Supplementary Information

Low-valent dialkoxytitanium(II): a useful tool for the synthesis of functionalized seven-membered ring compounds

Florent Bodinier[a], Youssouf Sanogo[a], Janick Ardisson[a], Marie-Isabelle Lannou[a], Geoffroy Sorin*[a]

Abstract: Herein, we describe an unprecedented access to all-carbon or heterocyclic seven-membered ring frameworks from 1,8-ene-ynes promoted by inexpensive low-valent titanium(II) species, readily available from Ti(O*i*Pr)$_4$ and Grignard reagent. A broad range of cycloheptane, azepane or oxepane derivatives has been obtained (19 examples) with moderate to good yields and an excellent selectivity (up to 95/5 d.r.).

[a] Unité CNRS UMR 8038 Université Paris de Paris, Faculté de Pharmacie, Sorbonne Paris Cité, 4 avenue de l'Observatoire, 75270 PARIS cedex 06, (France)

E-mail: geoffroy.sorin@parisdescartes.fr[a]

Contents

1/ General information

All reactions sensitive to moisture and/or air were carried out under argon atmosphere in dry, freshly distilled solvents under anhydrous conditions using oven-dried glassware, unless otherwise noted. THF and toluene were distilled over sodium/benzophenone system, DCM, DMSO and DMF were distilled over calcium hydride. Reactions were monitored by TLC (silica gel 60 F254plates) and visualization was accomplished with UV light (254 nm & 366 nm) and subsequent use of phosphomolybdic acid solution in EtOH (5%), $KMnO_4$ solution or vanillin/sulphuric acid solution in EtOH, followed by heating at 100-110 °C. Flash chromatography was performed with silica gel 60 (particle size 0.040-0.063 μm). Yield refers to chromatographically and spectroscopically pure compounds, unless otherwise noted. ^{1}H NMR spectra were recorded at 300 and 400 MHz. Chemical shifts are expressed in ppm, relative to the residual ^{1}H solvent signal ($CDCl_3$: δ = 7.26 ppm) as the internal reference. Coupling constants (*J*) are reported in hertz (Hz). The following abbreviations are used to designate the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; quint. = quintet, sext. = sextet, sept. = septet, m = multiplet; br = broad. ^{1}H NMR assignments were confirmed by 2D COSY spectra. The given multiplicities reflect apparent signal patterns. Diastereomer ratio (*dr*) was estimated by ^{1}H NMR spectroscopic analysis (300 and 400 MHz), unless otherwise noted. ^{13}C NMR spectra were recorded at 75 MHz and 100 MHz. Chemical shifts are given in ppm relative to the residual ^{13}C solvent signal ($CDCl_3$: δ = 77.16 ppm). ^{13}C NMR assignments were confirmed by 2D HSQC and HMBC spectra. Coupling constants (*J*) are given in Hz for all NMR spectroscopic data. IR spectra were recorded with a FT-IR spectrometer. High-resolution mass spectra (HRMS) were measured on a mass spectrometer equipped with a TOF system and an electrospray ionization (ESI) ion source. Deuterated solvents were used as supplied.

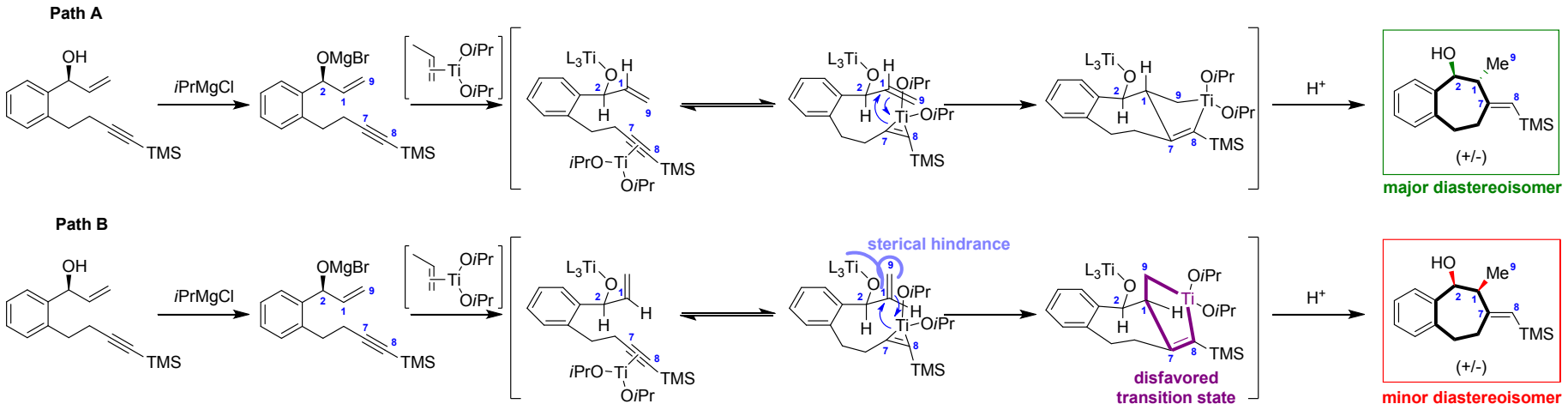
2/ Reaction optimization

Entry	Base	Time	T (°C)	Titanium	equiv	T (°C)	Time with Ti^{IV}	RMX	equiv	T (°C)	Solvant	Concentration	T (°C)	Time	Conversion
1	*i*PrMgCl	15 min	0	$Ti(OiPr)_4$	2	0	10 min	*i*PrMgCl	4	-40	toluene	0,1M	-40	5h30	-
2	*i*PrMgCl	15 min	0	$Ti(OiPr)_4$	2	0	10 min	*i*PrMgCl	4	-40	toluene	0,1M	-20	5h30	20%
3	*i*PrMgCl	15 min	0	$Ti(OiPr)_4$	2	0	10 min	*i*PrMgCl	4	-40	toluene	0,1M	0	2h	43%
4	*i*PrMgCl	15 min	0	$Ti(OiPr)_4$	2	0	10 min	*i*PrMgCl	4	-40	toluene	0,1M	RT	30 min	59%
5	*i*PrMgCl	15 min	0	$Ti(OiPr)_3Cl$	2	0	10 min	*i*PrMgCl	4	-40	toluene	0,1M	RT	1h	33%
6	*i*PrMgCl	15 min	0	$Ti(OiPr)_4$	2	0	10 min	*c*pentylMgBr	4	-40	toluene	0,1M	RT	1h	-
7	*n*BuLi	15 min	0	$Ti(OiPr)_4$	2	0	10 min	*n*BuLi	4	-40	toluene	0,1M	RT	1h	-
8	*i*PrMgCl	15 min	0	$Ti(OiPr)_4$	2	0	10 min	*i*PrMgCl	4	-40	Et_2O	0,1M	RT	1h	23%
9	*i*PrMgCl	15 min	0	$Ti(OiPr)_4$	2	0	10 min	*i*PrMgCl	4	-40	THF	0,1M	RT	1h	29%
10	*i*PrMgCl	15 min	0	$Ti(OiPr)_4$	2	0	10 min	*i*PrMgCl	4	-40	Dioxane	0,1M	RT	1h	-
11	*i*PrMgCl	15 min	0	$Ti(OiPr)_4$	1	0	10 min	*i*PrMgCl	2	-40	toluene	0,1M	RT	45 min	-
12	*i*PrMgCl	15 min	0	$Ti(OiPr)_4$	4	0	10 min	*i*PrMgCl	8	-40	toluene	0,1M	RT	30 min	50%
13	NaH	15 min	0	$Ti(OiPr)_4$	2	0	10 min	*i*PrMgCl	4	-40	toluene	0,1M	RT	30 min	22%
14	-	-	-	$Ti(OiPr)_4$	2	0	10 min	*i*PrMgCl	4	-40	toluene	0,1M	RT	30 min	-
15	*n*BuLi	15 min	-78	$Ti(OiPr)_4$	2	-78	10 min	*i*PrMgCl	4	-78	toluene	0,1M	-40	30 min	20%
16	*n*BuLi	15 min	-78	$Ti(OiPr)_4$	2	-78	10 min	*i*PrMgCl	4	-78	toluene	0,1M	RT	30 min	44%
17	*i*PrMgCl	15 min	0	$Ti(OiPr)_4$	2	0	10 min	*i*PrMgCl	4	-40	toluene	0,2 M	RT	30 min	42%
18	*i*PrMgCl	15 min	0	$Ti(OiPr)_4$	2	0	10 min	*i*PrMgCl	4	-40	toluene	0,05 M	RT	30 min	50%
19	*i*PrMgCl	15 min	0	$TiCl_2Cp_2$	1	0	10 min	*i*PrMgCl	2	-40	toluene	0,1M	RT	30 min	-
20	*i*PrMgCl	15 min	0	$TiCl_2Cp_2$	2	0	10 min	*i*PrMgCl	4	-40	toluene	0,1M	RT	30 min	-
21	*i*PrMgCl	30 min	0	$Ti(OiPr)_4$	2	0	10 min	*i*PrMgCl	4	-40	toluene	0,1M	RT	30 min	44%
22	*i*PrMgCl	15 min	0	$Ti(OiPr)_4$	2	0	20 min	*i*PrMgCl	4	-40	toluene	0,1M	RT	30 min	27%
23	*i*PrMgCl	3 min	0	$Ti(OiPr)_4$	2	0	10 min	*i*PrMgCl	4	-40	toluene	0,1M	RT	30 min	58%
24	*i*PrMgCl	15 min	0	$Ti(OiPr)_4$	2	0	2 min	*i*PrMgCl	4	-40	toluene	0,1M	RT	30 min	61%
25	*i*PrMgCl	3 min	0	$Ti(OiPr)_4$	2	0	2 min	*i*PrMgCl	4	-40	toluene	0,1M	RT	10 min	64%
26	*i*PrMgCl	3 min	0	$Ti(OiPr)_4$	1	0	2 min	*i*PrMgCl	2	-40	toluene	0,1M	RT	30 min	-
27	*i*PrMgCl	6 min	0	$Ti(OiPr)_4$	2	0	4 min	*i*PrMgCl	4	-40	toluene	0,1M	RT	10 min	64%*
28	*i*PrMgCl	6 min	0	$Ti(OiPr)_4$	2	0	4 min	*i*PrMgCl	4	-40	toluene	0,1M	45 directly	10 min	57%
29	*i*PrMgCl	6 min	0	$Ti(OiPr)_4$	2	0	-	*i*PrMgCl	4	-40	toluene	0,1M	RT	10 min	33%**

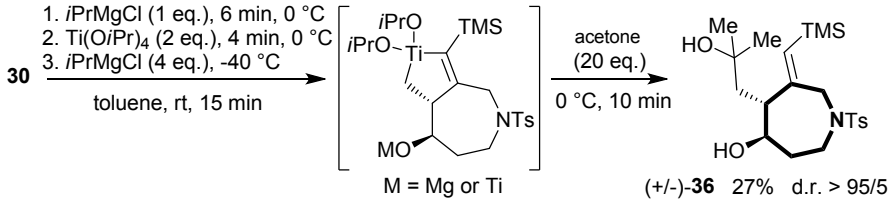
*6 min deprotonation and 4 min with Ti(IV) afforded a cleaner crude than 3 min deprotonation and 2 min with Ti(IV). The isolated yield is 60% with d.r. > 95:5. **i*PrMgCl was added immediately after $Ti(OiPr)_4$. Many degradation products were observed as well as a complete loss of diastereoselectivity

3/ Assumed mechanism

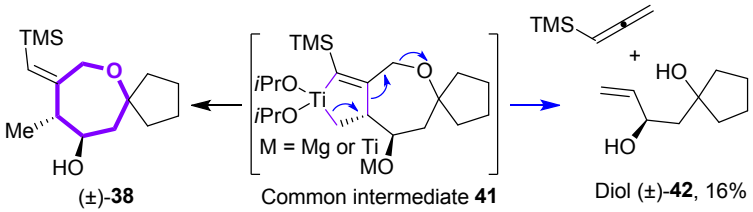
a/ Cyclization



b/ Trapping of the titanacyclopentene intermediate by acetone

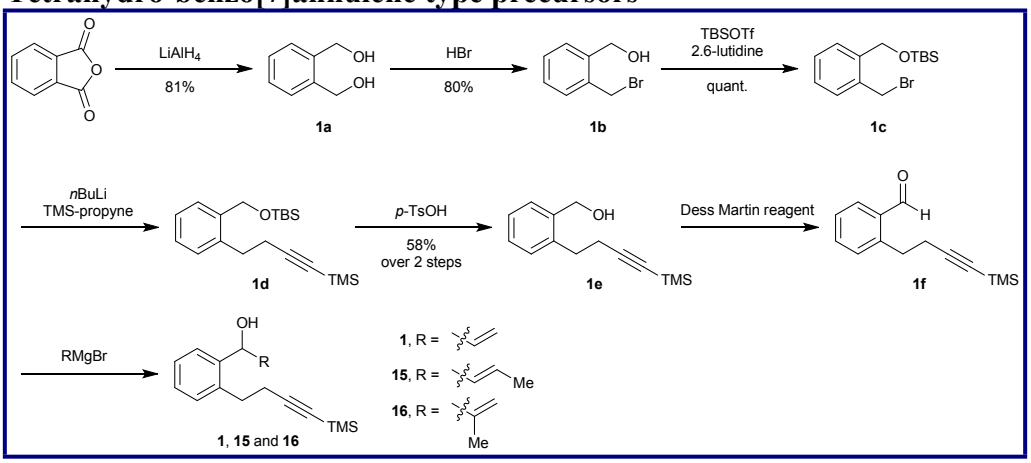


c/ Assumed elimination pathway for the oxepane derivative

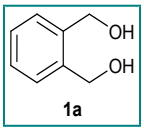


4/ Preparation of the cyclization precursors

a. Tetrahydro-benzo[7]annulene type precursors



1,2-phenylenedimethanol **1a**

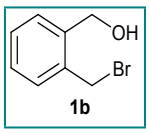


To a stirred solution of lithium aluminium hydride (9.5 g, 250 mmol, 2 equiv) in dry THF (100 mL, 2.5 M) was added dropwise, at 0 °C, a solution of phthalic anhydride (20.16 g, 136 mmol, 1 equiv) in dry THF (100 mL, 1.36 M). The green-grey solution was then stirred for 40 min at 0°C and overnight at room temperature. Reaction was quenched by a slow addition at 0 °C of water (10 mL), NaOH 15% (10 mL) and water (24 mL). The white precipitate was filtered through a Celite® pad and washed with ethyl acetate (100 mL). Concentration under reduced pressure afforded **1a** (15.17 g, 110 mmol, 81 %) as a colourless oil which solidify after a few minutes as a colourless cristal. Clean **1a** was used without further purification

Spectroscopic data were in accordance with those reported in literature[1].

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 - 7.29 (m, 4H), 4.71 (s, 4H), 3.22 (s, 2H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 139.6, 129.9, 128.8, 64.5

(2-(bromomethyl)phenyl)methanol **1b**



A solution of **1a** (5 g, 36 mmol, 1 equiv) in toluene (70 mL, 0.5 M) was heated at 70°C. At this temperature was slowly added a solution of HBr 48 % (4.6 mL, 41 mmol, 1.14 equiv) and the solution was stirred for 4 hours at 70 °C. After total completion, monitored by TLC, the heterogeneous mixture was cooled at 0°C, quenched by addition of a saturated $NaHCO_3$ solution (10 mL) and extracted by diethyl ether (3 × 40 mL). The combined organic layers were washed with water (60 mL), dried over

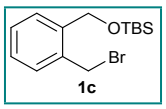
[1] M. Dow, F. Marchetti, K. A. Abrahams, L. Vaz, G. S. Besra, S. Warriner, A. Nelson, *Chem. Eur. J.,* 2017, **23**, 7207 – 7211

$MgSO_4$ and concentrated under reduced pressure, affording clean desired **1b** (5.823 g, 29 mmol, 80 %) as a brown solid which was used without further purifiction.

Spectroscopic data were in accordance with those reported in literature[2].

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 - 7.28 (m, 4H), 4.84 (d, J = 5.5 Hz, 2H), 4.64 (s, 2H), 1.92 (t, J = 5.5 Hz, 1H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 139.3, 135.9, 130.8, 129.4, 129.1, 128.6, 62.9, 31.1

((2-(bromomethyl)benzyl)oxy)(tert-butyl)dimethylsilane **1c**

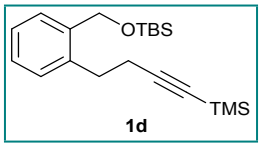


To a solution of **1b** (1.650 g, 8.21 mmol, 1 equiv) under argon atmosphere in dry dichloromethane (35 mL, 0.23M), was added at room temperature 2.6-lutidine (1.91 mL, 16.42 mmol, 2 equiv) and the mixture was stirred for 10 min. *Tert*-butyldimethylsilyl trifluoromethanesulfonate (2.64 mL, 12.31 mmol, 1.5 equiv) was then added dropwise and the solution was stirred at room temperature for 3 hours. After total completion, monitored by TLC, water (20 mL) was added and the aqueous layer was extracted by ethyl acetate (2 × 40 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the crude by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 80/20) afforded quantitatively pure **1c** (2.587 g, 8.21 mmol) as a light brown oil.

Spectroscopic data were in accordance with those reported in literature[3].

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 - 7.44 (m, 1H), 7.35 - 7.22 (m, 3H), 4.87 (s, 2H), 4.59 (s, 2H), 0.95 (s, 9H), 0.12 (s, 6H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 140.0, 135.0, 130.5, 129.1, 127.9, 127.8, 62.7, 31.2, 27.1, 26.2, -5.0

tert-butyldimethyl((2-(4-(trimethylsilyl)but-3-yn-1-yl)benzyl)oxy)silane **1d**



To a solution of 1-(trimethylsilyl)propyne (1.82 mL, 8.21 mmol, 1.5 equiv) under argon atmosphere in dry THF (10 mL, 0.8 M) was added dropwise at -78 °C a solution of *n*-butyllithium (13.14 mmol, 1.6 equiv). The bright yellow solution was stirred for 30 min at -78 °C and 30 min further at 0 °C before a dropwise addition of a solution of **1c** (2.587 g, 8.21 mmol, 1 equiv) in dry THF (10 mL, 0.8 M). The black solution was stirred for 4 hours at room temperature. After total completion, monitored by TLC, water (15 mL) was added and the aqueous layer was extracted by diethyl ether (3 × 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure afforded crude **1d** which was directly used without further purification.

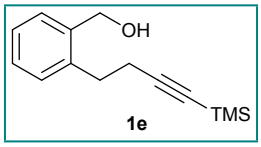
General procedure to remove the *tert*-butyldimethylsilyl group (GP1):
To a solution of the corresponding *tert*-butyldimethylsilylether (6.27 mmol, 1 equiv) in THF (100 mL, 0.06 M), was added *p*-TsOH.H_2O (2.386 g, 12.54 mmol, 2 equiv) and the mixture was stirred for 1h30

[2] R. Cao, P. Müller, S. J. Lippard, *J. Am. Chem. Soc.,* 2010, 132, **49**, 17366-17369

[3] R. P. Law, S. J. Atkinson, P. Bamborough, C. Chung, E. H. Demont, L. J. Gordon, M. Lindon, R. K. Prinjha, A. J. B. Watson, D. J. Hirst, *J. Med. Chem.,* 2018 61, **10**, 4317-4334

at room temperature. After total completion, monitored by TLC, a satured $NaHCO_3$ solution (50 mL) was added before extraction by ethyl acetate (2 × 50 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the crude by flash chromatography over silica gel afforded pure alcohol.

(2-(4-(trimethylsilyl)but-3-yn-1-yl)phenyl)methanol **1e**



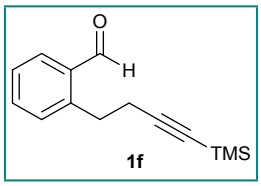
Compound **1e** was obtained from **1d** following **GP1** on 6.27 mmol scale (2.175 g). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 80/20) afforded pure **1e** as a colourless liquid (1.123 g, 4.83 mmol, 77 %).

Spectroscopic data were in accordance with literature[4].

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 - 7.35 (m, 1H), 7.27 - 7.21 (m, 3H), 4.74 (s, 2H), 2.93 (t, J = 7.2 Hz, 2H), 2.55 (t, J = 7.2 Hz, 2H), 0.13 (s, 9H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 139.0, 138.6, 129.9, 128.8, 128.2, 126.9, 106.8, 85.6, 63.4, 31.3, 22.1, 0.2

General procedure for the Dess-Martin oxidation (GP2):
To a solution of corresponding alcohol (6.88 mmol, 1 equiv) in dichloromethane (43 mL, 0.16 M), was added Dess-Martin reagent (3.210 g, 7.57 mmol, 1.1 equiv) and the mixture was stirred for 2h at room temperature. After total completion, monitored by TLC, a satured $NaHCO_3$ solution (50 mL) was added before extraction by dichloromethane (2 × 40 mL). The combined organic layers were washed with water (40 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Pentane and diethyl ether (80/20) were added and the white insoluble solid was filtered. The resulting filtrate was concentrated under reduced pressure, affording the desired clean aldehyde which was directly used without further purification.

2-(4-(trimethylsilyl)but-3-yn-1-yl)benzaldehyde **1f**



Clean compound **1f** was obtained from the corresponding alcohol **1e** following **GP2** on 6.88 mmol scale (1.600 g) as a yellow liquid.

Spectroscopic data were in accordance with literature[5].

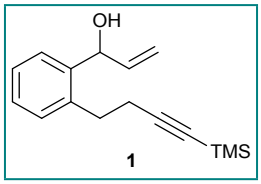
^{1}H NMR (300 MHz, $CDCl_3$): δ 10.26 (s, 1H), 7.86 - 7.83 (m, 1H), 7.56 - 7.51 (m, 1H), 7.44 - 7.39 (m, 1H), 7.35 - 7.32 (m, 1H), 3.24 (t, J = 7.2 Hz, 2H), 2.56 (t, J = 7.2 Hz, 2H), 0.10 (s, 9H)

General procedure for the addition of Grignard reagent on aldehydes (GP3):
To a solution of the corresponding aldehyde (6.88 mmol, 1 equiv) under argon atmosphere in dry THF (10 mL, 0.65 M), was added dropwise a solution of the corresponding Grignard reagent (8.26 mmol, 1.2

[4] C. Mukai, T. hirose, S. Teramoto, S. Kitgaki, *Tetrahedron,* 2005, **61**, 10983–10994
[5] B. M. Trost, S. Mahapatra, M. Hansen, *Angew. Chem. Int. Ed*., 2015, **54**, 6032 –6036

equiv) at 0 °C. The orange-brown mixture was stirred at room temperature for 2 hours. After total completion, monitored by TLC, the reaction was quenched by slow addition of a saturated NH_4Cl solution (20 mL) and extracted by ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the crude by flash chromatography over silica gel afforded pure desired allylic alcohol.

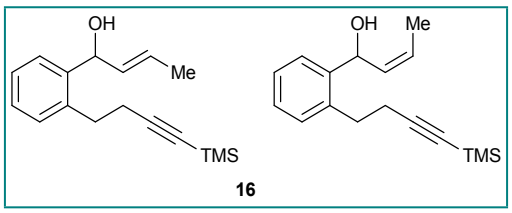
1-(2-(4-(trimethylsilyl)but-3-yn-1-yl)phenyl)prop-2-en-1-ol **1**



Compound **1** was obtained by addition of vinylmagnesium bromide on the aldehyde **1f** following **GP3** on 6.88 mmol scale (1.584 g). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 90/10) afforded pure **1** as an orange-yellow oil (1.634 g, 6.32 mmol, 92 % over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 - 7.42 (m, 1H), 7.28 - 7.20 (m, 3H), 6.09 (ddd, J = 17.2, 10.4, 5.2 Hz, 1H), 5.50 (d, J = 5.2 Hz, 1H), 5.36 (dd, J = 17.2, 1.2 Hz, 1H), 5.24 (dd, J = 10.4, 1.2 Hz, 1H), 2.95 (t, J = 7.6 Hz, 2H), 2.53 (t, J = 7.6 Hz, 2H), 1.94 (s, 1H), 0.14 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 140.1, 138.2, 130.0, 128.0, 127.1, 126.9, 115.2, 106.7, 85.7, 71.5, 31.4, 22.2, 0.2
HRMS (ESI): m/z calculated for $[M+H]^+$ 259.1513 g.mol^{-1}, found 259.1521 g.mol^{-1}, calculated for $[M+Na]^+$ 281.1332 g.mol^{-1}, found 281.1340 g.mol^{-1}
FTIR (film cm^{-1}): ν 3345, 2958, 2173, 1641, 1488, 1450, 1407, 1335, 1248, 1114, 1038, 988, 925, 837, 755, 697

(*E*)-1-(2-(4-(trimethylsilyl)but-3-yn-1-yl)phenyl)but-2-en-1-ol and (*Z*)-1-(2-(4-(trimethylsilyl)but-3-yn-1-yl)phenyl)but-2-en-1-ol **16A** and **16B**



Compounds **16A** and **16B** were obtained by the addition of prop-1-en-1-ylmagnesium bromide on the aldehyde **1f** following **GP3** on 1.27 mmol scale (293 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 95/5) afforded a clean inseparable mixture of **16A** and **16B** as a yellow oil (293 mg, 1.08 mmol, 85 % over 2 steps).

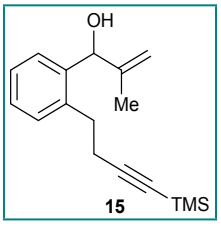
16A

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 – 7.52 (m, 1H), 7.29 – 7.17 (m, 3H), 5.79 (d, J = 6.8 Hz, 1H), 5.70 – 5.61 (m, 2H), 2.99 – 2.83 (m, 2H), 2.58 – 2.42 (m, 2H), 1.98 (s, 1H), 1.86 – 1.78 (m, 3H), 0.15 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 137.7, 132.8, 129.8, 127.6, 127.0, 126.9, 126.2, 106.9, 85.5, 66.4, 31.6, 21.9, 13.6, 0.2
HRMS (ESI): m/z calculated for $[M+H]^+$ 273.1669 g.mol^{-1}, found 273.1678 g.mol^{-1}, calculated for $[M+Na]^+$ 295.1489 g.mol^{-1}, found 295.1496 g.mol^{-1}
FTIR (film cm^{-1}): ν 3337, 3020, 2958, 2173, 1487, 1450, 1249, 1037, 971, 886, 838, 757, 698

16B

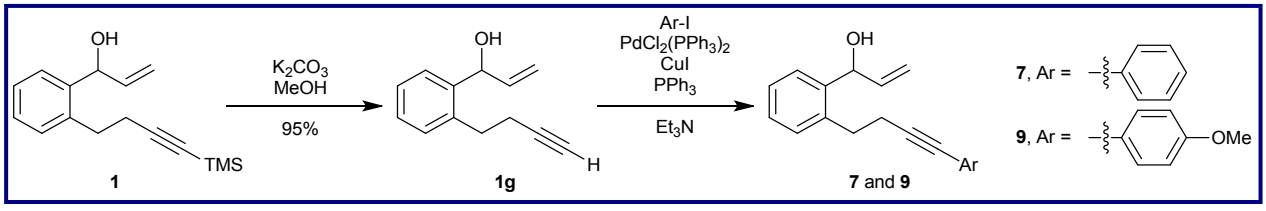
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.46 (m, 1H), 7.29 – 7.17 (m, 3H), 5.76 – 5.70 (m, 2H), 5.43 (d, J = 4.2 Hz, 1H), 2.99 – 2.83 (m, 2H), 2.58 – 2.42 (m, 2H), 2.01 (s, 1H), 1.74 – 1.71 (m, 3H), 0.15 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 137.8, 133.4, 129.9, 127.7, 127.5, 127.0, 126.5, 106.8, 85.5, 71.4, 31.5, 22.0, 17.9, 0.21
HRMS (ESI): m/z calculated for $[M+H]^+$ 273.1669 g.mol^{-1}, found 273.1678 g.mol^{-1}, calculated for $[M+Na]^+$ 295.1489 g.mol^{-1}, found 295.1496 g.mol^{-1}
FTIR (film cm^{-1}): ν 3337, 3020, 2958, 2173, 1487, 1450, 1249, 1037, 971, 886, 838, 757, 698

2-methyl-1-(2-(4-(trimethylsilyl)but-3-yn-1-yl)phenyl)prop-2-en-1-ol **15**



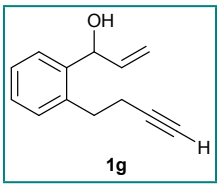
Compound **15** was obtained by the addition of prop-1-en-2-ylmagnesium bromide on the aldehyde **1f** following **GP3** on 1.74 mmol scale (400 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 90/10) afforded pure **15** as a yellow oil (371 mg, 1.36 mmol, 78 % over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.36 (m, 1H), 7.29 – 7.18 (m, 3H), 5.36 (s, 1H), 5.20 (dq, J = 1.6, 0.8 Hz, 1H), 5.04 - 5.03 (m, 1H), 3.05 – 2.86 (m, 2H), 2.53 (t, J = 7.5 Hz, 2H), 2.08 (s, 1H), 1.64 (dt, J = 1.6, 0.7 Hz, 3H), 0.15 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 139.5, 138.7, 130.0, 127.9, 127.0, 126.9, 111.6, 106.8, 85.5, 73.8, 31.4, 22.1, 19.5, 0.2
HRMS (ESI): m/z calculated for $[M+Na]^+$ 295.1489 g.mol^{-1}, found 295.1495 g.mol^{-1}
FTIR (film cm^{-1}): ν 3353, 2958, 2174, 1488, 1450, 1275, 1249, 1040, 993, 902, 838, 757, 699



General procedure for the methanolysis of silylated alkynes (GP4):
To a solution of the corresponding silylated alkyne (2.31 mmol, 1 equiv) in methanol (15 mL, 0.15 M) was added potassium carbonate (5.76 mmol, 2.5 equiv) and the heterogeneous mixture was vigorously stirred overnight at room temperature. After total completion, monitored by TLC, the mixture was concentrated under reduced pressure, diluted into water (30 mL) and extracted by ethyl acetate (2 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the crude over silica gel afforded pure corresponding desired terminal alkyne.

1-(2-(but-3-yn-1-yl)phenyl)prop-2-en-1-ol **1g**

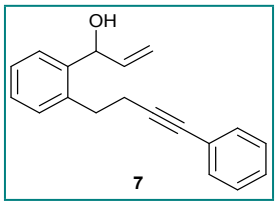


Compound **1g** was obtained from **1** following **GP4** on 2.31 mmol scale (600 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 50/50) afforded pure **1g** as a colourless oil (411 mg, 2.19 mmol, 95 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48-7.44 (m, 1H), 7.29-7.21 (m, 3H), 6.09 (ddd, J = 17.1, 10.5, 5.4 Hz, 1H), 5.50 (d, J = 5.4 Hz, 1H), 5.36 (dd, J = 17.1, 1.5 Hz, 1H), 5.24 (dd, J = 10.5, 1.5 Hz, 1H), 2.96 (t, J = 7.5 Hz, 2H), 2.50 (dt, J = 7.5, 2.7 Hz, 2H), 2.00 (t, J = 2.7 Hz, 1H), 1.92 (s, 1H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 140.4, 140.1, 138.1, 129.9, 128.1, 127.2, 127.0, 115.4, 84.0, 71.6, 69.3, 31.3, 20.7
HRMS (ESI): calculated for $[M+Na]^+$ 209.0937 g.mol^{-1}, found 209.0941 g.mol^{-1}
FTIR (film cm^{-1}): ν 3530, 3384, 3298, 3062, 2912, 2117, 1641, 1488, 1450, 1429, 1265, 1178, 1114, 1019, 988, 925, 756, 737, 702

General procedure for the Sonogashira coupling (GP5):
To a stirred solution of the corresponding iodophenyl derivative (1.2 mmol, 1.2 equiv) under argon atmosphere in distilled triethylamine (3 mL, 0.33 M) was added dropwise a solution of the corresponding alkyne (1 mmol, 1 equiv) in triethylamine (1 mL). $PdCl_2(PPh_3)_2$ (15 mg, 0.02 mmol, 2 mol%), CuI (9 mg, 0.04 mmol, 4 mol%) and PPh_3 (11 mg, 0.04 mmol, 4 mol%) were successively added and the heterogeneous yellow mixture was stirred with argon bubbling for 20 minutes. Further vigorous stirring overnight at room temperature gave a thick paste which was concentrated under reduced pressure. Purification of the crude over silica gel afforded pure desired coupling product.

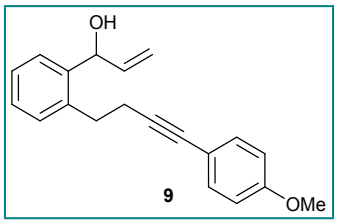
1-(2-(4-phenylbut-3-yn-1-yl)phenyl)prop-2-en-1-ol **7**



Compound **7** was obtained by coupling reaction between **1g** and iodobenzene following **GP5** on 1 mmol scale (186 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 85/15) afforded pure **7** as a yellow liquid (226 mg, 0.86 mmol, 86 %).

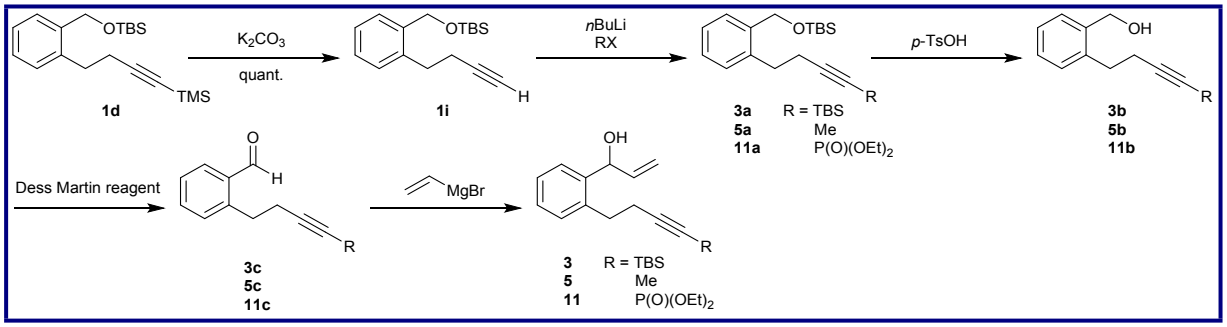
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.46 (m, 1H), 7.40 – 7.36 (m, 2H), 7.31 – 7.25 (m, 6H), 6.11 (ddd, J = 17.1, 10.4, 5.3 Hz, 1H), 5.57 (d, J = 5.3 Hz, 1H), 5.37 (dt, J = 17.1, 1.5 Hz, 1H), 5.24 (dt, J = 10.4, 1.5 Hz, 1H), 3.04 (t, J = 7.7 Hz, 2H), 2.73 (t, J = 7.7 Hz, 2H), 1.95 (s, 1H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 140.1, 138.3, 131.7, 130.0, 128.4, 128.1, 127.8, 127.1, 126.9, 123.8, 115.3, 89.5, 81.6, 71.6, 31.6, 21.7
HRMS (ESI): calculated for $[M+H]^+$ 263.1430 g.mol^{-1}, found 263.1437 g.mol^{-1}, calculated for $[M+Na]^+$ 285.1250 g.mol^{-1}, found 285.1256 g.mol^{-1}
FTIR (film cm^{-1}): ν 3351, 3060, 2906, 1640, 1597, 1571, 1489, 1441, 1338, 1265, 1018, 987, 924, 837, 752, 690

1-(2-(4-(4-methoxyphenyl)but-3-yn-1-yl)phenyl)prop-2-en-1-ol **9**

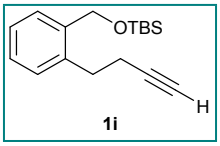


Compound **9** was obtained by coupling reaction between **1g** and 1-iodo-4-methoxybenzene following **GP5** on 0.46 mmol scale (86 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 60/40) afforded pure **9** as a yellow oil (101 mg, 0.34 mmol, 75 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.44 (m, 1H), 7.34 – 7.30 (m, 2H), 7.27 – 7.26 (m, 3H), 6.84 – 6.79 (m, 2H), 6.10 (ddd, J = 17.2, 10.4, 5.2 Hz, 1H), 5.60 – 5.54 (m, 1H), 5.36 (dt, J = 17.2, 1.5 Hz, 1H), 5.23 (dt, J = 10.4, 1.5 Hz, 1H), 3.79 (s, 3H), 3.03 (t, J = 7.8 Hz, 2H), 2.70 (t, J = 7.8 Hz, 2H), 2.03 (s, 1H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 140.4, 140.1, 138.3, 133.0, 129.9, 128.0, 127.0, 126.9, 115.9, 115.2, 114.0, 87.9, 81.4, 71.6, 55.4, 31.6, 21.7
HRMS (ESI): calculated for $[M+H]^+$ 293.1536 g.mol^{-1}, found 293.1543 g.mol^{-1}
FTIR (film cm^{-1}): ν 3394, 2918, 2837, 1605, 1508, 1462, 1441, 1288, 1243, 1172, 1106, 1030, 988, 927, 831, 756



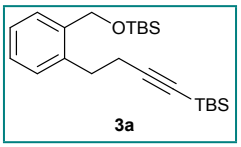
((2-(but-3-yn-1-yl)benzyl)oxy)(*tert*-butyl)dimethylsilane **1i**



Compound **1i** was obtained from **1d** following **GP4** on 15.8 mmol scale (5.50 g). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 90/10) afforded pure **1i** as a brown liquid (4.35 g, 15.8 mmol, quant.).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46-7.41 (m, 1H), 7.27-7.21 (m, 3H), 4.78 (s, 2H), 2.90 (t, J = 7.6 Hz, 2H), 2.51 (dt, J = 7.6, 2.4 Hz, 2H), 2.01 (t, J = 2.4 Hz, 1H), 0.96 (s, 9H), 0.13 (s, 6H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 138.9, 138.0, 129.2, 127.7, 127.5, 126.7, 84.2, 69.0, 63.5, 31.3, 26.1, 20.2, -5.0
HRMS (ESI): calculated for $[M+Na]^+$ 297.1645 g.mol^{-1}, found 297.1246 g.mol^{-1}
FTIR (film cm^{-1}): ν 3313, 2954, 2927, 2855, 1739, 1463, 1379, 1361, 1253, 1186, 1118, 1075, 1006, 835, 775, 753

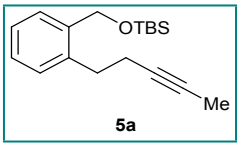
tert-butyl((2-(4-(*tert*-butyldimethylsilyl)but-3-yn-1-yl)benzyl)oxy)dimethylsilane **3a**



3a

To a solution of **1i** (1.0 g, 3.64 mmol, 1 equiv) under argon atmosphere in dry THF (8 mL, 0.45 M) was added dropwise at -78 °C a solution of *n*-butyllithium (4.0 mmol, 1.1 equiv). The dark solution was stirred for 30 min at -78 °C before a dropwise addition of *tert*-butyldimethylsilyl triflate (1.82 mL, 4.0 mmol, 1.1 equiv). The solution was stirred for 1 hour at -78°C. After total completion, monitored by TLC, water (30 mL) was added and the aqueous layer was extracted by ethyl acetate (2 × 30 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure affording crude **3a** which was directly used without further purification.

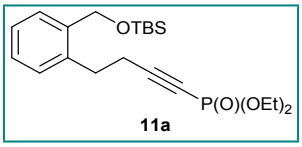
tert-butyldimethyl((2-(pent-3-yn-1-yl)benzyl)oxy)silane **5a**



5a

To solution of **1i** (1 g, 3.64 mmol, 1 equiv) under argon atmosphere in dry THF (36 mL, 0.1 M) was added dropwise at -78 °C a solution of *n*-butyllithium (5.46 mmol, 1.5 equiv). The dark solution was stirred for 30 min at -78 °C before dropwise addition of iodomethane (0.32 mL, 5.10 mmol, 1.4 equiv). The black mixture was slowly warmed to room temperature and then stirred for 3 hours. After total completion, monitored by TLC, the reaction was quenched by slow addition of a satured ammonium chloride solution (20 mL) and the aqueous layer was extracted by ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure affording crude **5a** which was directly used without further purification.

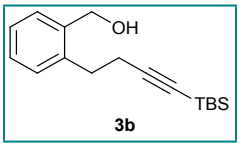
diethyl (4-(2-(((*tert*-butyldimethylsilyl)oxy)methyl)phenyl)but-1-yn-1-yl)phosphonate **11a**



11a

To a solution of **1i** (972 mg, 3.54 mmol, 1 equiv) under argon atmosphere in dry THF (10 mL, 0.35 M) was added dropwise at -78 °C a solution of *n*-butyllithium (3.89 mmol, 1.1 equiv). The dark solution was stirred for 1 hour at -78 °C before a dropwise addition of a solution of diethylchlorophosphate (0.56 mL, 3.89 mmol, 1.1 equiv) in 4 mL of dry THF. The solution was stirred for 1 hour at -78°C and 4 hour at room temperature. After total completion, monitored by TLC, a satured NH_4Cl solution (20 mL) was added and the aqueous layer was extracted by ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure affording crude **11a** which was directly used without further purification.

(2-(4-(*tert*-butyldimethylsilyl)but-3-yn-1-yl)phenyl)methanol **3b**

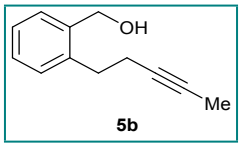


3b

Compound **3b** was obtained from **3a** following **GP1** on 3.64 mmol scale (1.415 g). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 90/10) afforded pure **3b** as a yellow liquid (703 mg, 2.55 mmol, 70 % over 2 steps).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.34 (m, 1H), 7.27-7.21 (m, 3H), 4.74 (s, 2H), 2.94 (t, J = 7.5 Hz, 2H), 2.56 (t, J = 7.5 Hz, 2H), 1.59 (bs, 1H), 0.88 (s, 9H), 0.06 (s, 6H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 139.0, 138.5, 129.9, 128.8, 128.3, 126.8, 107.2, 83.8, 63.5, 31.3, 29.9, 26.2, 22.0, -4.3
HRMS (ESI): calculated for $[M+H]^+$ 275.1826 g.mol^{-1}, found 275.1823 g.mol^{-1}
FTIR (film cm^{-1}): ν 3309, 2953, 2927, 2855, 2172, 1471, 1462, 1361, 1275, 1249, 1039, 1007, 836, 824, 809, 773, 751, 680

(2-(pent-3-yn-1-yl)phenyl)methanol **5b**

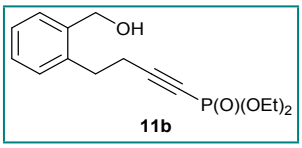


5b

Compound **5b** was obtained from **5a** following **GP1** on 3.64 mmol scale (1.050 g). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 80/20) afforded pure **5b** as a yellow liquid (371 mg, 2.11 mmol, 58 % over 2 steps).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.35 (m, 1H), 7.31-7.20 (m, 3H), 4.71 (s, 2H), 2.89 (t, J = 7.5 Hz, 2H), 2.45 (tq, J = 7.5 Hz, 2.7 Hz), 1.96 (s, 1H), 1.76 (t, J = 2.7 Hz, 3H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 139.3, 138.7, 129.7, 128.8, 128.3, 126.8, 78.9, 76.7, 63.3, 31.8, 20.9, 3.6
HRMS (ESI): calculated for $[M+H]^+$ 175.1117 g.mol^{-1}, found 175.1117 g.mol^{-1}
FTIR (film cm^{-1}): ν 3341, 3020, 2919, 1491, 1453, 1249, 1210, 1183, 1005, 836, 753

diethyl (4-(2-(hydroxymethyl)phenyl)but-1-yn-1-yl)phosphonate **11b**

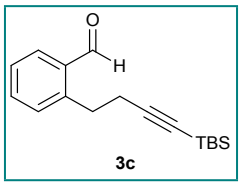


11b

Compound **11b** was obtained from **11a** following **GP1** on 3.54 mmol scale (1.453 g). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 50/50 to 20/80) afforded pure **11b** as a yellow liquid (673 mg, 2.27 mmol, 64 % over 2 steps).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.41 (m, 1H), 7.27-7.18 (m, 3H), 4.74 (s, 2H), 4.10-3.98 (m, 4H), 2.97 (t, J = 7.2 Hz, 2H), 2.67 (dt, J = 7.2, 4.5 Hz, 2H), 2.23 (s, 1H), 1.30 (t, J = 7.2 Hz, 6H)
^{31}P NMR (300 MHz, $CDCl_3$): δ -6.21 (s)l
^{13}C NMR (75 MHz, $CDCl_3$): δ 139.2, 137.6, 129.5, 128.6, 128.1, 127.1, 102.6 (d, J = 52.7 Hz), 71.5 (d, J = 301.6 Hz), 63.2, 63.1, 29.8 (d, J = 2.3 Hz), 21.4 (d, J = 4.5 Hz), 16.2, 16.1
HRMS (ESI): calculated for $[M+H]^+$ 297.1250 g.mol^{-1}, found 297.1247 g.mol^{-1}
FTIR (film cm^{-1}): ν 3394, 2984, 2930, 2203, 1455, 1393, 1245, 1163, 1015, 974, 889, 797, 756

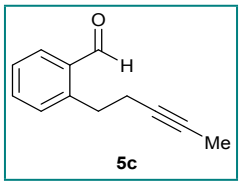
2-(4-(*tert*-butyldimethylsilyl)but-3-yn-1-yl)benzaldehyde **3c**



3c

Crude compound **3c** was obtained from the corresponding alcohol **3b** following **GP2** on 1.80 mmol scale (490 mg) and was directly used without purification.

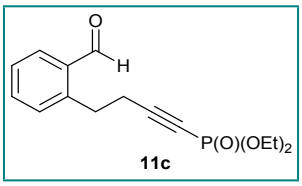
2-(pent-3-yn-1-yl)benzaldehyde **5c**



5c

Crude compound **5c** was obtained from the corresponding alcohol **5b** following **GP2** on 1.91 mmol scale (329 mg) and was directly used without purification.

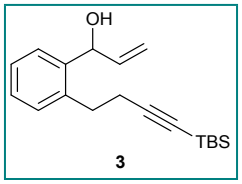
diethyl (4-(2-formylphenyl)but-1-yn-1-yl)phosphonate **11c**



11c

Crude compound **11c** was obtained from the corresponding alcohol **11b** following **GP2** on 2.27 mmol scale (673 mg) and was directly used without purification.

1-(2-(4-(*tert*-butyldimethylsilyl)but-3-yn-1-yl)phenyl)prop-2-en-1-ol **3**

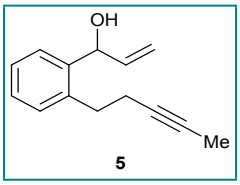


3

Compound **3** was obtained by the addition of vinylmagnesium bromide on the aldehyde **3c** following **GP3** on 1.80 mmol scale (490 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 80/20) afforded pure **3** as a yellow oil (351 mg, 1.17 mmol, 65 % over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 - 7.42 (m, 1H), 7.27 - 7.23 (m, 3H), 6.07 (ddd, J = 17.2, 10.4, 5.2 Hz, 1H), 5.44 (dt, J = 5.2, 1.6 Hz, 1H), 5.35-5.30 (m, 1H), 5.24-5.21 (m, 1H), 2.94 (t, J = 7.6 Hz, 2H), 2.53 (t, J = 7.6 Hz, 2H), 2.45 (s, 1H), 0.94 (s, 9H), 0.14 (s, 6H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 140.0, 138.1, 130.0, 127.8, 126.9, 126.8, 115.1, 107.2, 83.6, 71.4, 31.5, 26.2, 21.9, 16.6, -4.4
HRMS (ESI): calculated for $[M+H]^+$ 301.1982 g.mol^{-1}, found 301.1985 g.mol^{-1}, calculated for $[M+Na]^+$ 323.1802 g.mol^{-1}, found 323.1803 g.mol^{-1}
FTIR (film cm^{-1}): ν 3342, 2953, 2928, 2856, 2172, 1489, 1471, 1462, 1408, 1361, 1249, 1115, 1037, 1007, 989, 926, 884, 836, 824, 809, 773, 754, 679

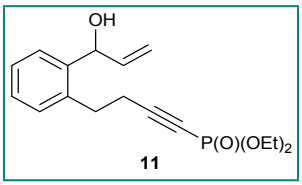
1-(2-(pent-3-yn-1-yl)phenyl)prop-2-en-1-ol **5**



Compound **5** was obtained by the addition of vinylmagnesium bromide on the aldehyde **5c** following **GP3** on 1.91 mmol scale (329 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 80/20) afforded pure **5** as a colourless oil (206 mg, 1.03 mmol, 54 % over 2 steps).

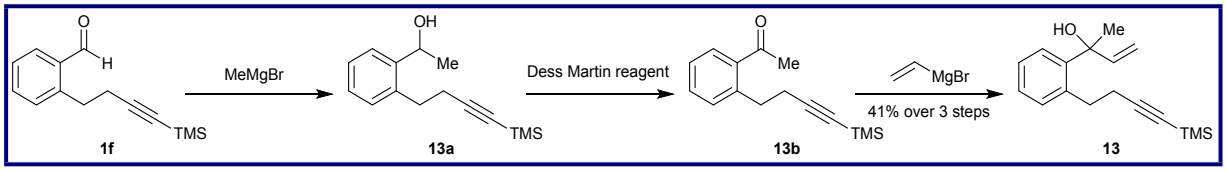
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.42 (m, 1H), 7.28 – 7.19 (m, 3H), 6.09 (ddd, J = 17.1, 10.4, 5.3 Hz, 1H), 5.52 (d, J = 5.3 Hz, 1H), 5.36 (dt, J = 17.2, 1.5 Hz, 1H), 5.23 (dt, J = 10.4, 1.5 Hz, 1H), 2.91 (t, J = 7.6 Hz, 2H), 2.47 – 2.41 (m, 2H), 1.99 (s, 1H), 1.77 (t, J = 2.5 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 140.1, 138.6, 129.8, 128.0, 127.0, 126.9, 115.2, 78.7, 76.7, 71.5, 31.9, 21.1, 3.6
HRMS (ESI): calculated for $[M+H]^+$ 201.1274 g.mol^{-1}, found 201.1279 g.mol^{-1}, calculated for $[M+Na]^+$ 223.1093 g.mol^{-1}, found 223.1097 g.mol^{-1}
FTIR (film cm^{-1}): ν 3354, 2918, 2852, 1640, 1603, 1488, 1450, 1338, 1247, 1178, 1112, 1019, 987, 924, 829, 753, 674

diethyl (4-(2-(1-hydroxyallyl)phenyl)but-1-yn-1-yl)phosphonate **11**

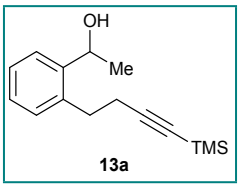


Compound **11** was obtained by the addition of vinylmagnesium bromide on the aldehyde **11c** following **GP3** on 2.27 mmol scale (673 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 50/50 to 20/80) afforded pure **11** as a viscous brown oil (460 mg, 1.43 mmol, 63 % over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.42 (m, 1H), 7.19-7.08 (m, 3H), 5.98 (ddd, J = 17.2, 10.4, 5.2 Hz, 1H), 5.40 (d, J = 5.2 Hz, 1H), 5.18-5.13 (m, 1H), 5.09-5.06 (m, 1H), 4.02-3.95 (m, 2H), 3.95-3.84 (m, 2H), 2.97-2.83 (m, 2H), 2.66-2.51 (m, 2H), 1.25 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.2 Hz)
^{31}P NMR (400 MHz, $CDCl_3$): δ -5.93(s)
^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 140.4, 136.4, 129.3, 127.4, 126.96, 126.94, 114.6, 102.7 (d, J = 210 Hz), 71.2 (d, J = 1199 Hz), 71.1, 63.0 (d, J = 22 Hz), 29.6, 21.2 (d, J = 17 Hz), 15.9 (t, J = 29 Hz)
HRMS (ESI): calculated for $[M+Na]^+$ 345.1226 g.mol^{-1}, found 345.1224 g.mol^{-1}
FTIR (film cm^{-1}): ν 3390, 2982, 2923, 2846, 2204, 1639, 1449, 1393, 1247, 1164, 1099, 1021, 979, 799, 760



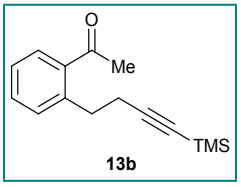
1-(2-(4-(trimethylsilyl)but-3-yn-1-yl)phenyl)ethanol **13a**



13a

Crude compound **13a** was obtained by the addition of methylmagnesium bromide on the aldehyde **1f** following **GP3** on 2.17 mmol scale (500 mg) and was directly used without purification.

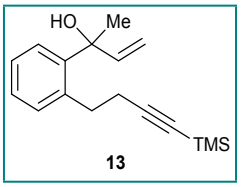
1-(2-(4-(trimethylsilyl)but-3-yn-1-yl)phenyl)ethanone **13b**



13b

Crude compound **13b** was obtained from **13a** following **GP2** and was directly used without purification.

