 8.0, 1.9 Hz, 2H), 7.15 (t, *J* = 8.0 Hz, 1H), 10.3 (bs, 6H). **^{13}C{1H} NMR** (126 MHz, $(CD_3)_2SO$): δ/ppm = 101.1,

107.3 (2C), 129.6, 146.3 (2C). **^{1}H/^{15}N HMQC NMR** (500/51 MHz, $(CD_3)_2SO$, optimized for *J* = 90 Hz): δ/ppm = 10.3/65.0.

Silylation procedure. Following a literature procedure,[1] a 500-mL flame-dried Schlenk flask equipped with a magnetic stirring bar and a rubber septum was charged with the solid *m*-phenylenedihydrazinonium dichloride salt **(S1)** (6.29 g, 29.8 mmol, 1.00 equiv) followed by dry THF (150 mL, 0.2 M) at room temperature. The resulting suspension was vigorously stirred and cooled to –5 °C. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 3.11 mL, 20.9 mmol, 0.70 equiv) and dry triethylamine (18.7 mL, 134 mmol, 4.50 equiv) were then successively added dropwise over 10 min. To the resulting mixture was dropwise added trimethylchlorosilane (11.4 mL, 89.4 mmol, 3.00 equiv) over 5 min. The obtained suspension was vigorously stirred for 1 h at –5 °C. The crude reaction mixture was then filtered over a fritted funnel and the filtrate was concentrated under reduced pressure to afford the crude silylated *m*-phenylenedihydrazine which was further evacuated under high vacuum (*ca.* 10^{-2} mbar) for 1 h. The title compound **S2** (3.35 g, 11.9 mmol, 47% *over 2 steps*) was obtained as a pale brown solid and was engaged in the subsequent oxidation step without any further purification.

M.p.: 29–32 °C (THF). **^{1}H NMR** (400 MHz, $CDCl_3$): δ/ppm = 0.11 (s, 18H), 2.89 (bs, 2H), 5.10 (bs, 2H), 6.24 (dd, *J* = 7.8, 2.2 Hz, 2H), 6.44 (t, *J* = 2.2 Hz, 1H), 6.95 (t, *J* = 7.8 Hz, 1H). **^{13}C{1H} NMR** (101 MHz, $CDCl_3$): δ/ppm = –0.81 (6C), 96.3, 103.5 (2C), 129.5, 153.3 (2C). **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, optimized for *J* = 7 Hz): δ/ppm = 0.11/5.55. **^{1}H/^{15}N HMQC NMR** (500/51 MHz, C_6D_6, optimized for *J* = 90 Hz): δ/ppm = 2.45/61.9, 4.60/86.7. **HRMS** (APCI) calculated for $C_{12}H_{27}N_4Si_2^+$ [(M+H)$^+$]: 283.1769; found: 283.1767. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3337, 3276, 2952, 1594, 1498, 1461, 1248, 1209, 1159, 1104, 1071, 958, 830.

1,3-bis((*E*)-(trimethylsilyl)diazenyl)benzene (1p)



1p
$C_{12}H_{22}N_4Si_2$
278.51 g/mol

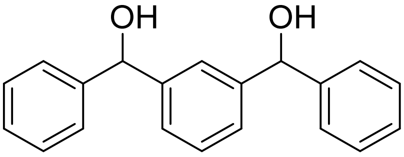
Oxidation of S2. Following a literature procedure,[1] a single-necked round-bottomed flask equipped with a magnetic stirring bar was charged in a glovebox with the bis-silylhydrazine **S2** (1.99 g, 7.05 mmol, 1.00 equiv) followed by dry hexamethyldisiloxane (40 mL, 0.2 M). To the resulting homogeneous, vigorously stirred solution was added solid DBAD (2.92 g, 17.7 mmol, 1.80 equiv) portion-wise over *ca.* 5 min at room temperature. The resulting suspension was further stirred 3 h at room temperature and the crude reaction mixture was then filtered over a fritted funnel. The blue filtrate was concentrated *in vacuo* to afford the crude silylated aryldiazene, which was then distilled under reduced pressure *via* a short path distillation (**b.p.**: 84–86 °C at 8×10^{-2} mbar) to afford the title compound **1p** (1.07 g, 3.84 mmol, 55%) as a deep blue liquid. Crystals suitable for X-Ray diffraction were obtained after spontaneous crystallization of a distillation fraction under reduced pressure (ca. 10^{-3} mbar).

Note: Bis-diazene **1p** was invariably contaminated with impurities arising from side-reactions of the hydrazine by-product BocHN–NHBoc (up to *ca*. 15 mol%) with the diazene **1p** itself. In fact, GC/MS analysis revealed the presence of Boc(Me_3Si)N–NHBoc and Boc(Me_3Si)N–N($SiMe_3$)Boc contaminants, which could not be removed by distillation or sublimation. Alternative oxidation protocols with other solvents, oxidants (e.g. DIAD or 1,3-di-*tert*-butylaziridinone) or lower temperature were thus investigated but did not improve the purity of **1p**. However, these impurities were not detrimental for the applications described in this manuscript and were easily removed after the reactions with carbonyl compounds.

M.p.: 25–27 °C (*n*-pentane). **^{1}H NMR** (500 MHz, C_6D_6): δ/ppm = 0.29 (s, 18H), 7.25 (t, *J* = 7.8 Hz, 1H), 8.04 (dd, *J* = 7.8, 1.9 Hz, 2H), 8.57 (t, *J* = 1.9 Hz, 1H). **^{13}C{1H} NMR** (126 MHz, C_6D_6): δ/ppm = –2.72 (6C), 111.5, 124.6 (2C), 129.6, 157.1 (2C). **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, C_6D_6, optimized for *J* = 7 Hz): δ/ppm = 0.29/12.6. **HRMS** (APCI) calculated for $C_{12}H_{23}N_4Si_2^+$ [$(M+H)^+$]: 279.1456; found: 279.1454. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3059, 2960, 2901, 1723, 1596, 1500, 1452, 1420, 1391, 1366, 1315, 1246, 1153, 1076, 837.

5. Reaction of **1p** with benzaldehyde and terephthalaldehyde

5.1. Synthesis of 1,3-phenylenebis(phenylmethanol) (**10pa**)



10pa
$C_{20}H_{18}O_2$
290.36 g/mol

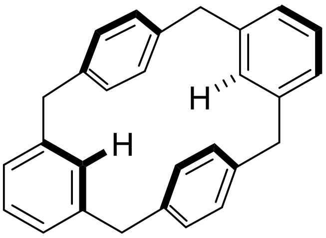
A 10-mL vial equipped with a magnetic stirring bar was charged with potassium trimethylsilanolate (Me_3SiOK, 20 mol%, 5.1 mg), THF (1 mL) and benzaldehyde (20 µL, 0.20 mmol, 1.4 equiv). To the resulting vigorously stirred mixture was then added dropwise a solution of **1p** (39 mg, 0.14 mmol, 1.0 equiv) in THF (1 mL) over 5 min at room temperature. Full conversion of the benzaldehyde was reached after 2 h. A solution of TBAF in THF (1 M, 2 mL, 10 equiv) was then added and the resulting mixture was stirred for 15 h at room temperature. The mixture was then quenched by the addition of H_2O (16 mL), the aqueous phase was extracted thrice with *tert*-butyl methyl ether and the combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (8:2 → 7:3) as eluent afforded the title compound **10pa** (19 mg, 0.065 mmol, 65%) as a white solid.

R_f = 0.29 (cyclohexane:*tert*-butyl methyl ether 6:4). **M.p.**: 121–124 °C (dichloromethane). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 2.39 (bs, 2H), 5.81 (s, 2H), 7.22–7.30 (m, 5H), 7.30–7.41 (m, 8H), 7.47 (m_c, 1H). **^{13}C{1H} NMR** (101 MHz, CD_2Cl_2): δ/ppm = 76.4 (2C), 124.78 (d_1 or d_2), 124.79 (d_1 or d_2), 125.95 (2C, d_1 or d_2), 125.99 (2C, d_1 or d_2), 126.83 (4C, d_1 or d_2), 126.84 (4C, d_1 or d_2), 127.9 (2C), 128.9 (4C), 129.0, 144.5 (2C), 144.87 (2C, d_1 or d_2), 144.90 (2C, d_1 or d_2). **HRMS** (APCI) calculated for $C_{20}H_{17}O^+$ $[(M–OH)^+]$: 273.1274; found: 273.1274. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3280, 3064, 3028, 2918, 1599, 1491, 1452, 1397, 1337, 1270, 1238, 1193, 1153, 1078, 1017, 954, 916.

Note: The two diastereomers d_1 and d_2 (d.r. = 50:50) are not separable by flash column chromatography (identical polarity) and display similar ^{1}H NMR spectroscopy signatures. However, they are partially distinguishable by ^{13}C NMR spectroscopy.

5.2. Synthesis of a cyclophane-like [4]arene macrocycle

1,5(1,3),3,7(1,4)-Tetrabenzenacyclooctaphane (11pm)



11pm
$C_{28}H_{24}$
360.50 g/mol

Macrocyclization procedure. A 250-mL flask equipped with a magnetic stirring bar was charged with 1,3-bis((*E*)-(trimethylsilyl)diazenyl)benzene (**1p**) (438 mg, 1.26 mmol, 1.00 equiv, 80%), THF (110 mL, 10^{-2} M) and terephthalaldehyde (141 mg, 1.05 mmol, 0.80 equiv). To the resulting vigorously stirred mixture was then added in a fine stream (over a few seconds) a solution of the potassium trimethylsilanolate (Me_3SiOK, 20 mol%, 32 mg) in THF (1 mL) at room temperature. Full conversion of the terephthalaldehyde was reached after 2 h. The reaction mixture was then concentrated under reduced pressure to afford a brown solid that was washed with *n*-pentane and further dried under high vacuum for 1 h.

A characterization by HRMS-APCI spectrometry of the crude solid revealed that other oligomers and macrocycles were formed. This crude residue was then directly used in the defunctionalization step without further purification.

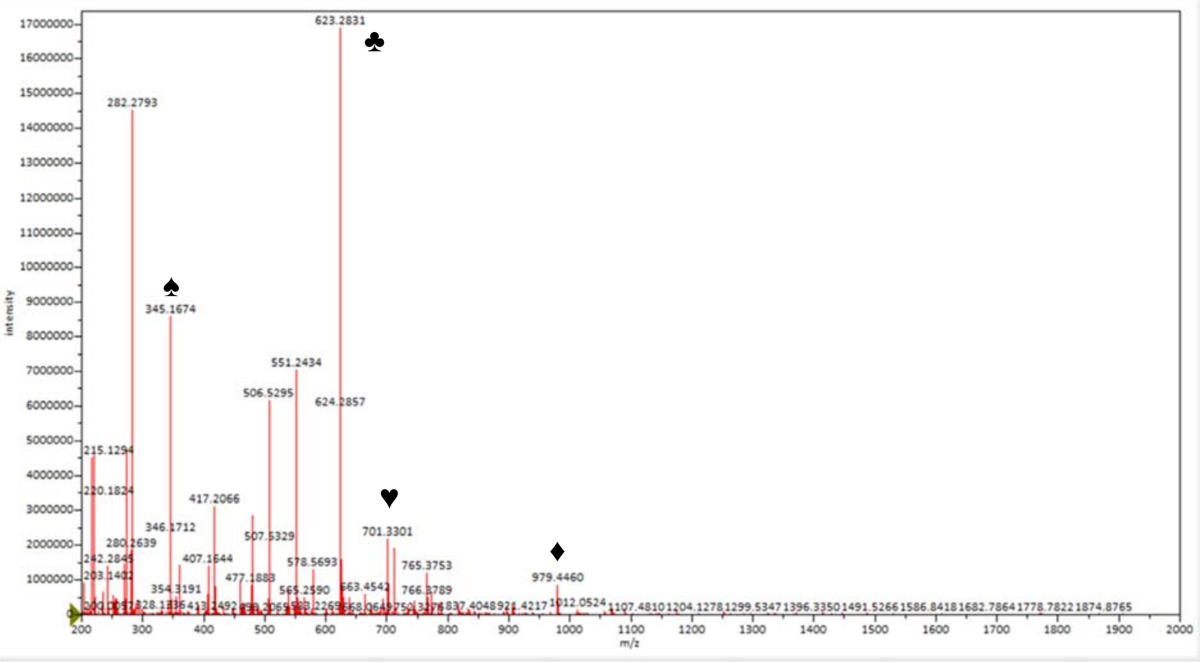
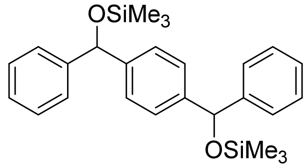
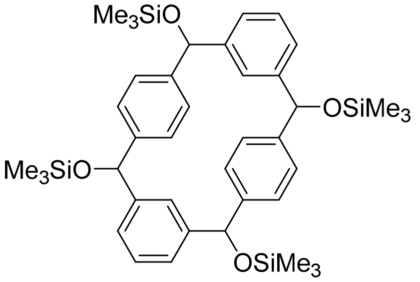
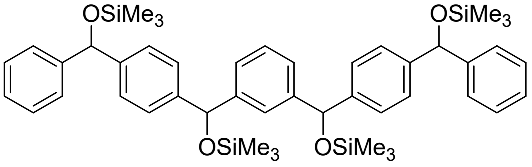


Figure S3. HRMS-APCI spectrum of the crude residue showing the presence or oligomers and macrocycles (c.f. **Table S6** for structures)

Table S6. HRMS-APCI spectrometry characterization of the major oligomers and macrocyles observed on **Figure S3**.

Signal	Attribution
♠	 **S7** $[(M{-}OSiMe_3)^+]$: 345.1674 (calculated: 345.1669)
♣	 **S8** $[(M{-}OSiMe_3)^+]$: 623.2831 (calculated: 623.2828)
♥	Cyclophane-like [6]arene macrocycle **S9** $[(M{-}OSiMe_3)^+]$: 701.3301 (calculated: 701.3297)
♦	 **S10** $[(M{-}OSiMe_3)^+]$: 979.4460 (calculated: 979.4455)

Defunctionalization procedure. According to a modified reported procedure,[4] a 50-mL flask equipped with a magnetic stirring bar was charged with trimethylsilyl iodide Me_3SiI (0.86 mL, 6.3 mmol, 12 equiv), dry acetonitrile (10 mL) and water H_2O (38 μL, 2.1 mmol, 4.0 equiv) under nitrogen. A precipitate is instantaneously formed in the reaction mixture. To the vigorously stirred resulting suspension was added dropwise a solution of the crude residue (containing **S8**) (374 mg, 0.525 mmol, 1.0 equiv) in dry acetonitrile (10 mL) at 0 °C over 15 min. The reaction was further stirred for 14 h at room temperature. A solution of NaOH (20 mol%) was added followed by a solution of sodium thiosulfate $Na_2S_2O_3$ (1.66 g, 20 equiv) in water and brine. The aqueous phase was extracted seven times with dichloromethane (7 × 15 mL) and the combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using dichlorometane:*n*-pentane (1:1) as eluent yielded a mixture of **11pm** and reduced **S7** as a pale

yellow solid. The resulting solid was triturated with distilled acetone and filtered off to afford the title compound **11pm** (18 mg, 0.051 mmol, 10%) as a white solid. Crystals suitable for X-Ray diffraction were obtained by recrystallization from a mixture of chloroform and ethanol (1:1).
R_f = 0.71 (dichlorometane:*n*-pentane 1:1). **M.p.**: > 221 °C (acetone). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ/ppm = 3.87 (s, 8H), 6.22 (s, 2H), 6.93 (s, 8H), 7.12 (d, *J* = 7.7 Hz, 4H), 7.22 (t, *J* = 7.7 Hz, 2H). **^{13}C{1H} NMR** (101 MHz, CD_2Cl_2): δ/ppm = 41.3 (4C), 126.6 (4C), 128.0 (2C), 128.5 (2C), 129.9 (8C), 138.5 (4C), 142.6 (4C). **HRMS** (APCI) calculated for $C_{28}H_{25}^+$ [(M+H)$^+$]: 361.1951; found: 361.1952. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3021, 2898, 2831, 1600, 1509, 1483, 1418, 1181, 1106, 928, 856, 808.

6. Crystallographic data

Data for the single crystal structure determination were collected with an Agilent SuperNova diffractometer equipped with a CCD area Atlas detector and a mirror monochromator by utilizing Cu-Kα radiation (λ = 1.5418 Å). Software packages used: CrysAlis PRO for data collection, cell refinement and data reduction,[6] SHELXS-97 for structure solution,[7] SHELXL-97 for structure refinement,[8] and Mercury 4.1[9] for graphics.

Table S7. Crystal data and structure refinement for **1p**.

Compound (CCDC number)	**1p** (1971069)	**11pm** (1971057)
Empirical formula	$C_{12}H_{22}N_4Si_2$	C28 H24
Formula weight	278.52	360.47
Temperature	150.00(10) K	150.00(10) K
Wavelength	1.54184 Å	1.54184 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 29.7476(6) Å α= 90°. b = 5.98427(9) Å β= 114.139(2)°. c = 30.9411(6) Å γ = 90°	a = 5.8507(2) Å α= 90°. b = 12.4136(5) Å β= 93.982(4)°. c = 13.4792(5) Å γ = 90°.
Volume	5026.42(16) $Å^3$	976.61(6) $Å^3$
Z	12	2
Density (calculated)	1.104 Mg/m^3	1.226 Mg/m^3
Absorption coefficient	1.844 mm^{-1}	0.519 mm^{-1}
F(000)	1800	384
Crystal size	0.22 x 0.10 x 0.08 mm^3	0.58 x 0.09 x 0.08 mm^3
Theta range for data collection	2.88 to 67.50°.	4.85 to 67.50°.
Index ranges	-34<=h<=35, -7<=k<=6, -35<=l<=37	-6<=h<=6, -14<=k<=14, -16<=l<=16
Reflections collected	31407	5694
Independent reflections	9048 [R(int) = 0.0509]	1749 [R(int) = 0.0235]
Completeness to theta = 67.50°	99.9 %	99.3 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.8635 and 0.6871	0.9577 and 0.7515
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	9048 / 24 / 542	1749 / 0 / 128
Goodness-of-fit on F^2	1.142	1.022

Final R indices [I>2sigma(I)]	R1 = 0.0637, wR2 = 0.1702	R1 = 0.1223, wR2 = 0.3200
R indices (all data)	R1 = 0.0764, wR2 = 0.1810	R1 = 0.1248, wR2 = 0.3207
Extinction coefficient	–	0.011(4)
Largest diff. peak and hole	0.373 and -0.375 e.Å^{-3}	0.603 and -0.344 e.Å^{-3}

6.1. Molecular structure of **1p**

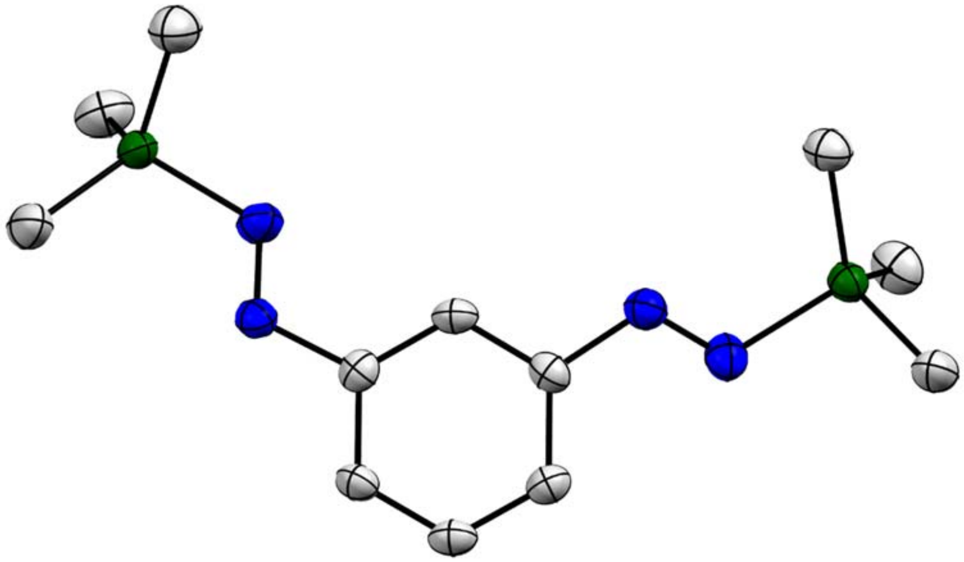
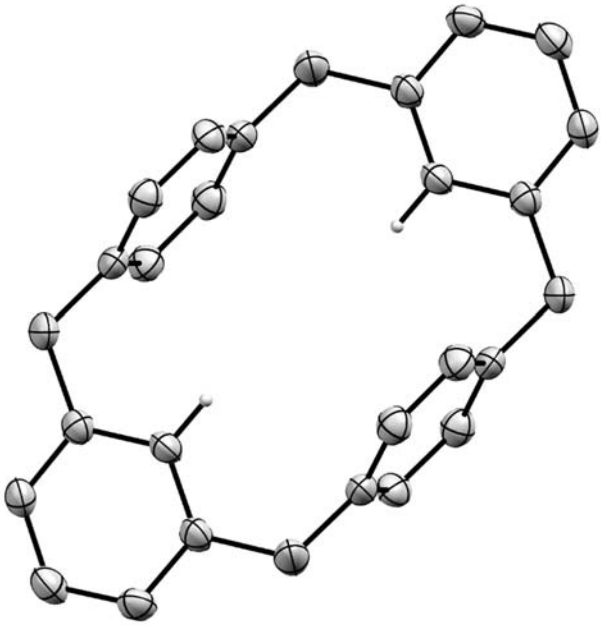


Figure S4. Molecular structure of **1p**. Thermal ellipsoids are shown at the 50% probability level and hydrogen atoms are omitted for clarity. C: gray; N: blue; Si: green.

6.2. Molecular structure of **11pm**



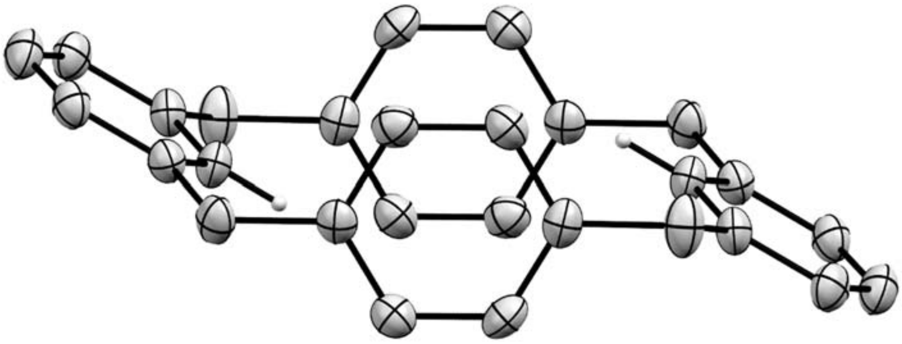


Figure S5. Top and side views of the molecular structure of **11pm**. Thermal ellipsoids are shown at the 50% probability level and all hydrogen atoms except the two pointing toward the center are omitted for clarity.

7. Calculation on the conformations of macrocycle **11pm**

7.1. General considerations

All DFT calculations have been performed using Gaussian09 version D.01 code[10] without imposing symmetry constraints. The Becke three-parameter hybrid functional B3LYP[11] (a) A. D. Becke, J. Chem. Phys.1993, 98, 5648; b) C. T. Lee, W. T. Yang, R. G. Parr, Phys. Review B.1988, 37, 785; c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, J. Phys. Chem.1994, 98, 11623; d) S. H. Vosko, L. Wilk, M. Nusair, Can. J. Phys.1980, 58, 1200) was used with Grimme's D3 empirical dispersion. (S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104) Structural optimizations were carried out using default cut-off values and were followed by a frequency calculation at the same level of theory to confirm the localization of a true minimum on the potential energy hypersurface (no negative harmonic vibrational frequencies).

7.2. Conformational analysis of macrocycle **11pm**

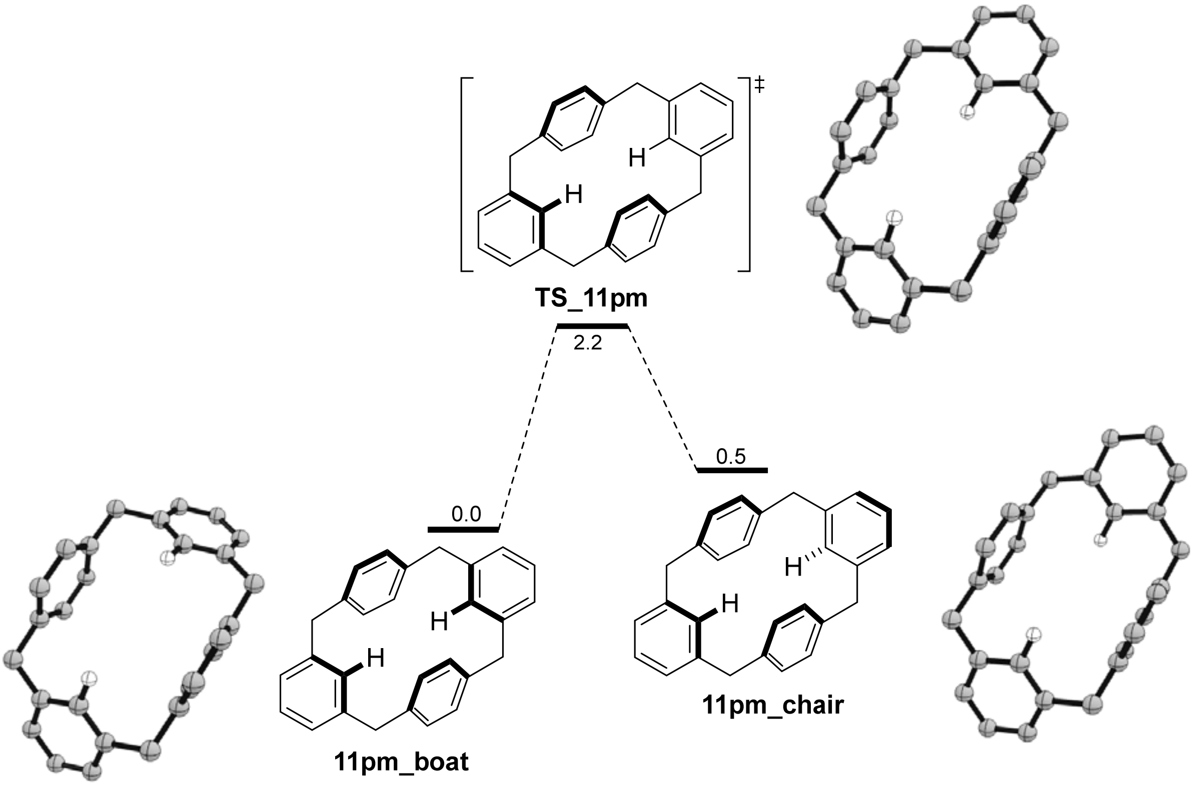


Figure S6. Conformational equilibrium between **11pm_boat** and **11pm_chair** *via* a half-chair transition structure **TS_11pm**. Gas phase Gibbs free energies computed at the B3LYP-D3/6-31+G(d,p) level of theory are given in kcal/mol.

7.3. Computed structure geometries

11pm_boat

Element	X	Y	Z
C	-4.08333492	-0.78511399	-0.99039602
C	-2.99777794	-0.91510701	-0.11335400
C	-2.45365310	0.24120100	0.45893300
C	-2.97013998	1.51261795	0.17968901
C	-4.05575895	1.62009895	-0.69987202
C	-4.60994911	0.47617999	-1.28049302
H	-4.51223421	-1.67109299	-1.45264399
H	-1.58987796	0.15297000	1.11285698
H	-4.46292114	2.60023689	-0.93669701
H	-5.44648409	0.56874597	-1.96796405
C	-2.36439204	2.74836206	0.83023697
H	-2.70418501	2.81020808	1.87215304
H	-2.75534010	3.64177608	0.32788801
C	-2.42449808	-2.28498697	0.22323500
H	-2.78016591	-2.58969903	1.21607900
H	-2.82576895	-3.02079391	-0.48432699
C	-0.84787297	2.76959991	0.80139500
C	-0.09391600	2.71497798	1.97660697
C	-0.16179100	2.81376004	-0.42398000
C	1.30626500	2.70613503	1.93415403
H	-0.60103500	2.67248797	2.93787193
C	1.22923601	2.80492496	-0.46613300
H	-0.73004401	2.83850002	-1.35079706
C	1.98798394	2.75159788	0.71521097
H	1.87032402	2.65705991	2.86285090
H	1.74052203	2.82287908	-1.42570496
C	-0.90898800	-2.33232903	0.20240700
C	-0.16683300	-2.51771808	1.37194705
C	-0.21038599	-2.15569210	-1.00376499
C	1.23362899	-2.52812910	1.34214103
H	-0.68352503	-2.65185189	2.31961608
C	1.18107903	-2.16584110	-1.03335798
H	-0.76858598	-1.99520195	-1.92318904
C	1.92780304	-2.35342693	0.14195301
H	1.78809702	-2.66987801	2.26704311
H	1.70209801	-2.01269388	-1.97554398
C	3.50283599	2.70874500	0.65140700
H	3.87463593	3.58995509	0.11424000
H	3.90700507	2.77838707	1.66961098
C	3.44368291	-2.33004403	0.09748900
H	3.83700204	-2.62467194	1.07904899
H	3.80286598	-3.08306503	-0.61460900
C	4.04985380	1.45612097	-0.01899700
C	3.53084707	0.19642900	0.30470300
C	5.08296204	1.53634405	-0.96259397
C	4.02133989	-0.97462600	-0.28593901

```
H            2.70571089      0.12876999      1.00903499
C            5.58373785      0.37745699     -1.56162405
H            5.49095583      2.50707102     -1.23420000
C            5.05516100     -0.87195802     -1.22663796
H            6.37954378      0.44899499     -2.29819894
H            5.44173288     -1.76974499     -1.70319998
=======================================================

                      1                      2                      3
                      A                      A                      A
 Frequencies --     14.5943                20.9457                28.4953
 Red. masses --      3.7273                 4.5735                 3.7020
 Frc consts  --      0.0005                 0.0012                 0.0018
 IR Inten    --      0.0007                 0.0054                 0.0044

 Sum of electronic and zero-point Energies=          -1081.133875
 Sum of electronic and thermal Energies=             -1081.112182
 Sum of electronic and thermal Enthalpies=           -1081.111238
 Sum of electronic and thermal Free Energies=        -1081.186910

HF =  -1081.57002242
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11pm_chair

```
=======================================================
Element               X               Y               Z
=======================================================
C           -2.48426890      0.13404000     -0.43325499
H           -1.51050603      0.17245799     -0.91483200
C           -3.12207294      1.33187497     -0.08743300
C           -4.35572386      1.27136004      0.57495099
H           -4.85972404      2.19148111      0.86114597
C           -4.93515396      0.03623400      0.87704498
H           -5.88752079     -0.00222200      1.39908004
C           -4.28718376     -1.14979601      0.52225900
H           -4.73828697     -2.10843897      0.76740998
C           -3.05301690     -1.11185396     -0.14093900
C           -2.34683895     -2.39778399     -0.54958600
H           -2.82491589     -3.24253607     -0.03928000
H           -2.49796796     -2.56386709     -1.62414706
C           -0.86003900     -2.39659595     -0.25165600
C            0.09019000     -2.32147789     -1.27898502
H           -0.24284101     -2.28811193     -2.31393504
C            1.45631003     -2.28232098     -0.99366802
H            2.17522311     -2.20712805     -1.80615997
C            1.91604197     -2.32292295      0.32916301
C            0.96605802     -2.39919209      1.35628498
H            1.29881203     -2.42787790      2.39144707
C           -0.40055501     -2.43304706      1.07118797
H           -1.12047100     -2.47617888      1.88513803
C            3.40094900     -2.25189209      0.62933302
H            3.92572689     -3.04548407      0.08369200
H            3.56193805     -2.45652103      1.69573295
C            4.03353786     -0.91200799      0.27854100
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C           5.26715088     -0.85148799     -0.38391599
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C           5.84656096      0.38363999     -0.68603802
H           6.79889679      0.42210099     -1.20812798
C           5.19860888      1.56966805     -0.33120999
H           5.64969492      2.52831292     -0.57638502
C           3.96448112      1.53172100      0.33206001
C           3.39575410      0.28582400      0.62440801
H           2.42201996      0.24740200      1.10604095
C           3.25831008      2.81764293      0.74073797
H           3.73638797      3.66240692      0.23045100
H           3.40943599      2.98370194      1.81530297
C           1.77151000      2.81645989      0.44280300
C           0.82127601      2.74135590      1.47012901
H           1.15430200      2.70799994      2.50508094
C          -0.54484200      2.70220089      1.18480599
H          -1.26375902      2.62701893      1.99729502
C          -1.00456798      2.74278903     -0.13802700
C          -0.05457900      2.81904507     -1.16514599
H          -0.38732901      2.84772110     -2.20030999
C           1.31203198      2.85289788     -0.88004303
H           2.03195190      2.89601803     -1.69399095
C          -2.48947406      2.67176008     -0.43820500
H          -2.65045810      2.87640095     -1.50460398
H          -3.01425409      3.46534801      0.10744100
========================================================
```

```
                      1                      2                      3
                      A                      A                      A
 Frequencies --     24.7263                26.1666                27.4043
 Red. masses --      3.9466                 4.2194                 3.7840
 Frc consts  --      0.0014                 0.0017                 0.0017
 IR Inten    --      0.0821                 0.0435                 0.0000

 Sum of electronic and zero-point Energies=          -1081.133635
 Sum of electronic and thermal Energies=             -1081.111981
 Sum of electronic and thermal Enthalpies=           -1081.111037
 Sum of electronic and thermal Free Energies=        -1081.186112

HF =  -1081.56990273
```

TS_11pm

```
========================================================
Element                 X                Y                Z
========================================================
C          -4.98532200     -1.19076896     -0.21488200
C          -3.58864594     -1.20366597     -0.09204000
C          -2.89597011      0.01470200     -0.11726400
C          -3.57425809      1.23341894     -0.26239499
C          -4.97109985      1.22135305     -0.37854800
C          -5.67332697      0.01524100     -0.35561600
H          -5.53466797     -2.12970209     -0.19720900
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H          -1.81528902     0.01529300    -0.02240700
H          -5.50918913     2.16045403    -0.48880300
H          -6.75630903     0.01534800    -0.44677401
C          -2.85417891     2.57902193    -0.31755799
H          -3.33516598     3.25310397     0.40294600
H          -3.03522301     3.02163792    -1.30601597
C          -2.89192700    -2.55225492     0.07398200
H          -3.28624392    -3.02930689     0.98042798
H          -3.20135498    -3.19753790    -0.75902897
C          -1.36565804     2.55473709    -0.05513500
C          -0.86317998     2.60926199     1.25008297
C          -0.44766501     2.46587801    -1.11238396
C           0.51396102     2.58801603     1.49183404
H          -1.55546403     2.66763210     2.08693790
C           0.92537397     2.44357395    -0.87193102
H          -0.81522298     2.41296101    -2.13464808
C           1.42882597     2.51193595     0.43551999
H           0.87945598     2.63312292     2.51523209
H           1.61844099     2.36237311    -1.70576501
C          -1.38154995    -2.53654194     0.14516400
C          -0.71505201    -2.60472393     1.37337601
C          -0.60591602    -2.46696806    -1.02314305
C           0.68240303    -2.62260294     1.43412495
H          -1.29264295    -2.65365791     2.29357195
C           0.78650397    -2.47981501    -0.96277398
H          -1.10241497    -2.40560293    -1.98887098
C           1.45416796    -2.56869411     0.26863301
H           1.17622995    -2.68562794     2.40116405
H           1.36709797    -2.42020202    -1.88040602
C           2.92595506     2.48042893     0.68242699
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H           3.36068797    -3.32677102    -0.36899900
C           3.59379601     1.21121001     0.17577900
C           3.02262092    -0.03777600     0.45060900
C           4.77658176     1.26124501    -0.57256401
C           3.60244989    -1.22701800    -0.00406800
H           2.08816409    -0.08056500     1.00356603
C           5.37025499     0.08195400    -1.03285301
H           5.22852516     2.22270894    -0.80471998
C           4.78545618    -1.15535700    -0.75359601
H           6.28248215     0.12920500    -1.62157595
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=========================================================

                      1                       2                       3
                      A                       A                       A
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 Frc consts  --      0.0016                 0.0004                 0.0014
 IR Inten    --      0.0297                 0.0400                 0.0072
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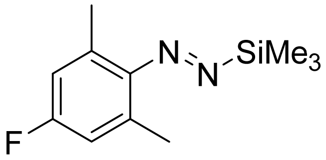
 Sum of electronic and thermal Enthalpies=           -1081.110659
 Sum of electronic and thermal Free Energies=        -1081.183412

HF =  -1081.56851930
```

8. Preparation of diazene **S3**

All the diazenes were synthesized according to a procedure we reported recently using di-*tert*-butyl azodicarboxylate as an oxidant. Diazene **S3** was not reported before and its synthesis has been carried out according to the following procedure.

8.1. Synthesis of (*E*)-1-(4-fluoro-2,6-dimethylphenyl)-2-(trimethylsilyl)diazene (**1o**)



S3

$C_{11}H_{17}FN_2Si$

224.35 g/mol

Following a reported literature procedure,[1] a single-neck round-bottom flask equipped with a magnetic stirring bar was charged in a glovebox with the corresponding silylated arylhydrazine (1.46 g, 6.43 mmol, 1.00 equiv) followed by dry *n*-pentane (0.5 M). To the resulting homogeneous, vigorously stirred solution was added portion–wise as a solid di-*tert*-butyl azodicarboxylate (DBAD, 1.44 g, 6.10 mmol, 0.950 equiv) at room temperature. The resulting suspension was further stirred 1 h at room temperature and the crude reaction mixture was then filtered over a fritted funnel. The blue filtrate was concentrated *in vacuo* to afford the crude silylated aryldiazene, which was then distilled under reduced pressure *via* a short path distillation (**b.p.**: 53–55 °C at 2.1×10^{-1} mbar) to afford the title compound **1o** (0.890 g, 3.97 mmol, 62%) as a deep blue liquid.

^{1}H NMR (500 MHz, CD_2Cl_2): δ/ppm = 0.38 (s, 9H), 2.17 (s, 3H), 6.78 (d, *J* = 9.4 Hz, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = –2.55 (3C), 18.3 (2C), 115.6 (d, *J* = 21.9 Hz, 2C), 131.7 (d, *J* = 9.5 Hz, 2C), 154.3 (d, *J* = 2.3 Hz), 161.7 (d, *J* = 245.9 Hz). **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2): δ/ppm = –116.5. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.38/12.6. **HRMS** (APCI) calculated for $C_{11}H_{18}FN_2Si^+$ [$(M+H)^+$]: 225.1218; found: 225.1215. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2962, 2928, 1589, 1502, 1377, 1297, 1248, 1124, 1020, 841.

9. General procedures (GP) for the silylarylation of carbonyl compounds

9.1. General procedure for the silylarylation of aldehydes (GPS1)

A 10-mL vial equipped with a magnetic stirring bar was charged with sodium trimethysilanolate (Me_3SiONa, 10 mol%, 4.5 mg), THF (1 mL) and the corresponding aldehyde (0.4 mmol, prior to adding the solvent when solid). To the resulting vigorously stirred mixture was then added dropwise a solution of the silylated aryldiazene (0.48 mmol, 1.2 equiv) in THF (1 mL) over 5 min. Nitrogen evolution starts almost instantaneously and generally ends within 5 min after the addition of the diazene is complete. When full conversion of the aldehyde was reached (usually < 5 min reaction time as judged by TLC or ^{1}H NMR analysis), the crude mixture was concentrated by rotary evaporation and the resulting crude residue was directly purified by flash column chromatography on silica gel.

9.2. General procedure for the silylarylation of ketones (GPS2)

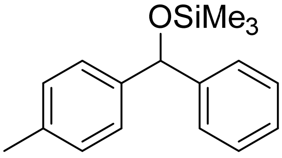
A 10-mL vial equipped with a magnetic stirring bar was charged with potassium trimethylsilanolate (Me_3SiOK, 10 mol%, 5.1 mg), THF (1 mL) and the corresponding ketone (0.400 mmol, prior to adding the solvent when solid). To the resulting vigorously stirred mixture was then added dropwise a solution of the silylated aryldiazene (0.48 mmol, 1.2 equiv) in THF (1 mL) over 5 min. Nitrogen evolution starts almost instantaneously and generally ends within 5 min after the addition of the diazene is complete. When full conversion of the ketone was reached (usually < 5 min reaction time as judged by TLC or ^{1}H NMR analysis), the crude mixture was concentrated by rotary evaporation and the resulting crude residue was directly purified by flash column chromatography on silica gel.

9.3. General procedure for the silylarylation of esters (GPS3)

A 10-mL vial equipped with a magnetic stirring bar was charged with Me_3SiOK (20 mol%, 7.7 mg), THF (1 mL) and the ester (0.30 mmol; prior to adding the solvent when solid). To the resulting vigorously stirred mixture is slowly added *via* a syringe pump (4 mL/h, 3 mL syringe, 9.65 mm diameter) a solution of the silylated aryldiazene (0.48 mmol, 3.0 equiv) in THF (2 mL) over 30 min. When full conversion of the ester was reached (usually 1 hour reaction time as judged by TLC or ^{1}H NMR analysis), the crude mixture was concentrated by rotary evaporation and the resulting crude residue was directly purified by flash column chromatography on silica gel.

10. Characterization data

Trimethyl(phenyl(*p*-tolyl)methoxy)silane (3aa)

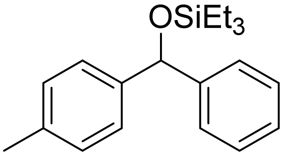


3aa
$C_{17}H_{22}OSi$
270.45 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (92 mg, 0.48 mmol, 1.2 equiv) and benzaldehyde (41 µL, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **3aa** (76 mg, 0.28 mmol, 70%) as a colorless liquid.

R_f = 0.54 (cyclohexane:*tert*-butyl methyl ether 99:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.07 (s, 9H), 2.31 (s, 3H), 5.75 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.19–7.24 (m, 3H), 7.29 (m_c, 2H), 7.34 (d, *J* = 8.0 Hz, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.13 (3C), 21.2, 76.7, 126.7 (2C), 126.7 (2C), 127.3, 128.5 (2C), 129.2 (2C), 137.1, 142.6, 145.7. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.07, 5.74/18.4. **HRMS** (APCI) calculated for $C_{17}H_{21}OSi^+$ [$(M–H)^+$]: 269.1356; found: 269.1357. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3025, 2954, 2861, 1491, 1450, 1249, 1188, 1084, 1061, 1023, 882, 834.

Triethyl(phenyl(*p*-tolyl)methoxy)silane (3ba)

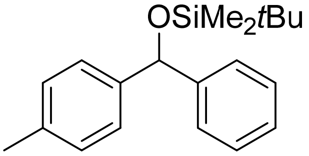


3ba
$C_{20}H_{28}OSi$
312.53 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (0.11 g, 0.48 mmol, 1.2 equiv) and benzaldehyde (41 µL, 0.40 mmol, 1.0 equiv) and using Me_3SiOK (5.1 mg, 40 µmol, 10 mol%) instead of Me_3SiONa as catalyst. Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **3ba** (95 mg, 0.30 mmol, 76%) as a colorless liquid.

R_f = 0.85 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.58 (q, *J* = 8.0 Hz, 6H), 0.89 (t, *J* = 8.0 Hz, 9H), 2.30 (s, 3H), 5.74 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.20 (tt, J = 7.3, 1.3 Hz, 1H), 7.24–7.31 (m, 4H), 7.37 (d, J = 8.0 Hz, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 5.19 (3C), 6.95 (3C), 21.2, 76.6, 126.5 (4C), 127.2, 128.5 (2C), 129.2 (2C), 137.1, 142.9, 146.1. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for J = 7 Hz): δ/ppm = 0.58, 0.89, 5.74/19.9. **HRMS** (APCI) calculated for $C_{20}H_{27}OSi^+$ [$(M–H)^+$]: 311.1826; found: 311.1826. **IR** (ATR): ṽ/cm^{-1} = 3024, 2952, 2910, 2874, 1510, 1452, 1412, 1237, 1188, 1084, 1062, 1004, 843.

tert-Butyldimethyl(phenyl(*p*-tolyl)methoxy)silane (3ca)

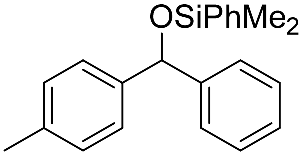


3ca
$C_{20}H_{28}OSi$
312.53 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (0.10 g, 0.44 mmol, 1.1 equiv) and benzaldehyde (41 µL, 0.40 mmol, 1.0 equiv) using Me_3SiOK (5.1 mg, 40 µmol, 10 mol%) as catalyst and 18-C-6 (10.6 mg, 40 µmol, 10 mol%) as ligand for potassium. Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **3ca** (85 mg, 0.30 mmol, 68%) as a colorless liquid.