2-(2-(4-(trimethylsilyl)but-3-yn-1-yl)phenyl)but-3-en-2-ol **13**



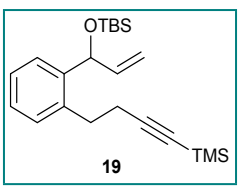
13

Compound **13** was obtained by the addition of vinylmagnesium bromide on the ketone **13b** following **GP3** on 2.17 mmol scale (530 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 98/2) afforded pure **13** as a colourless oil (244 mg, 0.89 mmol, 41 % over 3 steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.40 (m, 1H), 7.31 – 7.14 (m, 3H), 6.22 (ddd, J = 17.4, 10.6, 1.0 Hz, 1H), 5.15 (dt, J = 17.4, 1.0 Hz, 1H), 5.13 (dt, J = 10.6, 1.0 Hz, 1H), 3.21 – 2.97 (m, 2H), 2.58 – 2.49 (m, 2H), 1.72 (s, 3H), 0.13 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 143.5, 139.6, 131.7, 127.6, 126.3, 126.1, 112.7, 107.7, 85.4, 75.9, 32.5, 30.4, 22.6, 0.3
HRMS (ESI): calculated for $[M+H]^+$ 273.1669 g.mol^{-1}, found 273.1672 g.mol^{-1}, calculated for $[M+Na]^+$ 295.1489 g.mol^{-1}, found 295.1488 g.mol^{-1}
FTIR (film cm^{-1}): ν 3453, 2959, 2172, 1673, 1487, 1445, 1407, 1368, 1335, 1248, 1216, 1098, 1044, 994, 922, 838, 757, 698

b. Protected alcohol

tert-butyldimethyl((1-(2-(4-(trimethylsilyl)but-3-yn-1-yl)phenyl)allyl)oxy)silane **19**

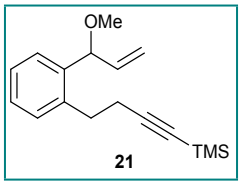


19

To a solution of **1** (250 mg, 0.97 mmol, 1 equiv) under argon atmosphere in dry dichloromethane (5 mL, 0.23M), was added at room temperature 2.6-lutidine (0.22 mL, 1.94 mmol, 2 equiv) and the mixture was stirred for 10 min. *Tert*-butyldimethylsilyl trifluoromethanesulfonate (0.31 mL, 1.45 mmol, 1.5 equiv) was then added dropwise and the solution was stirred at room temperature for 2 hours. After total completion, monitored by TLC, water (10 mL) was added and the aqueous layer was extracted by ethyl acetate (2 × 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the crude by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 90/10) afforded pure **19** (315 mg, 0.84 mmol, 87 %) as a brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.42 (m, 1H), 7.25 – 7.14 (m, 3H), 5.95 (ddd, J = 17.0, 10.3, 5.2 Hz, 1H), 5.36 (ddd, J = 5.2, 1.6, 1.6 Hz, 1H), 5.23 (ddd, J = 17.0, 1.6, 1.6 Hz, 1H), 5.07 (ddd, J = 10.3, 1.6, 1.6 Hz, 1H), 2.94 – 2.89 (m, 2H), 2.53 – 2.42 (m, 2H), 0.91 (s, 9H), 0.16 (s, 9H), 0.08 (s, 3H), -0.04 (s, 3H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 141.2, 137.1, 129.5, 127.2, 126.7, 113.7, 106.9, 85.2, 77.4, 73.1, 31.5, 26.0, 21.6, 18.4, 0.3, -4.5, -4.6
HRMS (ESI): m/z, calculated for $[M+H]^+$ 373.2383 g.mol^{-1}, found 373.2375 g.mol^{-1}, calculated for $[M+Na]^+$ 395.2202 g.mol^{-1}, found 395.2196 g.mol^{-1}
FTIR (film cm^{-1}): ν 2956, 2929, 2897, 2857, 2175, 1471, 1462, 1407, 1249, 1128, 1101, 1064, 1034, 988, 921, 833, 774, 753, 697, 676

(4-(2-(1-methoxyallyl)phenyl)but-1-yn-1-yl)trimethylsilane **21**

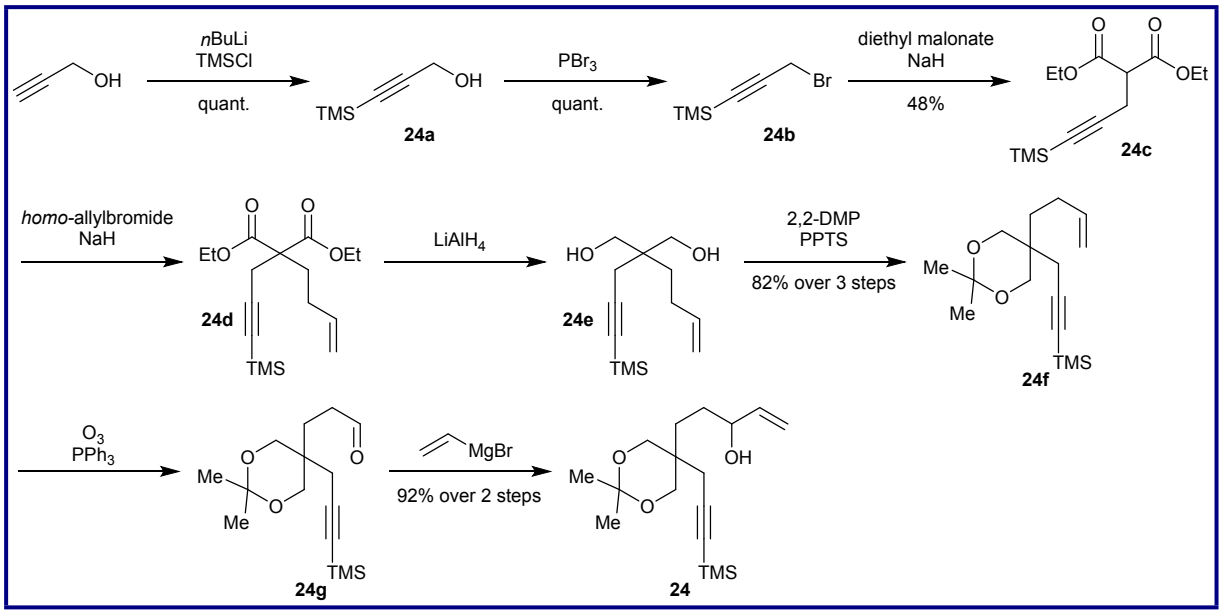


21

To a suspension of NaH (60 mg, 1.5 mmol, 1.5 equiv) under argon atmosphere in dry THF (3 mL, 0.5M), was added at 0 °C a solution of **1** (258 mg, 1 mmol, 1 equiv) in dry THF (1 mL). Stirring was kept 30 minutes at 0 °C before dropwise addition of iodomethane (0.1 mL, 1.5 mmol, 1.5 equiv) and the mixture was stirred overnight at room temperature. After total completion, monitored by TLC, a satured NH_4Cl solution (25 mL) was added and the aqueous layer was extracted by ethyl acetate (2 × 25 mL). The combined organic layers were washed with brine (25 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the crude by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 80/20) afforded pure **21** (227 mg, 0.83 mmol, 83 %) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.37 (m, 1H), 7.28 – 7.20 (m, 3H), 5.97 (ddd, J = 16.9, 10.6, 6.3 Hz, 1H), 5.25 (dt, J = 7.8, 1.4 Hz, 1H), 5.21 (d, J = 1.3 Hz, 1H), 4.88 (dt, J = 6.2, 1.3 Hz, 1H), 3.32 (s, 3H), 2.94 – 2.87 (m, 2H), 2.52 – 2.45 (m, 2H), 0.15 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 138.4, 129.9, 127.8, 127.2, 127.0, 116.7, 106.7, 85.3, 81.2, 77.4, 56.6, 31.7, 21.8, 0.2
HRMS (ESI): m/z calculated for $[M+H]^+$ 273.1669 g.mol^{-1}, found 273.1672 g.mol^{-1}
FTIR (film cm^{-1}): ν 3073, 3020, 2958, 2931, 2898, 2820, 2174, 1488, 1450, 1337, 1249, 1082, 1041, 991, 926, 885, 839, 756, 699

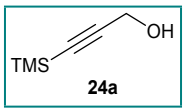
c. Spiro-ketal type precursors



General procedure for the silylation of a terminal alkyne with an alcohol (GP6):

To a stirred solution of the corresponding terminal alkyne (35.7 mmol, 1 equiv) in dry THF (75 mL, 0.5 M) under argon atmosphere was added dropwise a *n*butyllithium solution (75 mmol, 2 equiv) at -78°C. Stirring was kept at this temperature for 30 minutes before the dropwise addition of freshly distilled trimethylsilyl chloride (9.1 mL, 71.4 mmol, 2.1 equiv). Stirring was kept further 30 minutes at -78°C before slow addition of a concentrated HCl solution (25 mL). The aqueous layer was extracted by ethyl acetate (2 × 30 mL). The combined organic layers were washed with a satured $NaHCO_3$ solution (50 mL), dried over $MgSO_4$, and concentrated under reduced pressure.

3-(trimethylsilyl)prop-2-yn-1-ol **24a**

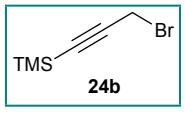


Compound **24a** was obtained from commercially available propargylic alcohol following **GP6** on 35.7 mmol scale (2.07 mL). Pure **24a** was quantitatively obtained after concentration under reduced pressure (4.578 g, 35.7 mmol) as a clear yellow liquid.

Spectroscopic data were in accordance with those reported in literature[6].

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.27 (s, 2H), 0.18 (s, 9H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 103.9, 90.8, 51.8, -0.1

(3-bromoprop-1-yn-1-yl)trimethylsilane **24b**



To a stirred solution of **24a** (4.578 g, 35.7 mmol, 1 equiv) in dry Et_2O (35 mL, 1 M) under argon atmosphere was added dropwise at room temperature phosphorus tribromide (12.5 mL, 12.5 mmol, 1 M in CH_2Cl_2, 0.35 equiv). After stirring overnight at room temperature, a satured $NaHCO_3$ solution (80

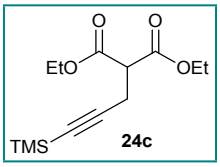
[6] M. Bourkhis, H. Gaspard, P. Rullière, D.K.C de Almeida, D. Listunov, E. Joly, R. Abderrahim, M.C. de Mattos, M.C.F. de Oliveira, V. Maraval, R. Chauvin, Y. Génisson, *ChemMedChem,* 2018, **13**, 1124-1130

mL) was slowly added. The aqueous layer was extracted by Et_2O (2 × 45 mL). The combined organic layers were dried over $MgSO_4$, and cautiously concentrated under reduced pressure (700 mbar at 30°C) affording quantitatively pure **24b** (6.824 g, 35.7 mmol) as a yellow liquid and was used without further purification.

Spectroscopic data were in accordance with those reported in literature[7].

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.91 (s, 2H), 0.18 (s, 9H)

diethyl 2-(3-(trimethylsilyl)prop-2-yn-1-yl)malonate **24c**

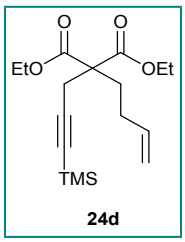


Commercially available diethylmalonate (16.3 mL, 107.1 mmol, 3 equiv) was added dropwise at 0°C to a solution of sodium hydride (1.43 g, 35.7 mmol, 60% in mineral oil, 1 equiv) in dry THF (85 mL, 0.4 M) under argon atmosphere. After stirring 30 minutes at room temperature, **24b** (6.824 g, 35.7 mmol, 1 equiv) was added dropwise at 0°C. The dark-brown solution was then vigorously stirred overnight at room temperature. After total completion, monitored by TLC, the reaction was quenched by slow addition of water (50 mL). The aqueous layer was extracted by ethyl acetate (3 × 50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. Distillation under reduced pressure (15 mbar, 65°C) of the crude mixture afforded pure **24c** (4.647 g, 17.14 mmol, 48 %) as a colourless liquid.

Spectroscopic data were I accordance with those reported in literature[8].

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.22 (q, J = 7.2 Hz, 4H), 3.55 (t, J = 7.8 Hz, 1H), 2.80 (d, J = 7.8 Hz, 2H), 1.28 (t, J = 7.2 Hz, 6H), 0.12 (s, 9H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 102.4, 76.6, 61.8, 51.5, 20.0, 14.2, 0.1

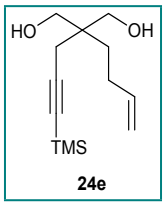
diethyl 2-(but-3-en-1-yl)-2-(3-(trimethylsilyl)prop-2-yn-1-yl)malonate **24d**



24c (4.624 g, 17.1 mmol, 1 equiv) was added dropwise at 0°C to a solution of sodium hydride (750 mg, 18.8 mmol, 60% in mineral oil, 1.1 equiv) in dry DMF (15 mL, 1.25 M) under argon atmosphere. After stirring 30 minutes, allyl bromide (1.91 mL, 18.8 mmol, 1.1 equiv) was added dropwise. The dark solution was then vigorously stirred overnight at room temperature. After total completion, monitored by TLC, the reaction was quenched by slow addition of a satured NH_4Cl solution (50 mL). The aqueous layer was extracted by diethyl ether (2 × 45 mL). The combined organic layers were washed by brine (50 mL), dried over $MgSO_4$ and concentrated under reduced pressure affording crude **24d** which was directly used without further purification.

2-(but-3-en-1-yl)-2-(3-(trimethylsilyl)prop-2-yn-1-yl)propane-1,3-diol **24e**

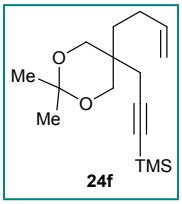
[7] F. Kolundžić, A. Murali, P. Pérez-Galán, J.O. Bauer, C. Strohmann, K. Kumar, H. Waldmann, *Angew. Chem. Int. Ed.,* 2014, **53**, 8122-8126
[8] B.M. Trost, M.T. Rudd, M.G. Costa, P.I. Lee, A.E. Poerantz, *Org. Lett.,* 2004, 6, **23**, 4235-4238



24e

To a stirred solution of $LiAlH_4$ (1.3 g, 34.2 mmol, 2 equiv) in dry THF (35 mL, 1 M) under argon atmosphere was dropwise added a solution of **24d** (5.548 g, 17.1 mmol, 1 equiv) in dry THF (15 mL, 1.25 M) via cannula at 0°C. The green-grey solution was then stirred 4 h at room temperature. After total completion, monitored by TLC, water (4 mL) was added dropwise at 0°C, followed by NaOH 15% (4 mL) and water (12 mL). The white precipitate was filtered through a Celite® pad and washed with ethyl acetate (60 mL). The organic layer was washed by water (40 mL), brine (40 mL), dried over $MgSO_4$ and concentrated under pressure affording crude **24e** which was directly used without further purification.

(3-(5-(but-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-5-yl)prop-1-yn-1-yl)trimethylsilane **24f**



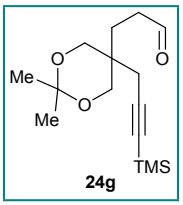
24f

To a solution of **24d** (4.111 g, 17.1 mmol, 1 equiv) in 85 mL of dichloromethane, were successively added 2,2-dimethoxypropane (10.4 mL, 85 mmol, 5 equiv) and pyridinium *p*-toluenesulfonate (430 mg, 1.71 mmol, 0.2 equiv). The solution was then stirred overnight at room temperature. After total completion, monitored by TLC, a satured $NaHCO_3$ solution (60 mL) was added and the aqueous layer was extracted by dichloromethane (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the crude by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 90/10) afforded pure **24f** (3.933 g, 14.0 mmol, 83 % over 3 steps) as a colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.80 (ddt, J = 17.1, 10.2, 6.6 Hz, 1H), 5.04 (ddt, J = 17.1, 1.8, 1.5, 1H), 4.99-4.93 (m, 1H), 3.71-3.61 (m, 4H), 2.45 (s, 2H), 2.06-1.98 (m, 2H), 1.48-1.40 (m, 8H), 0.14 (s, 9H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 138.7, 114.9, 114.8, 103.6, 98.2, 87.4, 67.2, 32.2, 27.2, 26.3, 23.7, 21.5, 0.2
HRMS (ESI): calculated for $[M+H]^+$ 281.1931 g.mol^{-1}, found 281.1930 g.mol^{-1}
FTIR (film cm^{-1}): ν 2992, 2957, 2860, 2174, 1642, 1453, 1370, 1249, 1196, 1155, 1120, 1072, 1038, 838, 759, 732, 698

General procedure for the ozonolysis reactions (GP7):
A stirred solution of the corresponding alkene (6.96 mmol, 1 equiv) in dichloromethane (14 mL, 0.5M) was bubbled with ozone at -78°C. After total completion, monitored by TLC, triphenylphosphine (2.74 g, 10.4 mmol, 1.5 equiv) was slowly added at -78°C. The orange mixture was allowed to warm to room temperature and stirred for 2 hours. Concentration under reduced pressure afforded the crude desired aldehyde with triphenylphosphine and triphenylphosphine oxide which was directly further used without purification.

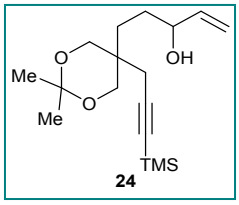
3-(2,2-dimethyl-5-(3-(trimethylsilyl)prop-2-yn-1-yl)-1,3-dioxan-5-yl)propanal **24g**



24g

Crude aldehyde **24g** was obtained from **24f** following **GP7** on 6.96 mmol scale (1.952 g).

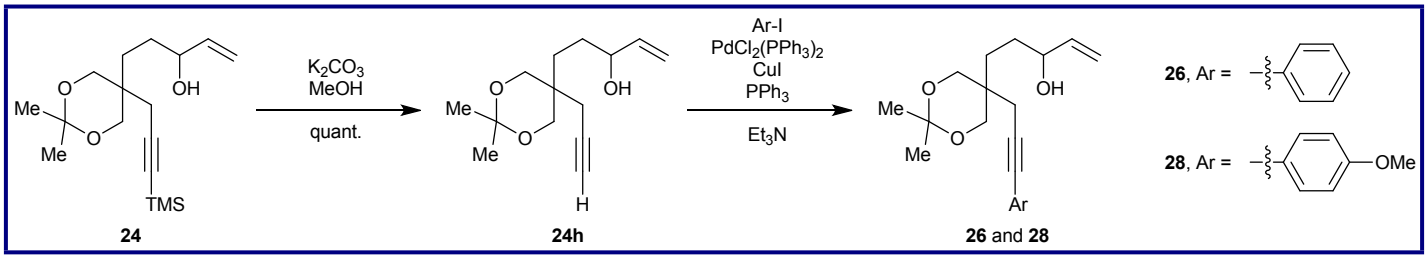
5-(2,2-dimethyl-5-(3-(trimethylsilyl)prop-2-yn-1-yl)-1,3-dioxan-5-yl)pent-1-en-3-ol **24**



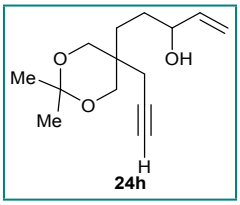
24

Compound **24** was obtained by addition of vinylmagnesium bromide on the aldehyde **24g** following **GP3** on 6.96 mmol scale (1.95 g). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 70/30) afforded pure **24** a colourless liquid (1.982 g, 6.38 mmol, 92 % over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.84 (ddd, J = 16.8, 10.4, 6.0 Hz, 1H), 5.23 (dd, J = 16.8, 1.2 Hz, 1H), 5.12 (dd, J = 10.4, 1.2 Hz, 1H), 4.05 (br s, 1H), 3.67-3.58 (m, 4H), 2.45 (d, J = 16.8 Hz, 1H), 2.38 (d, J = 16.8 Hz, 1H), 1.76 (br s, 1H), 1.52-1.45 (m, 3H), 1.43-1.33 (m, 7H), 0.12 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 115.3, 103.6, 98.3, 87.4, 73.6, 67.3, 67.2, 35.1, 28.3, 26.2, 23.6, 21.5, 0.2
HRMS (ESI): calculated for $[M+H]^+$ 311.2037 g.mol^{-1}, found 311.2044 g.mol^{-1}
FTIR (film cm^{-1}): ν 3447, 2992, 2921, 2861, 2173, 1644, 1453, 1426, 1371, 1249, 1195, 1155, 1121, 1078, 1038, 990, 922, 839, 759, 731, 698



5-(2,2-dimethyl-5-(prop-2-yn-1-yl)-1,3-dioxan-5-yl)pent-1-en-3-ol **24h**

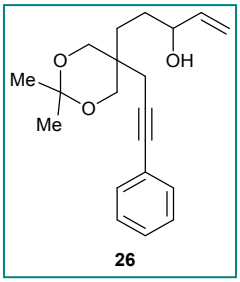


24h

Compound **24h** was obtained from **24** following **GP4** on 1.61 mmol scale (500 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 70/30) afforded quantitatively pure **24h** as a colourless oil (383 mg, 1.61 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.86 (ddd, J = 17.1, 10.5, 6.3 Hz, 1H), 5.24 (dd, J = 17.1, 1.2 Hz, 1H), 5.14 (dd, J = 10.5, 1.2 Hz, 1H), 4.07 (br s, 1H), 3.65 (s, 4H), 2.51-2.38 (m, 2H), 2.00 (t, J = 2.7 Hz, 1H), 1.53-1.40 (m, 10H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 115.4, 98.3, 80.9, 73.6, 71.0, 67.3, 67.2, 35.0, 29.9, 28.3, 26.8, 22.2, 21.0

5-(2,2-dimethyl-5-(3-phenylprop-2-yn-1-yl)-1,3-dioxan-5-yl)pent-1-en-3-ol **26**

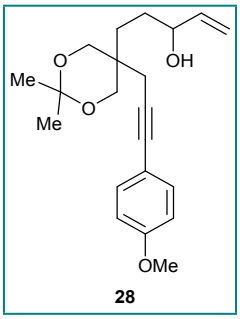


26

Compound **26** was obtained by coupling reaction between **24h** and iodobenzene following **GP5** on 0.5 mmol scale (120 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 70/30) afforded pure **26** as a yellow oil (137 mg, 0.44 mmol, 88 % over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.34 (m, 2H), 7.26-7.23 (m, 3H), 5.84 (ddd, J = 16.8, 10.4, 6.4 Hz, 1H), 5.21 (dd, J = 16.8, 1.2 Hz, 1H), 5.09 (dd, J = 10.4, 1.2 Hz, 1H), 4.06 (br s, 1H), 3.72-3.62 (m, 4H), 2.65 (d, J = 17.2 Hz, 1H), 2.59 (d, J = 17.2 Hz, 1H), 1.74 (br s, 1H), 1.56-1.48 (m, 3H), 1.47-1.37 (m, 7H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 131.7, 128.3, 127.8, 123.8, 115.4, 98.3, 86.5, 83.1, 73.6, 67.4, 67.3, 35.5, 30.0, 28.5, 26.6, 23.2, 21.2
HRMS (ESI): calculated for $[M+H]^+$ 315.1955 g.mol^{-1}, found 315.1955 g.mol^{-1}, calculated for $[M+Na]^+$ 337.1774 g.mol^{-1}, found 337.1773 g.mol^{-1}
FTIR (film cm^{-1}): ν 3434, 2991, 2938, 2862, 1598, 1490, 1452, 1442, 1371, 1253, 1195, 1121, 1076, 1043, 990, 921, 828, 755, 731, 690

5-(5-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-2,2-dimethyl-1,3-dioxan-5-yl)pent-1-en-3-ol **28**



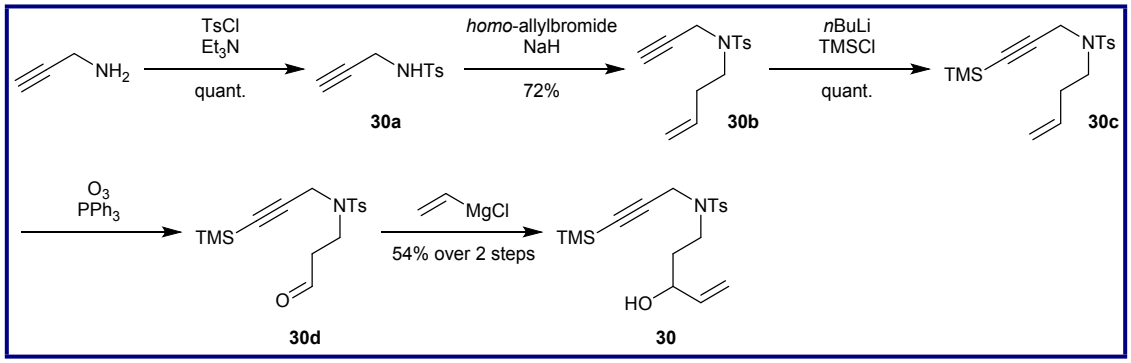
28

Compound **28** was obtained by coupling reaction between **24h** and 1-iodo-4-methoxybenzene following **GP5** on 0.5 mmol scale (120 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 60/40) afforded pure **28** as a yellow oil (144 mg, 0.42 mmol, 84 % over 2 steps).

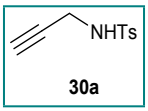
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.29 (m, 2H), 6.81-6.79 (m, 2H), 5.86 (ddd, J = 16.8, 10.4, 6.4 Hz, 1H), 5.24 (dd, J = 16.8, 1.2 Hz, 1H), 5.12 (dd, J = 10.4, 1.2 Hz, 1H), 4.08 (br s, 1H), 3.79 (s, 3H), 3.74-3.65 (m, 4H), 2.64 (d, J = 8.8 Hz, 1H), 2.59 (d, J = 8.8 Hz, 1H), 1.76 (br s, 1H), 1.59-1.50 (m, 3H), 1.49-1.39 (m, 7H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 140.9, 133.0, 116.0, 115.3, 113.9, 98.3, 84.8, 82.9, 73.6, 67.4, 67.3, 55.4, 35.5, 30.1, 28.5, 26.5, 23.2, 21.3
HRMS (ESI): calculated for calculated for $[M+H]^+$ 345.1988 g.mol^{-1}, found 345.2059 g.mol^{-1}, calculated for $[M+Na]^+$ 367.1880 g.mol^{-1}, found 367.1878 g.mol^{-1}
FTIR (film cm^{-1}): ν 3452, 2991, 2937, 2862, 1606, 1508, 1453, 1372, 1287, 1244, 1195, 1172, 1076, 1030, 991, 924, 828, 750, 687, 666

d. Azepane type precursors



4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **30a**

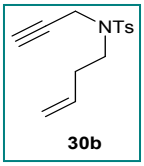


To a stirred solution of commercially available propargylamine (3.84 mL, 60 mmol, 1.2 equiv) in dry dichloromethane (50 mL, 1.2 M) under argon atmosphere was added triethylamine (9.5 mL, 70 mmol, 1.4 equiv), followed by tosyl chloride (9.53 g, 50 mmol, 1 equiv) portionwise at 0°C. After stirring overnight at room temperature, water (50 mL) was added. The aqueous layer was extracted by dichloromethane (2 × 50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure affording quantitatively pure **30a** (10.463 g, 50 mmol) as a white solid which was used without further purification.

Spectroscopic data were in accordance with those reported in literature[9].

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 4.41 (s, 1H), 3.82 (d, J = 2.7 Hz, 2H), 2.43 (s, 3H), 2.10 (t, J = 2.7 Hz, 1H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 143.9, 136.5, 129.8, 127.5, 78.1, 73.1, 32.9, 21.7

N-(but-3-en-1-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **30b**



To a stirred solution of sodium hydride (1.05 g, 26.3 mmol, 60% in mineral oil, 1.1 equiv) in dry DMF (26 mL, 1 M) under argon atmosphere was added dropwise a solution of **30a** (5 g, 23.9 mmol, 1 equiv) in dry DMF (5 mL) via cannula at 0°C. After stirring 30 minutes at 0°C, *homo*-allyl bromide (2.55 mL, 25.1 mmol, 1.05 equiv) was added dropwise. The orange-brown solution was then stirred overnight at

[9] N. Cabrera-Lobera, M.T. Quirós, W.W. Brennessel, M.L. Neidig, E. Buñuel, D.J. Cárdenas, *Org. Lett.,* 2019, 21, **16**, 6552-6556

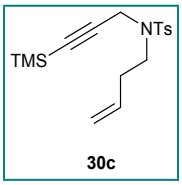
room temperature. After total completion, monitored by TLC, a satured NH_4Cl solution (50 mL) was slowly added. The aqueous layer was extracted by diethylether (2 × 45 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 75/25) afforded pure **30b** (4.530 g, 17.2 mmol, 72 %) as a colourless liquid.

Spectroscopic data were in accordance with those reported in literature[10].

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 – 7.63 (m, 2H), 7.33 – 7.26 (m, 2H), 5.77 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.19 – 4.95 (m, 2H), 4.14 (d, J = 2.5 Hz, 2H), 3.35 – 3.12 (m, 2H), 2.42 (s, 3H), 2.40 – 2.25 (m, 2H), 2.03 (t, J = 2.5 Hz, 1H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 143.6, 136.0, 134.6, 129.6, 127.8, 117.4, 76.7, 73.9, 45.8, 36.5, 32.3, 21.7

General procedure for the silylation of a terminal alkyne (GP8):
To a stirred solution of the corresponding terminal alkyne (17 mmol, 1 equiv) in dry THF (35 mL, 0.5 M) under argon atmosphere was added dropwise a *n*butyllithium solution (18.7 mmol, 1.1 equiv) at -78°C. Stirring was kept at this temperature for 30 minutes before the dropwise addition of freshly distilled trimethylsilyl chloride (2.4 mL, 18.7 mmol, 1.1 equiv). Stirring was kept further 30 minutes at -78°C before slow addition of a satured NH_4Cl solution (30 mL). The aqueous layer was extracted by ethyl acetate (2 × 20 mL). The combined organic layers were washed with a satured $NaHCO_3$ solution (30 mL), dried over $MgSO_4$, and concentrated under reduced pressure.

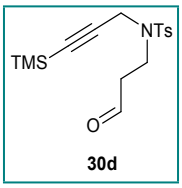
N-(but-3-en-1-yl)-4-methyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)benzenesulfonamide **30c**



30c

Crude compound **30c** was obtained from **30b** following **GP8** on 17 mmol scale (4.477 g) and was directly used without purification.

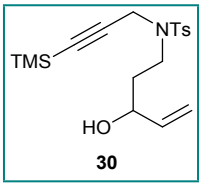
4-methyl-*N*-(3-oxopropyl)-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)benzenesulfonamide **30d**



30d

Crude aldehyde **30d** was obtained from **30c** following **GP7** on 8.94 mmol scale (3 g).

N-(3-hydroxypent-4-en-1-yl)-4-methyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)benzenesulfonamide **30**

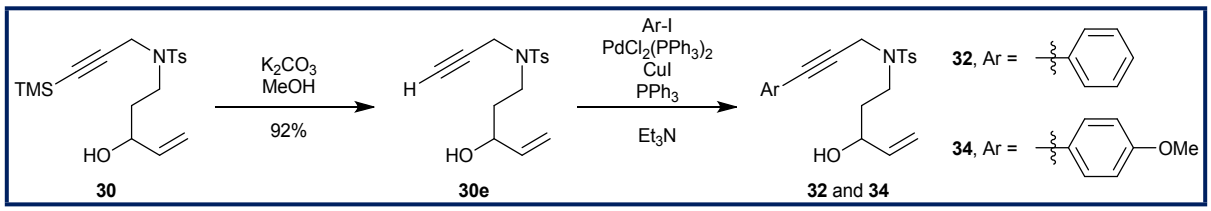


30

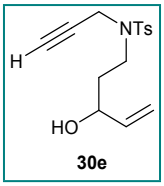
[10] T. Heesgaard Jepsen, E. Glibstrup, F. Crestey, A. A. Jensen, J. Langgaard Kristensen, *Beilstein J. Org. Chem.,* 2017, **13**, 988-994

Compound **30** was obtained by addition of vinylmagnesium bromide on the crude aldehyde **30d** following **GP3** on 8.94 mmol scale (1.95 g). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 80/20) afforded pure **30** as a white solid (1.765 g, 4.83 mmol, 54 % over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.71 (m, 2H), 7.32 – 7.27 (m, 2H), 5.90 (ddd, J = 17.2, 10.5, 5.7 Hz, 1H), 5.29 (dt, J = 17.3, 1.5 Hz, 1H), 5.13 (dt, J = 10.5, 1.4 Hz, 1H), 4.34 – 4.28 (m, 1H), 4.25 (d, J = 18.7 Hz, 1H), 4.05 (d, J = 18.7 Hz, 1H), 3.46 (dddd, J = 13.9, 8.9, 6.1, 1.0 Hz, 1H), 3.21 (ddd, J = 14.0, 6.6, 4.5 Hz, 1H), 2.45 (d, J = 4.6 Hz, 1H), 2.41 (s, 3H), 1.84 (dddd, J = 14.1, 8.9, 6.6, 3.9 Hz, 1H), 1.72 – 1.61 (m, 1H), 0.00 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 140.3, 135.7, 129.7, 127.9, 114.9, 98.0, 91.2, 69.4, 43.0, 37.7, 34.7, 21.7, -0.3
HRMS (ESI): calculated for $[M+H]^+$ 366.1554 g.mol^{-1}, found 366.1550 g.mol^{-1}, calculated for $[M+Na]^+$ 388.1373 g.mol^{-1}, found 388.1380 g.mol^{-1}, calculated for $[M+K]^+$ 404.1112 g.mol^{-1}, found 404.1110 g.mol^{-1}
FTIR (film cm^{-1}): ν 3532, 2958, 2924, 2177, 1598, 1495, 1426, 1345, 1249, 1158, 1119, 1090, 990, 918, 840, 813, 759, 735, 662
Mp 55°C



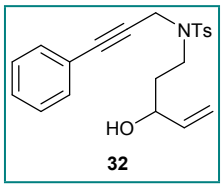
N-(3-hydroxypent-4-en-1-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **30e**



Compound **30e** was obtained from **30** following **GP4** on 4.1 mmol scale (1.5 g). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 60/40) afforded pure **30e** as a very viscous orange oil (1.109 mg, 3.77 mmol, 92 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 – 7.72 (m, 2H), 7.32 – 7.28 (m, 2H), 5.90 (ddd, J = 17.1, 10.5, 5.7 Hz, 1H), 5.32 – 5.25 (m, 1H), 5.15 – 5.12 (m, 1H), 4.34 – 4.28 (m, 1H), 4.24 (dd, J = 18.4, 2.6 Hz, 1H), 4.06 (dd, J = 18.4, 2.6 Hz, 1H), 3.52 – 3.42 (m, 1H), 3.22 (ddd, J = 14.1, 6.8, 4.5 Hz, 1H), 2.42 (s, 3H), 2.35 (br s, 1H), 2.05 (t, J = 2.6 Hz, 1H), 1.90 – 1.79 (m, 1H), 1.67 (dddd, J = 13.9, 9.1, 6.4, 4.5 Hz, 1H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 143.8, 140.3, 135.7, 129.7, 127.8, 115.0, 76.8, 74.0, 69.5, 43.2, 36.8, 34.8, 21.7
HRMS (ESI): calculated for $[M+H]^+$ 294.1158 g.mol^{-1}, found 294.1162 g.mol^{-1}, calculated for $[M+Na]^+$ 316.0978 g.mol^{-1}, found 316.0981 g.mol^{-1}, calculated for $[M+K]^+$ 332.0717 g.mol^{-1}, found 332.0711 g.mol^{-1}
FTIR (film cm^{-1}): ν 3525, 3286, 2926, 1734, 1598, 1495, 1429, 1329, 1306, 1289, 1245, 1185, 1155, 1120, 1090, 1018, 992, 924, 883, 814, 742, 704, 657

N-(3-hydroxypent-4-en-1-yl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide **32**

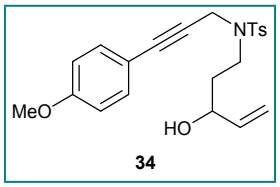


32

Compound **32** was obtained by coupling reaction between **30e** and iodobenzene following **GP5** on 1.87 mmol scale (550 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 70/30) afforded pure **32** as a bright yellow and very viscous oil (465 mg, 1.25 mmol, 67 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.76 (m, 2H), 7.29 – 7.21 (m, 5H), 7.11 – 7.04 (m, 2H), 5.92 (ddd, J = 17.2, 10.5, 5.7 Hz, 1H), 5.30 (dt, J = 17.2, 1.5 Hz, 1H), 5.14 (dt, J = 10.5, 1.4 Hz, 1H), 4.47 (d, J = 18.6 Hz, 1H), 4.39 – 4.32 (m, 1H), 4.26 (d, J = 18.6 Hz, 1H), 3.54 (dddd, J = 14.0, 8.9, 6.2, 1.0 Hz, 1H), 3.29 (ddd, J = 13.9, 6.6, 4.6 Hz, 1H), 2.45 (d, J = 4.5 Hz, 1H), 2.34 (s, 3H), 1.93 – 1.84 (m, 1H), 1.72 (dddd, J = 14.0, 9.1, 6.2, 4.6 Hz, 1H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 140.3, 135.8, 131.6, 129.7, 128.6, 128.3, 127.9, 122.2, 115.0, 85.9, 81.9, 69.5, 43.3, 37.6, 34.8, 21.7
HRMS (ESI): calculated for $[M+H]^+$ 370.1471 g.mol^{-1}, found 370.1465 g.mol^{-1}, calculated for $[M+Na]^+$ 392.1291 g.mol^{-1}, found 392.1295 g.mol^{-1}, calculated for $[M+K]^+$ 408.1030 g.mol^{-1}, found 408.1026 g.mol^{-1}
FTIR (film cm^{-1}): ν 3525, 2924, 1598, 1490, 1442, 1343, 1329, 1305, 1287, 1155, 1118, 1089, 1069, 1028, 1018, 991, 881, 813, 756, 713, 690, 656

N-(3-hydroxypent-4-en-1-yl)-*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide **34**

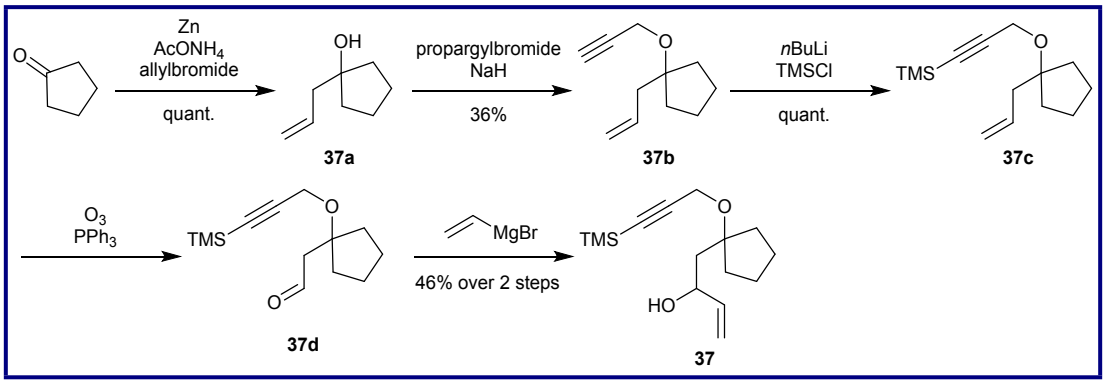


34

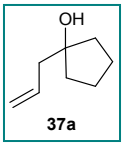
Compound **34** was obtained by coupling reaction between **30e** and 1-iodo-4-methoxybenzene following **GP5** on 1.87 mmol scale (550 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 70/30) afforded pure **34** as a yellow oil (229 mg, 0.58 mmol, 31 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.69 (m, 2H), 7.26 – 7.24 (m, 2H), 7.07 – 6.92 (m, 2H), 6.79 – 6.68 (m, 2H), 5.91 (ddd, J = 17.3, 10.5, 5.7 Hz, 1H), 5.29 (dt, J = 17.3, 1.5 Hz, 1H), 5.12 (dt, J = 10.5, 1.4 Hz, 1H), 4.44 (d, J = 18.6 Hz, 1H), 4.38 – 4.31 (m, 1H), 4.24 (d, J = 18.6 Hz, 1H), 3.78 (s, 3H), 3.57 – 3.47 (m, 1H), 3.28 (ddd, J = 14.0, 6.6, 4.6 Hz, 1H), 2.55 (d, J = 4.5 Hz, 1H), 2.35 (s, 3H), 1.88 (dddd, J = 14.2, 8.8, 6.6, 3.9 Hz, 1H), 1.71 (dddd, J = 13.9, 9.1, 6.2, 4.7 Hz, 1H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 143.6, 140.3, 135.7, 133.0, 129.6, 127.8, 114.8, 114.2, 113.8, 85.7, 80.3, 69.4, 55.3, 43.1, 37.6, 34.8, 21.5
HRMS (ESI): calculated for $[M+H]^+$ 400.1577 g.mol^{-1}, found 400.1568 g.mol^{-1}, calculated for $[M+Na]^+$ 422.1396 g.mol^{-1}, found 422.1390 g.mol^{-1}, calculated for $[M+K]^+$ 438.1136 g.mol^{-1}, found 438.1124 g.mol^{-1}
FTIR (film cm^{-1}): ν 3526, 2926, 2238, 1606, 1508, 1456, 1442, 1342, 1330, 1290, 1246, 1156, 1118, 1107, 1028, 991, 916, 882, 832, 813, 799, 771, 670

e. Oxepane type precursors



1-allylcyclopentanol **37a**

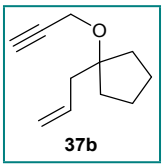


To a vigorously stirred solution of commercially available cyclopentanone (2.66 mL, 30 mmol, 1 equiv) in THF (120 mL, 0.25 M) were successively added at 0°C zinc dust (2.95 g, 45 mmol, 1.5 equiv), ammonium acetate (3.70 g, 45 mmol, 1.5 equiv) and allyl bromide (3.9 mL, 45 mmol, 1.5 equiv). The dark-grey heterogeneous mixture was stirred 1 hour at 0°C before slow addition of a satured $NaHCO_3$ solution (100 mL) and stirred further 20 minutes. The white precipitate was filtered through a Celite® pad and washed with ethyl acetate (30 mL). The aqueous layer was extracted by ethyl acetate (3 × 40 mL) The combined organic layers were washed with brine (40 mL), dried over $MgSO_4$ and concentrated under pressure affording quantitatively pure **37a** as a colourless liquid which was used without further purification.

Spectroscopic data were in accordance with those reported in literature[11].

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.95 (ddt, J = 18.0, 9.3, 7.5 Hz, 1H), 5.23-5.21 (m, 1H), 5.19-5.16 (m, 1H), 2.39 (d, J = 7.5 Hz, 2H), 1.90-1.81 (m, 2H), 1.74-1.61 (m, 6H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 134.7, 118.7, 81.4, 46.0, 39.5, 24.0

1-allyl-1-(prop-2-yn-1-yloxy)cyclopentane **37b**

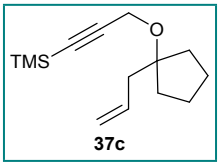


To a stirred solution of sodium hydride (0.96 g, 24 mmol, 60% in mineral oil, 1.6 equiv) in dry THF (50 mL, 0.5 M) under argon atmosphere was added dropwise a solution of **37a** (1.89 g, 15 mmol, 1 equiv) in 5 mL of THF at 0°C via cannula. After stirring 30 minutes at room temperature, propargyl bromide (2 mL, 18 mmol, 80% in toluene, 1.2 equiv) was added dropwise and the mixture was stirred overnight at room temperature. After total completion, monitored by TLC, water (20 mL) was slowly added. The aqueous layer was extracted by ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$ and concentrated under pressure. Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 8/2) afforded pure **37b** (877 mg, 5.4 mmol, 36 %) as a bright yellow oil.

[11] N.A. Weires, Y. Slutskyy, L.E. Overman, *Angew. Chem. Int. Ed.,* 2019, **58**, 8561-8565

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.93 (ddt, J = 17.7, 9.7, 7.0 Hz, 1H), 5.17-5.15 (m, 1H), 5.11 (br s, 1H), 4.11 (d, J = 2.6 Hz, 2H), 2.43 (m, 3H), 1.92-1.78 (m, 4H), 1.66-1.53 (m, 4H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 134.6, 117.4, 88.0, 81.4, 73.2, 50.8, 40.9, 36.1, 23.9
HRMS (ESI): compound not detected
FTIR (film cm^{-1}): ν 3293, 2924, 2854, 2115, 1959, 1737, 1456, 1258, 1160, 1070, 751

(3-((1-allylcyclopentyl)oxy)prop-1-yn-1-yl)trimethylsilane **37c**

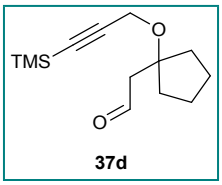


37c

Compound **37c** was obtained from **37b** following **GP8** on 5.23 mmol scale (860 mg). Pure **37c** was quantitatively obtained after concentration under reduced pressure (1.236 g, 5.23 mmol) as an orange-red oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.88 (ddt, J = 17.7, 9.7, 7.0 Hz, 1H), 5.09-5.04 (m, 2H), 4.07 (s, 2H), 2.36 (d, J = 7.0 Hz, 2H), 1.87-1.72 (m, 4H), 1.62-1.46 (m, 4H), 0.16 (s, 9H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 134.8, 117.3, 103.5, 89.7, 88.0, 51.6, 40.9, 36.1, 23.9, 0.0
FTIR (film cm^{-1}): ν 2958, 2175, 1640, 1438, 1356, 1334, 1250, 1064, 996, 913, 841, 760, 699

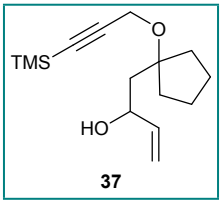
2-(1-((3-(trimethylsilyl)prop-2-yn-1-yl)oxy)cyclopentyl)acetaldehyde **37d**



37d

Crude aldehyde **37d** was obtained from **37c** following **GP7** on 2.61 mmol scale (618 mg).

1-(1-((3-(trimethylsilyl)prop-2-yn-1-yl)oxy)cyclopentyl)but-3-en-2-ol **37**

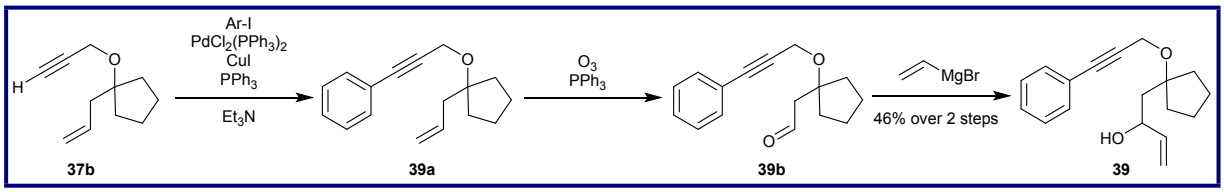


37

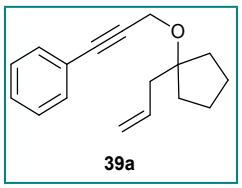
Compound **37** was obtained by addition of vinylmagnesium bromide on the crude aldehyde **37d** following **GP3** on 2.61 mmol scale (622 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 90/10) afforded pure **37** as a colourless liquid (317 mg, 1.20 mmol, 46 % over 3 steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.86 (ddd, J = 17.2, 10.6, 5.7 Hz, 1H), 5.27 (dd, J = 17.2, 1.3 Hz, 1H), 5.07 (dd, J = 10.6, 1.3 Hz, 1H), 4.46-4.42 (m, 1H), 4.11 (d, J = 15.7 Hz, 1H), 4.04 (d, J = 15.7 Hz, 1H), 3.39 (br s, 1H), 2.05-1.95 (m, 3H), 1.85-1.71 (m, 2H), 1.67-1.56 (m, 4H), 1.46-1.39 (m, 1H), 0.16 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 113.9, 102.4, 90.6, 89.2, 70.7, 51.5, 42.8, 36.2, 36.2, 23.7, 23.5, -0.2
HRMS (ESI): calculated for $[M+Na]^+$ 289.1594 $g.mol^{-1}$, found 2891598 $g.mol^{-1}$

FTIR (film cm^{-1}): *v* 3450, 2959, 2176, 1645, 1449, 1365, 1250, 1057, 992, 920, 840, 760, 699



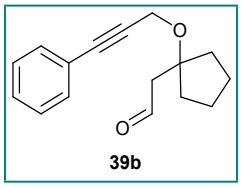
(3-((1-allylcyclopentyl)oxy)prop-1-yn-1-yl)benzene **39a**



Compound **39a** was obtained by coupling reaction between **37b** and iodobenzene following **GP5** on 2.14 mmol scale (352 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 95/5) afforded pure **39a** as a red oil (434 mg, 1.80 mmol, 84 %).

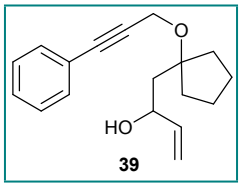
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.42 (m, 2H), 7.31-7.27 (m, 3H), 5.93 (ddt, *J* = 16.5, 11.0, 7.0 Hz, 1H), 5.15-5.11 (m, 1H), 5.09-5.07 (m, 2H), 4.30 (s, 2H), 2.45-2.42 (m, 2H), 1.93-1.78 (m, 2H), 1.63-1.52 (m, 5H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 134.8, 131.8, 128.3, 123.1, 117.4, 88.0, 86.9, 84.9, 51.6, 41.0, 36.2, 27.1, 23.9

2-(1-((3-phenylprop-2-yn-1-yl)oxy)cyclopentyl)acetaldehyde **39b**



Crude aldehyde **39b** was obtained from **39a** following **GP7** on 1.80 mmol scale (434 mg).

1-(1-((3-phenylprop-2-yn-1-yl)oxy)cyclopentyl)but-3-en-2-ol **39**



Compound **39** was obtained by addition of vinylmagnesium bromide on the crude aldehyde **39b** following **GP3** on 1.80 mmol scale (436 mg). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 90/10) afforded pure **39** as a yellow oil (165 mg, 0.61 mmol, 34 % over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.41 (m, 2H), 7.35-7.27 (m, 3H), 5.89 (ddd, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.28 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.08 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.51-4.47 (m, 1H), 4.35 (d, *J* =

15.4 Hz, 1H), 4.27 (d, *J* = 15.4 Hz, 1H), 3.47 (br s, 1H), 2.12-2.02 (m, 3H), 1.86-1.76 (m, 2H), 1.71-1.57 (m, 4H), 1.52-1.44 (m, 1H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 131.9, 128.5, 128.3, 128.3, 122.8, 114.1, 89.3, 86.0, 85.7, 70.9, 51.6, 42.9, 36.4, 36.4, 23.8, 23.7
HRMS (ESI): calculated for $[M+H]^+$ 271.1693 g.mol^{-1}, found 271.1690 g.mol^{-1}, calculated for $[M+Na]^+$ 293.1512 g.mol^{-1}, found 293.1509 g.mol^{-1}
FTIR (film cm^{-1}): *v* 3455, 2956, 2871, 1645, 1598, 1490, 1442, 1370, 1335, 1259, 1214, 1176, 1046, 993, 947, 844, 755, 690

5/ Cyclization reactions

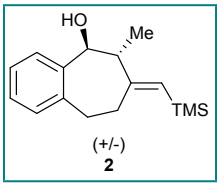
General procedure A (GP-A):
To a solution of the corresponding cyclization precursor (0.4 mmol, 1 equiv) under argon atmosphere in dry toluene (4 mL, 0.1 M), was added dropwise a solution of isopropylmagnesium chloride in diethyl ether (0.4 mmol, 1 equiv) at 0 °C. After stirring for 6 min, titanium isopropoxide (0.24 mL, 0.8 mmol, 2 equiv) was added dropwise and the light yellow mixture was stirred for 4 min at 0 °C. Isopropylmagnesium chloride in diethyl ether (1.6 mmol, 4 equiv) was added dropwise at -40 °C and the cooling bath was immediately removed before stirring the dark solution for 10 min at room temperature. After total completion, monitored by TLC, water (2 mL) and HCl (10 mL, 0.1 M) were successively added and the heterogeneous mixture was vigorously stirred until solubilisation of the grey salts. The aqueous layer was extracted by diethyl ether (3 × 15 mL), the combined organic layers were successively washed with a saturated $NaHCO_3$ solution (20 mL), brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the crude by flash chromatography over silica gel afforded pure desired cyclized product.

General procedure B (GP-B):
To a solution of the corresponding cyclization precursor (0.4 mmol, 1 equiv) under argon atmosphere in dry toluene (4 mL, 0.1 M), was added dropwise a solution of isopropylmagnesium chloride in diethyl ether (0.4 mmol, 1 equiv) at 0 °C. After stirring for 3 min, titanium isopropoxide (0.24 mL, 0.8 mmol, 2 equiv) was added dropwise and the light yellow mixture was stirred for 2 min at 0 °C. Isopropylmagnesium chloride in diethyl ether (1.6 mmol, 4 equiv) was added dropwise at -40 °C and the cooling bath was immediately removed before stirring the dark solution for 10 min at room temperature. After total completion, monitored by TLC, water (2 mL) and HCl (10 mL, 0.1 M) were successively added and the heterogeneous mixture was vigorously stirred until solubilisation of the grey salts. The aqueous layer was extracted by diethyl ether (3 × 15 mL), the combined organic layers were successively washed with a saturated $NaHCO_3$ solution (20 mL), brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the crude by flash chromatography over silica gel afforded pure desired cyclized product.

General procedure C (GP-C):
To a solution of the corresponding cyclization precursor (0.4 mmol, 1 equiv) under argon atmosphere in dry toluene (4 mL, 0.1 M), was added dropwise a solution of isopropylmagnesium chloride in diethyl ether (0.4 mmol, 1 equiv) at 0 °C. After stirring for 6 min, titanium isopropoxide (0.24 mL, 0.8 mmol, 2 equiv) was added dropwise and the light yellow mixture was stirred for 4 min at 0 °C. Isopropylmagnesium chloride in diethyl ether (1.6 mmol, 4 equiv) was added dropwise at -40 °C and the cooling bath was immediately removed before stirring the dark solution for 10 min at room temperature. After total completion, monitored by TLC, acetone (0.6 mL, 8 mmol, 20 equiv) was added dropwise at 0 °C. Stirring was kept for 10 minutes at 0 °C. After total completion, monitored by TLC, water (2 mL) and HCl (10 mL, 0.1 M) were successively added and the heterogeneous mixture was vigorously stirred until solubilisation of the grey salts. The aqueous layer was extracted by diethyl ether (3 × 15 mL), the combined organic layers were successively washed with a saturated $NaHCO_3$ solution (20 mL), brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the crude by flash chromatography over silica gel afforded pure desired cyclized product.

a. Tetrahydro-benzo[7]annulene type

(+/-)-(5*S*,6*R*,*E*)-6-methyl-7-((trimethylsilyl)methylene)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-ol **2**

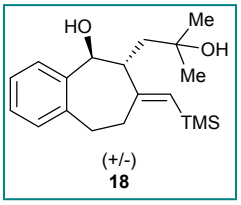


Cyclization was performed following **GP-A** starting from **1** (104 mg, 0.4 mmol). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 95/5) afforded **2** as a colourless oil (63 mg, 0.24 mmol, 60 %).