R$_f$ = 0.84 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = –0.02 (s, 3H), –0.01 (s, 3H), 0.92 (s, 9H), 2.30 (s, 3H), 5.74 (s, 1H), 7.10 (d, J = 8.0 Hz, 2H), 7.19 (tt, J = 7.3, 1.9 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.28 (m_c, 2H), 7.35 (dd, J = 7.3, 1.9 Hz, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = –4.76, –4.72, 18.6, 21.2, 26.0 (3C), 76.9, 126.5 (4C), 127.2, 128.5 (2C), 129.2 (2C), 137.1, 142.9, 146.1. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for J = 7 Hz): δ/ppm = –0.02, –0.01, 0.92, 5.74/20.0. **HRMS** (APCI) calculated for $C_{20}H_{27}OSi^+$ [$(M–H)^+$]: 311.1826; found: 311.1828. **IR** (ATR): ṽ/cm^{-1} = 3060, 3025, 2952, 2927, 2884, 2855, 1511, 1462, 1359, 1251, 1189, 1084, 1063, 880, 832.

Dimethyl(phenyl)(phenyl(*p*-tolyl)methoxy)silane (3da)



3da

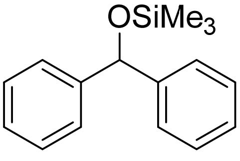
$C_{22}H_{24}OSi$

332.52 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (0.12 g, 0.48 mmol, 1.2 equiv) and benzaldehyde (41 µL, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **3da** (0.11 g, 0.34 mmol, 86%) as an orange oil.

R$_f$ = 0.52 (cyclohexane:*tert*-butyl methyl ether 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 0.29 (s, 6H), 2.31 (s, 3H), 5.73 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.18–7.22 (m, 3H), 7.25–7.29 (m, 2H), 7.30–7.36 (m, 4H), 7.39 (tt, *J* = 7.2, 2.5 Hz, 1H), 7.54 (dd, *J* = 8.0, 1.3 Hz, 2H). **^{13}C{1H} NMR** (126 MHz, $CDCl_3$): δ/ppm = –0.91, –0.88, 21.2, 76.8, 126.6 (2C), 126.7 (2C), 127.1, 127.9 (2C), 128.3 (2C), 129.0 (2C), 129.7, 133.8 (2C), 136.8, 138.0, 141.9, 145.0. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, optimized for *J* = 7 Hz): δ/ppm = 0.29, 5.73, 7.54/8.27. **HRMS** (APCI) calculated for $C_{22}H_{23}OSi^+$ [(M–H)$^+$]: 331.1513; found: 331.1507. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3023, 2955, 2860, 1510, 1491, 1450, 1426, 1251, 1188, 1115, 1058, 861.

(Benzhydryloxy)trimethylsilane (3ea)



3ea

$C_{16}H_{20}OSi$

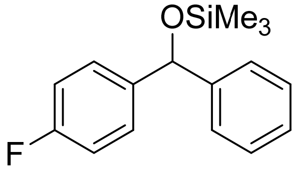
256.42 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (86 mg, 0.48 mmol, 1.2 equiv) and benzaldehyde (41 µL, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **3ea** (74 mg, 0.29 mmol, 72%) as a dark orange liquid.

R$_f$ = 0.58 (cyclohexane). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.08 (s, 9H), 5.78 (s, 1H), 7.22 (tt, *J* = 7.4, 1.5 Hz, 2H), 7.30 (m$_c$, 4H), 7.34–7.36 (m, 4H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.11 (3C), 76.9, 126.8 (4C), 127.4 (2C), 128.6 (4C), 145.5 (2C). **^{1}H,^{29}Si HMQC NMR**

(500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.08, 5.78/18.7. **HRMS** (APCI) calculated for $C_{16}H_{19}OSi^+$ [$(M–H)^+$]: 255.1200; found: 255.1200. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3061, 3027, 2955, 2863, 1598, 1491, 1451, 1249, 1186, 1088, 1060, 1025, 880, 834.

((4-Fluorophenyl)(phenyl)methoxy)trimethylsilane (3ia)



3ia

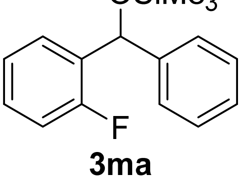
$C_{16}H_{19}FOSi$

274.41 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (94 mg, 0.48 mmol, 1.2 equiv) and benzaldehyde (41 µL, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **3ia** (0.11 g, 0.40 mmol, 99%) as a yellow liquid.

R$_f$ = 0.81 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.08 (s, 9H), 5.76 (s, 1H), 6.99 (m$_c$, 2H), 7.21 (tt, *J* = 7.3, 2.1 Hz, 1H), 7.27–7.32 (m, 2H), 7.32–7.38 (m, 4H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.09 (3C), 76.2, 115.3 (d, *J* = 22.4 Hz, 2C), 126.8 (2C), 127.6, 128.5 (d, *J* = 8.1 Hz, 2C), 128.7 (2C), 141.5 (d, *J* = 2.7 Hz), 145.3, 162.3 (d, *J* = 244.4 Hz). **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$): δ/ppm = –116.0. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.08, 5.76/18.9. **HRMS** (APCI) calculated for $C_{16}H_{19}FOSi^+$ [M^+]: 274.1184; found: 274.1187. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3063, 3028, 2956, 2864, 1603, 1506, 1451, 1250, 1220, 1185, 1155, 1061, 881, 836.

((2-Fluorophenyl)(phenyl)methoxy)trimethylsilane (3ma)



3ma

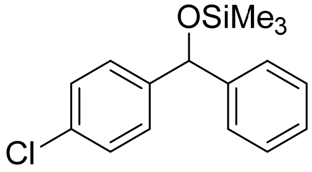
$C_{16}H_{19}FOSi$

274.41 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (94 mg, 0.48 mmol, 1.2 equiv) and benzaldehyde (41 µL, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **3ma** (71 mg, 0.26 mmol, 65%) as a pale orange liquid.

R$_f$ = 0.81 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.10 (s, 9H), 6.13 (s, 1H), 7.00 (m$_c$, 1H), 7.15 (m$_c$, 1H), 7.21–7.26 (m, 2H), 7.29–7.33 (m, 2H), 7.39 (m$_c$, 2H), 7.55 (m$_c$, 1H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = –0.02 (3C), 70.1 (d, *J* = 2.4 Hz), 115.4 (d, *J* = 23.0 Hz), 124.6 (d, *J* = 3.5 Hz), 126.7 (2C), 127.6, 128.4 (d, *J* = 4.7 Hz), 128.6 (2C), 129.1 (d, *J* = 8.3 Hz), 132.6 (d, *J* = 14.2 Hz), 144.4, 159.7 (d, *J* = 244.7 Hz). **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2): δ/ppm = –119.6. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.10, 6.13/19.6. **HRMS** (APCI) calculated for $C_{16}H_{18}FOSi^+$ [(M–H)$^+$]: 273.1105; found: 273.1107. **IR** (ATR): ṽ/cm^{-1} = 3067, 3032, 2957, 2898, 1586, 1485, 1454, 1251, 1224, 1190, 1108, 1060, 879, 836.

((4-Chlorophenyl)(phenyl)methoxy)trimethylsilane (3ja)

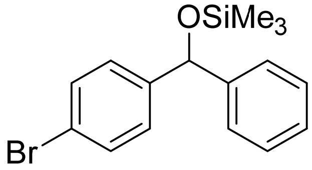


3ja
$C_{16}H_{19}ClOSi$
290.86 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (0.10 g, 0.48 mmol, 1.2 equiv) and benzaldehyde (41 µL, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **3ja** (94 mg, 0.32 mmol, 81%) as a red liquid.

R$_f$ = 0.57 (cyclohexane). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.07 (s, 9H), 5.75 (s, 1H), 7.20–7.25 (m, 1H), 7.26–7.33 (m, 8H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.08 (3C), 76.2, 126.8 (2C), 127.7, 128.2 (2C), 128.7 (2C), 128.7 (2C), 133.0, 144.2, 145.0. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.07, 5.75/19.1. **HRMS** (APCI) calculated for $C_{16}H_{18}ClOSi^+$ [(M–H)$^+$]: 289.0810; found: 289.0811. **IR** (ATR): ṽ/cm^{-1} = 3061, 3027, 2955, 2862, 1597, 1488, 1451, 1403, 1250, 1186, 1062, 1013, 880, 835.

((4-Bromophenyl)(phenyl)methoxy)trimethylsilane (3ka)

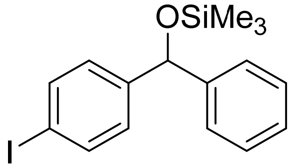


3ka
$C_{16}H_{19}BrOSi$
335.32 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (0.12 g, 0.48 mmol, 1.2 equiv) and benzaldehyde (41 µL, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (95:5) as eluent afforded the title compound **3ka** (0.12 g, 0.35 mmol, 87%) as a dark red liquid.

R$_f$ = 0.47 (cyclohexane). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.08 (s, 9H), 5.73 (s, 1H), 7.21–7.26 (m, 3H), 7.28–7.33 (m, 4H), 7.43 (m$_c$, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.08 (3C), 76.3, 121.1, 126.8 (2C), 127.7, 128.6 (2C), 128.7 (2C), 131.6 (2C), 144.7, 144.9. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.08, 5.73/19.2. **HRMS** (APCI) calculated for $C_{16}H_{19}BrOSi^+$ [M$^+$]: 334.0383; found: 334.0387. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3061, 3026, 2955, 2861, 1589, 1484, 1451, 1398, 1249, 1185, 1064, 1009, 880, 835.

((4-Iodophenyl)(phenyl)methoxy)trimethylsilane (3la)



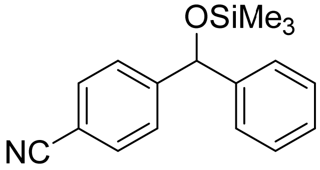
3la
$C_{16}H_{19}IOSi$
382.02 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (0.16 g, 0.48 mmol, 1.2 equiv, 90%) and benzaldehyde (41 µL, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **3la** (0.13 g, 0.33 mmol, 83%) as a purple liquid.

R$_f$ = 0.35 (cyclohexane). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.07 (s, 9H), 5.71 (s, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.20–7.32 (m, 5H), 7.63 (d, *J* = 8.4 Hz, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.07 (3C), 76.3, 92.6, 128.8 (2C), 127.7, 128.7 (2C), 128.8 (2C), 137.7 (2C), 144.9, 145.4. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.07, 5.71/19.3. **HRMS** (APCI) calculated for $C_{16}H_{19}IOSi^+$ [M$^+$]: 382.0244; found: 382.0246. **IR**

(ATR): $\tilde{\nu}$/cm^{-1} = 3060, 3026, 2954, 2895, 2859, 1585, 1480, 1450, 1395, 1249, 1187, 1062, 1004, 879, 835.

4-(Phenyl((trimethylsilyl)oxy)methyl)benzonitrile (3ha)



3ha

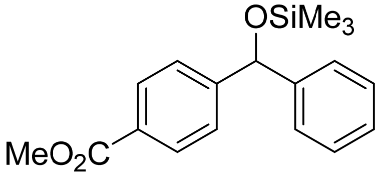
$C_{17}H_{19}NOSi$

281.43 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (98 mg, 0.48 mmol, 1.2 equiv) and benzaldehyde (41 µL, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (95:5) as eluent afforded the title compound **3ha** (81 mg, 0.29 mmol, 72%) as a colorless liquid.

R$_f$ = 0.54 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.07 (s, 9H), 5.79 (s, 1H), 7.22–7.28 (m, 1H), 7.31 (m$_c$, 4H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.02 (3C), 76.3, 111.2, 119.2, 126.9 (2C), 127.3 (2C), 128.0, 128.9 (2C), 132.5 (2C), 144.2, 150.7. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.07, 5.79/19.8. **HRMS** (APCI) calculated for $C_{17}H_{20}NOSi^+$ [(M+H)$^+$]: 282.1309; found: 282.1309. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3029, 2955, 2852, 2226, 1604, 1492, 1451, 1408, 1251, 1189, 1064, 1019, 878, 836.

Methyl 4-(phenyl((trimethylsilyl)oxy)methyl)benzoate (3ga)



3ga

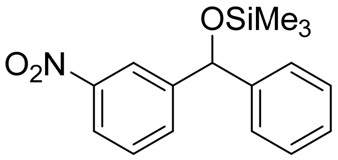
$C_{18}H_{22}O_3Si$

314.46 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (94 mg, 0.48 mmol, 1.2 equiv) and benzaldehyde (40.8 µL, 0.40 mmol, 1.00 equiv) and using $SiMe_3OK$ (5.1 mg, 40 µmol, 10 mol%) instead of $SiMe_3ONa$ as catalyst. Full conversion of the aldehyde was reached after 14 h. Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (97:3) as eluent afforded the title compound **3ga** (0.10 g, 0.32 mmol, 80%) as a pale yellow liquid.

R$_f$ = 0.55 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.08 (s, 9H), 3.87 (s, 3H), 5.82 (s, 1H), 7.23 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.27–7.36 (m, 4H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.08 (3C), 52.3, 76.6, 126.7 (2C), 126.9 (2C), 127.8, 128.8 (2C), 129.5, 129.9 (2C), 144.7, 150.5, 167.1. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.08, 5.82/19.3. **HRMS** (APCI) calculated for $C_{18}H_{23}O_3Si^+$ [(M+H)$^+$]: 315.1411; found: 315.1416. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3028, 2952, 2897, 1719, 1609, 1491, 1434, 1410, 1274, 1250, 1187, 1085, 1062, 1018, 878, 836.

Trimethyl((4-nitrophenyl)(phenyl)methoxy)silane (3na)



3na

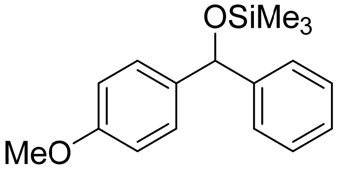
$C_{16}H_{19}NO_3Si$

301.42 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (0.12 g, 0.52 mmol, 1.3 equiv) and benzaldehyde (41 µL, 0.40 mmol, 1.0 equiv) and using $SiMe_3OK$ (5.1 mg, 40 µmol, 10 mol%) instead of $SiMe_3ONa$ as catalyst. Full conversion of the aldehyde was reached after 14 h. Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **3na** (81 mg, 0.27 mmol, 67%) as a yellow liquid.

R$_f$ = 0.25 (cyclohexane). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.10 (s, 9H), 5.86 (s, 1H), 7.26 (tt, *J* = 6.9, 1.8 Hz, 1H), 7.30–7.37 (m, 4H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.70 (m$_c$, 1H), 8.06 (m$_c$, 1H), 8.23 (m$_c$, 1H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.06 (3C), 76.1, 121.4, 122.4, 126.9 (2C), 128.1, 128.9 (2C), 129.6, 132.8, 144.2, 147.8, 148.8. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.10, 5.86/20.0. **HRMS** (APCI) calculated for $C_{16}H_{20}NO_3Si^+$ [(M+H)$^+$]: 302.1207; found: 302.1209. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3062, 3029, 2955, 2865, 1525, 1452, 1347, 1250, 1189, 1092, 1063, 892, 836.

((4-Methoxyphenyl)(phenyl)methoxy)trimethylsilane (3fa)



3fa

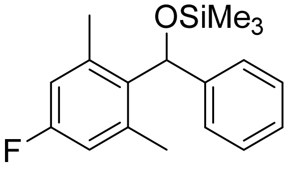
$C_{17}H_{22}O_2Si$

286.45 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (0.10 g, 0.48 mmol, 1.2 equiv) and benzaldehyde (41 µL, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **3fa** (94 mg, 0.33 mmol, 82%) as a yellow liquid.

R$_f$ = 0.71 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.07 (s, 9H), 3.77 (s, 3H), 5.74 (s, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 7.21 (tt, *J* = 7.2, 2.0 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.27–7.32 (m, 2H), 7.32–7.36 (m, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.13 (3C), 55.6, 76.4, 113.9 (2C), 126.7 (2C), 127.3, 128.1 (2C), 128.5 (2C), 137.7, 145.8, 159.2. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.07, 5.74/18.4. **HRMS** (APCI) calculated for $C_{17}H_{22}O_2Si^+$ [M$^+$]: 286.1384; found: 286.1384. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3026, 2953, 2900, 2834, 1609, 1509, 1451, 1300, 1244, 1170, 1060, 1031, 882, 835.

((4-Fluoro-2,6-dimethylphenyl)(phenyl)methoxy)trimethylsilane (3oa)



3oa

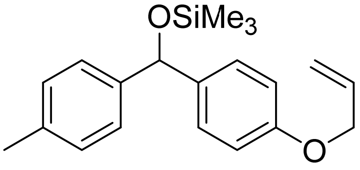
$C_{18}H_{23}FOSi$

302.46 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (0.11 g, 0.48 mmol, 1.2 equiv) and benzaldehyde (41 µL, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **3oa** (88 mg, 0.29 mmol, 73%) as a colorless liquid.

R$_f$ = 0.70 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.08 (s, 9H), 2.26 (s, 6H), 6.23 (s, 1H), 6.72 (m$_c$, 2H), 7.18–7.24 (m, 3H), 7.25–7.30 (m, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = –0.02 (3C), 21.0 (2C), 71.3, 115.6 (d, *J* = 19.9 Hz, 2C), 125.9 (2C), 126.8, 128.3 (2C), 136.7 (d, *J* = 5.9 Hz, 2C), 139.9 (d, *J* = 6.8 Hz), 144.3, 161.9 (d, *J* = 243.9 Hz). **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2): δ/ppm = –117.8. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.08, 6.23/17.7. **HRMS** (APCI) calculated for $C_{18}H_{23}FOSi^+$ [M$^+$]: 302.1497; found: 302.1500. **IR** (ATR): ṽ/cm^{-1} = 3059, 3027, 2955, 1600, 1476, 1447, 1297, 1249, 1173, 1126, 1061, 1024, 881, 835.

((4-(Allyloxy)phenyl)(*p*-tolyl)methoxy)trimethylsilane (3ec)

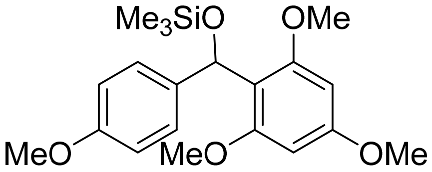


3ec
$C_{20}H_{26}O_2Si$
326.51 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (92 mg, 0.52 mmol, 1.3 equiv) and 4-allyloxybenzaldehyde (63 µL, 0.40 mmol, 1.00 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (98:2) as eluent afforded the title compound **3ec** (0.11 g, 0.33 mmol, 83%) as a dark orange liquid.

R$_f$ = 0.74 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.06 (s, 9H), 2.30 (s, 3H), 4.50 (m$_c$, 2H), 5.25 (m$_c$, 1H), 5.38 (m$_c$, 1H), 5.70 (s, 1H), 6.04 (m$_c$, 1H), 6.81–6.85 (m, 2H), 7.08–7.12 (m, 2H), 7.18–7.23 (m, 4H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.13 (3C), 21.2, 69.2, 76.3, 114.7 (2C), 117.5, 126.6 (2C), 128.0 (2C), 129.2 (2C), 134.0, 137.0, 138.1, 142.8, 158.1. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.06, 5.70/17.9. **HRMS** (APCI) calculated for $C_{20}H_{26}O_2Si^+$ [M$^+$]: 326.1697; found: 326.1692. **IR** (ATR): ṽ/cm^{-1} = 3020, 2954, 2859, 1609, 1506, 1456, 1422, 1300, 1245, 1170, 1064, 1020, 883, 834.

((4-Methoxyphenyl)(2,4,6-trimethoxyphenyl)methoxy)trimethylsilane (3fb)

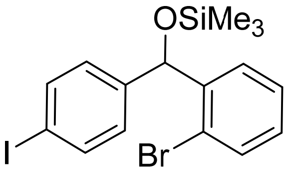


3fb
$C_{20}H_{28}O_5Si$
376.52 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (0.10 g, 0.48 mmol, 1.2 equiv) and 2,4,6-trimethoxybenzaldehyde (80 mg, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (9:1) as eluent afforded the title compound **3fb** (0.13 g, 0.36 mmol, 89%) as a yellow liquid.