Cyclization was also performed following **GP-A** starting from **1** (388 mg, 1.5 mmol). Purification by flash chromatography over silica gel (cyclohexane/ethyl acetate 1/0 to 95/5) afforded **2** as a colourless oil (157 mg, 0.60 mmol, 40 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 - 7.44 (m, 1H), 7.26 - 7.22 (m, 1H), 7.21 - 7.17 (m, 1H), 7.12 - 7.10 (m, 1H), 5.42 (s, 1H), 4.87 (s, 1H), 2.87 (ddd, J = 14.2, 8.2, 1.9 Hz, 1H), 2.79 (dq, J = 6.9, 1.8 Hz, 1H), 2.69 - 2.61 (m, 1H), 2.46 (ddd, J = 13.5, 8.5, 1.8 Hz, 1H), 2.29 (ddd, J = 13.3, 10.9, 1.9 Hz, 1H), 1.99 (s, 1H), 0.86 (d, J = 6.9 Hz, 3H), 0.17 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 141.3, 139.5, 129.3, 127.2, 126.4, 126.4, 125.9, 75.8, 52.0, 35.5, 33.0, 14.7, 0.6
HRMS (ESI): calculated for $[M-H]^-$ 259.1524 g.mol^{-1}, found 259.1521 g.mol^{-1}, calculated for $[M+H]^+$ 261.1669 g.mol^{-1}, found 261.1677 g.mol^{-1}, calculated for $[M+Na]^+$ 283.1489 g.mol^{-1}, found 283.1498 g.mol^{-1}
FTIR (film cm^{-1}): ν 3392, 2953, 2926, 2853, 1608, 1486, 1454, 1355, 1295, 1247, 1038, 1025, 995, 892, 848, 754, 690, 659

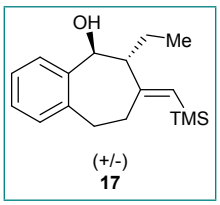
(+/-)-(5S,6R,E)-6-(2-hydroxy-2-methylpropyl)-7-((trimethylsilyl)methylene)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ol **18**



Cyclization was performed following **GP-C** starting from **1** (104 mg, 0.4 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 1/0 to 60/40) afforded **18** as a yellow oil (34 mg, 0.11 mmol, 27 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ *7.54* (dt, J = 7.7, 1.2 Hz, 1H), 7.26 (td, J = 7.5, 1.5 Hz, 1H), 7.17 (td, J = 7.3, 1.2 Hz, 1H), 7.09 (dd, J = 7.4, 1.5 Hz, 1H), 5.46 (s, 1H), 4.90 (d, J = 2.0 Hz, 1H), 3.05 (td, J = 6.3, 5.8, 2.0 Hz, 1H), 2.84 (ddd, J = 14.1, 6.7, 1.6 Hz, 1H), 2.67 – 2.58 (m, 1H), 2.54 (d, J = 13.3 Hz, 1H), 1.97 (ddd, J = 13.7, 12.5, 1.6 Hz, 1H), 1.45 – 1.36 (m, 1H), 1.19 (s, 3H), 1.15 (s, 3H), 1.03 (dd, J = 14.7, 5.6 Hz, 1H), 0.15 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8, 141.6, 138.8, 128.9, 126.7, 126.3, 126.3, 125.9, 74.5, 71.2, 54.9, 41.7, 35.6, 31.7, 31.3, 28.5, 0.5
HRMS (ESI): calculated for $[M+H]^+$ 319.2088 g.mol^{-1}, found 319.2083 g.mol^{-1}, calculated for $[M+Na]^+$ 341.1907 g.mol^{-1}, found 341.1908 g.mol^{-1}
FTIR (film cm^{-1}): ν 3312, 2953, 1604, 1454, 1364, 1275, 1247, 1153, 1125, 1040, 926, 836, 752, 706, 689, 663

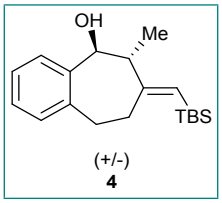
(+/-)-(5*S*,6*R*,*E*)-6-ethyl-7-((trimethylsilyl)methylene)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-ol **17**



Cyclization was performed following **GP-A** starting from **16** (109 mg, 0.4 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 1/0 to 90/10) afforded **17** as a colourless oil (22 mg, 0.08 mmol, 20 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 - 7.55 (m, 1H), 7.28 - 7.24 (m, 1H), 7.20 - 7.16 (m, 1H), 7.12 - 7.10 (m, 1H), 5.40 (s, 1H), 4.98 (s, 1H), 2.84 (ddd, J = 14.4, 7.2, 2.0 Hz, 1H), 2.65-2.59 (m, 1H), 2.58 - 2.49 (m, 2H), 2.07-2.00 (m, 2H), 1.45-1.34 (m, 1H), 0.78-0.71 (m, 4H), 0.86, 0.17 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 141.5, 139.0, 129.0, 127.8, 126.9, 126.3, 125.3, 74.5, 60.9, 35.3, 31.9, 20.2, 12.1, 0.6
HRMS (ESI): m/z calculated for $[M+H]^+$ 275.1826 g.mol^{-1}, found 275.1833 g.mol^{-1}, calculated for $[M+Na]^+$ 297.1645 g.mol^{-1}, found 297.1654 g.mol^{-1}
FTIR (film cm^{-1}): ν 3375, 2955, 2871, 1603, 1485, 1454, 1356, 1246, 1101, 1030, 904, 847, 834, 779, 752, 706, 689, 669

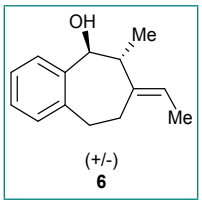
(+/-)-(5*S*,6*R*,*E*)-7-((tert-butyldimethylsilyl)methylene)-6-methyl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-ol **4**



Cyclization was performed following **GP-A** starting from **3** (120 mg, 0.4 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 1/0 to 90/10) afforded **4** as a colourless oil (67 mg, 0.22 mmol, 55 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.46 (m, 1H), 7.27-7.23 (m, 1H), 7.21-7.17 (m, 1H), 7.12-7.10 (m, 1H), 5.42 (s, 1H), 4.90 (s, 1H), 2.87-2.81 (m, 2H), 2.67-2.60 (m, 1H), 2.50 (ddd, J = 13.6, 8.0, 1.6 Hz, 1H), 2.27-2.21 (m, 1H), 2.03 (s, 1H), 0.93 (s, 9H), 0.83 (d, J = 7.2 Hz, 3H), 0.15 (s, 3H), 0.14 (s, 3H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 141.3, 139.4, 129.2, 127.1, 126.3, 126.1, 123.0, 75.5, 52.7, 35.3, 32.7, 26.7, 17.1, 14.6, -3.6, -3.6
HRMS (ESI): calculated for $[M+H]^+$ 303.2139 g.mol^{-1}, found 303.2141 g.mol^{-1}, calculated for $[M+Na]^+$ 325.1958 g.mol^{-1}, found 325.1959 g.mol^{-1}
FTIR (film cm^{-1}): ν 3369, 2952, 2926, 2854, 1605, 1470, 1462, 1360, 1248, 1038, 1024, 1007, 995, 835, 824, 809, 779, 771, 753, 707, 670

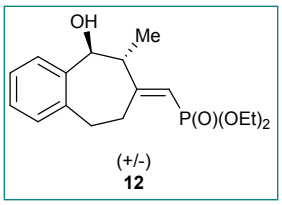
(+/-)-(5*S*,6*R*,*E*)-7-ethylidene-6-methyl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-ol **6**



Cyclization was performed following **GP-A** starting from **5** (80 mg, 0.4 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 1/0 to 90/10) afforded **6** as a colourless oil (38 mg, 0.19 mmol, 47 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 7.5 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.18 (td, 1H), 7.12 (dd, J = 7.3 Hz, 1H), 5.46 (q, J = 6.6 Hz, 1H), 4.88 (d, J = 1.9 Hz, 1H), 2.82 (ddd, J = 14.2, 7.9, 1.8 Hz, 1H), 2.73 (qd, J = 7.1, 1.9 Hz, 1H), 2.62 (ddd, J = 13.9, 11.3, 1.7 Hz, 1H), 2.53 (ddd, J = 13.9, 7.9, 1.7 Hz, 1H), 2.11 – 2.01 (m, 2H), 1.69 (d, J = 6.6 Hz, 3H), 0.81 (d, J = 7.1 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 141.5, 139.8, 129.3, 127.0, 126.2, 126.2, 120.0, 76.1, 49.3, 35.1, 26.3, 14.3, 12.9
HRMS (ESI): calculated for $[M+Na]^+$ 225.1250 g.mol^{-1}, found 225.1255 g.mol^{-1}
FTIR (film cm^{-1}): ν 3374, 1962, 2928, 2857, 1485, 1453, 1372, 1024, 994, 829, 775, 753, 661

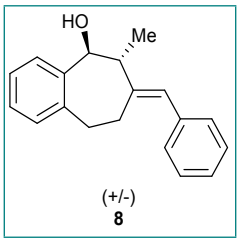
(+/-)-diethyl ((E)-((5S,6R)-5-hydroxy-6-methyl-8,9-dihydro-5H-benzo[7]annulen-7(6H)-ylidene)methyl)phosphonate **12**



Cyclization was performed following **GP-A** starting from **11** (129 mg, 0.4 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 50/50 to 5/95) afforded **12** as a colourless oil (40 mg, 0.12 mmol, 30 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (dt, J = 7.5, 1.1 Hz, 1H), 7.23 (td, J = 7.5, 1.5 Hz, 1H), 7.16 (td, J = 7.4, 1.5 Hz, 1H), 7.09 (dd, J = 7.4, 1.5 Hz, 1H), 5.53 (d, J = 19.1 Hz, 1H), 4.92 (s, 1H), 4.20 – 3.87 (m, 4H), 3.23 (s, 1H), 3.16 (dd, J = 13.7, 7.7 Hz, 1H), 2.97 – 2.79 (m, 2H), 2.65 (ddd, J = 14.2, 11.6, 1.7 Hz, 1H), 2.30 (ddt, J = 14.0, 11.6, 2.4 Hz, 1H), 1.39 – 1.19 (m, 6H), 0.81 (d, J = 7.0 Hz, 3H)
^{31}P NMR (400 MHz, $CDCl_3$): δ 17.90 (s)
^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6 (d, J = 6.6 Hz), 140.7, 138.8, 129.1, 127.2, 126.4, 126.2, 112.8 (d, J = 186.7 Hz), 74.0, 61.6 (d, J = 5.9 Hz), 61.5 (d, J = 5.6 Hz), 51.0 (d, J = 22.3 Hz), 33.6 (d, J = 2.4 Hz), 29.7 (d, J = 7.6 Hz), 16.5 (d, J = 3.0 Hz), 16.4 (d, J = 2.9 Hz), 14.1
HRMS (ESI): calculated for $[M+H]^+$ 325.1563 g.mol^{-1}, found 325.1567 g.mol^{-1}, calculated for $[M+Na]^+$ 347.1383 g.mol^{-1}, found 347.1390 g.mol^{-1}, calculated for $[M+K]^+$ 363.1122 g.mol^{-1}, found 363.1132 g.mol^{-1}
FTIR (film cm^{-1}): ν 3369, 2978, 2930, 1616, 1455, 1392, 1368, 1217, 1163, 1097, 1048, 1020, 955, 834, 810, 793, 779, 755, 736, 672

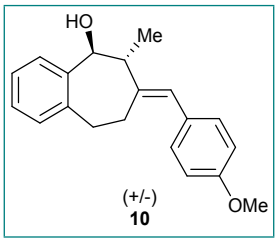
(+/-)-(5(5*S*,6*R*,*E*)-7-benzylidene-6-methyl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-ol **8**



Cyclization was performed following **GP-A** starting from **7** (105 mg, 0.4 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 1/0 to 80/20) afforded **8** as a colourless oil (64 mg, 0.24 mmol, 60 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.29 - 7.21 (m, 5H), 7.13 (d, J = 7.3 Hz, 1H), 6.54 (s, 1H), 5.08 (s, 1H), 2.94 – 2.84 (m, 2H), 2.85 – 2.77 (m, 1H), 2.73 (t, J = 12.6 Hz, 1H), 2.17 – 2.10 (m, 2H), 0.91 (d, J = 7.0 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 141.2, 139.4, 138.0, 129.3, 129.2, 128.2, 127.1, 126.4, 126.3, 126.2, 125.9, 75.5, 49.7, 35.1, 26.8, 14.1
HRMS (ESI): calculated for $[M+Na]^+$ 287.1406 g.mol^{-1}, found 287.1414 g.mol^{-1}
FTIR (film cm^{-1}): ν 3390, 3057, 3021, 2965, 2930, 1488, 1453, 1275, 1262, 1180, 1102, 1038, 1024, 997, 917, 892, 855, 753, 740, 699, 666

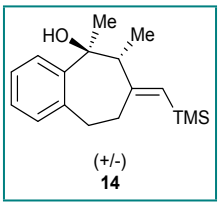
(+/-)-(5*S*,6*R*,*E*)-7-(4-methoxybenzylidene)-6-methyl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-ol **10**



Cyclization was performed following **GP-A** starting from **9** (100 mg, 0.34 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 1/0 to 80/20) afforded **10** as a yellow oil (39 mg, 0.16 mmol, 39 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 7.6 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.23 - 7.16 (m, 3H), 7.16 – 7.12 (m, 1H), 6.92 – 6.89 (m, 2H), 6.47 (s, 1H), 5.06 (s, 1H), 3.84 (s, 3H), 2.93 – 2.84 (m, 2H), 2.83 – 2.76 (m, 1H), 2.72 (t, J = 12.7 Hz, 1H), 2.17 – 2.10 (m, 2H), 0.90 (d, J = 7.0 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 144.7, 141.2, 139.4, 130.4, 130.4, 129.2, 127.1, 126.3, 125.9, 125.7, 113.7, 75.6, 55.4, 49.7, 35.2, 26.8, 14.1
HRMS (ESI): calculated for $[M+H]^+$ 295.1693 g.mol^{-1}, found 295.1702 g.mol^{-1}
FTIR (film cm^{-1}): ν 3395, 2918, 2836, 1606, 1508, 1462, 1441, 1288, 1243, 1172, 1106, 1030, 989, 927, 831, 756

(+/-)-(5*S*,6*R*,*E*)-5,6-dimethyl-7-((trimethylsilyl)methylene)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-ol **14**

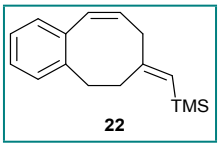


Cyclization was performed following **GP-A** starting from **13** (109 mg, 0.4 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 1/0 to 80/20) afforded **14** as a colourless oil (47 mg, 0.17 mmol, 43 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.71 (m, 1H), 7.27-7.23 (m, 1H), 7.17-7.14 (m, 1H), 7.09-7.07 (m, 1H), 5.39 (s, 1H), 2.98-2.90 (m, 1H), 2.79 (ddd, J = 14.4, 5.2, 2.8 Hz, 1H), 2.71 (q, J = 6.8 Hz, 1H), 2.59 (ddd, J = 13.2, 4.8 Hz, 2.4 Hz, 1H), 2.30 (dt, J = 13.2, 2.8 Hz, 1H), 1.86 (s, 1H), 1.53 (s, 3H), 0.87 (d, J = 6.8 Hz, 3H), 0.14 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 144.9, 137.6, 130.7, 127.0, 126.7, 126.7, 126.4, 77.06, 57.7, 36.4, 31.2, 28.6, 14.8, 0.6
HRMS (ESI): calculated for $[M-H]^-$ 273.1673 g.mol^{-1}, found 273.1680 g.mol^{-1}, calculated for $[M+H]^+$ 275.1826 g.mol^{-1}, found 275.1828 g.mol^{-1}, calculated for $[M+Na]^+$ 297.1645 g.mol^{-1}, found 297.1646 g.mol^{-1}
FTIR (film cm^{-1}): ν 3480, 2952, 1608, 1484, 1451, 1370, 1278, 1245, 1121, 1063, 1016, 995, 883, 844, 835, 759, 749, 715, 688

b. Protected alcohol

((E)-((Z)-5,6-dihydrobenzo[8]annulen-7(8H)-ylidene)methyl)trimethylsilane **22**

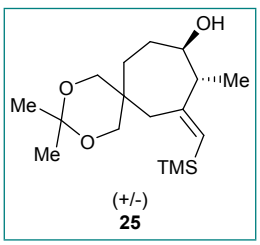


Cyclization was performed following **GP-A** starting from **21** (82 mg, 0.3 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 1/0 to 97/3) afforded **22** as a white solid (27 mg, 0.11 mmol, 37 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.48 (m, 1H), 7.23 – 7.07 (m, 3H), 6.77 (d, J = 15.3 Hz, 1H), 6.11 (dt, J = 15.3, 7.4 Hz, 1H), 5.45 (s, 1H), 3.06 (d, J = 7.4 Hz, 2H), 2.88 – 2.77 (m, 2H), 2.38 – 2.25 (m, 2H), 0.19 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 139.1, 135.3, 131.1, 130.2, 127.7, 127.5, 127.1, 126.6, 125.4, 45.9, 36.6, 34.2, 0.6
HRMS (ESI): compound not detected
FTIR (film cm^{-1}): ν 3019, 2952, 2925, 1608, 1482, 1451, 1246, 963, 834, 746, 688
Mp 62-64°C

c. Spiro-ketal type precursors

(+/-)-(9*R*,10*R*,*E*)-3,3,10-trimethyl-11-((trimethylsilyl)methylene)-2,4-dioxaspiro[5.6]dodecan-9-ol **25**

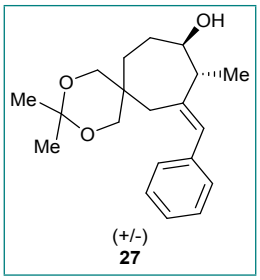


Cyclization was performed following **GP-B** starting from **24** (124 mg, 0.4 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 1/0 to 80/20) afforded **25** as a yellow oil (66 mg, 0.21 mmol, 53 %).

Cyclization was also performed following **GP-B** starting from **24** (310 mg, 1 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 1/0 to 60/40) afforded **25** as a yellow oil (150 mg, 0.48 mmol, 48 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.36 (s, 1H), 3.72 (ddd, J = 6.1, 4.0, 3.0 Hz, 1H), 3.65 (dd, J = 11.6, 1.1 Hz, 1H), 3.59 (dd, J = 11.6, 1.1 Hz, 1H), 3.58 (dd, J = 11.5, 1.1 Hz, 1H), 3.46 (dd, J = 11.5, 1.1 Hz, 1H), 2.48 (d, J = 14.4 Hz, 1H), 2.42 (qd, J = 7.2, 3.0 Hz, 1H), 2.04 (d, J = 14.4 Hz, 1H), 1.78 – 1.65 (m, 2H), 1.68 – 1.56 (m, 1H), 1.54 – 1.39 (m, 2H), 1.41 (s, 3H), 1.39 (s, 3H), 1.11 (d, J = 7.2 Hz, 3H), 0.13 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 128.3, 98.2, 71.7, 69.9, 69.7, 47.5, 41.6, 34.8, 29.9, 25.9, 24.1, 23.8, 17.4, 0.7
HRMS (ESI): calculated for $[M+H]^+$ 313.2193 g.mol^{-1}, found 313.2193 g.mol^{-1}, calculated for $[M+Na]^+$ 335.2013 g.mol^{-1}, found 335.2015 g.mol^{-1}
FTIR (film cm^{-1}): ν 3447, 2927, 2859, 1602, 1453, 1370, 1246, 1196, 1157, 1121, 1083, 1036, 832, 753, 732, 689

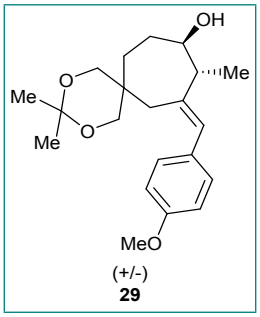
(+/-)-(9*R*,10*R*,*E*)-11-benzylidene-3,3,10-trimethyl-2,4-dioxaspiro[5.6]dodecan-9-ol **27**



Cyclization was performed following **GP-B** starting from **26** (94 mg, 0.3 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 1/0 to 90/10) afforded **27** as a colourless oil (39 mg, 0.12 mmol, 41 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.29 (m, 2H), 7.22-7.20 (m, 3H), 6.48 (s, 1H), 3.86 (dt, J = 6.8, 3.2 Hz, 1H), 3.40 (d, J = 11.6 Hz, 1H), 3.33 (d, J = 11.6 Hz, 1H), 3.29 (d, J = 11.6 Hz, 1H), 3.25 (d, J = 11.6 Hz, 1H), 2.60-2.55 (m, 2H), 1.99 (d, J = 14.4, 1H), 1.79-1.58 (m, 4H), 1.51 (m, 1H), 1.30 (s, 3H), 1.24 (s, 3H), 1.23 (d, J = 7.3 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8, 138.4, 129.1, 128.8, 128.4, 126.5, 97.9, 72.8, 69.6, 69.3, 47.4, 36.0, 34.4, 29.0, 25.8, 25.2, 22.3, 16.0
HRMS (ESI): calculated for $[M+H]^+$ 317.2111 g.mol^{-1}, found 317.2112 g.mol^{-1}, calculated for $[M+Na]^+$ 339.1931 g.mol^{-1}, found 339.1932 g.mol^{-1}
FTIR (film cm^{-1}): ν 3453, 2989, 2927, 2860, 1493, 1452, 1370, 1347, 1259, 1195, 1114, 1053, 1030, 990, 968, 933, 919, 878, 830, 732, 699

(+/-)-(9*R*,10*R*,*E*)-11-(4-methoxybenzylidene)-3,3,10-trimethyl-2,4-dioxaspiro[5.6]dodecan-9-ol **29**

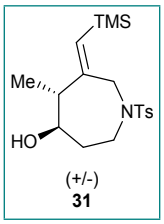


Cyclization was performed following **GP-B** starting from **28** (90 mg, 0.26 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 1/0 to 80/20) afforded **29** as a colourless oil (49 mg, 0.14 mmol, 54 %).
Only ^1H NMR are available due to the high unstability of the product and its rapid decomposition occurring even during neat at -20°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 – 7.11 (m, 2H), 6.89 – 6.80 (m, 2H), 6.40 (s, 1H), 3.85 (dt, J = 7.2, 3.6 Hz, 1H), 3.80 (s, 3H), 3.42 (d, J = 11.6 Hz, 1H), 3.36 (d, J = 11.6 Hz, 1H), 3.31 – 3.25 (m, 2H), 2.58 (d, J = 14.3 Hz, 1H), 2.56 – 2.49 (m, 1H), 1.97 (d, J = 14.3 Hz, 1H), 1.80 – 1.55 (m, 5H), 1.49 (ddd, J = 14.7, 8.3, 1.9 Hz, 1H), 1.32 (s, 3H), 1.28 (s, 3H), 1.21 (d, J = 7.1 Hz, 3H)
HRMS (ESI): calculated for $[M+H]^+$ 347.2217 g.mol^{-1}, found 347.2214 g.mol^{-1}
FTIR (film cm^{-1}): ν 3453, 2989, 2925, 2857, 1606, 1508, 1454, 1370, 1245, 1196, 1177, 1156, 1120, 1033, 991, 969, 933, 881, 832, 751, 732

d. Azepane type

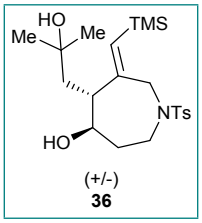
(+/-)-(4*R*,5*R*,*Z*)-5-methyl-1-tosyl-6-((trimethylsilyl)methylene)azepan-4-ol **31**



Cyclization was performed following **GP-A** starting from **30** (146 mg, 0.4 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 1/0 to 40/60) afforded **31** as a white solid (75 mg, 0.2 mmol, 51 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.64 (m, 2H), 7.35 – 7.30 (m, 2H), 5.55 (s, 1H), 4.11 (d, J = 13.7 Hz, 1H), 3.76 – 3.70 (m, 1H), 3.63 (d, J = 13.7 Hz, 1H), 3.42 – 3.35 (m, 1H), 2.91 (q, J = 7.1 Hz, 1H), 2.67 (ddd, J = 14.6, 10.8, 1.9 Hz, 1H), 2.43 (s, 3H), 1.92 (ddt, J = 14.4, 10.8, 3.4 Hz, 1H), 1.86 – 1.77 (m, 1H), 1.64 (bs, 1H), 1.18 (d, J = 7.1 Hz, 3H), -0.02 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 143.6, 135.5, 130.4, 129.9, 127.1, 71.0, 53.9, 43.9, 41.9, 38.0, 21.6, 16.7, 0.1
HRMS (ESI): calculated for $[M+H]^+$ 368.1710 g.mol^{-1}, found 368.1707 g.mol^{-1}, calculated for $[M+Na]^+$ 390.1530 g.mol^{-1}, found 390.1526 g.mol^{-1}
FTIR (film cm^{-1}): ν 3526, 2951, 2923, 1599, 1451, 1335, 1248, 1158, 1107, 1089, 1030, 935, 851, 835, 814, 757, 733, 713, 656
Mp 87°C

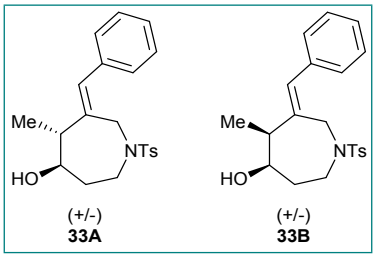
(+/-)-(4R,5R,Z)-5-(2-hydroxy-2-methylpropyl)-1-tosyl-6-((trimethylsilyl)methylene)azepan-4-ol **36**



Cyclization was performed following **GP-C** starting from **30** (73 mg, 0.2 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 50/50 to 0/1) afforded **36** as a colourless liquid (23 mg, 0.05 mmol, 27 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.62 (m, 2H), 7.36 – 7.29 (m, 2H), 5.62 (s, 1H), 4.07 (d, J = 13.7 Hz, 1H), 3.77 – 3.72 (m, 1H), 3.69 (d, J = 13.7 Hz, 1H), 3.28 (dt, J = 14.0, 4.6 Hz, 1H), 2.97 (td, J = 5.9, 3.2 Hz, 1H), 2.76 (dt, J = 20.2, 6.4 Hz, 1H), 2.43 (s, 3H), 2.00 (dd, J = 14.9, 5.9 Hz, 1H), 1.88 (td, J = 7.2, 3.8 Hz, 2H), 1.80 (dd, J = 14.9, 5.9 Hz, 1H), 1.68 (bs, 1H), 1.28 (s, 3H), 1.21 (s, 3H), -0.05 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 143.6, 135.2, 132.2, 129.9, 127.2, 73.9, 71.4, 52.7, 50.2, 42.7, 40.8, 36.5, 31.8, 28.4, 21.6, -0.1
HRMS (ESI): calculated for $[M+H]^+$ 426.2129 g.mol^{-1}, found 426.2116 g.mol^{-1}, calculated for $[M+Na]^+$ 448.1948 g.mol^{-1}, found 448.1941 g.mol^{-1}, calculated for $[M+K]^+$ 464.1688 g.mol^{-1}, found 464.1675 g.mol^{-1}
FTIR (film cm^{-1}): ν 3359, 2952, 1599, 1444, 1335, 1248, 1158, 1091, 1035, 914, 851, 835, 752, 736, 716, 660

(+/-)-(4*R*,5*R*,*Z*)-6-benzylidene-5-methyl-1-tosylazepan-4-ol **33A** and (+/-)-(4R,5S,Z)-6-benzylidene-5-methyl-1-tosylazepan-4-ol **33B**

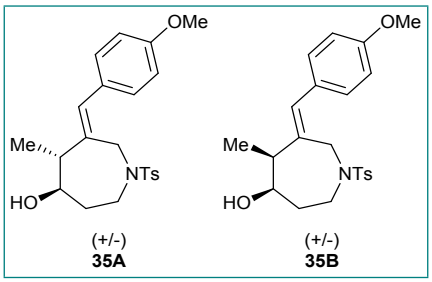


Cyclization was performed following **GP-A** starting from **32** (148 mg, 0.4 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 50/50 to 20/80) afforded a clean mixture of **33A** and **33B** (*syn*/*anti* 40/60) as a colourless oil (63 mg, 0.17 mmol, 42 %).

33A
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 – 7.59 (m, 2H), 7.33 – 7.17 (m, 5H), 7.10 – 7.03 (m, 2H), 6.56 (s, 1H), 4.25 – 4.21 (m, 1H), 4.00 (dd, J = 10.9, 1.4 Hz, 1H), 3.85 (s, 1H), 3.24 (ddd, J = 3.3, 3.3, 2.8 Hz, 1H), 3.04 – 2.93 (m, 1H) 2.86 (ddd, J = 14.5, 10.1, 2.0 Hz, 1H), 2.39 (s, 3H), 1.95 (dddd, J = 14.5, 10.1, 4.1, 2.8 Hz, 1H), 1.89 – 1.79 (m, 2H), 1.32 (d, J = 7.1 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 137.1, 136.3, 135.8, 131.0, 130.0, 128.9, 128.3, 127.1, 127.0, 72.1, 49.8, 43.1, 42.4, 37.1, 21.6, 16.0
HRMS (ESI): calculated for $[M+H]^+$ 372.1628 g.mol^{-1}, found 372.1629 g.mol^{-1}, calculated for $[M+Na]^+$ 394.1447 g.mol^{-1}, found 394.1451 g.mol^{-1}
FTIR (film cm^{-1}): ν 3526, 2923, 1598, 1493, 1445, 1329, 1305, 1289, 1184, 1154, 1090, 1030, 1018, 963, 923, 907, 885, 699, 657

33B
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 – 7.59 (m, 2H), 7.33 – 7.17 (m, 5H), 7.10 – 7.03 (m, 2H), 6.56 (s, 1H), 4.25 – 4.21 (m, 1H), 3.96 (dd, J = 10.6, 1.4 Hz, 1H), 3.76 – 3.67 (m, 1H), 3.27 (ddd, J = 6.4, 3.3, 3.3 Hz, 1H), 3.06 – 3.02 (m, 1H), 2.73 (m, 1H), 2.40 (s, 3H), 2.06 (dddd, J = 14.8, 10.0, 3.6, 2.7 Hz, 1H), 1.84 – 1.73 (m, 2H), 1.34 (d, J = 7.0 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 136.9, 136.3, 135.5, 131.6, 129.8, 128.9, 128.3, 127.1, 127.1, 73.3, 48.4, 47.8, 42.1, 35.4, 21.6, 16.3
HRMS (ESI): calculated for $[M+H]^+$ 372.1628 g.mol^{-1}, found 372.1629 g.mol^{-1}, calculated for $[M+Na]^+$ 394.1447 g.mol^{-1}, found 394.1451 g.mol^{-1}
FTIR (film cm^{-1}): ν 3526, 2923, 1598, 1493, 1445, 1329, 1305, 1289, 1184, 1154, 1090, 1030, 1018, 963, 923, 907, 885, 699, 657

(+/-)-(4*R*,5*R*,*Z*)-6-(4-methoxybenzylidene)-5-methyl-1-tosylazepan-4-ol **35A** and (+/-)-(4*R*,5*S*,*Z*)-6-(4-methoxybenzylidene)-5-methyl-1-tosylazepan-4-ol **35B**



Cyclization was performed following **GP-A** starting from **34** (160 mg, 0.4 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 1/0 to 50/50) afforded a clean mixture of **35A** and **35B** (*syn*/*anti* 31/69) as a yellow oil (23 mg, 0.06 mmol, 14 %).

35A

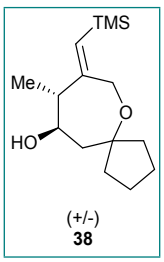
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 – 7.61 (m, 2H), 7.31 – 7.23 (m, 2H), 7.06 – 6.97 (m, 2H), 6.86 – 6.77 (m, 2H), 6.50 (s, 1H), 4.24 (d, J = 14.3 Hz, 1H), 3.98 (dd, J = 14.3, 1.4 Hz, 1H), 3.86 – 3.83 (m, 1H), 3.81 (s, 3H), 3.30 – 3.26 (m, 1H), 3.02 – 2.95 (m, 1H), 2.84 (dd, J = 10.3, 2.0 Hz, 1H), 2.41 (s, 3H), 2.00 – 1.87 (m, 1H), 1.87 – 1.80 (m, 1H), 1.68 (s, 1H), 1.31 (d, J = 7.2 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 143.4, 136.0, 135.5, 130.4, 130.2, 130.0, 128.8, 127.1, 113.8, 72.0, 55.4, 50.0, 43.0, 42.4, 37.2, 21.6, 16.7
HRMS (ESI): calculated for $[M+H]^+$ 402.1733 g.mol^{-1}, found 402.1731 g.mol^{-1}, calculated for $[M+Na]^+$ 424.1553 g.mol^{-1}, found 424.1548 g.mol^{-1}, calculated for $[M+K]^+$ 440.1292 g.mol^{-1}, found 440.1290 g.mol^{-1}
FTIR (film cm^{-1}): ν 3525, 2926, 1606, 1574, 1508, 1456, 1331, 1304, 1290, 1247, 1156, 1106, 1089, 1030, 964, 908, 887, 833, 813, 733, 703, 666, 657

35B

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 – 7.61 (m, 2H), 7.31 – 7.23 (m, 2H), 7.06 – 6.97 (m, 2H), 6.86 – 6.77 (m, 2H), 6.50 (s, 1H), 4.25 (d, J = 13.6 Hz, 1H), 3.94 (dd, J = 13.6, 1.1 Hz, 1H), 3.81 (s, 3H), 3.72 – 3.68 (m, 1H), 3.33 – 3.30 (m, 1H), 2.80 (dd, J = 10.3, 2.0 Hz, 1H), 2.76 – 2.64 (m, 1H), 2.42 (s, 3H), 2.09 – 2.00 (m, 1H), 1.80 – 1.72 (m, 1H), 1.68 (s, 1H), 1.33 (d, J = 7.2 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 143.4, 135.7, 135.1, 131.5, 130.2, 130.0, 128.8, 127.2, 113.8, 73.2, 55.45, 48.4, 48.1, 42.0, 35.3, 21.6, 15.9
HRMS (ESI): calculated for $[M+H]^+$ 402.1733 g.mol^{-1}, found 402.1731 g.mol^{-1}, calculated for $[M+Na]^+$ 424.1553 g.mol^{-1}, found 424.1548 g.mol^{-1}, calculated for $[M+K]^+$ 440.1292 g.mol^{-1}, found 440.1290 g.mol^{-1}
FTIR (film cm^{-1}): ν 3525, 2926, 1606, 1574, 1508, 1456, 1331, 1304, 1290, 1247, 1156, 1106, 1089, 1030, 964, 908, 887, 833, 813, 733, 703, 666, 657

e. Oxepane type

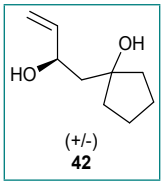
(+/-)-(9*R*,10*R*,*Z*)-9-methyl-8-((trimethylsilyl)methylene)-6-oxaspiro[4.6]undecan-10-ol **38**



Cyclization was performed following **GP-A** starting from **37** (106 mg, 0.4 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 1/0 to 80/20) afforded **38** as a yellow oil (46 mg, 0.17 mmol, 43 %).

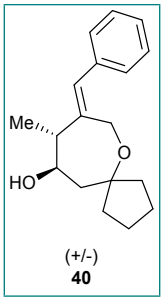
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.34 (d, J = 1.5 Hz 1H), 4.26 (dd, J = 15.7, 1.5 Hz, 1H), 4.16 (dd, J = 15.7, 1.5 Hz, 1H), 3.84 (br s, 1H), 2.92 (dq, J = 6.9, 3.2 Hz, 1H), 1.91-1.80 (m, 4H), 1.75-1.66 (m, 2H), 1.65-1.56 (m, 2H), 1.53 (br s, 1H), 1.49-1.37 (m, 2H), 1.14 (d, J = 6.9 Hz, 3H), 0.11 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 123.4, 85.7, 71.6, 66.8, 44.7, 44.6, 38.2, 38.2, 23.6, 23.5, 14.1, 0.0
HRMS (ESI): calculated for $[M+Na]^+$ 291.1751 g.mol^{-1}, found 291.1754 g.mol^{-1}
FTIR (film cm^{-1}): ν 3392, 2953, 2873, 1604, 1440, 1363, 1247, 1211, 1101, 1088, 1036, 987, 833, 765, 747, 730, 689

1-(2-hydroxybut-3-en-1-yl)cyclopentanol **42**



^{1}H NMR (300 MHz, $CDCl_3$): δ 5.88 (ddd, J = 17.2, 10.6, 5.9 Hz, 1H), 5.25 (dd, J = 17.2, 1.0, 1H), 5.08 (dd, J = 10.6, 1.0 Hz, 1H), 4.48 (dt, J = 7.9, 1.8 Hz, 1H), 3.34-3.19 (br m, 1H), 2.99-2.86 (br m, 1H), 1.95-1.77 (m, 4H), 1.73-1.53 (m, 6H)
^{13}C NMR (75 MHz, $CDCl_3$): δ 141.2, 114.3, 83.0, 72.2, 46.3, 41.9, 38.5, 23.8, 23.5
HRMS (ESI): calculated for $[M+H]^+$ 157.1223 g.mol^{-1}, found 157.1224 g.mol^{-1}, calculated for $[M+Na]^+$ 179.1048 g.mol^{-1}, found 179.1043 g.mol^{-1}
FTIR (film cm^{-1}): ν 3359, 2957, 2873, 1709, 1435, 1319, 1039, 993, 909, 854, 731

(+/-)-(9*R*,10*R*,*Z*)-8-benzylidene-9-methyl-6-oxaspiro[4.6]undecan-10-ol **40**



Cyclization was performed following **GP-A** starting from **39** (108 mg, 0.4 mmol). Purification by flash chromatography over silica gel (pentane/diethyl ether 1/0 to 60/40) afforded **40** as a yellow oil (30 mg, 0.11 mmol, 28 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.32 (m, 2H), 7.28 – 7.15 (m, 3H), 6.35 (s, 1H), 4.41 (d, J = 15.6 Hz, 1H), 4.34 (d, J = 15.7 Hz, 1H), 3.98 (dt, J = 8.6, 3.9 Hz, 1H), 3.02 (qd, J = 7.2, 3.5 Hz, 1H), 1.98 (dd, J = 14.3, 9.3 Hz, 1H), 1.84 (dd, J = 14.3, 4.1 Hz, 1H), 1.81 – 1.73 (m, 1H), 1.68 – 1.63 (m, 2H), 1.59 – 1.52 (m, 3H), 1.51 – 1.37 (m, 2H), 1.29 (d, J = 7.2 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 137.2, 129.0, 128.3, 126.7, 125.7, 85.6, 72.0, 63.5, 44.2, 43.4, 39.0, 37.6, 23.8, 23.6, 13.8
HRMS (ESI): calculated for $[M+Na]^+$ 295.1668 g.mol^{-1}, found 295.1673 g.mol^{-1}
FTIR (film cm^{-1}): ν 3412, 3023, 2958, 2871, 1598, 1493, 1444, 1332, 1211, 1094, 1079, 1030, 989, 917, 867, 753, 699

6/ References

[1] M. Dow, F. Marchetti, K. A. Abrahams, L. Vaz, G. S. Besra, S. Warriner, A. Nelson, *Chem. Eur. J.,* 2017, **23**, 7207 – 7211

[2] R. Cao, P. Müller, S. J. Lippard, *J. Am. Chem. Soc.,* 2010, 132, **49**, 17366-17369

[3] R. P. Law, S. J. Atkinson, P. Bamborough, C. Chung, E. H. Demont, L. J. Gordon, M. Lindon, R. K. Prinjha, A. J. B. Watson, D. J. Hirst, *J. Med. Chem.,* 2018, 61, **10**, 4317-4334

[4] J.A. Bergman, K. Hahne, J. Song, C.A. Hrycyna, R.A. Gibbs, *ACS Med. Chem. Lett.,* 2012, **3**, 15-19

[5] B. M. Trost, S. Mahapatra, M. Hansen, *Angew. Chem. Int. Ed*., 2015, **54**, 6032 –6036

[6] M. Bourkhis, H. Gaspard, P. Rullière, D.K.C de Almeida, D. Listunov, E. Joly, R. Abderrahim, M.C. de Mattos, M.C.F. de Oliveira, V. Maraval, R. Chauvin, Y. Génisson, *ChemMedChem.,* 2018, **13**, 1124-1130

[7] F. Kolundžić, A. Murali, P. Pérez-Galán, J.O. Bauer, C. Strohmann, K. Kumar, H. Waldmann, *Angew. Chem. Int. Ed.,* 2014, **53**, 8122-8126

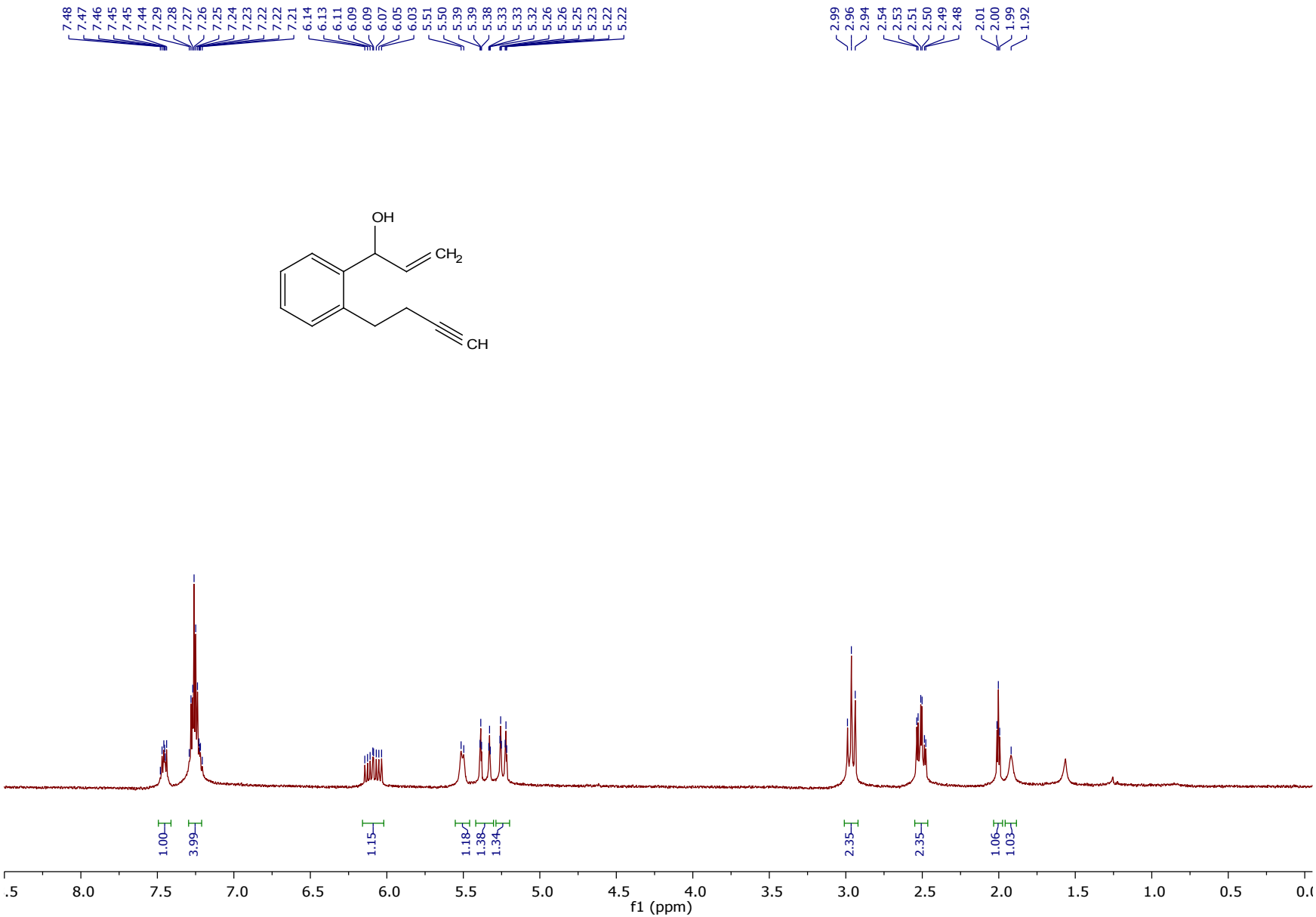
[8] B.M. Trost, M.T. Rudd, M.G. Costa, P.I. Lee, A.E. Poerantz, *Org. Lett.,* 2004, 6, **23**, 4235-4238

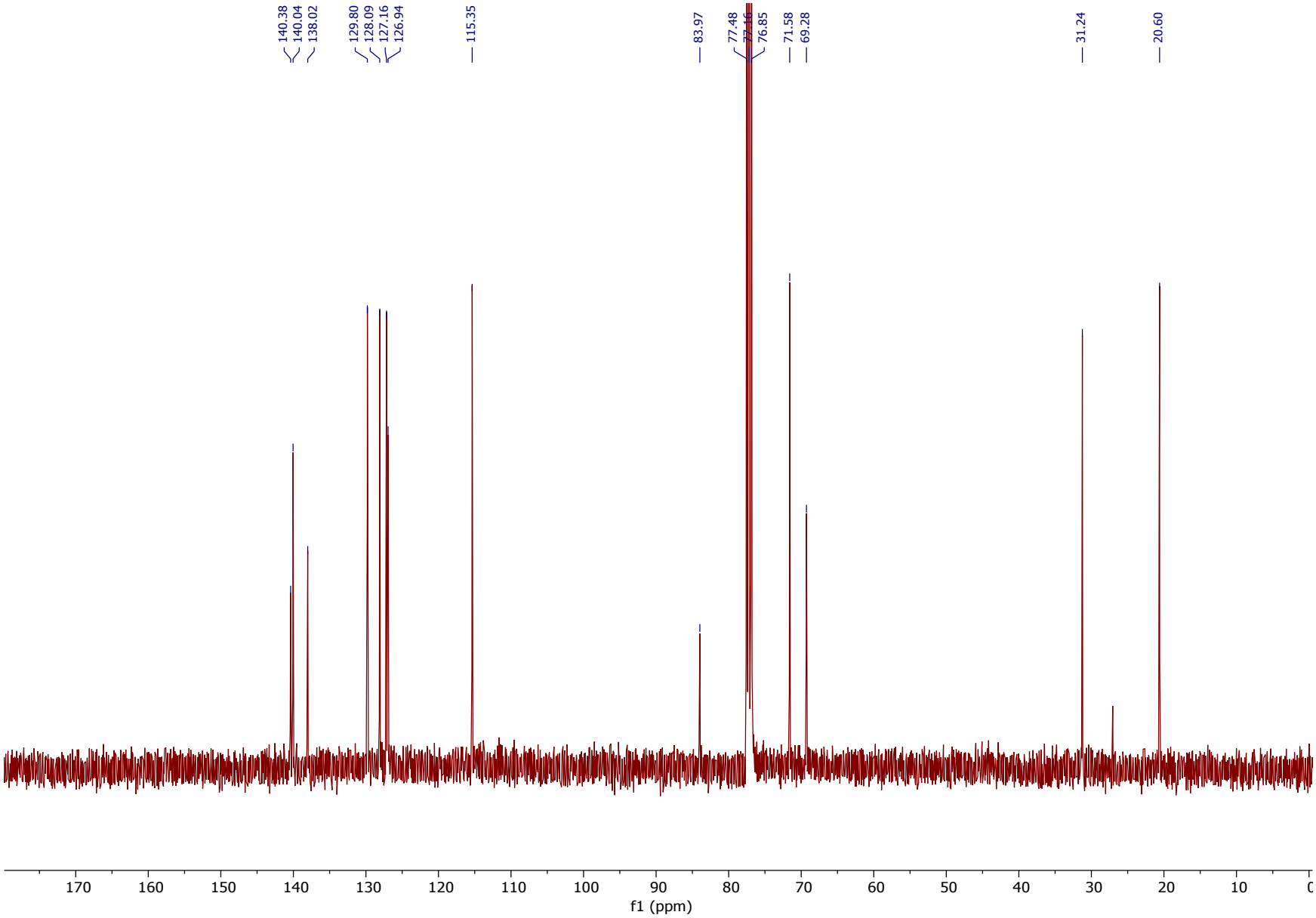
[9] N. Cabrera-Lobera, M.T. Quirós, W.W. Brennessel, M.L. Neidig, E. Buñuel, D.J. Cárdenas, *Org. Lett.,* 2019, 21, **16**, 6552-6556

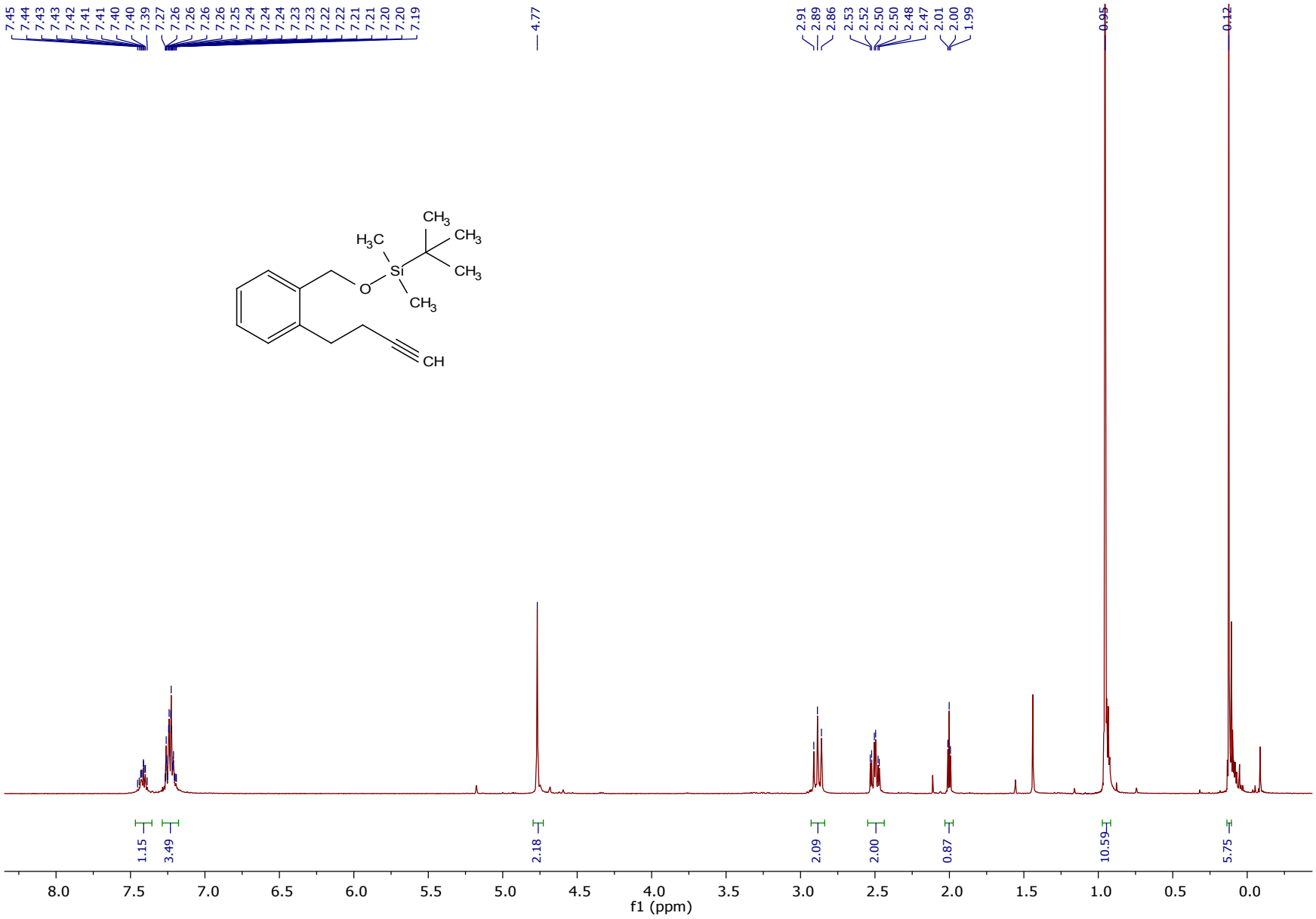
[10] T. Heesgaard Jepsen, E. Glibstrup, F. Crestey, A. A. Jensen, J. Langgaard Kristensen, *Beilstein J. Org. Chem.,* 2017, **13**, 988-994

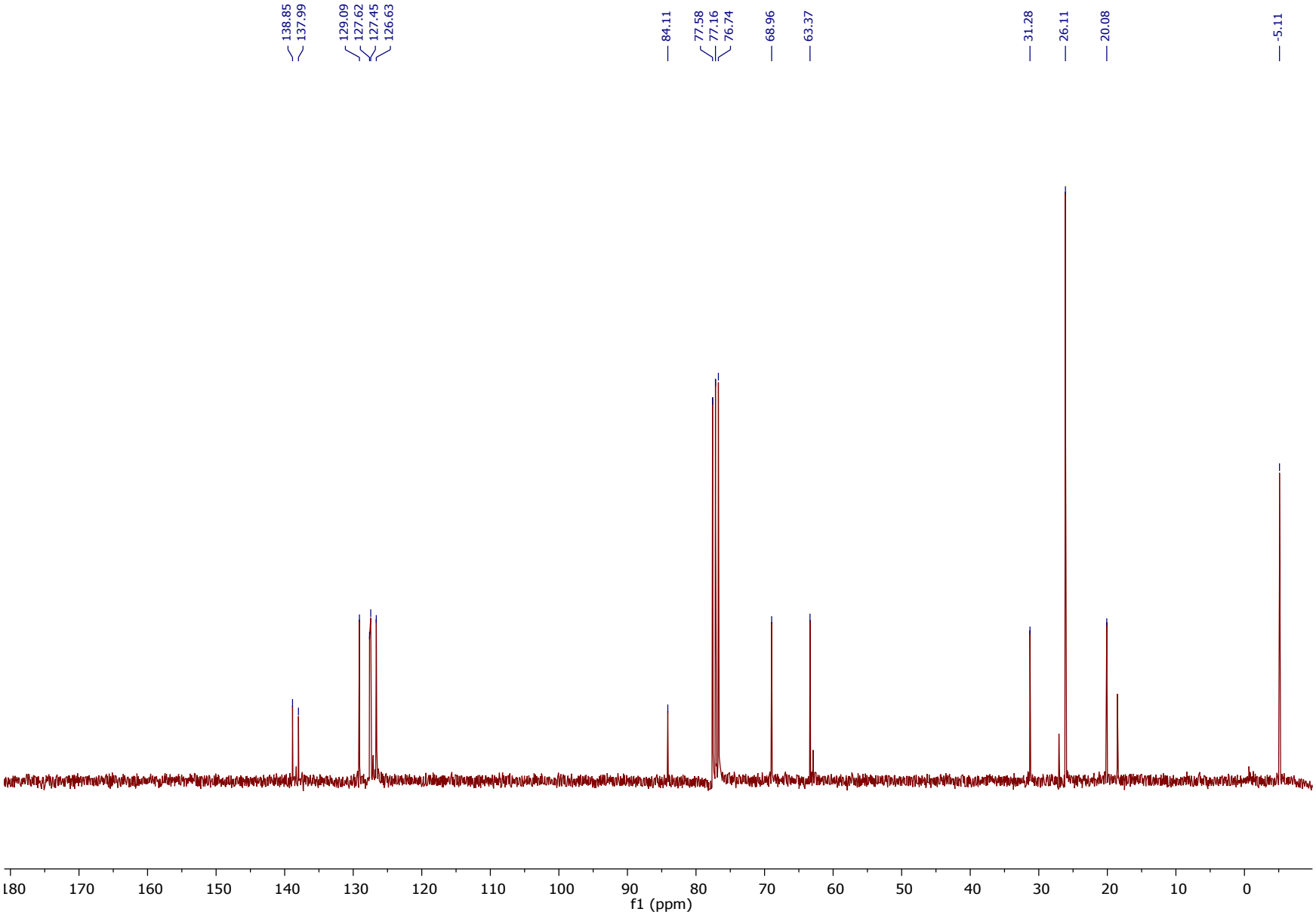
[11] N.A. Weires, Y. Slutskyy, L.E. Overman, *Angew. Chem. Int. Ed.,* 2019, **58**, 8561-8565

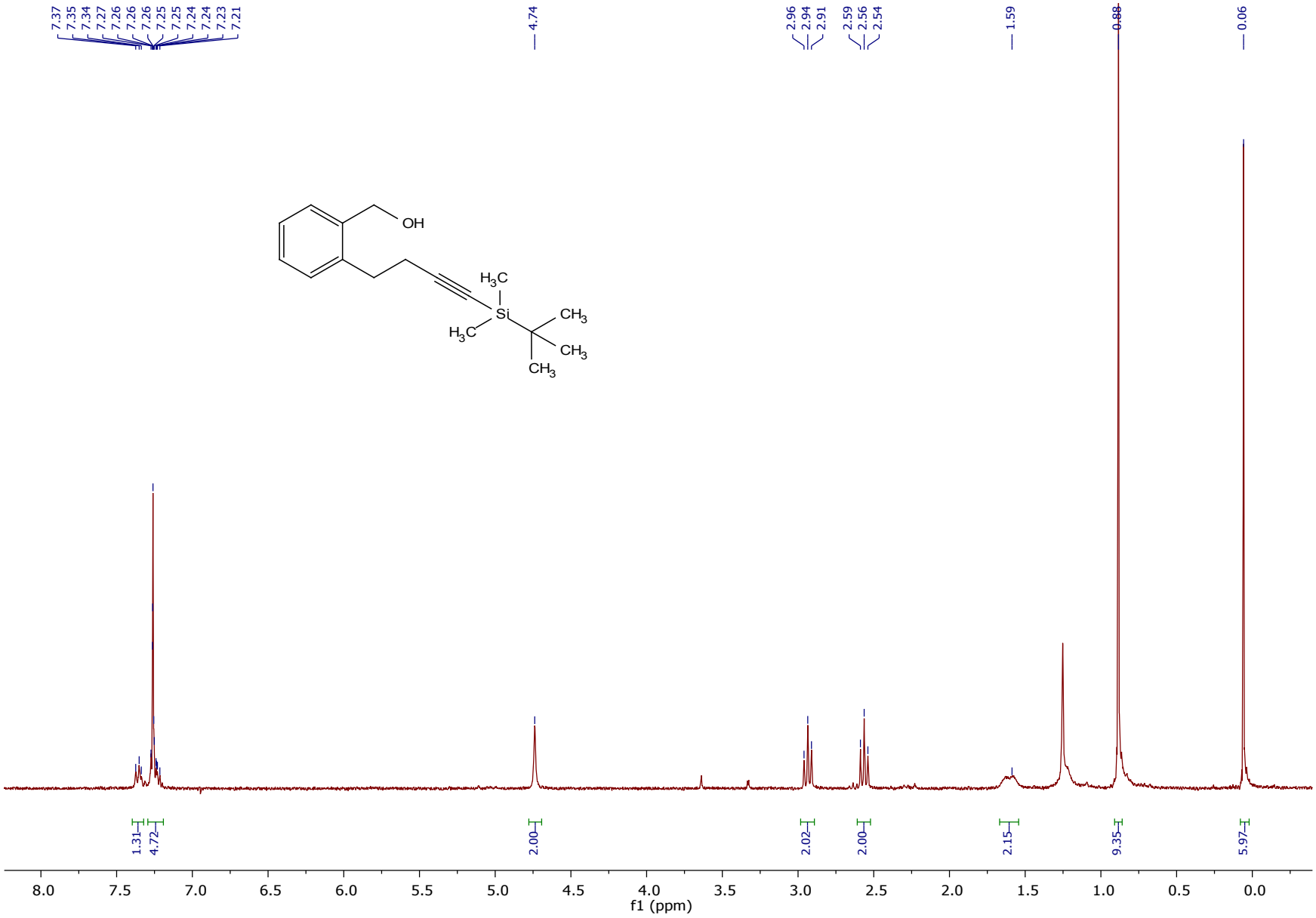
7/ NMR spectra

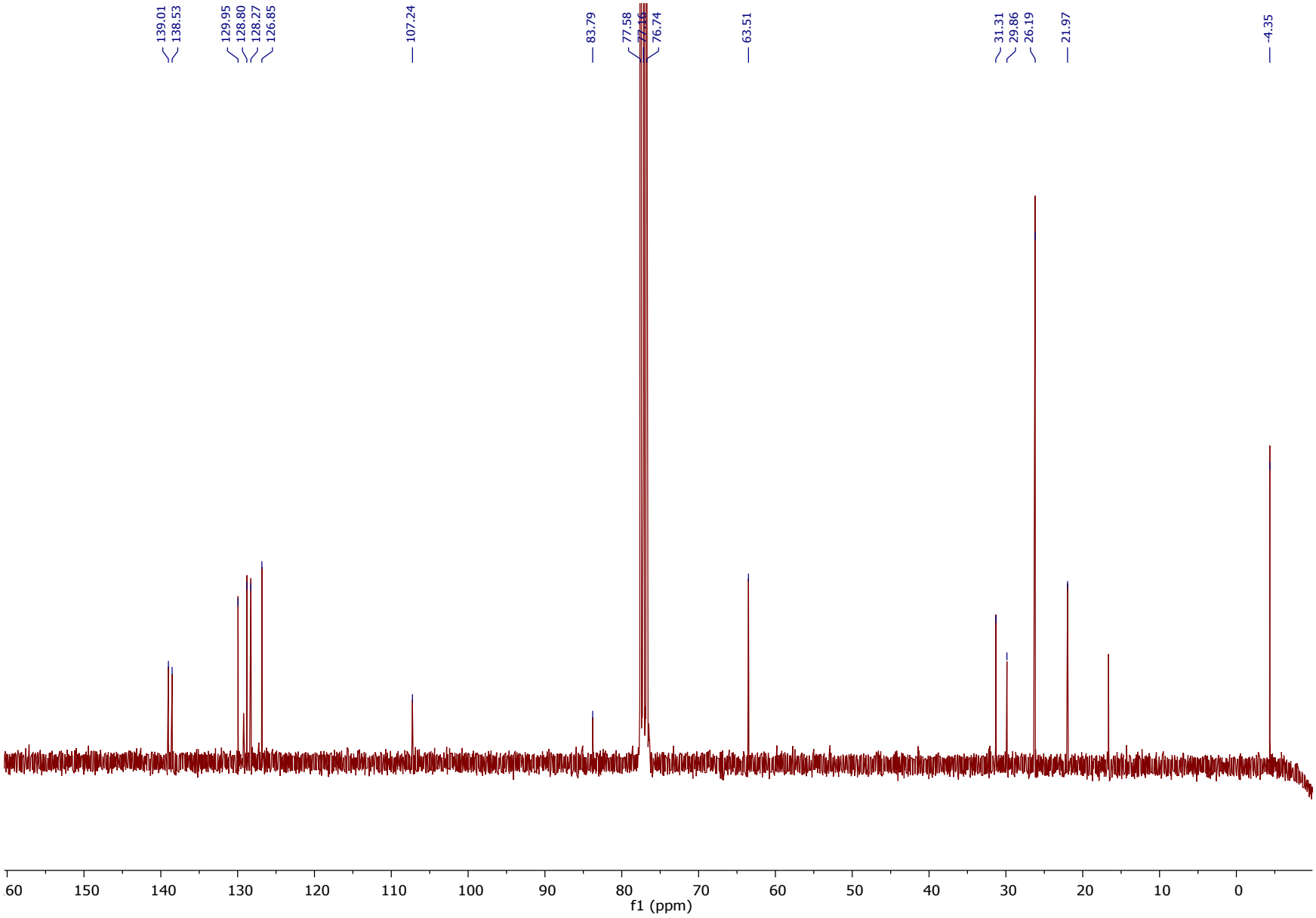

7.48
7.47
7.46
7.45
7.45
7.44
7.29
7.28
7.27
7.26
7.25
7.24
7.23
7.22
7.22
7.21
6.14
6.13
6.11
6.09
6.09
6.07
6.05
6.03
5.51
5.50
5.39
5.39
5.38
5.33
5.33
5.32
5.26
5.26
5.25
5.23
5.22
5.22
2.99
2.96
2.94
2.54
2.53
2.51
2.50
2.49
2.48
2.01
2.00
1.99
1.92
OH
CH2
CH
1.00
3.99
1.15
1.18
1.38
1.34
2.35
2.35
1.06
1.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

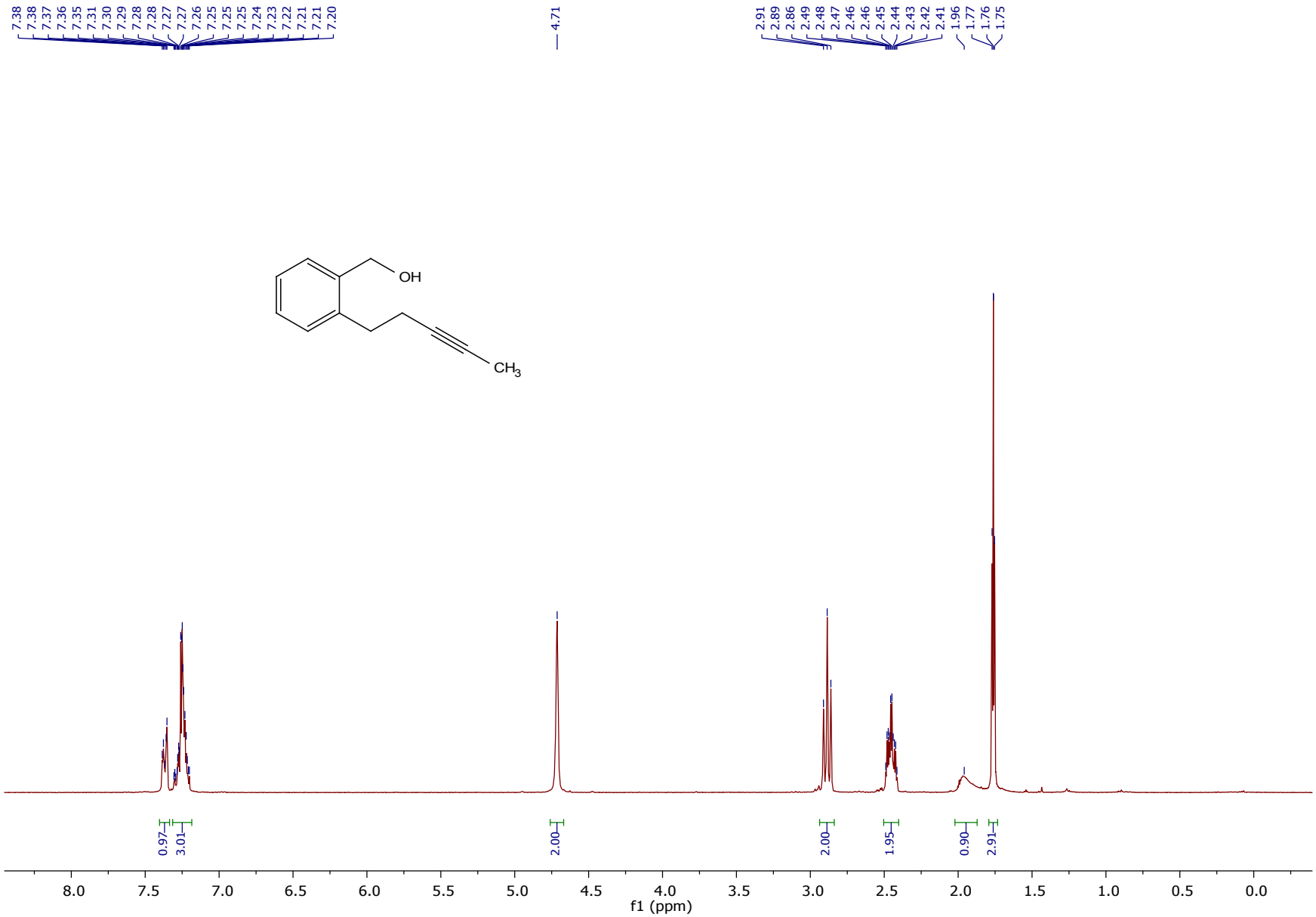

140.38
140.04
138.02
129.80
128.09
127.16
126.94
115.35
83.97
77.48
77.16
76.85
71.58
69.28
31.24
20.60
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

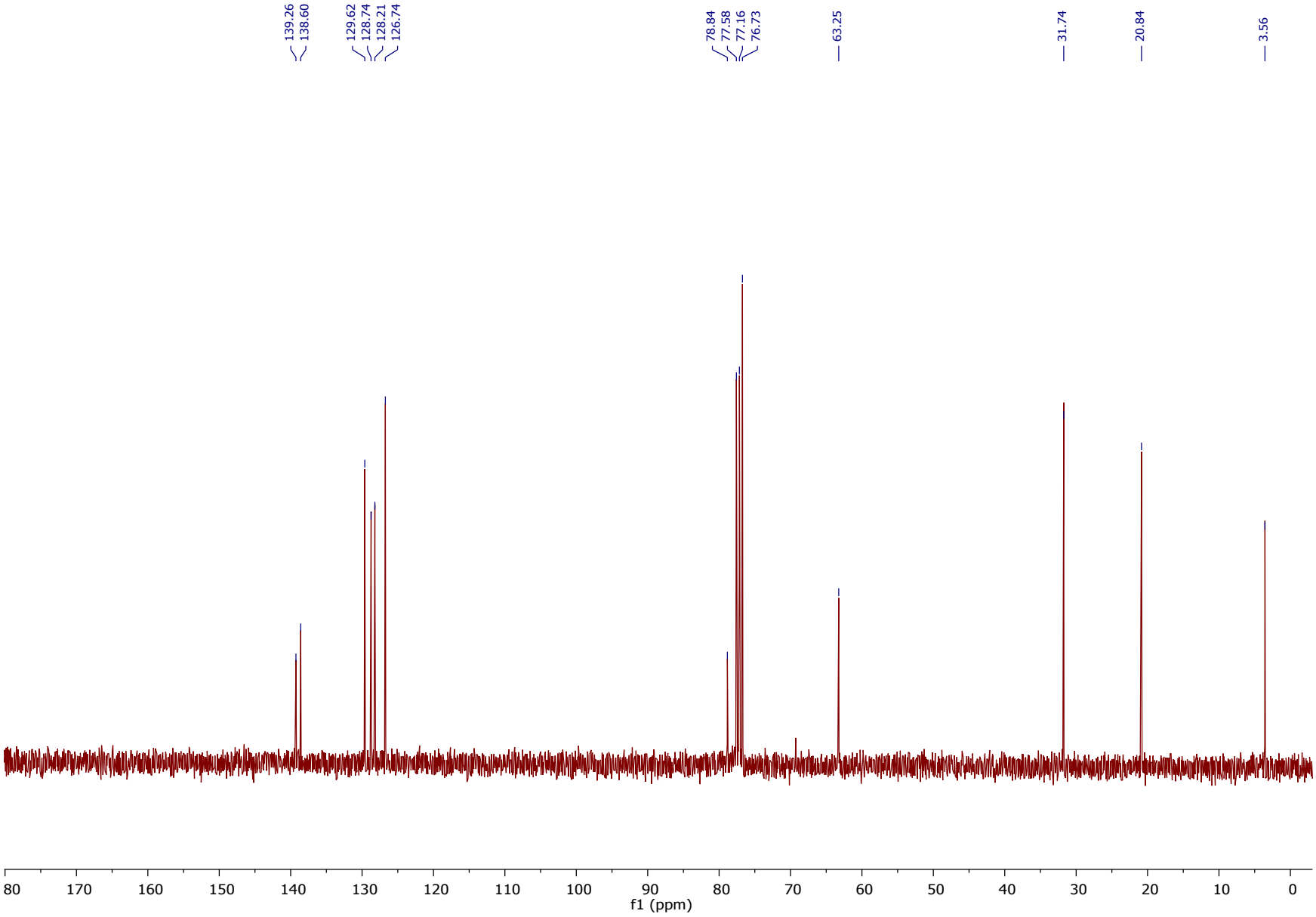

7.45 7.44 7.43 7.43 7.42 7.41 7.41 7.40 7.40 7.39 7.27 7.26 7.26 7.26 7.25 7.24 7.24 7.24 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.20 7.19
4.77
2.91 2.89 2.86 2.53 2.52 2.50 2.50 2.48 2.47 2.01 2.00 1.99
0.95
0.12
CH3
H3C
CH3
Si
CH3
O
CH3
CH
1.15
3.49
2.18
2.09
2.00
0.87
10.59
5.75
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

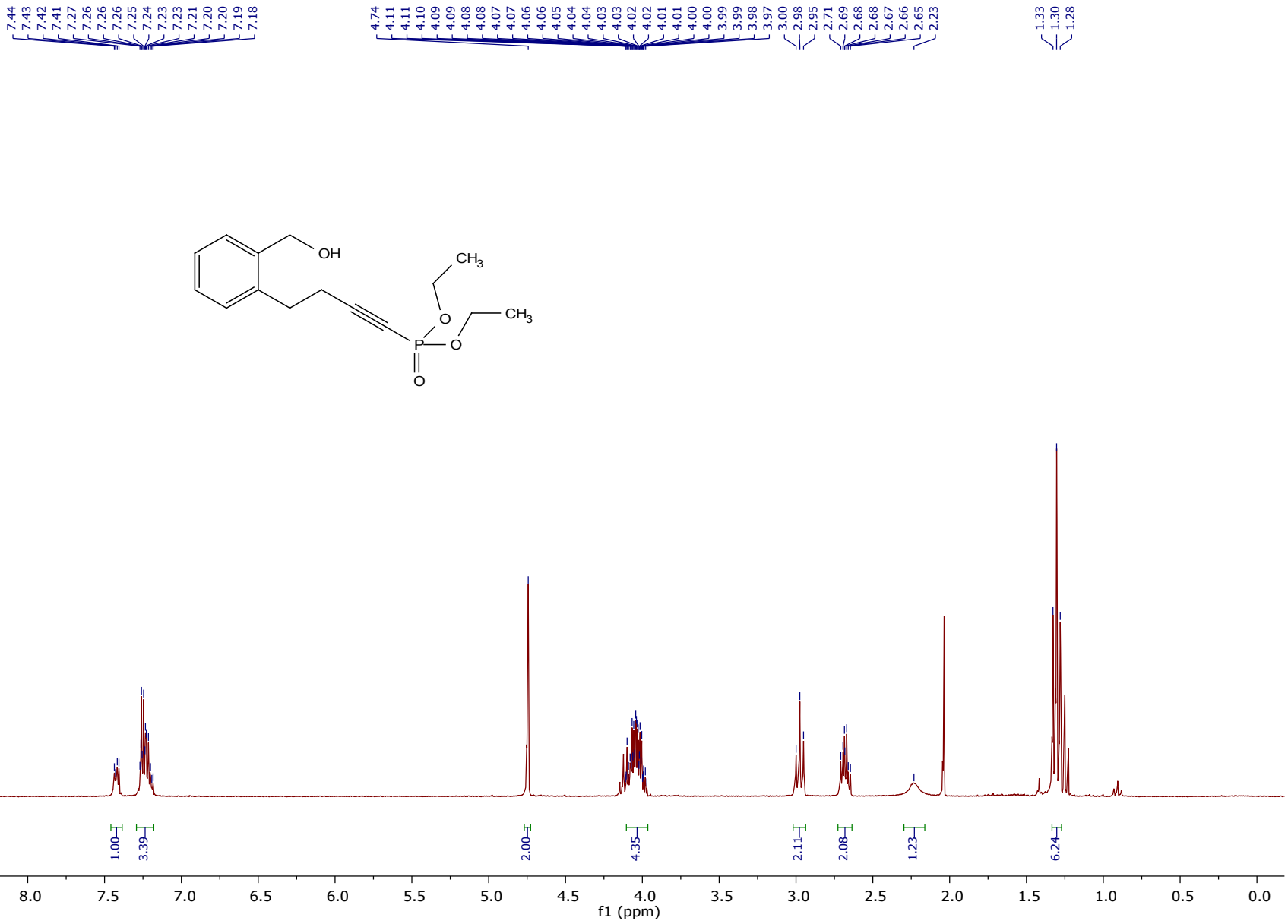

138.85
137.99
129.09
127.62
127.45
126.63
84.11
77.58
77.16
76.74
68.96
63.37
31.28
26.11
20.08
-5.11
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

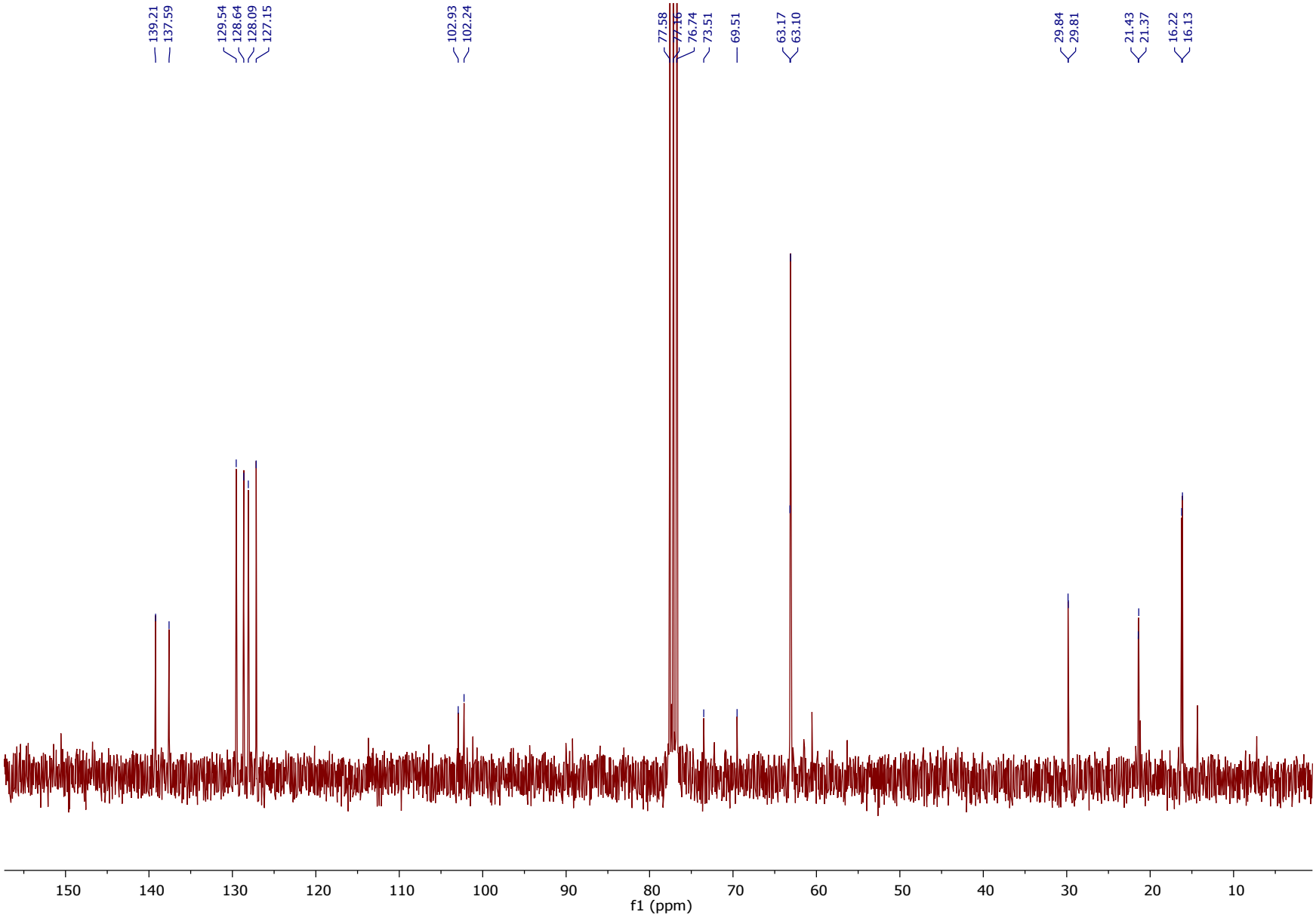

7.37
7.35
7.34
7.27
7.26
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.21
4.74
2.96
2.94
2.91
2.59
2.56
2.54
1.59
0.88
0.06
OH
H3C
Si
CH3
H3C
CH3
CH3
1.31
4.72
2.00
2.02
2.00
2.15
9.35
5.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

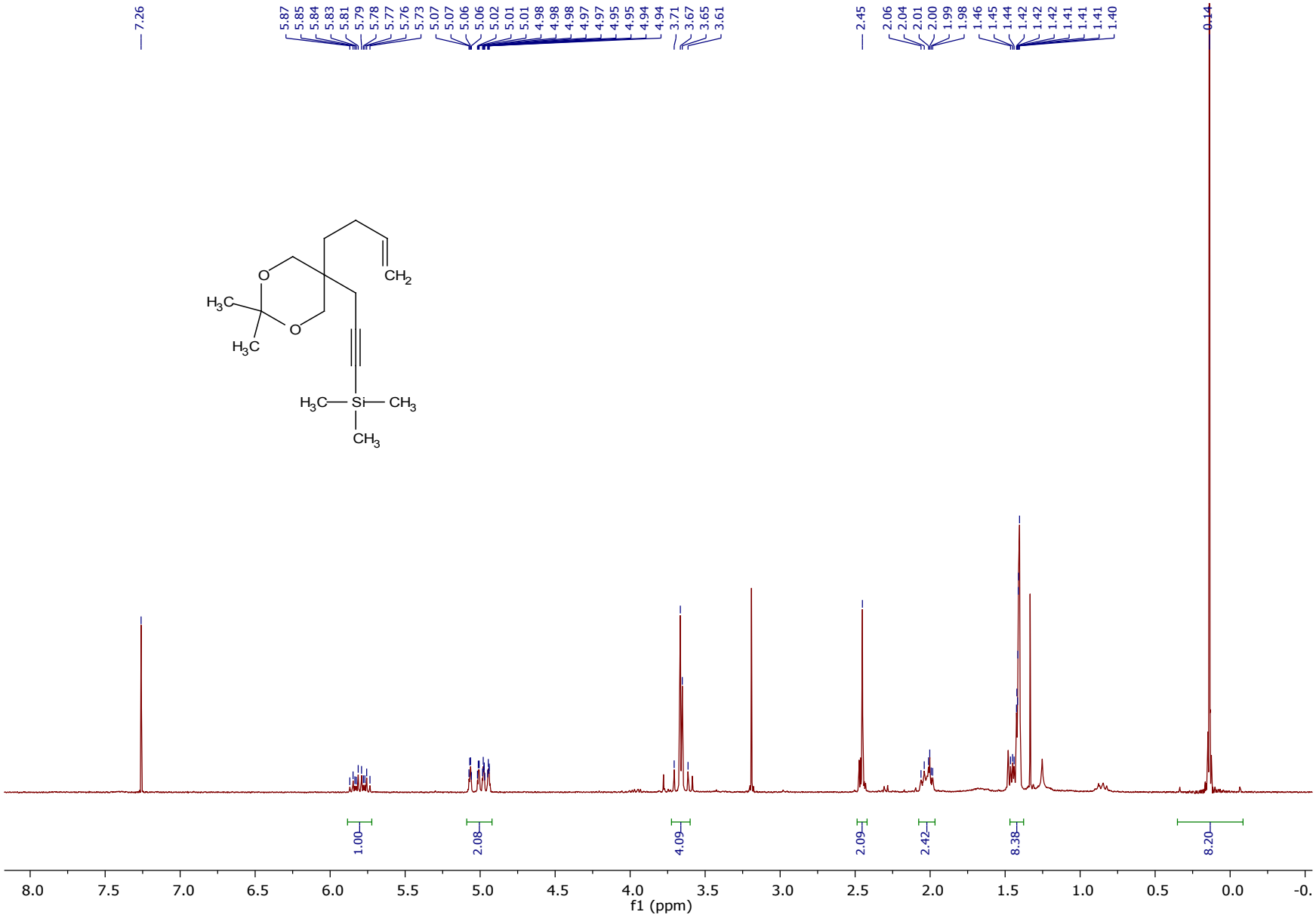

139.01
138.53
129.95
128.80
128.27
126.85
107.24
83.79
77.58
77.16
76.74
63.51
31.31
29.86
26.19
21.97
-4.35
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

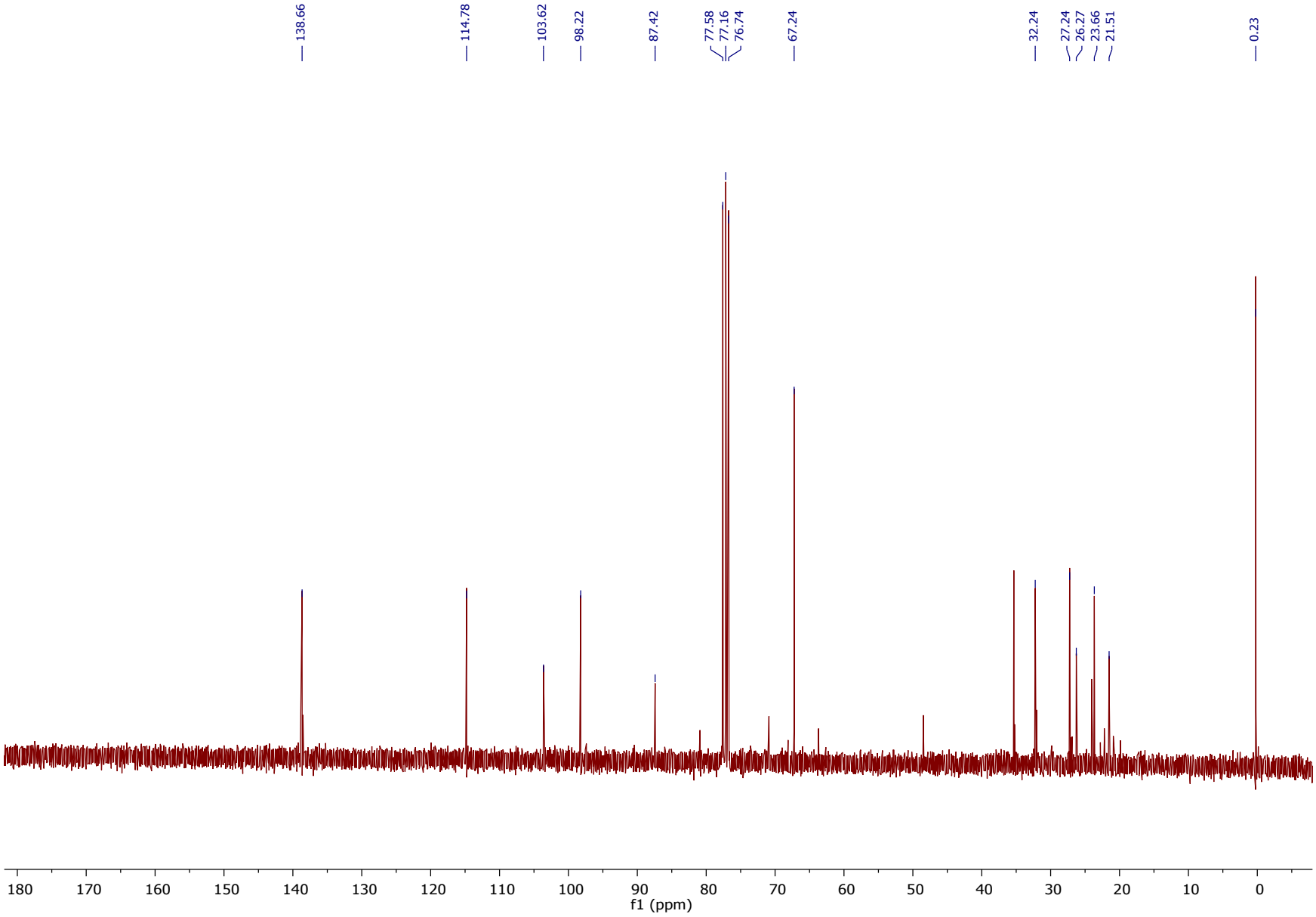

7.38
7.38
7.37
7.36
7.35
7.31
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.25
7.24
7.23
7.22
7.21
7.21
7.20
4.71
2.91
2.89
2.86
2.49
2.48
2.47
2.46
2.46
2.45
2.44
2.43
2.42
2.41
1.96
1.77
1.76
1.75
OH
CH3
0.97
3.01
2.00
2.00
1.95
0.90
2.91
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

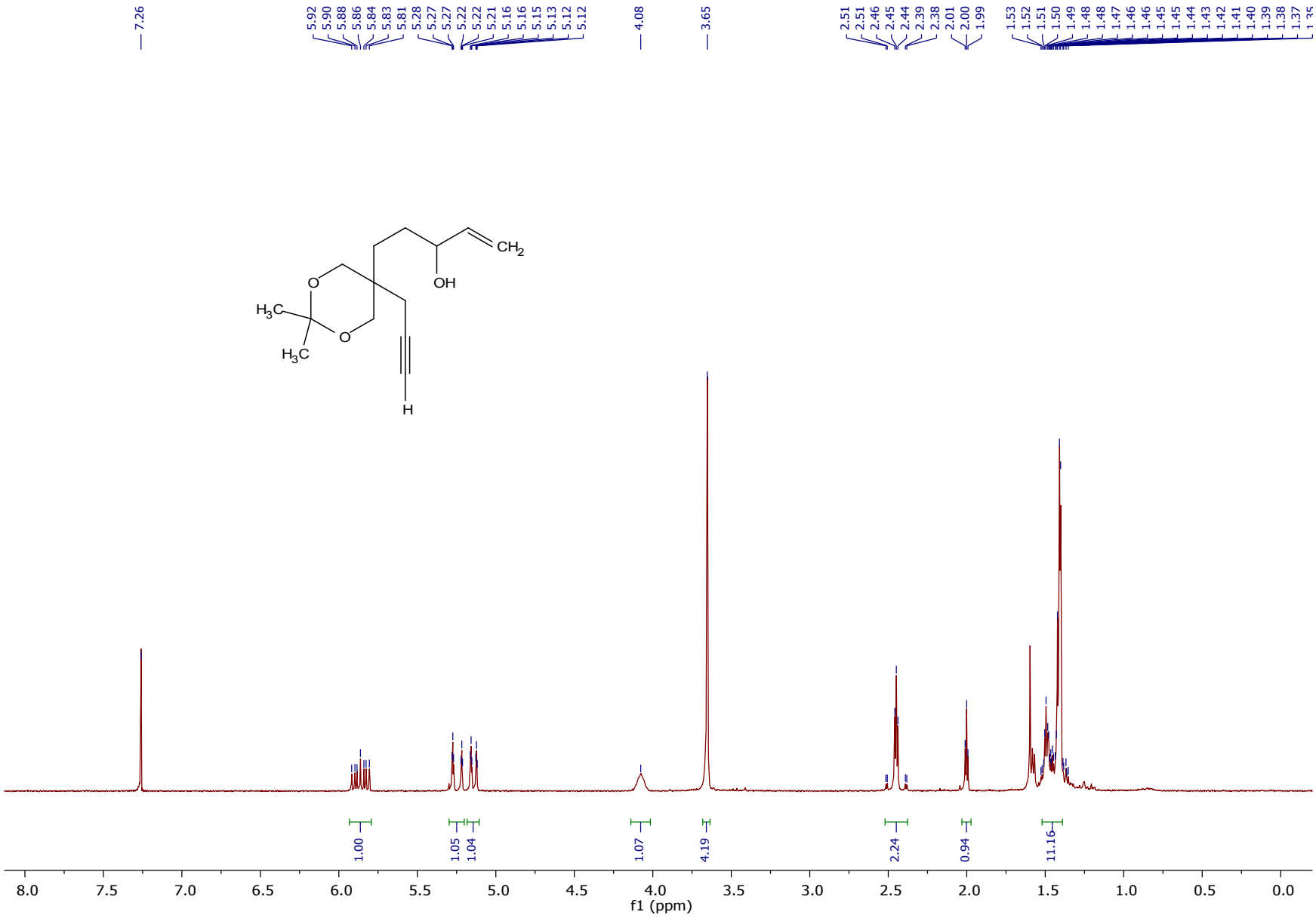

139.26
138.60
129.62
128.74
128.21
126.74
78.84
77.58
77.16
76.73
63.25
31.74
20.84
3.56
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

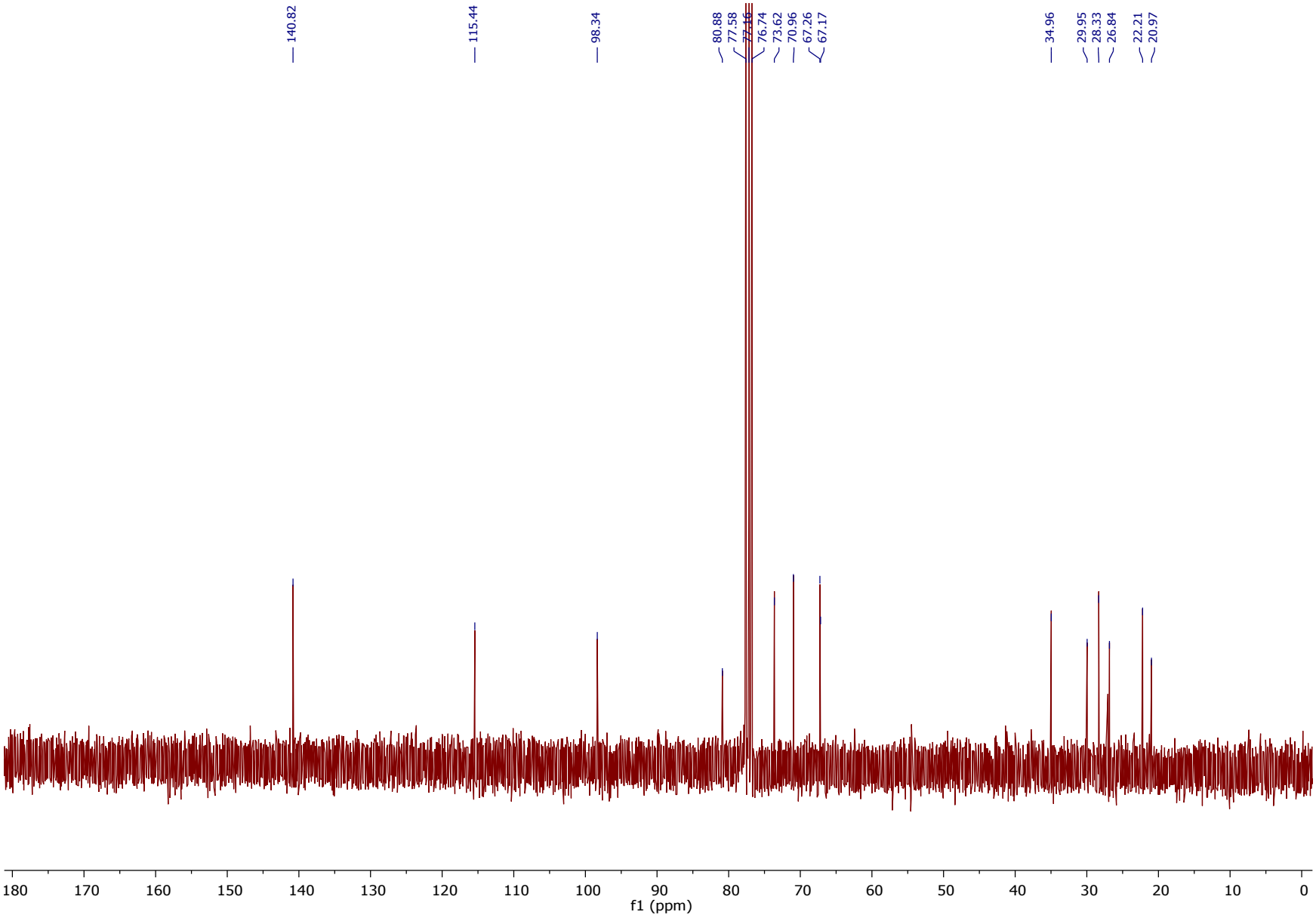

7.44 7.43 7.42 7.41 7.27 7.26 7.26 7.26 7.25 7.24 7.23 7.23 7.21 7.20 7.20 7.19 7.18
4.74 4.11 4.11 4.10 4.09 4.09 4.08 4.08 4.07 4.07 4.06 4.06 4.05 4.04 4.04 4.03 4.03 4.02 4.02 4.01 4.01 4.00 4.00 3.99 3.99 3.98 3.97 3.00 2.98 2.95 2.71 2.69 2.68 2.68 2.67 2.66 2.65 2.23
1.33 1.30 1.28
OH
CH3
CH3
O
O
P
O
O
1.00 3.39 2.00 4.35 2.11 2.08 1.23 6.24
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

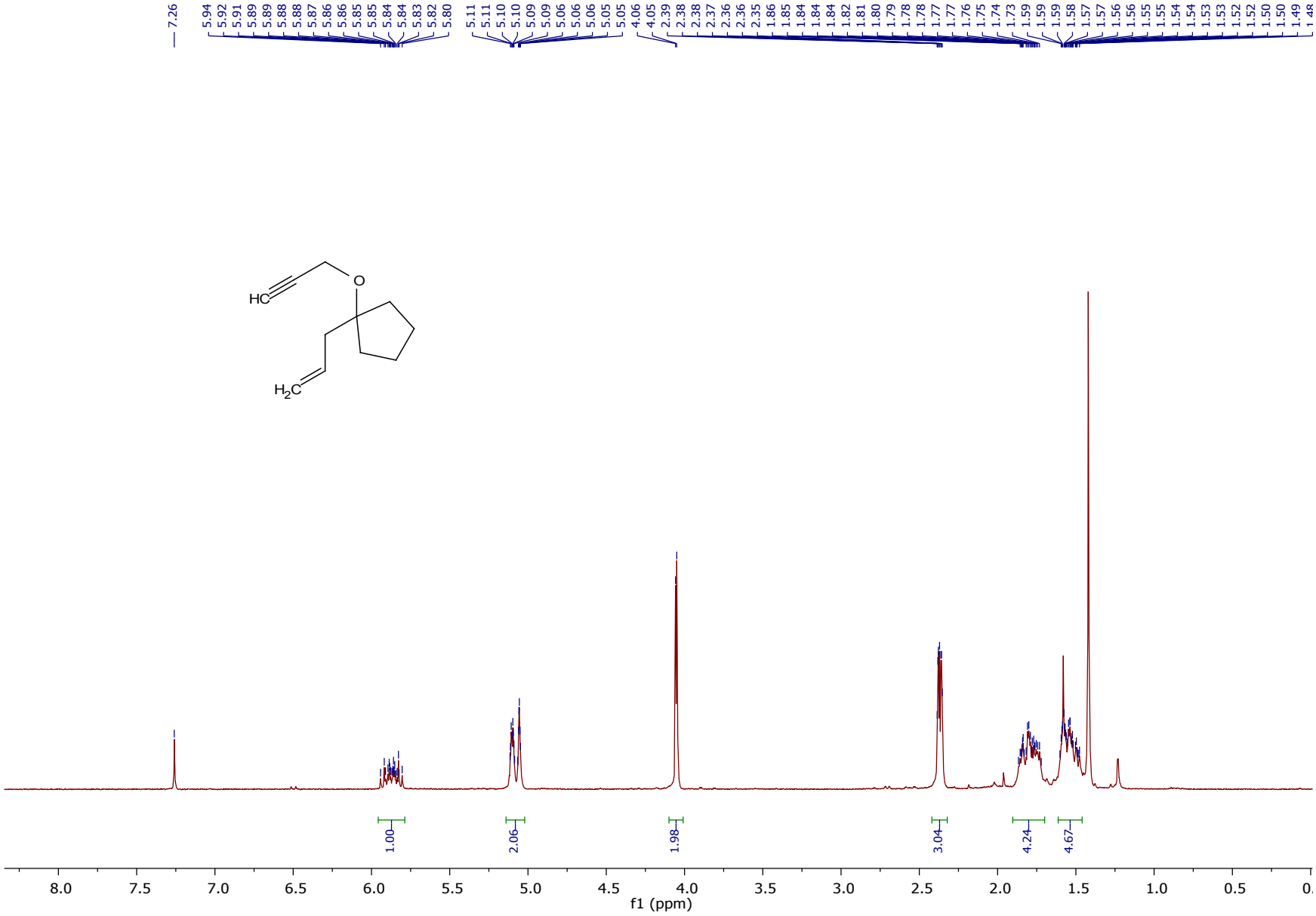

139.21
137.59
129.54
128.64
128.09
127.15
102.93
102.24
77.58
77.16
76.74
73.51
69.51
63.17
63.10
29.84
29.81
21.43
21.37
16.22
16.13
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

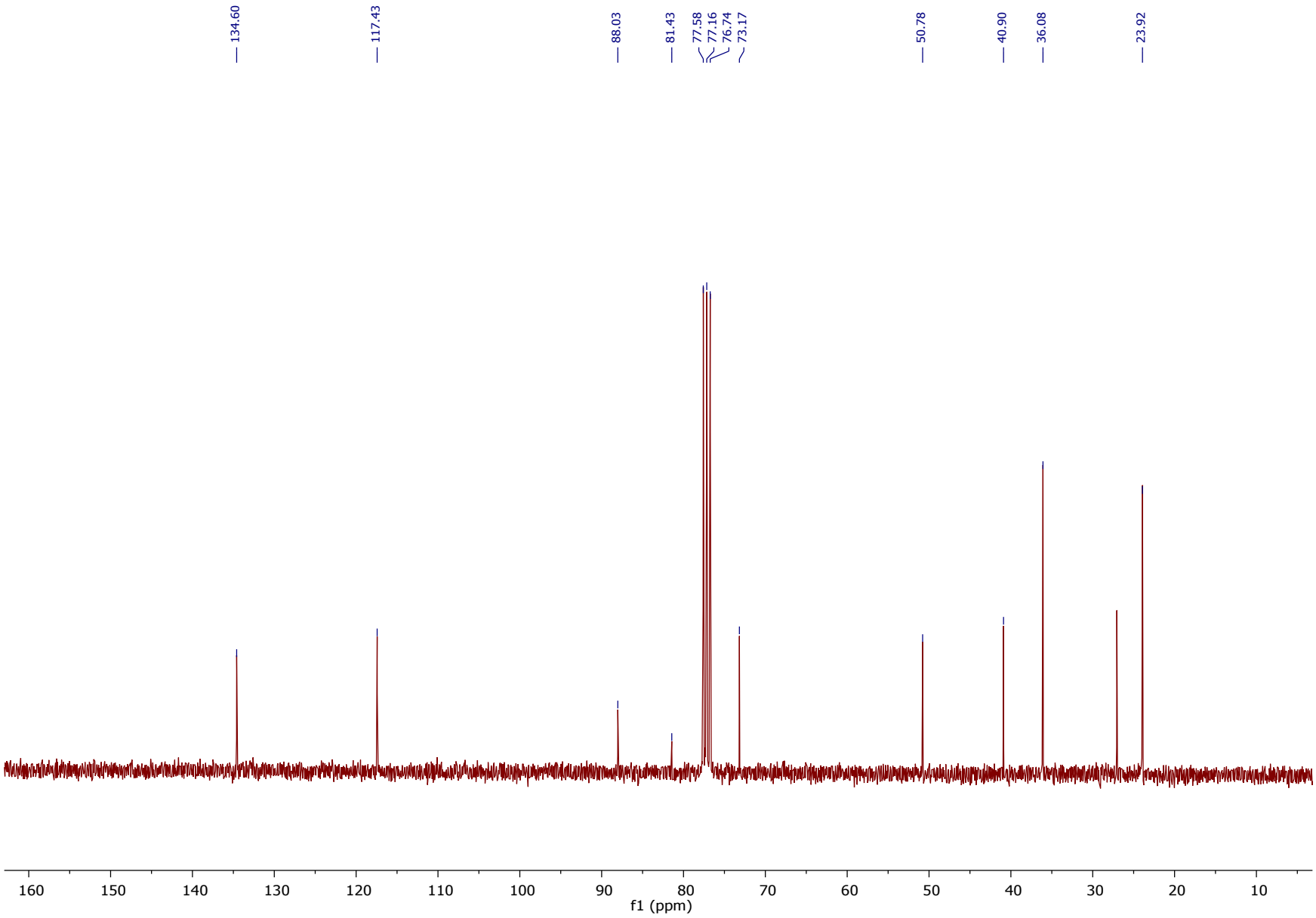

7.26
5.87
5.85
5.84
5.83
5.81
5.79
5.78
5.77
5.76
5.73
5.07
5.07
5.06
5.06
5.02
5.01
5.01
4.98
4.98
4.98
4.97
4.97
4.95
4.95
4.94
4.94
3.71
3.67
3.65
3.61
2.45
2.06
2.04
2.01
2.00
1.99
1.98
1.46
1.45
1.44
1.42
1.42
1.42
1.41
1.41
1.41
1.40
0.14
O
O
CH2
H3C
H3C
H3C
Si
CH3
CH3
1.00
2.08
4.09
2.09
2.42
8.38
8.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

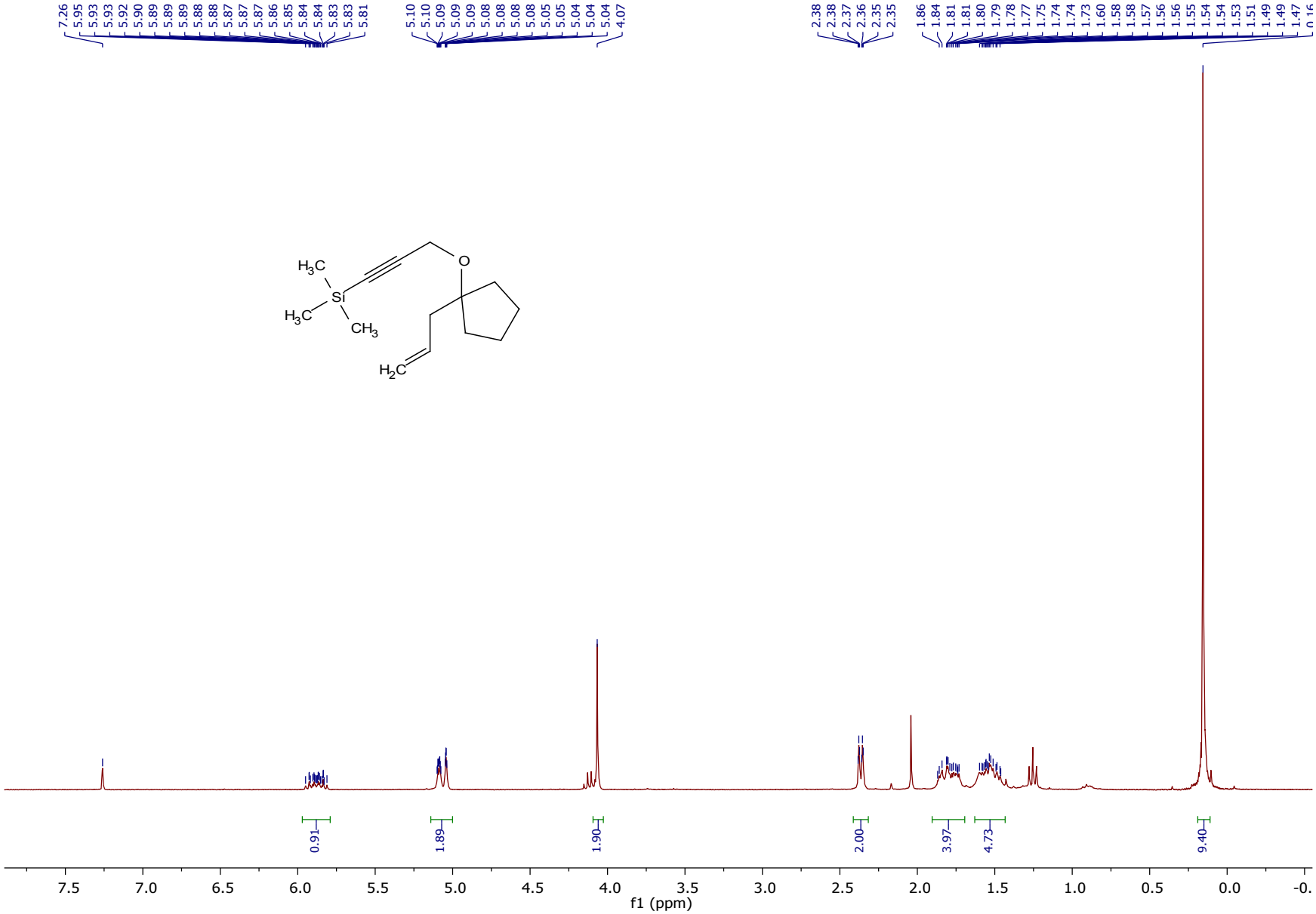

138.66
114.78
103.62
98.22
87.42
77.58
77.16
76.74
67.24
32.24
27.24
26.27
23.66
21.51
0.23
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

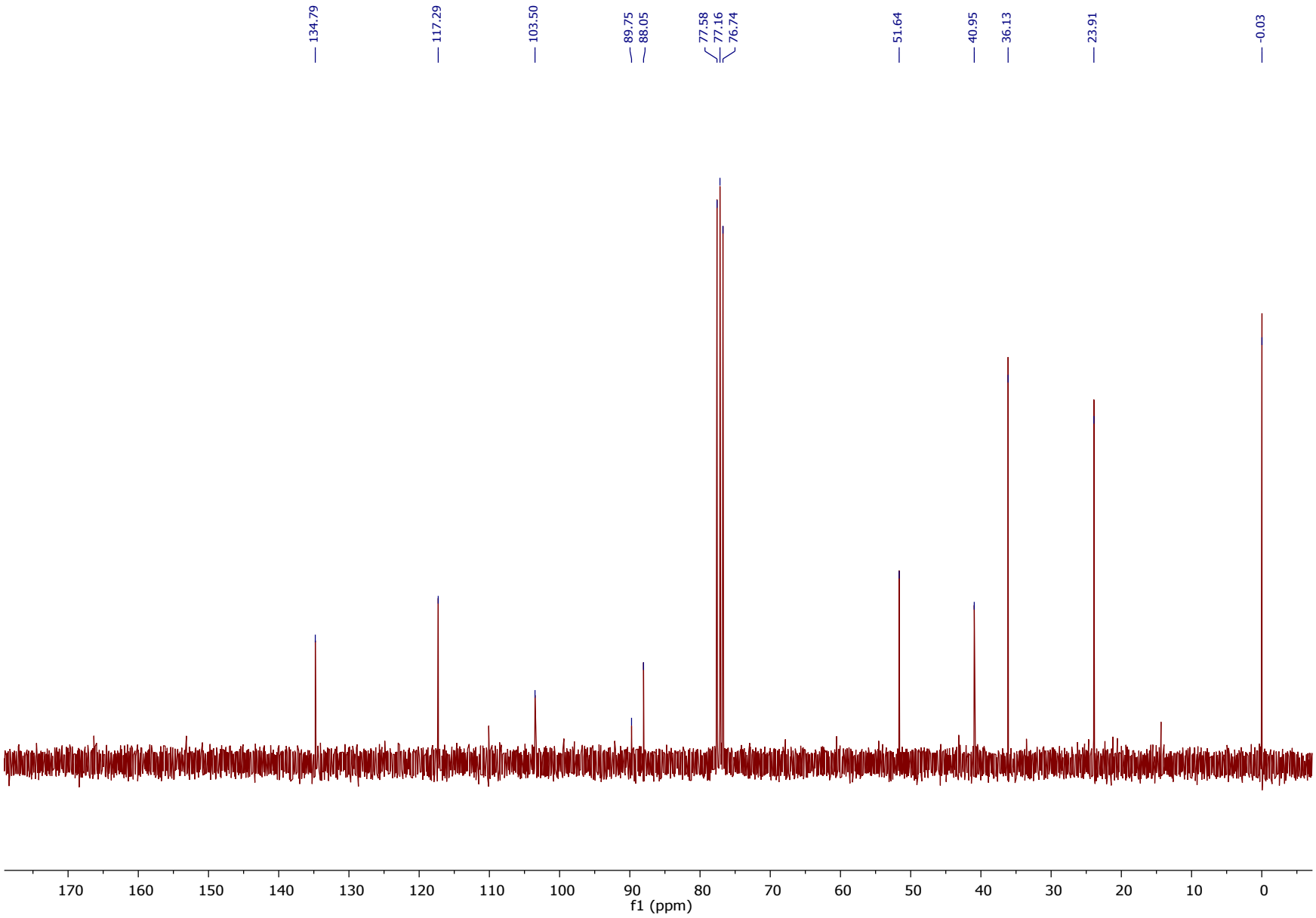

7.26
5.92
5.90
5.88
5.86
5.84
5.83
5.81
5.28
5.27
5.27
5.22
5.22
5.21
5.16
5.16
5.15
5.13
5.12
5.12
4.08
3.65
2.51
2.51
2.46
2.45
2.44
2.39
2.38
2.01
2.00
1.99
1.53
1.52
1.51
1.50
1.49
1.48
1.48
1.47
1.46
1.46
1.45
1.45
1.44
1.43
1.42
1.41
1.40
1.39
1.38
1.37
CH2
OH
O
H3C
O
H3C
H
1.00
1.05
1.04
1.07
4.19
2.24
0.94
11.16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