R$_f$ = 0.33 (cyclohexane:*tert*-butyl methyl ether 7:3). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.03 (s, 9H), 3.69 (s, 6H), 3.75 (s, 3H), 3.79 (s, 3H), 6.11 (s, 2H), 6.36 (s, 1H), 6.78 (d, *J* = 8.9 Hz, 2H), 7.22 (d, *J* = 8.9 Hz, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = –0.03 (3C), 55.5, 55.6, 56.1 (2C), 66.8, 91.7 (2C), 113.0 (2C), 114.1, 127.0 (2C), 138.2, 158.2, 159.7 (2C), 161.3. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.03, 6.36/16.4. **HRMS** (APCI) calculated for $C_{20}H_{28}O_5Si^+$ [M$^+$]: 376.1701; found: 376.1694. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2997, 2952, 2903, 2835, 1558, 1508, 1455, 1416, 1242, 1202, 1148, 1117, 1034, 887, 835.

((2-Bromophenyl)(4-iodophenyl)methoxy)trimethylsilane (3lf)



3lf

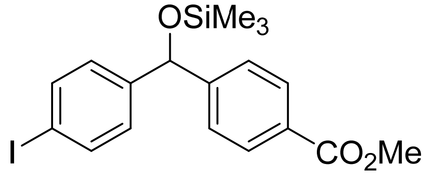
$C_{16}H_{18}BrIOSi$

461.21 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (0.16 g, 0.48 mmol, 1.2 equiv, 90%) and 2-bromobenzaldehyde (48 µL, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **3lf** (0.12 g, 0.26 mmol, 65%) as a red solid.

R$_f$ = 0.27 (cyclohexane). **M.p.**: 56–60 °C (dichloromethane). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.08 (s, 9H), 6.12 (s, 1H), 7.11–7.17 (m, 3H), 7.31–7.35 (m, 1H), 7.51 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.58 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.06 (3C), 74.6, 92.9, 122.3, 128.2, 129.2 (3C), 129.4, 132.9, 137.7 (2C), 143.8, 143.9. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.08, 6.12/19.8. **HRMS** (APCI) calculated for $C_{16}H_{18}BrIOSi^+$ [M$^+$]: 459.9349; found: 459.9346. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3057, 2954, 2910, 1585, 1461, 1437, 1399, 1367, 1248, 1183, 1055, 1005, 875, 835.

Methyl 4-((4-iodophenyl)((trimethylsilyl)oxy)methyl)benzoate (3lg)



3lg

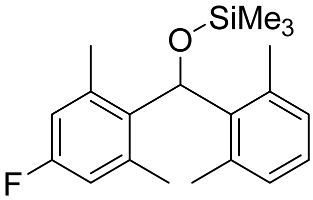
$C_{18}H_{21}IO_3Si$

440.35 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (0.16 g, 0.48 mmol, 1.2 equiv, 90%) and methyl 4-formylbenzoate (68 mg, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (98:2) as eluent afforded the title compound **3lg** (99 mg, 0.22 mmol, 56%) as a dark orange liquid.

R$_f$ = 0.52 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.08 (s, 9H), 3.86 (s, 3H), 5.75 (s, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.05 (3C), 52.3, 76.0, 93.0, 126.7 (2C), 128.9 (2C), 129.7, 130.0 (2C), 137.8 (2C), 144.6, 149.9, 167.0. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.08, 5.75/20.0. **HRMS** (APCI) calculated for $C_{18}H_{22}IO_3Si^+$ [(M+H)$^+$]: 441.0377; found: 441.0372. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2950, 2895, 2863, 1718, 1609, 1577, 1481, 1434, 1411, 1274, 1249, 1187, 1107, 1072, 1005, 877, 836.

((2,6-Dimethylphenyl)(4-fluoro-2,6-dimethylphenyl)methoxy)trimethylsilane (3od)



3od

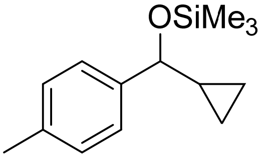
$C_{20}H_{27}FOSi$

330.52 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (0.11 g, 0.48 mmol, 1.2 equiv) and 2,6-dimethylbenzaldehyde (55 mg, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **3od** (79 mg, 0.24 mmol, 60%) as a pale yellow liquid.

R$_f$ = 0.84 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.02 (s, 9H), 2.24 (s, 12H), 6.40 (s, 1H), 6.67 (m$_c$, 2H), 6.93 (d, *J* = 7.4 Hz, 2H), 7.03 (t, *J* = 7.4 Hz, 1H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.56 (3C), 22.0 (4C), 73.4, 116.1 (d, *J* = 19.9 Hz, 2C,), 127.3, 130.2 (2C), 136.5 (d, *J* = 2.8 Hz), 137.3 (2C), 140.0 (d, *J* = 7.1 Hz, 2C), 140.1, 161.5 (d, *J* = 243.7 Hz). **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2): δ/ppm = –118.9. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.02, 6.40/15.1. **HRMS** (APCI) calculated for $C_{20}H_{27}FOSi^+$ [M^+]: 330.1810; found: 330.1813. **IR** (ATR): ṽ/cm^{-1} = 3061, 2957, 1599, 1474, 1293, 1249, 1163, 1127, 1078, 1023, 875, 834.

(Cyclopropyl(*p*-tolyl)methoxy)trimethylsilane (3ak)

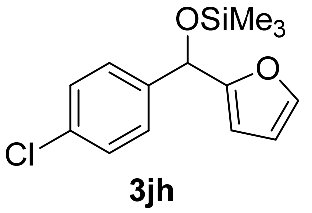


3ak
$C_{14}H_{22}OSi$
234.41 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (92 mg, 0.48 mmol, 1.2 equiv) and cyclopropanecarboxaldehyde (28 mg, 0.40 mmol, 1.0 equiv). The crude residue was purified by filtration over a pad of silica gel eluted with *tert*-butyl methyl ether that afforded the title compound **3ak** (84 mg, 0.36 mmol, 90%) as an orange liquid.

^{1}H NMR (500 MHz, CD_2Cl_2): δ/ppm = 0.03 (s, 9H), 0.27–0.33 (m, 1H), 0.39–0.44 (m, 2H), 0.47–0.54 (m, 1H), 1.05–1.13 (m, 1H), 2.33 (s, 3H), 4.08 (d, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.28 (3C), 2.75, 3.80, 20.2, 21.2, 78.2, 126.3 (2C), 129.1 (2C), 137.0, 142.8. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.03, 4.08/16.5. **HRMS** (APCI) calculated for $C_{14}H_{21}OSi^+$ [$(M–H)^+$]: 233.1356; found: 233.1354. **IR** (ATR): ṽ/cm^{-1} = 3080, 3006, 2955, 2860, 1511, 1249, 1131, 1053, 1017, 947, 877, 835.

((4-Chlorophenyl)(furan-2-yl)methoxy)trimethylsilane (3jh)

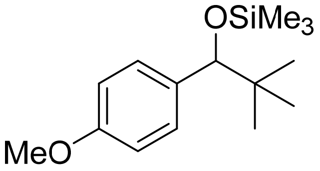


3jh
$C_{14}H_{17}ClO_2Si$
280.82 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (0.10 g, 0.48 mmol, 1.2 equiv) and furfural (34 µL, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (95:5) as eluent afforded the title compound **3jh** (82 mg, 0.29 mmol, 73%) as a dark orange liquid.

R$_f$ = 0.75 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.10 (s, 9H), 5.76 (s, 1H), 6.10 (d, *J* = 3.3 Hz, 1H), 6.31 (dd, *J* = 3.3, 1.9 Hz, 1H), 7.31–7.37 (m, 5H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = –0.11 (3C), 69.9, 107.6, 110.6, 128.3 (2C), 128.7 (2C), 133.5, 141.0, 142.7, 156.6. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.10, 5.76/20.0. **HRMS** (APCI) calculated for $C_{14}H_{17}ClO_2Si^+$ [M$^+$]: 280.0681; found: 280.0684. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2956, 1596, 1489, 1404, 1250, 1142, 1066, 1012, 876, 836.

(1-(4-Methoxyphenyl)-2,2-dimethylpropoxy)trimethylsilane (3fl)



3fl

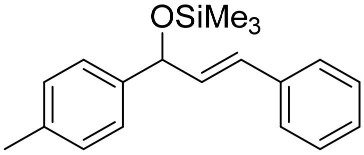
$C_{15}H_{26}O_2Si$

266.46 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (0.10 g, 0.48 mmol, 1.2 equiv) and pivalaldehyde (46 µL, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (98:2) as eluent afforded the title compound **3fl** (83 mg, 0.31 mmol, 76%) as an orange liquid.

R$_f$ = 0.28 (cyclohexane). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = –0.05 (s, 9H), 0.83 (s, 9H), 3.78 (s, 3H), 4.24 (s, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.03 (3C), 26.1 (3C), 36.4, 55.5, 82.6, 112.8 (2C), 129.3 (2C), 135.4, 159.0. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = –0.05, 4.24/16.4. **HRMS** (APCI) calculated for $C_{15}H_{25}O_2Si^+$ [(M–H)$^+$]: 265.1618; found: 265.1614. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2952, 2904, 2866, 1611, 1510, 1462, 1390, 1359, 1286, 1244, 1172, 1110, 1070, 1038, 883, 828.

(*E*)-Trimethyl((3-phenyl-1-(*p*-tolyl)allyl)oxy)silane (3ai)



3ai

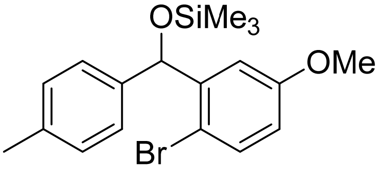
$C_{19}H_{24}OSi$

296.49 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (92 mg, 0.48 mmol, 1.2 equiv) and *trans*-cinnamaldehyde (50 µL, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **3ai** (87 mg, 0.29 mmol, 73%) as a dark orange liquid.