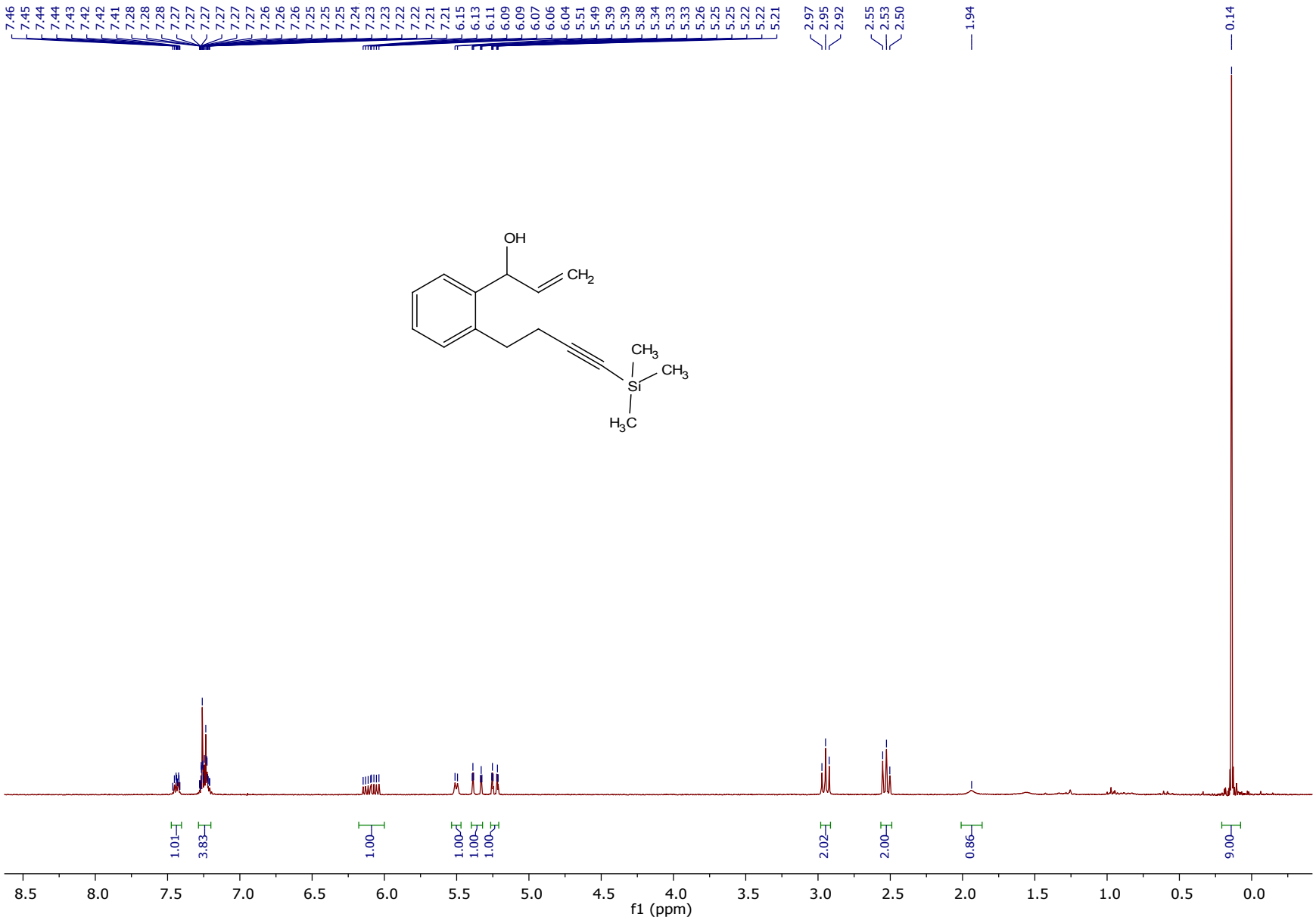

140.82
115.44
98.34
80.88
77.58
77.16
76.74
73.62
70.96
67.26
67.17
34.96
29.95
28.33
26.84
22.21
20.97
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

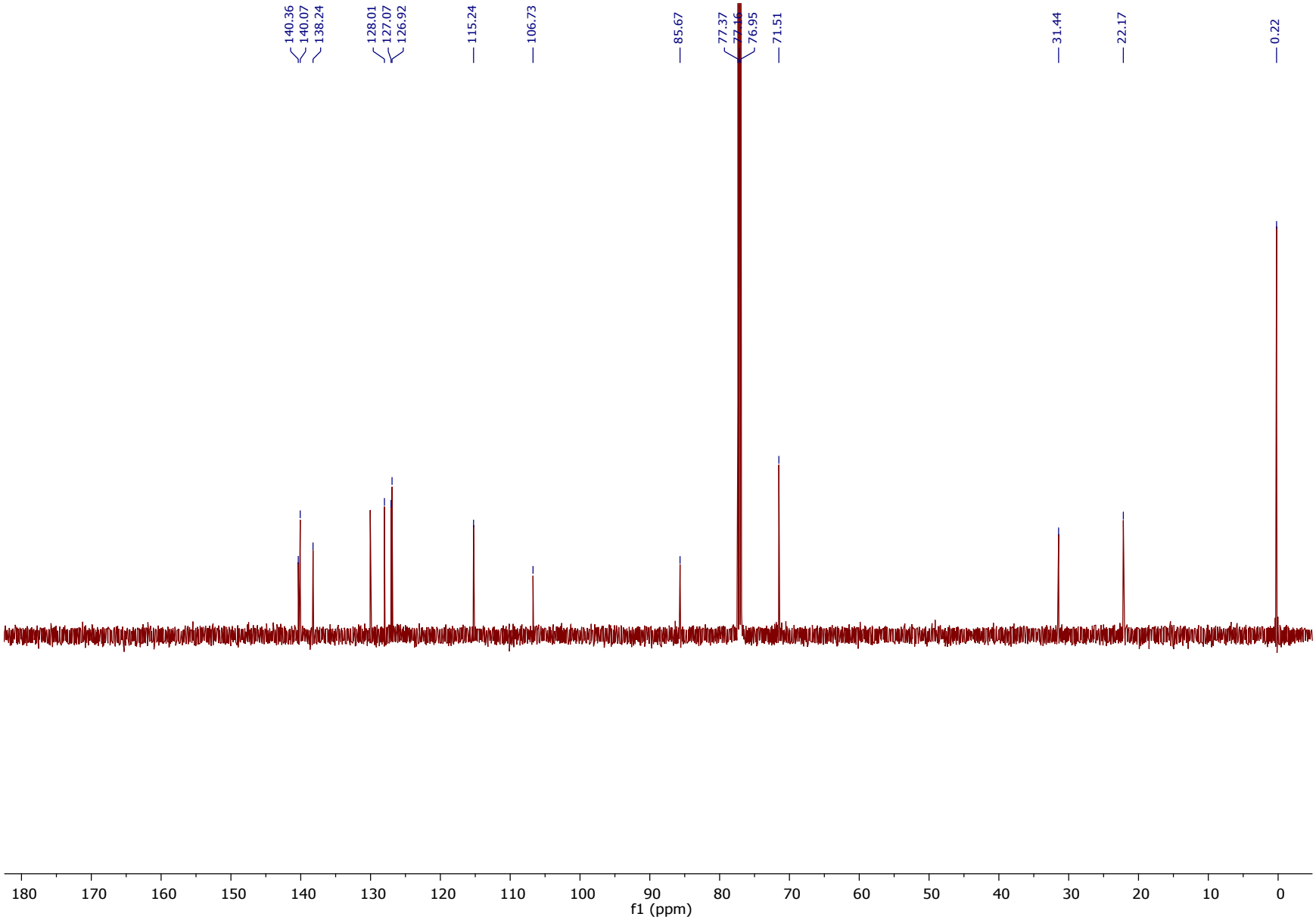

7.26
5.94 5.92 5.91 5.89 5.89 5.88 5.88 5.87 5.86 5.86 5.85 5.85 5.84 5.84 5.83 5.82 5.80
5.11 5.11 5.10 5.10 5.09 5.09 5.06 5.06 5.06 5.05 5.05
4.06 4.05 2.39 2.38 2.38 2.37 2.36 2.36 2.35 1.86 1.85 1.84 1.84 1.84 1.82 1.81 1.80 1.79 1.78 1.78 1.77 1.77 1.76 1.75 1.74 1.73 1.59 1.59 1.59 1.58 1.57 1.57 1.56 1.56 1.55 1.55 1.54 1.54 1.53 1.53 1.52 1.52 1.50 1.50 1.49
HC
O
H2C
1.00
2.06
1.98
3.04
4.24
4.67
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

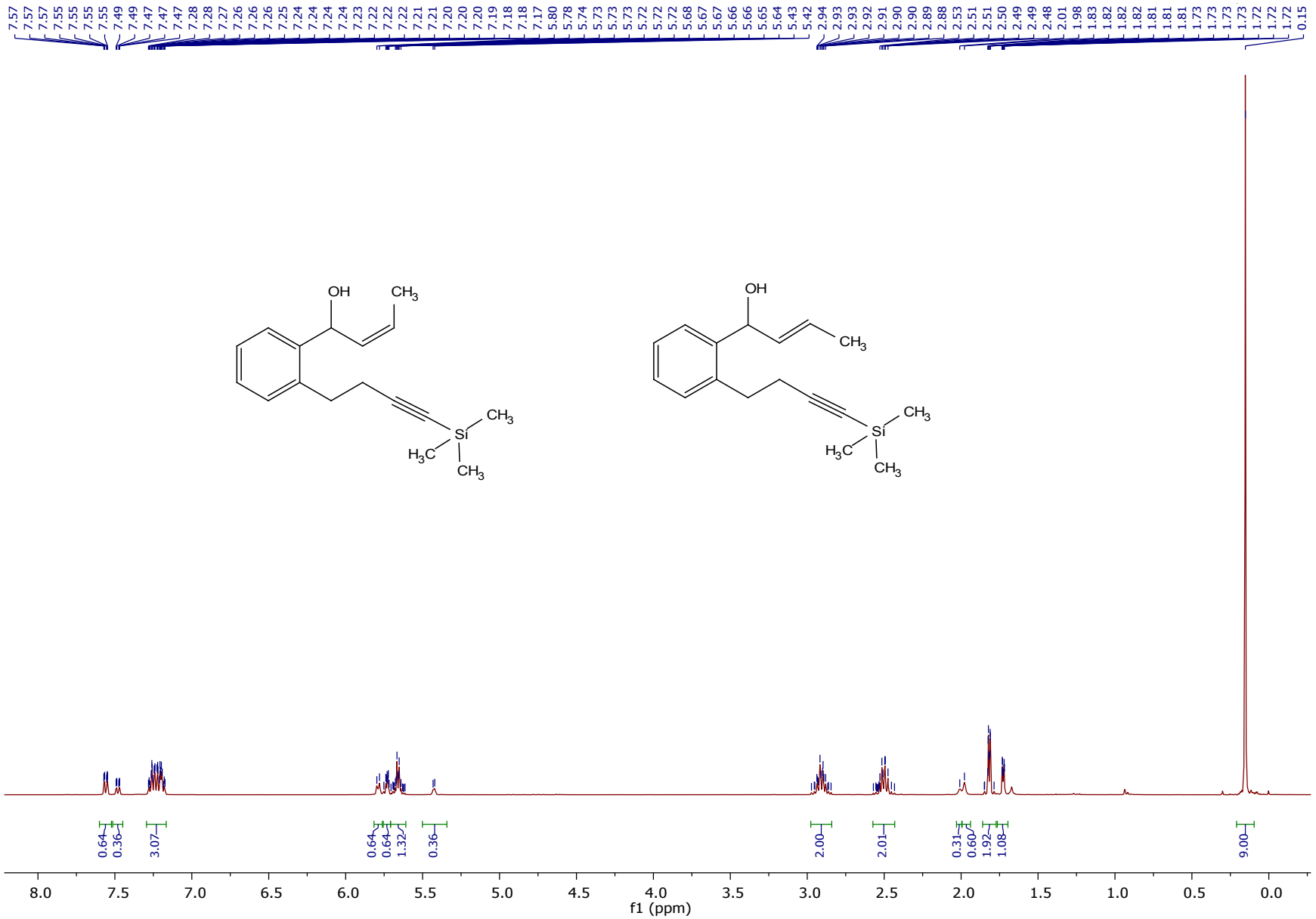

134.60
117.43
88.03
81.43
77.58
77.16
76.74
73.17
50.78
40.90
36.08
23.92
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

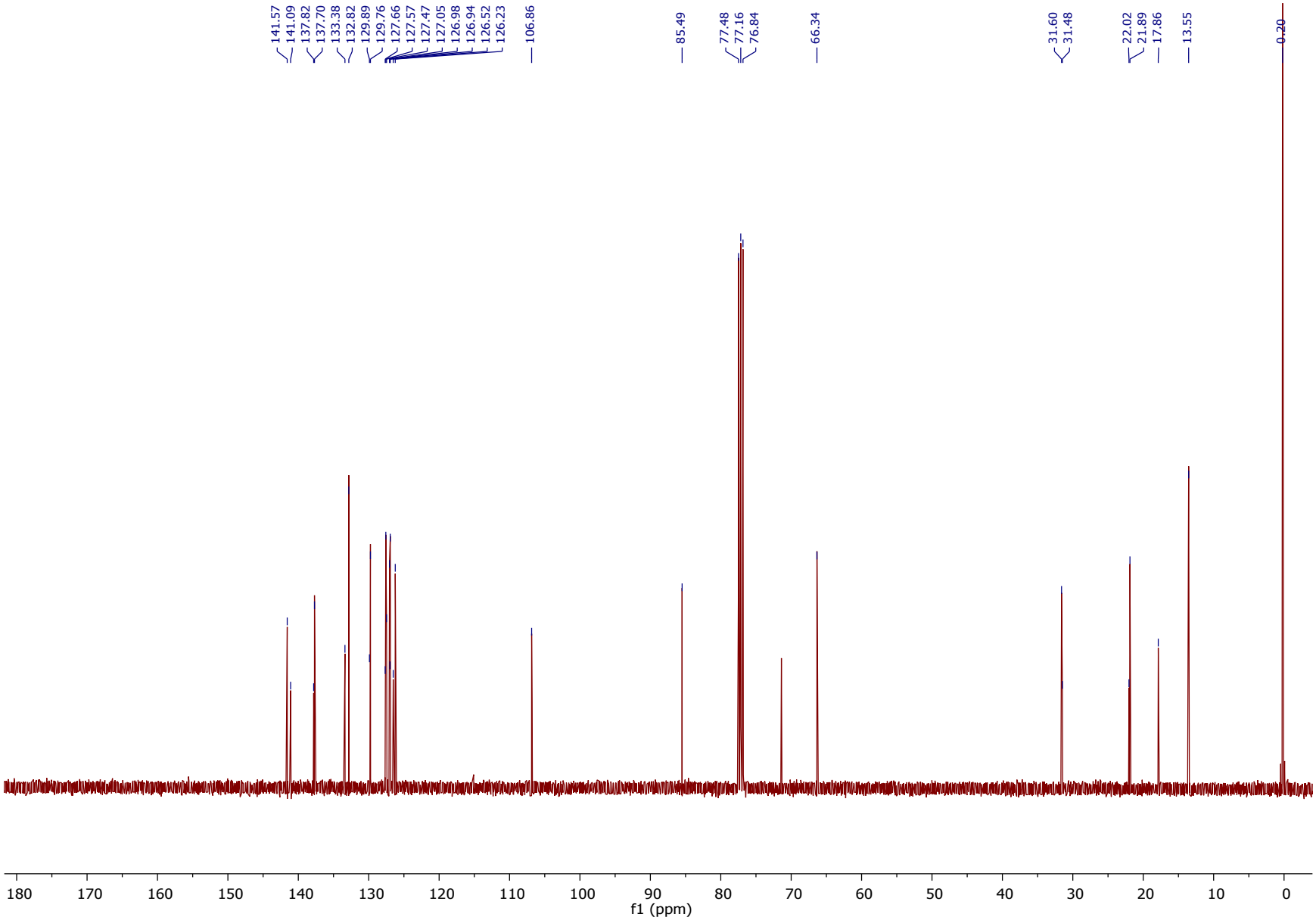

7.26 5.95 5.93 5.93 5.92 5.90 5.89 5.89 5.89 5.88 5.88 5.87 5.87 5.87 5.86 5.85 5.84 5.84 5.83 5.83 5.81
5.10 5.10 5.09 5.09 5.09 5.08 5.08 5.08 5.08 5.05 5.05 5.04 5.04 5.04 4.07
2.38 2.38 2.37 2.36 2.35 2.35
1.86 1.84 1.81 1.81 1.80 1.79 1.78 1.77 1.75 1.74 1.74 1.73 1.60 1.58 1.58 1.57 1.56 1.56 1.55 1.54 1.54 1.53 1.51 1.49 1.49 1.47
H3C
Si
H3C
CH3
O
H2C
0.91
1.89
1.90
2.00
3.97
4.73
9.40
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

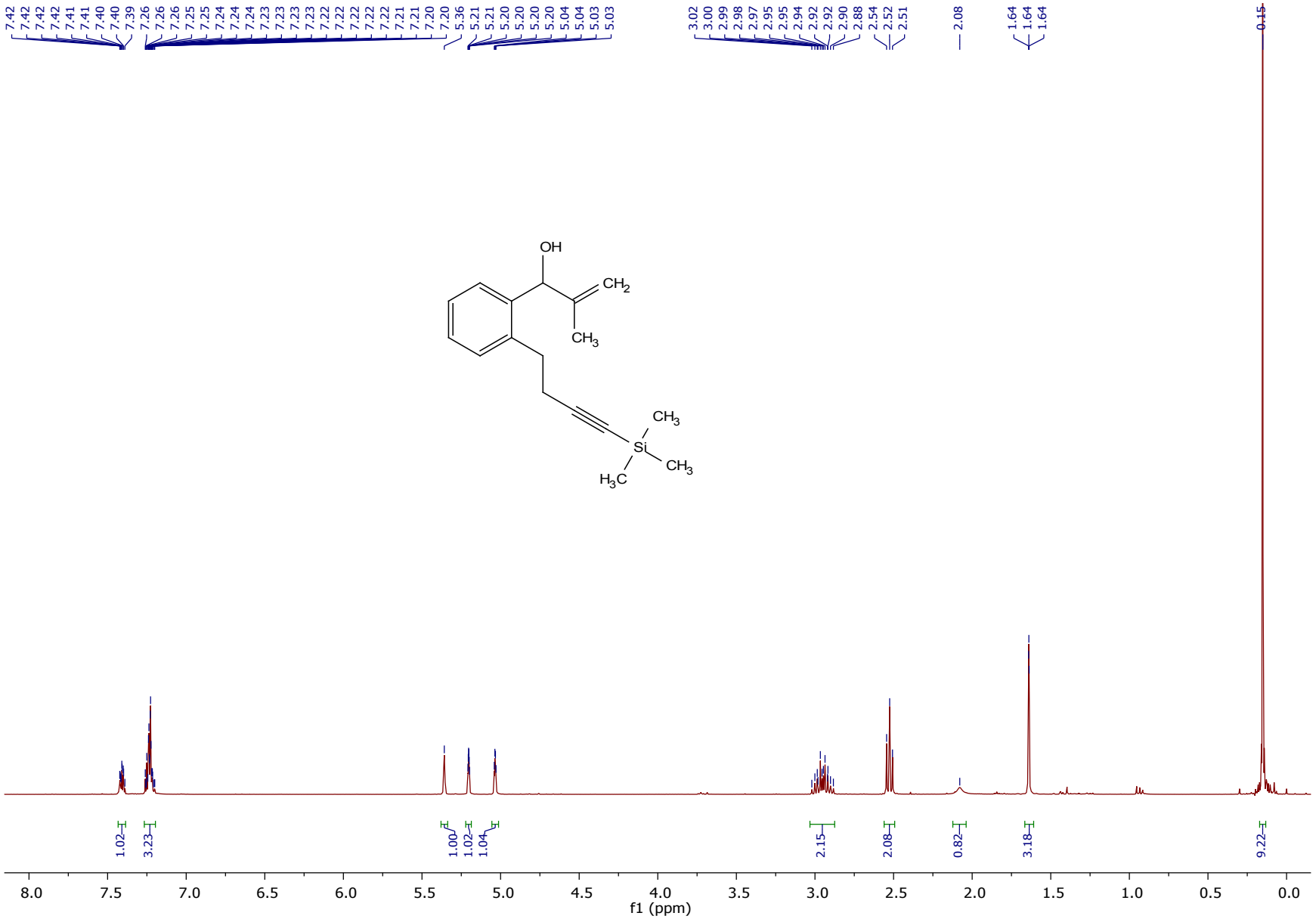

134.79
117.29
103.50
89.75
88.05
77.58
77.16
76.74
51.64
40.95
36.13
23.91
-0.03
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

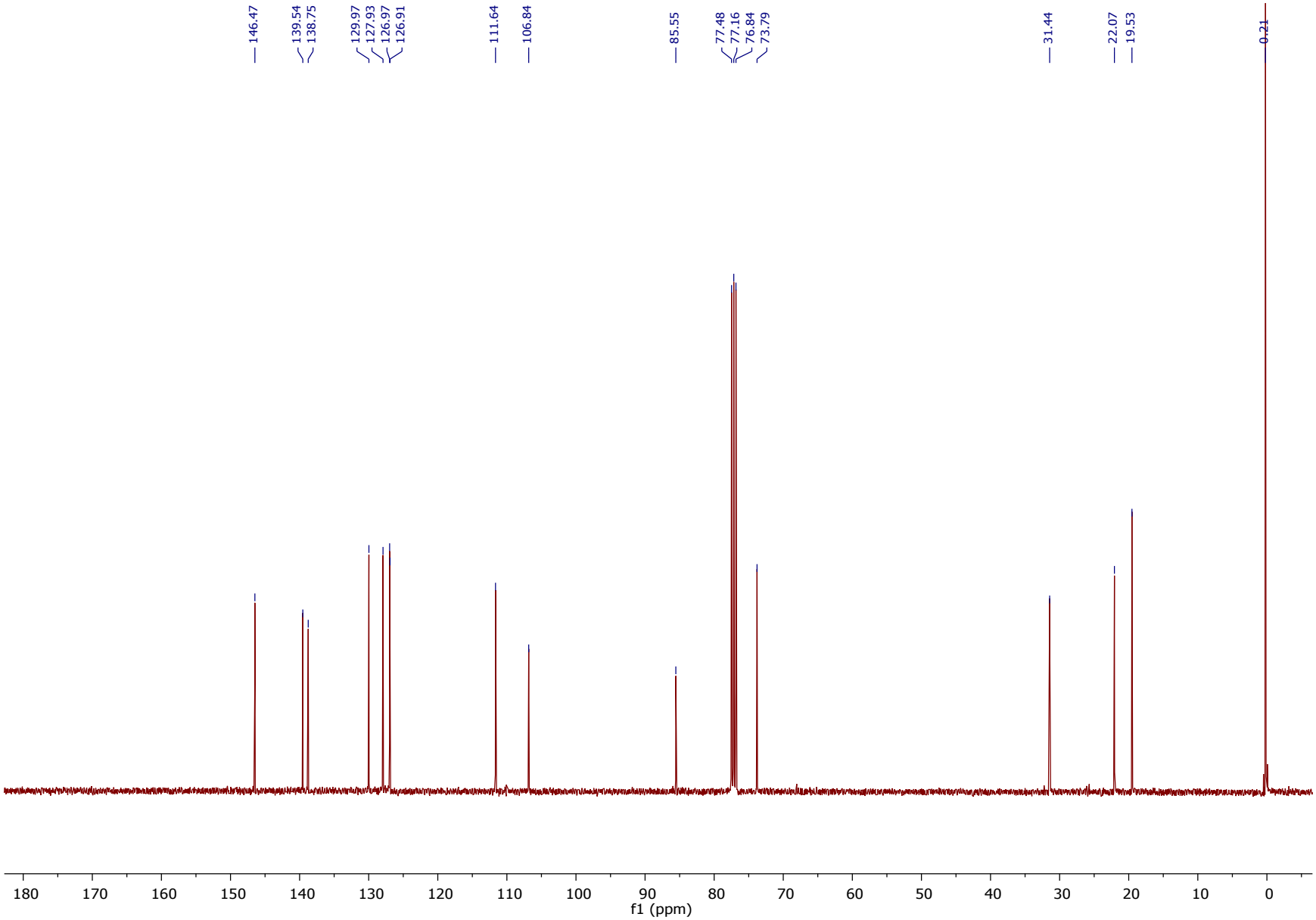

7.46 7.45 7.44 7.44 7.43 7.42 7.42 7.41 7.28 7.28 7.27 7.27 7.27 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.25 7.24 7.23 7.23 7.22 7.22 7.21 7.21 6.15 6.13 6.11 6.09 6.09 6.07 6.06 6.04 5.51 5.49 5.39 5.39 5.38 5.34 5.33 5.33 5.26 5.25 5.25 5.22 5.22 5.21
2.97 2.95 2.92
2.55 2.53 2.50
1.94
0.14
OH
CH2
CH3
CH3
Si
H3C
1.01 3.83 1.00 1.00 1.00 1.00 2.02 2.00 0.86 9.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

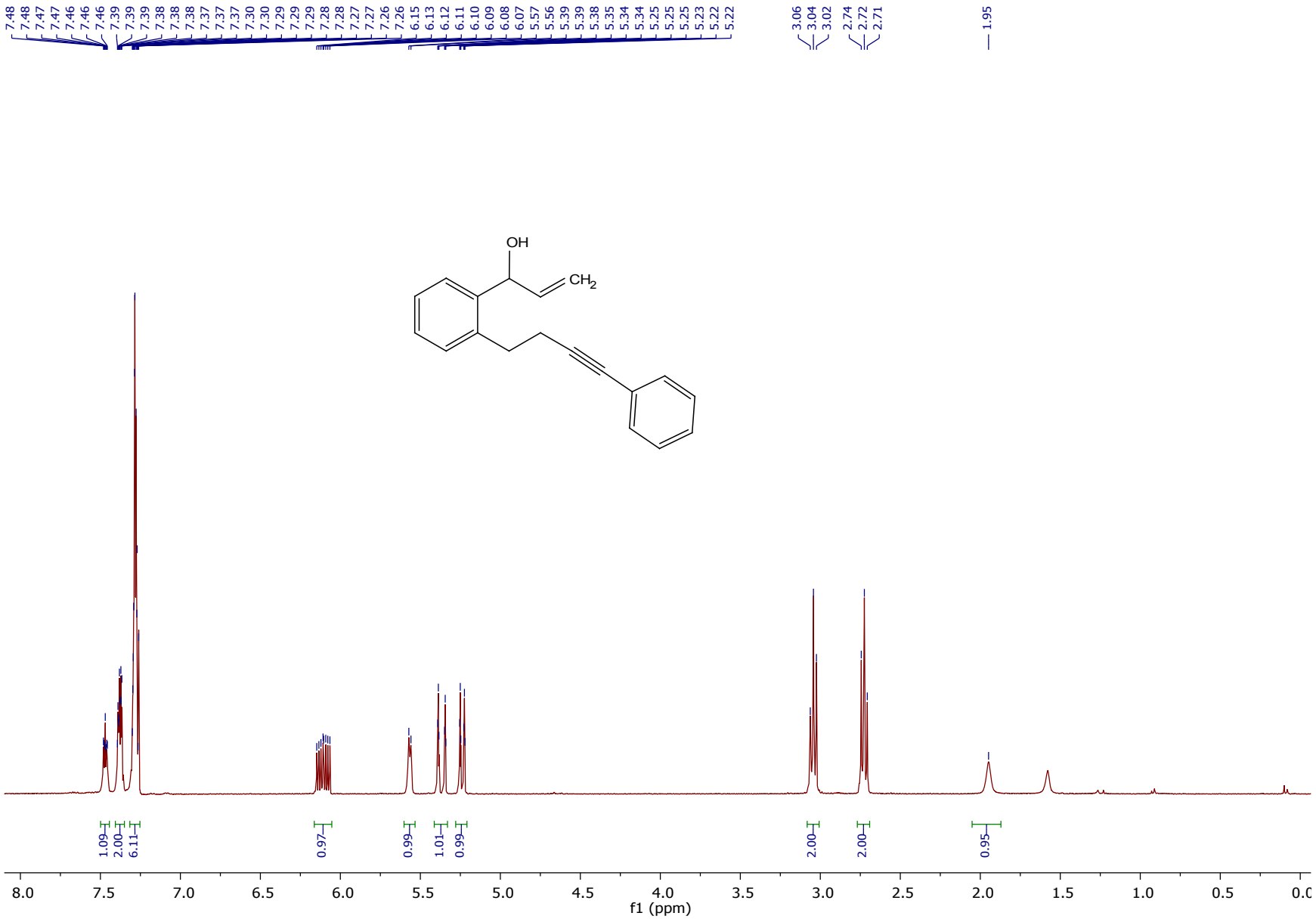

140.36
140.07
138.24
128.01
127.07
126.92
115.24
106.73
85.67
77.37
77.16
76.95
71.51
31.44
22.17
0.22
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

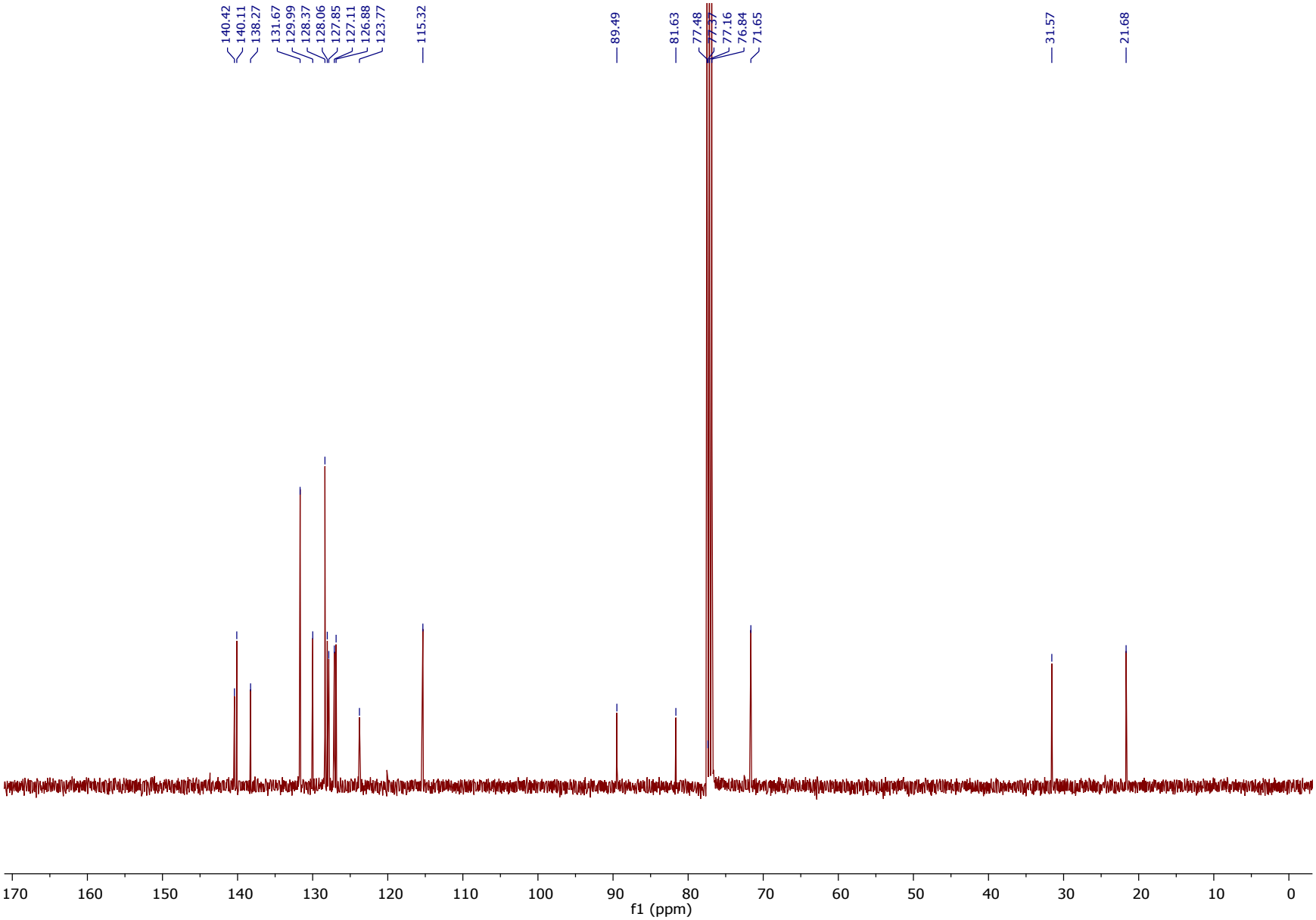

7.57 7.57 7.57 7.55 7.55 7.55 7.55 7.49 7.49 7.47 7.47 7.47 7.28 7.28 7.27 7.26 7.26 7.26 7.25 7.24 7.24 7.24 7.24 7.23 7.22 7.22 7.22 7.21 7.21 7.20 7.20 7.20 7.19 7.18 7.18 7.17 5.80 5.78 5.74 5.73 5.73 5.73 5.72 5.72 5.72 5.68 5.67 5.67 5.66 5.66 5.65 5.64 5.43 5.42 2.94 2.93 2.93 2.92 2.91 2.90 2.90 2.89 2.88 2.53 2.51 2.51 2.50 2.49 2.49 2.48 2.01 1.98 1.83 1.82 1.82 1.82 1.81 1.81 1.81 1.73 1.73 1.73 1.73 1.72 1.72 1.72 0.15
OH
CH3
Si
H3C
CH3
CH3
OH
CH3
Si
H3C
CH3
CH3
0.64
0.36
3.07
0.64
0.64
1.32
0.36
2.00
2.01
0.31
0.60
1.92
1.08
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

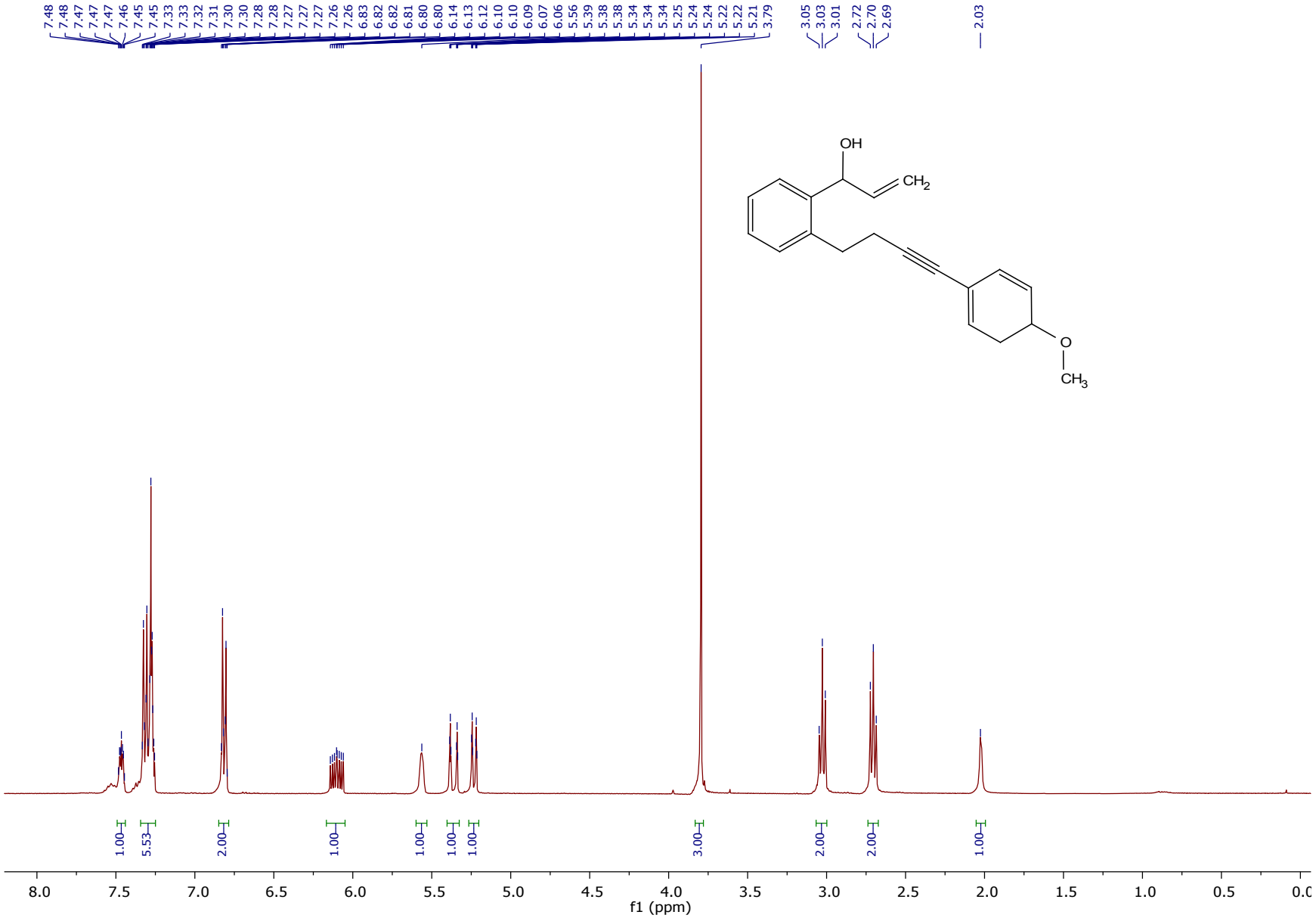

141.57
141.09
137.82
137.70
133.38
132.82
129.89
129.76
127.66
127.57
127.47
127.05
126.98
126.94
126.52
126.23
106.86
85.49
77.48
77.16
76.84
66.34
31.60
31.48
22.02
21.89
17.86
13.55
0.20
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

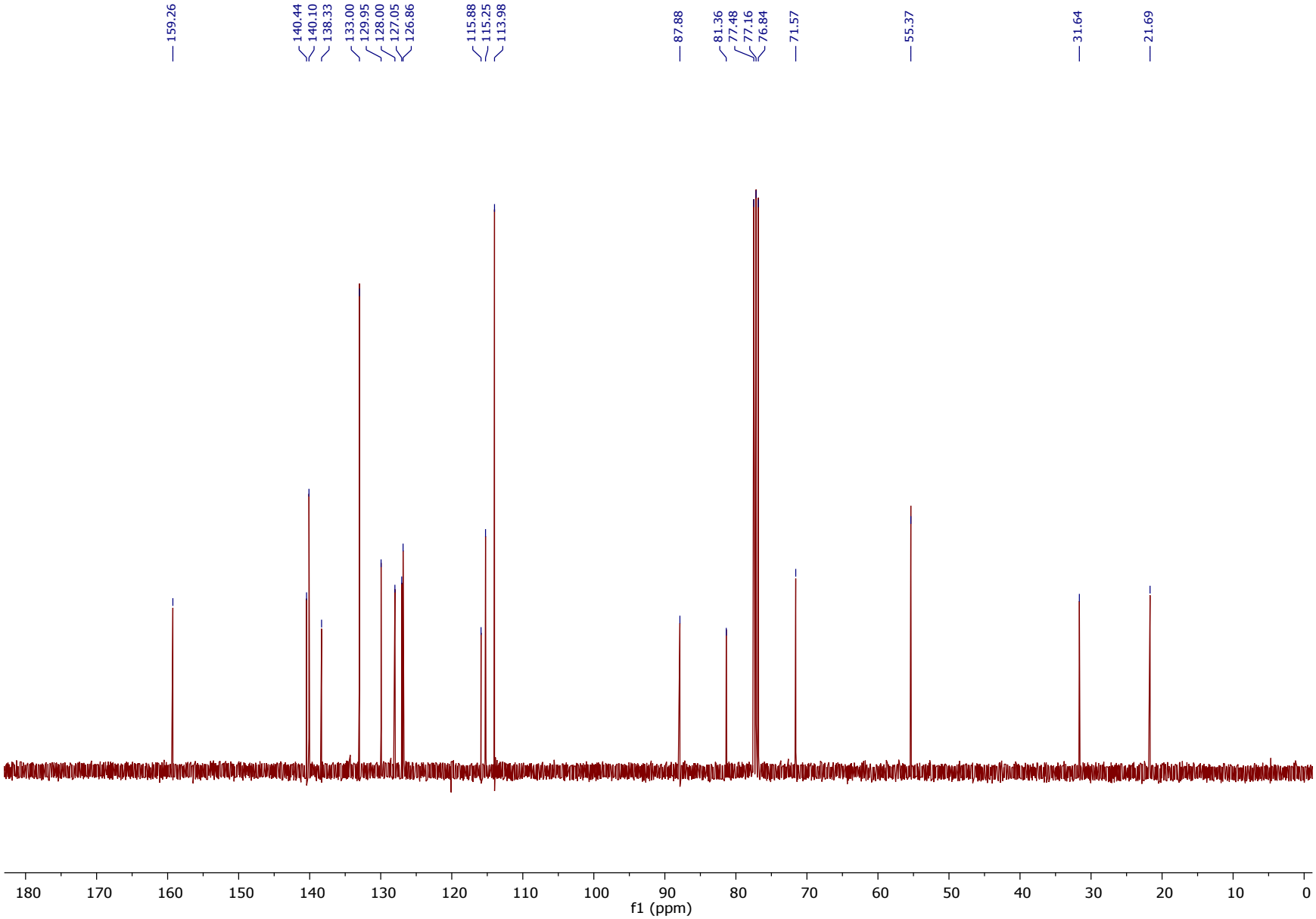

7.42 7.42 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.26 7.26 7.26 7.25 7.25 7.24 7.24 7.24 7.23 7.23 7.23 7.23 7.22 7.22 7.22 7.22 7.21 7.21 7.20 7.20 5.36 5.21 5.21 5.20 5.20 5.20 5.20 5.04 5.04 5.03 5.03
3.02 3.00 2.99 2.98 2.97 2.95 2.95 2.94 2.92 2.92 2.90 2.88 2.54 2.52 2.51
2.08
1.64 1.64 1.64
0.15
OH
CH2
CH3
CH3
Si
CH3
H3C
1.02 3.23 1.00 1.02 1.04 2.15 2.08 0.82 3.18 9.22
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

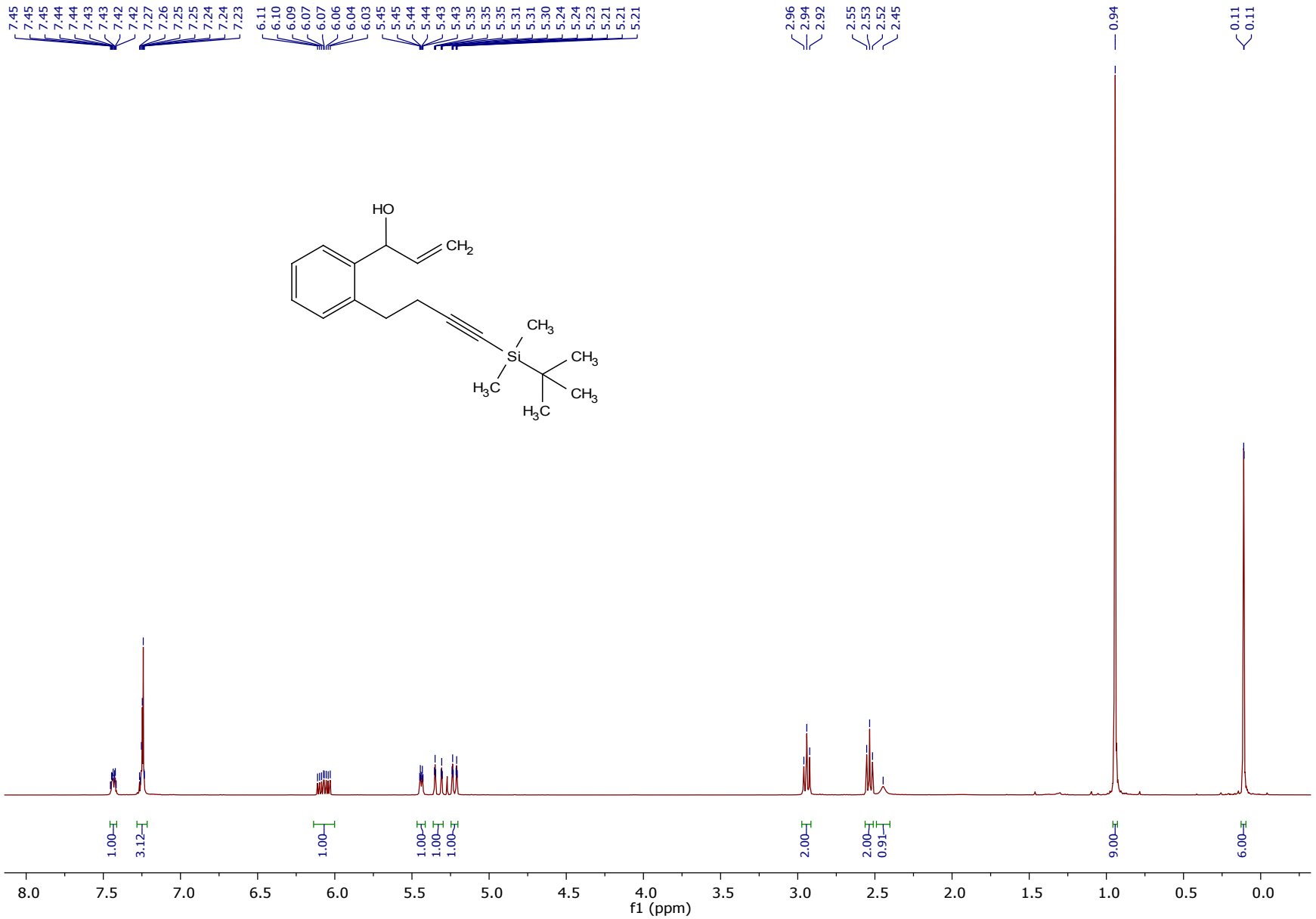

146.47
139.54
138.75
129.97
127.93
126.97
126.91
111.64
106.84
85.55
77.48
77.16
76.84
73.79
31.44
22.07
19.53
0.21
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

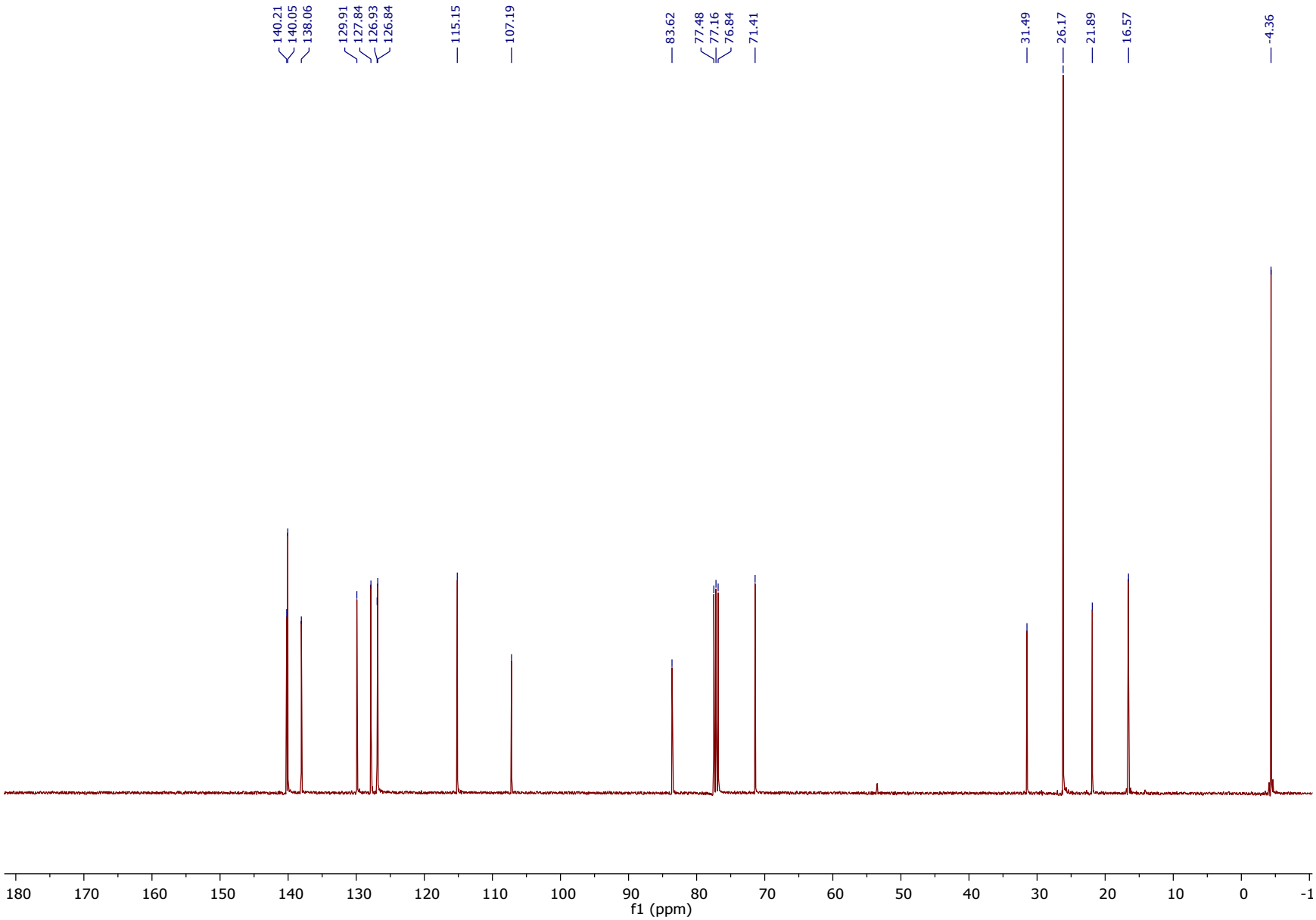

7.48 7.48 7.47 7.47 7.46 7.46 7.46 7.39 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.37 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.26 6.15 6.13 6.12 6.11 6.10 6.09 6.08 6.07 5.57 5.56 5.39 5.39 5.38 5.35 5.34 5.34 5.25 5.25 5.25 5.23 5.22 5.22
3.06 3.04 3.02 2.74 2.72 2.71
1.95
OH
CH2
1.09 2.00 6.11 0.97 0.99 1.01 0.99 2.00 2.00 0.95
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

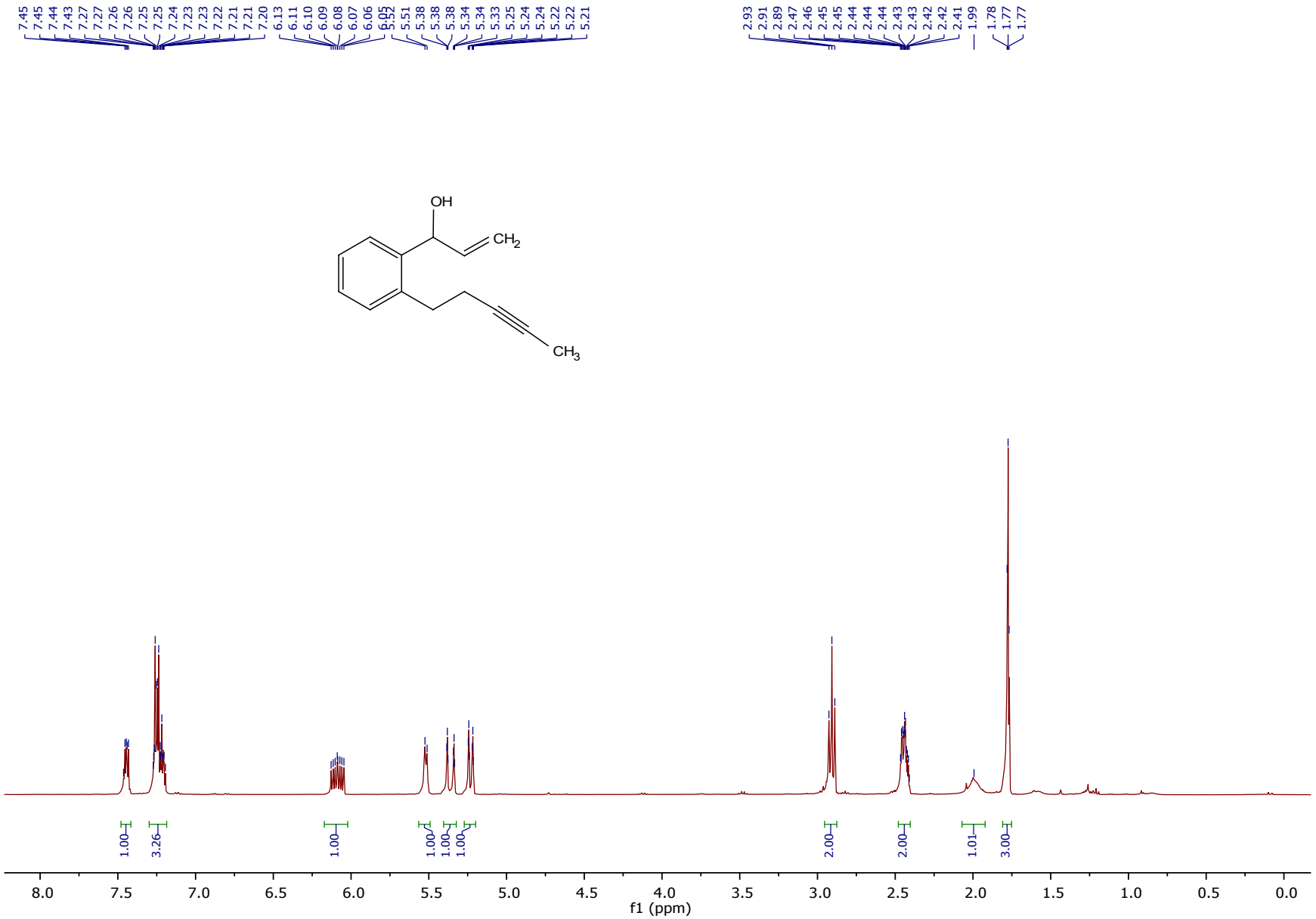

140.42
140.11
138.27
131.67
129.99
128.37
128.06
127.85
127.11
126.88
123.77
115.32
89.49
81.63
77.48
77.37
77.16
76.84
71.65
31.57
21.68
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