R$_f$ = 0.81 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.14 (s, 9H), 2.34 (s, 3H), 5.33 (d, *J* = 6.5 Hz, 1H), 6.30 (dd, *J* = 15.8, 6.5 Hz, 1H), 6.61 (d, *J* = 15.8 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.22 (tt, *J* = 7.3, 1.9 Hz, 1H), 7.27–7.32 (m, 4H), 7.38 (d, *J* = 8.0 Hz, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.32 (3C), 21.2, 75.7, 126.6 (2C), 126.8 (2C), 127.9, 128.9 (2C), 129.2, 129.3 (2C), 133.5, 137.4, 137.4, 141.2. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.14, 5.33/18.1. **HRMS** (APCI) calculated for $C_{19}H_{23}OSi^+$ [(M–H)$^+$]: 295.1513; found: 295.1512. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3024, 2954, 2858, 1598, 1510, 1447, 1301, 1249, 1097, 1055, 964, 887, 835.

((2-Bromo-5-methoxyphenyl)(*p*-tolyl)methoxy)trimethylsilane (3ae)



3ae

$C_{18}H_{23}BrO_2Si$

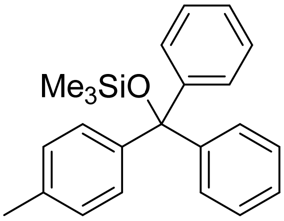
379.37 g/mol

Prepared according to **GPS1** from the corresponding silylated aryldiazene (0.74 g, 3.8 mmol, 1.2 equiv) and 2-bromo-5-methoxybenzaldehyde (0.69 g, 3.2 mmol, 1.0 equiv) using Me_3SiONa (18.0 mg, 0.16 mmol, **5 mol%**) as catalyst. Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **3ae** (0.69 g, 1.8 mmol, 57%) as an orange oil.

Note: No exotherm was noticed upon dropwise addition of diazene **1a** on that larger scale.

R$_f$ = 0.26 (cyclohexane:*tert*-butyl methyl ether 99:1). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ/ppm = 0.11 (s, 9H), 2.32 (s, 3H), 3.79 (s, 3H), 6.08 (s, 1H), 6.71 (dd, *J* = 8.7, 3.1 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 3.1 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 1H). **^{13}C{1H} NMR** (101 MHz, CD_2Cl_2): δ/ppm = 0.15 (3C), 21.2, 55.8, 75.1, 112.6, 114.6, 115.1, 127.3 (2C), 129.2 (2C), 133.5, 137.5, 140.7, 145.4, 159.8. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.11/19.0. **HRMS** (APCI) calculated for $C_{18}H_{23}BrO_2Si^+$ [M$^+$]: 378.0645; found: 378.0637. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3002, 2953, 2834, 1592, 1510, 1465, 1413, 1249, 1227, 1158, 1128, 1070, 1013, 880, 837.

(Diphenyl(*p*-tolyl)methoxy)trimethylsilane (7aa)

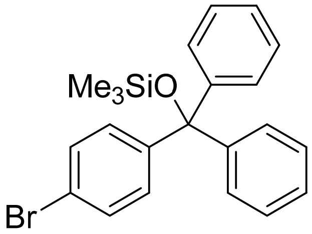


7aa
$C_{23}H_{26}OSi$
346.55 g/mol

Prepared according to **GPS2** from the corresponding silylated aryldiazene (92 mg, 0.48 mmol, 1.2 equiv) and benzophenone (73 mg, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the title compound **7aa** (95 mg, 0.27 mmol, 69%) as a colorless liquid.

R$_f$ = 0.82 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = –0.16 (s, 9H), 2.32 (s, 3H), 7.10 (d, *J* = 8.3 Hz, 2H), 7.23 (tt, *J* = 7.3, 2.3 Hz, 2H), 7.26–7.30 (m, 6H), 7.40–7.44 (m, 4H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 1.72 (3C), 21.1, 84.7, 127.2 (2C), 128.0 (4C), 128.7 (4C), 128.7 (2C), 128.8 (2C), 137.1, 144.5, 147.8 (2C). **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = –0.16/12.0. **HRMS** (APCI) calculated for $C_{23}H_{26}OSi^+$ [M$^+$]: 346.1747; found: 346.1742. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3057, 3023, 2953, 1596, 1489, 1445, 1404, 1249, 1219, 1159, 1067, 1031, 883, 834.

((4-Bromophenyl)diphenylmethoxy)trimethylsilane (7ka)

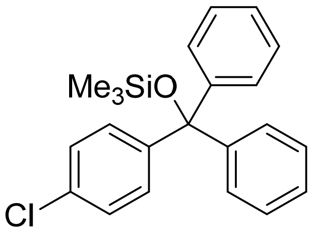


7ka
$C_{22}H_{23}BrOSi$
411.41 g/mol

Prepared according to **GPS2** from the corresponding silylated aryldiazene (0.12 g, 0.48 mmol, 1.2 equiv) and benzophenone (73 mg, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the title compound **7ka** (0.13 g, 0.32 mmol, 79%) as a pale yellow solid.

R_f = 0.85 (cyclohexane:*tert*-butyl methyl ether 9:1). **M.p.**: 79–83 °C (dichloromethane). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = –0.15 (s, 9H), 7.25 (tt, *J* = 7.1, 3.0 Hz, 2H), 7.30 (m_c, 4H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.38–7.44 (m, 6H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 1.71 (3C), 84.6, 121.2, 127.6 (2C), 128.2 (4C), 128.8 (4C), 130.4 (2C), 131.1 (2C), 146.9 (2C), 147.1. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = –0.15/12.5. **HRMS** (APCI) calculated for $C_{22}H_{23}BrOSi^+$ [M$^+$]: 410.0696; found: 410.0695. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3052, 3024, 2952, 2923, 2852, 1579, 1483, 1443, 1389, 1317, 1248, 1207, 1160, 1068, 1032, 1007, 907, 876, 834, 813.

((4-Chlorophenyl)diphenylmethoxy)trimethylsilane (7ja)

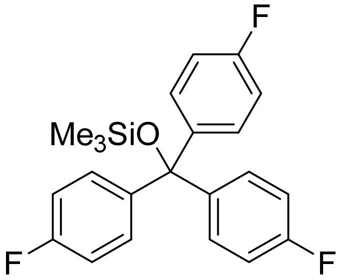


7ja
$C_{22}H_{23}ClOSi$
366.96 g/mol

Prepared according to **GPS2** from the corresponding silylated aryldiazene (0.10 g, 0.48 mmol, 1.2 equiv) and benzophenone (73 mg, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (98:2) as eluent afforded the title compound **7ja** (71 mg, 0.20 mmol, 49%) as a colorless liquid.

R$_f$ = 0.84 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = –0.15 (s, 9H), 7.22–7.32 (m, 8H), 7.37–7.41 (m, 6H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 1.71 (3C), 84.5, 127.5 (2C), 128.1 (2C), 128.2 (4C), 128.8 (4C), 130.1 (2C), 133.0, 146.6, 147.0 (2C). **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = –0.15/12.4. **HRMS** (APCI) calculated for $C_{22}H_{23}ClOSi^+$ [M$^+$]: 366.1201; found: 366.1198. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3058, 3028, 2953, 2895, 1595, 1486, 1445, 1397, 1249, 1213, 1162, 1068, 1013, 881, 835.

Trimethyl(tris(4-fluorophenyl)methoxy)silane (7ib)

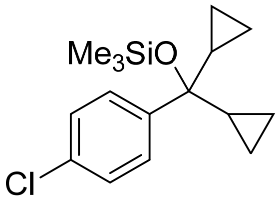


7ib
$C_{22}H_{21}F_3OSi$
386.49 g/mol

Prepared according to **GPS2** from the corresponding silylated aryldiazene (87 mg, 0.48 mmol, 1.2 equiv) and 4,4'-difluorobenzophenone (87 mg, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **7ib** (0.12 g, 0.31 mmol, 76%) as a white solid.

R$_f$ = 0.81 (cyclohexane:*tert*-butyl methyl ether 9:1). **M.p.**: 78–82 °C (dichloromethane). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = –0.14 (s, 9H), 7.00 (m$_c$, 6H), 7.36 (m$_c$, 6H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 1.72 (3C), 83.8, 114.9 (d, *J* = 21.6 Hz, 6C), 130.4 (d, *J* = 7.8 Hz, 6C), 143.2 (d, *J* = 3.0 Hz, 3C), 162.3 (d, *J* = 245.9 Hz, 3C). **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$): δ/ppm = –116.6. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = –0.14/12.7. **HRMS** (APCI) calculated for $C_{22}H_{21}F_3OSi^+$ [M$^+$]: 386.1308; found: 386.1305. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3064, 2968, 2898, 1598, 1499, 1406, 1251, 1219, 1156, 1070, 1013, 884, 833.

((4-Chlorophenyl)dicyclopropylmethoxy)trimethylsilane (7jd)

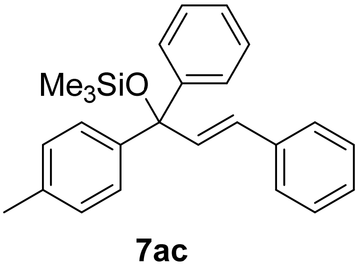


7jd
$C_{16}H_{23}ClOSi$
294.89 g/mol

Prepared according to **GPS2** from the corresponding silylated aryldiazene (77 mg, 0.36 mmol, 1.2 equiv) and dicyclopropylmethanone (34 µL, 0.30 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the title compound **7jd** (48 mg, 0.16 mmol, 54%) as a yellow liquid.

R$_f$ = 0.40 (cyclohexane). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 0.08 (s, 9H), 0.26–0.32 (m, 2H), 0.49–0.58 (m, 4H), 0.60–0.66 (m, 2H), 0.97–1.05 (m, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 0.92 (2C), 2.36 (3C), 3.54 (2C), 20.4 (2C), 77.6, 127.9 (2C), 128.0 (2C), 132.4, 148.5. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.08/10.7. **HRMS** (APCI) calculated for $C_{16}H_{22}ClOSi^+$ [(M–H)$^+$]: 293.1123; found: 293.1116. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3086, 3008, 2955, 2925, 2853, 1485, 1397, 1249, 1134, 1067, 1024, 973, 933, 876, 835.

(*E*)-((1,3-Diphenyl-1-(*p*-tolyl)allyl)oxy)trimethylsilane (7ac)

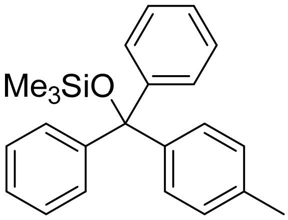


7ac
$C_{25}H_{28}OSi$
372.58 g/mol