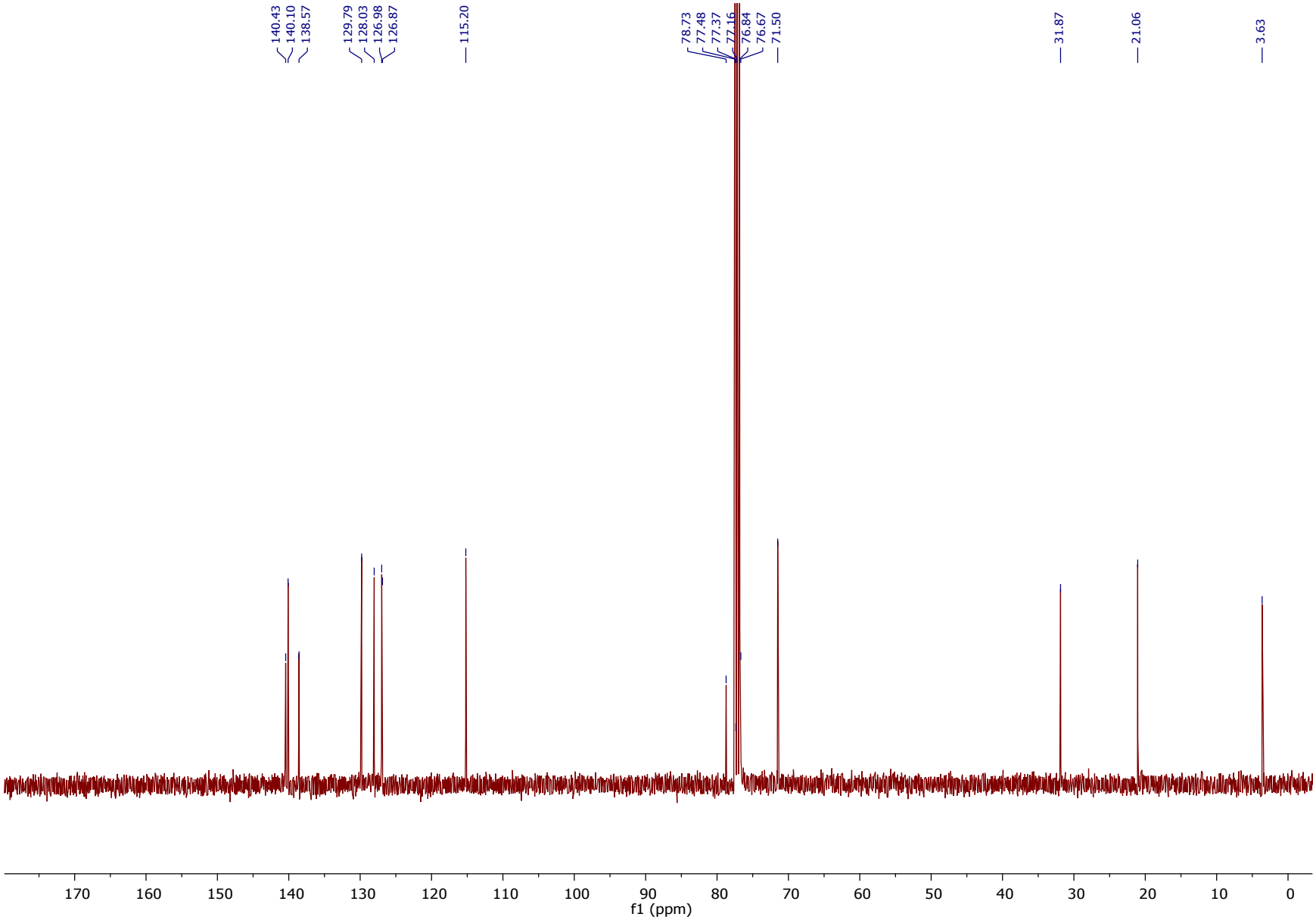

7.48 7.48 7.47 7.47 7.47 7.46 7.45 7.45 7.33 7.33 7.32 7.31 7.30 7.30 7.28 7.28 7.27 7.27 7.27 7.26 7.26 6.83 6.82 6.82 6.81 6.80 6.80 6.14 6.13 6.12 6.10 6.10 6.09 6.07 6.06 5.56 5.39 5.38 5.38 5.34 5.34 5.34 5.25 5.24 5.24 5.22 5.22 5.21 3.79
3.05 3.03 3.01
2.72 2.70 2.69
2.03
OH
CH2
O
CH3
1.00 5.53 2.00 1.00 1.00 1.00 1.00 3.00 2.00 2.00 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

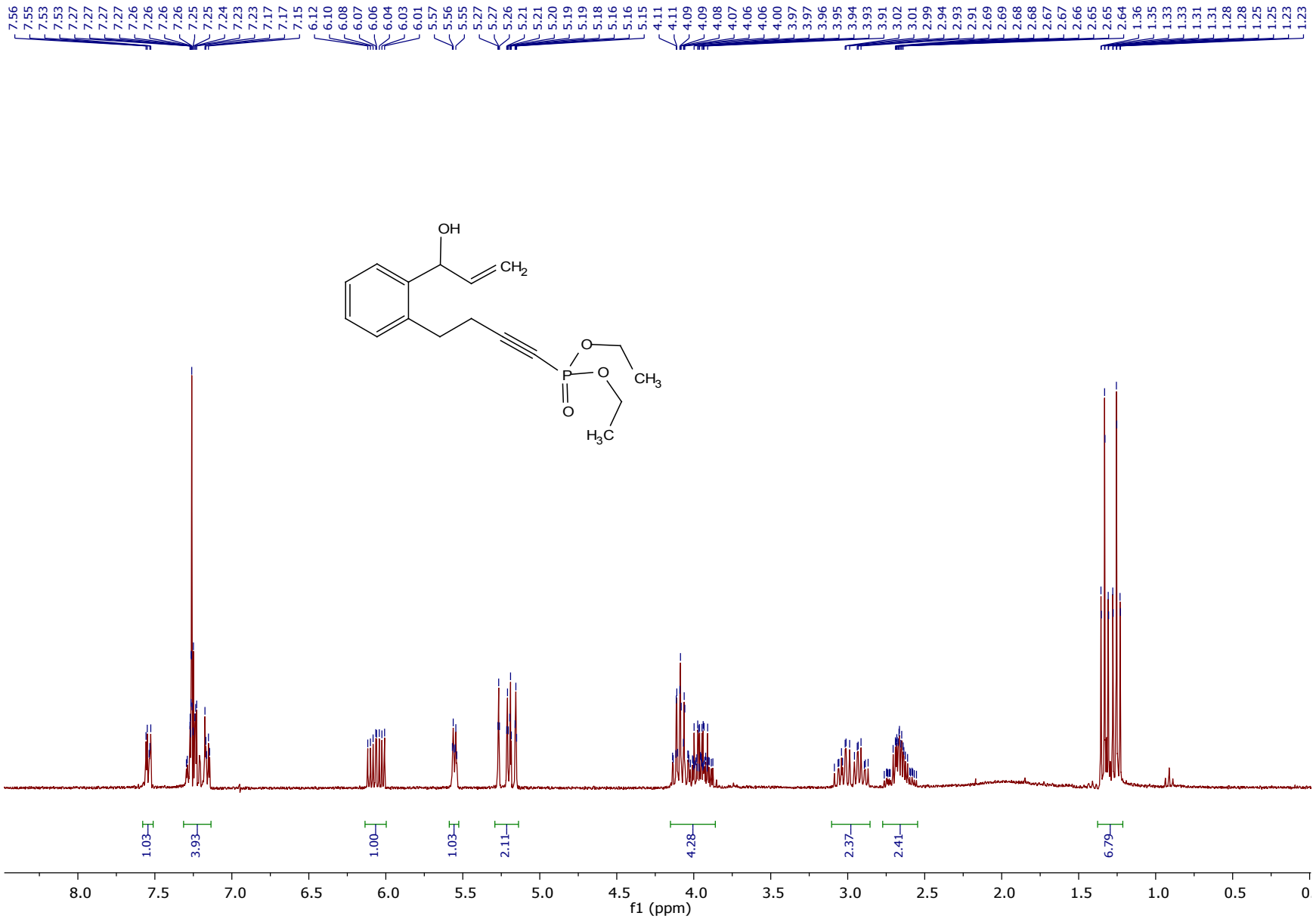

159.26
140.44
140.10
138.33
133.00
129.95
128.00
127.05
126.86
115.88
115.25
113.98
87.88
81.36
77.48
77.16
76.84
71.57
55.37
31.64
21.69
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

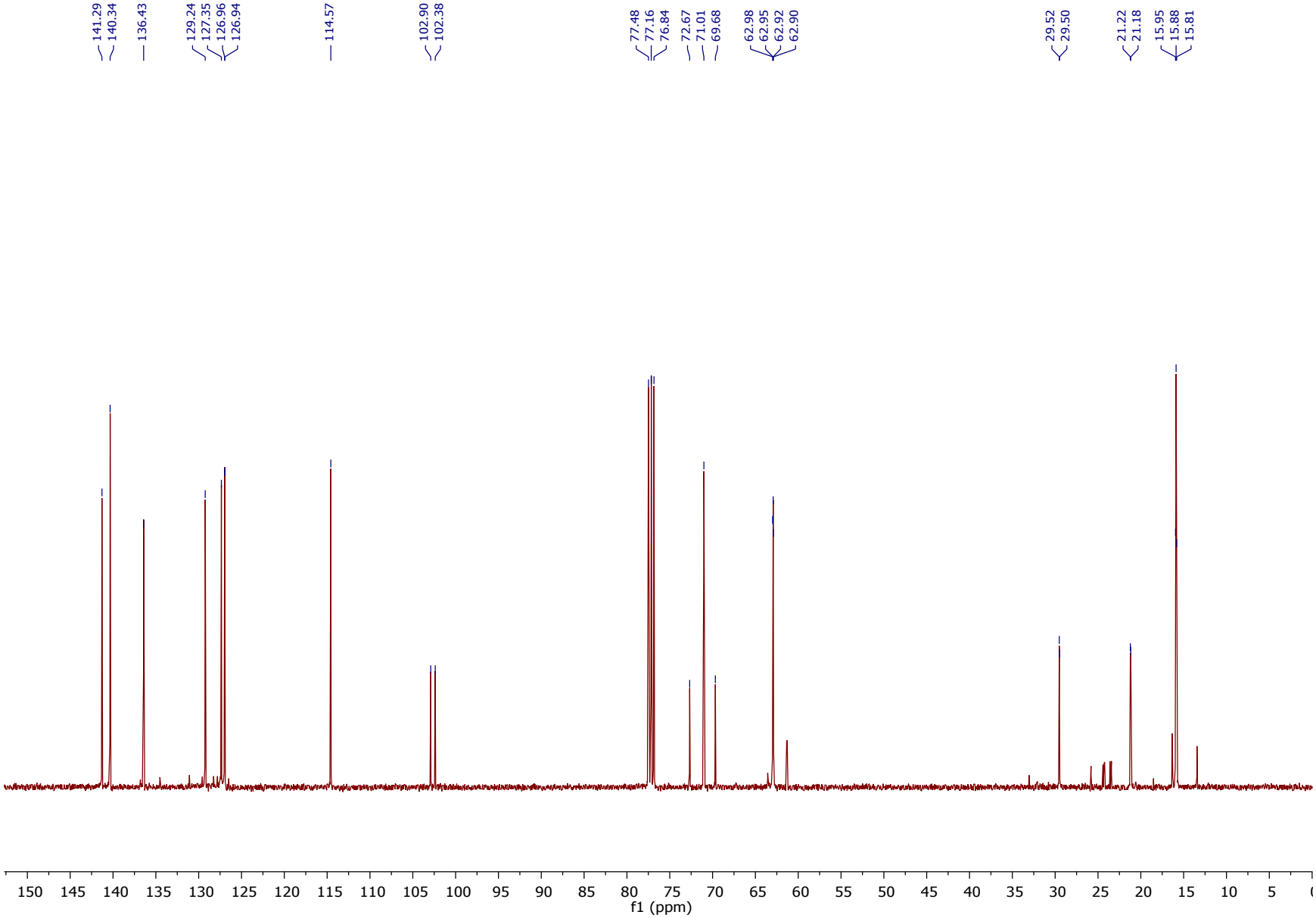

7.45 7.45 7.45 7.44 7.44 7.43 7.43 7.42 7.42 7.27 7.26 7.25 7.25 7.24 7.24 7.23
6.11 6.10 6.09 6.07 6.07 6.06 6.04 6.03
5.45 5.45 5.44 5.44 5.43 5.43 5.35 5.35 5.35 5.31 5.31 5.30 5.24 5.24 5.23 5.21 5.21 5.21
2.96 2.94 2.92
2.55 2.53 2.52 2.45
0.94
0.11 0.11
HO
CH2
CH3
Si
CH3
H3C
CH3
H3C
1.00 3.12 1.00 1.00 1.00 1.00 2.00 2.00 0.91 9.00 6.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

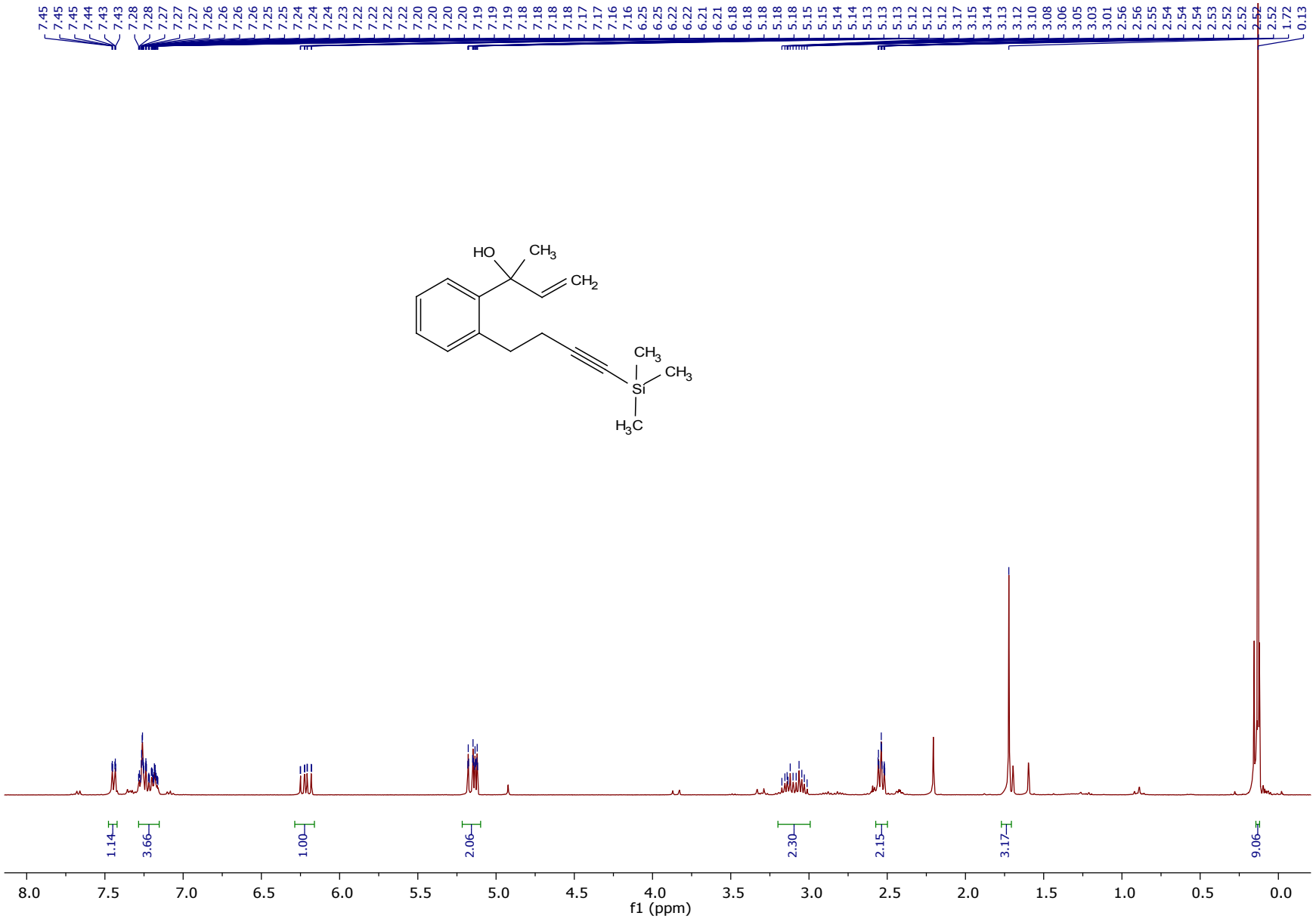

140.21
140.05
138.06
129.91
127.84
126.93
126.84
115.15
107.19
83.62
77.48
77.16
76.84
71.41
31.49
26.17
21.89
16.57
-4.36
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

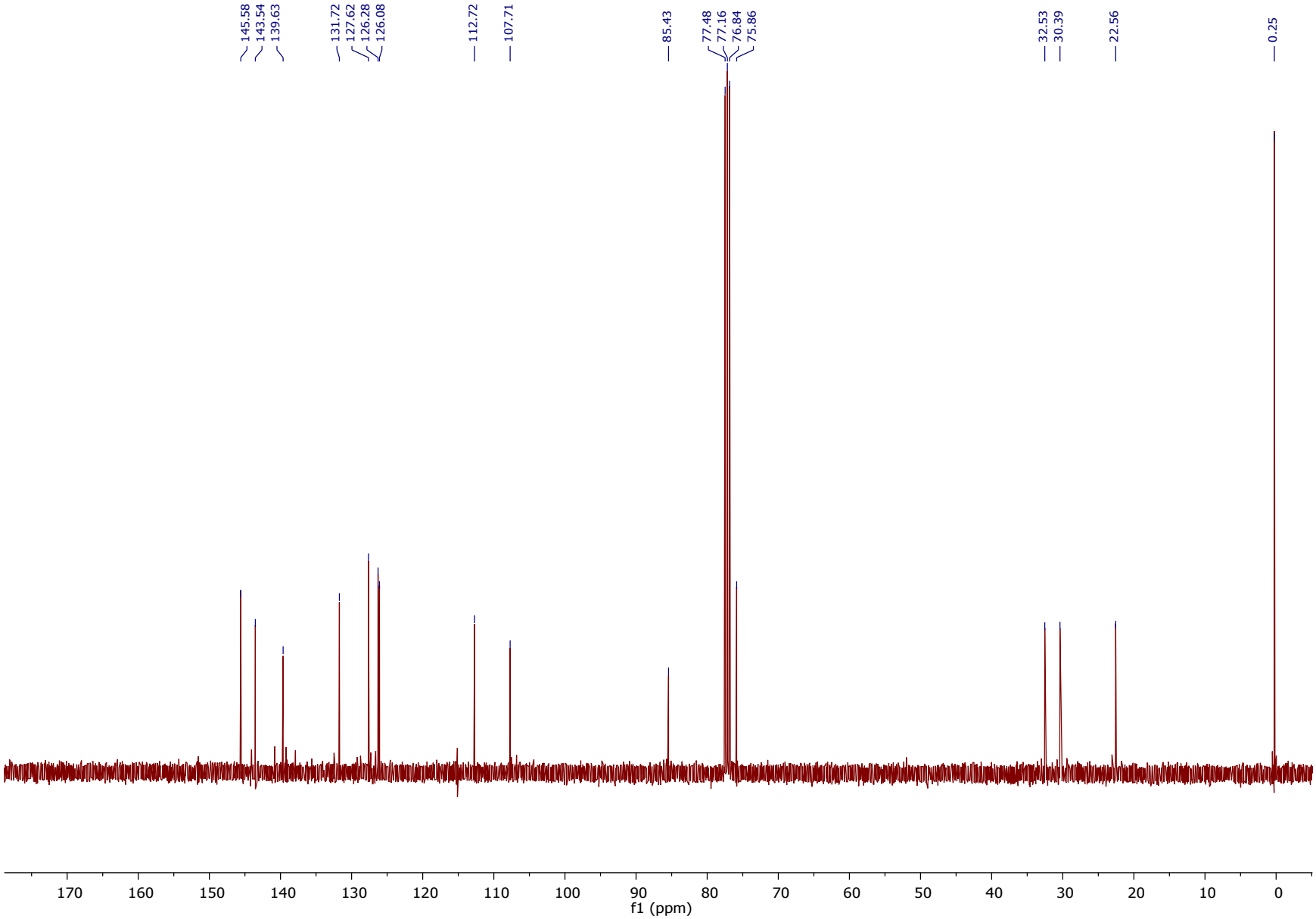

7.45 7.45 7.44 7.43 7.27 7.27 7.26 7.26 7.25 7.25 7.24 7.23 7.23 7.22 7.21 7.21 7.20 6.13 6.11 6.10 6.09 6.08 6.07 6.06 6.05 5.52 5.51 5.38 5.38 5.34 5.34 5.33 5.25 5.24 5.24 5.22 5.22 5.21
2.93 2.91 2.89 2.47 2.46 2.45 2.45 2.44 2.44 2.44 2.43 2.43 2.42 2.42 2.41 1.99 1.78 1.77 1.77
OH
CH2
CH3
1.00 3.26 1.00 1.00 1.00 1.00 2.00 2.00 1.01 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

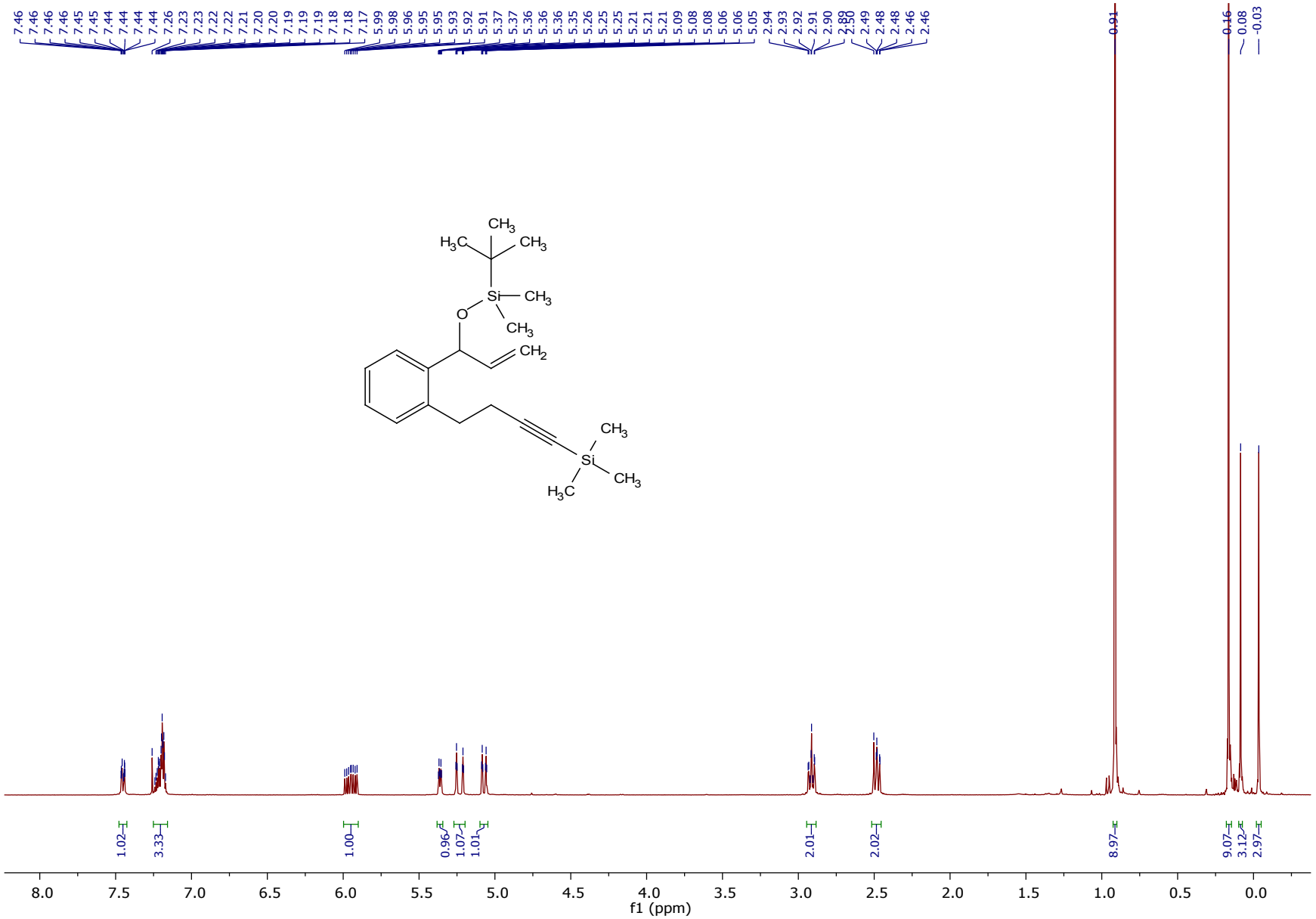

140.43
140.10
138.57
129.79
128.03
126.98
126.87
115.20
78.73
77.48
77.37
77.16
76.84
76.67
71.50
31.87
21.06
3.63
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

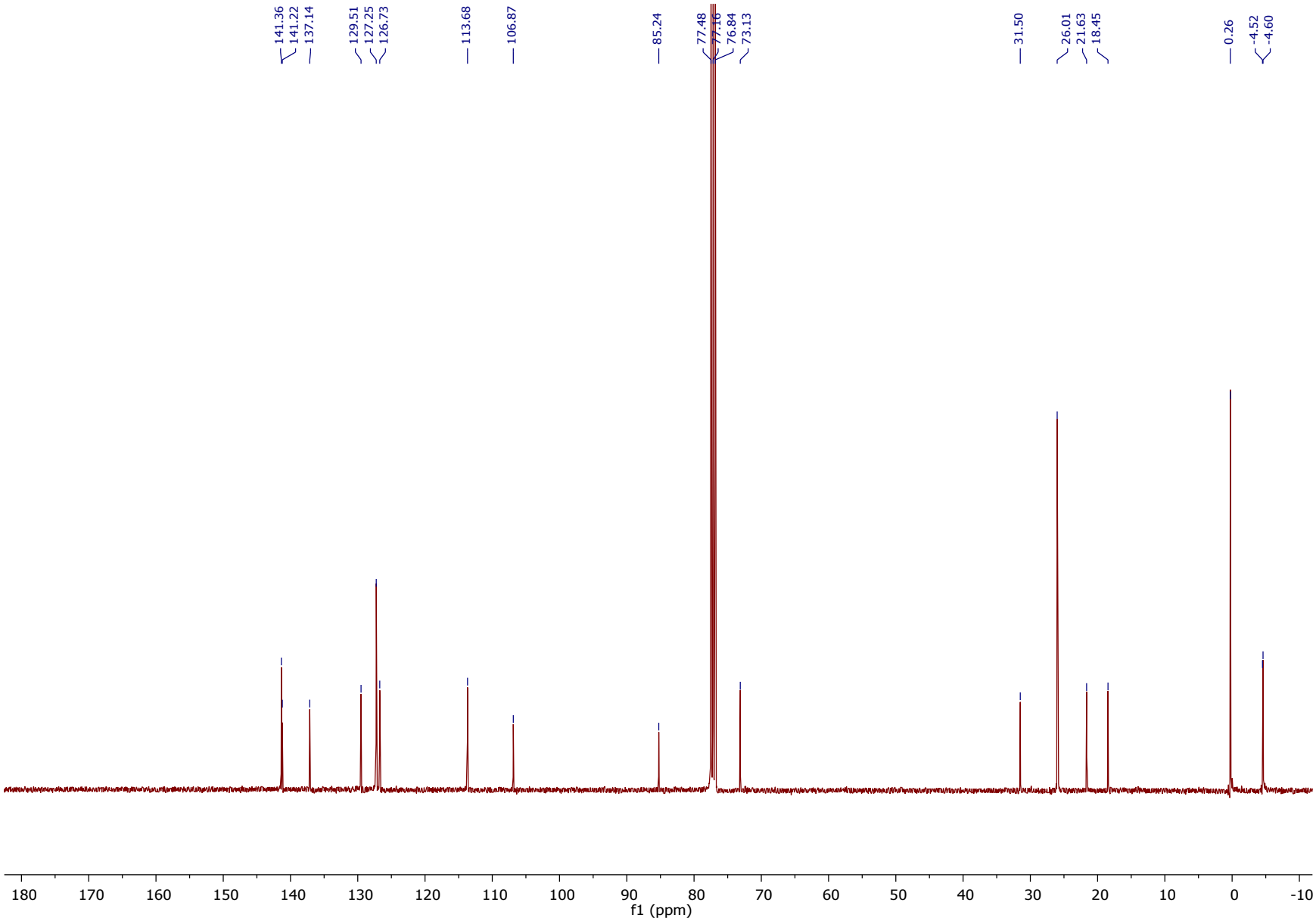

7.56 7.55 7.53 7.53 7.27 7.27 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.24 7.23 7.23 7.17 7.17 7.15 6.12 6.10 6.08 6.07 6.06 6.04 6.03 6.01 5.57 5.56 5.55 5.27 5.27 5.26 5.21 5.21 5.20 5.19 5.19 5.18 5.16 5.16 5.15 4.11 4.11 4.09 4.09 4.08 4.07 4.06 4.06 4.00 3.97 3.97 3.96 3.95 3.94 3.93 3.91 3.02 3.01 2.99 2.94 2.93 2.91 2.69 2.69 2.68 2.68 2.67 2.67 2.66 2.65 2.65 2.64 1.36 1.35 1.33 1.33 1.31 1.31 1.28 1.28 1.25 1.25 1.23 1.23
OH
CH2
O
P
O
O
CH3
O
H3C
1.03
3.93
1.00
1.03
2.11
4.28
2.37
2.41
6.79
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

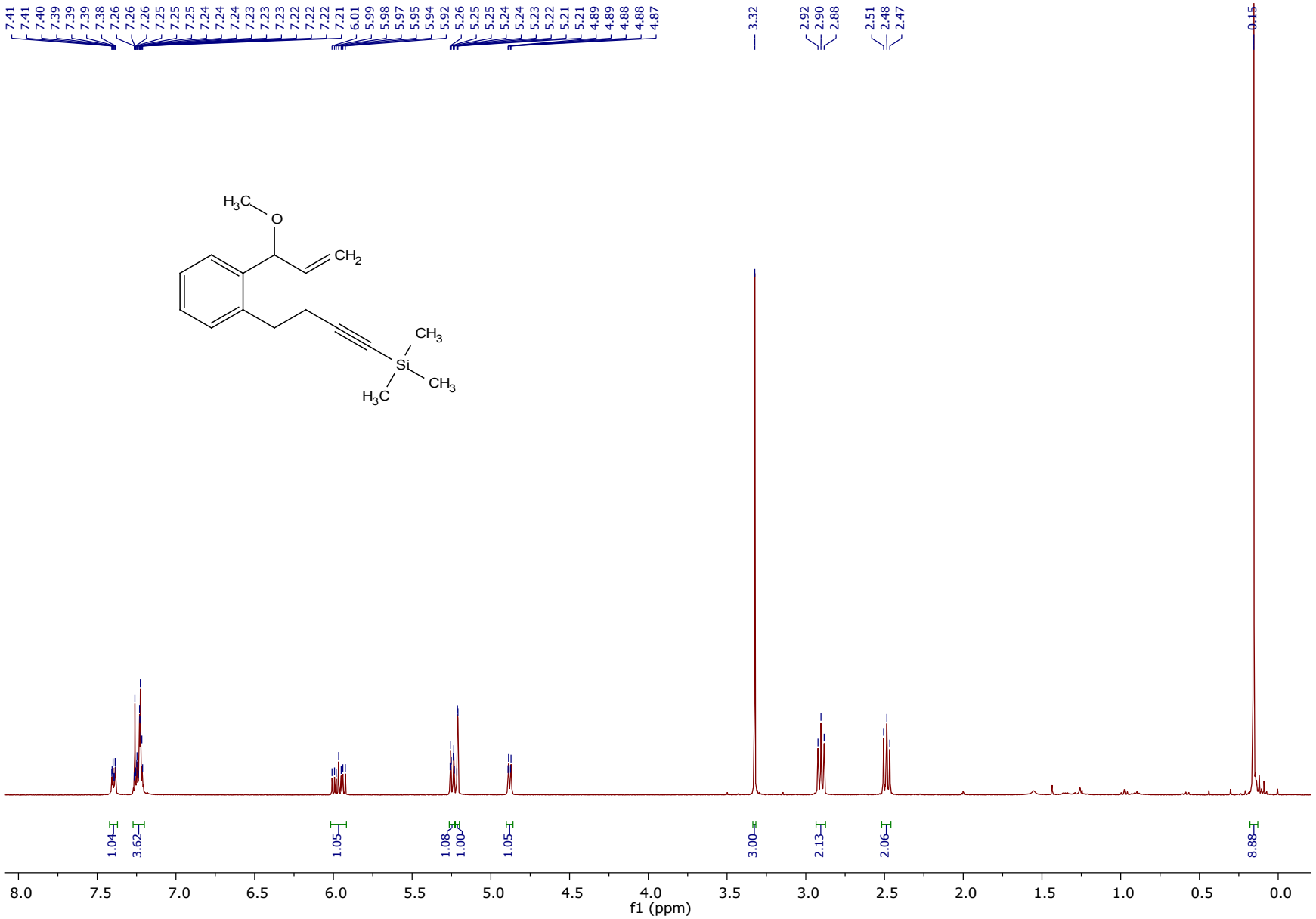

141.29
140.34
136.43
129.24
127.35
126.96
126.94
114.57
102.90
102.38
77.48
77.16
76.84
72.67
71.01
69.68
62.98
62.95
62.92
62.90
29.52
29.50
21.22
21.18
15.95
15.88
15.81
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

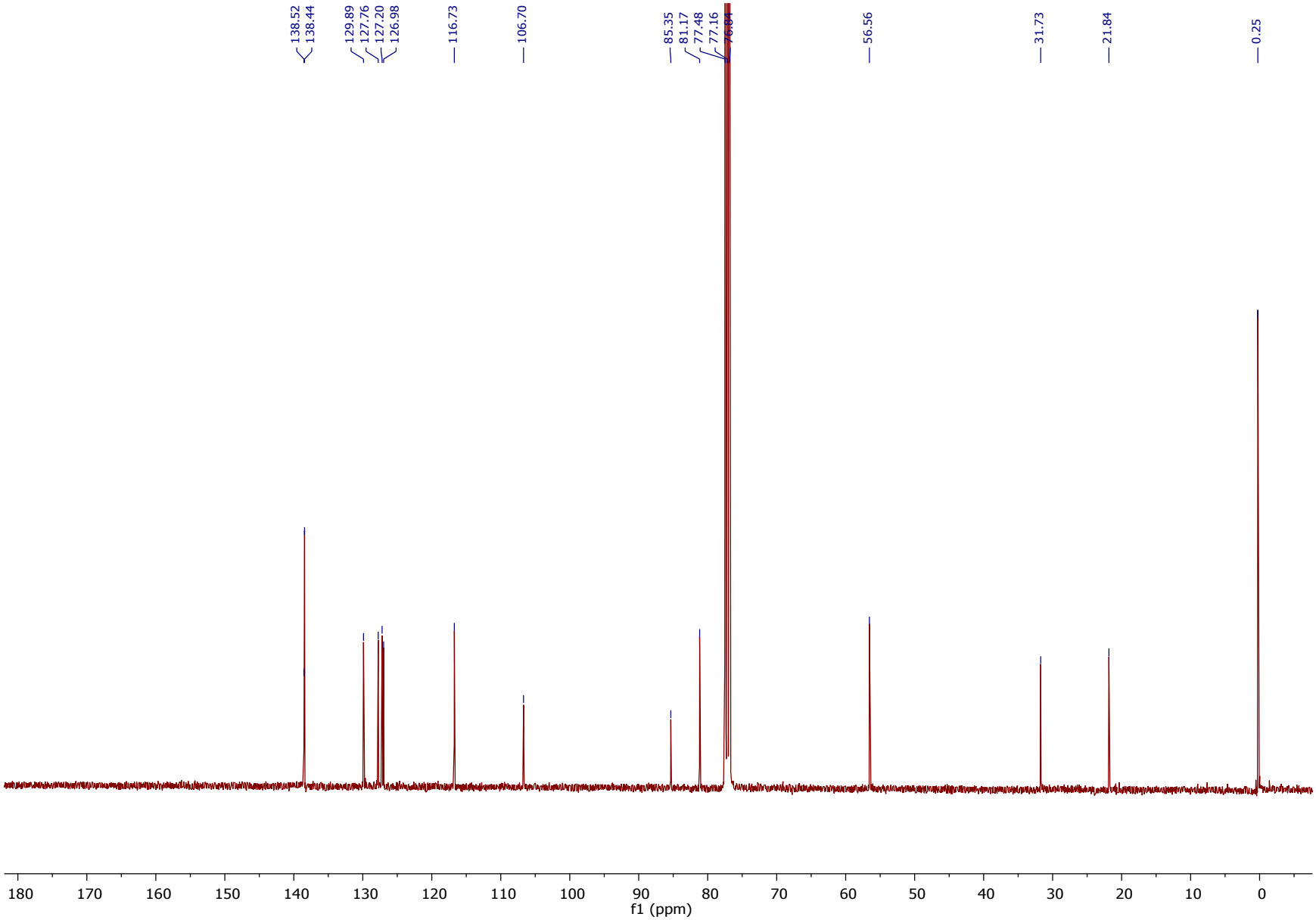

HO
CH3
CH2
CH3
CH3
Si
H3C
1.14
3.66
1.00
2.06
2.30
2.15
3.17
9.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

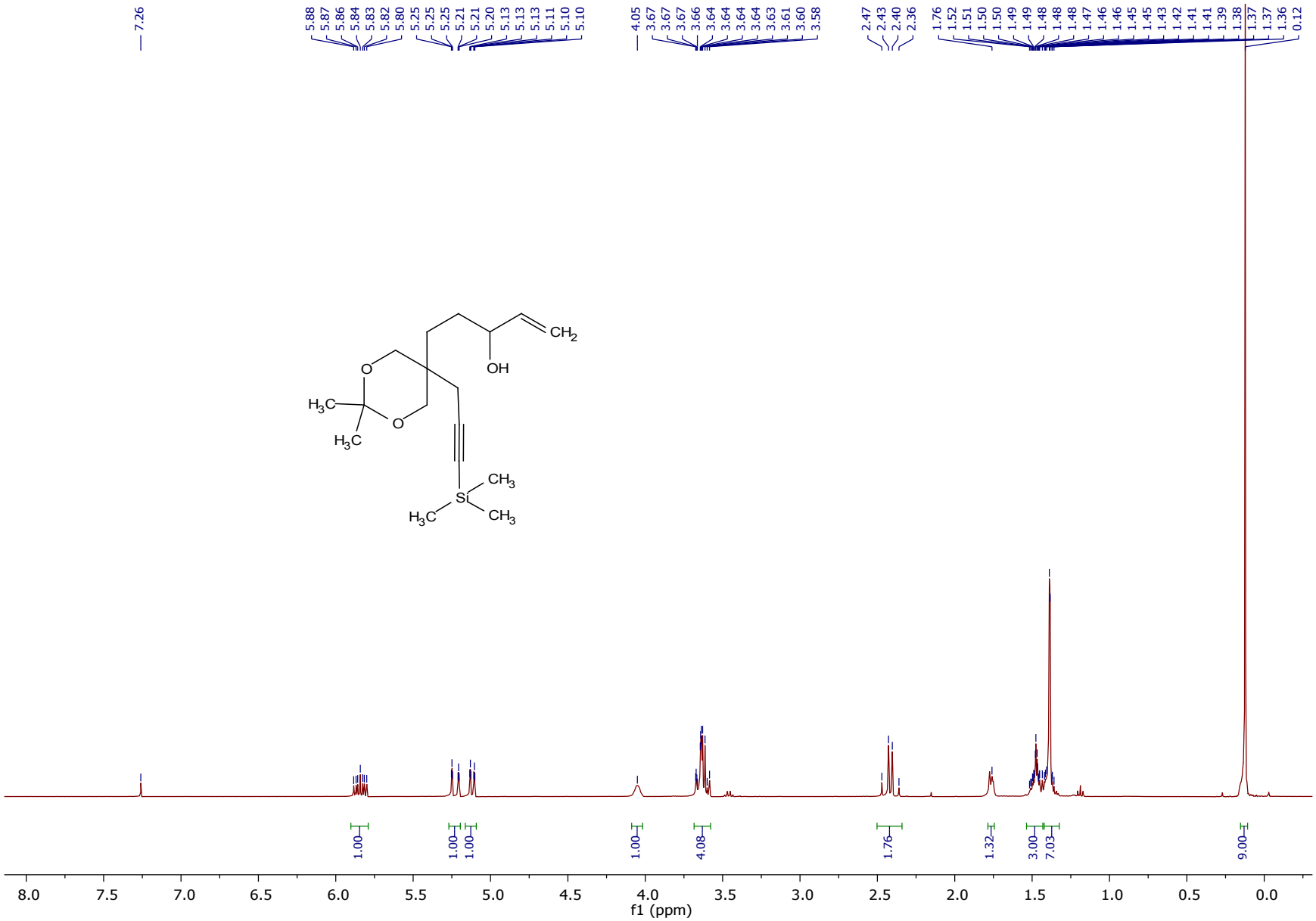

145.58
143.54
139.63
131.72
127.62
126.28
126.08
112.72
107.71
85.43
77.48
77.16
76.84
75.86
32.53
30.39
22.56
0.25
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

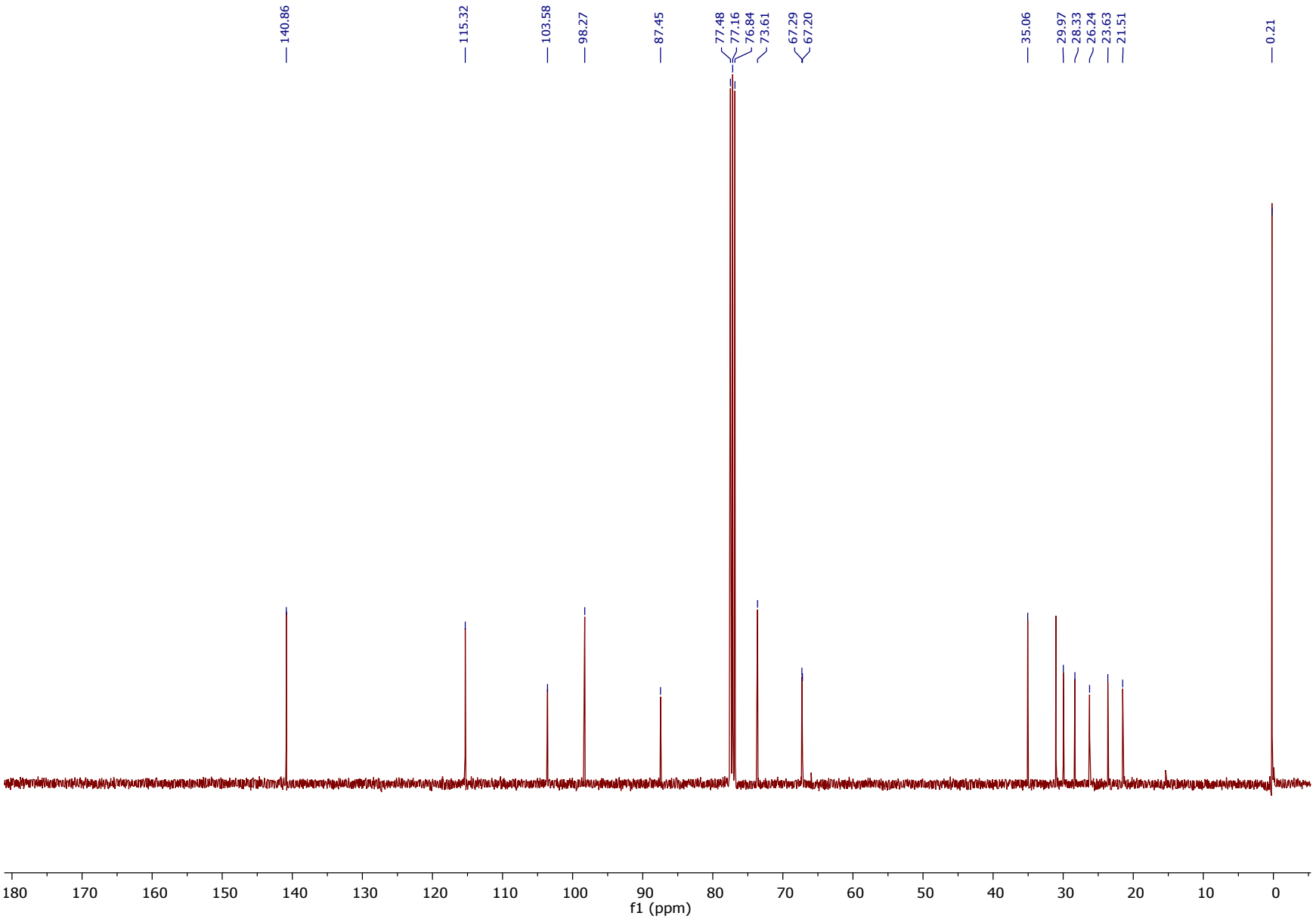

7.46 7.46 7.46 7.46 7.45 7.45 7.44 7.44 7.44 7.44 7.26 7.23 7.23 7.22 7.22 7.21 7.20 7.20 7.19 7.19 7.19 7.18 7.18 7.17 5.99 5.98 5.96 5.95 5.95 5.93 5.92 5.91 5.37 5.37 5.36 5.36 5.36 5.35 5.26 5.25 5.25 5.21 5.21 5.21 5.09 5.08 5.08 5.06 5.06 5.05 2.94 2.93 2.92 2.91 2.90 2.89 2.50 2.49 2.48 2.48 2.46 2.46
0.91
0.16
0.08
-0.03
CH3
H3C
CH3
Si
CH3
O
CH3
CH2
CH3
Si
CH3
H3C
1.02
3.33
1.00
0.96
1.07
1.01
2.01
2.02
8.97
9.07
3.12
2.97
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

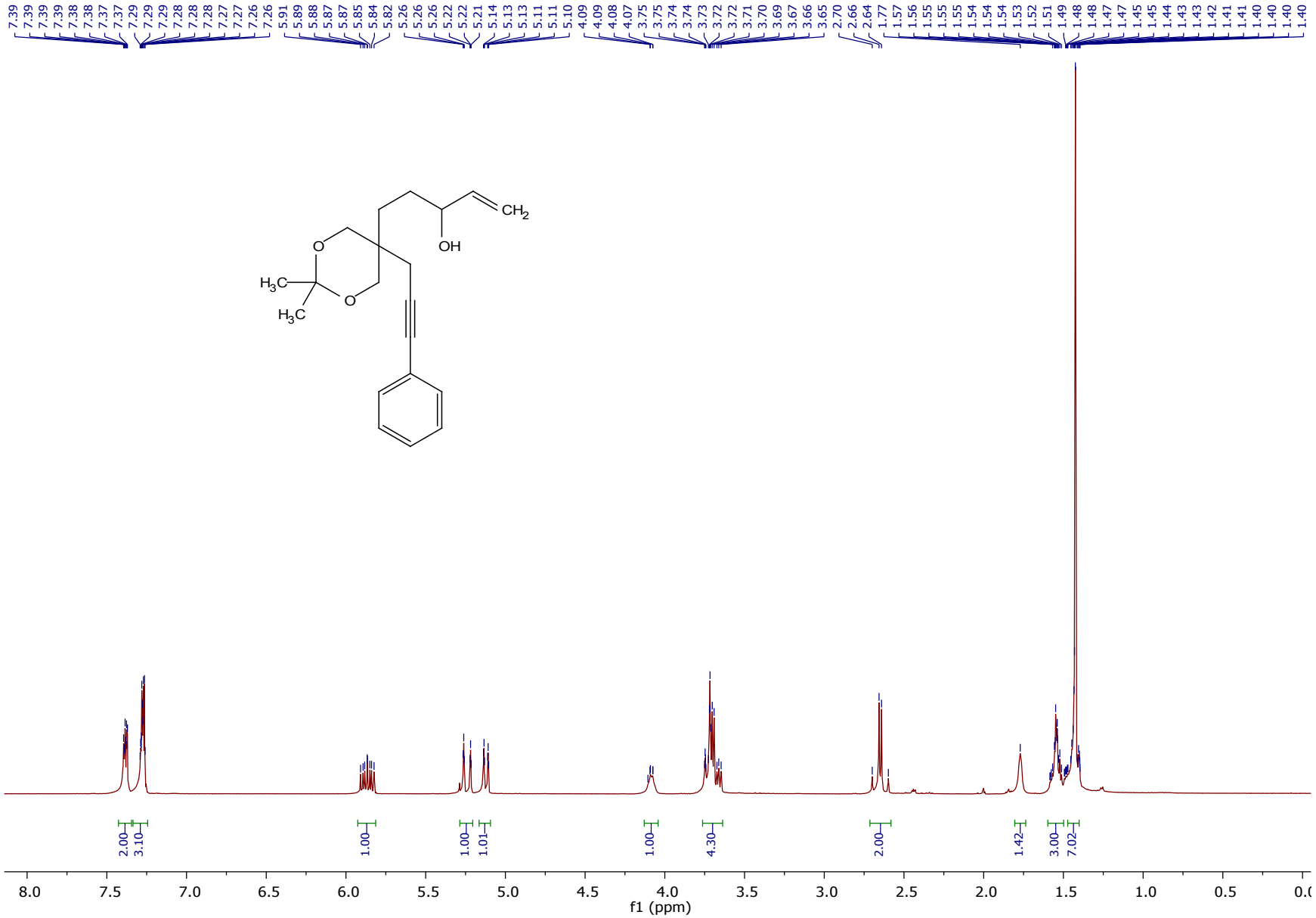

141.36
141.22
137.14
129.51
127.25
126.73
113.68
106.87
85.24
77.48
77.16
76.84
73.13
31.50
26.01
21.63
18.45
0.26
-4.52
-4.60
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

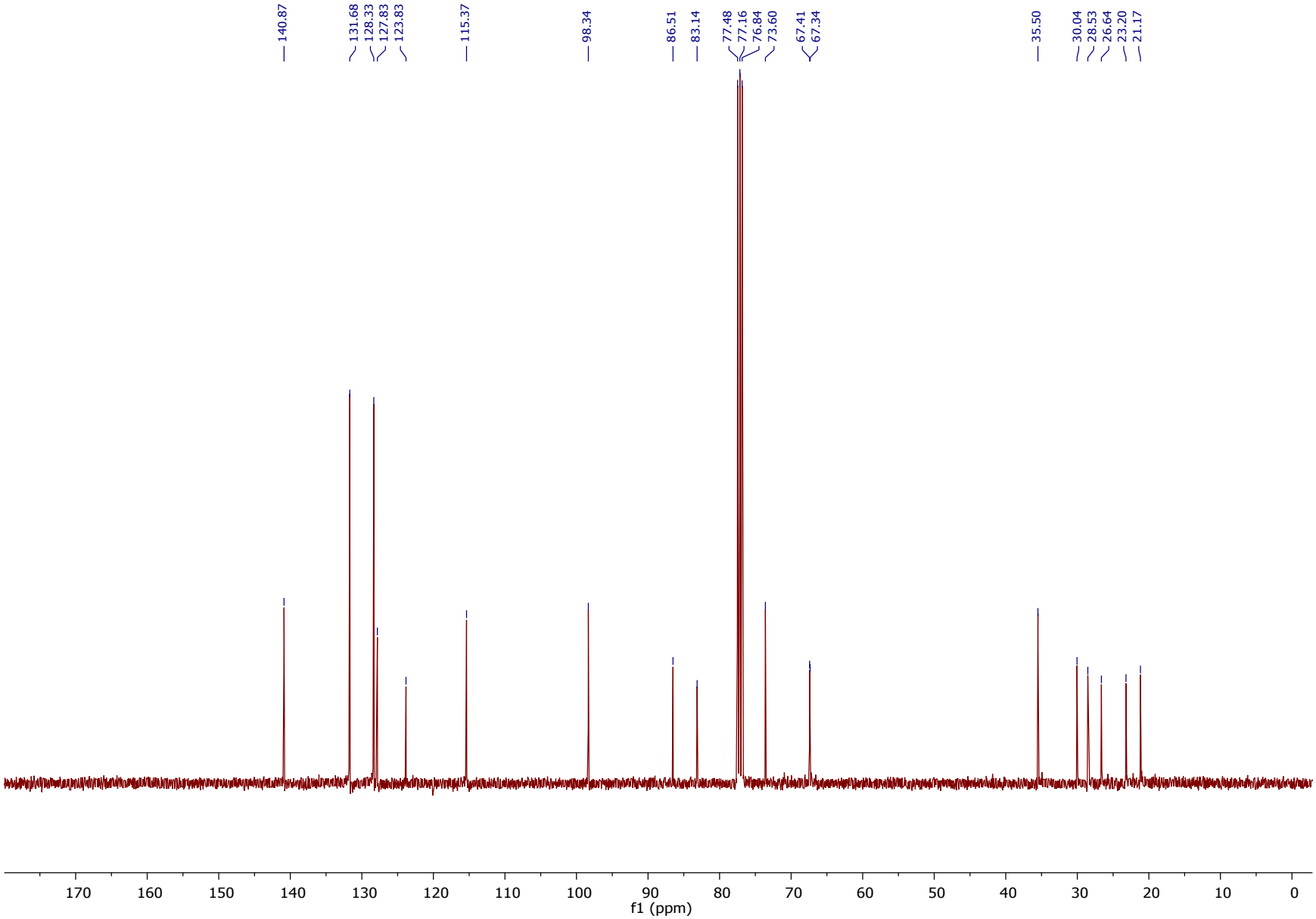

7.41 7.41 7.40 7.39 7.39 7.39 7.38 7.26 7.26 7.26 7.25 7.25 7.25 7.24 7.24 7.24 7.24 7.23 7.23 7.23 7.23 7.22 7.22 7.22 7.21 6.01 5.99 5.98 5.97 5.95 5.94 5.92 5.26 5.25 5.25 5.24 5.24 5.23 5.22 5.21 5.21 4.89 4.89 4.88 4.88 4.87
3.32
2.92 2.90 2.88
2.51 2.48 2.47
0.15
H3C O CH2 CH3 Si CH3 H3C
1.04 3.62 1.05 1.08 1.00 1.05 3.00 2.13 2.06 8.88
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

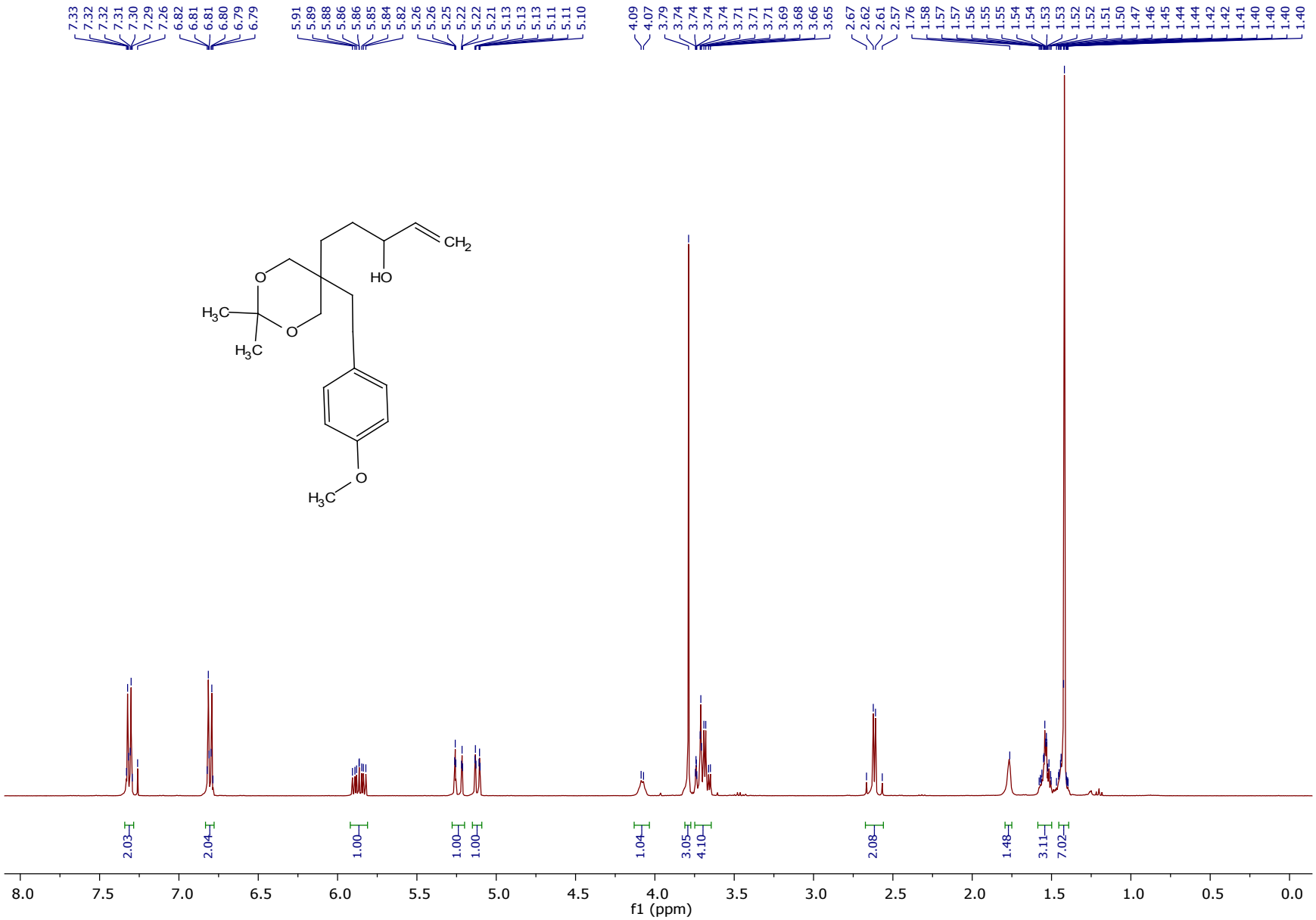

138.52
138.44
129.89
127.76
127.20
126.98
116.73
106.70
85.35
81.17
77.48
77.16
76.84
56.56
31.73
21.84
0.25
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

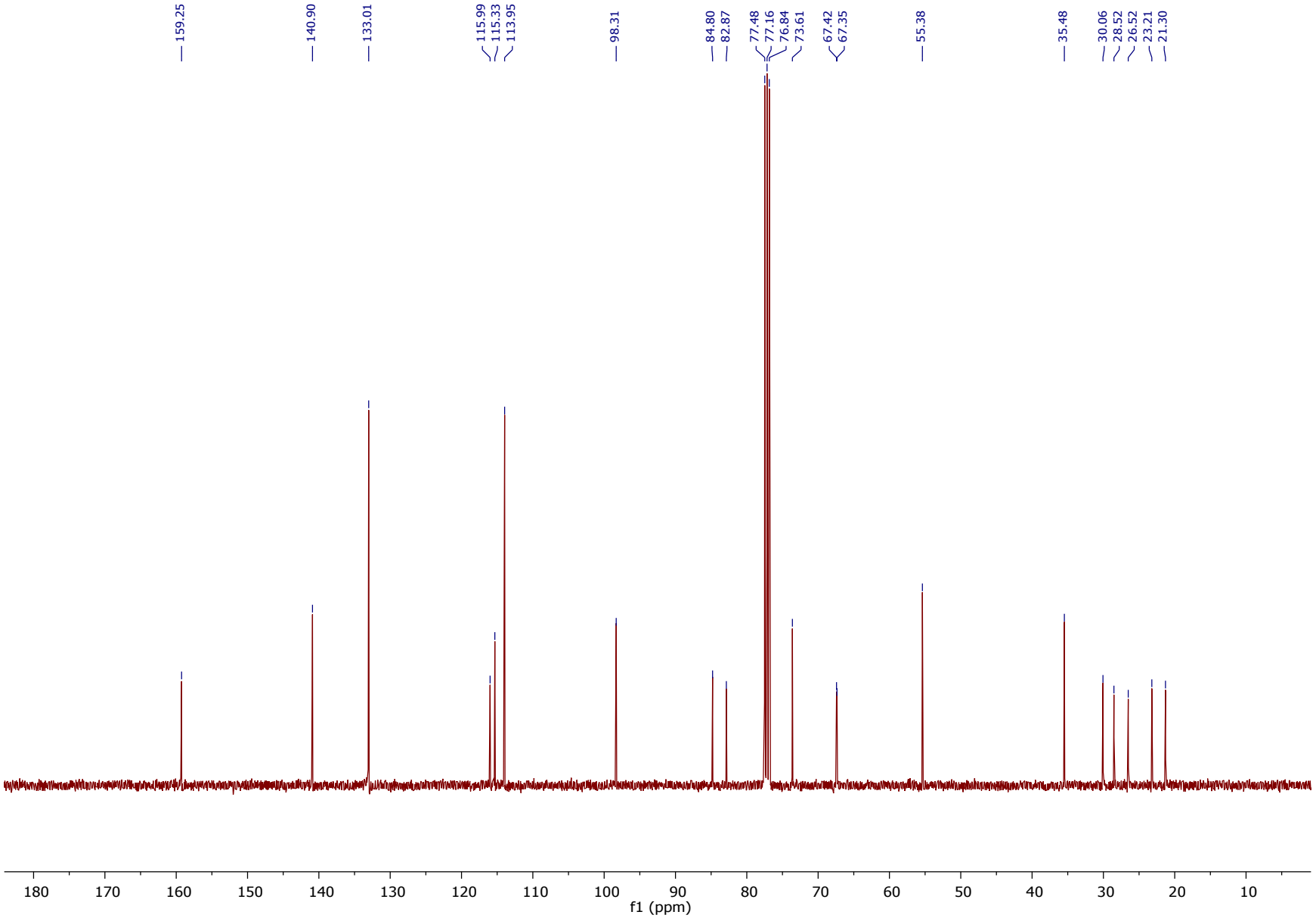

7.26
5.88 5.87 5.86 5.84 5.83 5.82 5.80
5.25 5.25 5.21 5.21 5.20 5.13 5.13 5.13 5.11 5.10 5.10
4.05
3.67 3.67 3.67 3.66 3.64 3.64 3.64 3.64 3.63 3.61 3.60 3.58
2.47 2.43 2.40 2.36
1.76 1.52 1.51 1.50 1.50 1.49 1.49 1.48 1.48 1.48 1.47 1.46 1.46 1.45 1.45 1.43 1.42 1.41 1.41 1.39 1.38 1.37 1.37 1.36 0.12
CH2
OH
O
H3C
O
H3C
CH3
Si
H3C
CH3
1.00 1.00 1.00 1.00 4.08 1.76 1.32 3.00 7.03 9.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

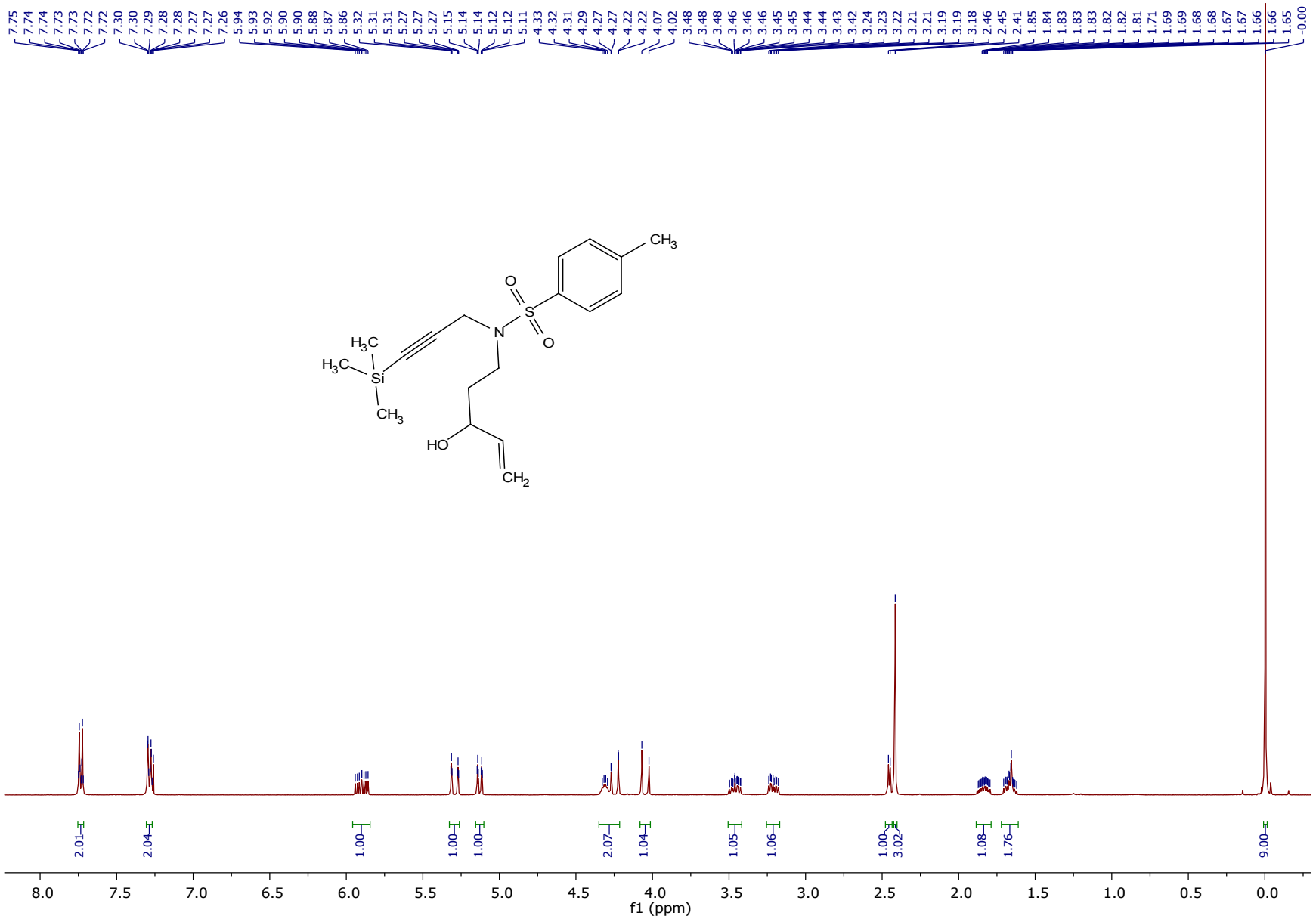

140.86
115.32
103.58
98.27
87.45
77.48
77.16
76.84
73.61
67.29
67.20
35.06
29.97
28.33
26.24
23.63
21.51
0.21
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

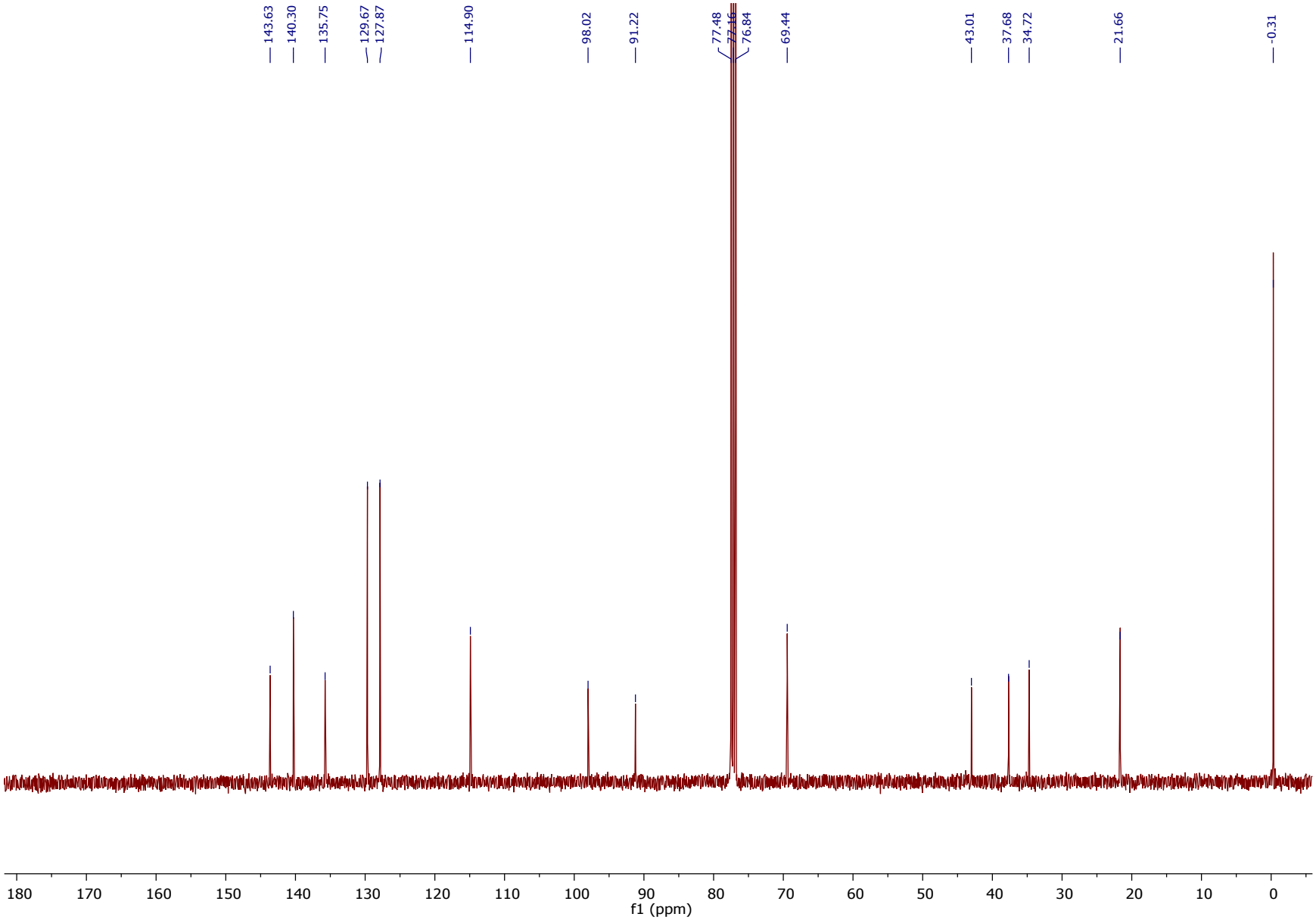

7.39 7.39 7.39 7.39 7.38 7.38 7.37 7.37 7.29 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.26 7.26
5.91 5.89 5.88 5.87 5.87 5.85 5.84 5.82 5.26 5.26 5.26 5.22 5.22 5.21 5.14 5.13 5.13 5.11 5.11 5.10
4.09 4.09 4.08 4.07 3.75 3.75 3.74 3.74 3.73 3.72 3.72 3.71 3.70 3.69 3.67 3.66 3.65
2.70 2.66 2.64 1.77 1.57 1.56 1.55 1.55 1.55 1.54 1.54 1.54 1.53 1.52 1.51 1.49 1.48 1.48 1.47 1.47 1.45 1.45 1.44 1.43 1.43 1.42 1.41 1.41 1.40 1.40 1.40
CH2
OH
O
O
H3C
H3C
2.00
3.10
1.00
1.00
1.01
1.00
4.30
2.00
1.42
3.00
7.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

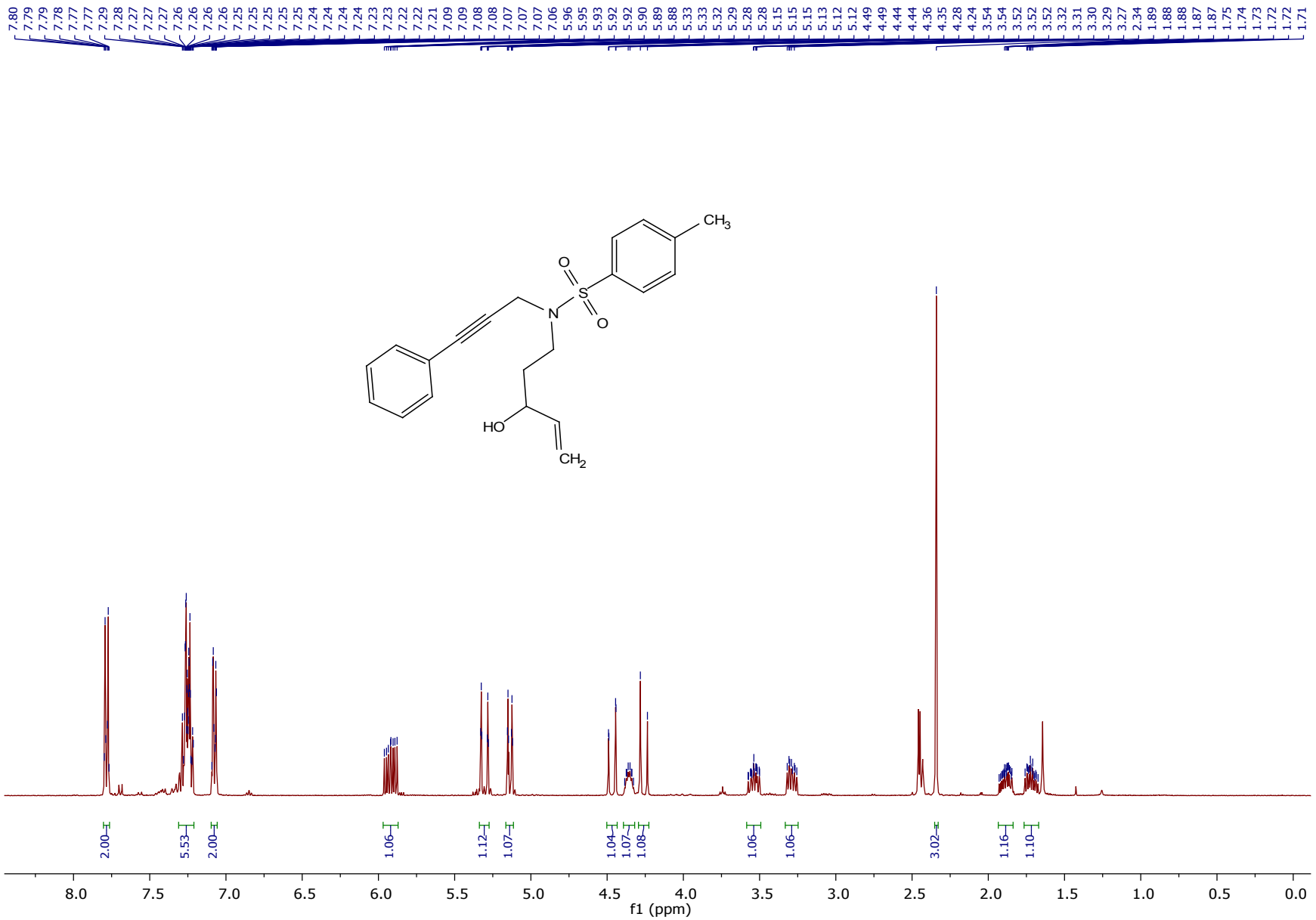

140.87
131.68
128.33
127.83
123.83
115.37
98.34
86.51
83.14
77.48
77.16
76.84
73.60
67.41
67.34
35.50
30.04
28.53
26.64
23.20
21.17
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

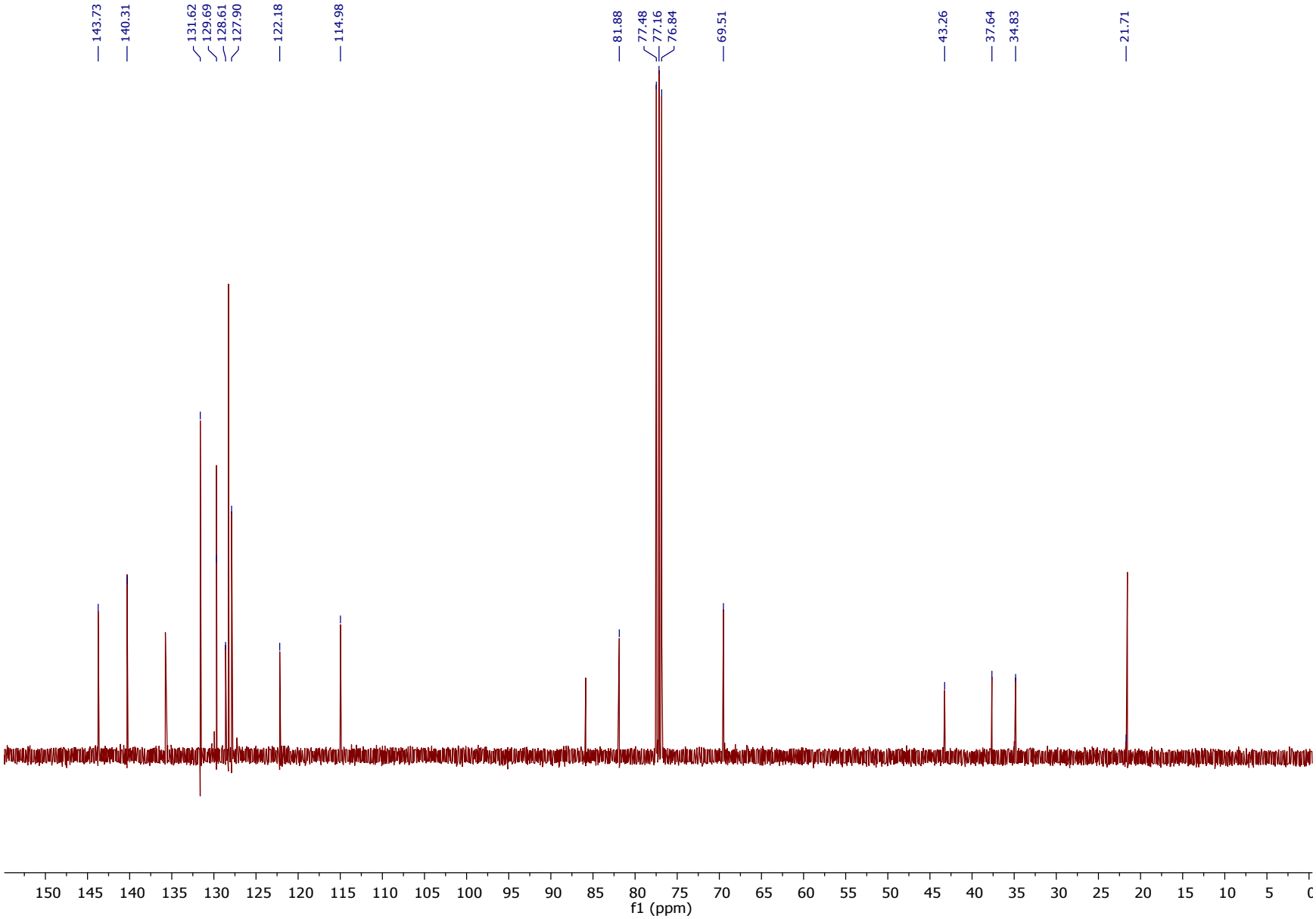

7.33 7.32 7.32 7.31 7.30 7.29 7.26 6.82 6.81 6.81 6.80 6.79 6.79
5.91 5.89 5.88 5.86 5.86 5.85 5.84 5.82 5.26 5.26 5.25 5.22 5.22 5.21 5.13 5.13 5.13 5.11 5.11 5.10
4.09 4.07 3.79 3.74 3.74 3.74 3.74 3.71 3.71 3.71 3.69 3.68 3.66 3.65 2.67 2.62 2.61 2.57 1.76 1.58 1.57 1.57 1.56 1.55 1.55 1.54 1.54 1.53 1.53 1.52 1.52 1.51 1.50 1.47 1.46 1.45 1.44 1.44 1.42 1.42 1.41 1.40 1.40 1.40
CH2
HO
O
H3C
O
H3C
O
H3C
2.03 2.04 1.00 1.00 1.00 1.04 3.05 4.10 2.08 1.48 3.11 7.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

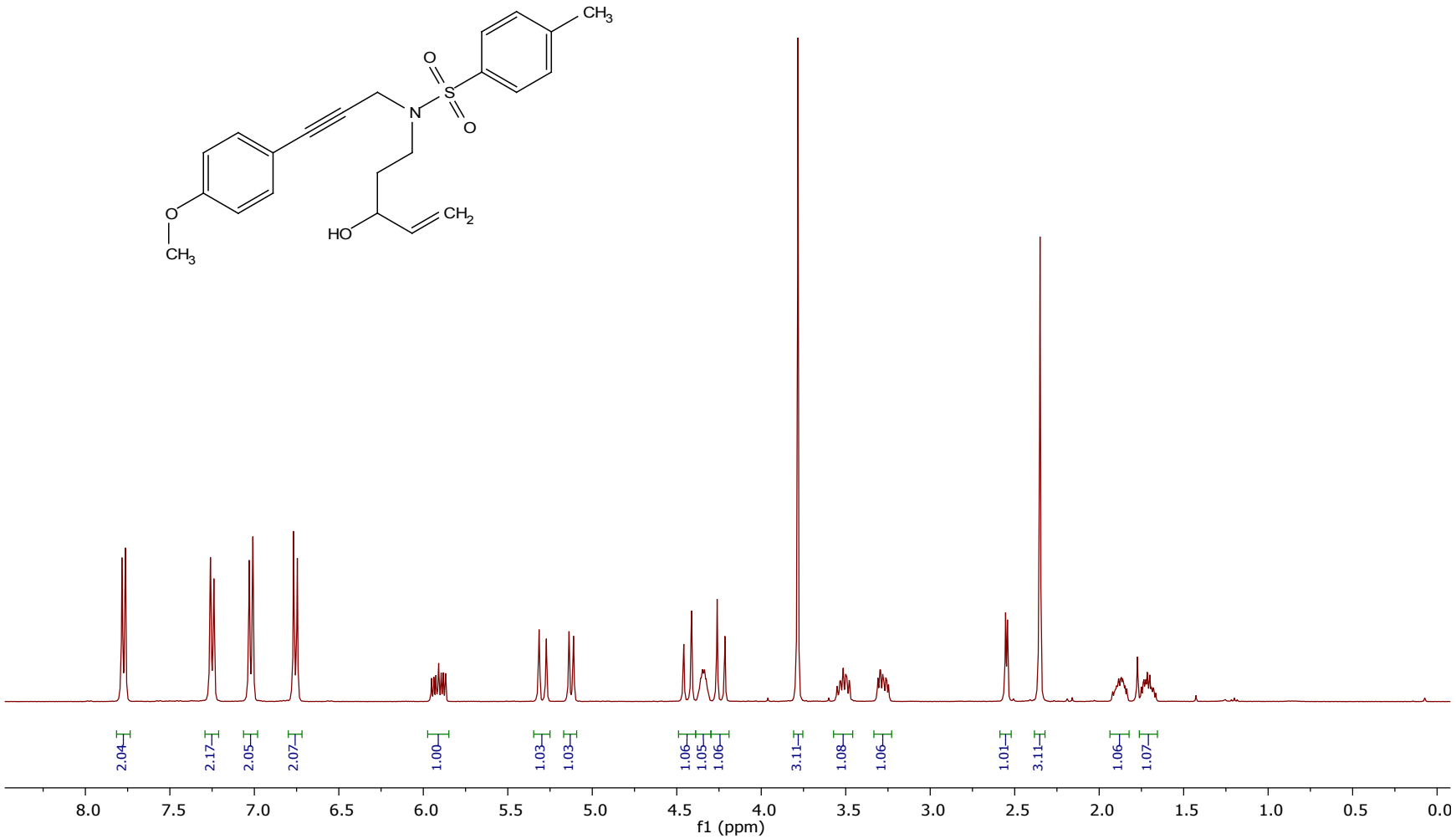

159.25
140.90
133.01
115.99
115.33
113.95
98.31
84.80
82.87
77.48
77.16
76.84
73.61
67.42
67.35
55.38
35.48
30.06
28.52
26.52
23.21
21.30
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

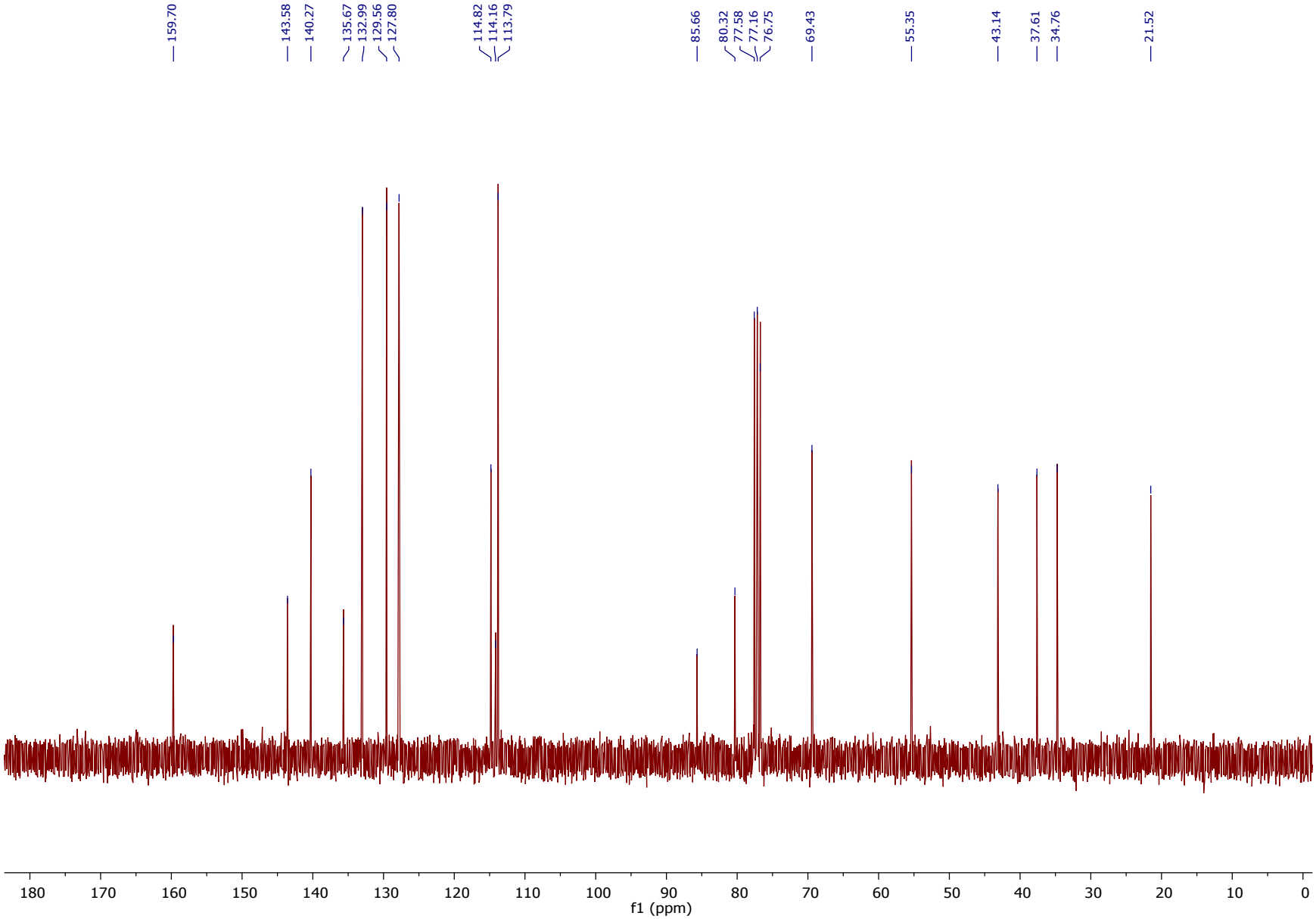

7.75 7.74 7.74 7.73 7.73 7.72 7.72 7.30 7.30 7.29 7.28 7.28 7.27 7.27 7.26 5.94 5.93 5.92 5.90 5.90 5.88 5.87 5.86 5.32 5.31 5.31 5.27 5.27 5.27 5.15 5.14 5.14 5.12 5.12 5.11 4.33 4.32 4.31 4.29 4.27 4.27 4.22 4.22 4.07 4.02 3.48 3.48 3.48 3.46 3.46 3.46 3.45 3.45 3.44 3.44 3.43 3.42 3.24 3.23 3.22 3.21 3.21 3.19 3.19 3.18 2.46 2.45 2.41 1.85 1.84 1.83 1.83 1.83 1.82 1.82 1.81 1.71 1.69 1.69 1.68 1.68 1.67 1.67 1.66 1.66 1.65 -0.00
CH3
O
S
O
N
H3C
H3C
Si
CH3
HO
CH2
2.01 2.04 1.00 1.00 1.00 2.07 1.04 1.05 1.06 1.00 3.02 1.08 1.76 9.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

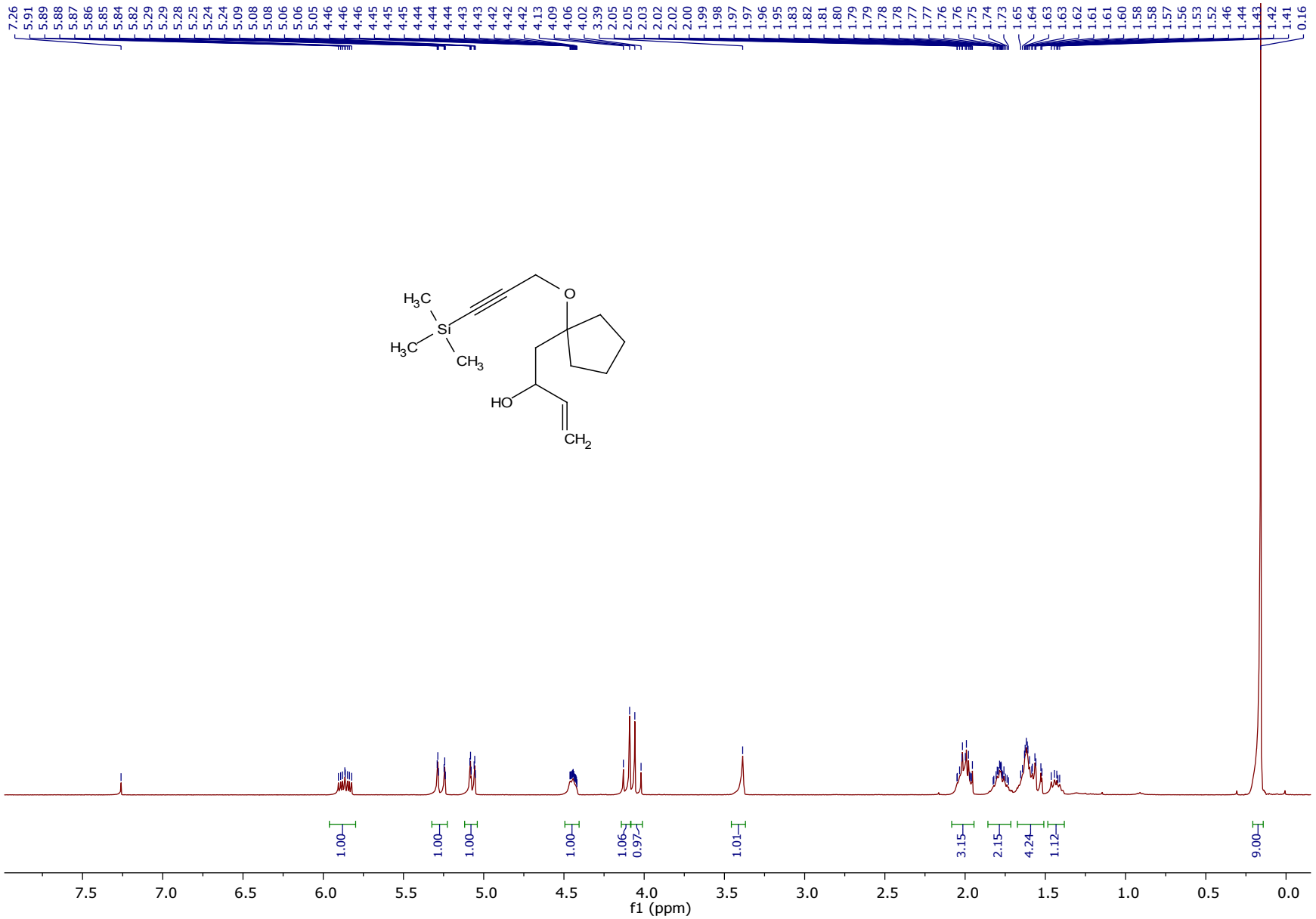

143.63
140.30
135.75
129.67
127.87
114.90
98.02
91.22
77.48
77.16
76.84
69.44
43.01
37.68
34.72
21.66
-0.31
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

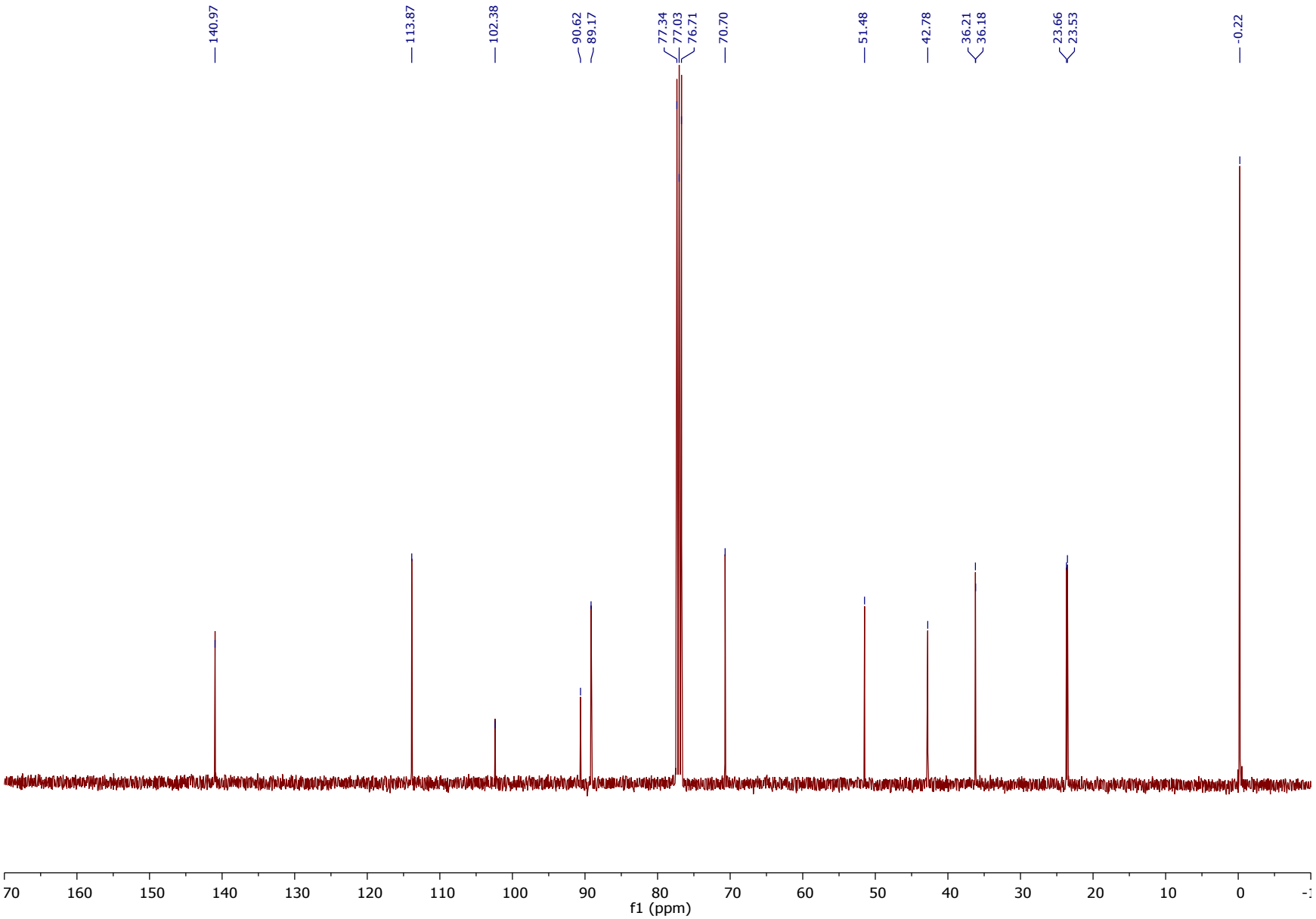

7.80 7.79 7.79 7.78 7.77 7.77 7.29 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.25 7.25 7.24 7.24 7.24 7.24 7.23 7.23 7.22 7.22 7.21 7.09 7.09 7.08 7.08 7.07 7.07 7.07 7.06 5.96 5.95 5.93 5.92 5.92 5.90 5.89 5.88 5.33 5.33 5.32 5.29 5.28 5.28 5.15 5.15 5.15 5.13 5.12 5.12 4.49 4.49 4.44 4.44 4.36 4.35 4.28 4.24 3.54 3.54 3.52 3.52 3.52 3.32 3.31 3.30 3.29 3.27 2.34 1.89 1.88 1.88 1.87 1.87 1.75 1.74 1.73 1.72 1.72 1.71
CH3
O
S
O
N
HO
CH2
2.00 5.53 2.00 1.06 1.12 1.07 1.04 1.07 1.08 1.06 1.06 3.02 1.16 1.10
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

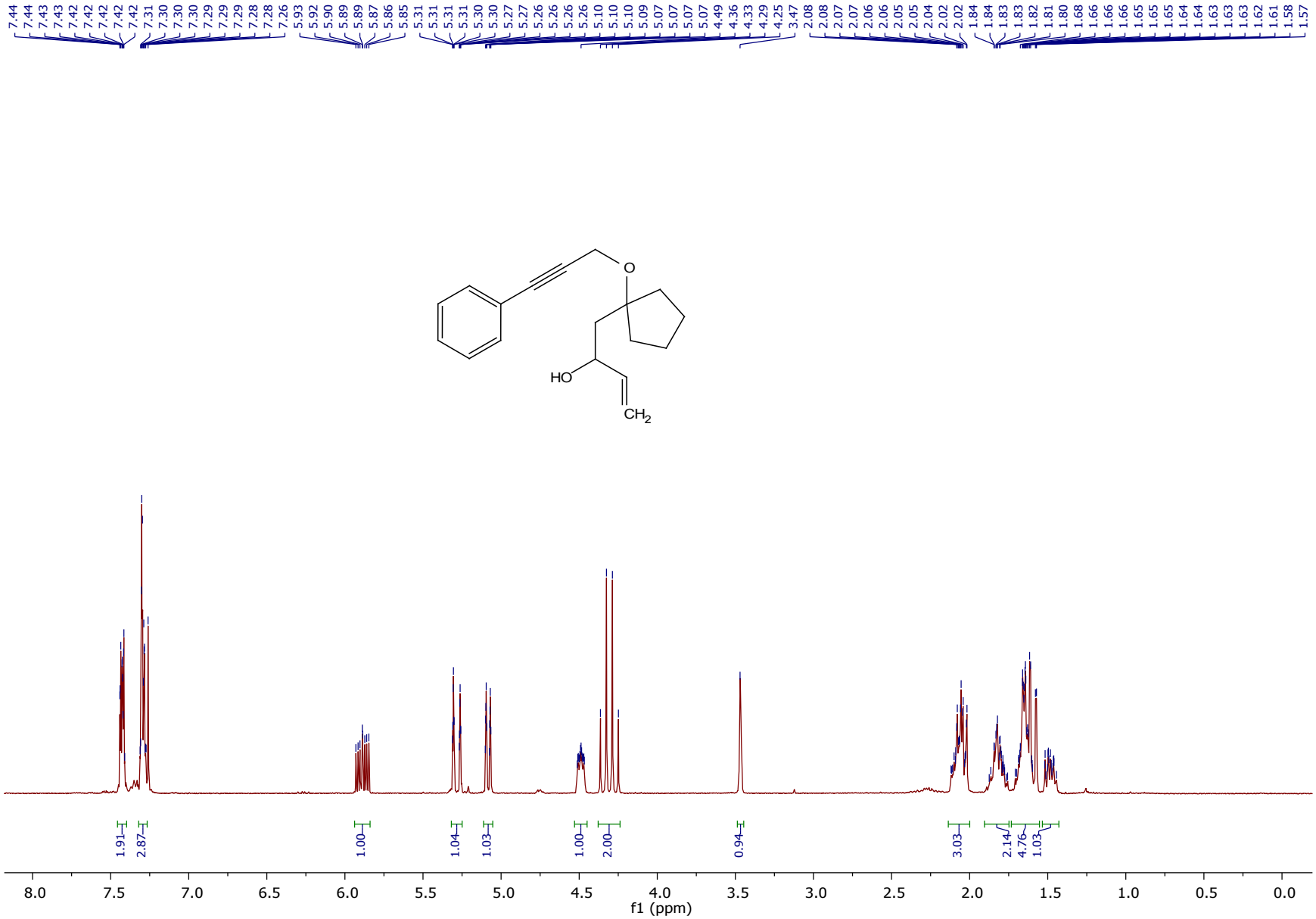

143.73
140.31
131.62
129.69
128.61
127.90
122.18
114.98
81.88
77.48
77.16
76.84
69.51
43.26
37.64
34.83
21.71
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

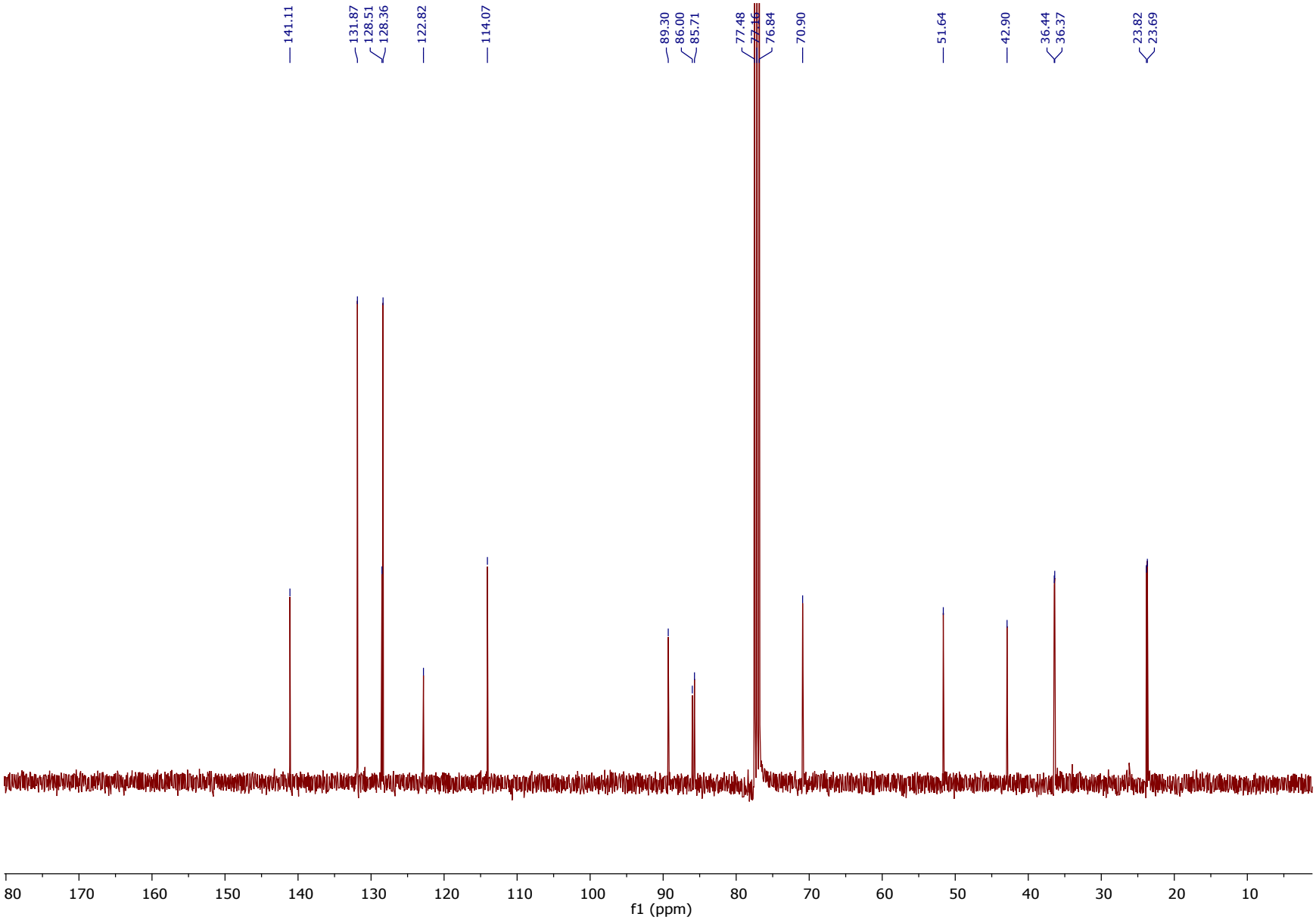

CH3
O
S
O
N
O
CH2
HO
O
CH3
2.04
2.17
2.05
2.07
1.00
1.03
1.03
1.06
1.05
1.06
3.11
1.08
1.06
1.01
3.11
1.06
1.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

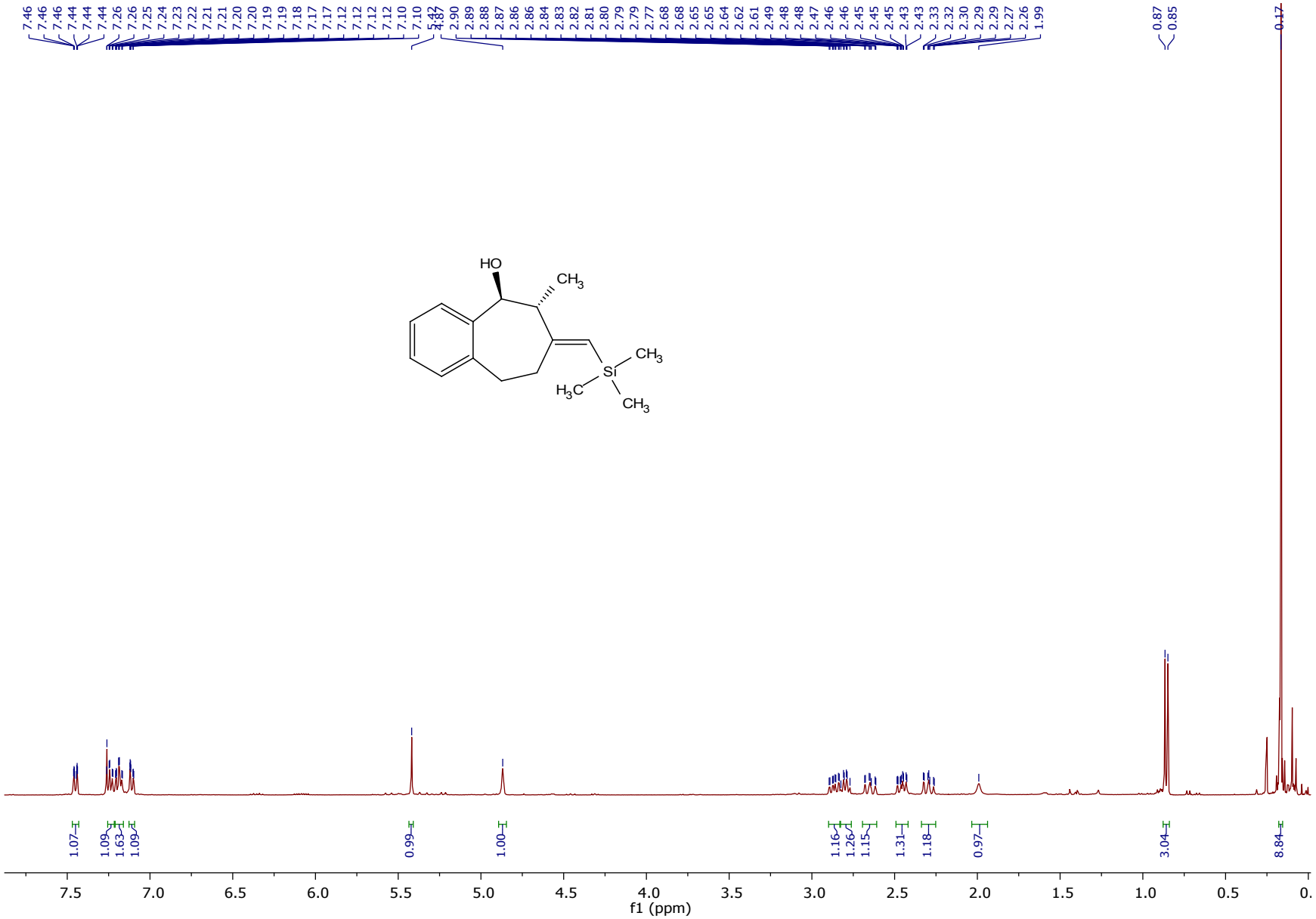

159.70
143.58
140.27
135.67
132.99
129.56
127.80
114.82
114.16
113.79
85.66
80.32
77.58
77.16
76.75
69.43
55.35
43.14
37.61
34.76
21.52
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

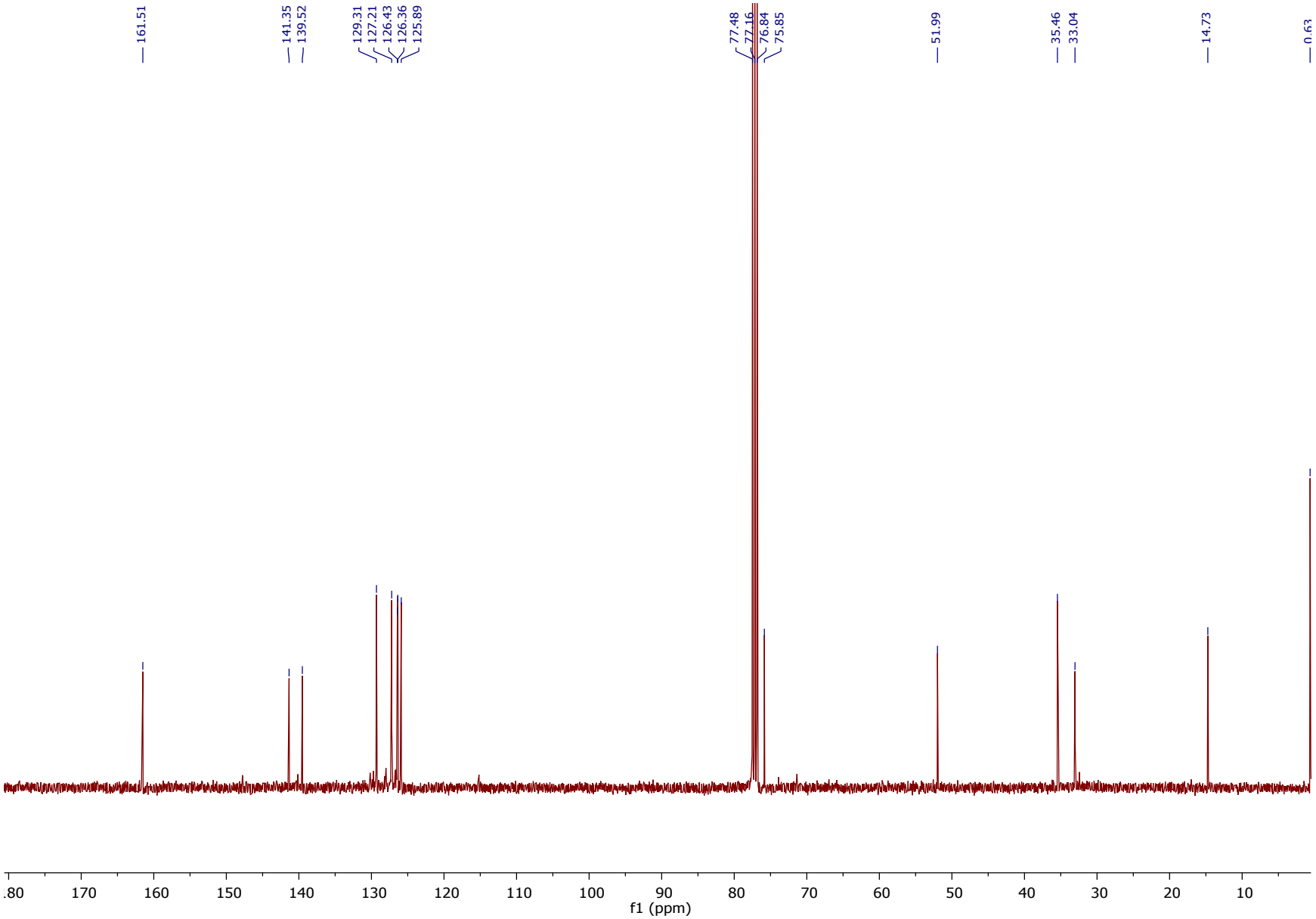

7.26 5.91 5.89 5.88 5.87 5.86 5.85 5.84 5.82 5.29 5.29 5.28 5.25 5.24 5.24 5.09 5.08 5.08 5.06 5.06 5.05 4.46 4.46 4.45 4.45 4.45 4.44 4.44 4.44 4.43 4.43 4.42 4.42 4.42 4.13 4.09 4.06 4.02 3.39 2.05 2.05 2.03 2.02 2.02 2.00 1.99 1.98 1.97 1.97 1.96 1.95 1.83 1.82 1.81 1.80 1.79 1.79 1.78 1.78 1.77 1.77 1.76 1.76 1.75 1.74 1.73 1.65 1.64 1.63 1.63 1.62 1.61 1.61 1.60 1.58 1.58 1.57 1.56 1.53 1.52 1.46 1.44 1.43 1.42 1.41 0.16
H3C
Si
H3C
CH3
O
HO
CH2
1.00 1.00 1.00 1.00 1.06 0.97 1.01 3.15 2.15 4.24 1.12 9.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