Prepared according to **GPS2** from the corresponding silylated aryldiazene (92 mg, 0.48 mmol, 1.2 equiv) and *trans*-chalcone (86 mg, 0.40 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **7ac** (96 mg, 0.26 mmol, 65%) as a yellow oil.

R$_f$ = 0.88 (cyclohexane:*tert*-butyl methyl ether 9:1).**^{1}H NMR** (400 MHz, CD_2Cl_2): δ/ppm = 0.00 (s, 9H), 2.33 (s, 3H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.82 (d, *J* = 15.8 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.23 (tt, *J* = 7.3, 2.4 Hz, 2H), 7.26–7.34 (m, 6H), 7.38–7.42 (m, 4H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 2.18 (3C), 21.1, 82.2, 127.0 (2C), 127.3, 127.8 (2C), 127.9 (2C), 128.0, 128.2 (2C), 128.9 (2C), 129.0 (2C), 130.5, 136.3, 137.2, 137.3, 144.1, 147.4. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = 0.00/12.7. **HRMS** (APCI) calculated for $C_{25}H_{28}OSi^+$ [M$^+$]: 372.1904; found: 372.1904. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3056, 3024, 2953, 1598, 1491, 1445, 1249, 1134, 1055, 1016, 892, 834.

(Diphenyl(*p*-tolyl)methoxy)trimethylsilane (9ea)

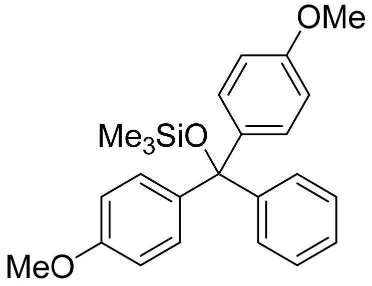


9ea
$C_{23}H_{26}OSi$
346.55 g/mol

Prepared according to **GPS3** from the corresponding silylated aryldiazene (0.19 g, 0.90 mmol, 3.0 equiv) and methyl *p*-toluate (45 mg, 0.30 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the title compound **9ea** (75 mg, 0.22 mmol, 73%) as a colorless liquid.

The NMR spectroscopic and mass spectrometric data were in accordance with those of title compound **7aa** synthesized from the (*E*)-1-(*p*-tolyl)-2-(trimethylsilyl)diazene and benzophenone.

(Bis(4-methoxyphenyl)(phenyl)methoxy)trimethylsilane (9fb)



9fb

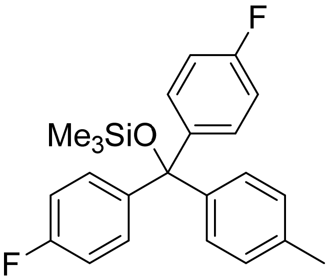
$C_{24}H_{28}O_3Si$

392.57 g/mol

Prepared according to **GPS3** from the corresponding silylated aryldiazene (0.19 g, 0.90 mmol, 3.0 equiv) and methyl benzoate (38 µL, 0.30 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (99:1) as eluent afforded the title compound **9fb** (77 mg, 0.20 mmol, 67%) as a yellow oil.

R_f = 0.65 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = –0.15 (s, 9H), 3.78 (s, 6H), 6.81 (d, *J* = 8.8 Hz, 4H), 7.21 (tt, *J* = 7.4, 2.3 Hz, 1H), 7.24–7.32 (m, 6H), 7.42 (m_c, 2H). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ/ppm = 1.74 (3C), 55.6 (2C), 84.2, 113.2 (4C), 126.9, 127.9 (2C), 128.2 (2C), 130.1 (4C), 139.8 (2C), 148.4, 159.0 (2C). **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = –0.15/11.3. **HRMS** (APCI) calculated for $C_{24}H_{27}O_3Si^+$ [(M–H)$^+$]: 391.1724; found: 391.1714. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2999, 2952, 2899, 2833, 1606, 1504, 1442, 1410, 1298, 1245, 1172, 1066, 1032, 885, 829.

(Bis(4-fluorophenyl)(*p*-tolyl)methoxy)trimethylsilane (9ia)



9ia

$C_{23}H_{24}F_2OSi$

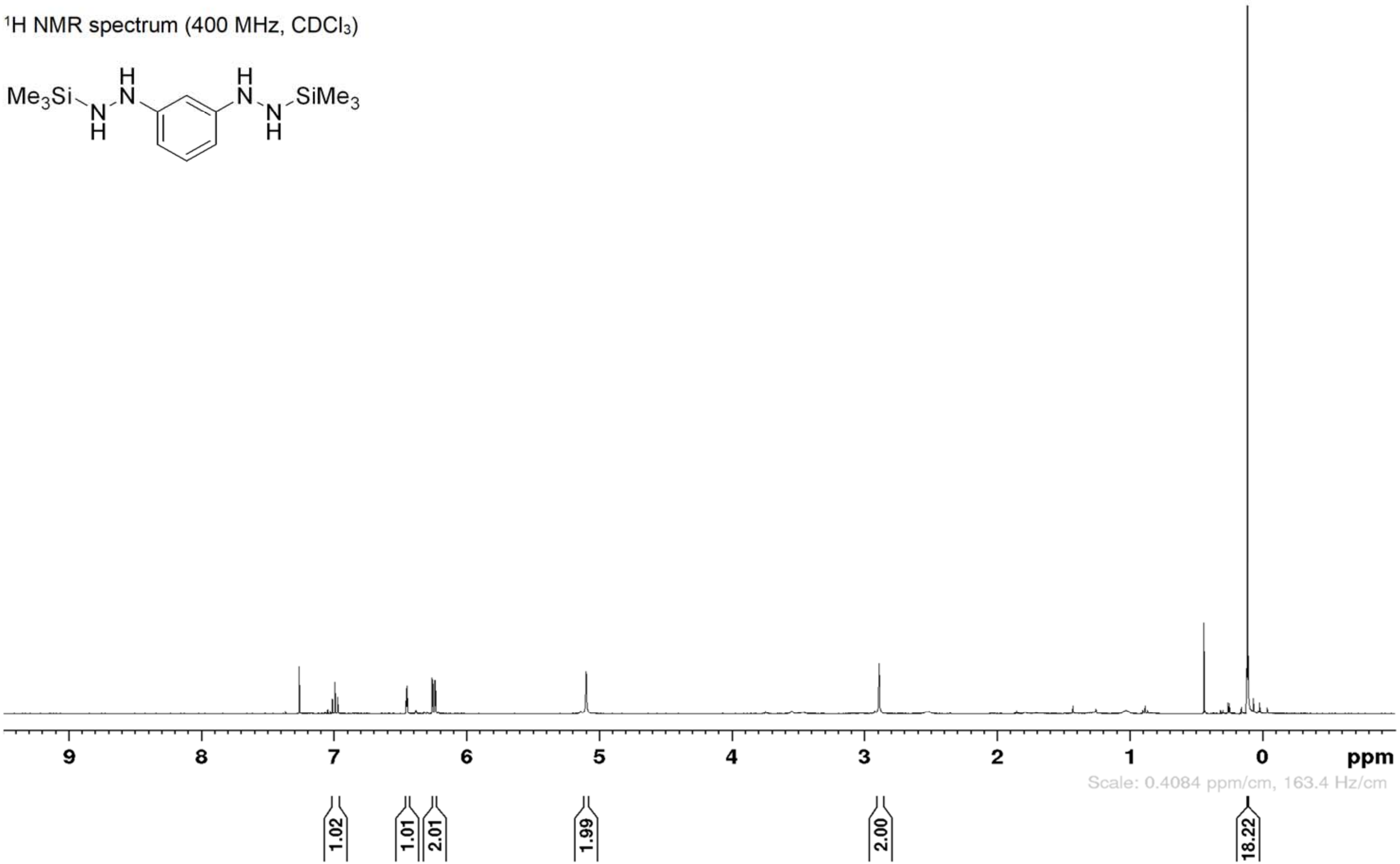
382.53 g/mol

Prepared according to **GPS3** from the corresponding silylated aryldiazene (0.19 g, 0.90 mmol, 3.0 equiv) and methyl *p*-toluate (45 mg, 0.30 mmol, 1.0 equiv). Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the title compound **9ia** (78 mg, 0.20 mmol, 68%) as a yellow liquid.

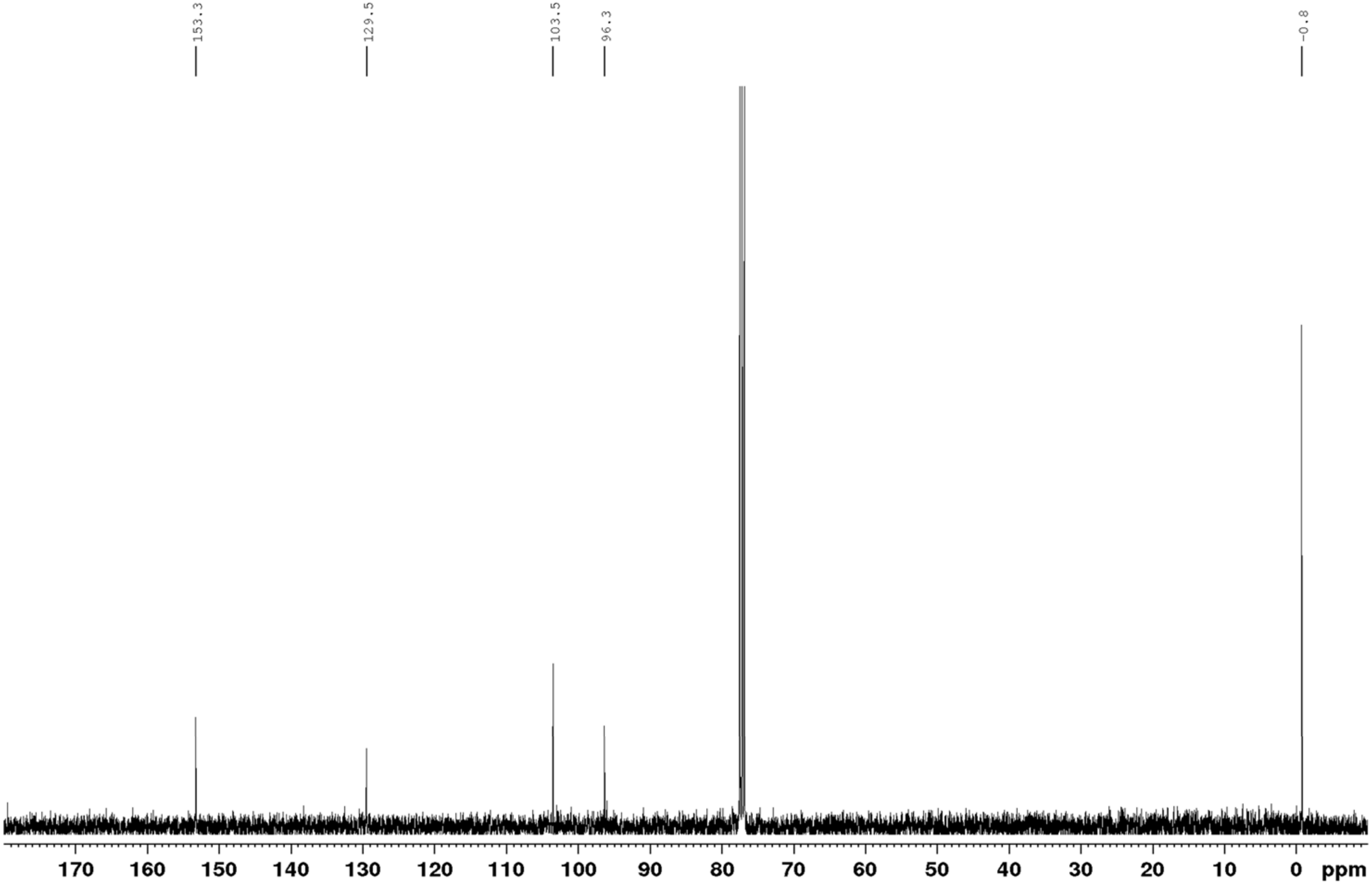
R$_f$ = 0.77 (cyclohexane:*tert*-butyl methyl ether 9:1). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ/ppm = –0.15 (s, 9H), 2.32 (s, 3H), 6.94–7.02 (m, 4H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.34–7.41 (m, 4H). **^{13}C{1H} NMR** (101 MHz, CD_2Cl_2): δ/ppm = 1.70 (3C), 21.1, 83.9, 114.7 (d, *J* = 21.5 Hz, 4C), 128.5 (2C), 128.8 (2C), 130.3 (d, *J* = 8.0 Hz, 4C), 137.4, 143.7 (d, *J* = 3.4 Hz, 2C), 144.1, 162.2 (d, *J* = 245.5 Hz, 2C). **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2): δ/ppm = –117.0. **^{1}H,^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, optimized for *J* = 7 Hz): δ/ppm = –0.14/12.2. **HRMS** (APCI) calculated for $C_{23}H_{24}F_2OSi^+$ [M$^+$]: 382.1559; found: 382.1559. **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 3024, 2954, 1600, 1501, 1452, 1406, 1250, 1223, 1156, 1075, 1014, 923, 886, 832.

1,3-Bis(2-(trimethylsilyl)hydrazineyl)benzene

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

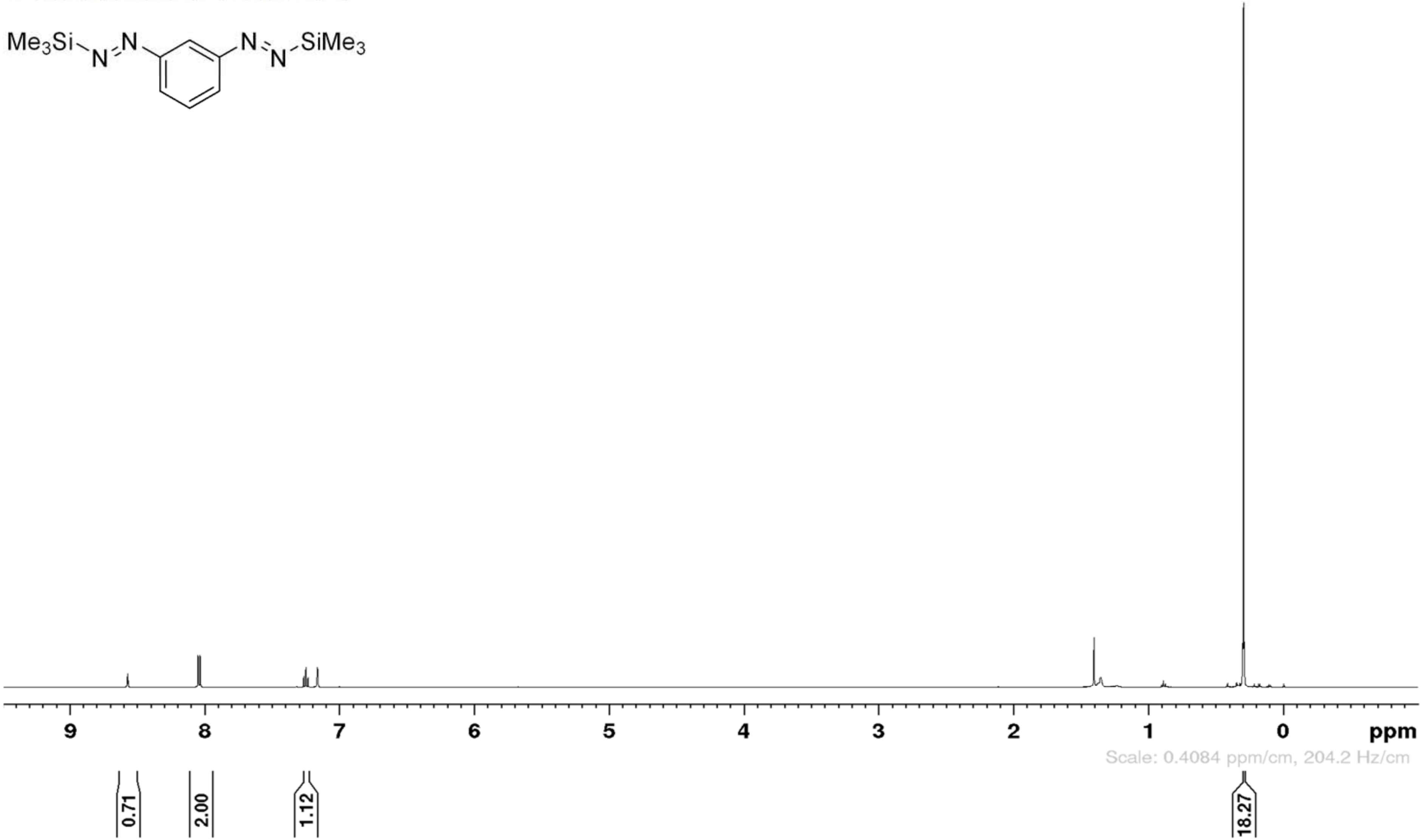


$^{13}C\{^{1}H\}$ NMR (101 MHz, CDCl$_3$)

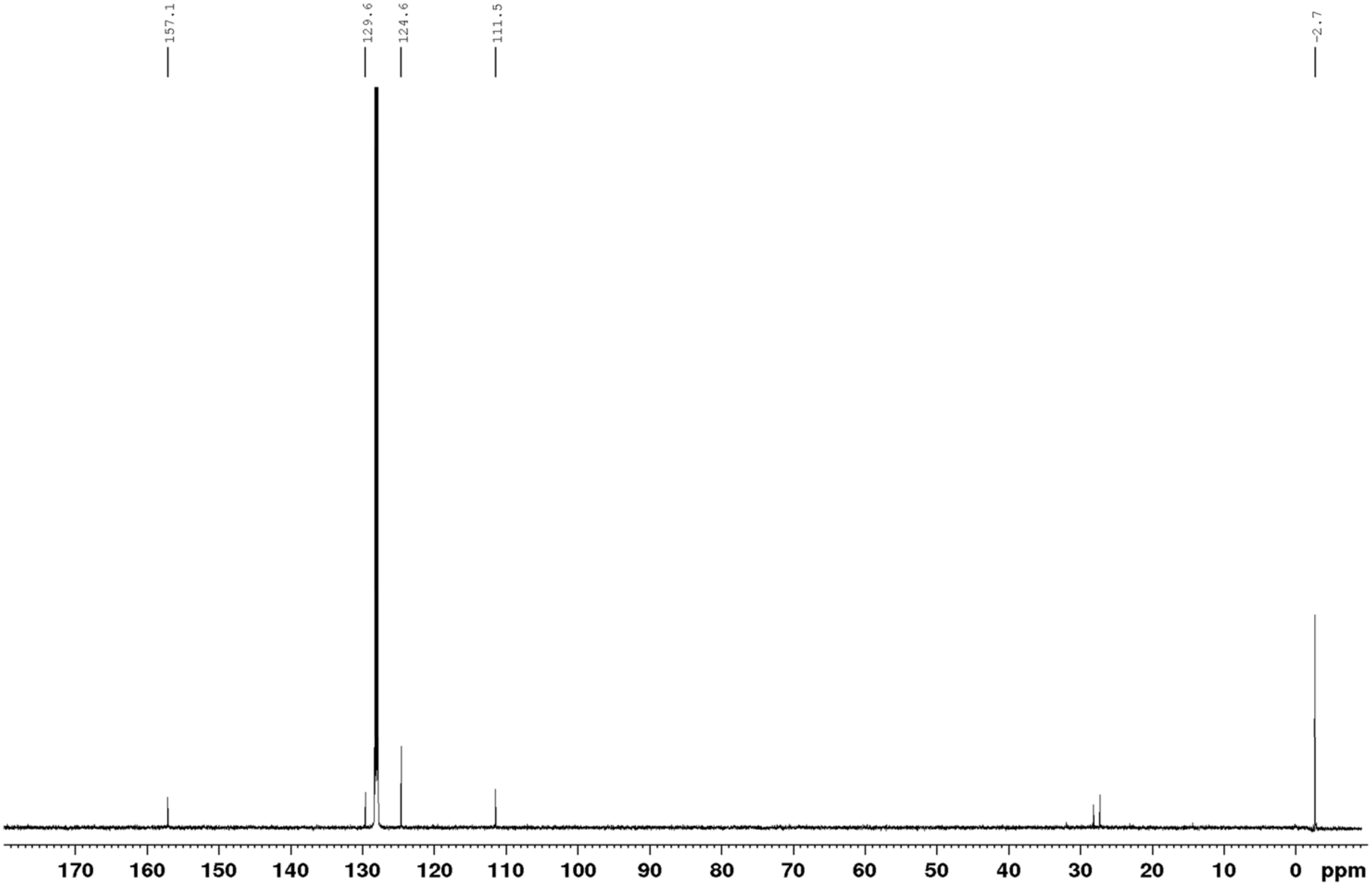


1,3-Bis((*E*)-(trimethylsilyl)diazenyl)benzene

^{1}H NMR spectrum (500 MHz, C_6D_6)

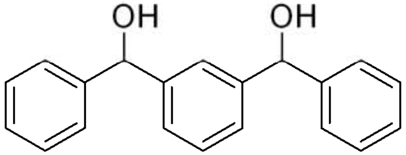


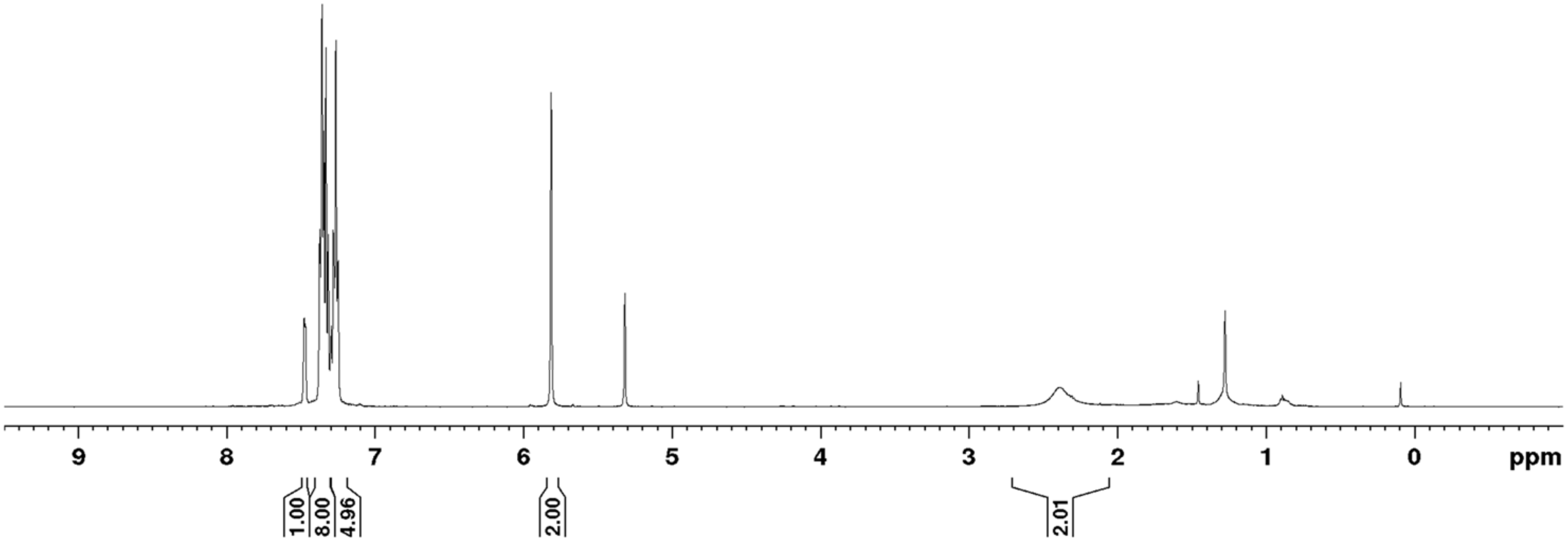
$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6)



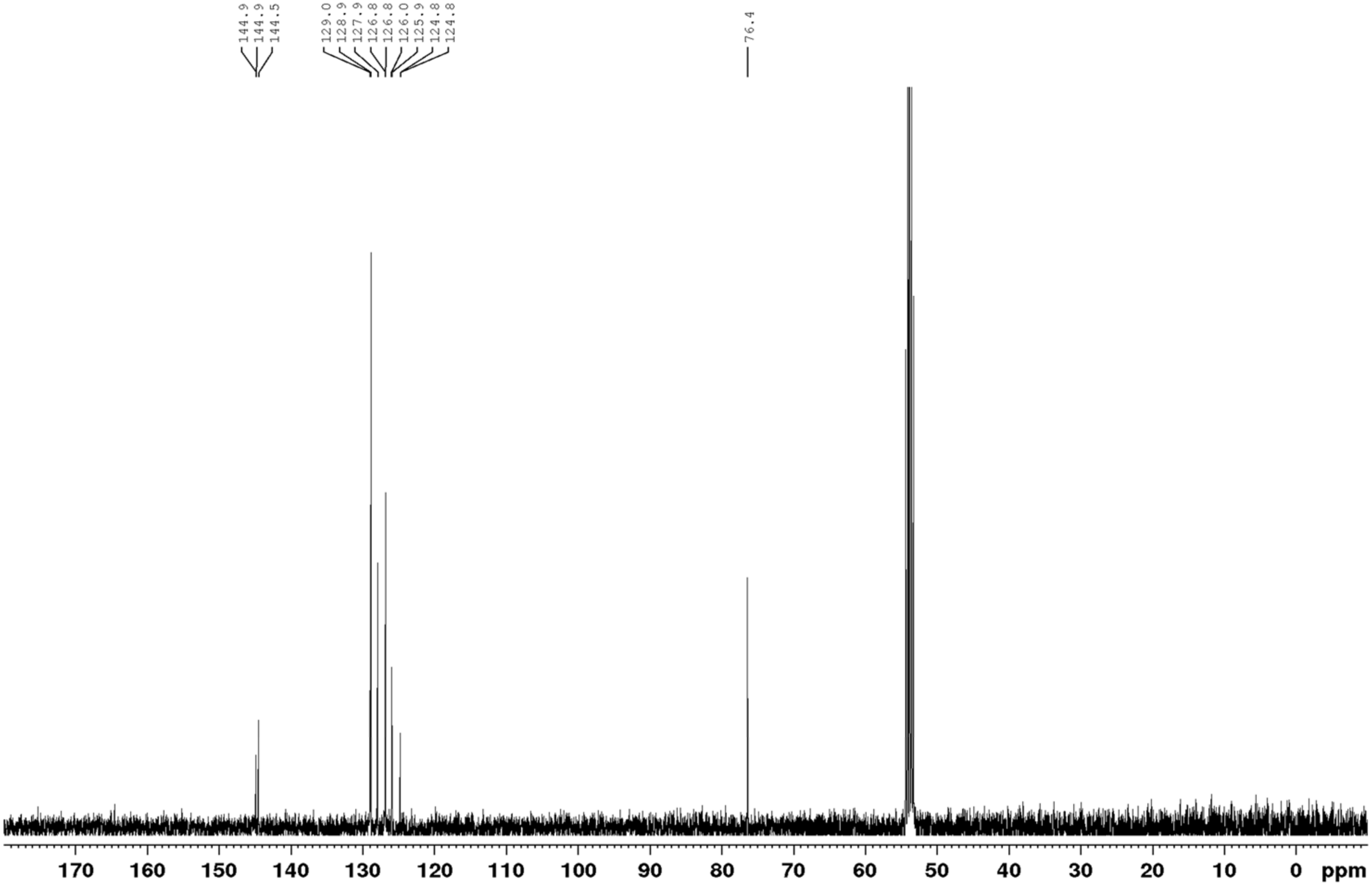
1,3-Phenylenebis(phenylmethanol)

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)



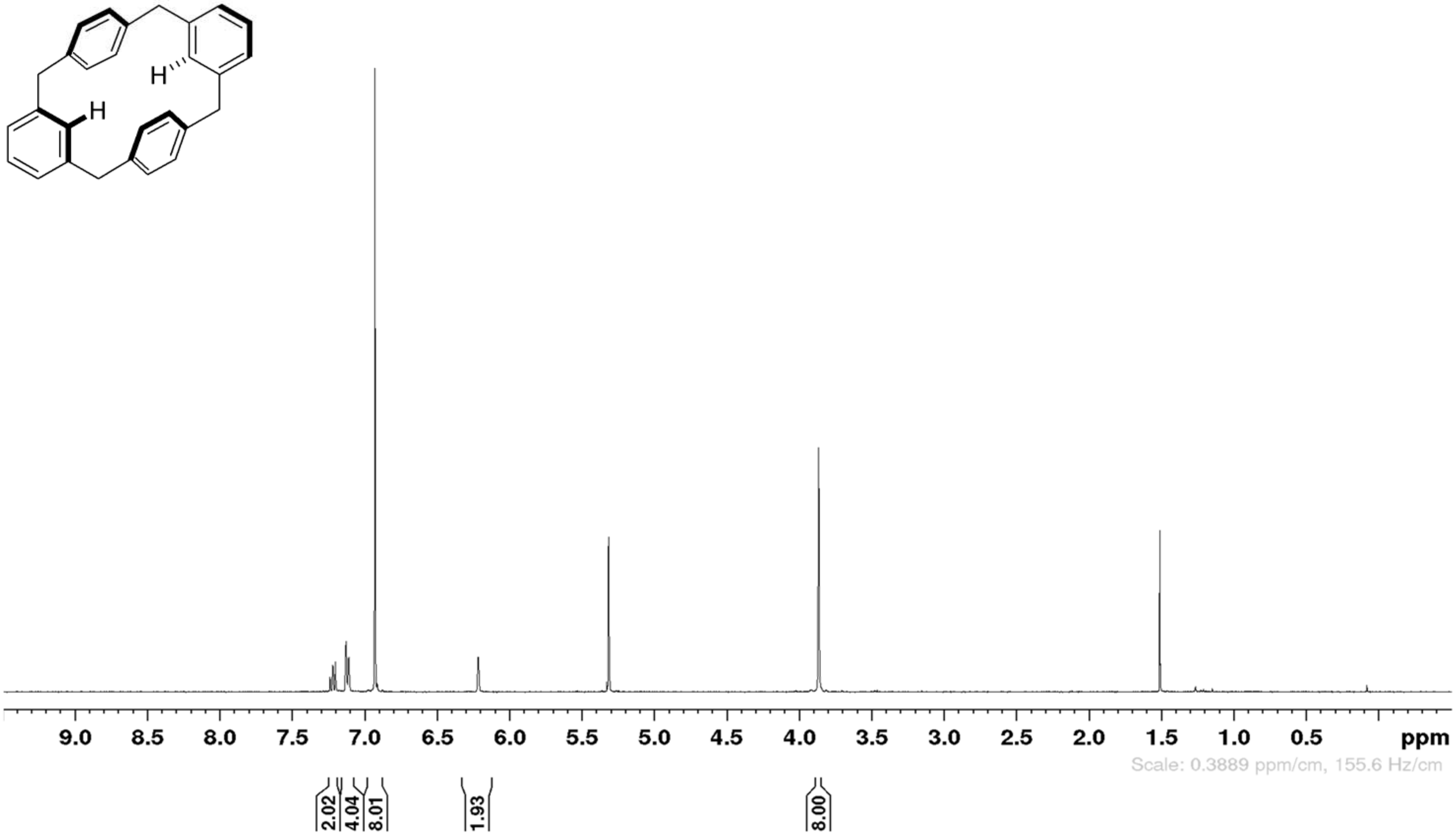


$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2)

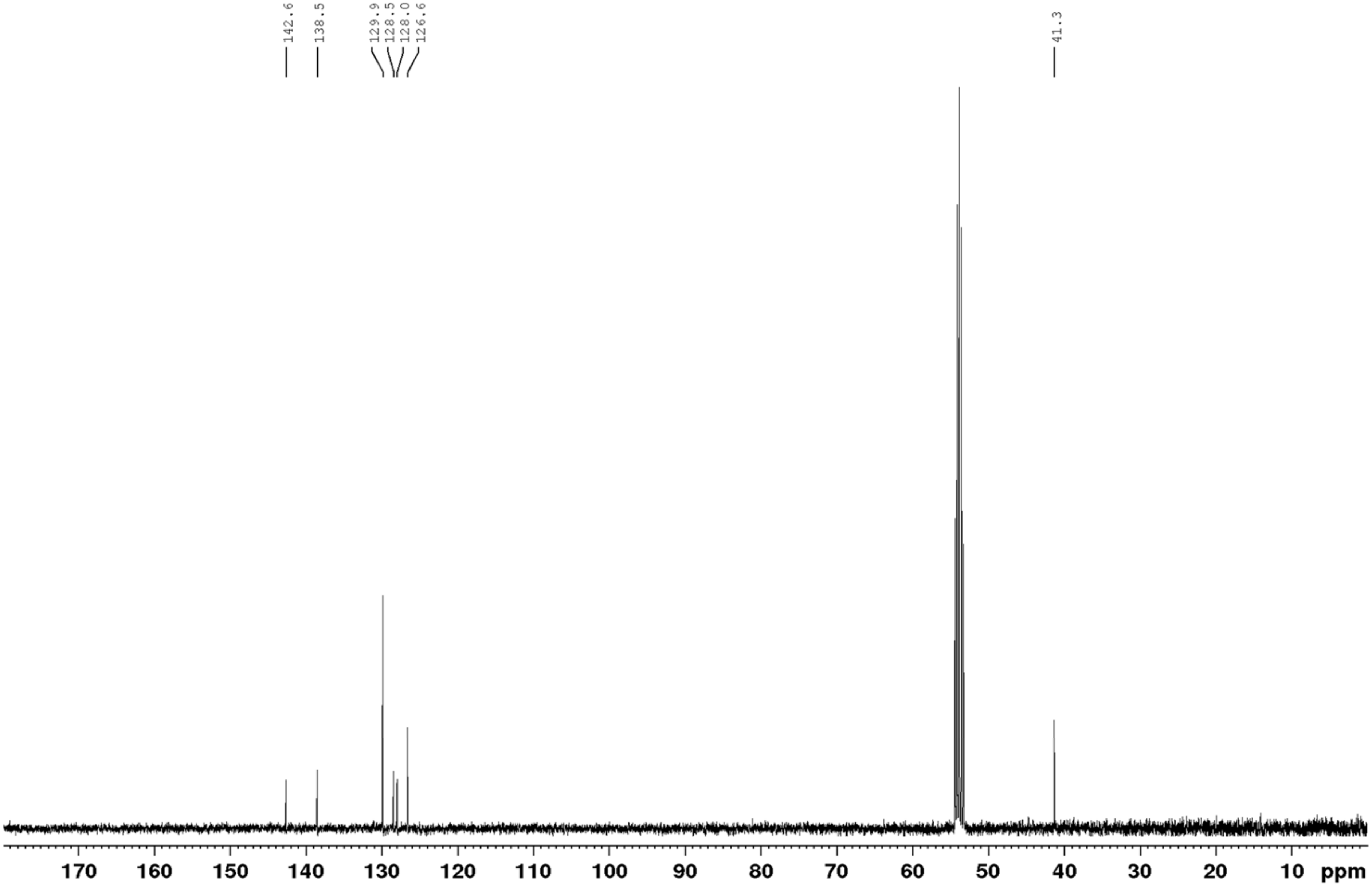


1,5(1,3),3,7(1,4)-Tetrabenzenacyclooctaphane

^{1}H NMR spectrum (400 MHz, CD_2Cl_2)



$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2)



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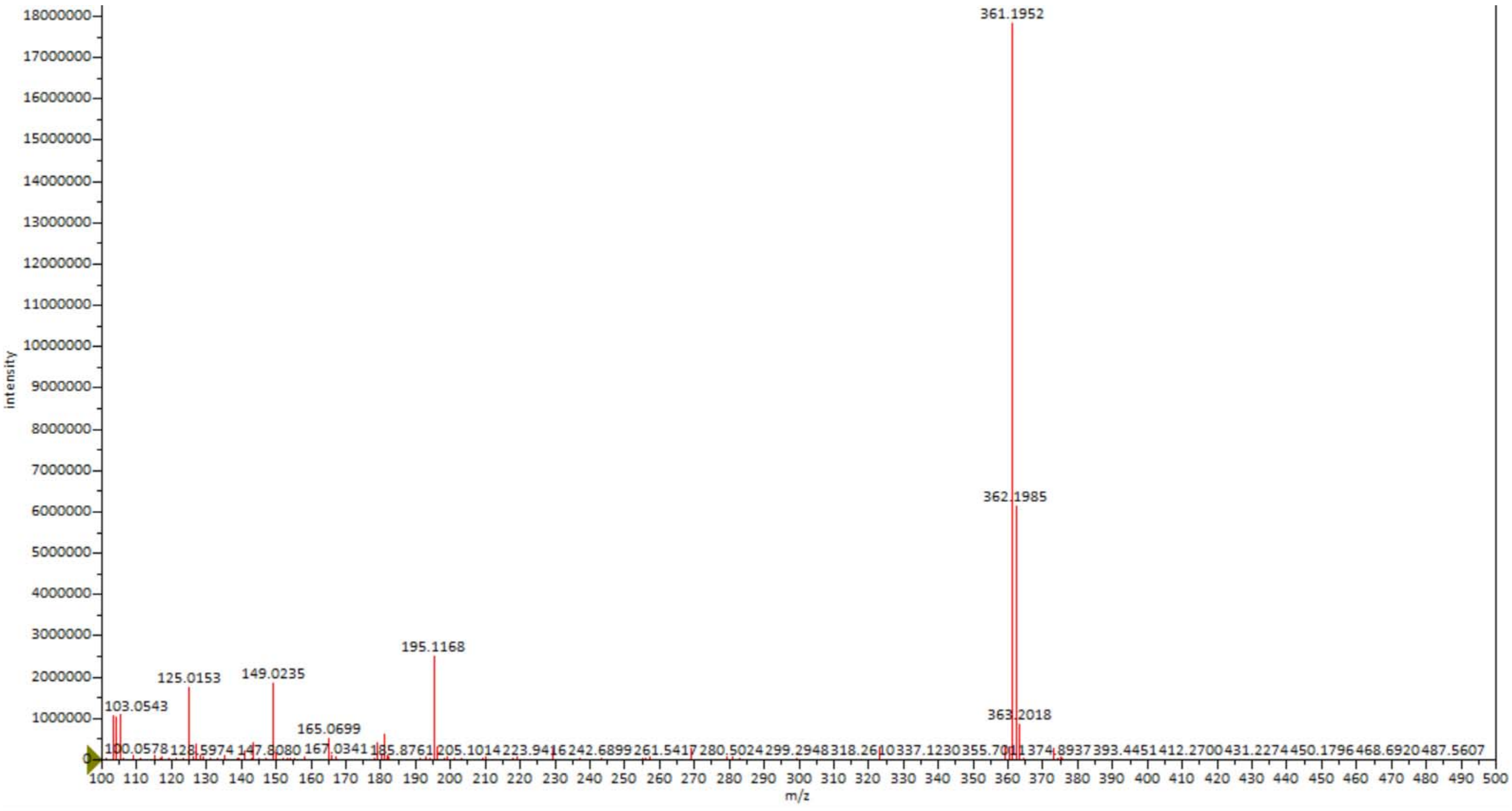
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337.1230
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374.8937
393.4451
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intensity
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15000000
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330
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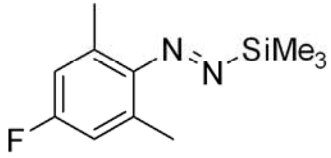
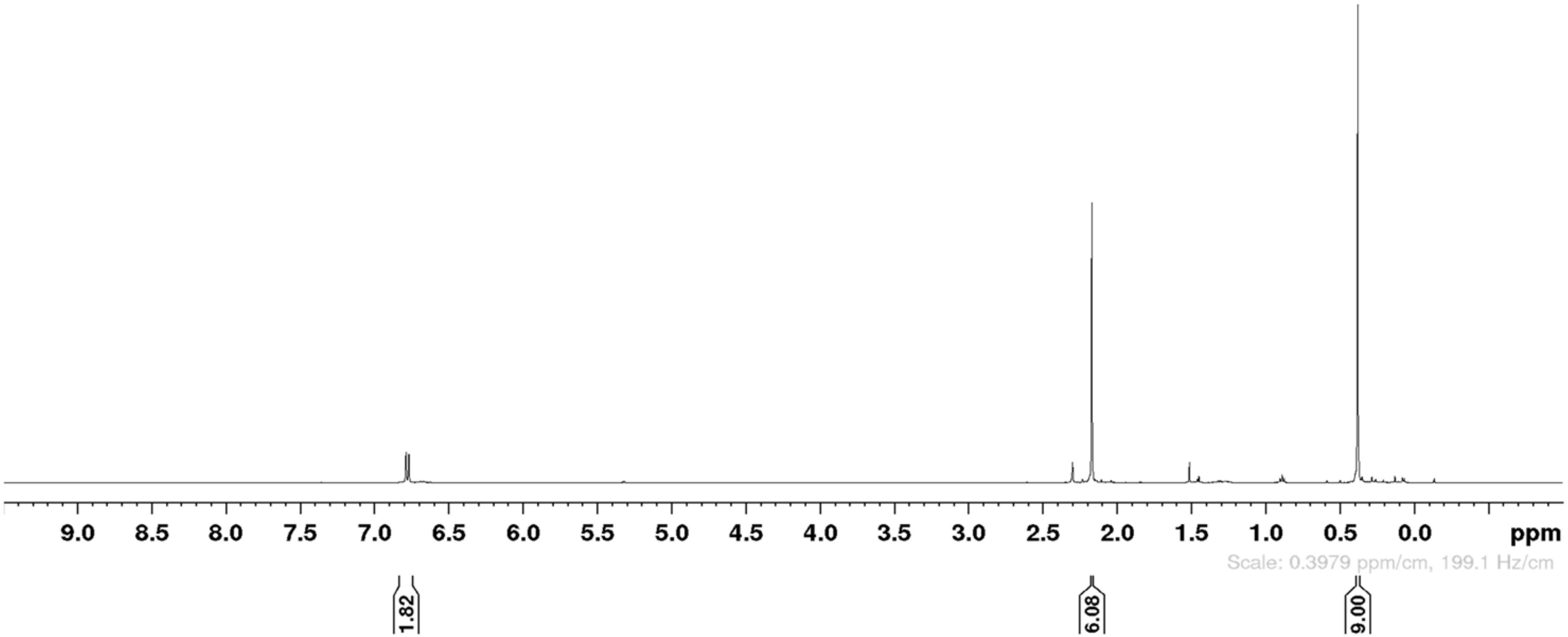
350
360
370
380
390
400
410
420
430
440
450
460
470
480
490
500
m/z

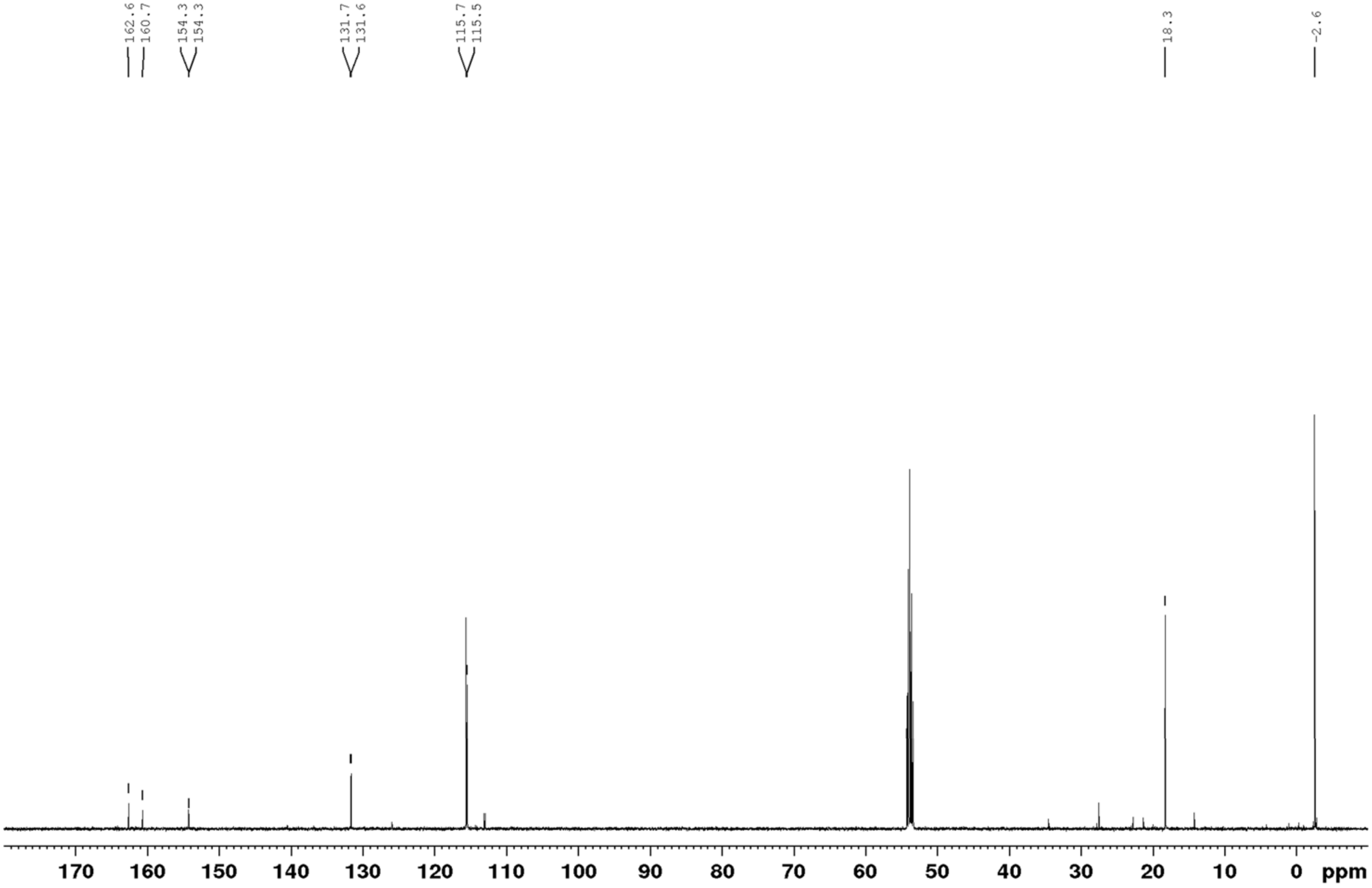
(*E*)-1-(4-Fluoro-2,6-dimethylphenyl)-2-(trimethylsilyl)diazene

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

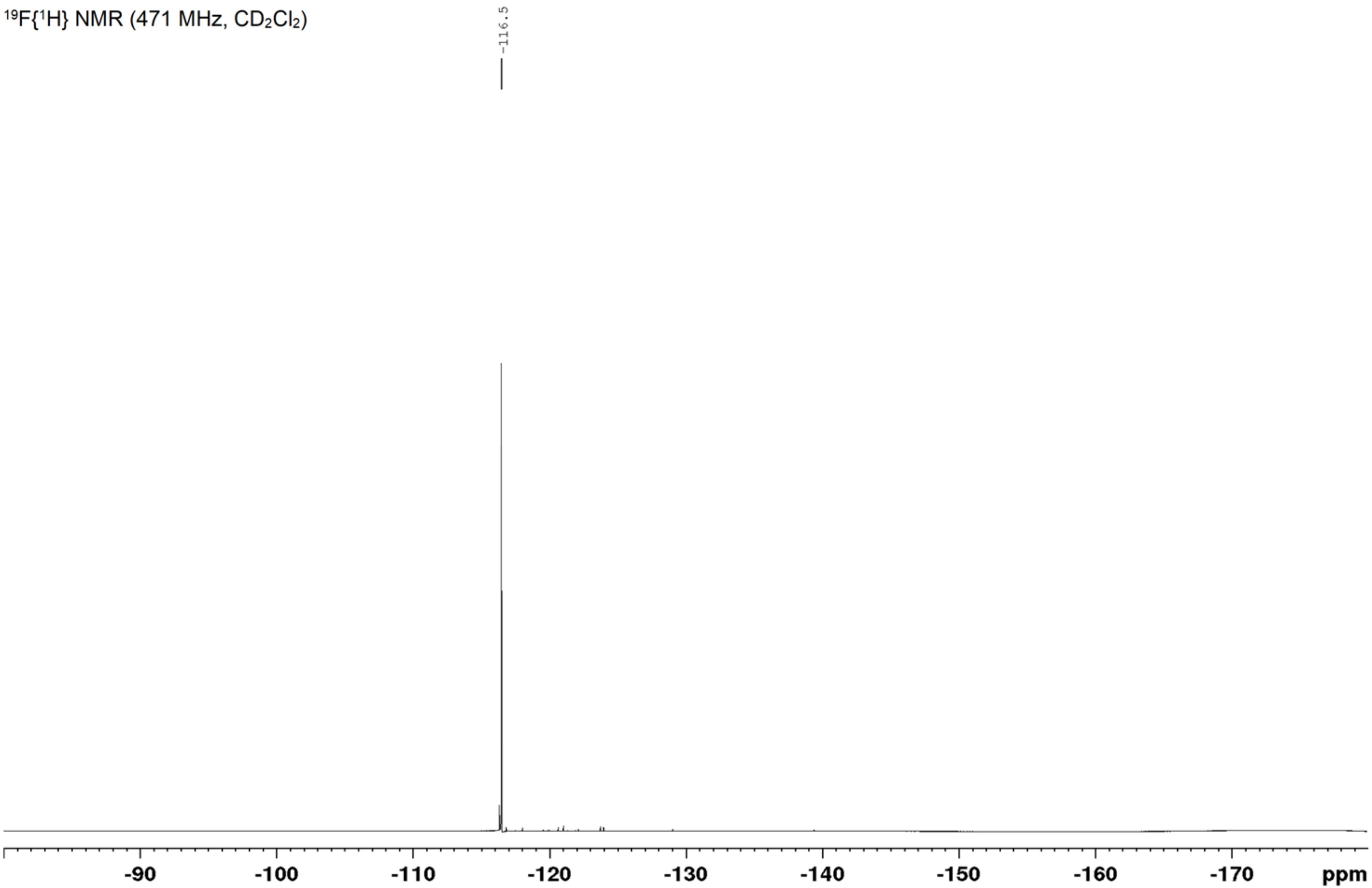




$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)

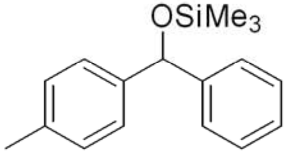


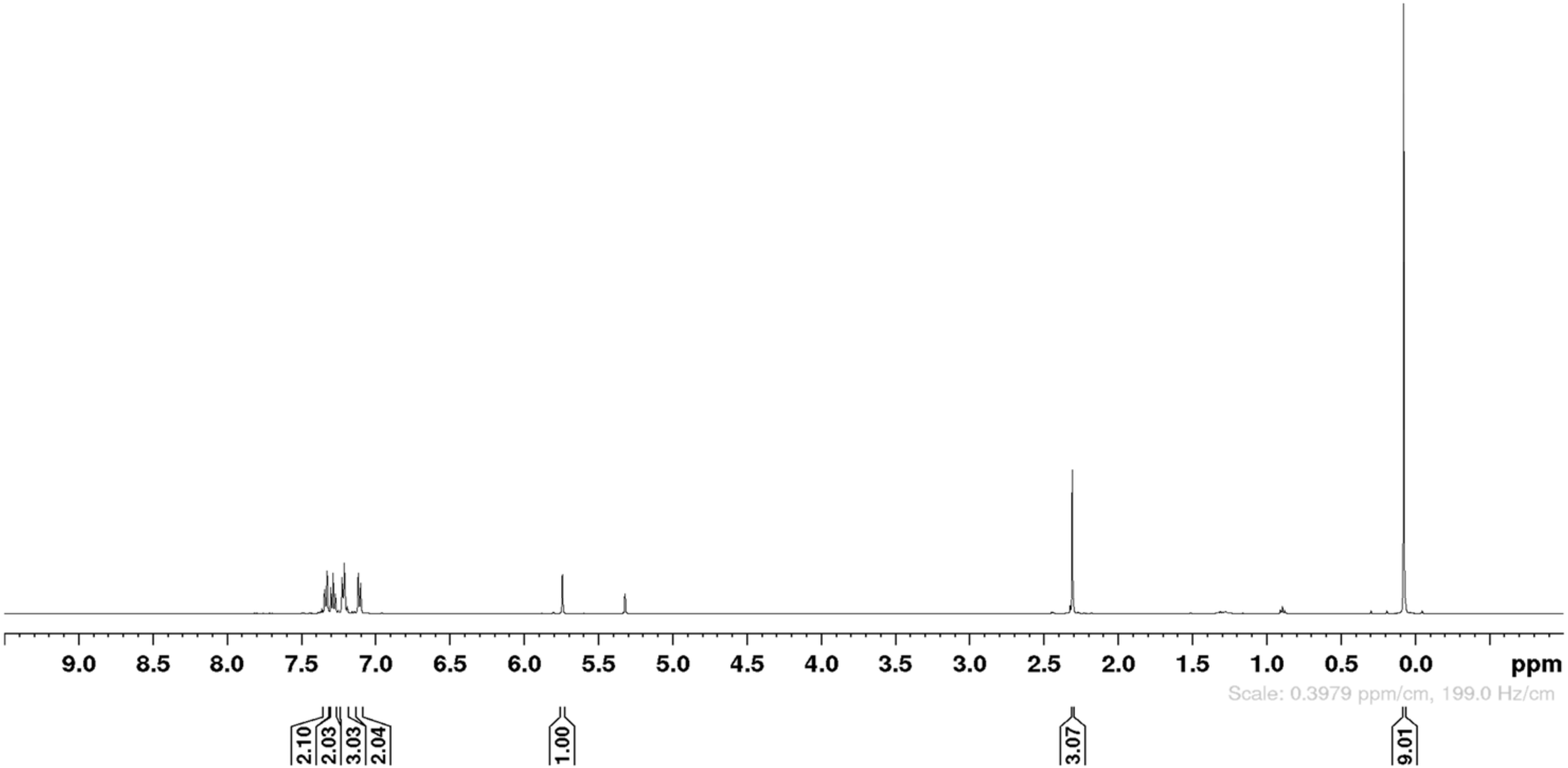
$^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2)



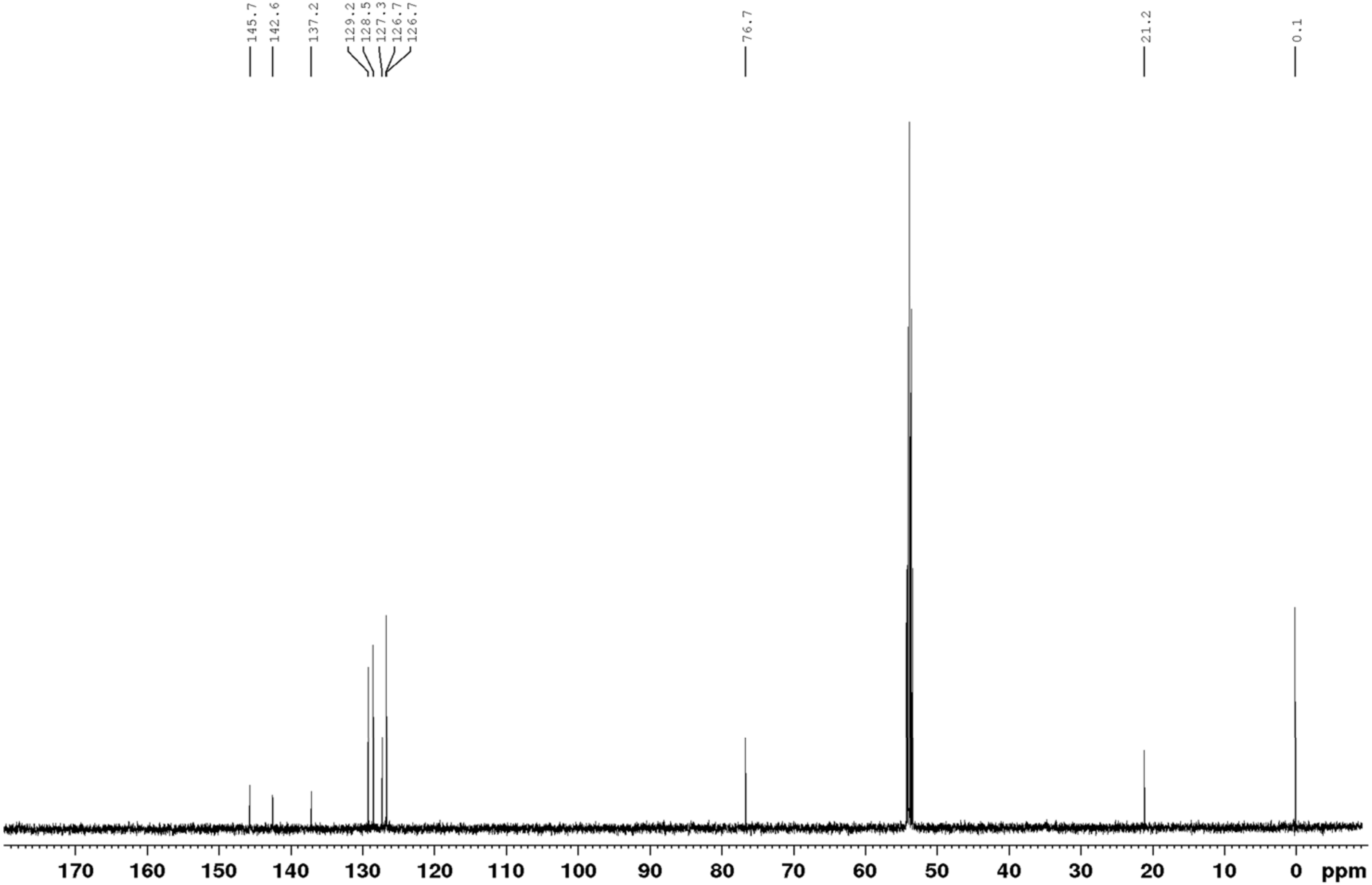
Trimethyl(phenyl(*p*-tolyl)methoxy)silane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)



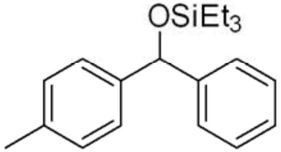


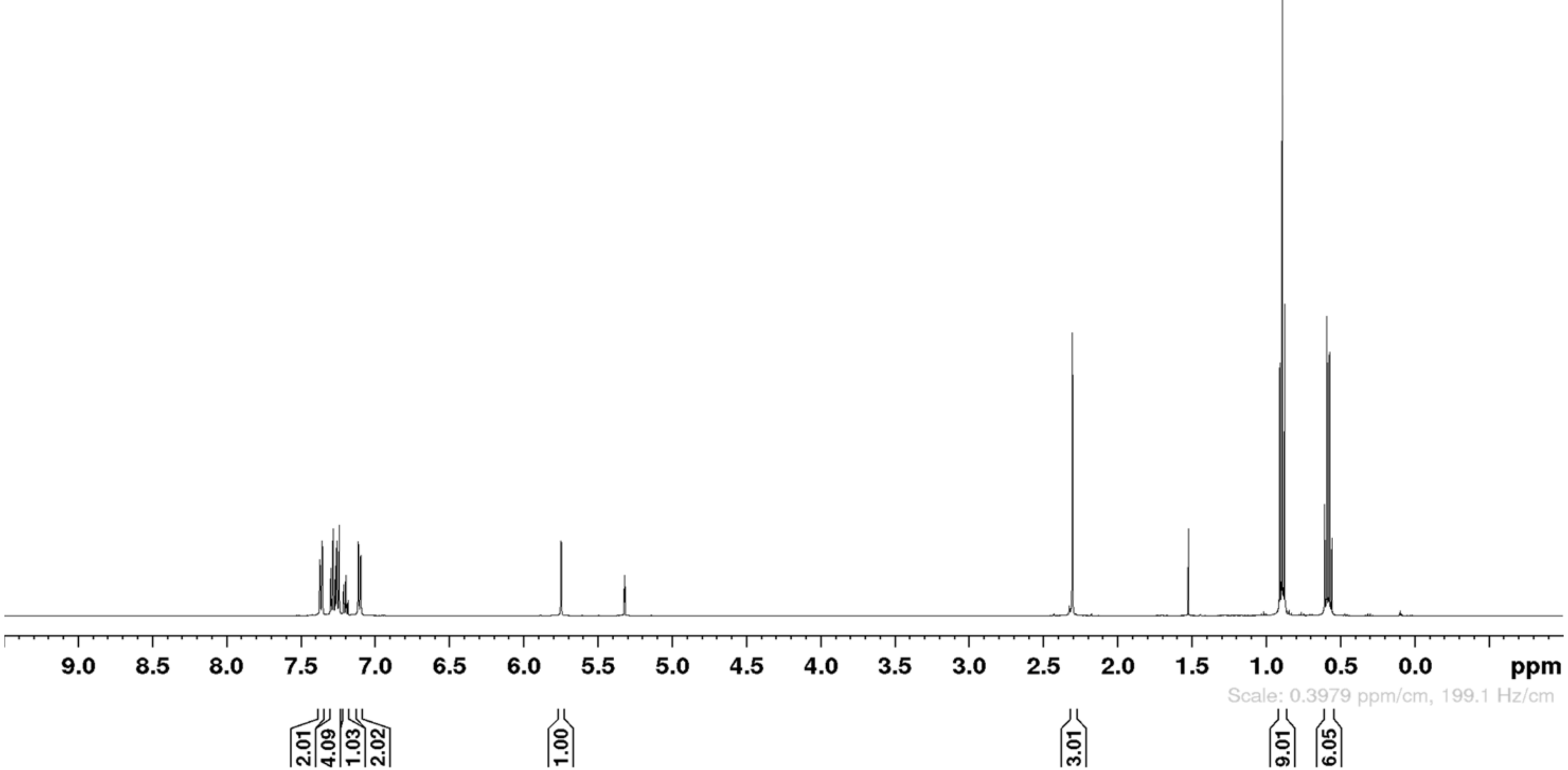
$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2)



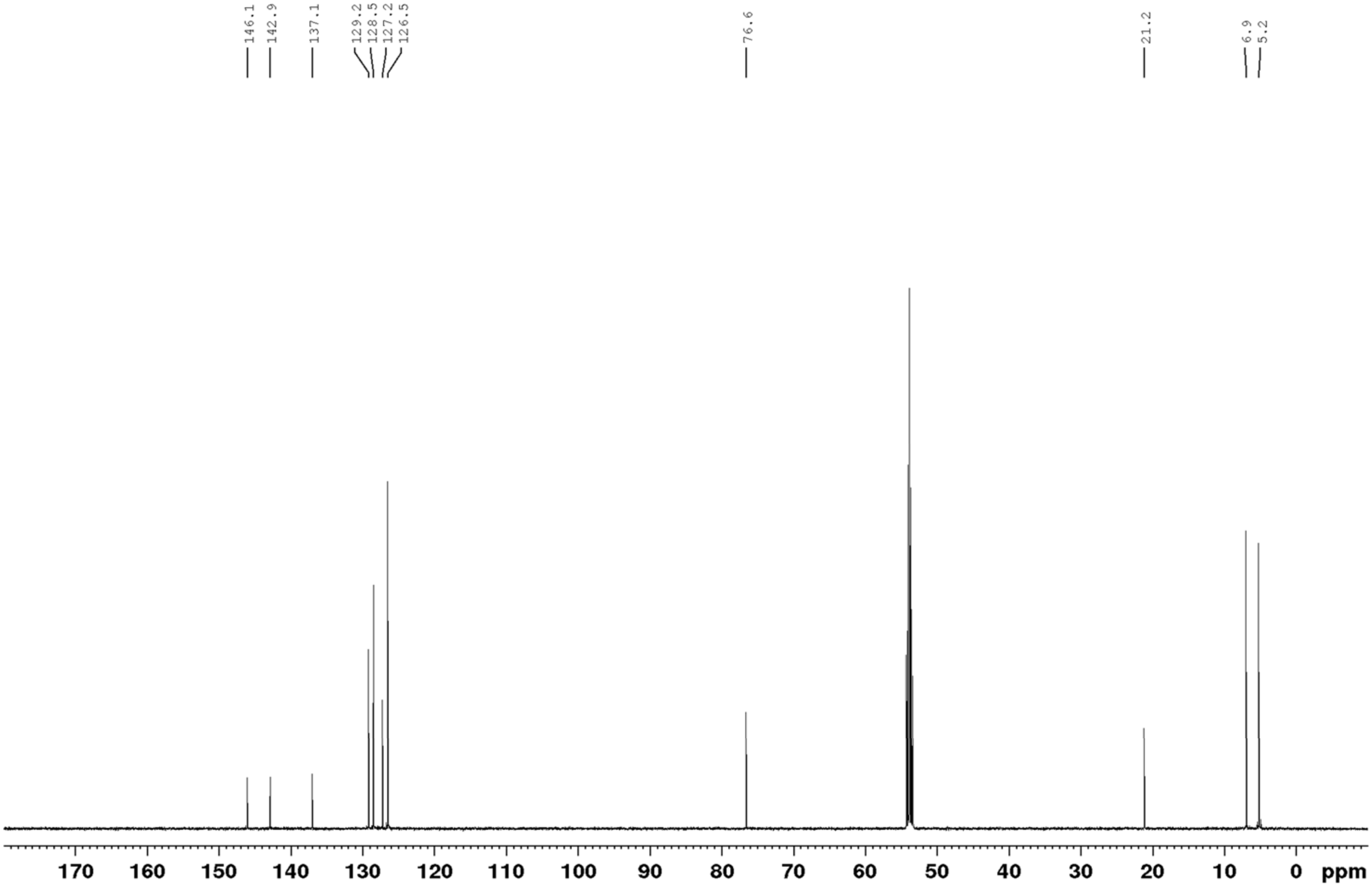
Triethyl(phenyl(*p*-tolyl)methoxy)silane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)



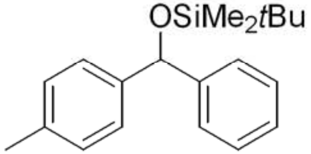


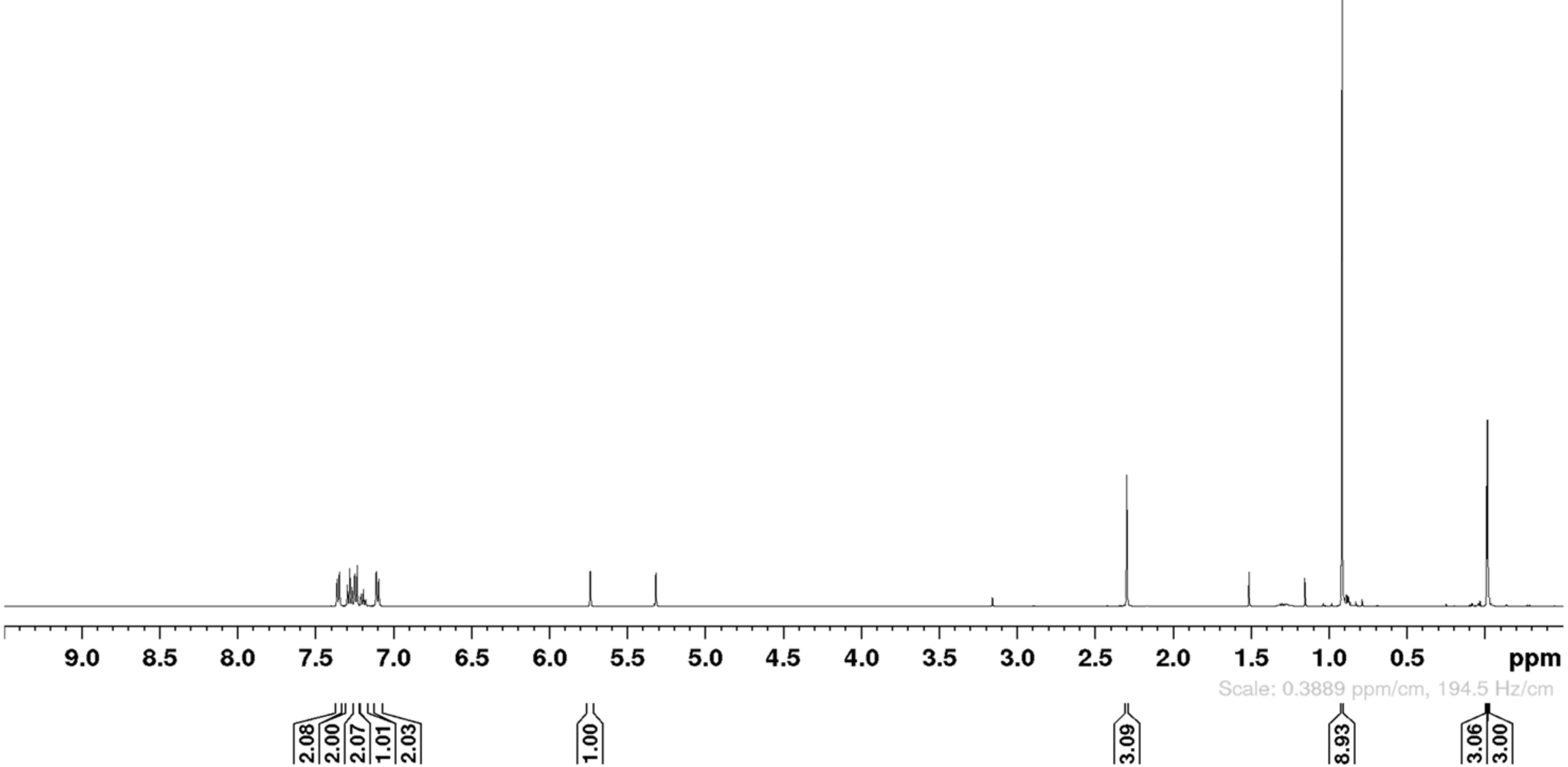
$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)



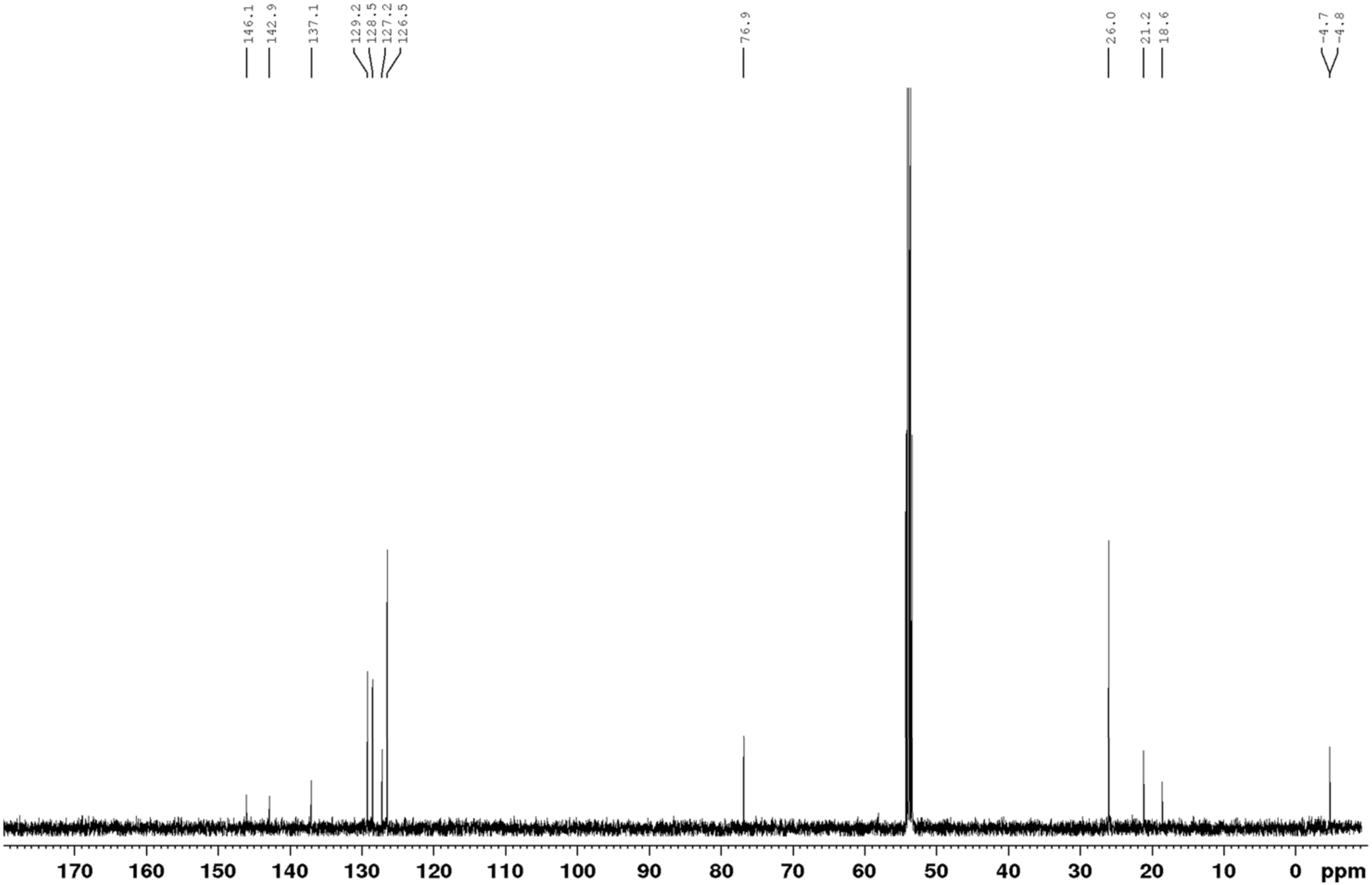
***tert*-Butyldimethyl(phenyl(*p*-tolyl)methoxy)silane**

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)



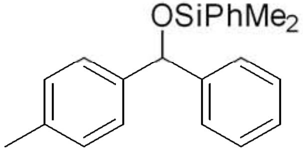


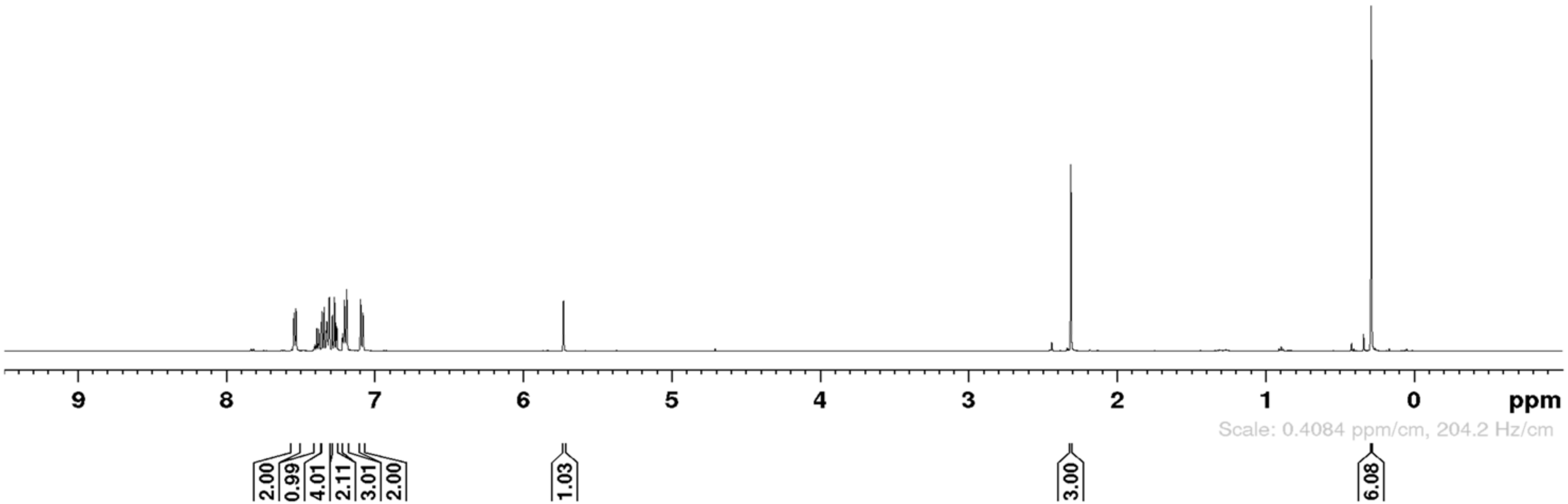
$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)



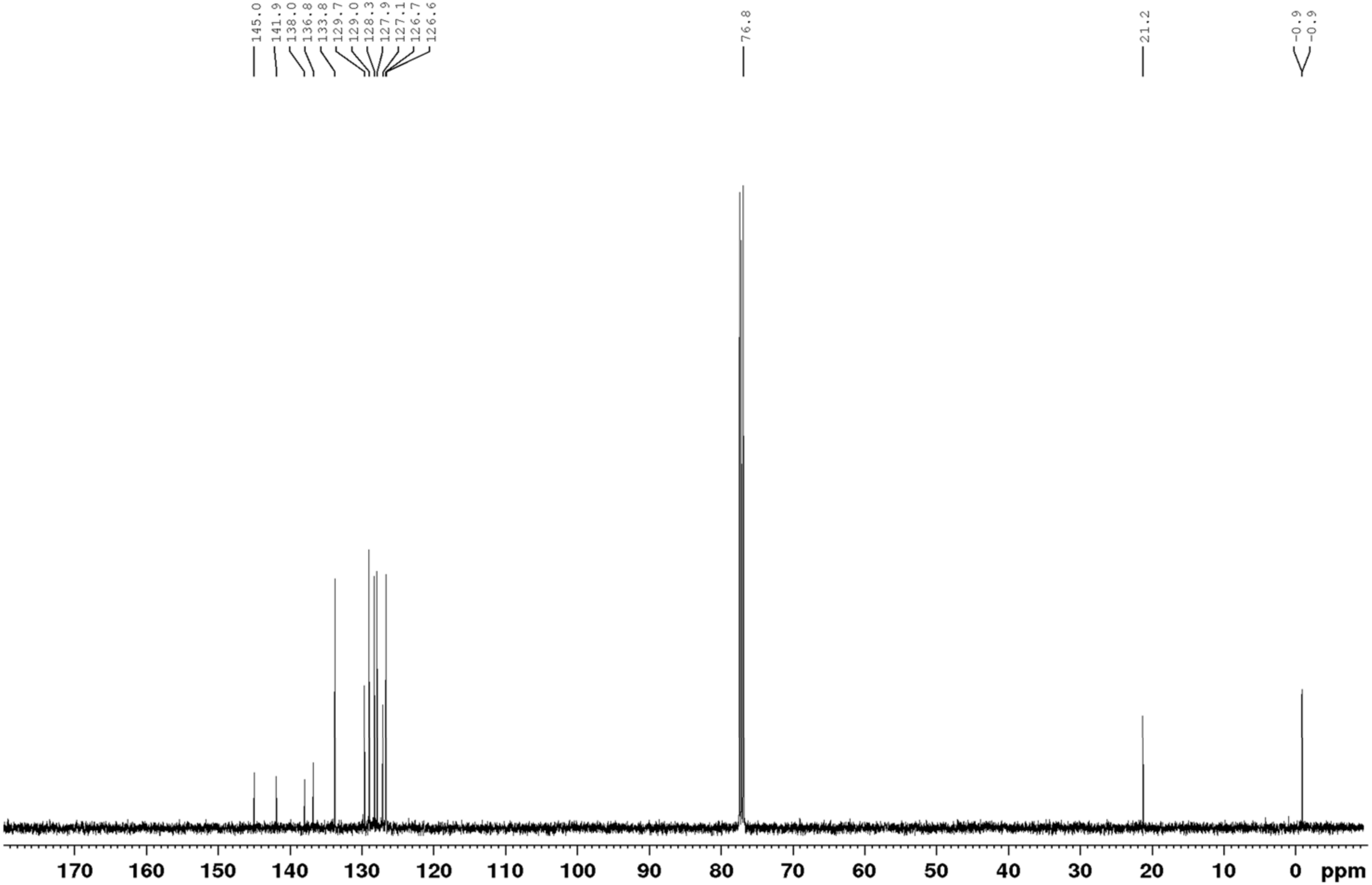
Dimethyl(phenyl)(phenyl(*p*-tolyl)methoxy)silane

^{1}H NMR spectrum (500 MHz, $CDCl_3$)



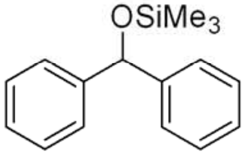


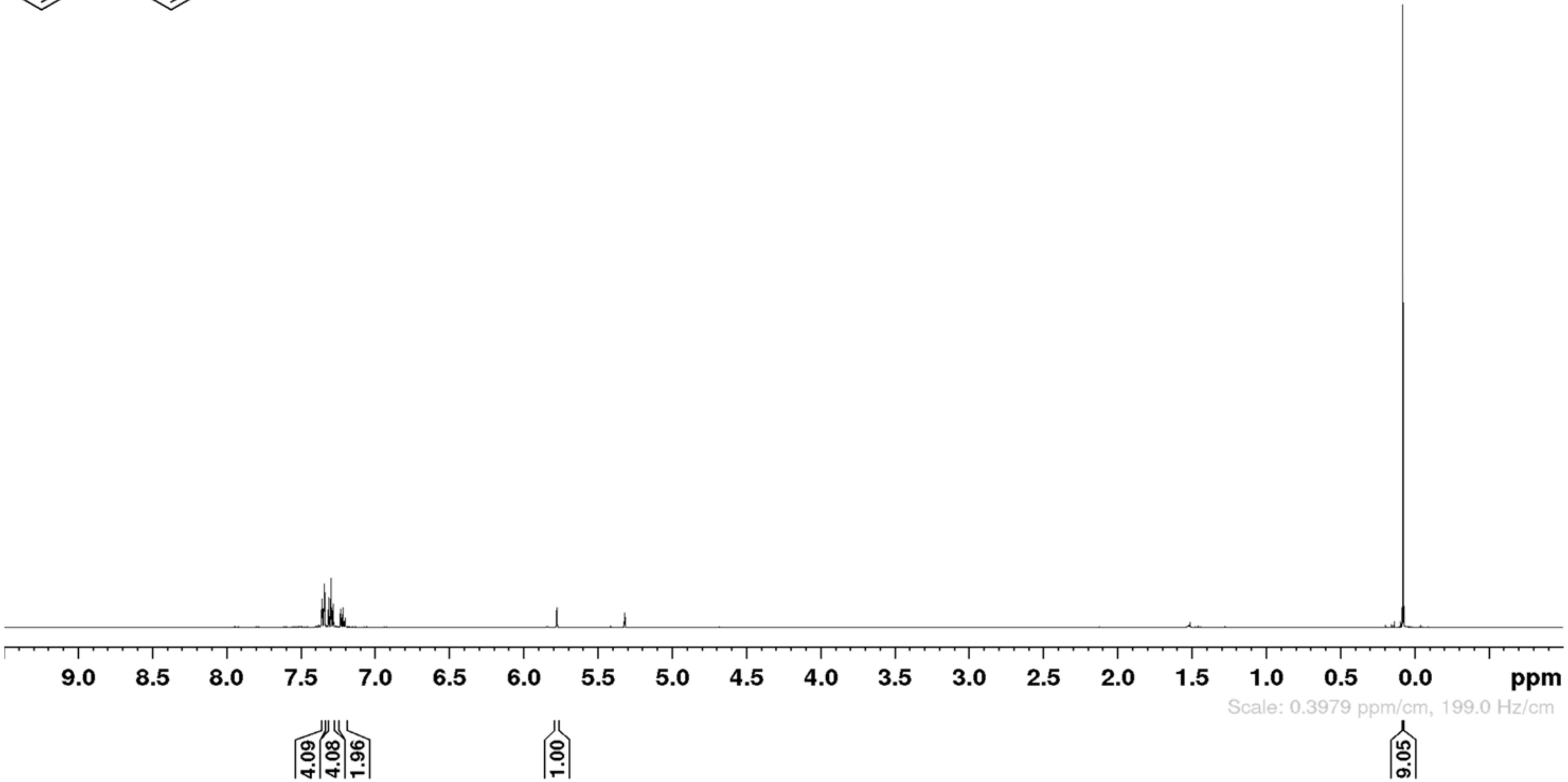
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



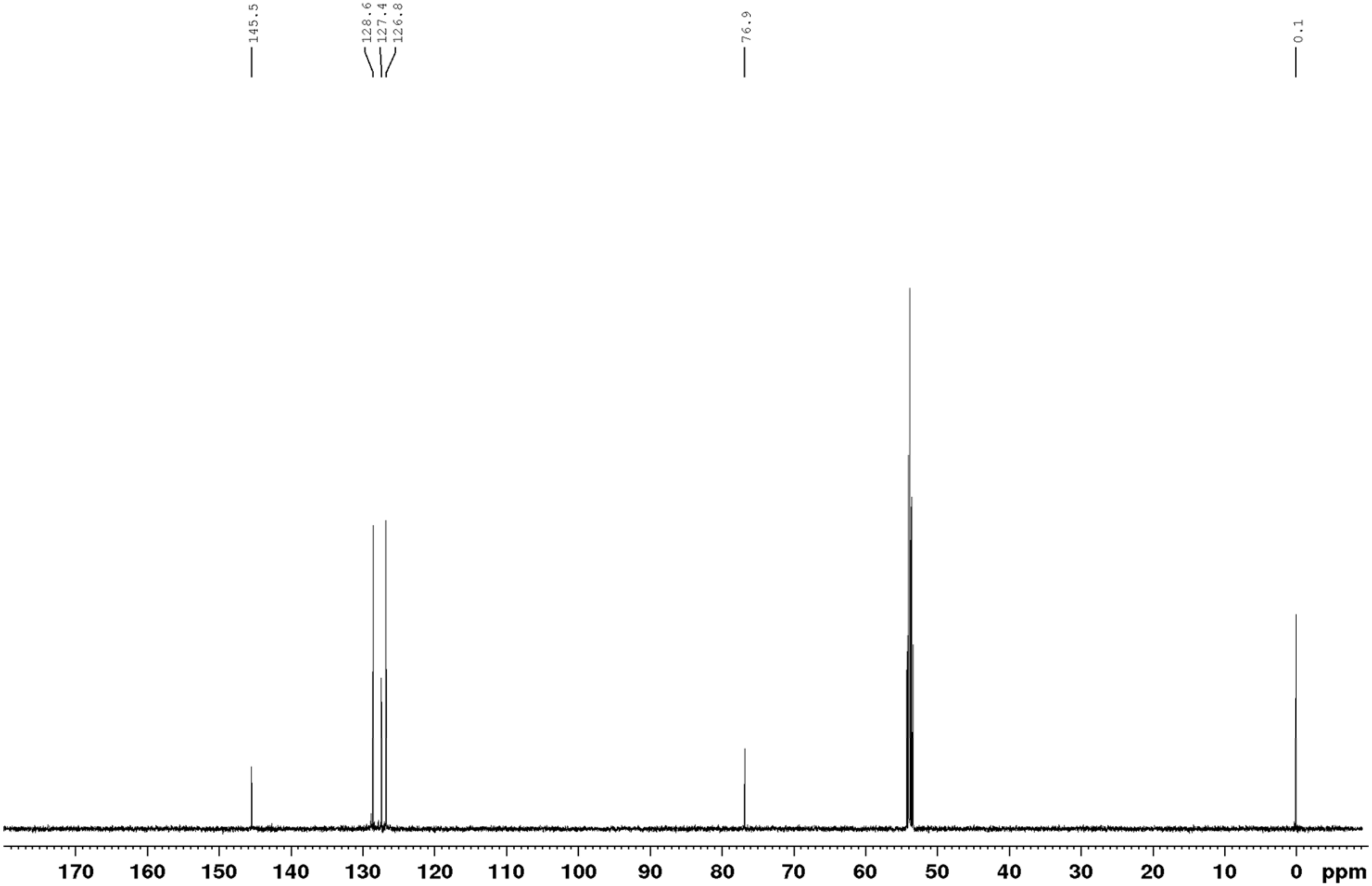
(Benzhydryloxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)



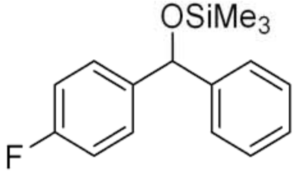


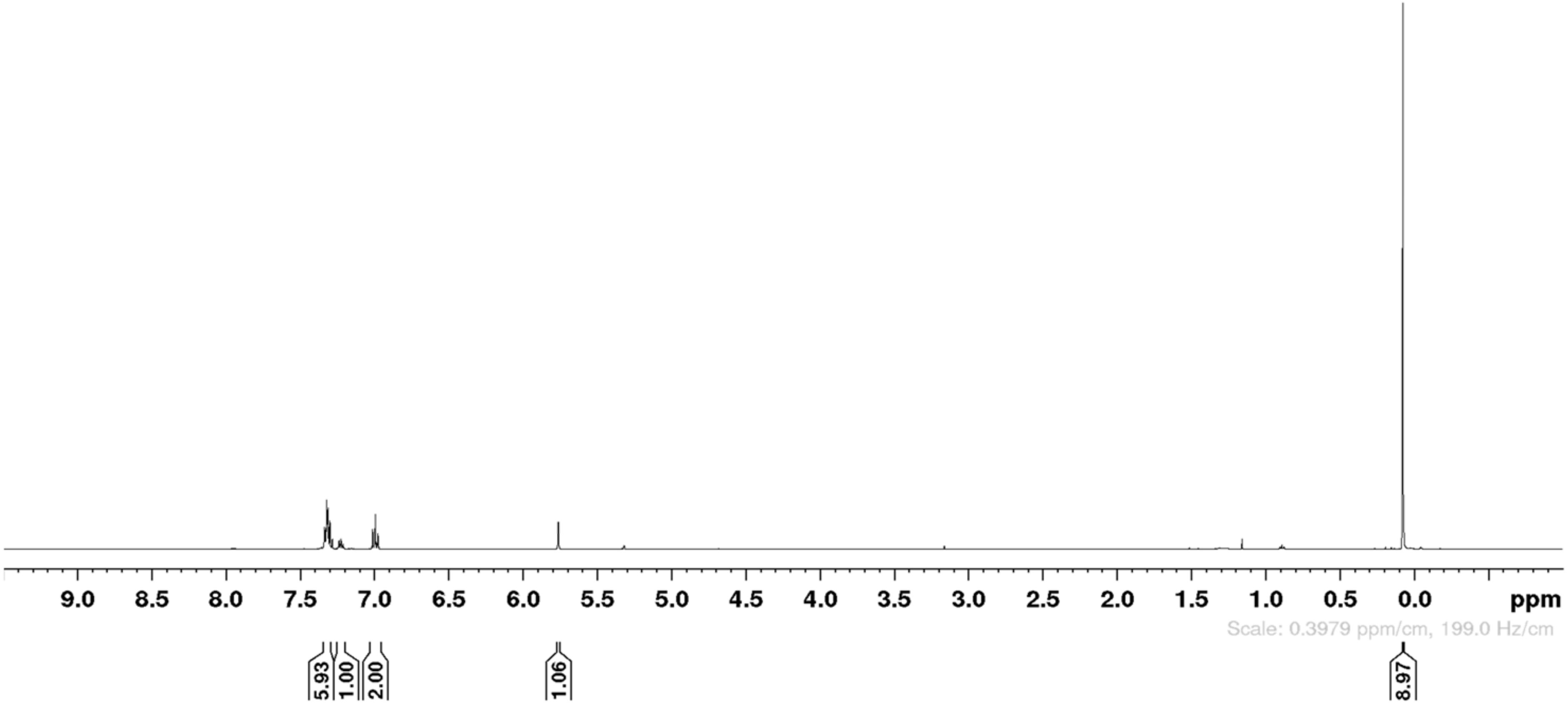
$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)



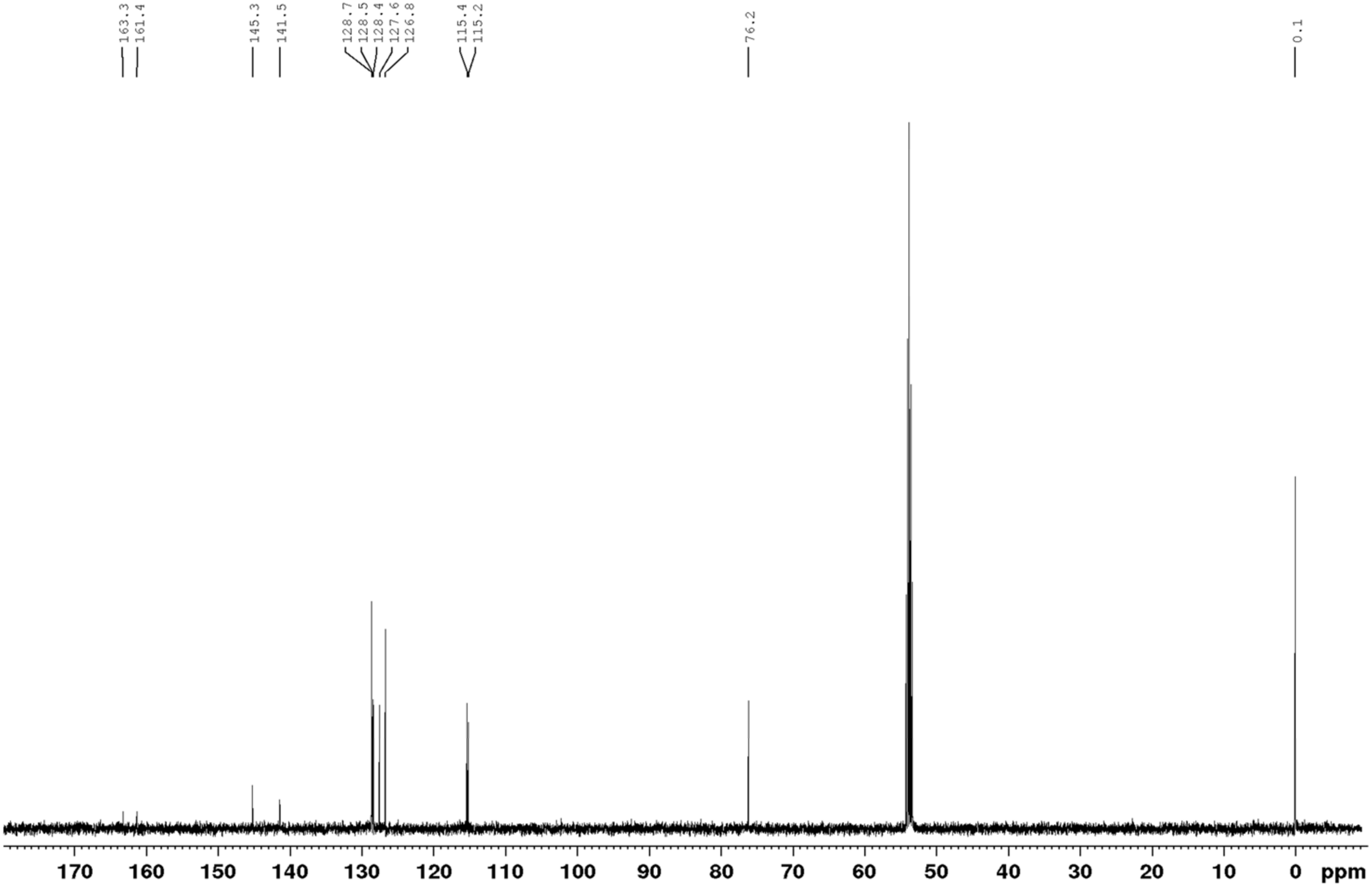
((4-Fluorophenyl)(phenyl)methoxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

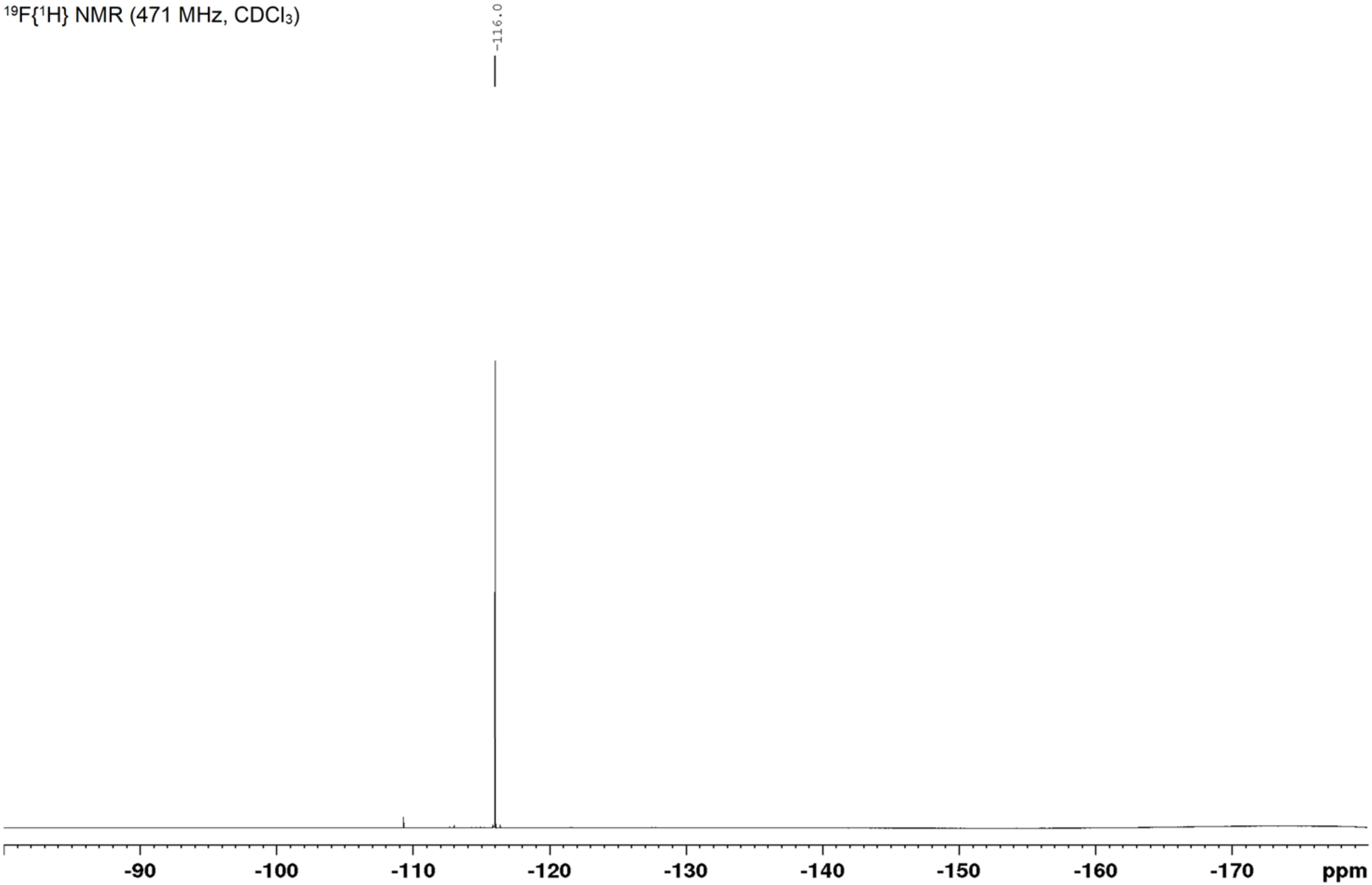




^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2)

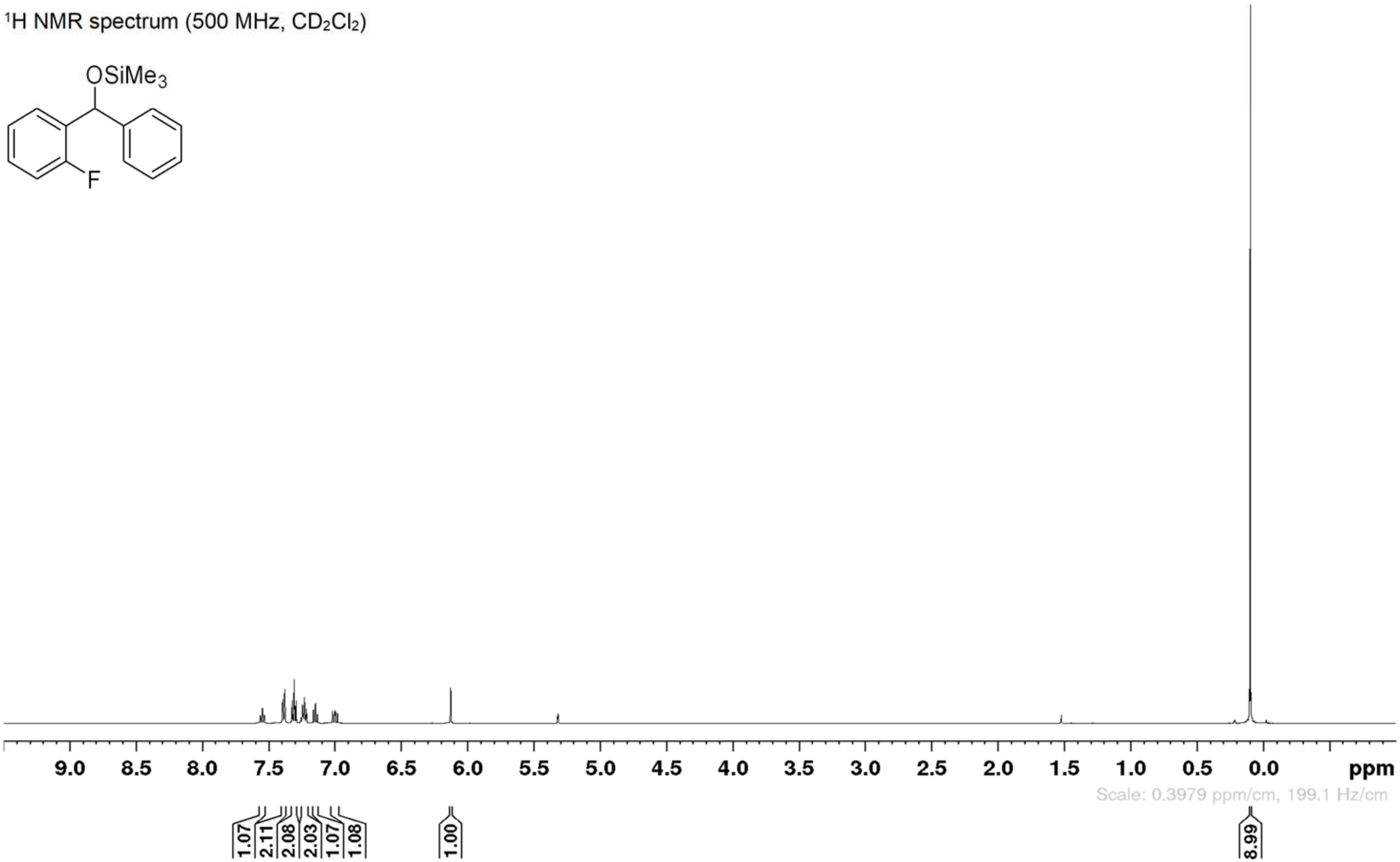


$^{19}F\{^{1}H\}$ NMR (471 MHz, CDCl$_3$)

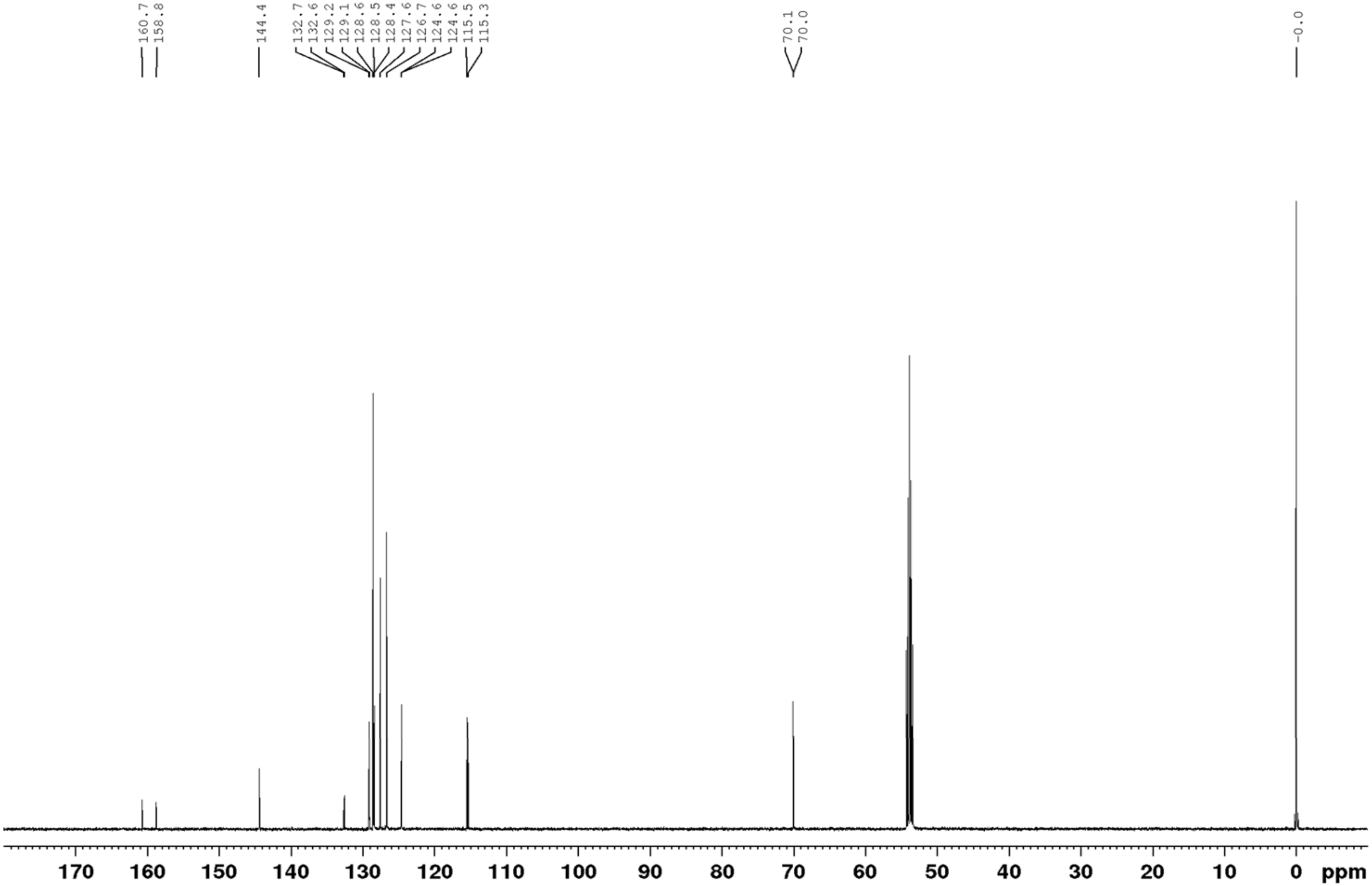


((2-Fluorophenyl)(phenyl)methoxy)trimethylsilane

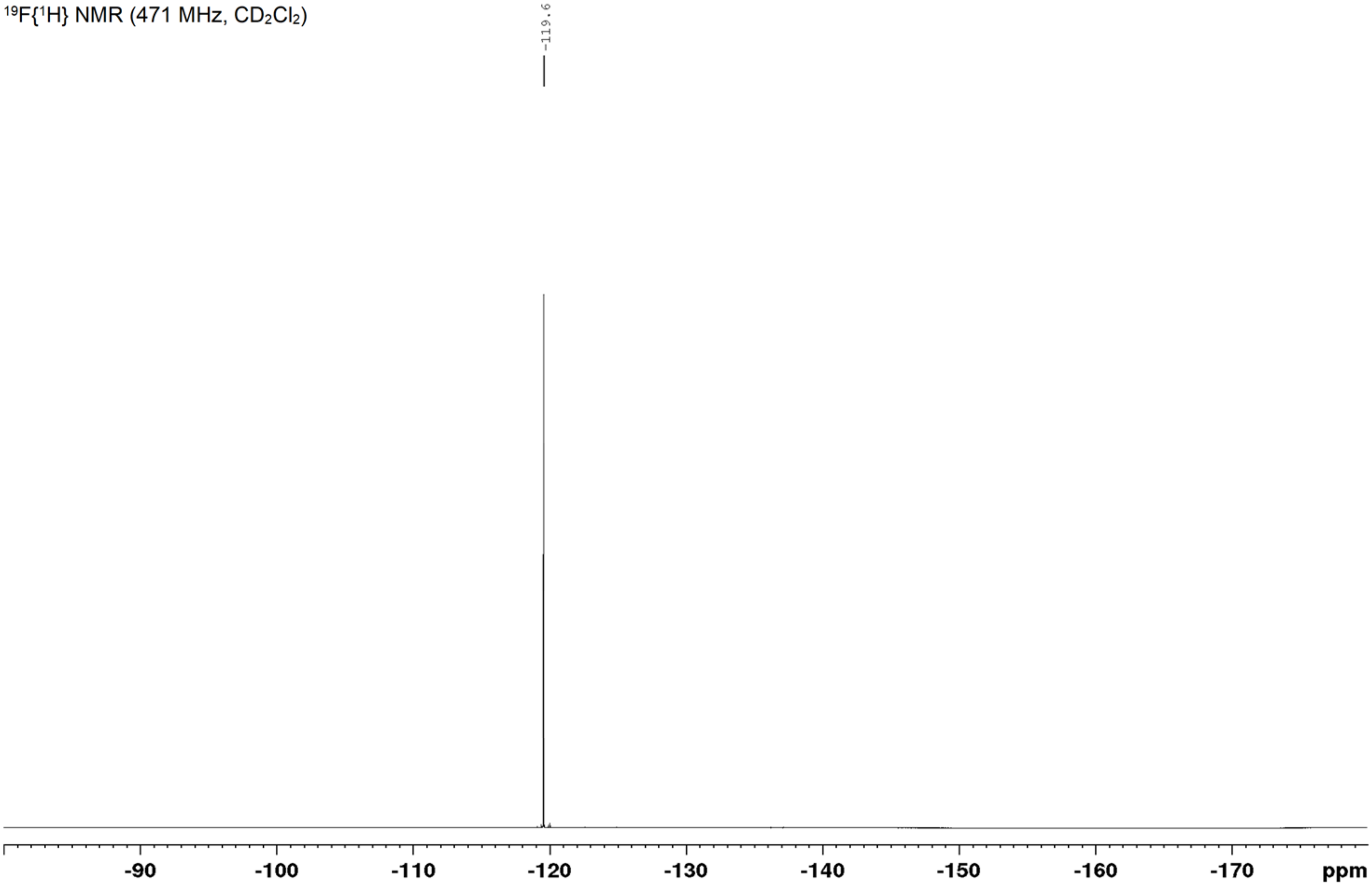
^{1}H NMR spectrum (500 MHz, CD_2Cl_2)



$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)

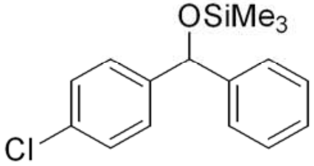


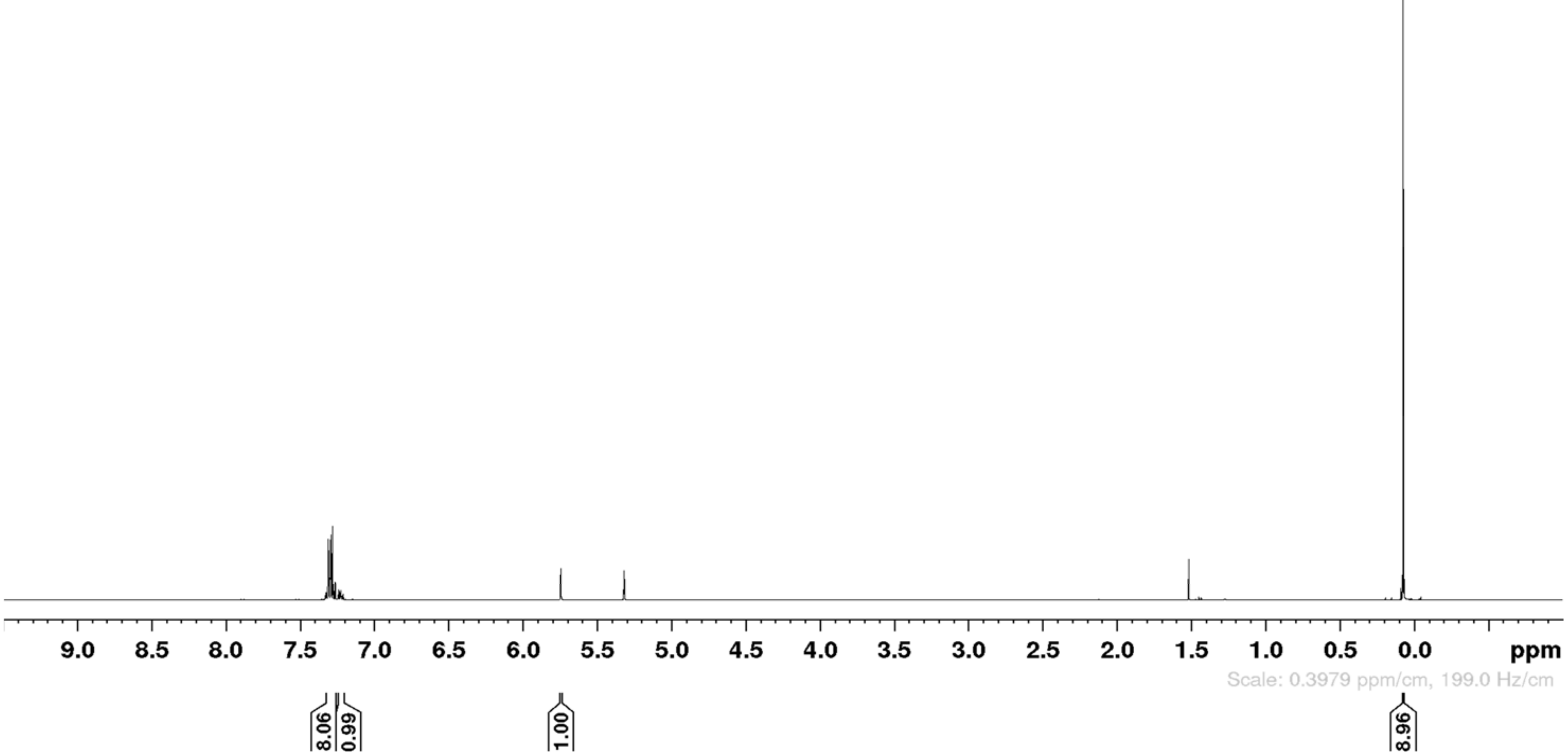
$^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2)



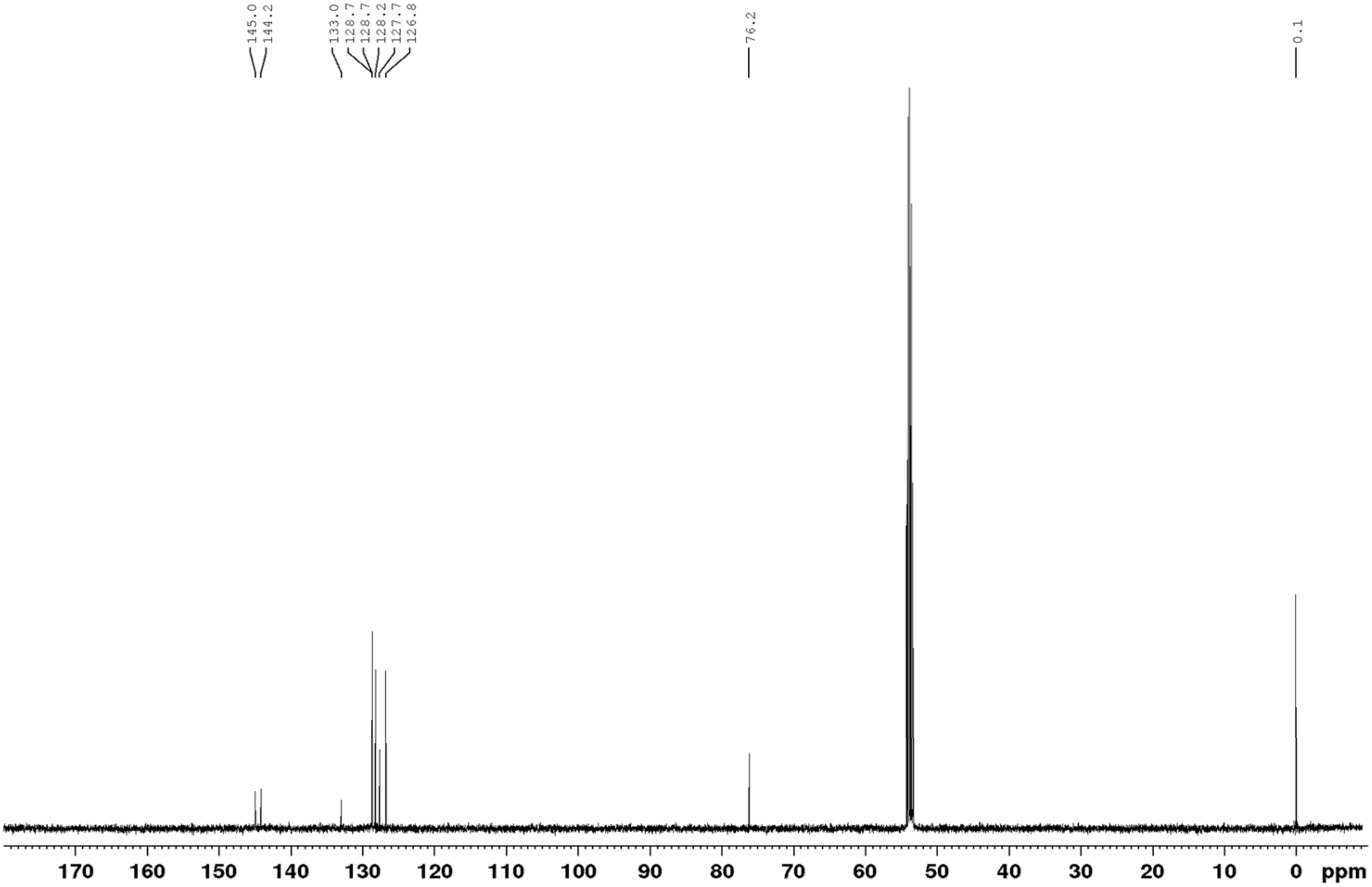
((4-Chlorophenyl)(phenyl)methoxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)



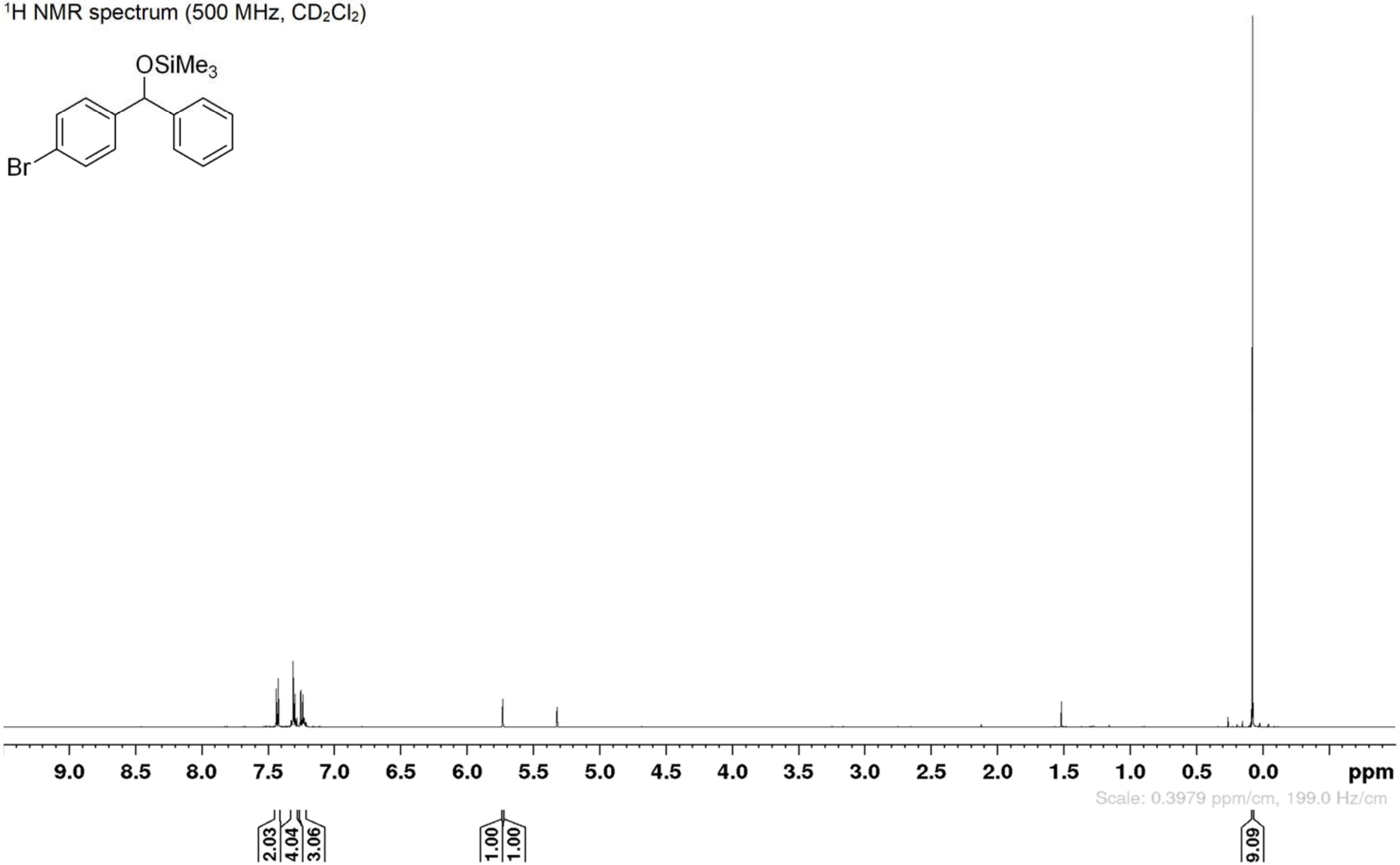


$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)

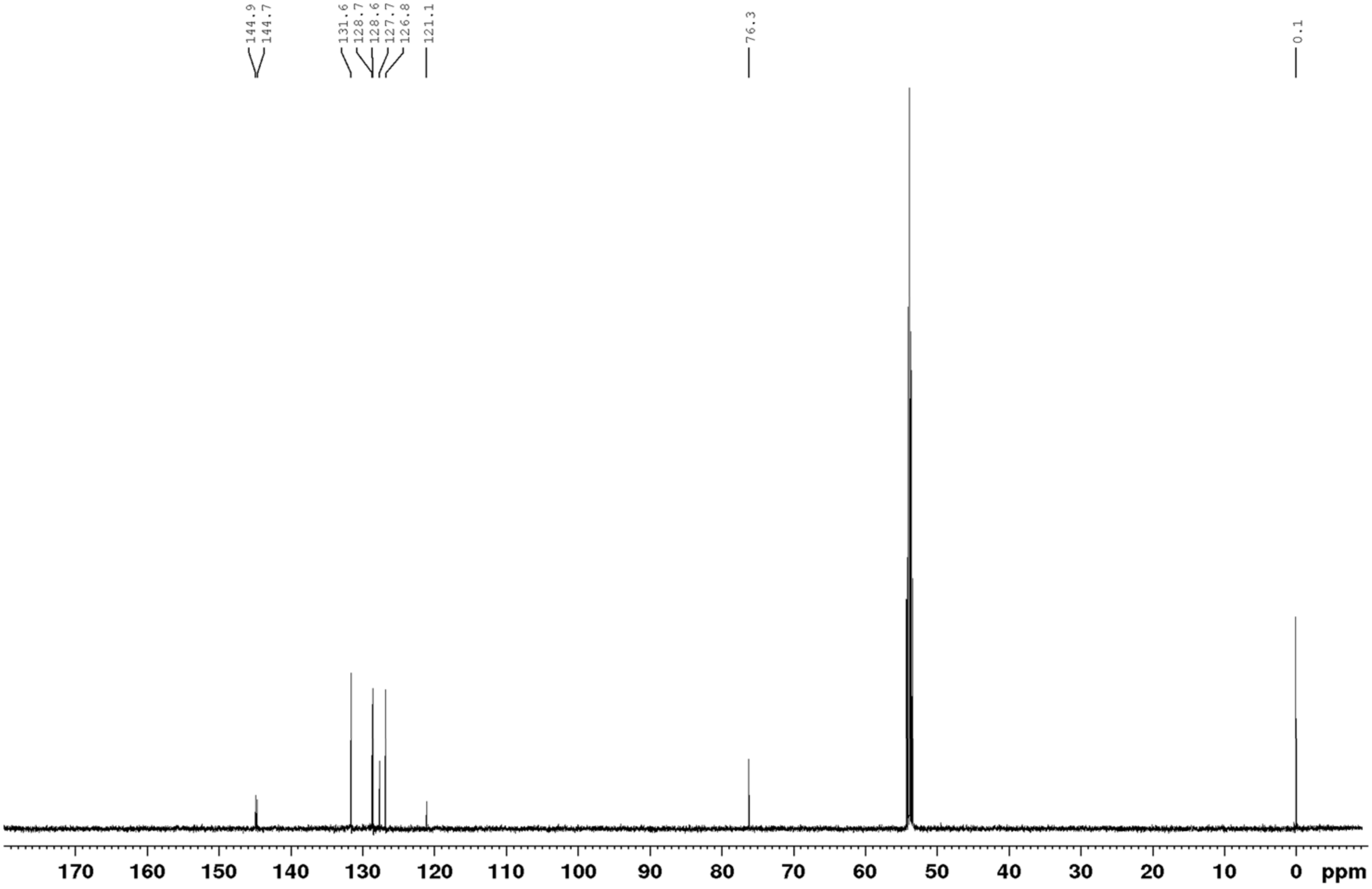


((4-Bromophenyl)(phenyl)methoxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

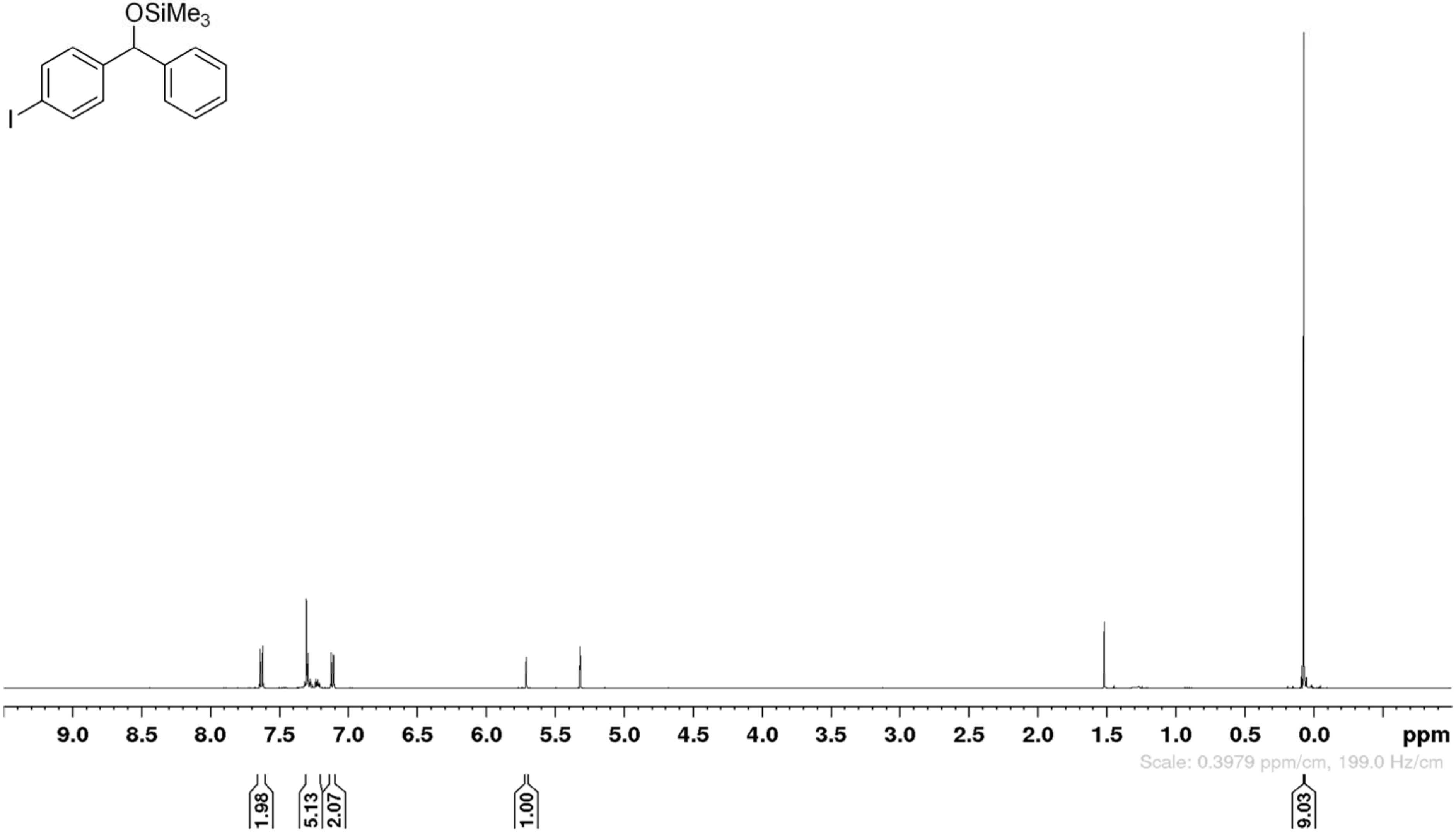


$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2)

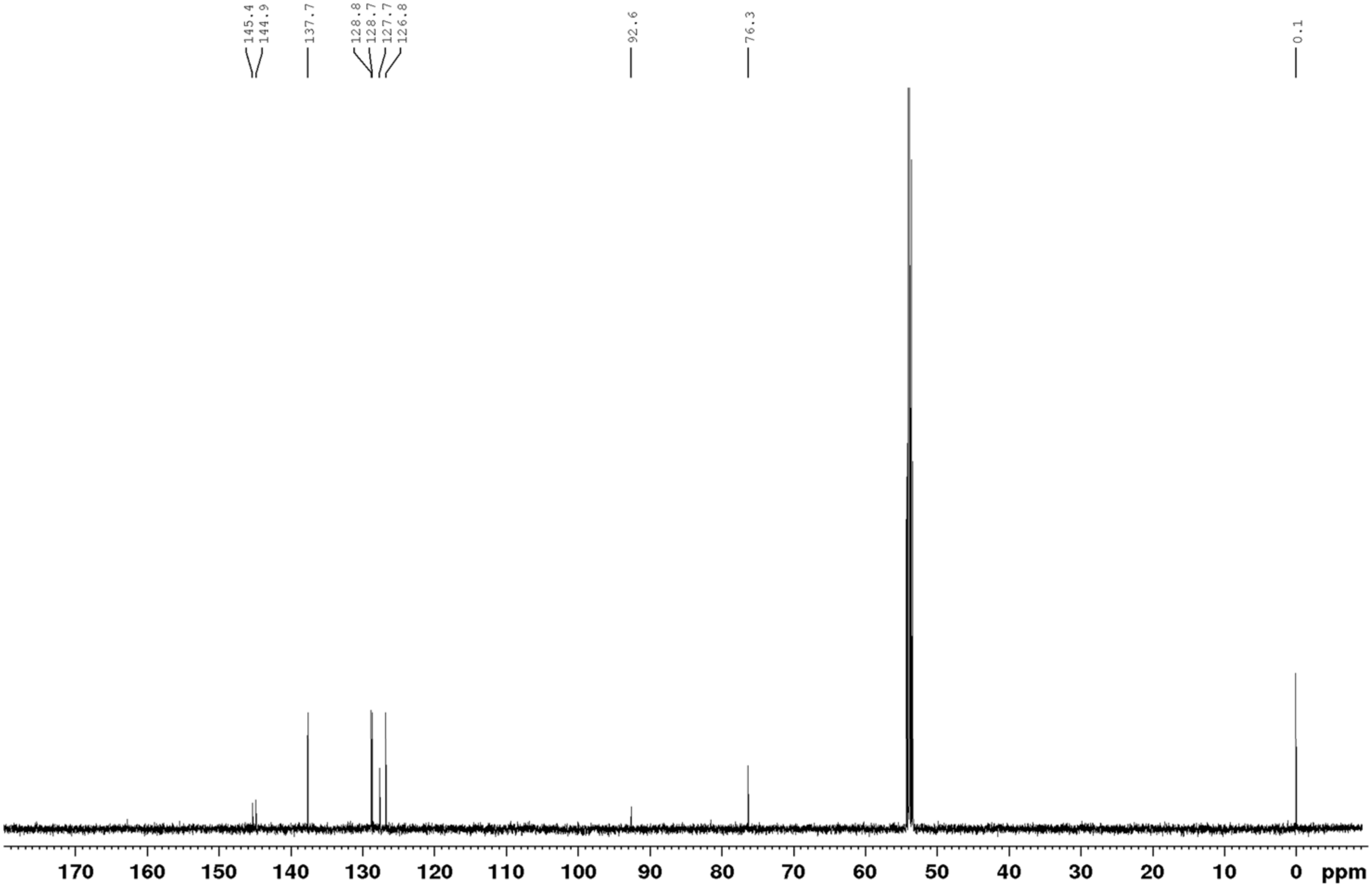


((4-Iodophenyl)(phenyl)methoxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

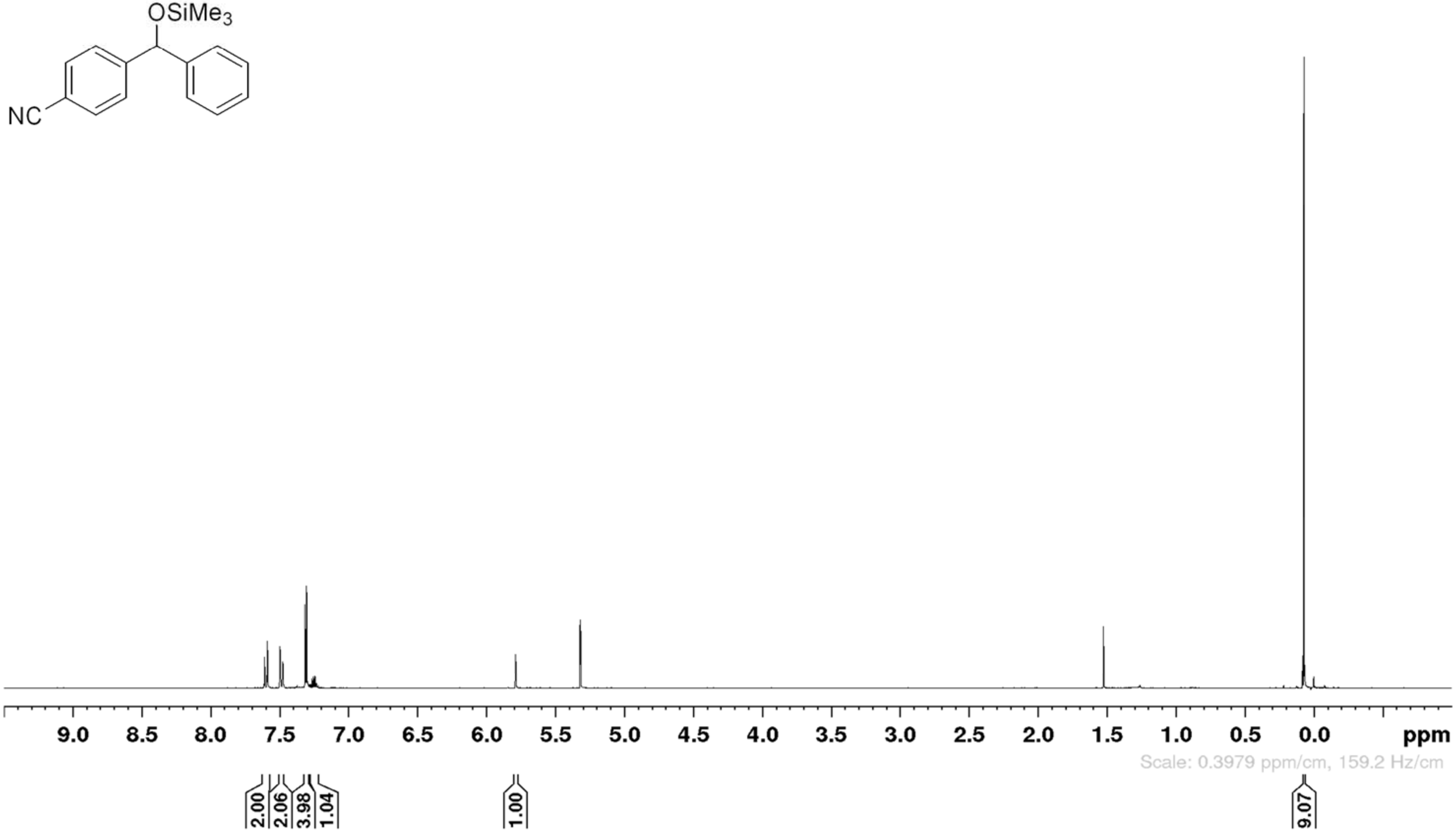


$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2)

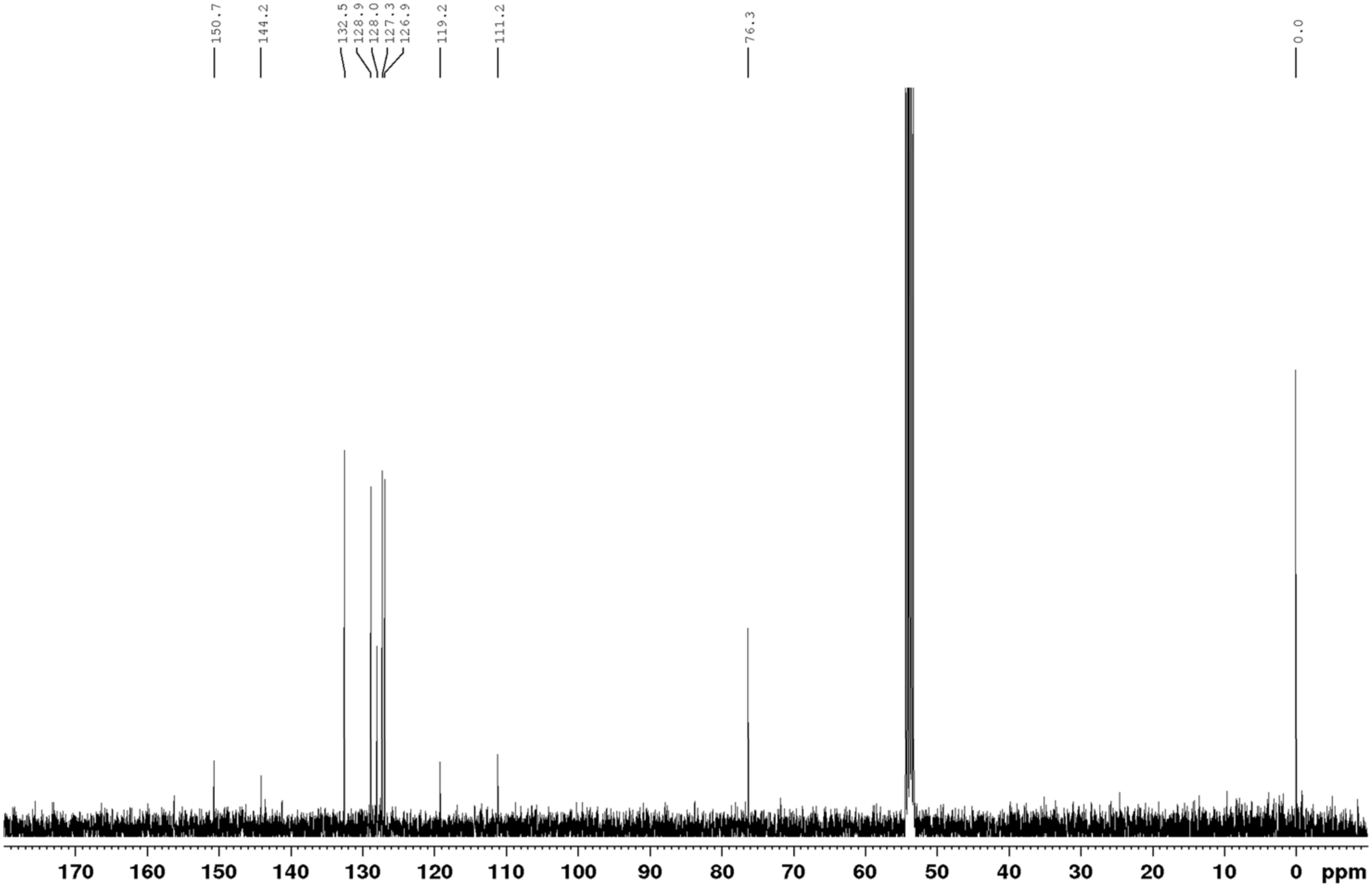


4-(Phenyl((trimethylsilyl)oxy)methyl)benzonitrile

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

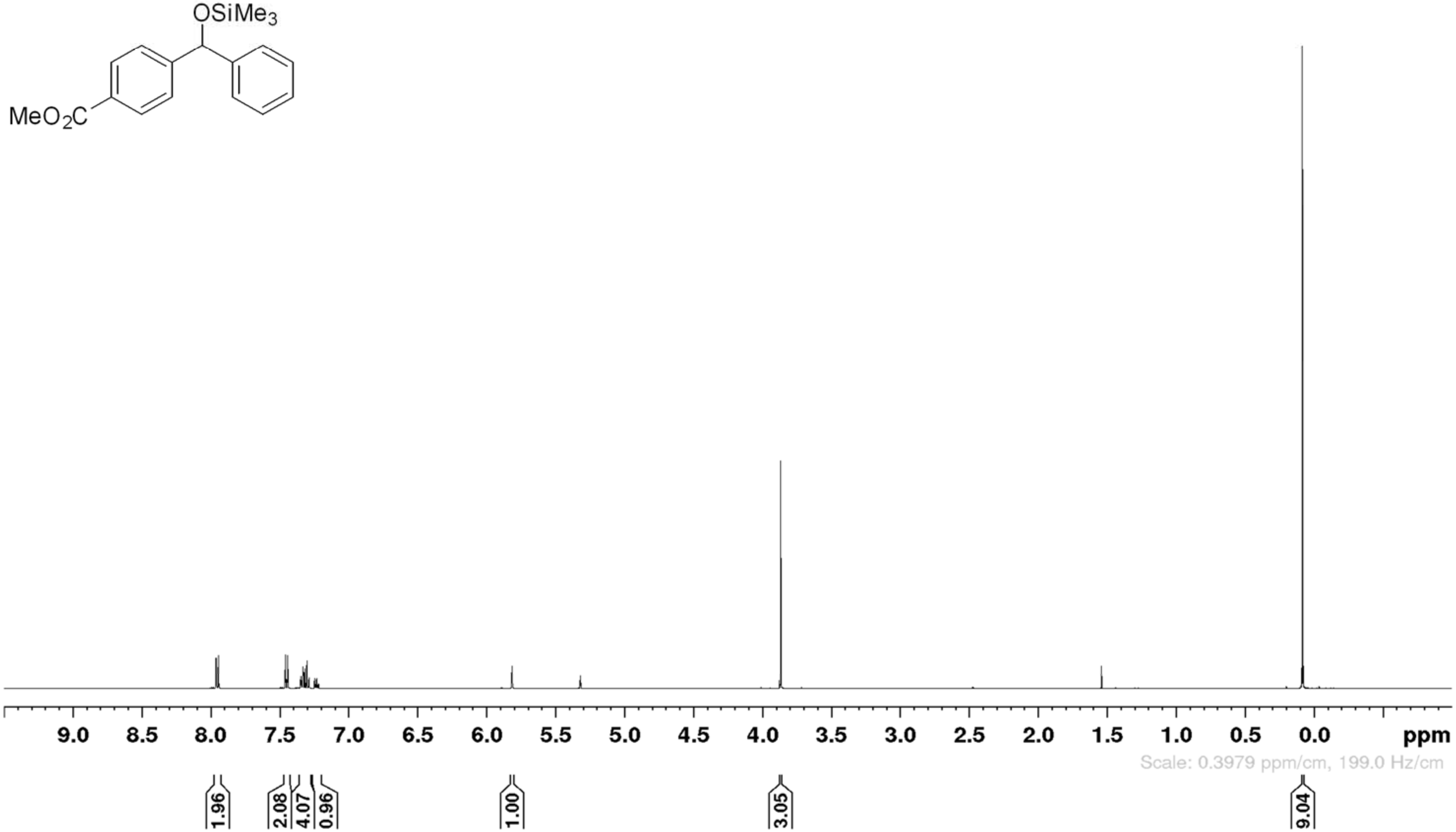


$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)

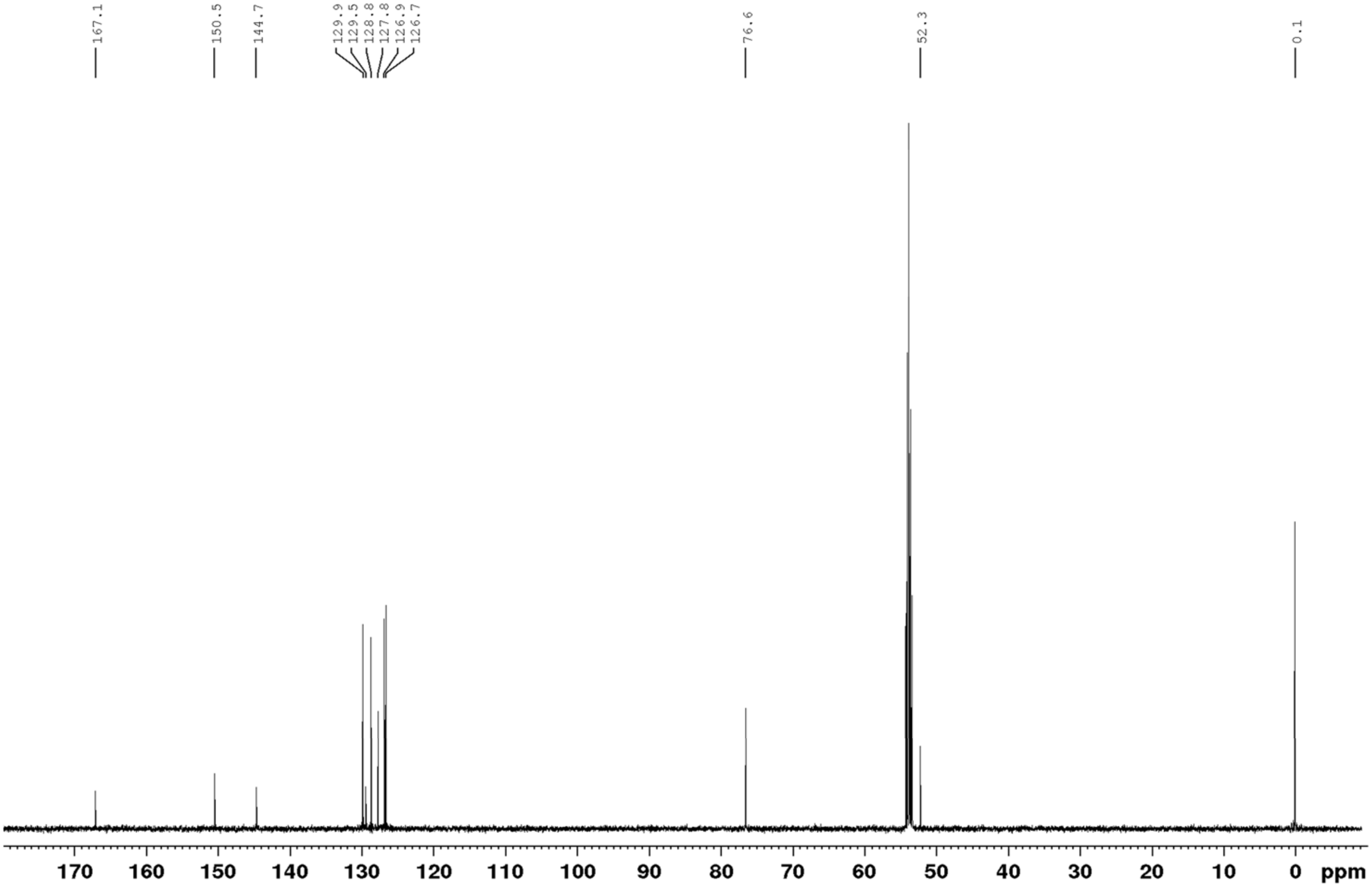


Methyl 4-(phenyl((trimethylsilyl)oxy)methyl)benzoate

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

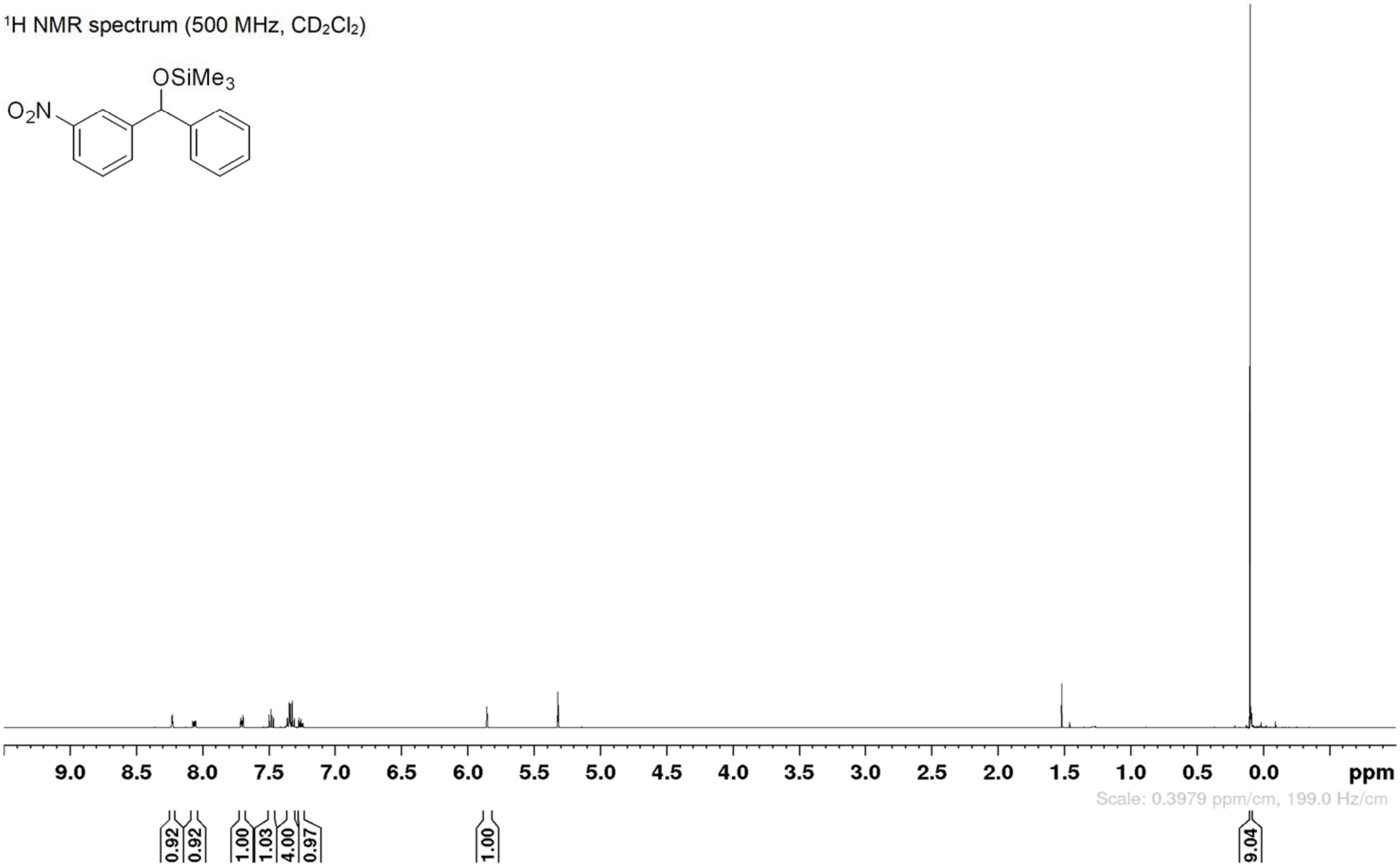


$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)

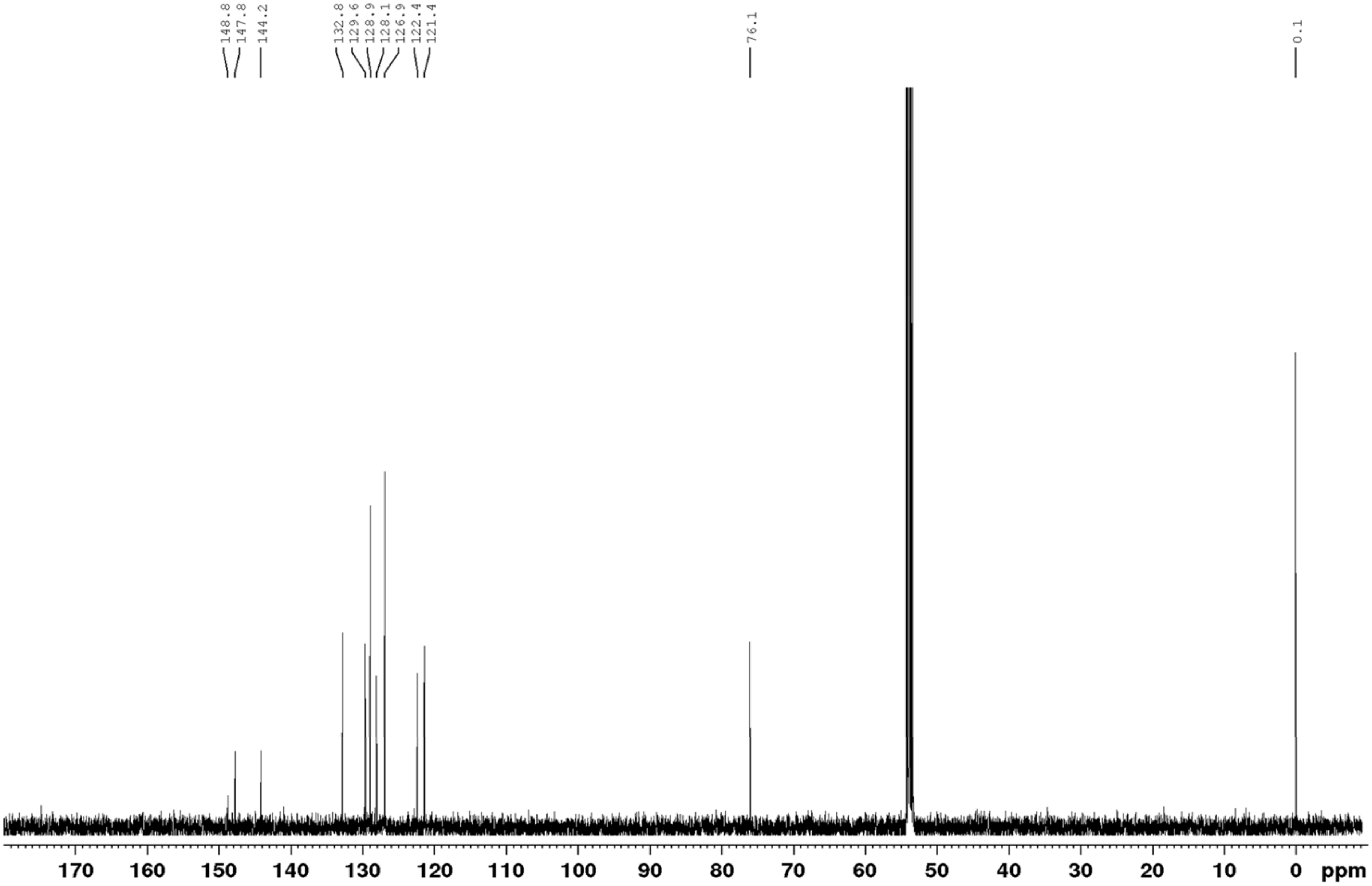


Trimethyl((4-nitrophenyl)(phenyl)methoxy)silane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

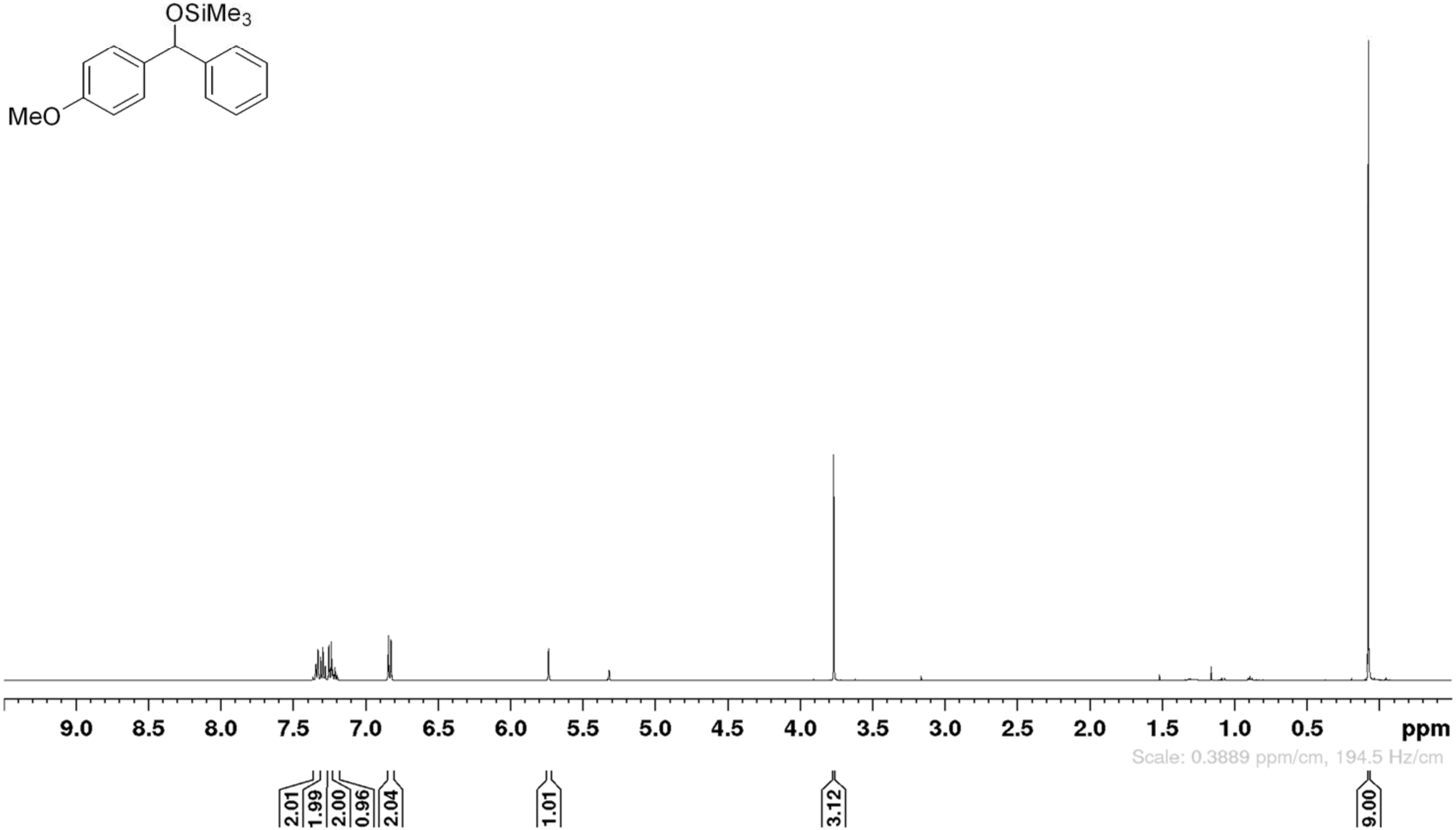


$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2)

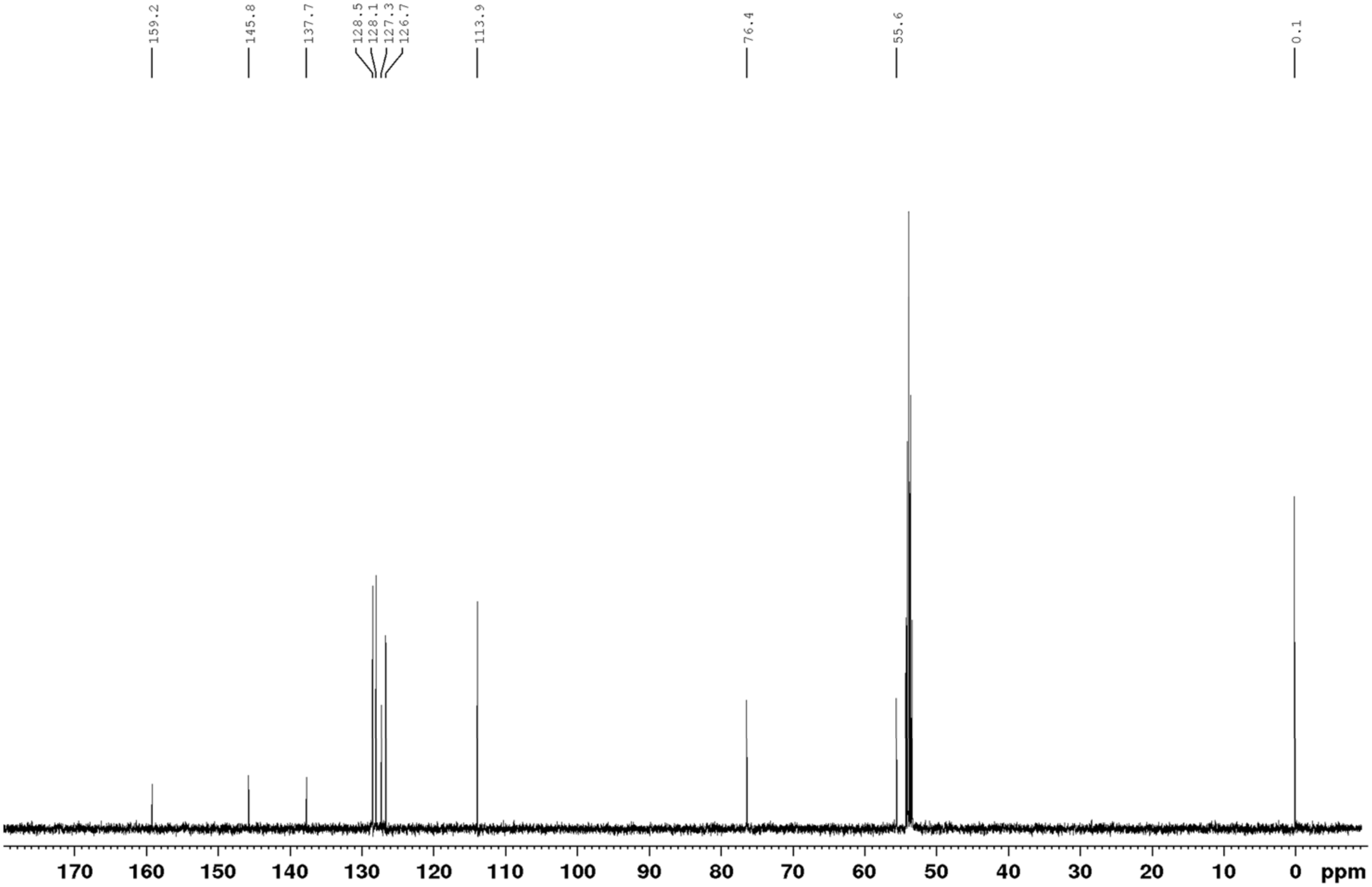


((4-Methoxyphenyl)(phenyl)methoxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

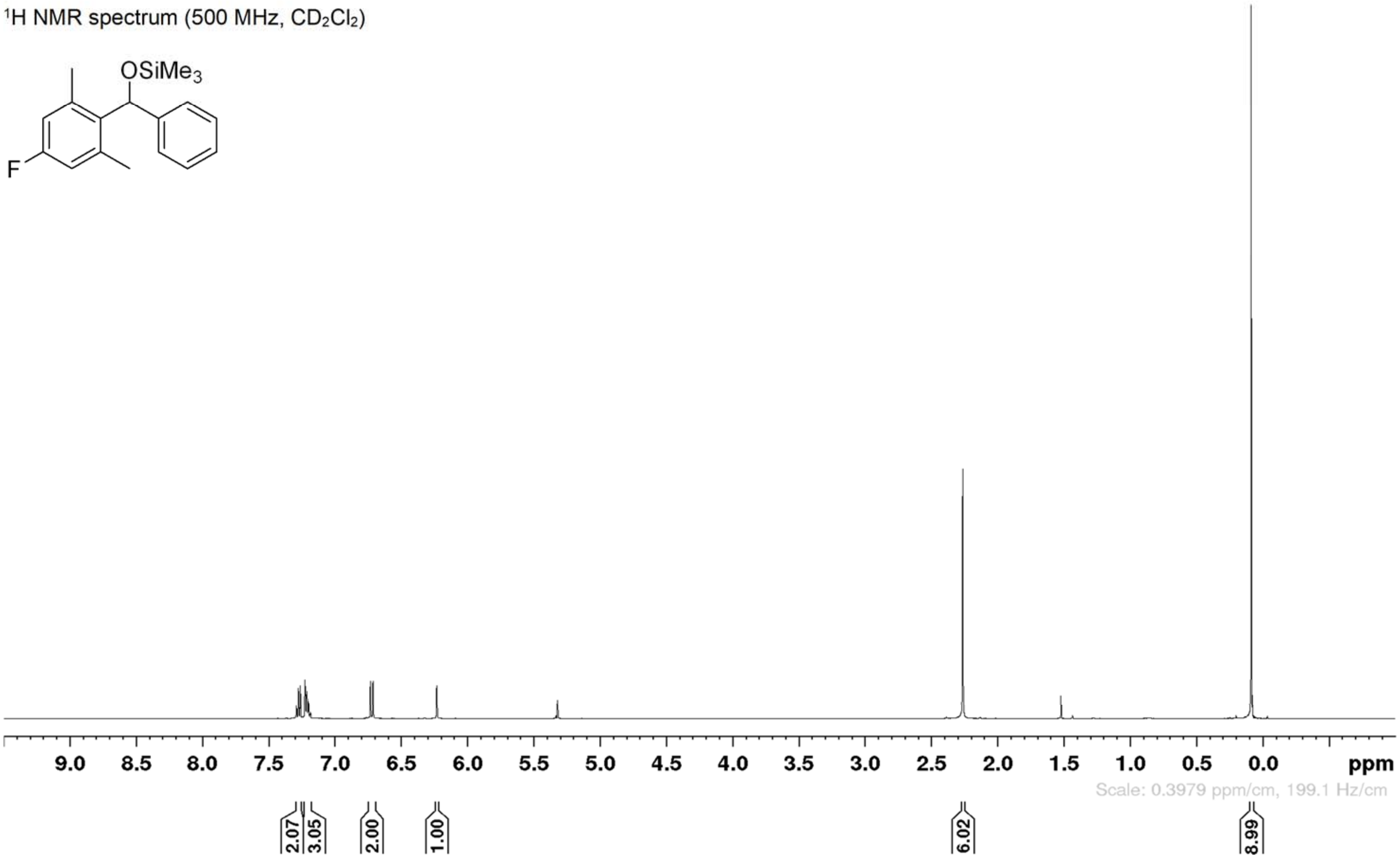


$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2)

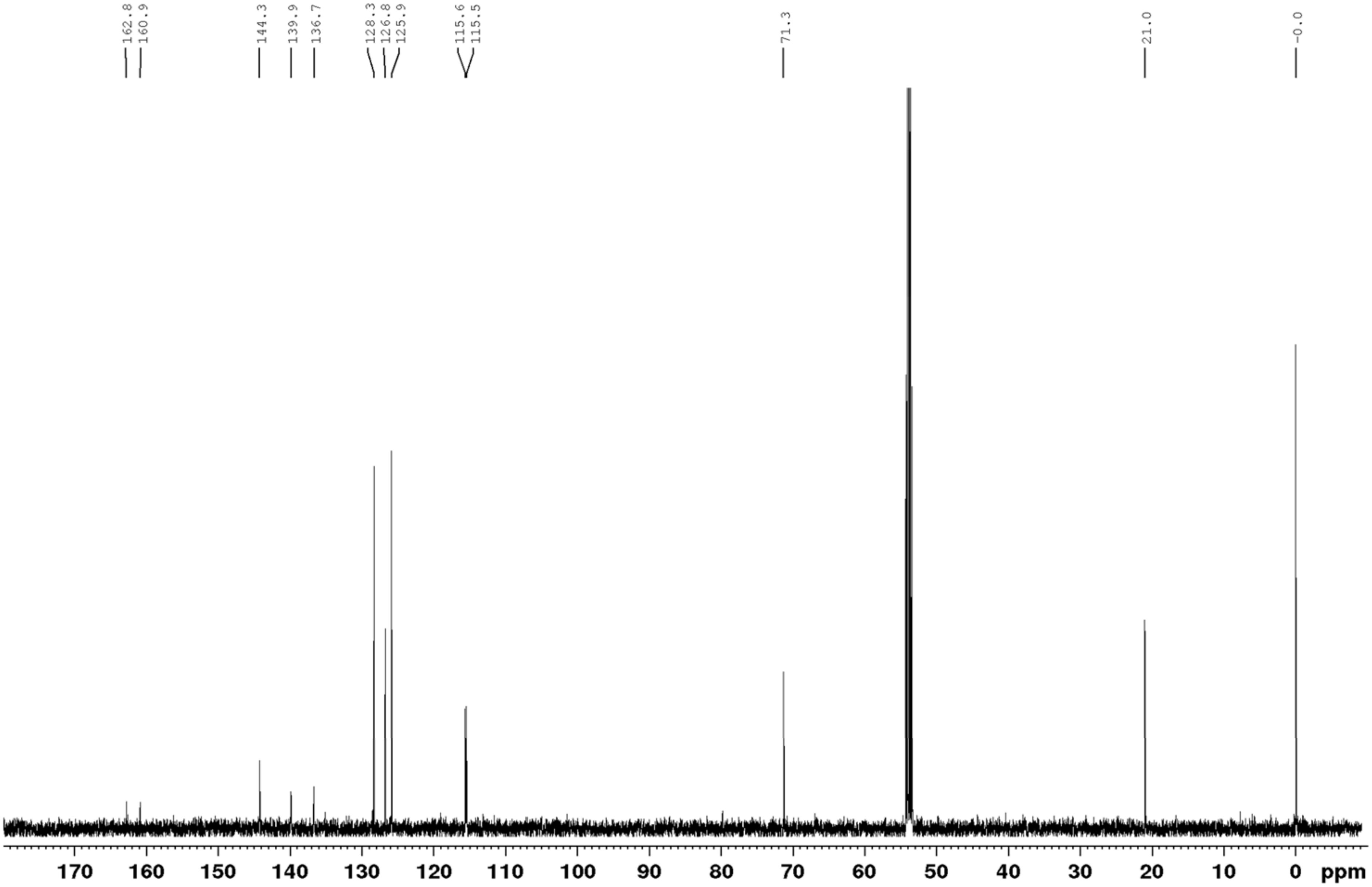


((4-Fluoro-2,6-dimethylphenyl)(phenyl)methoxy)trimethylsilane

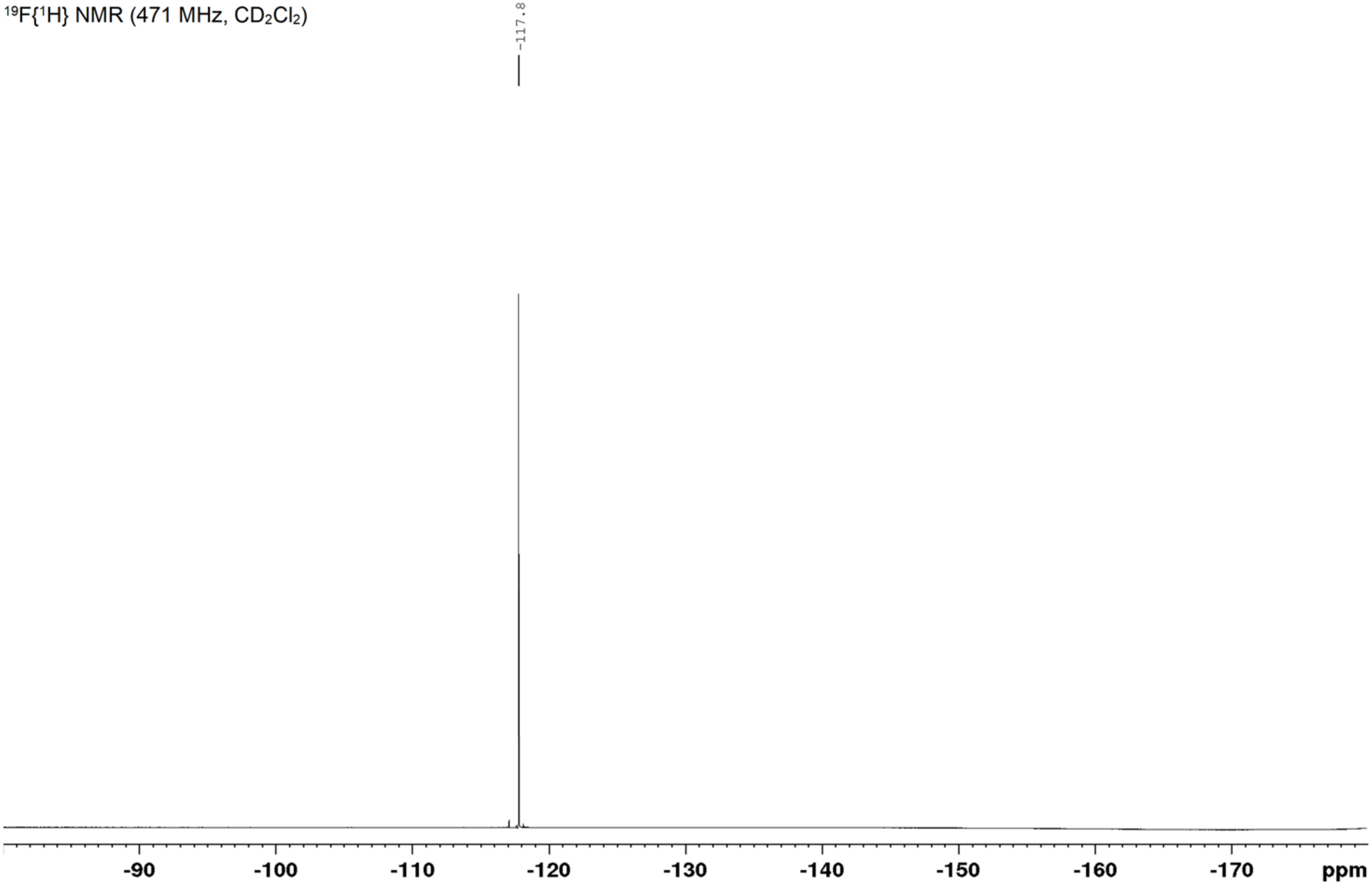
^{1}H NMR spectrum (500 MHz, CD_2Cl_2)



$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)

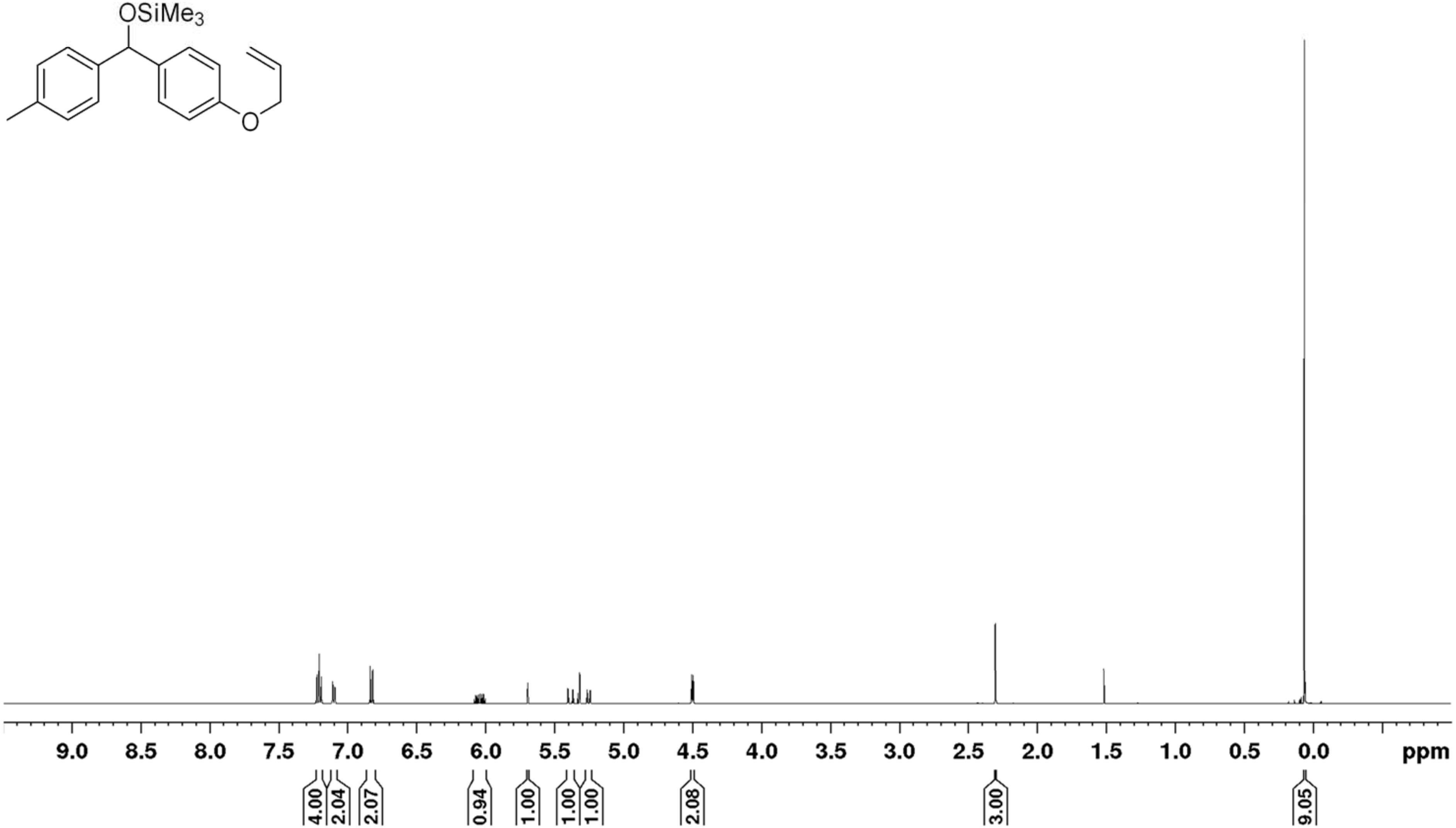


$^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2)

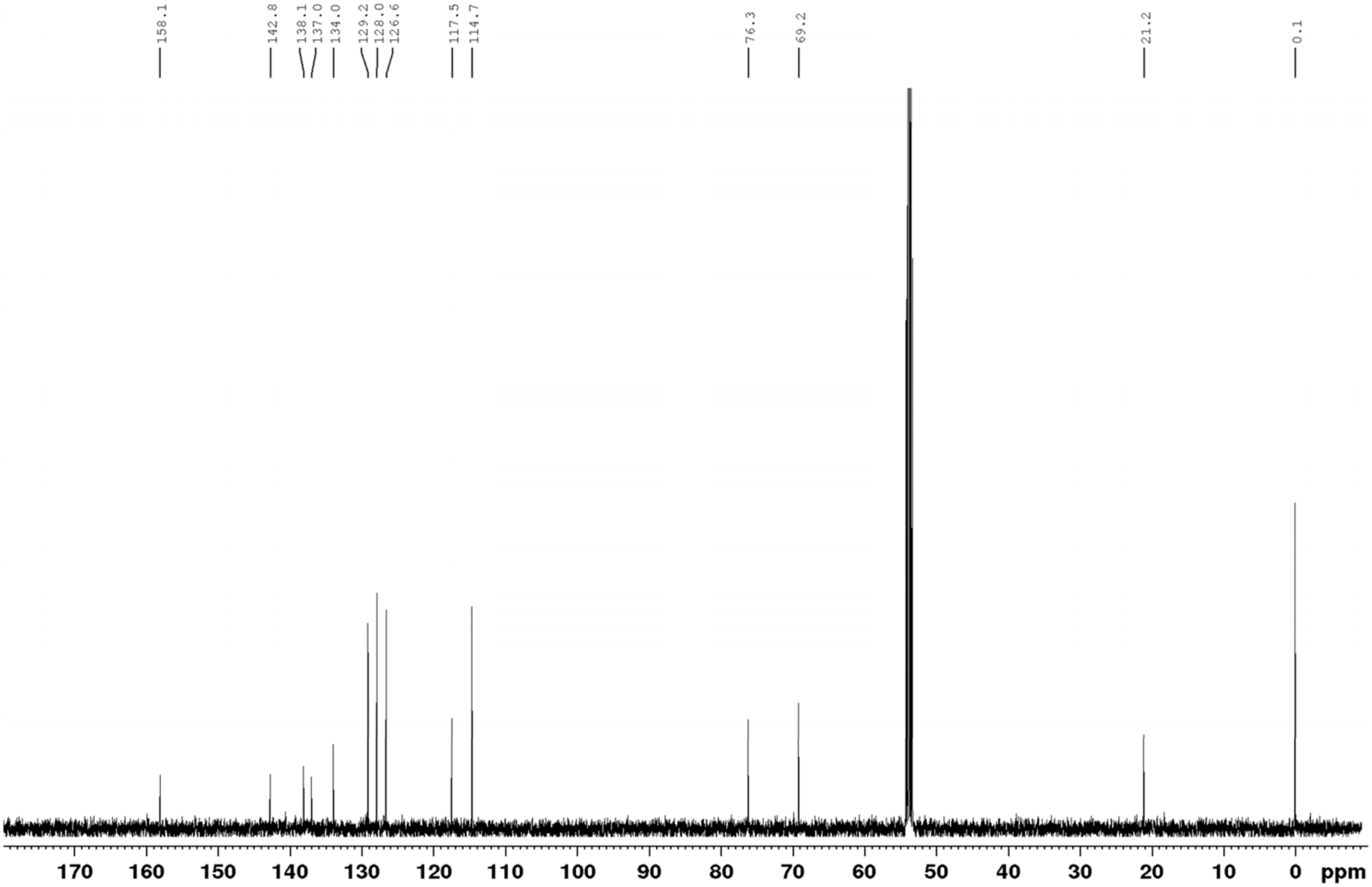


((4-(Allyloxy)phenyl)(*p*-tolyl)methoxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

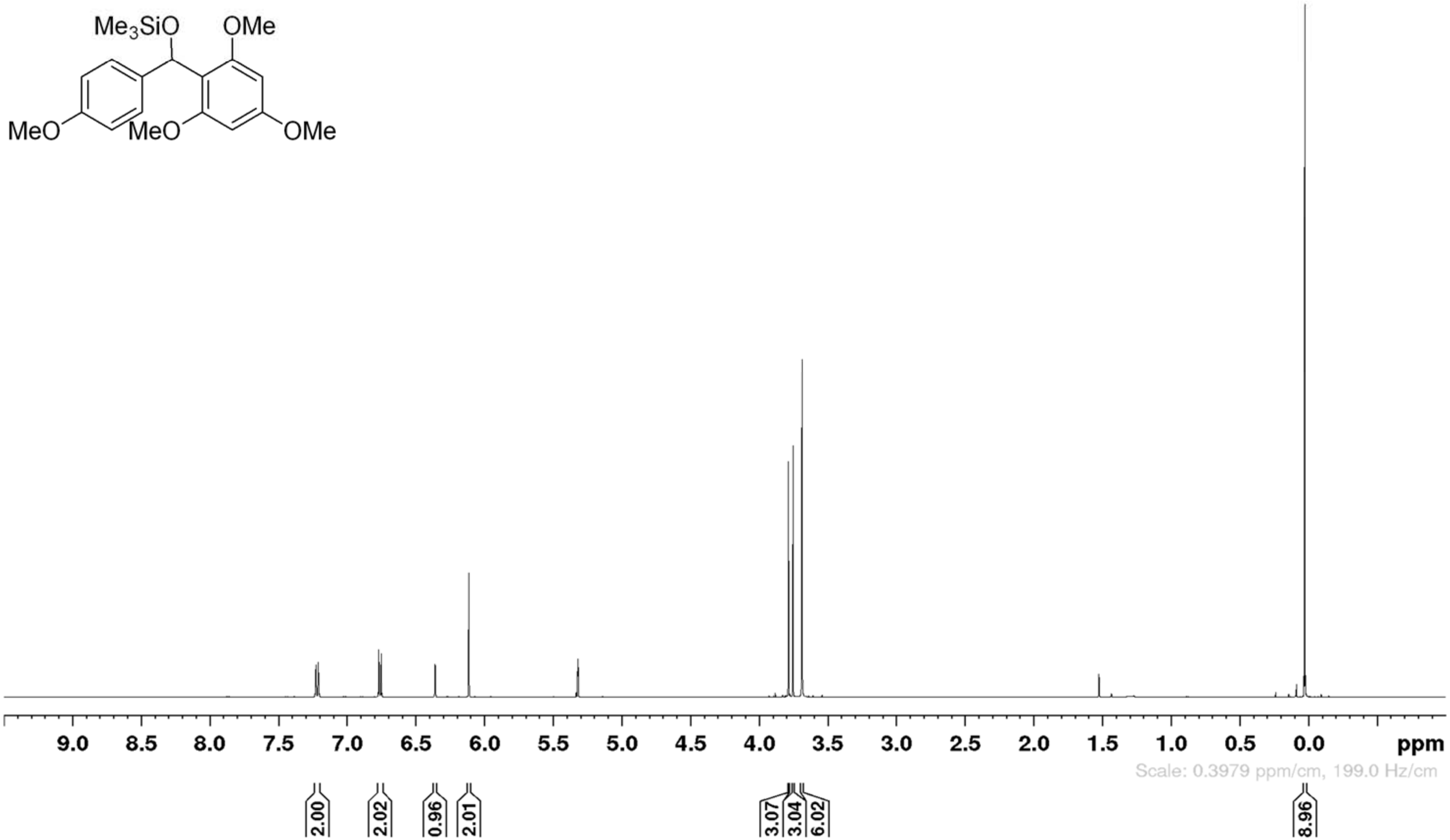


$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)

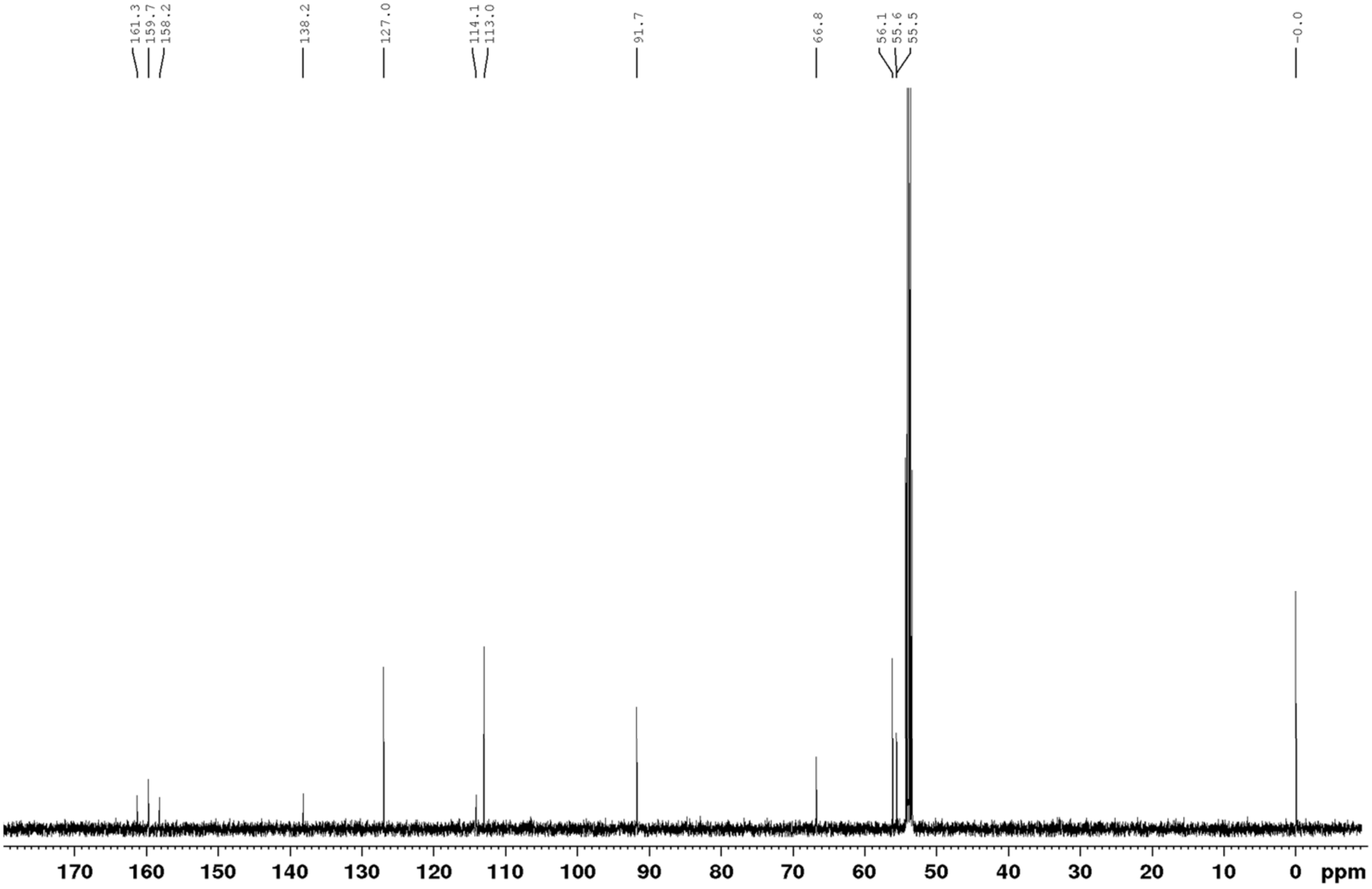


((4-Methoxyphenyl)(2,4,6-trimethoxyphenyl)methoxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

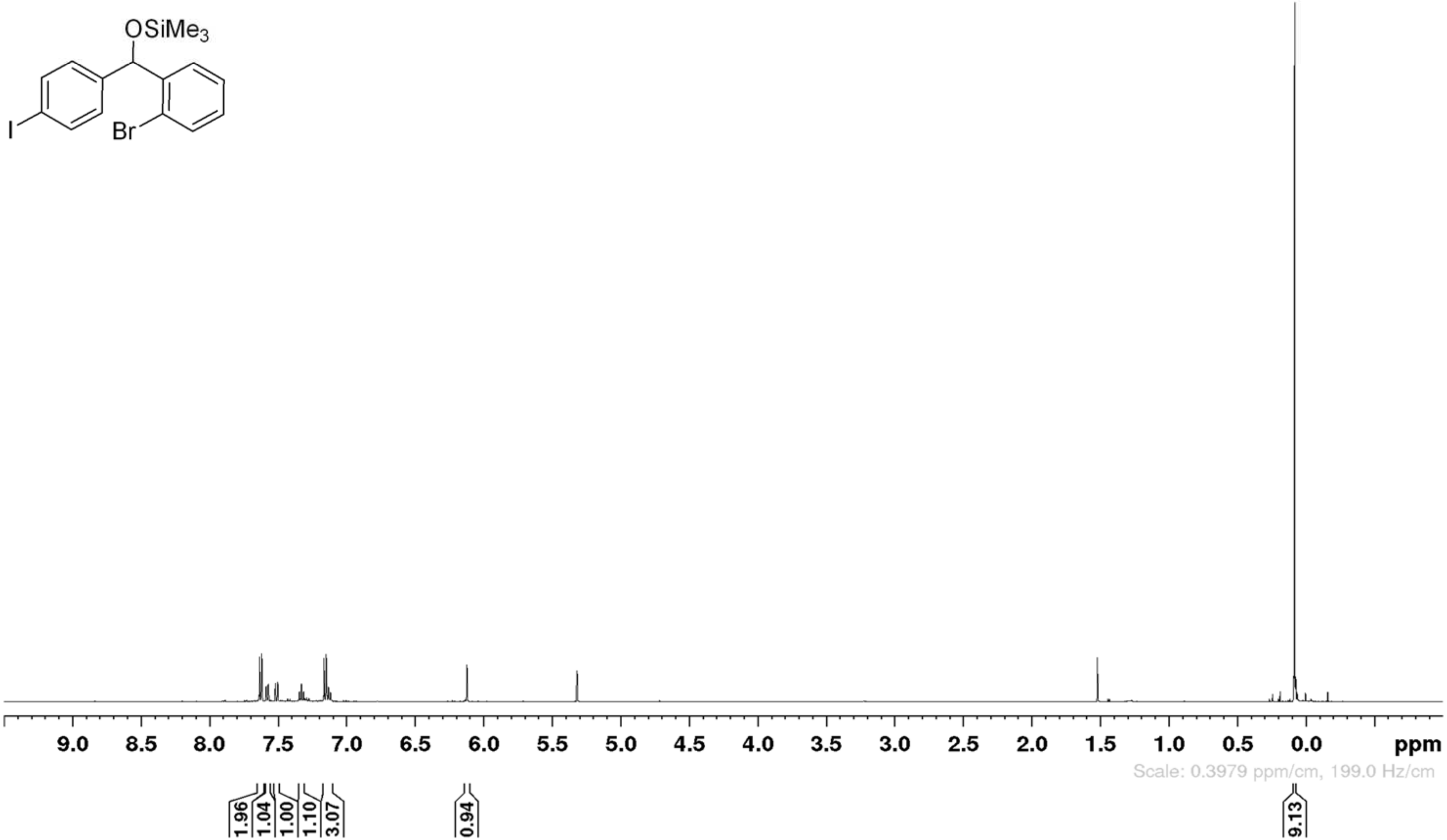


$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)

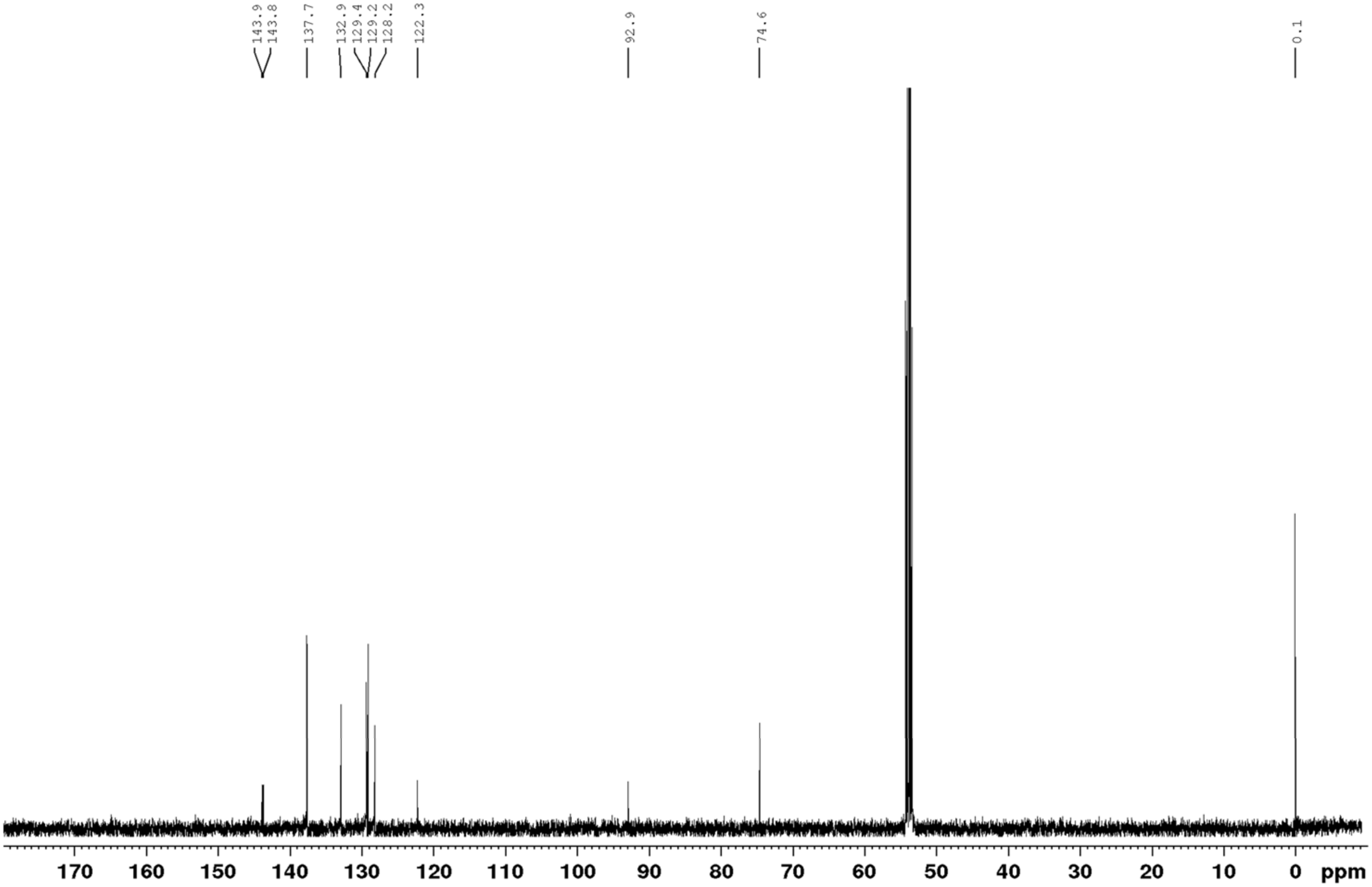


((2-Bromophenyl)(4-iodophenyl)methoxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

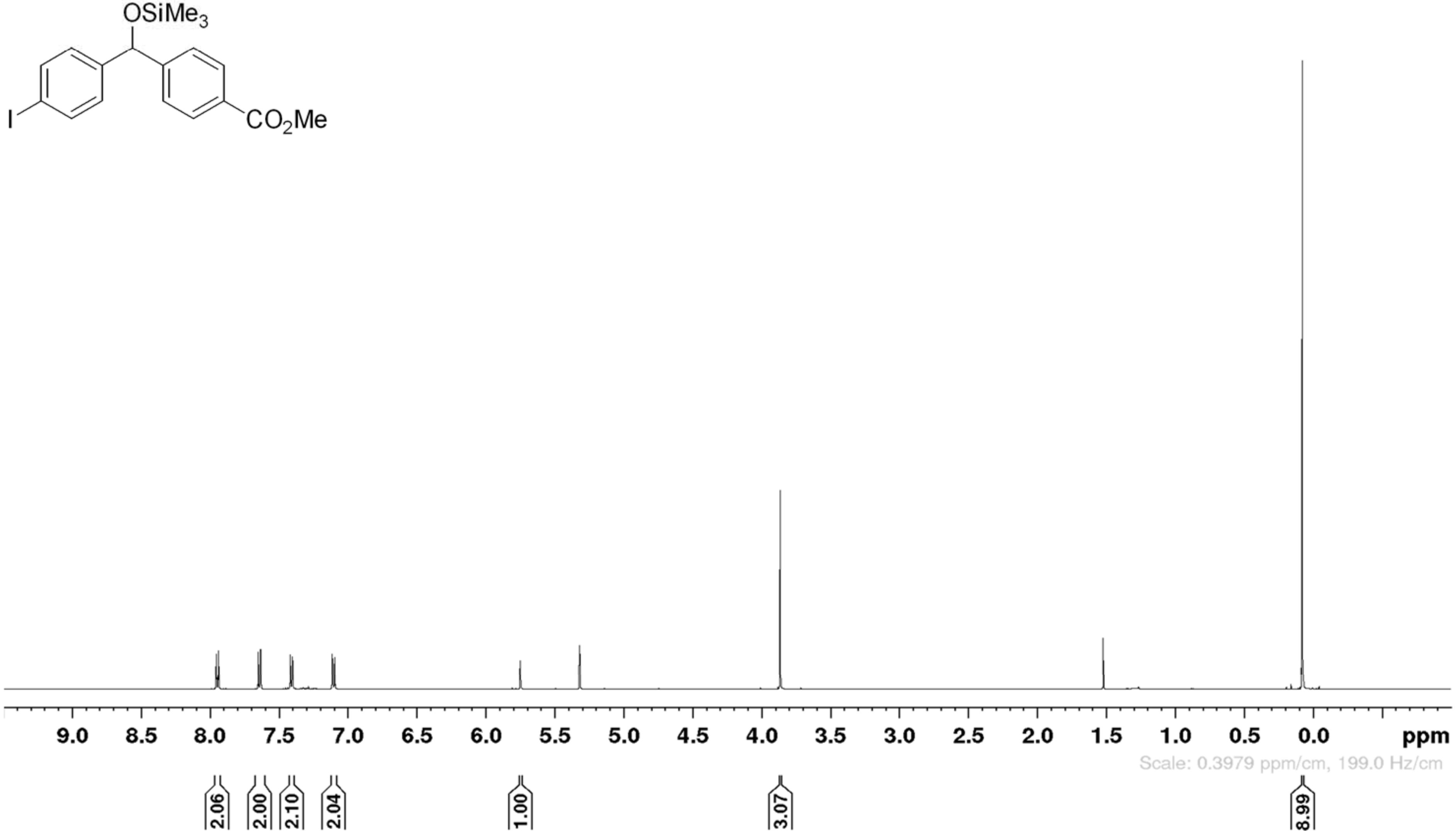


$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)

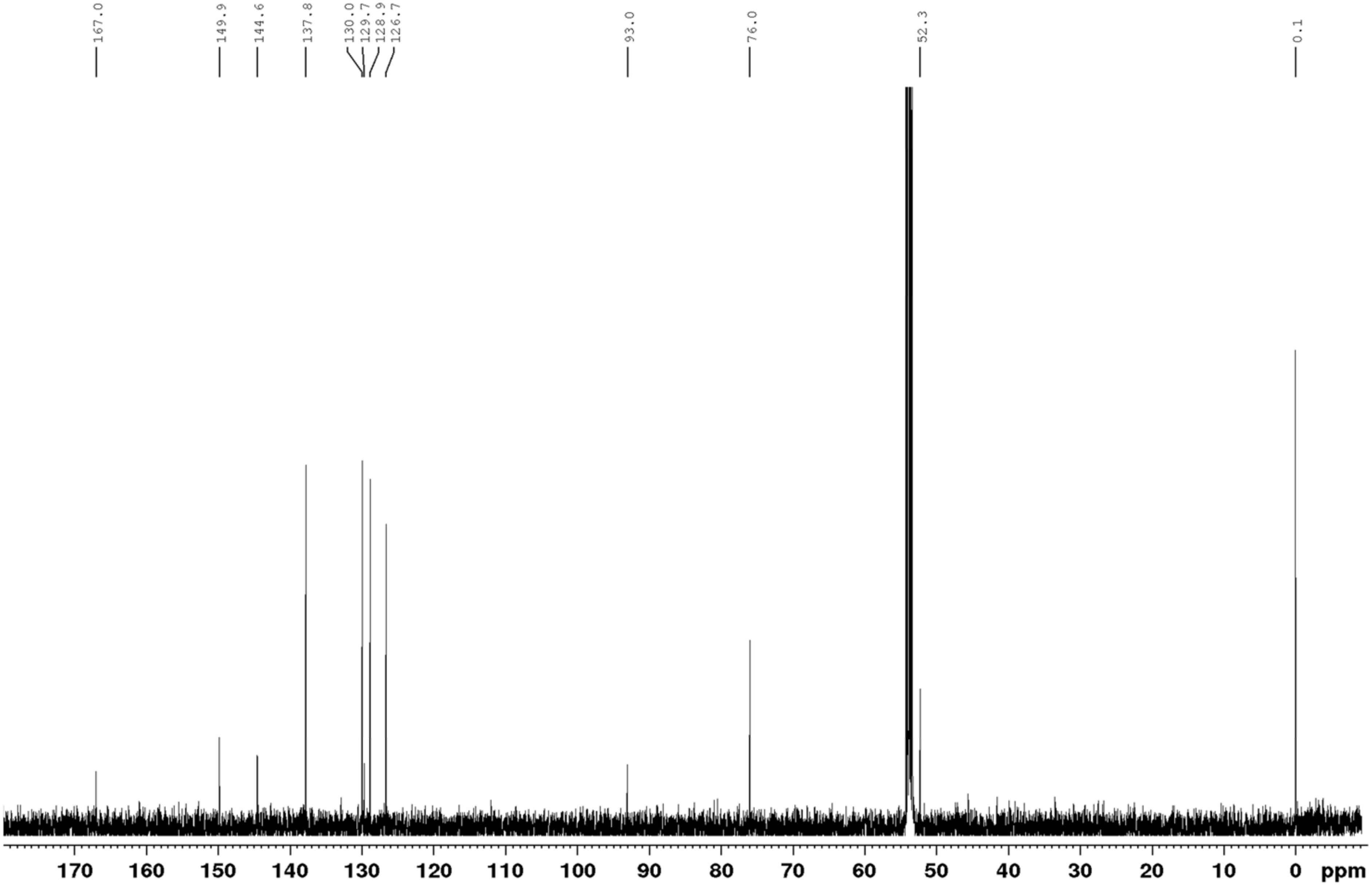


Methyl 4-((4-iodophenyl)((trimethylsilyl)oxy)methyl)benzoate

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

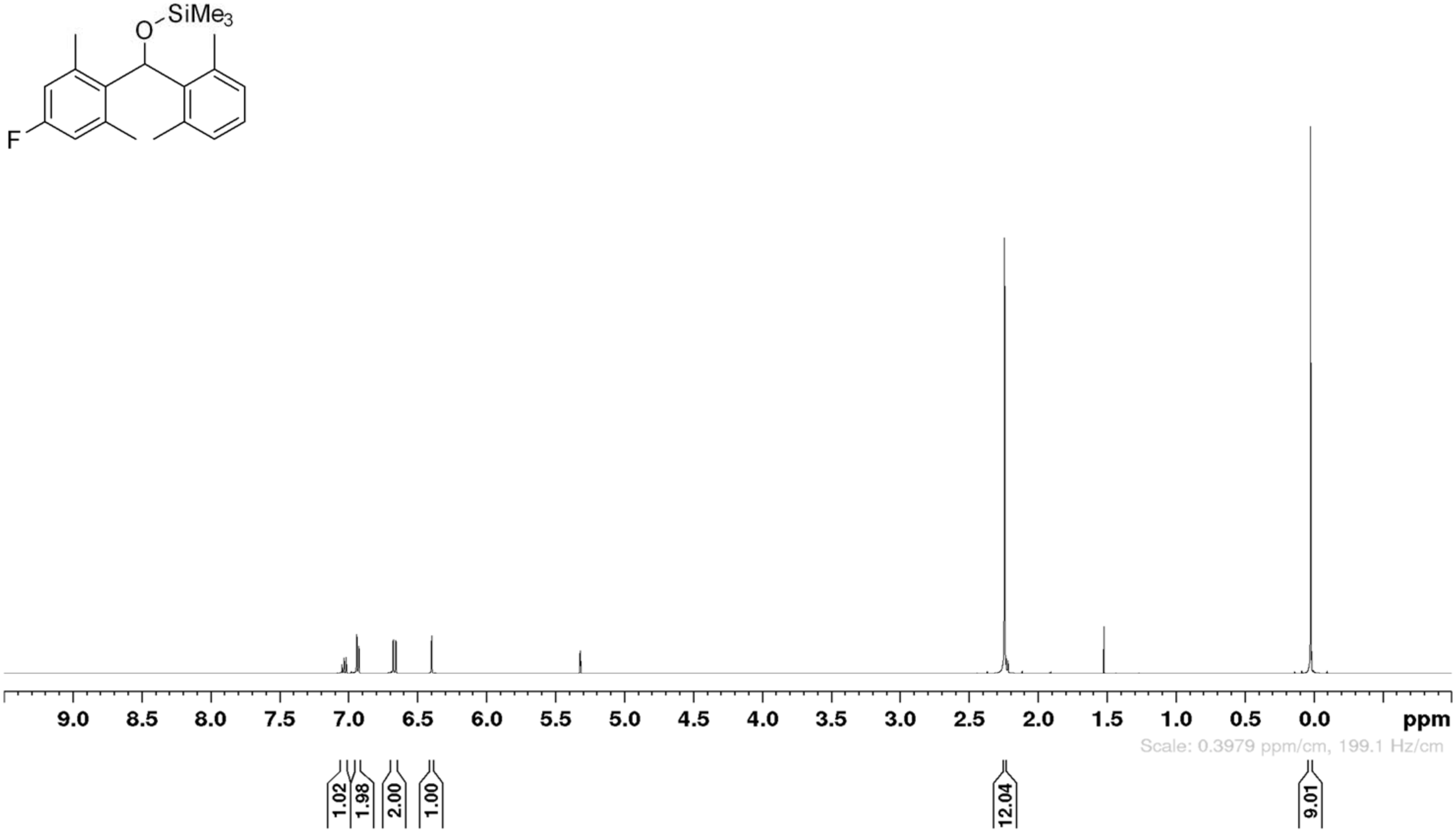


$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2)

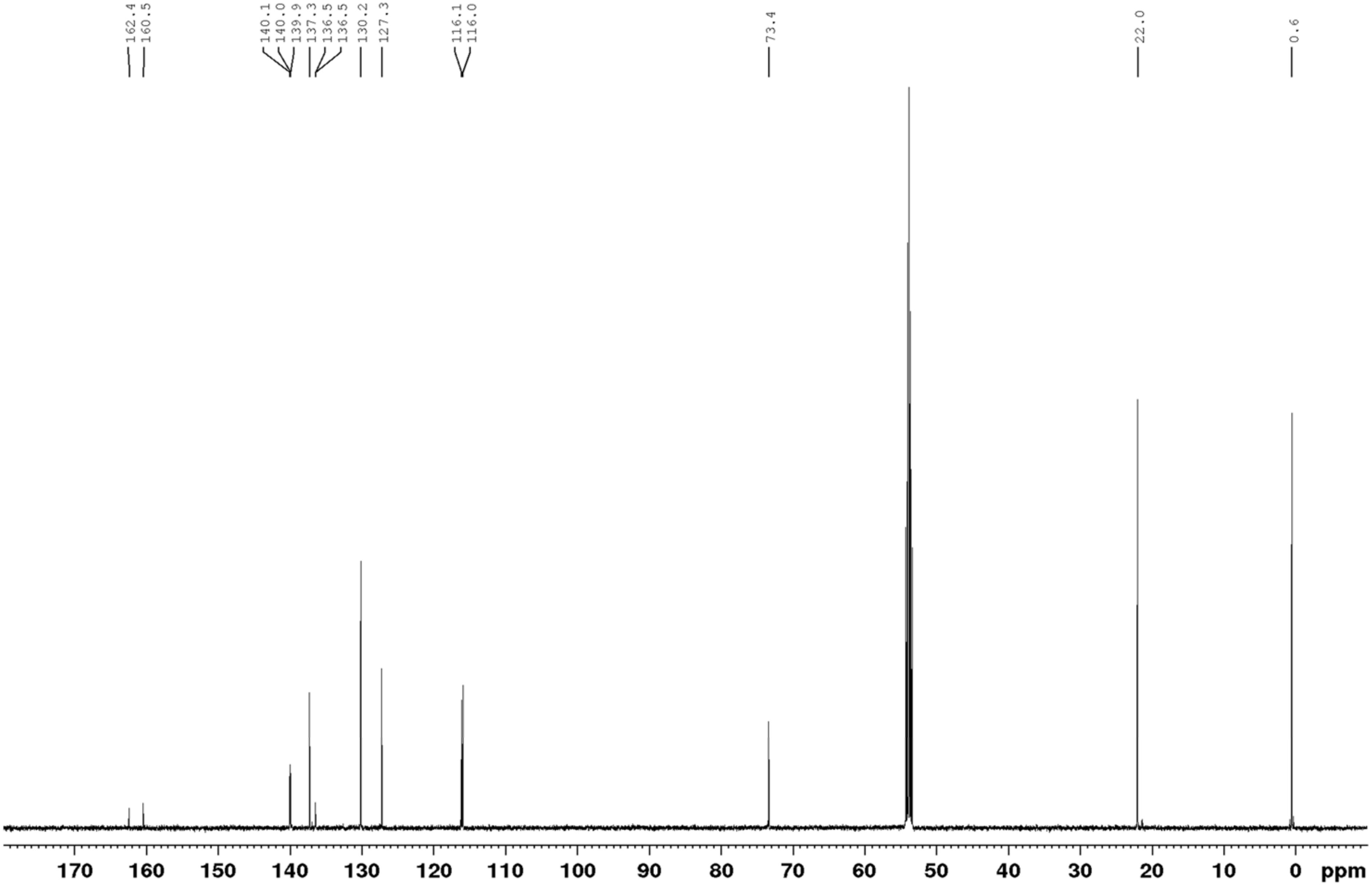


((2,6-Dimethylphenyl)(4-fluoro-2,6-dimethylphenyl)methoxy)trimethylsilane

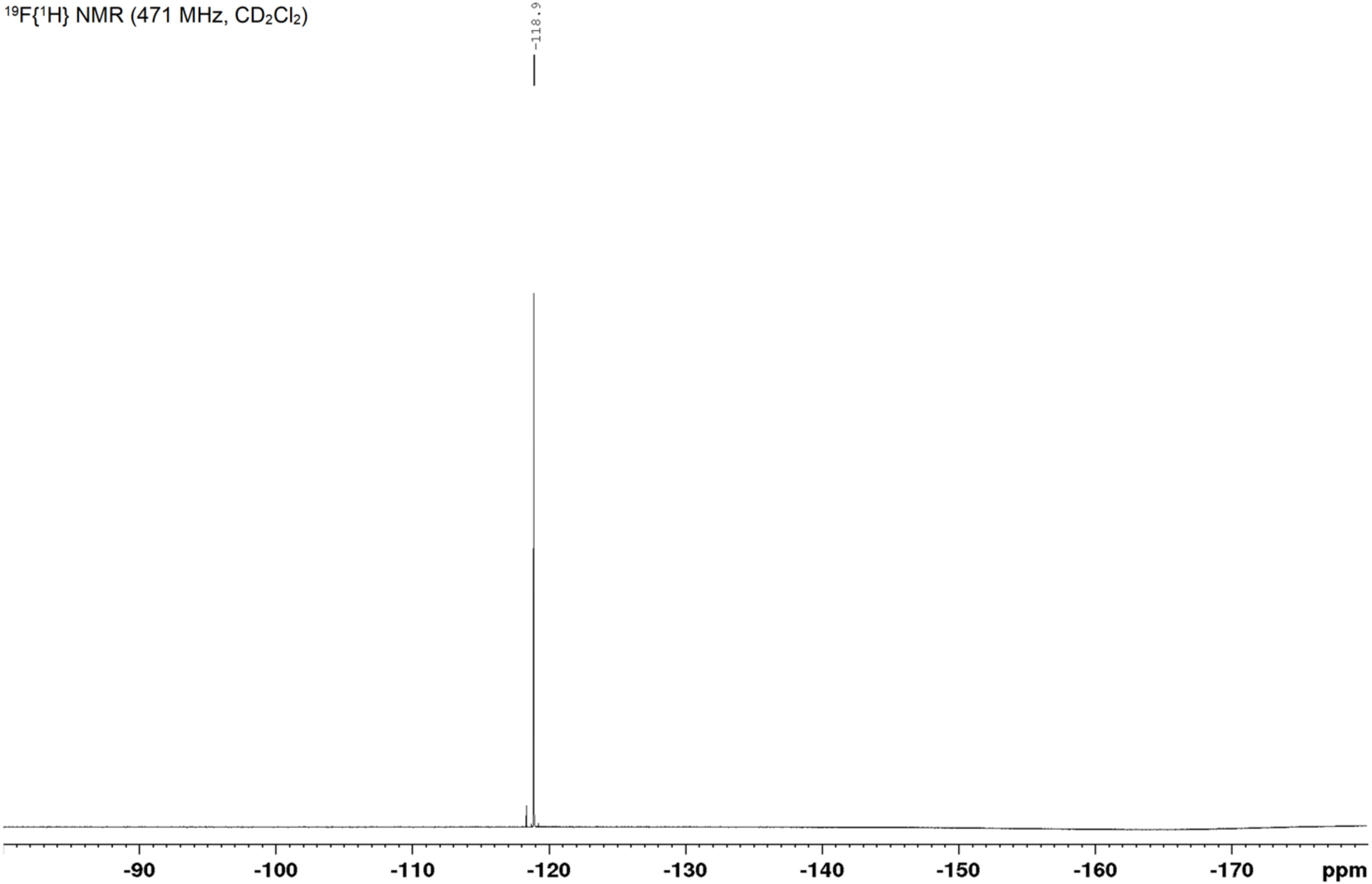
^{1}H NMR spectrum (500 MHz, CD_2Cl_2)



$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)

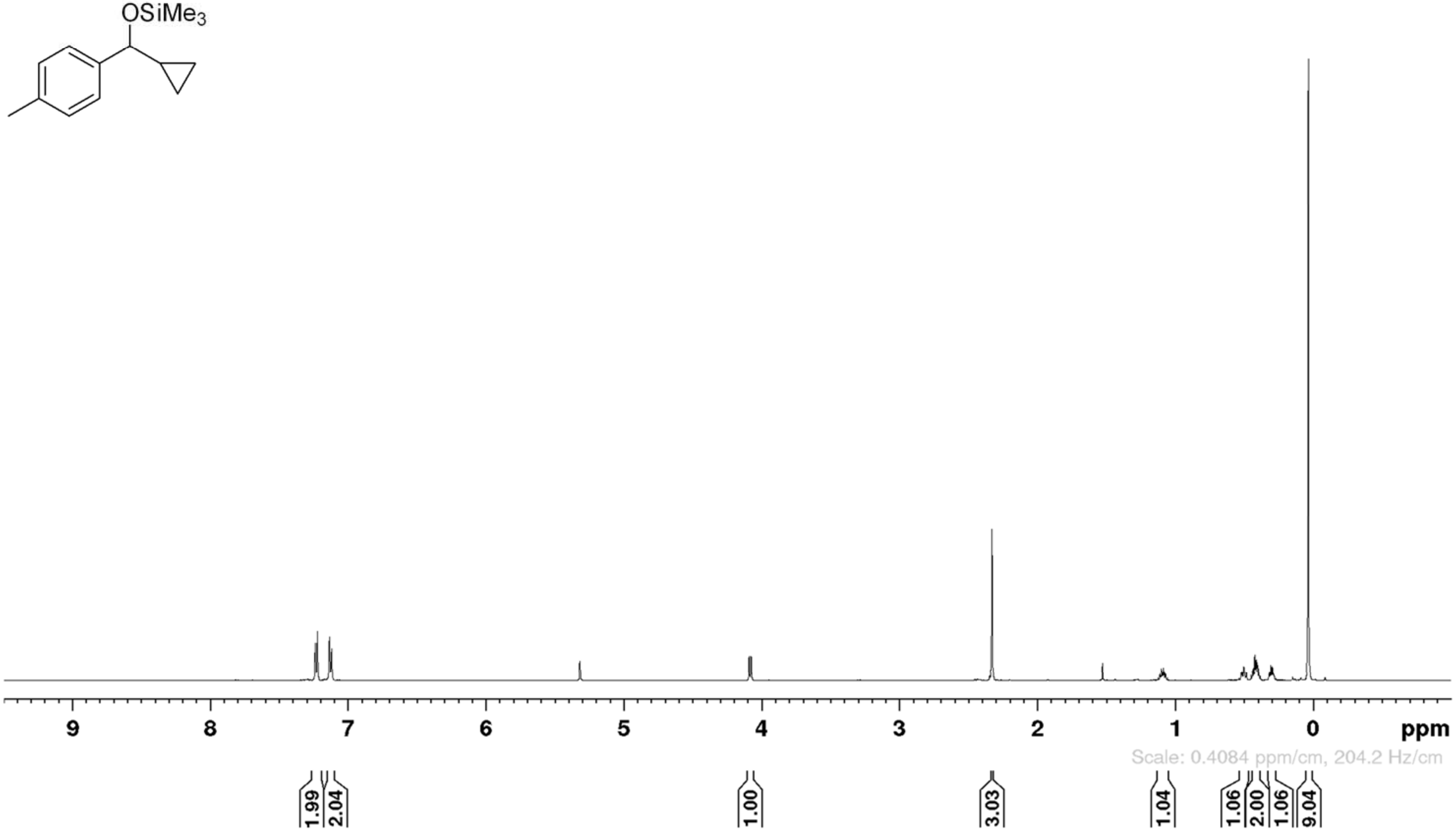


$^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2)

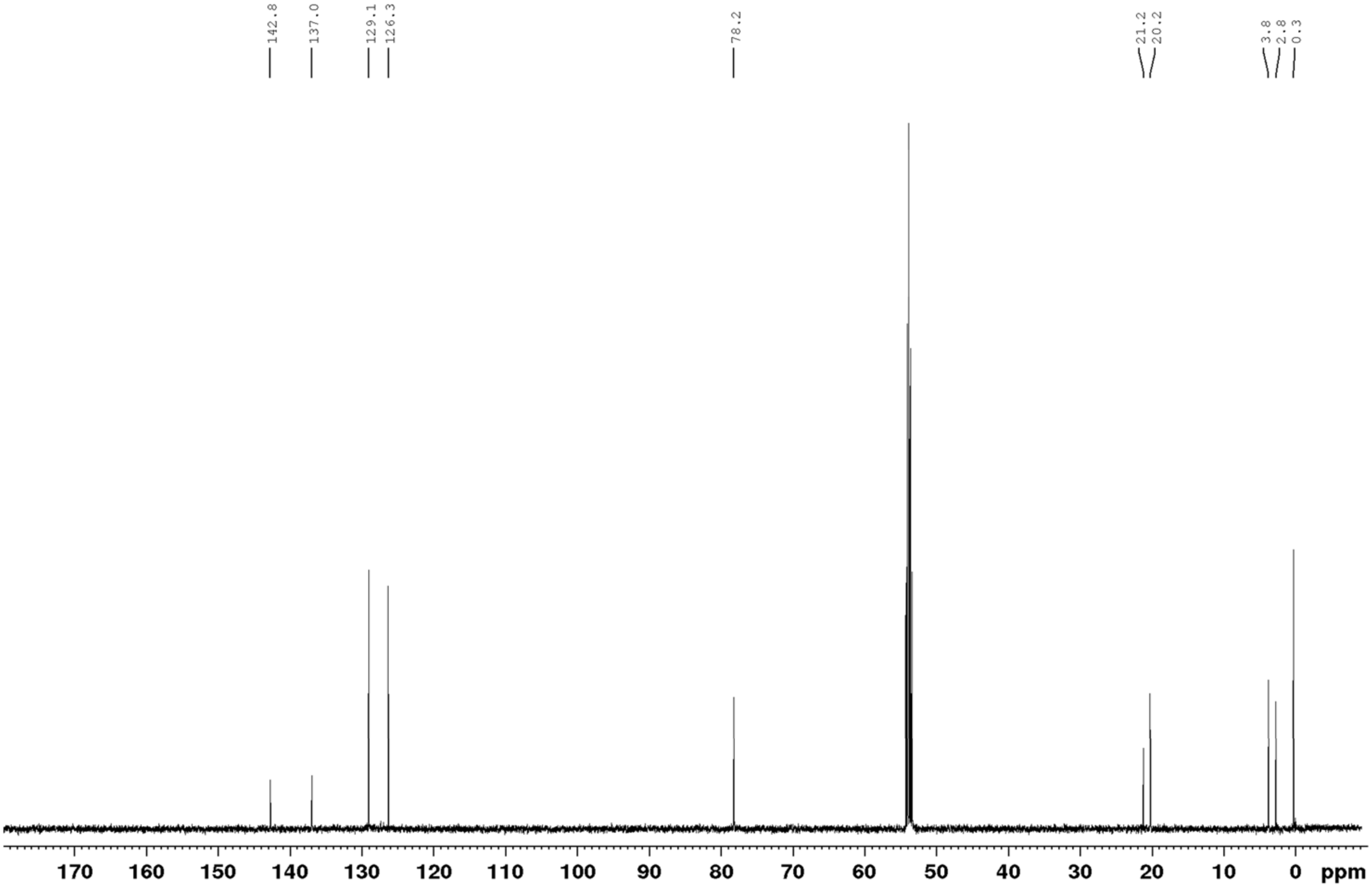


(Cyclopropyl(*p*-tolyl)methoxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

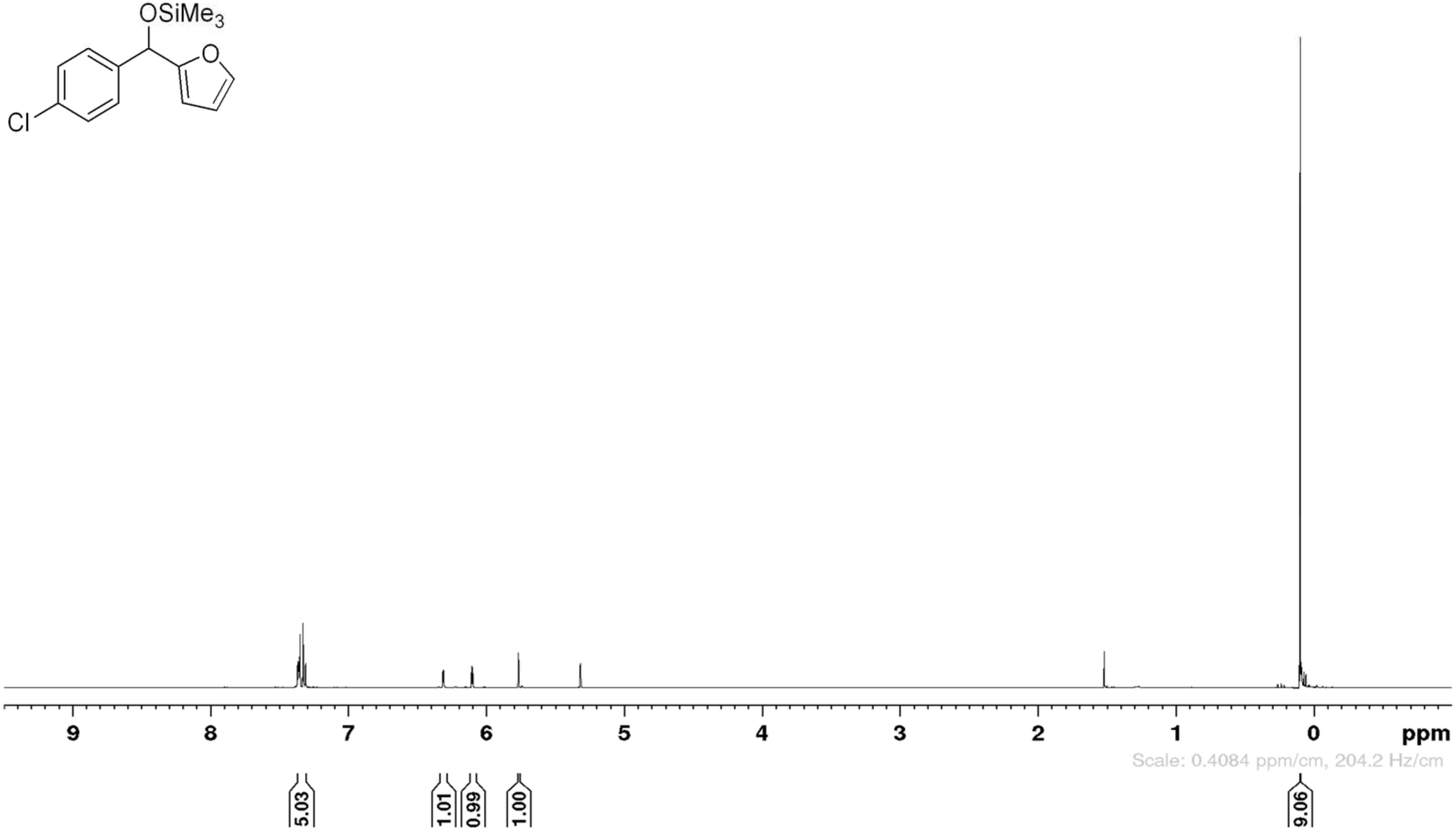


$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2)

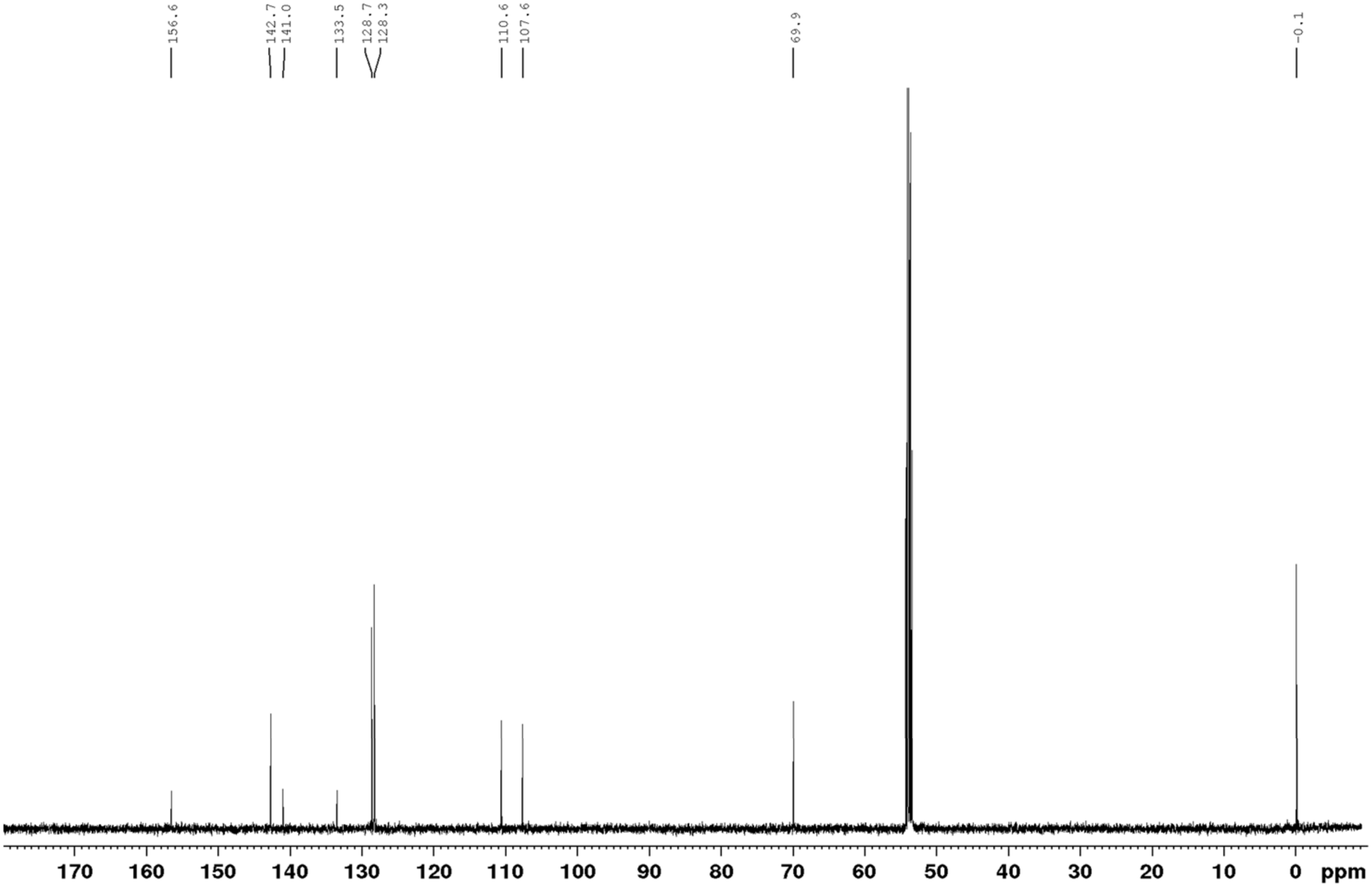


((4-Chlorophenyl)(furan-2-yl)methoxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

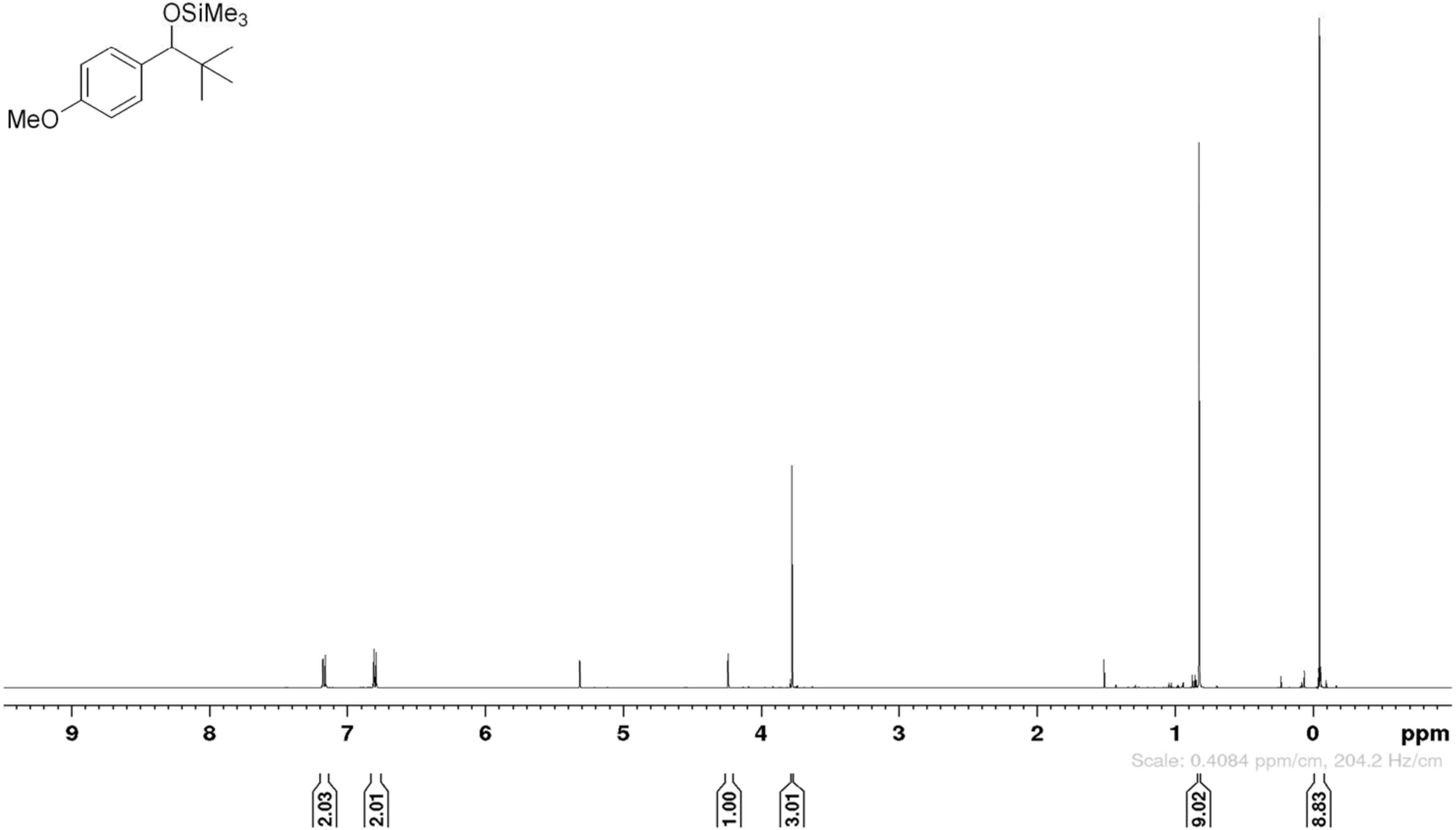


$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)

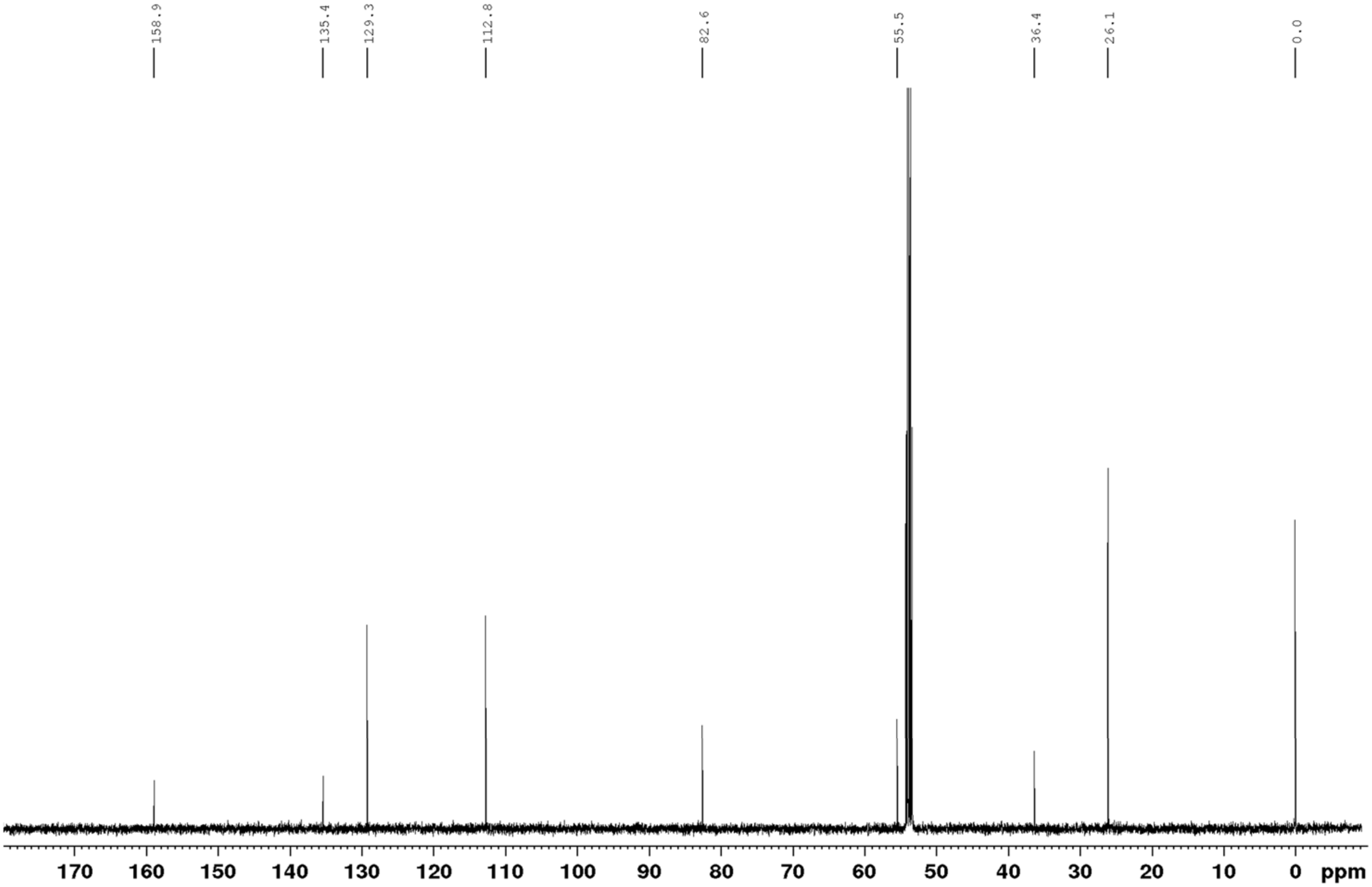


(1-(4-Methoxyphenyl)-2,2-dimethylpropoxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

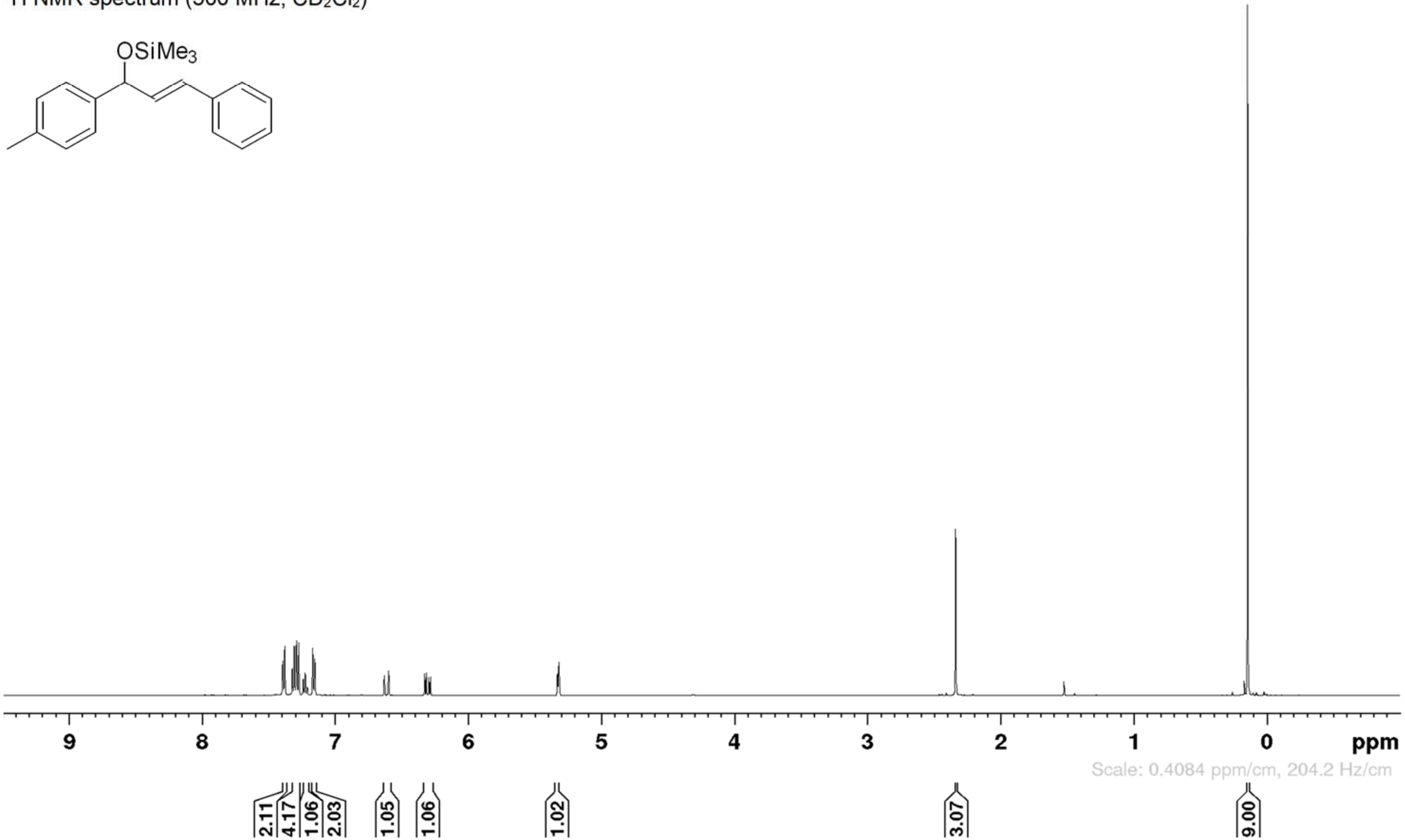


$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)

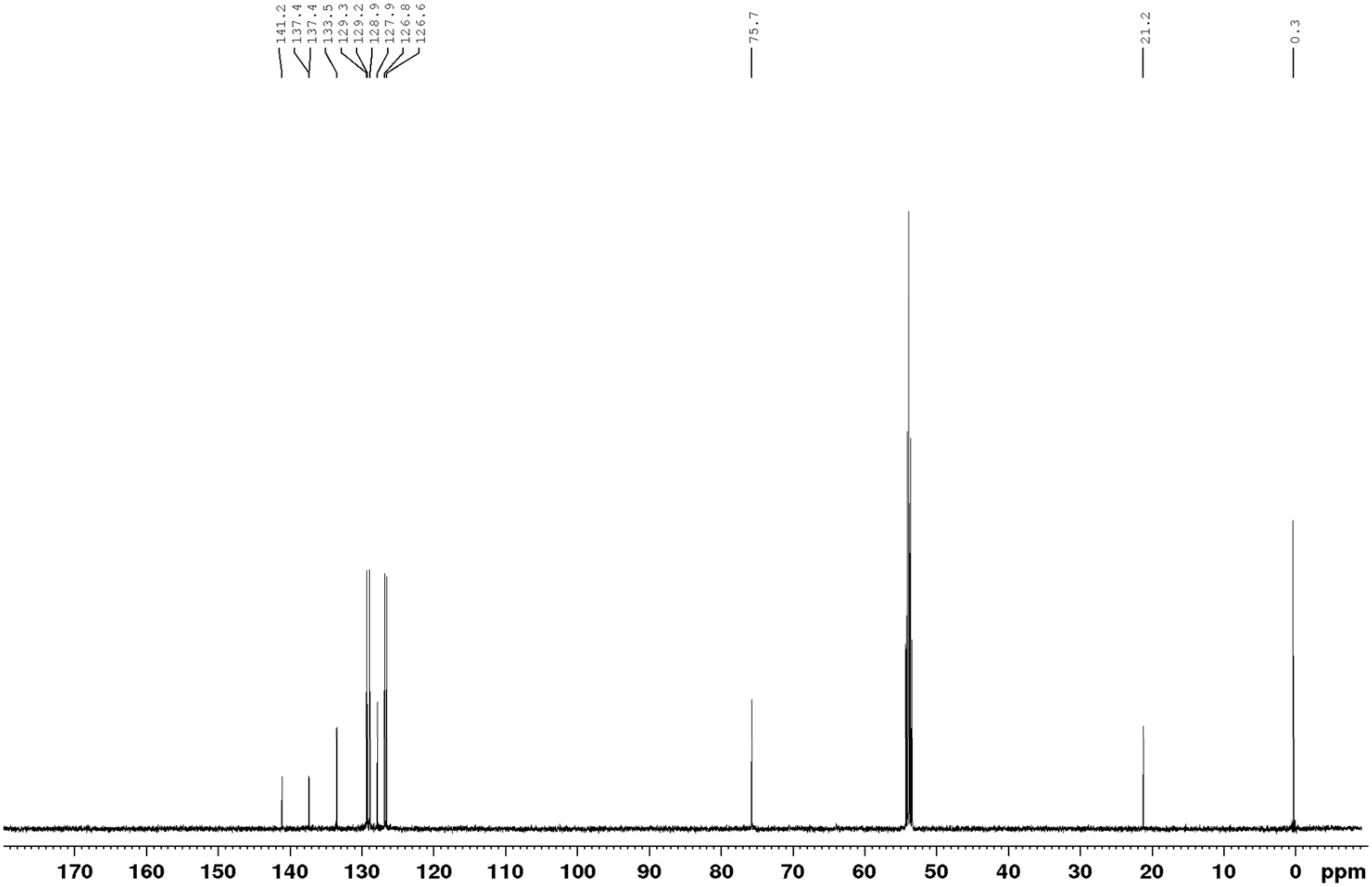


(*E*)-Trimethyl((3-phenyl-1-(*p*-tolyl)allyl)oxy)silane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

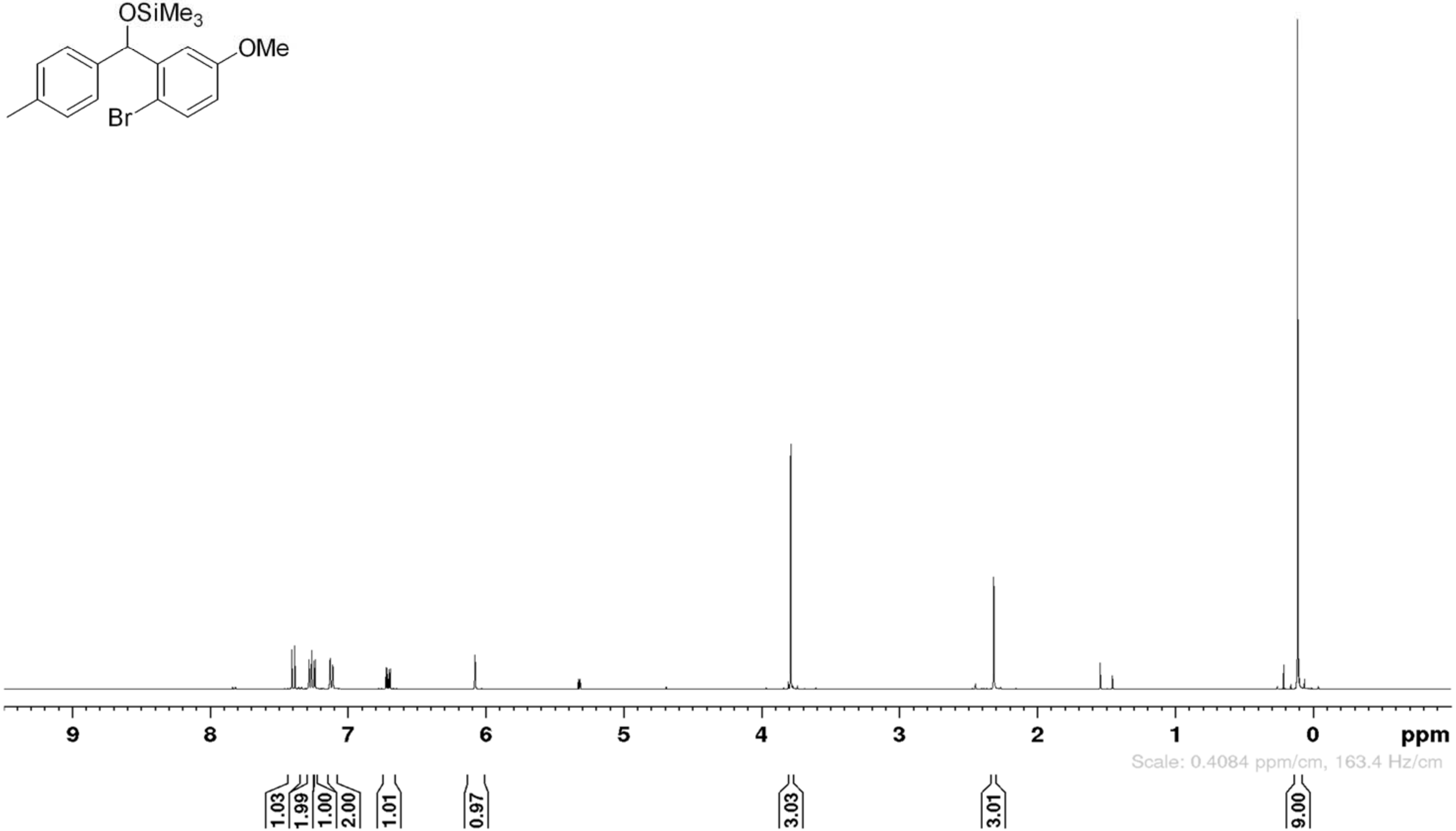


$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)

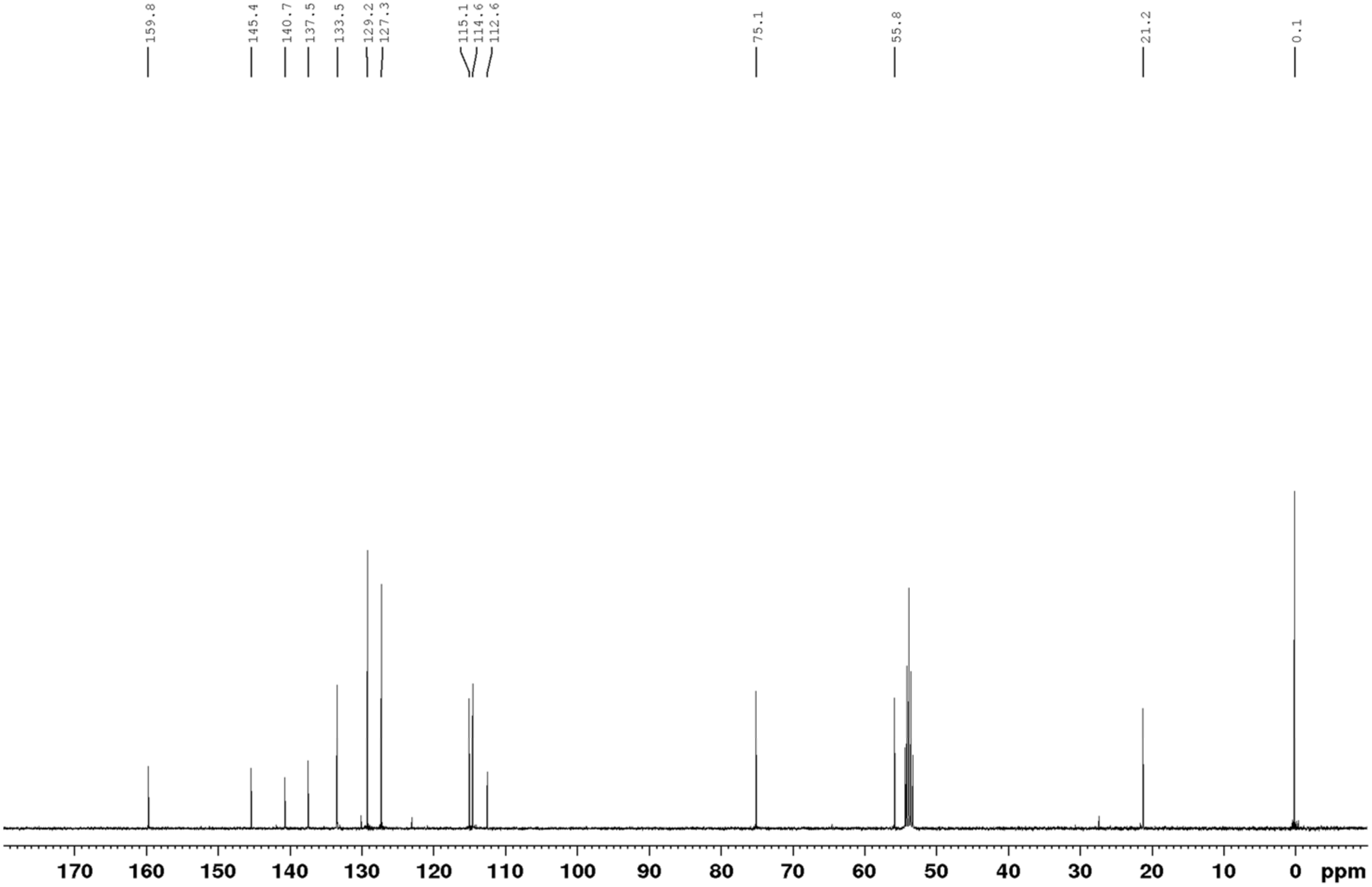


((2-Bromo-5-methoxyphenyl)(*p*-tolyl)methoxy)trimethylsilane

^{1}H NMR spectrum (400 MHz, CD_2Cl_2)

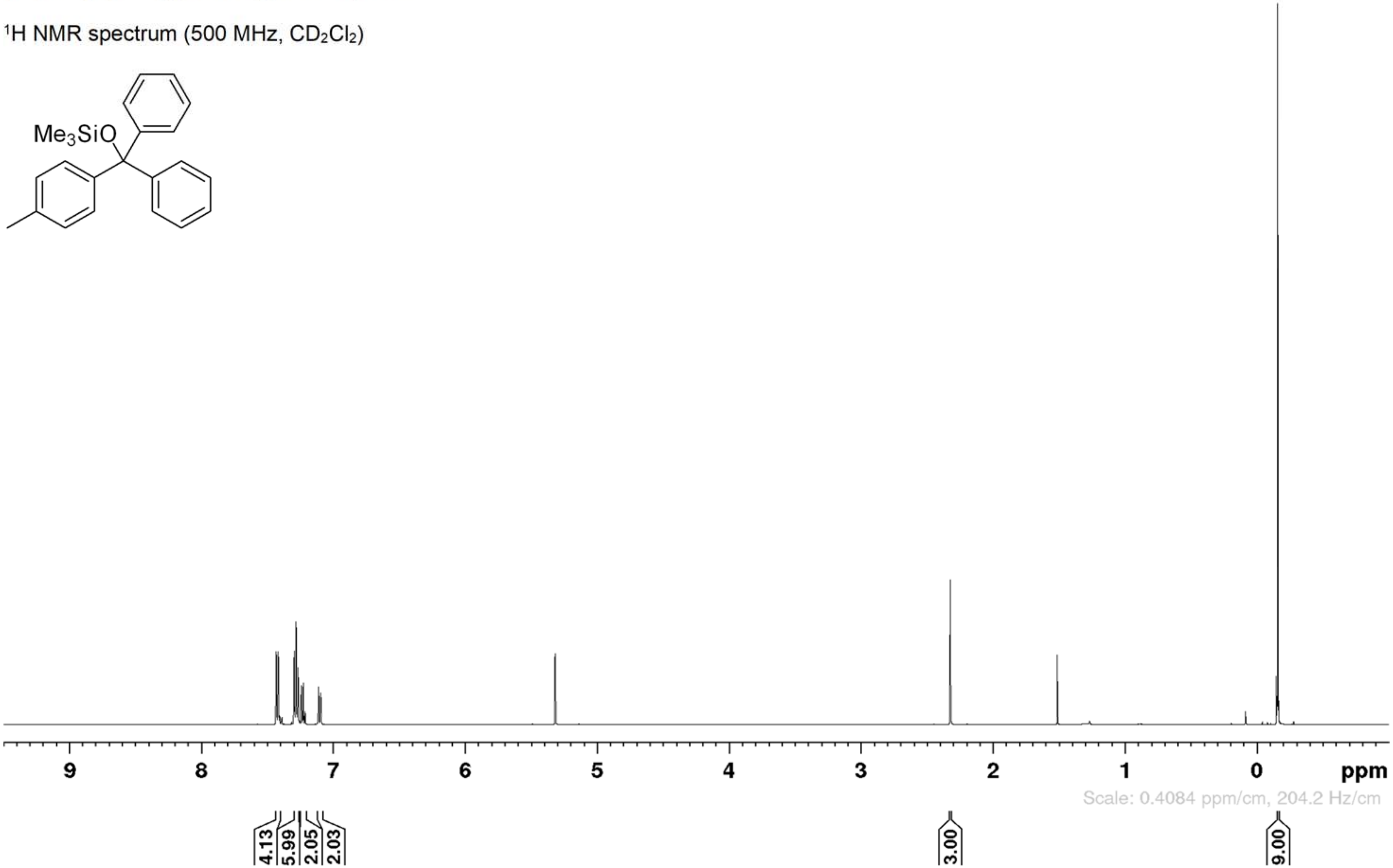


$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2)

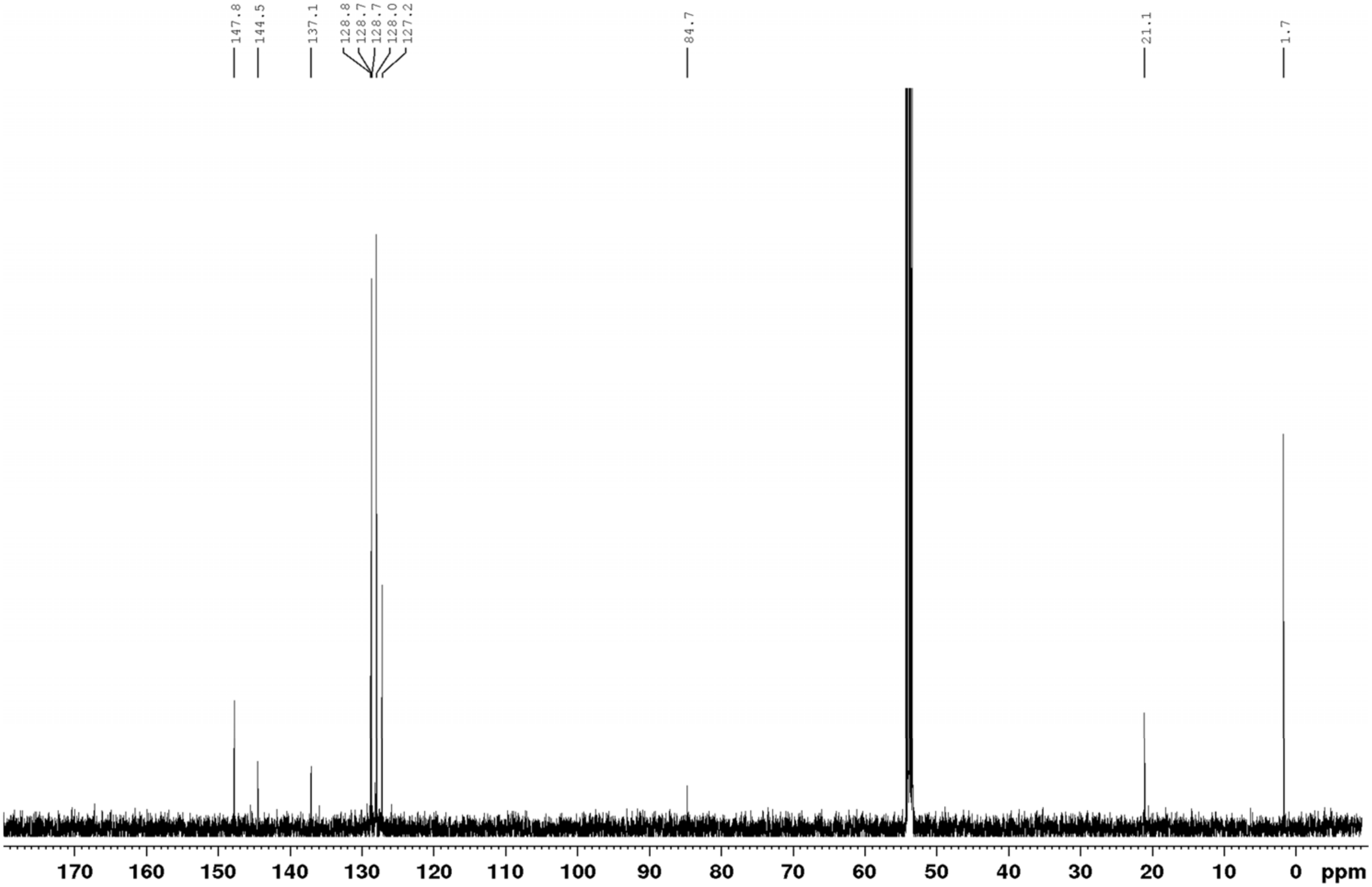


(Diphenyl(*p*-tolyl)methoxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

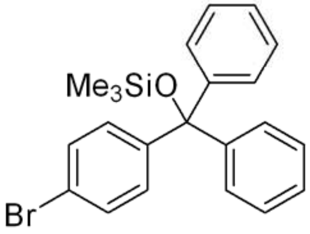


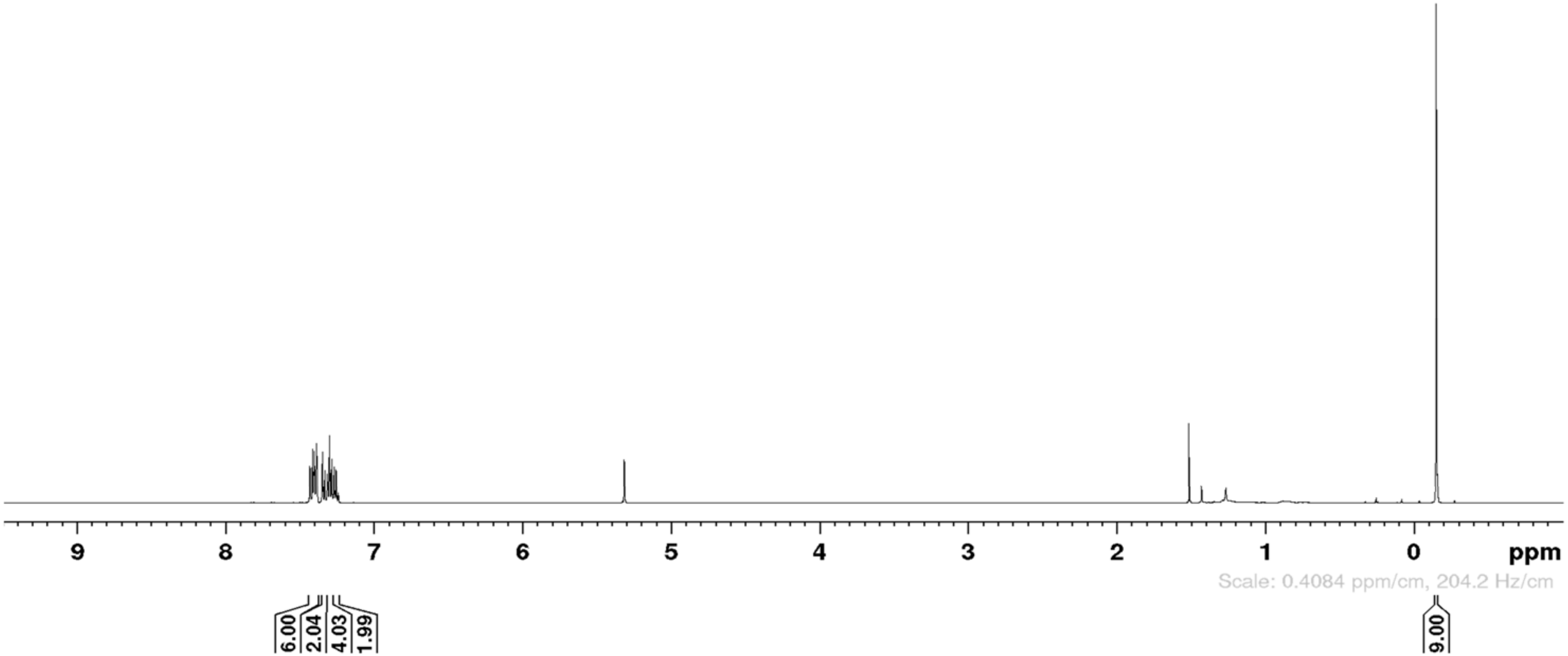
$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)



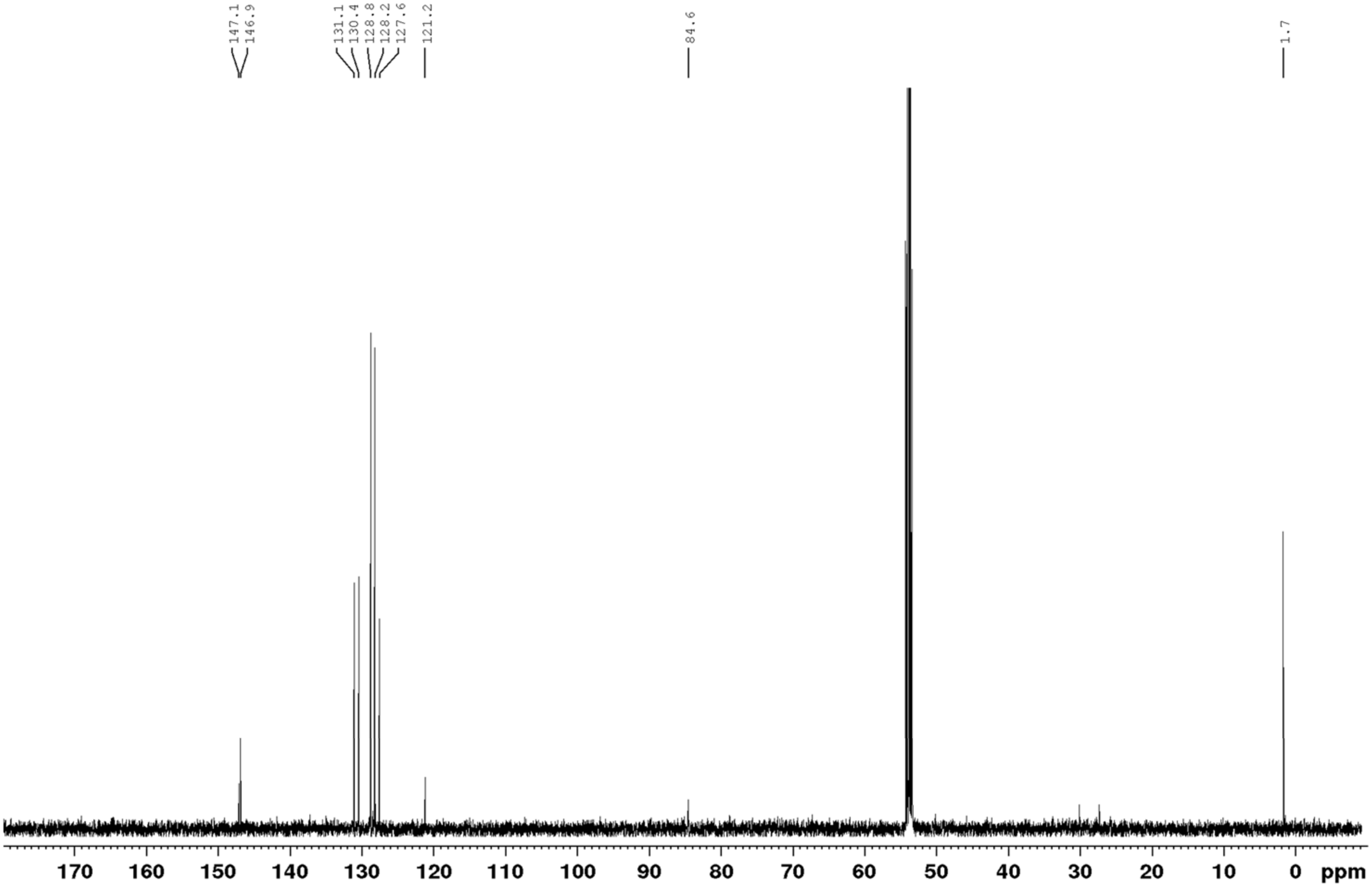
((4-Bromophenyl)diphenylmethoxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)



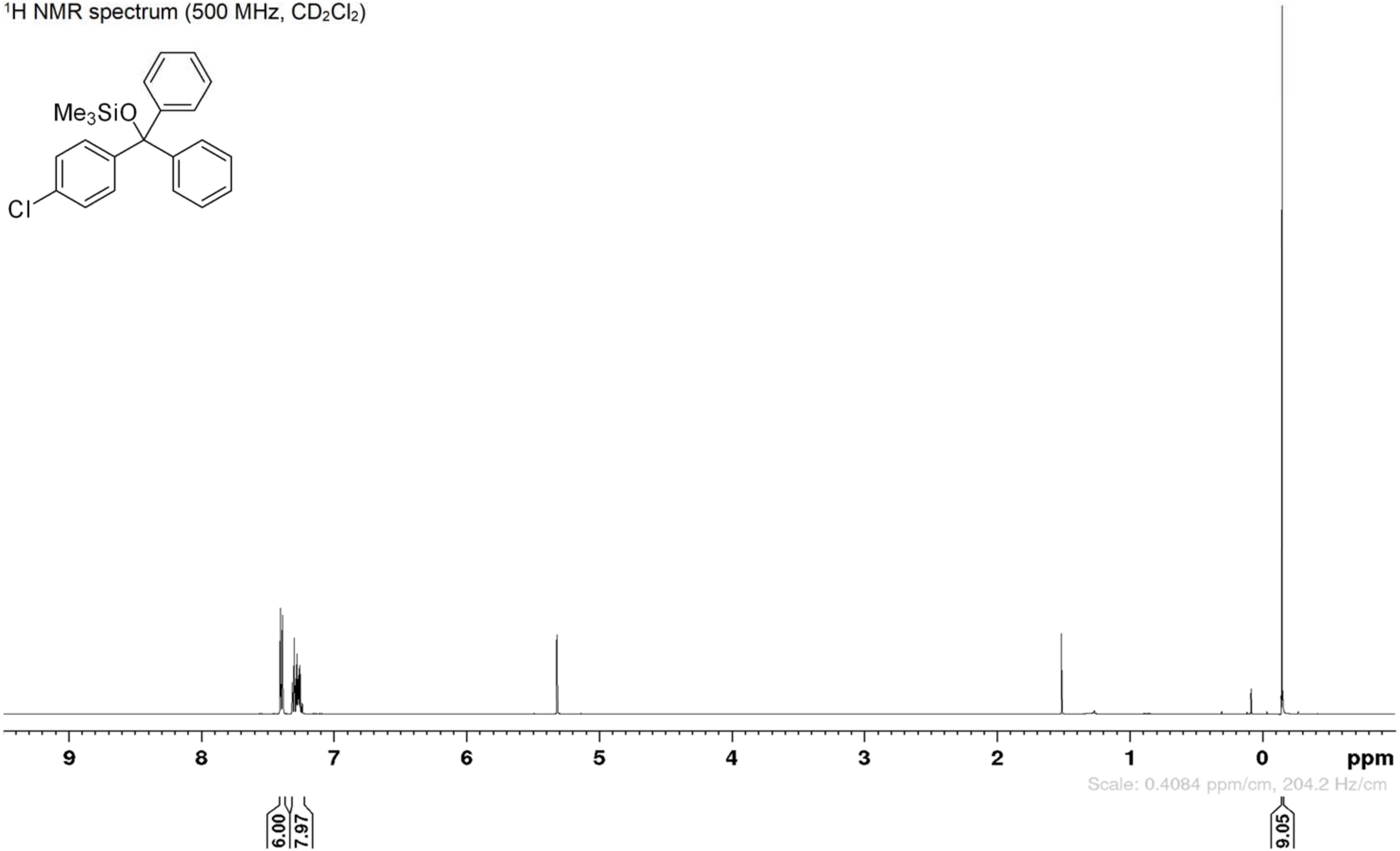


$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)

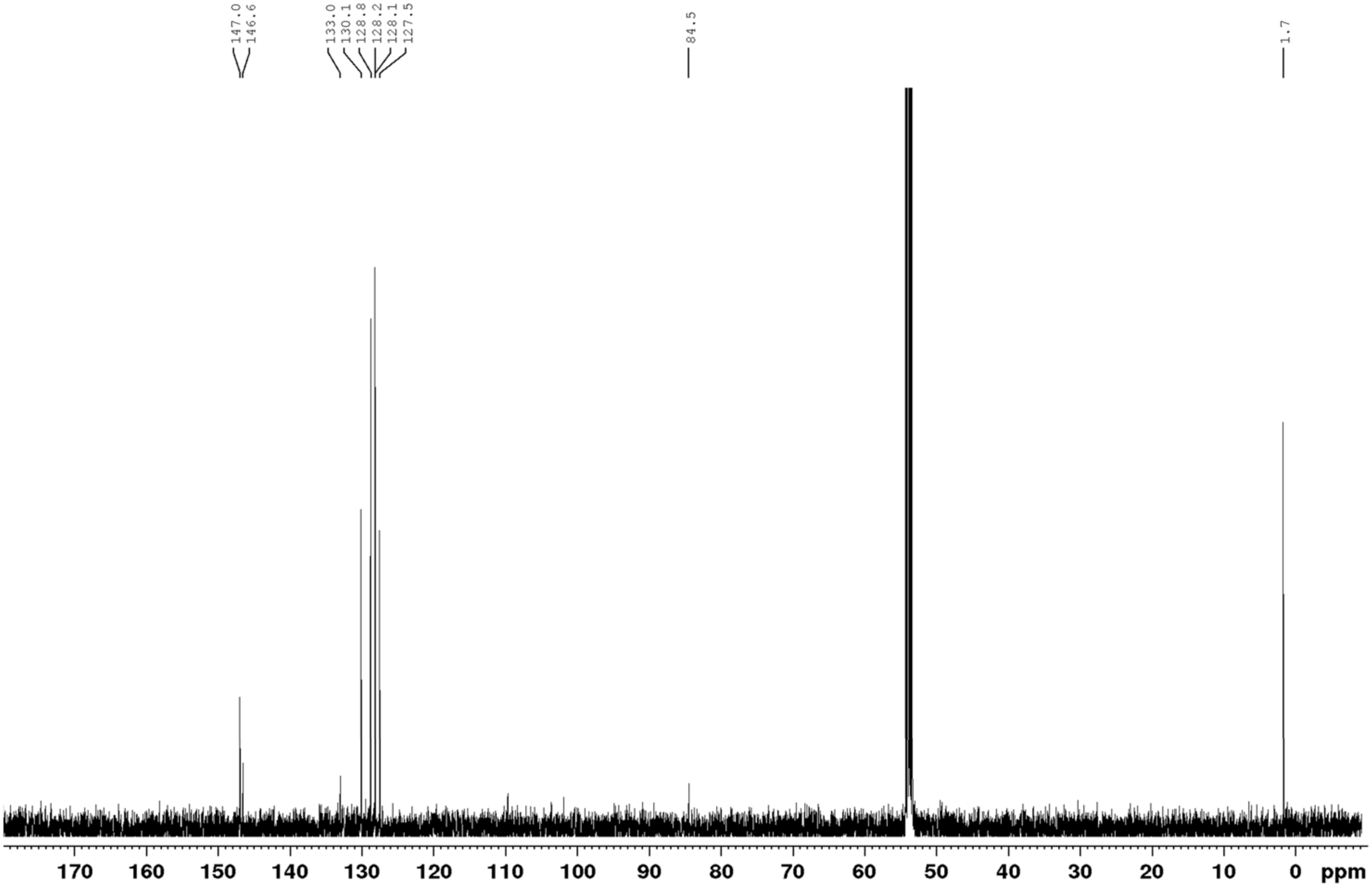


((4-Chlorophenyl)diphenylmethoxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

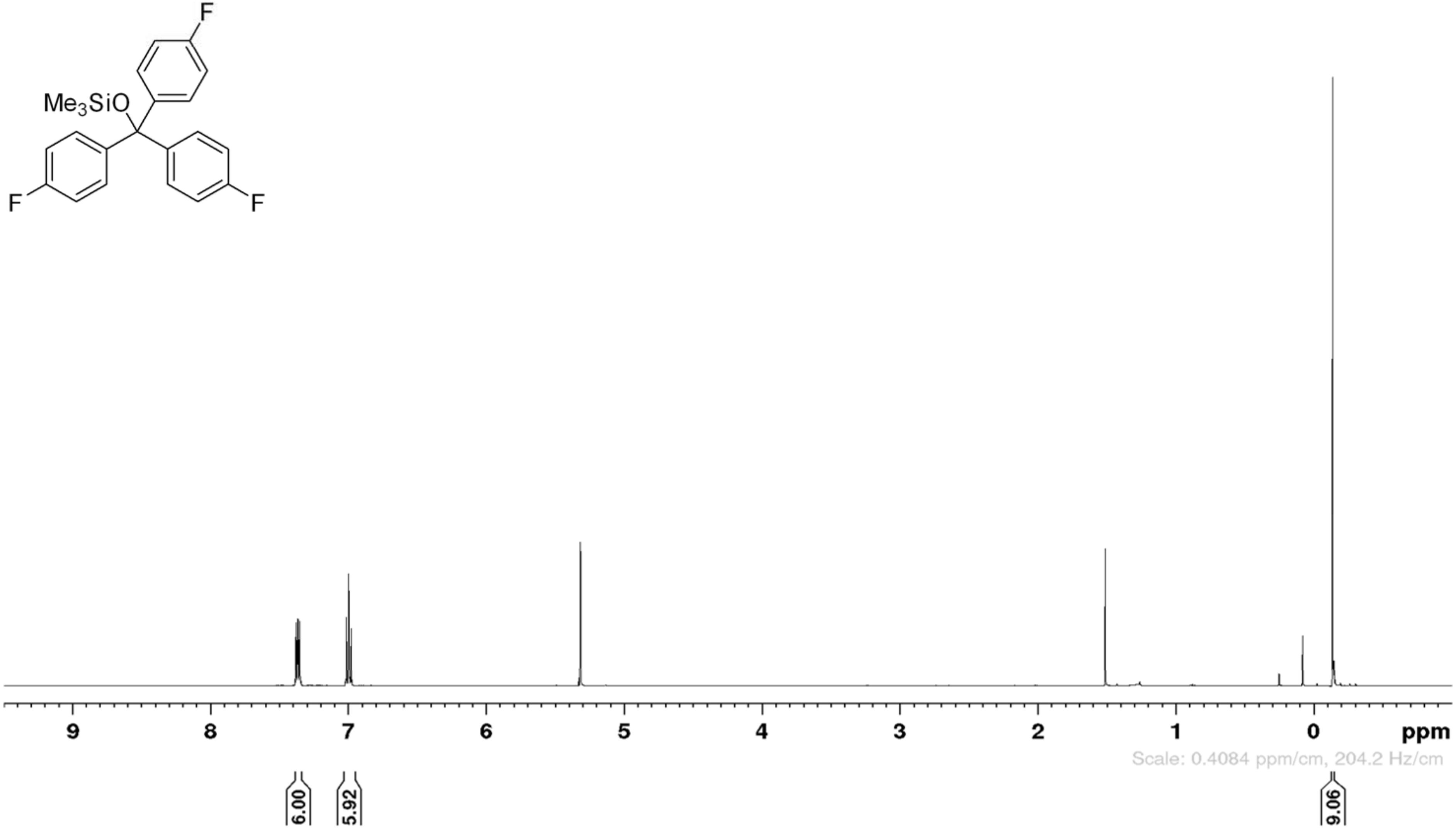


$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)

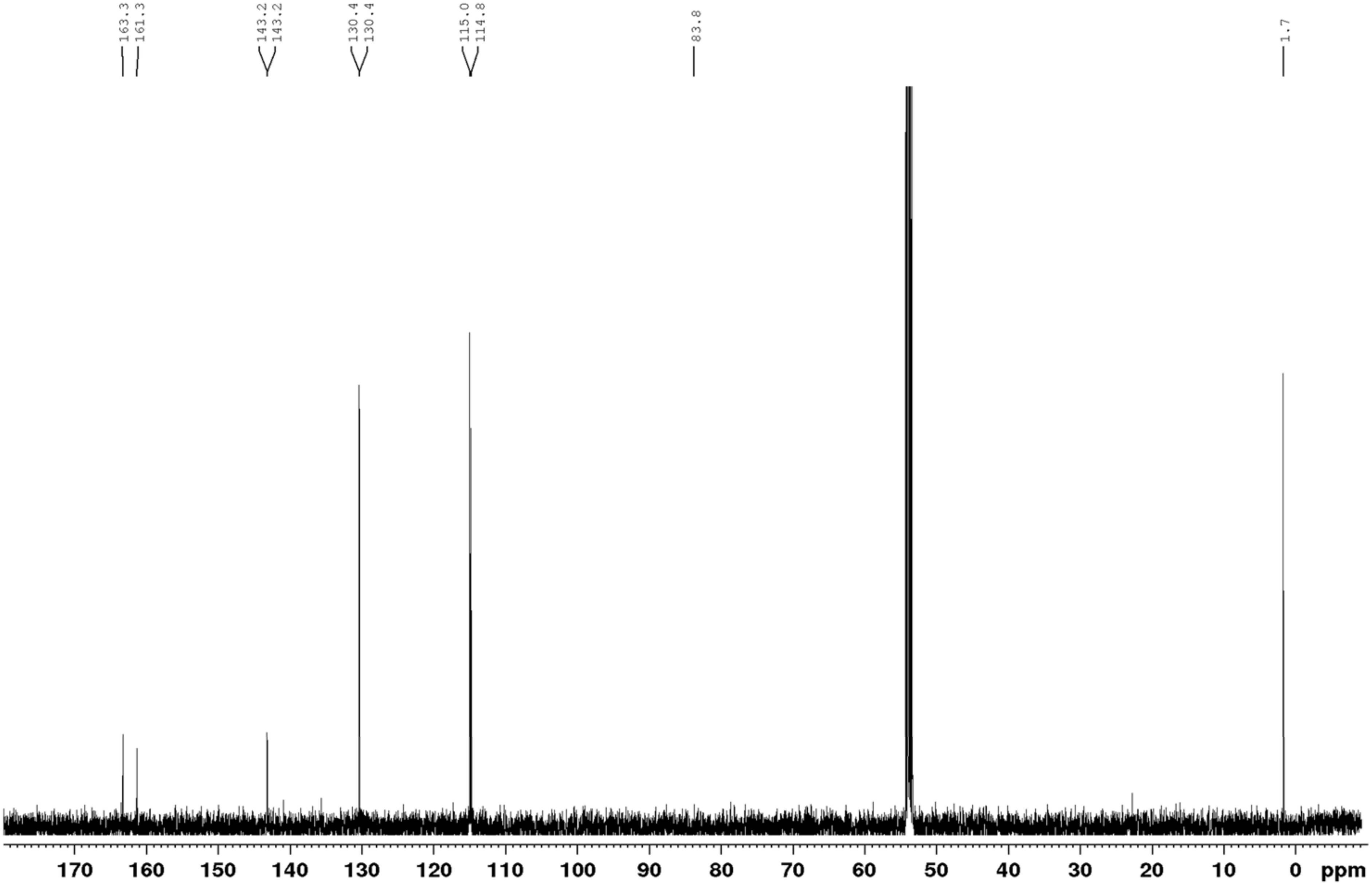


Trimethyl(tris(4-fluorophenyl)methoxy)silane

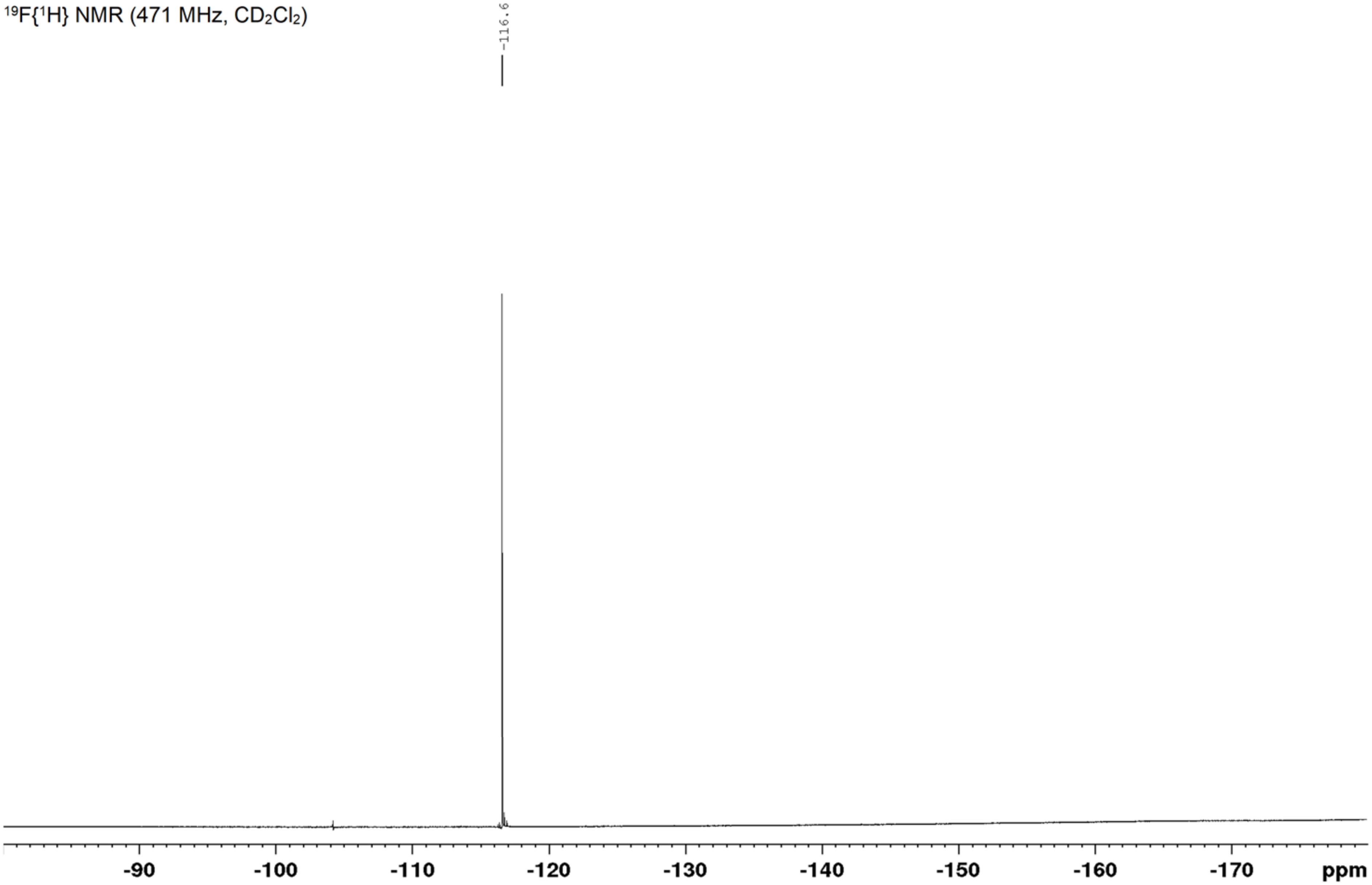
^{1}H NMR spectrum (500 MHz, CD_2Cl_2)



$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2)

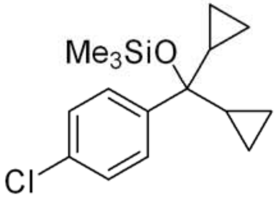


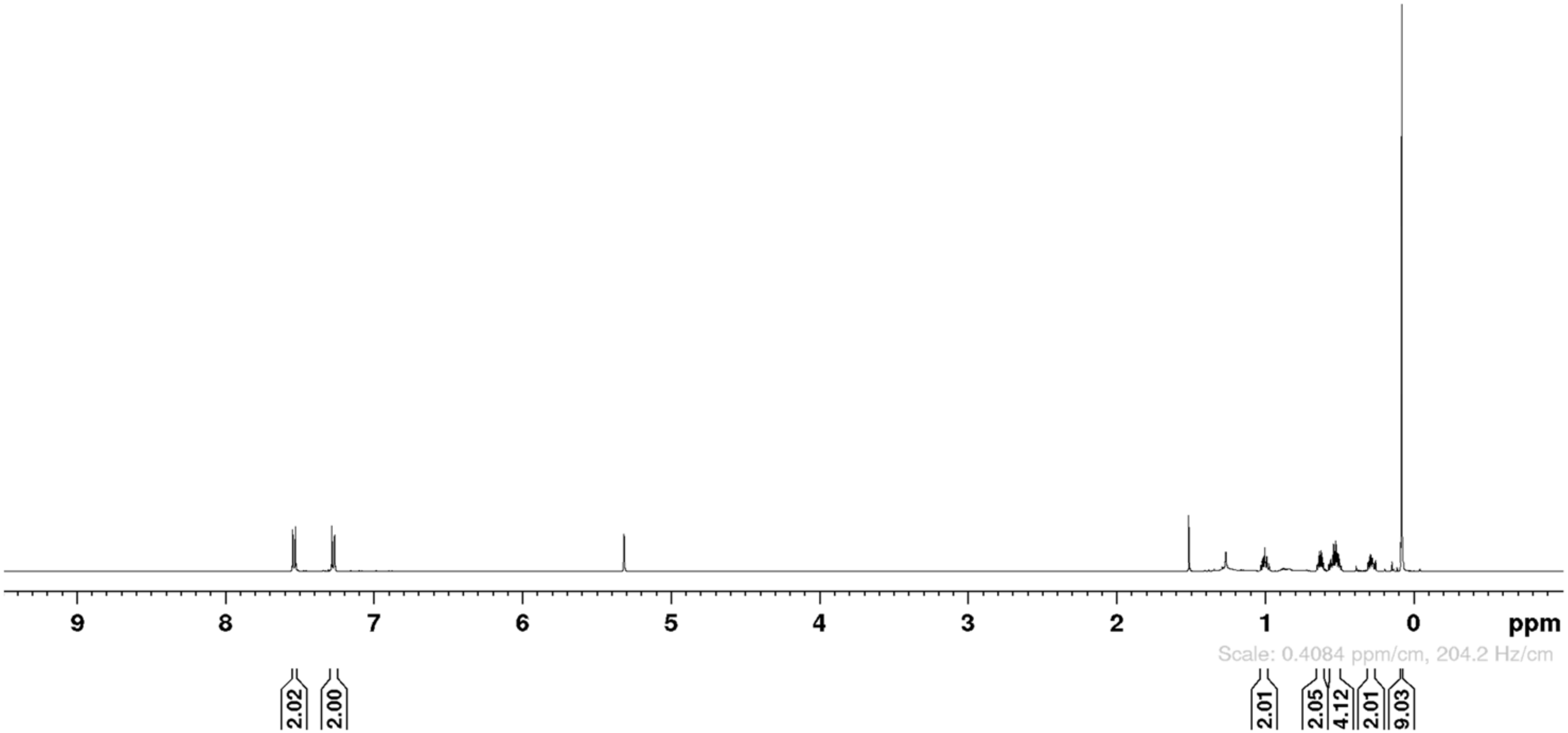
$^{19}F\{^1H\}$ NMR (471 MHz, CD_2Cl_2)



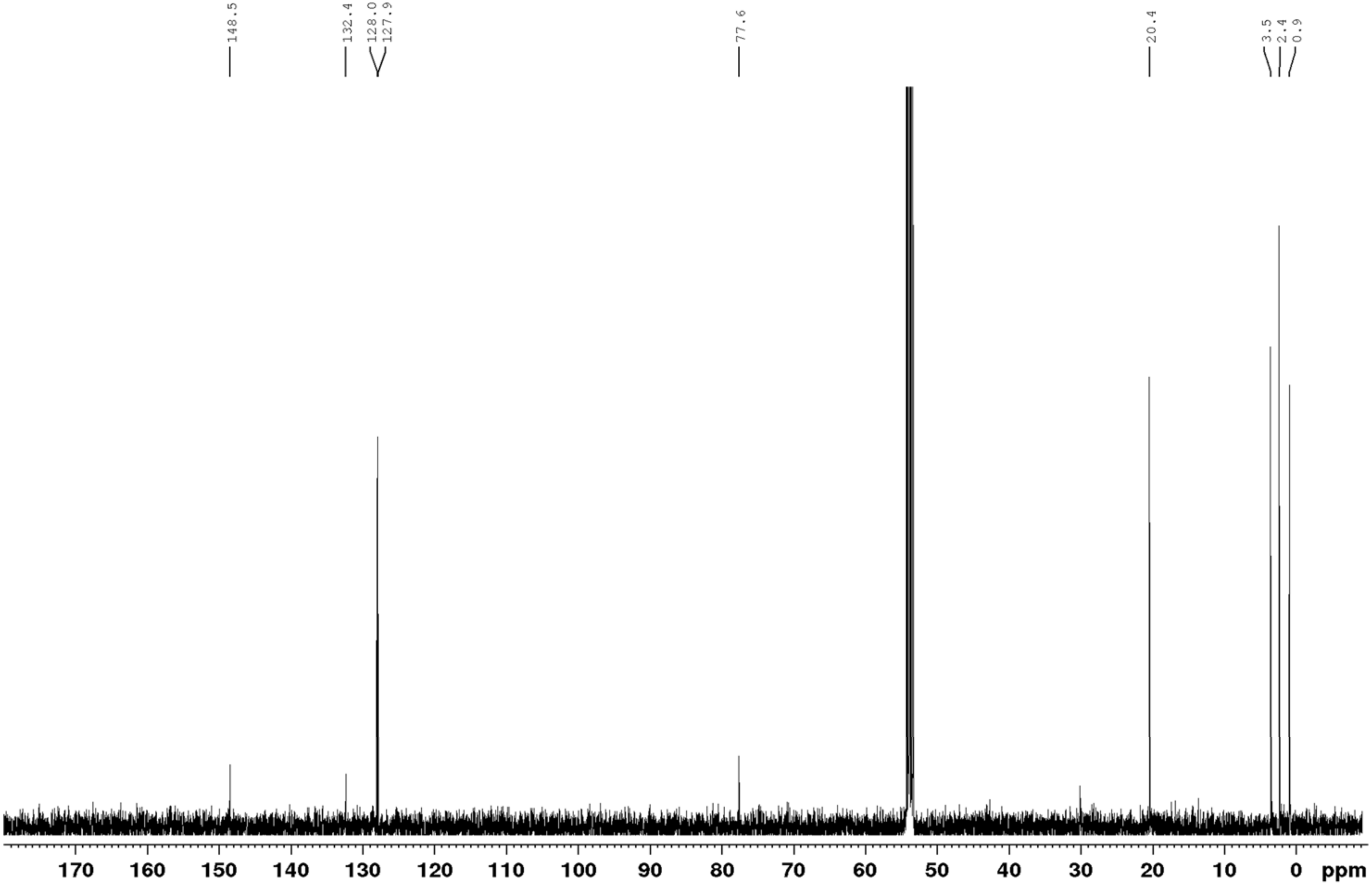
((4-Chlorophenyl)dicyclopropylmethoxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)



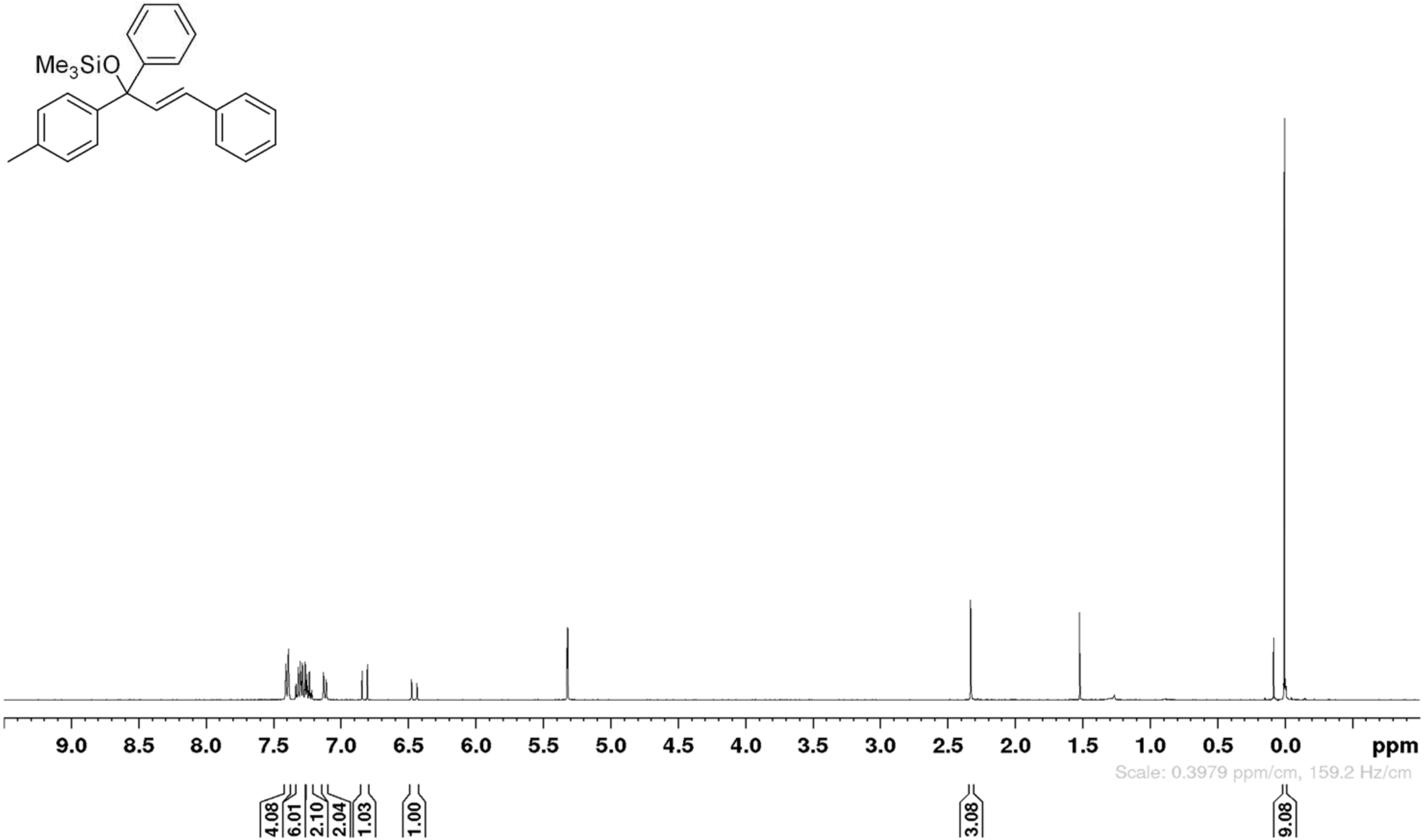


$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)

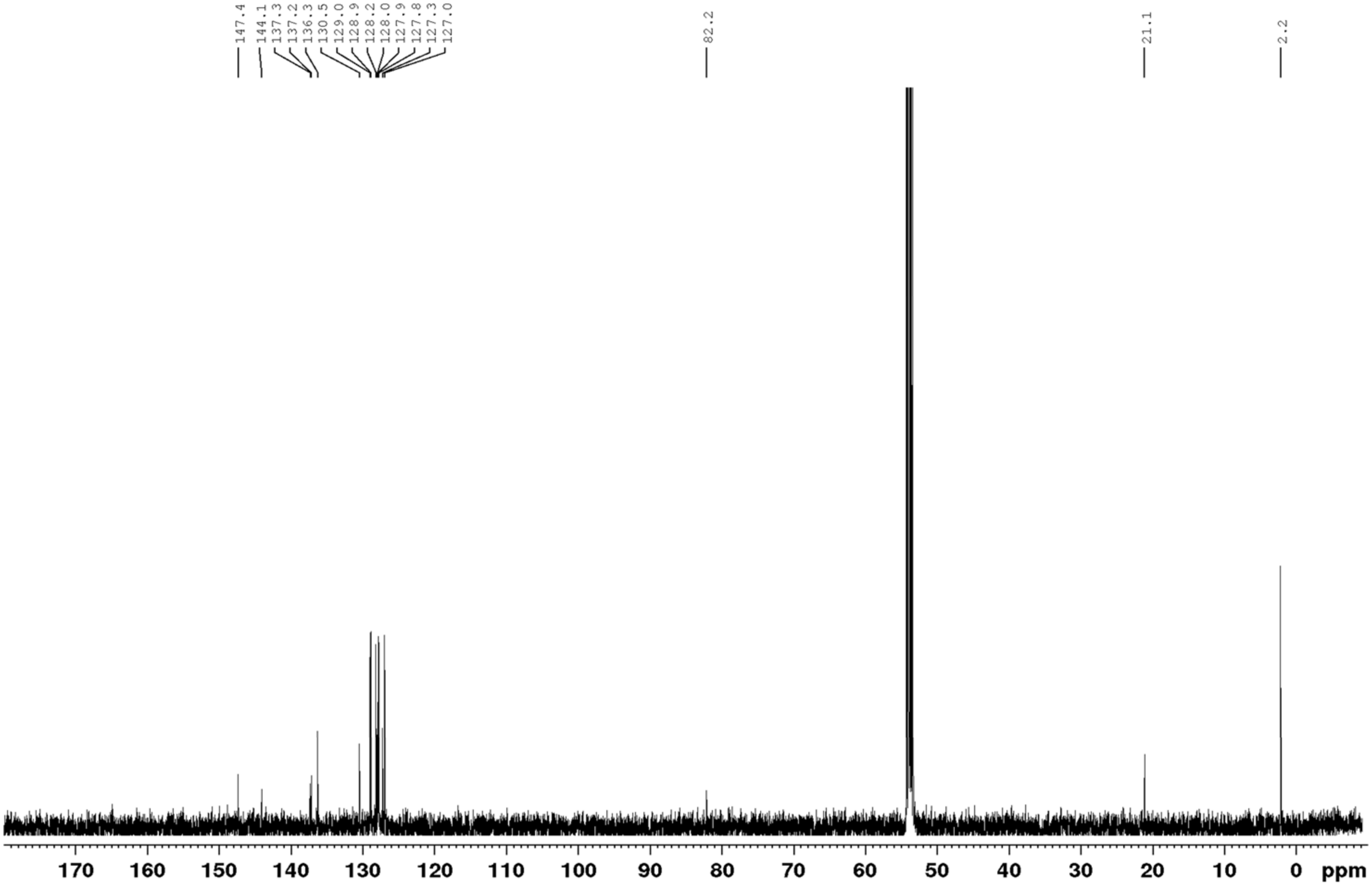


(*E*)-((1,3-Diphenyl-1-(*p*-tolyl)allyl)oxy)trimethylsilane

^{1}H NMR spectrum (400 MHz, CD_2Cl_2)

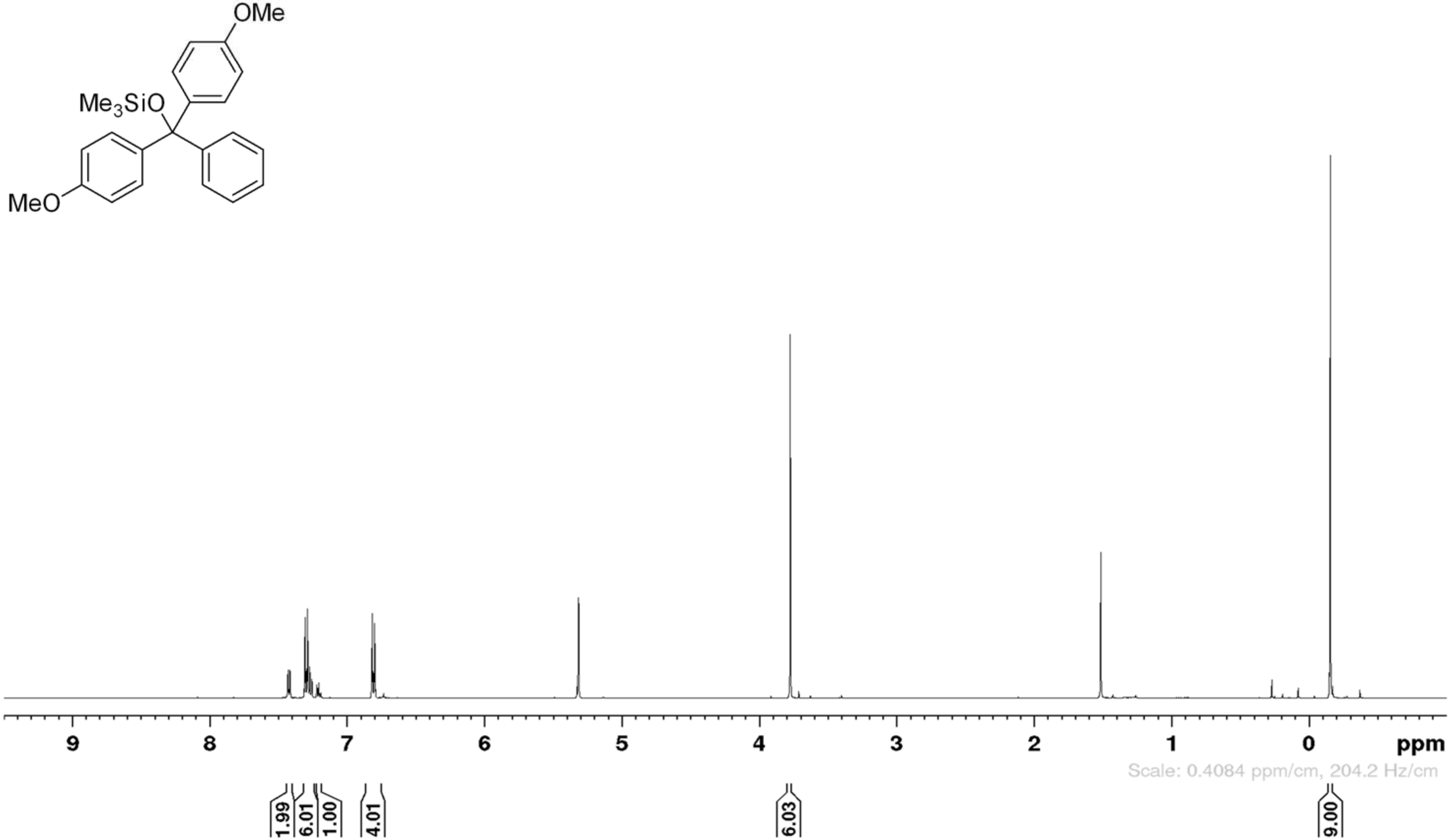


$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2)

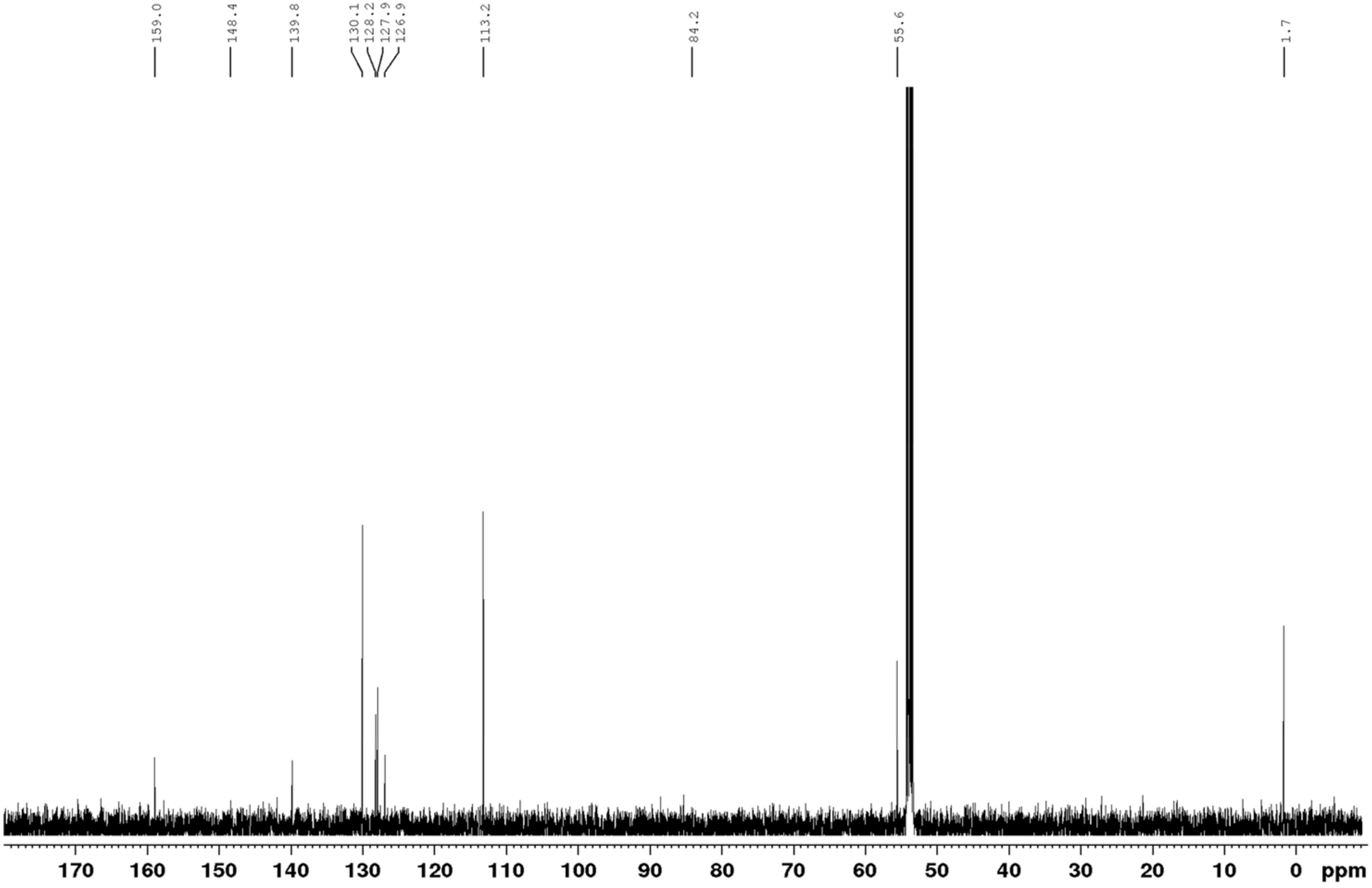


(Bis(4-methoxyphenyl)(phenyl)methoxy)trimethylsilane

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

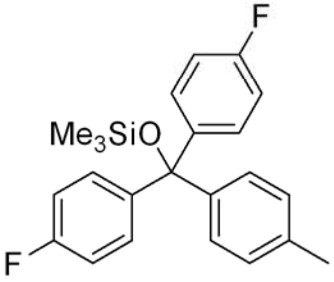


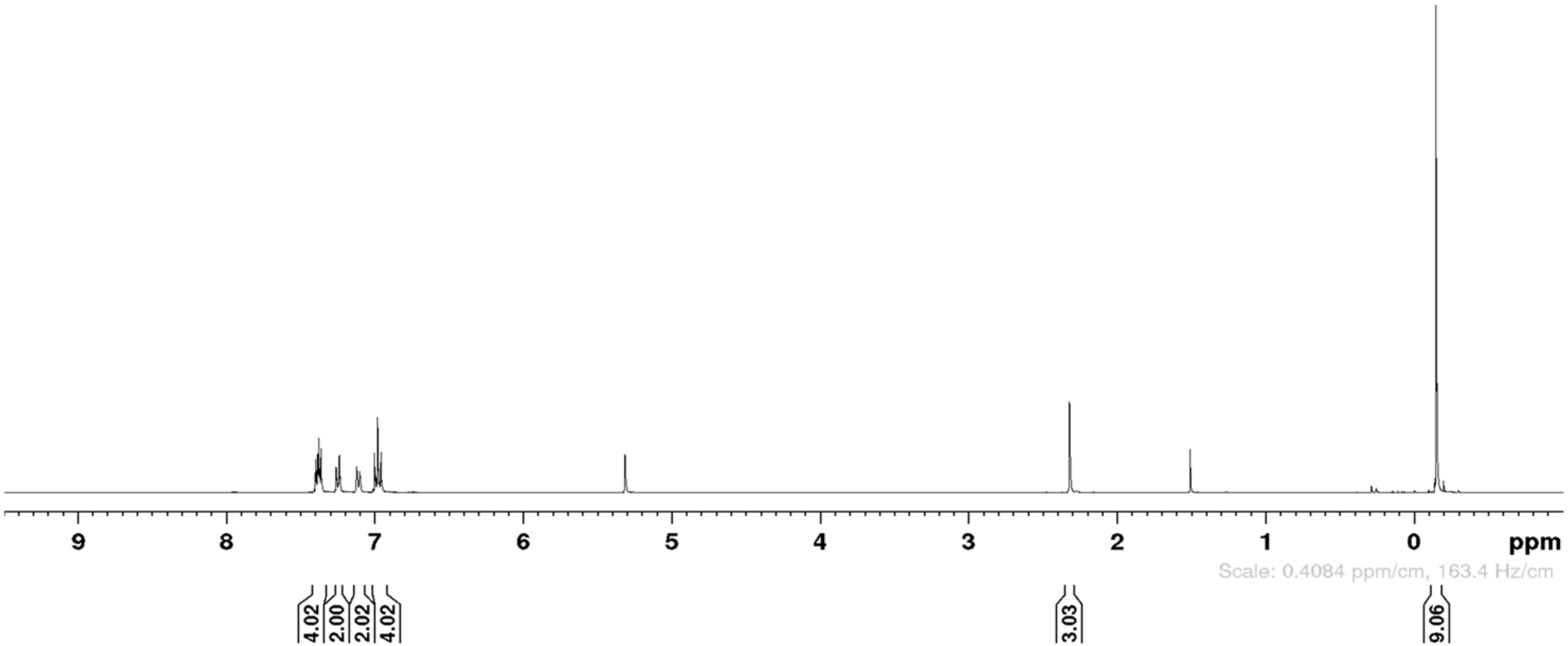
$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2)



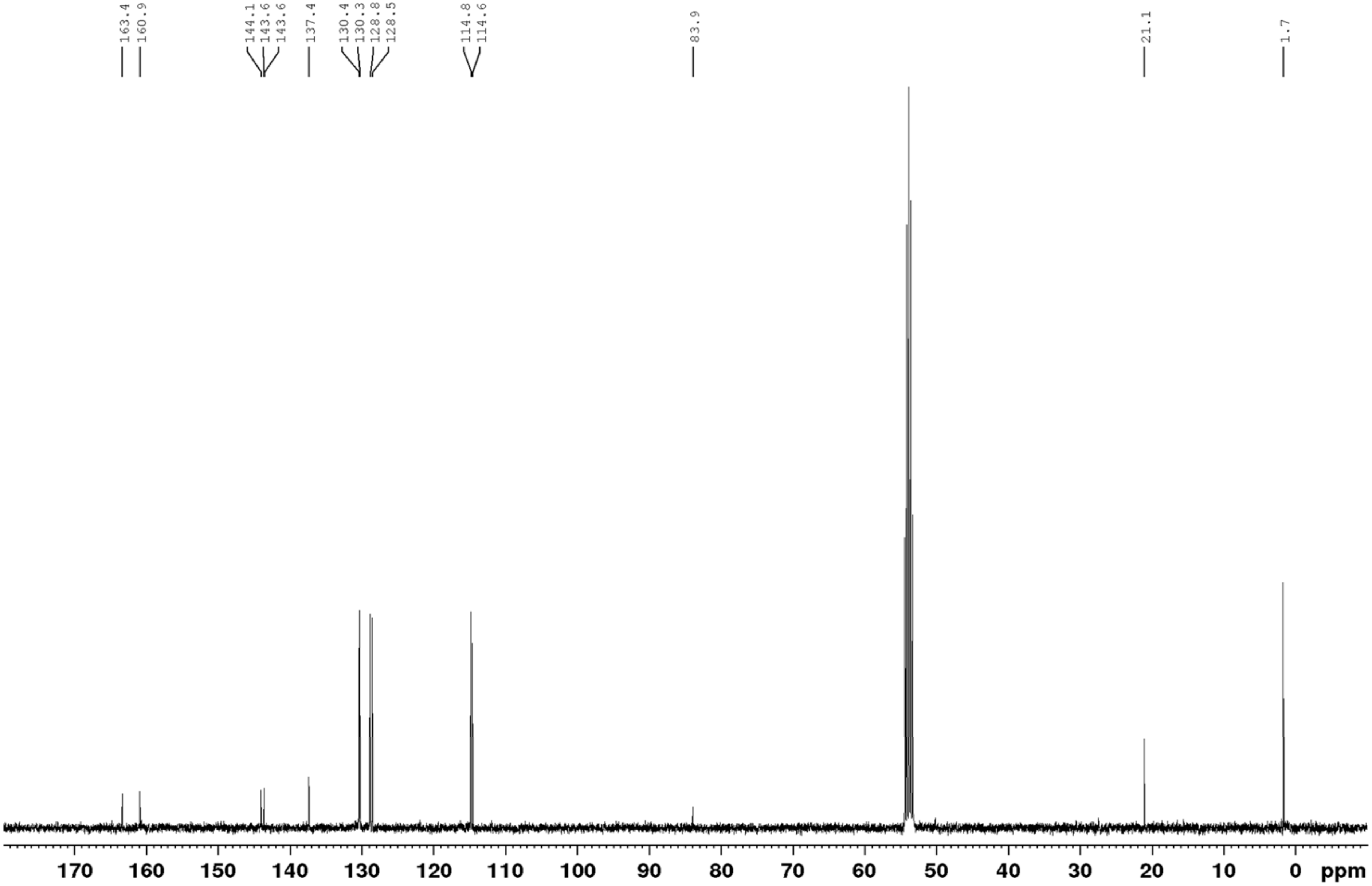
(Bis(4-fluorophenyl)(*p*-tolyl)methoxy)trimethylsilane

^{1}H NMR spectrum (400 MHz, CD_2Cl_2)

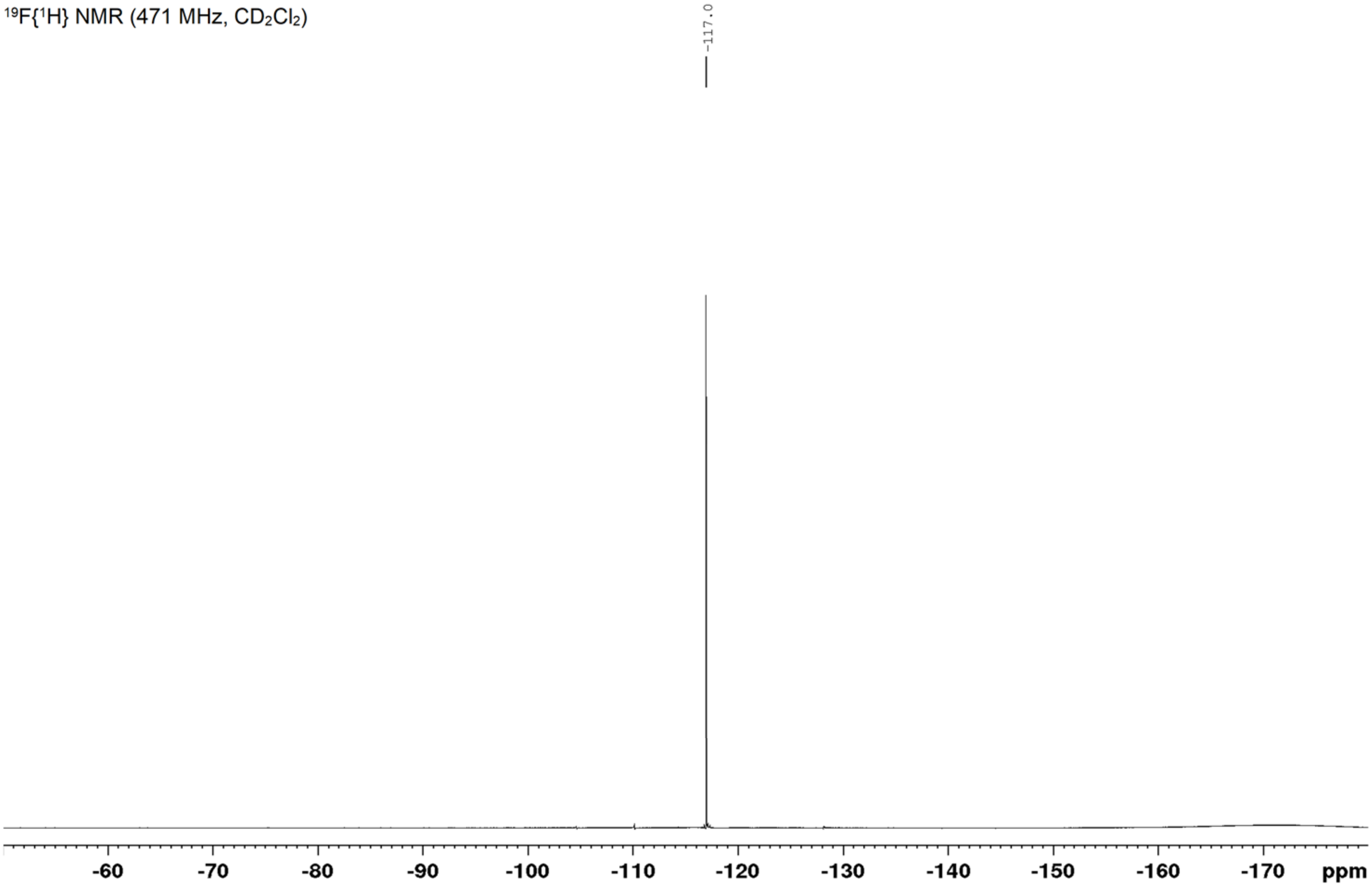




$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2)



$^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2)



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