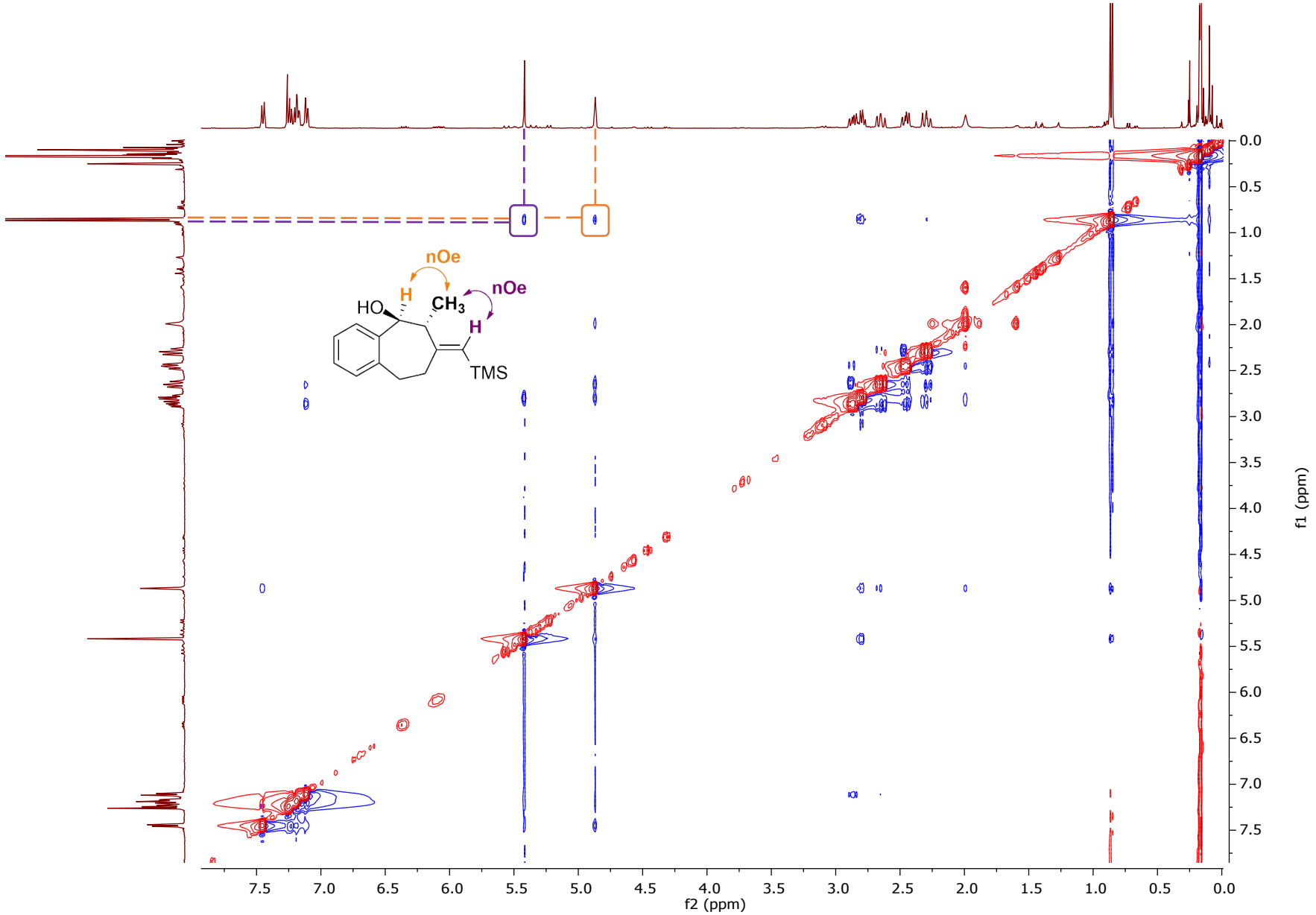

140.97
113.87
102.38
90.62
89.17
77.34
77.03
76.71
70.70
51.48
42.78
36.21
36.18
23.66
23.53
-0.22
f1 (ppm)

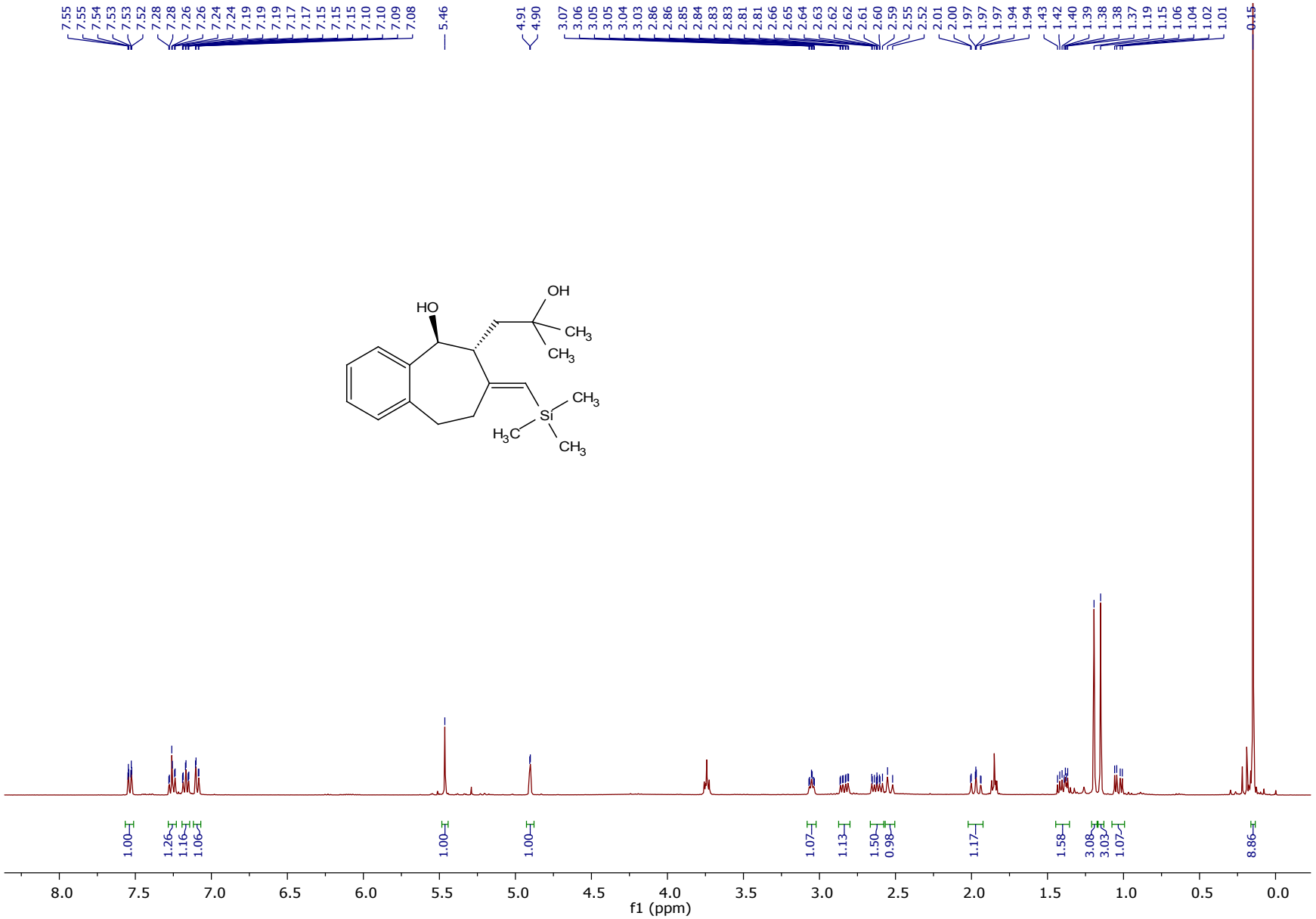

7.44 7.44 7.43 7.43 7.42 7.42 7.42 7.42 7.42 7.31 7.30 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.26 5.93 5.92 5.90 5.89 5.89 5.87 5.86 5.85 5.31 5.31 5.31 5.30 5.30 5.27 5.27 5.26 5.26 5.26 5.26 5.10 5.10 5.09 5.07 5.07 5.07 5.07 4.49 4.36 4.33 4.29 4.25 3.47 2.08 2.08 2.07 2.07 2.06 2.06 2.05 2.05 2.04 2.02 2.02 1.84 1.84 1.83 1.83 1.82 1.81 1.80 1.68 1.66 1.66 1.66 1.65 1.65 1.65 1.64 1.64 1.63 1.63 1.63 1.62 1.61 1.58 1.57
O
HO
CH2
1.91 2.87 1.00 1.04 1.03 1.00 2.00 0.94 3.03 2.14 4.76 1.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

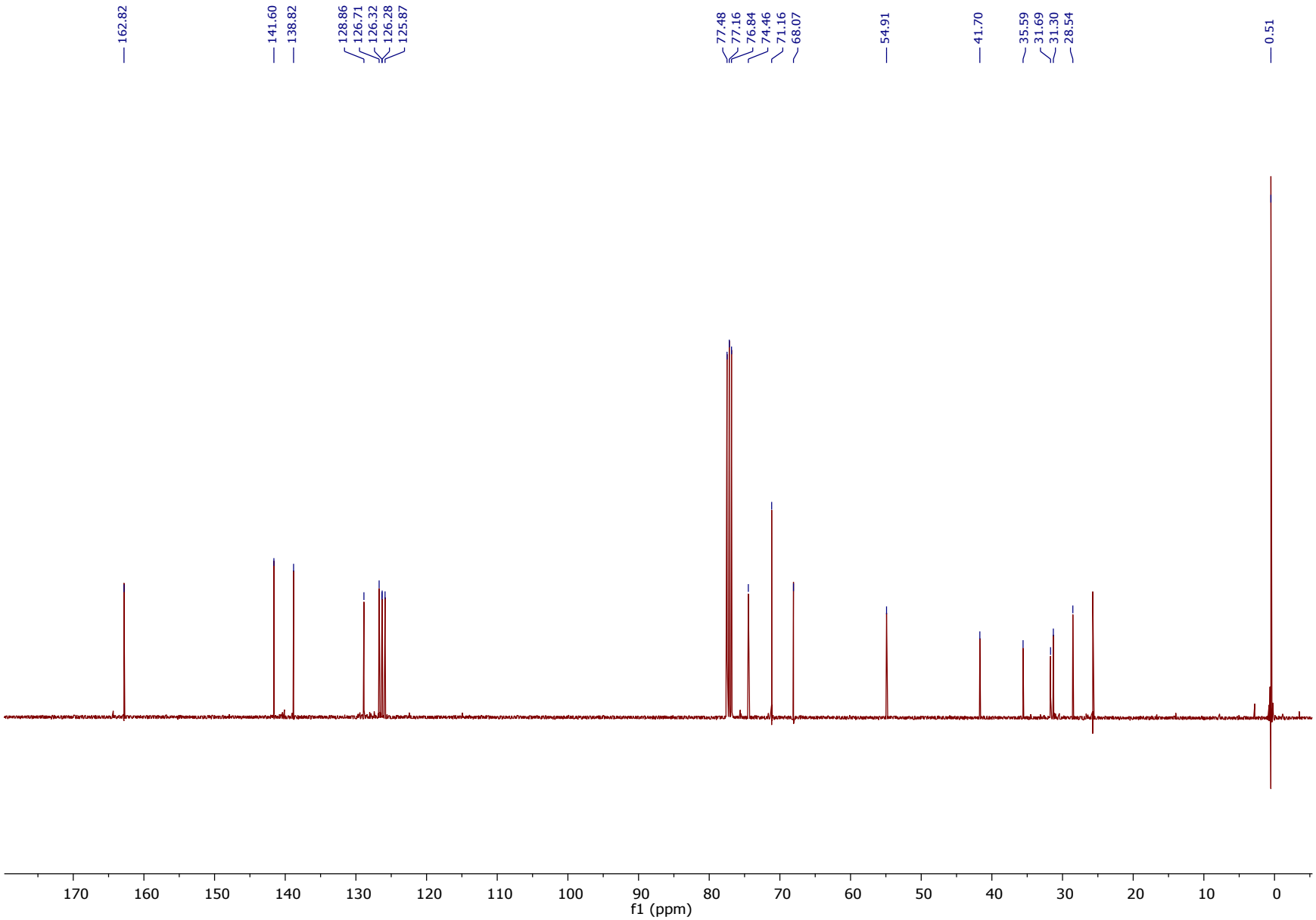

141.11
131.87
128.51
128.36
122.82
114.07
89.30
86.00
85.71
77.48
77.16
76.84
70.90
51.64
42.90
36.44
36.37
23.82
23.69
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

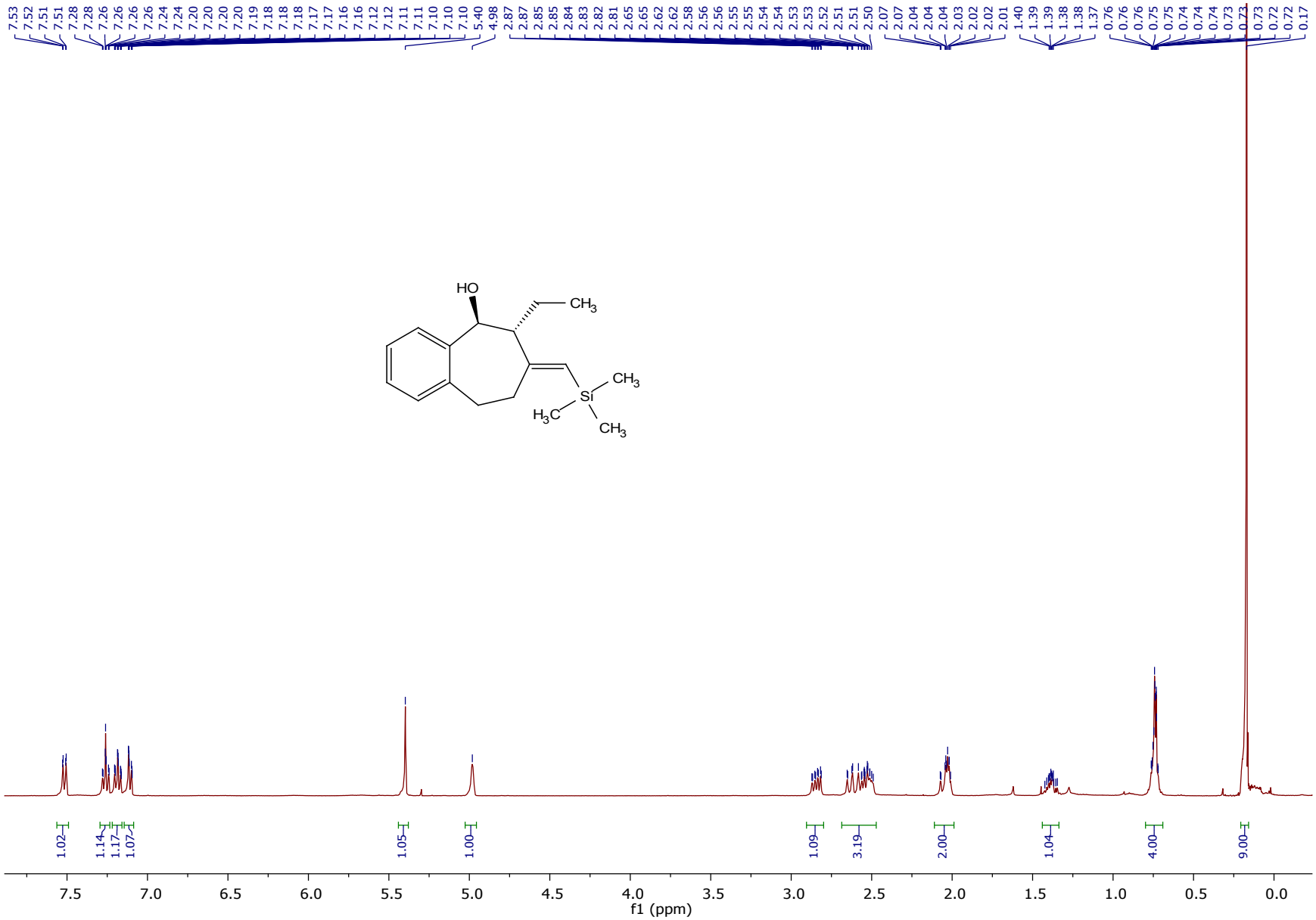

7.46 7.46 7.46 7.44 7.44 7.44 7.26 7.25 7.24 7.23 7.22 7.21 7.21 7.20 7.20 7.19 7.19 7.18 7.17 7.17 7.12 7.12 7.12 7.12 7.10 7.10 5.42 5.42 2.90 2.89 2.88 2.87 2.86 2.86 2.84 2.83 2.82 2.81 2.80 2.79 2.79 2.77 2.68 2.68 2.65 2.65 2.64 2.62 2.61 2.49 2.48 2.48 2.47 2.46 2.46 2.45 2.45 2.45 2.43 2.43 2.33 2.32 2.30 2.29 2.29 2.27 2.26 1.99
0.87 0.85
0.17
HO
CH3
CH3
Si
H3C
CH3
1.07 1.09 1.63 1.09 0.99 1.00 1.16 1.26 1.15 1.31 1.18 0.97 3.04 8.84
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

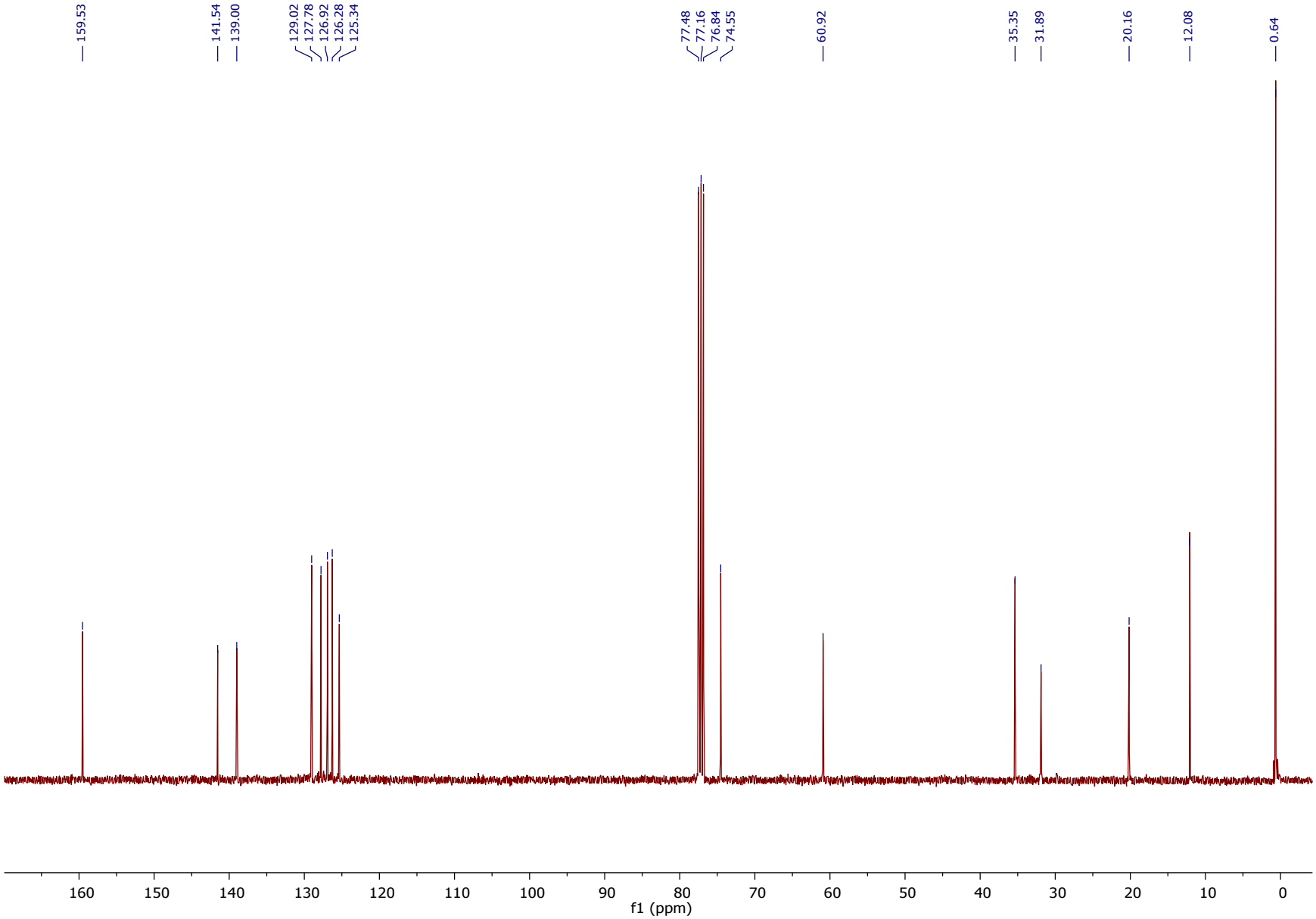

161.51
141.35
139.52
129.31
127.21
126.43
126.36
125.89
77.48
77.16
76.84
75.85
51.99
35.46
33.04
14.73
0.63
f1 (ppm)

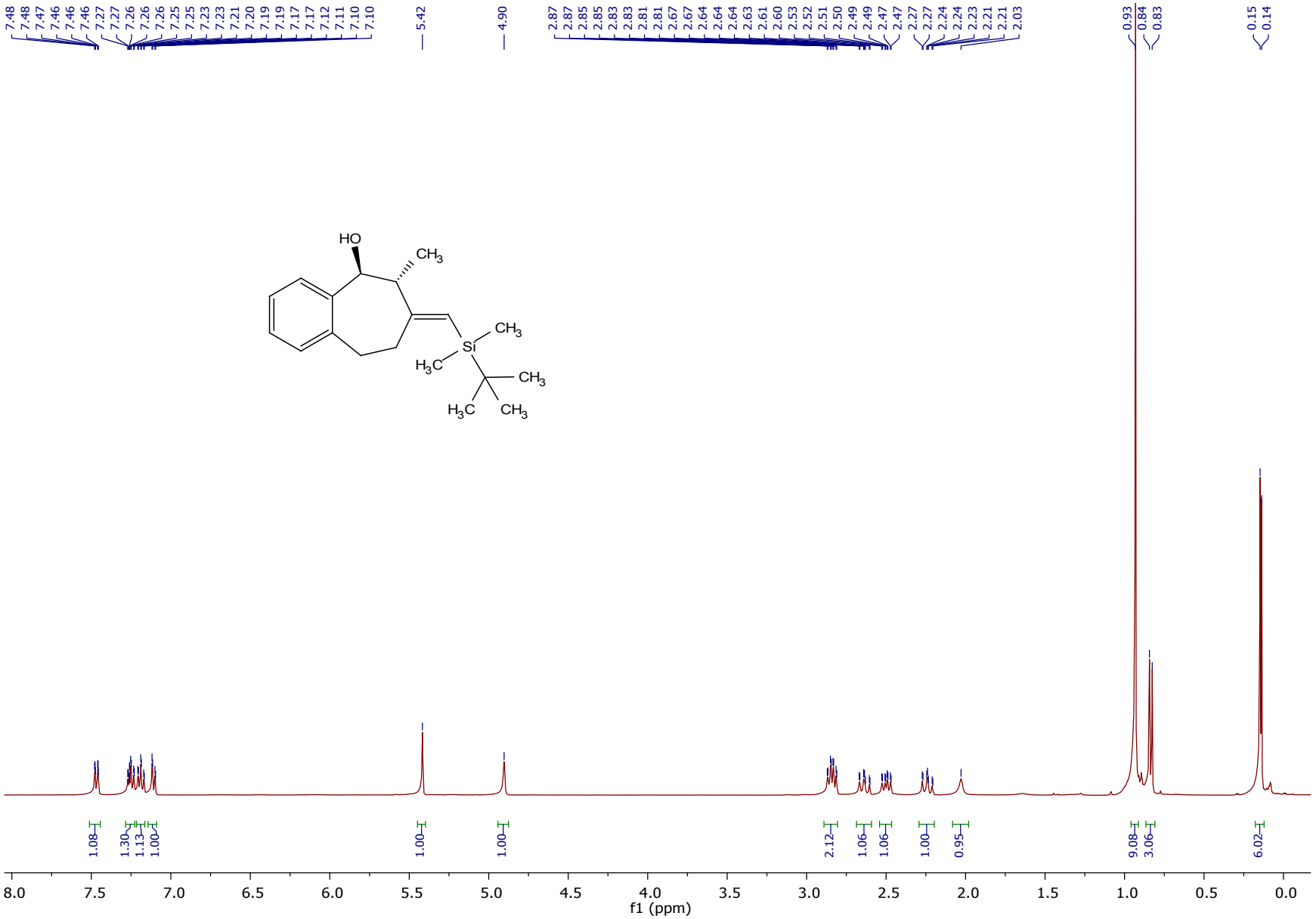

nOe
nOe
H
HO
CH3
H
TMS
f2 (ppm)
f1 (ppm)

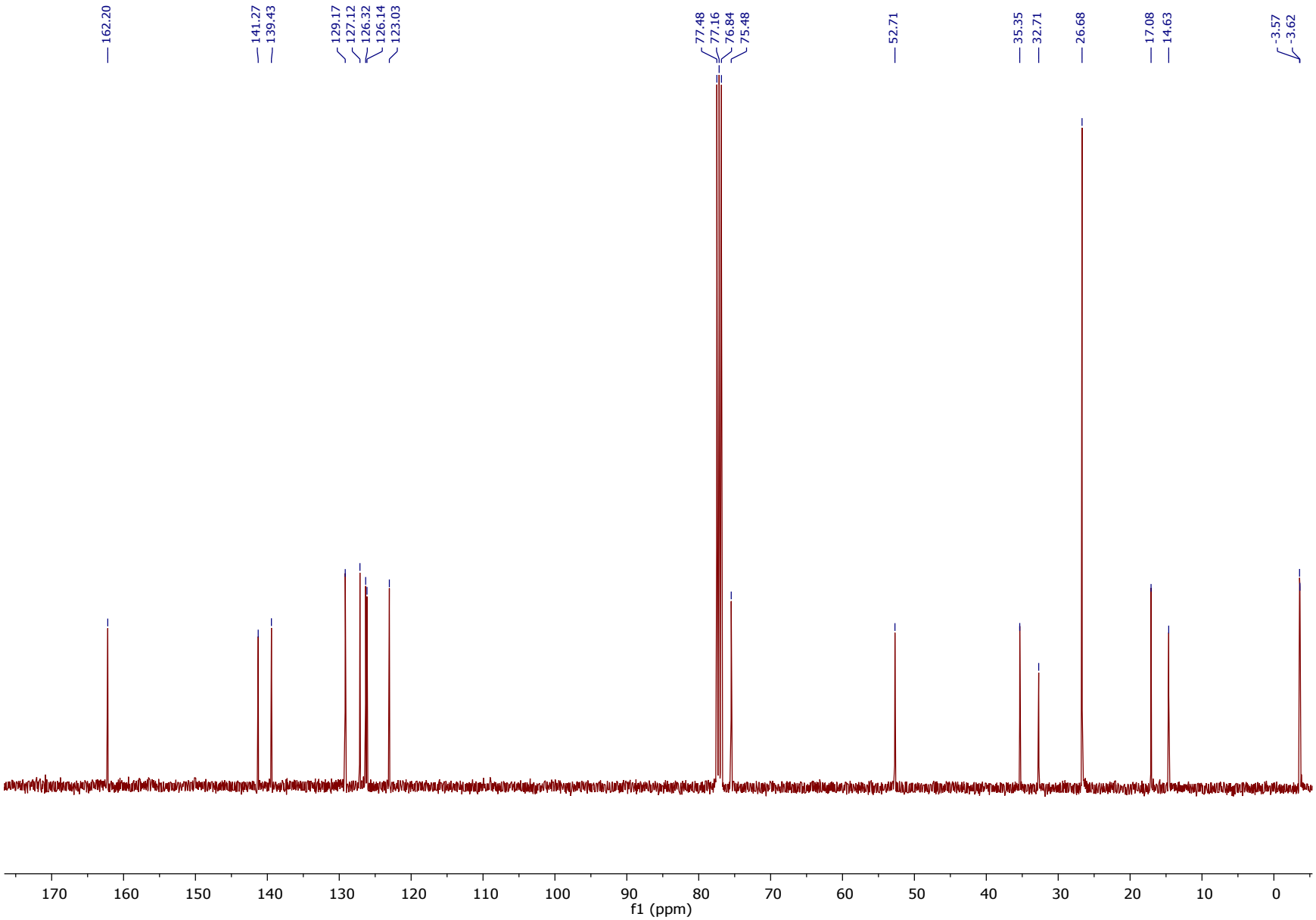

7.55 7.55 7.54 7.53 7.53 7.52 7.28 7.28 7.26 7.26 7.24 7.24 7.19 7.19 7.19 7.17 7.17 7.15 7.15 7.15 7.10 7.09 7.08 5.46
4.91 4.90 3.07 3.06 3.05 3.05 3.04 3.03 2.86 2.86 2.85 2.84 2.83 2.83 2.81 2.81 2.66 2.65 2.64 2.63 2.62 2.62 2.61 2.60 2.59 2.55 2.52 2.01 2.00 1.97 1.97 1.97 1.94 1.94 1.43 1.42 1.40 1.39 1.38 1.38 1.37 1.19 1.15 1.06 1.04 1.02 1.01 0.15
HO
OH
CH3
CH3
CH3
Si
H3C
CH3
1.00 1.26 1.16 1.06 1.00 1.00 1.07 1.13 1.50 0.98 1.17 1.58 3.08 3.03 1.07 8.86
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

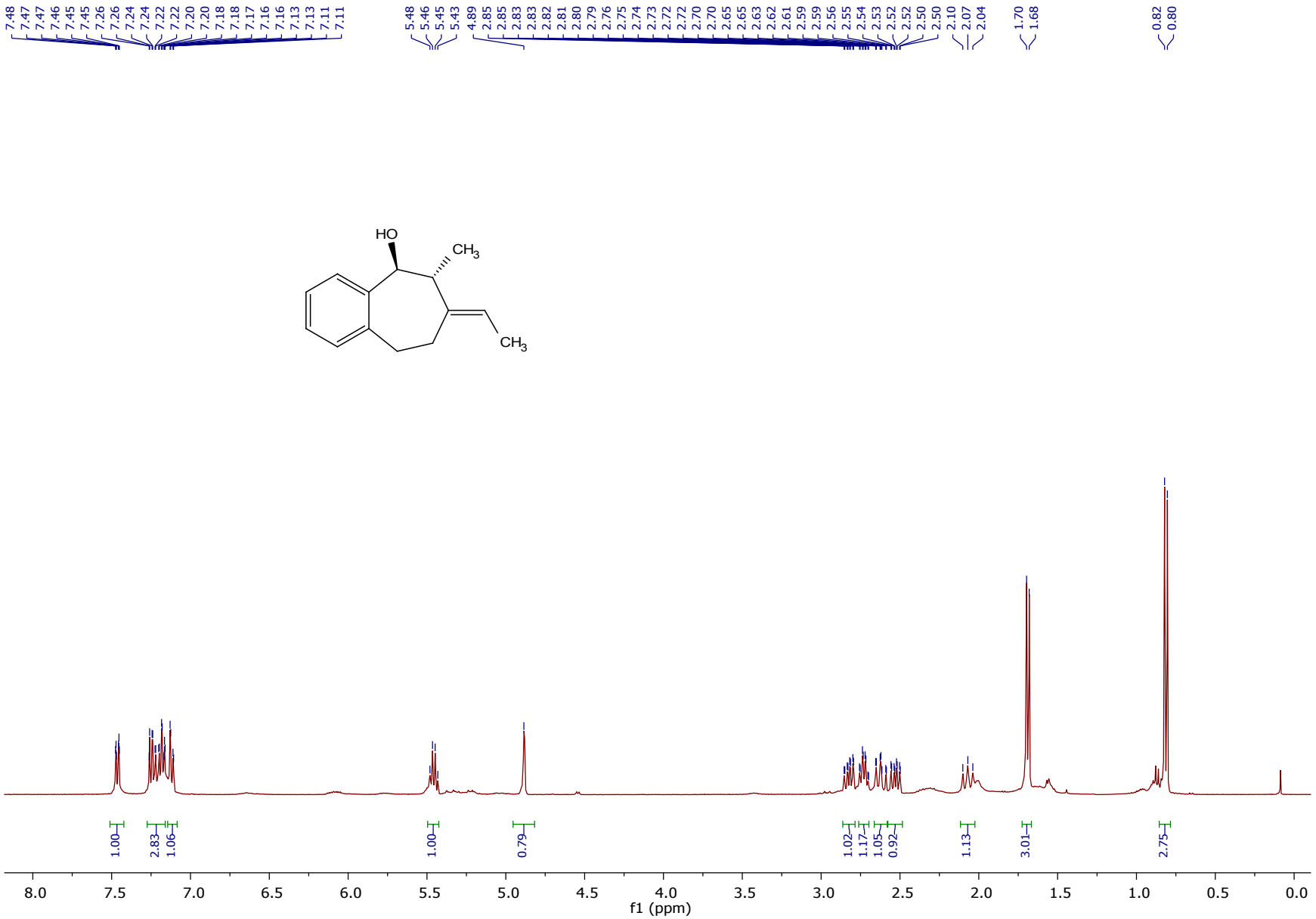

162.82
141.60
138.82
128.86
126.71
126.32
126.28
125.87
77.48
77.16
76.84
74.46
71.16
68.07
54.91
41.70
35.59
31.69
31.30
28.54
0.51
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

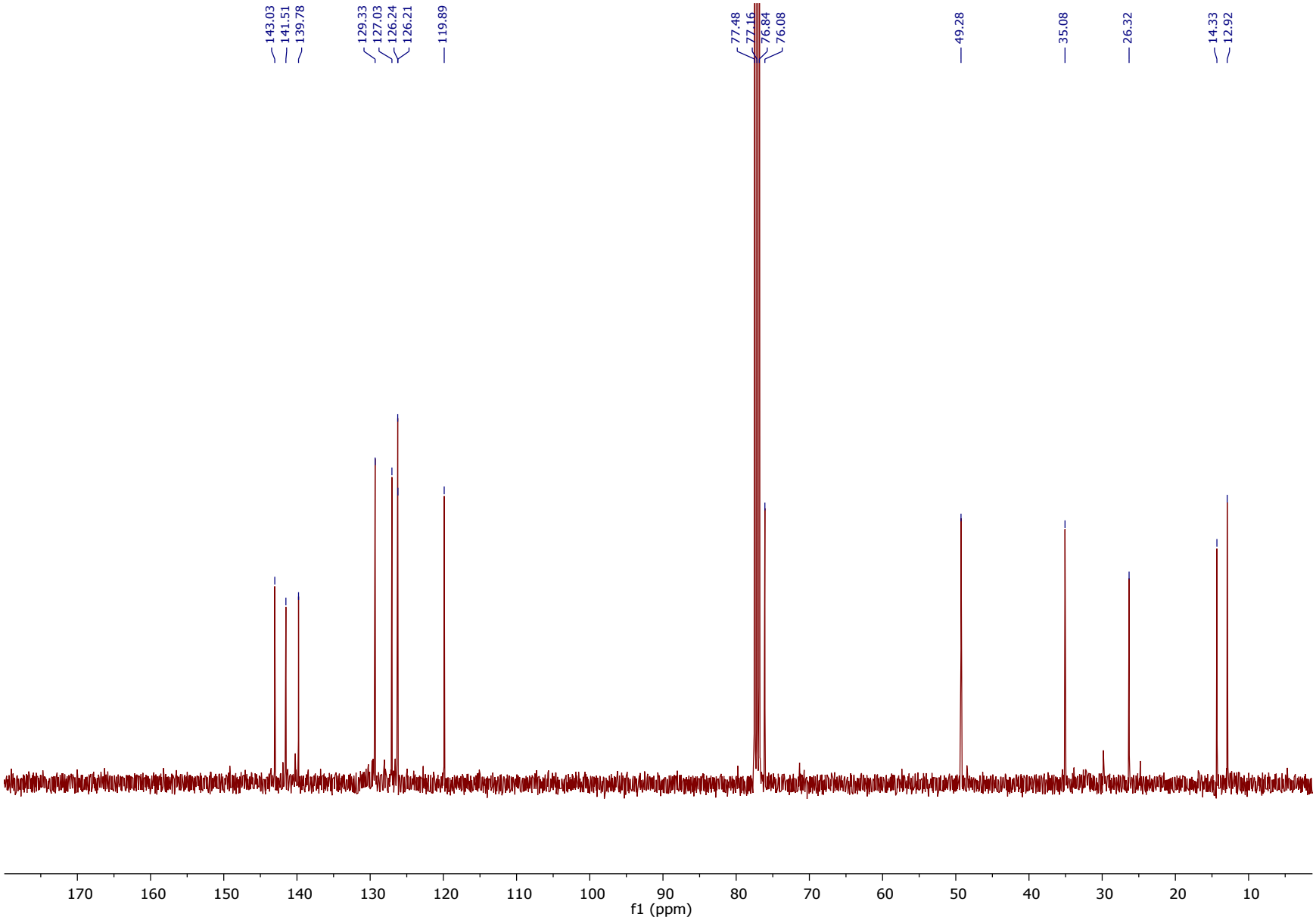

7.53 7.52 7.51 7.51 7.28 7.28 7.26 7.26 7.26 7.26 7.24 7.24 7.20 7.20 7.20 7.20 7.19 7.18 7.18 7.18 7.17 7.17 7.16 7.16 7.12 7.12 7.11 7.11 7.10 7.10 7.10 5.40 4.98 2.87 2.87 2.85 2.85 2.84 2.83 2.82 2.81 2.65 2.65 2.62 2.62 2.58 2.56 2.56 2.55 2.55 2.54 2.54 2.53 2.53 2.52 2.51 2.51 2.50 2.07 2.07 2.04 2.04 2.04 2.03 2.02 2.02 2.01 1.40 1.39 1.39 1.38 1.38 1.37 0.76 0.76 0.76 0.75 0.75 0.74 0.74 0.74 0.73 0.73 0.73 0.72 0.72 0.17
HO
CH3
CH3
Si
H3C
CH3
1.02 1.14 1.17 1.07 1.05 1.00 1.09 3.19 2.00 1.04 4.00 9.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

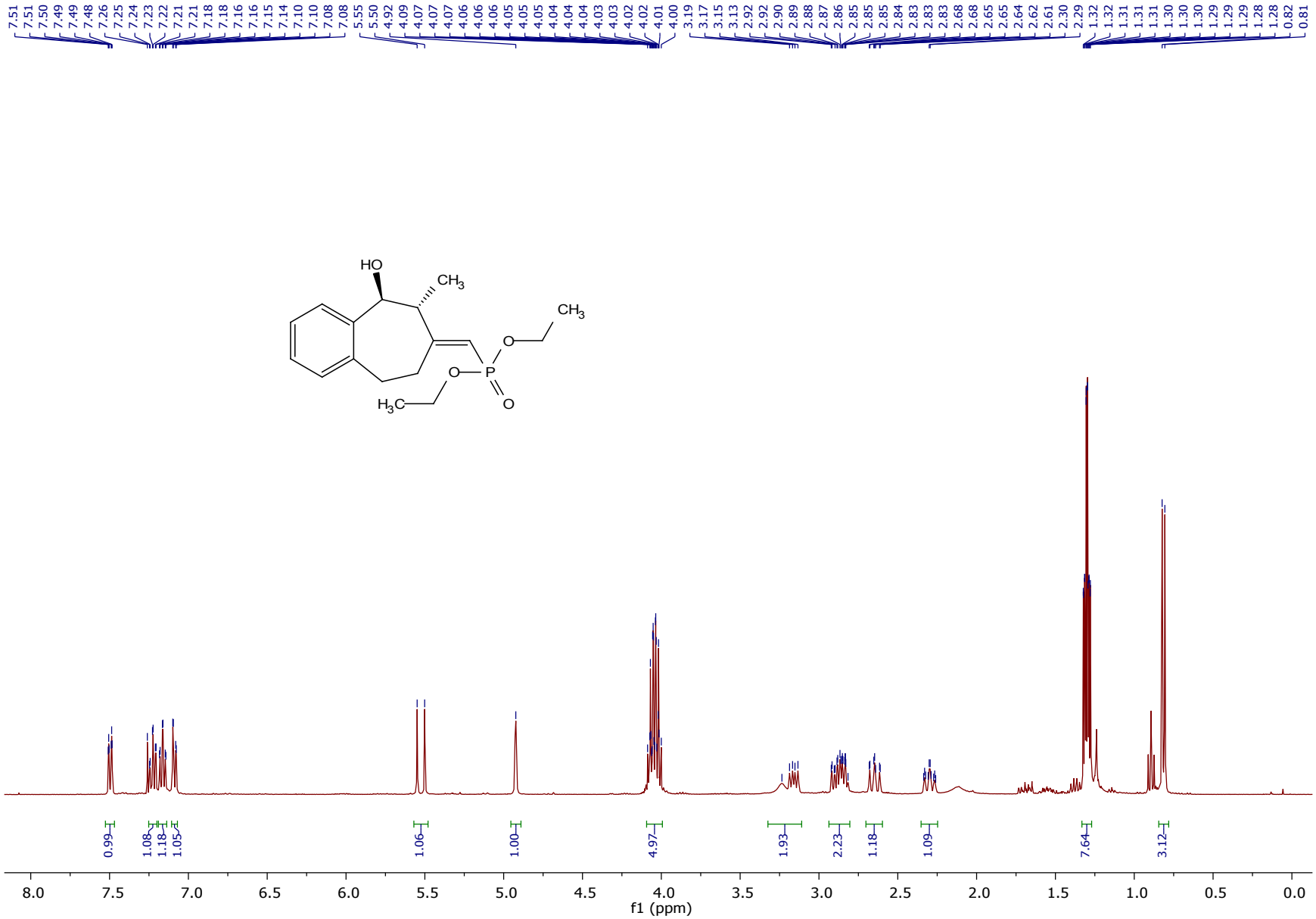

159.53
141.54
139.00
129.02
127.78
126.92
126.28
125.34
77.48
77.16
76.84
74.55
60.92
35.35
31.89
20.16
12.08
0.64
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

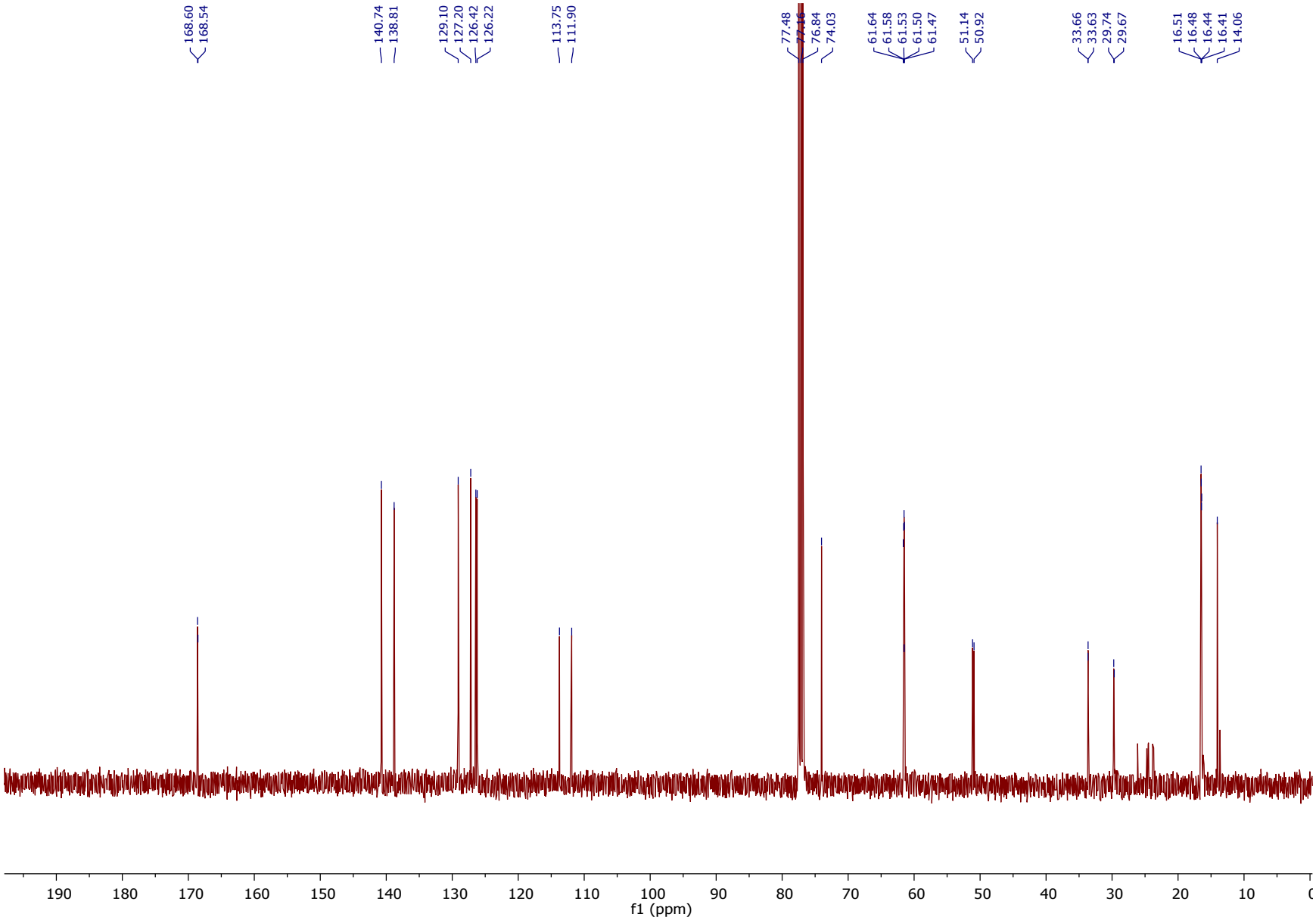

7.48 7.48 7.47 7.46 7.46 7.46 7.27 7.27 7.26 7.26 7.25 7.23 7.23 7.21 7.20 7.19 7.17 7.17 7.12 7.11 7.10 7.10
5.42
4.90
2.87 2.87 2.85 2.85 2.83 2.83 2.81 2.81 2.67 2.67 2.64 2.64 2.63 2.61 2.60 2.53 2.52 2.51 2.50 2.49 2.49 2.47 2.47 2.27 2.27 2.24 2.24 2.23 2.21 2.21 2.03
0.93 0.84 0.83
0.15 0.14
HO
CH3
CH3
Si
H3C
CH3
H3C
CH3
1.08 1.30 1.13 1.00 1.00 1.00 2.12 1.06 1.06 1.00 0.95 9.08 3.06 6.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

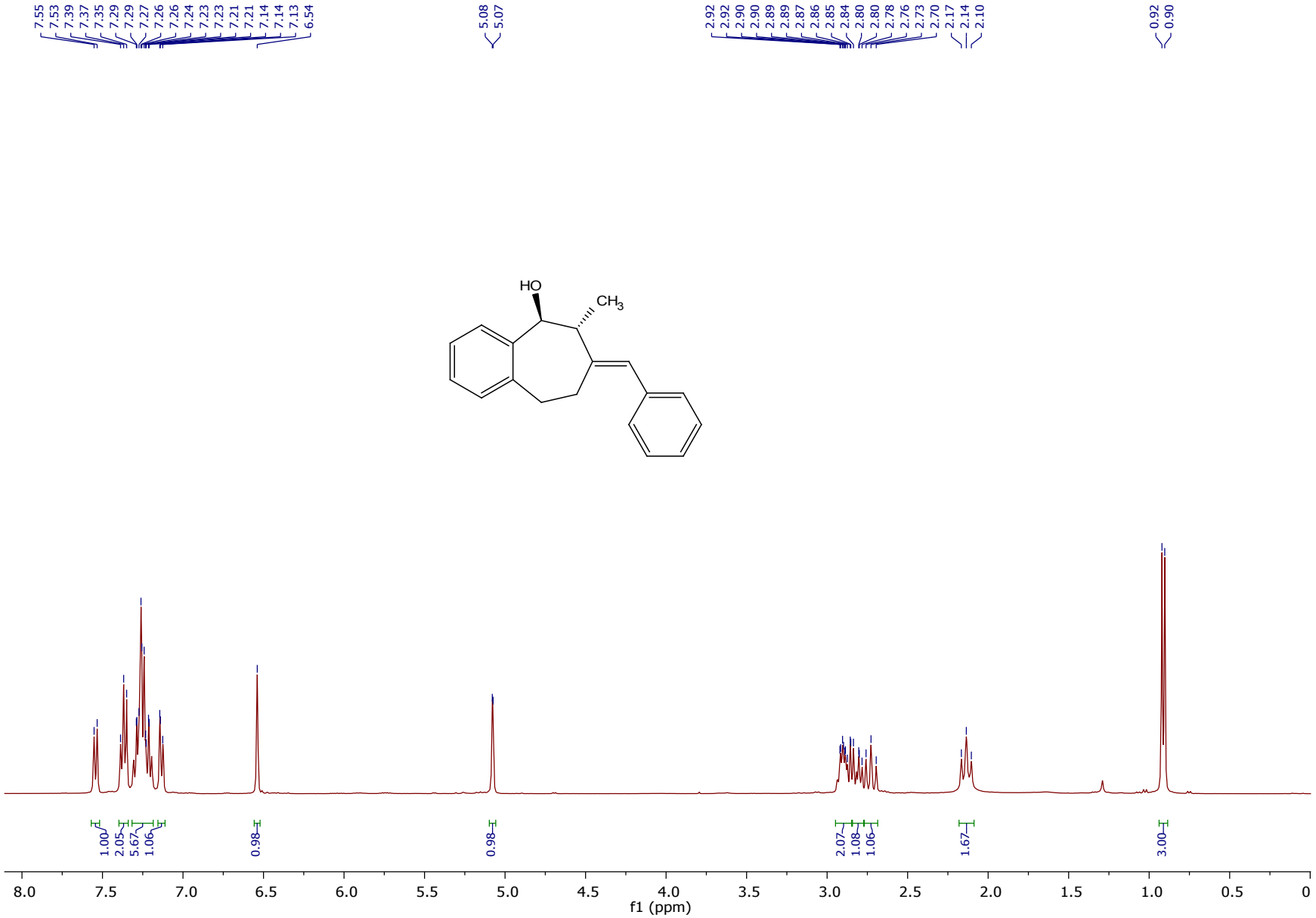

162.20
141.27
139.43
129.17
127.12
126.32
126.14
123.03
77.48
77.16
76.84
75.48
52.71
35.35
32.71
26.68
17.08
14.63
-3.57
-3.62
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

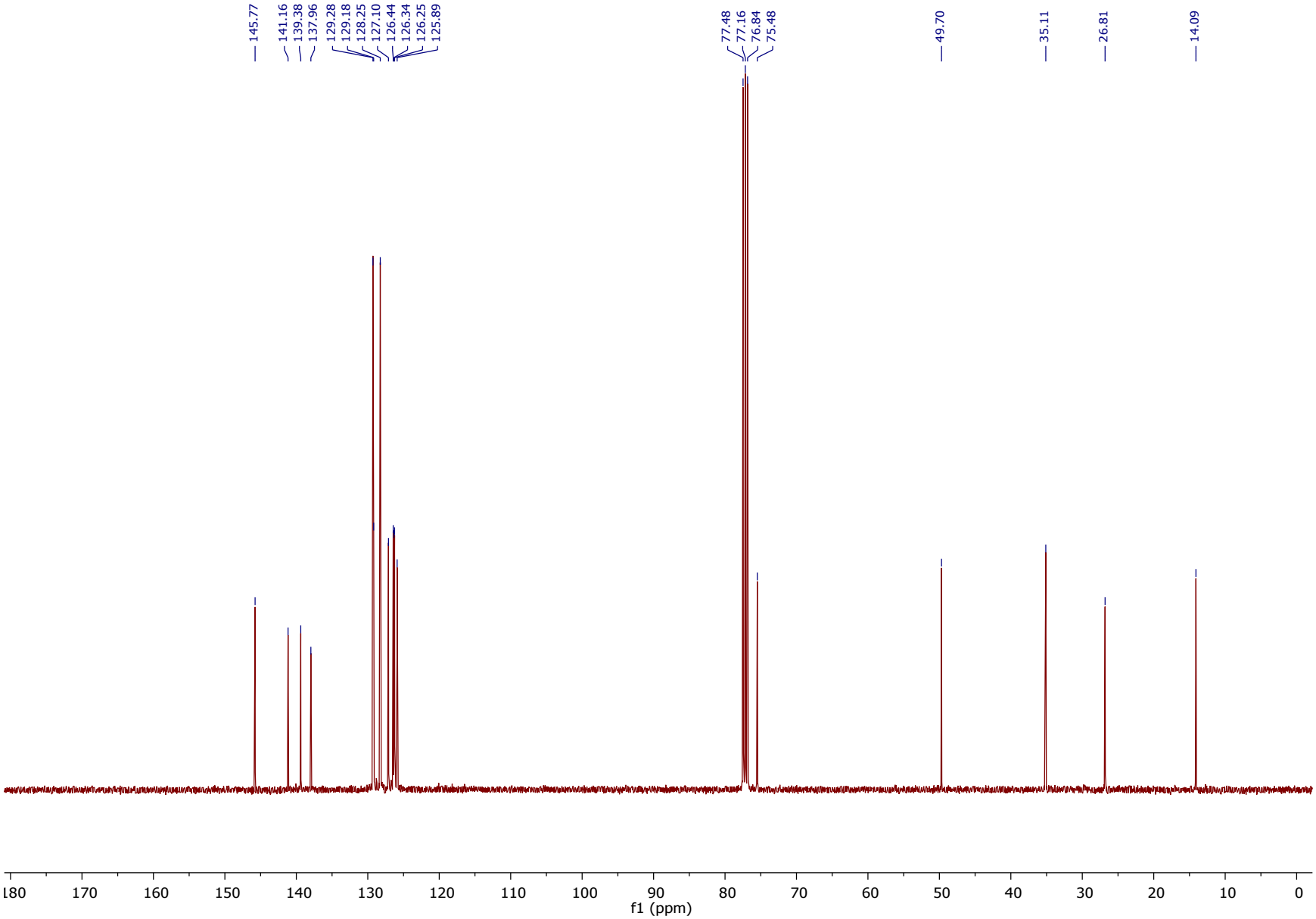

7.48 7.47 7.47 7.46 7.45 7.45 7.26 7.26 7.24 7.24 7.22 7.22 7.20 7.20 7.18 7.18 7.17 7.16 7.16 7.13 7.13 7.11 7.11
5.48 5.46 5.45 5.43 4.89 2.85 2.85 2.83 2.83 2.82 2.81 2.80 2.79 2.76 2.75 2.74 2.73 2.72 2.72 2.70 2.70 2.65 2.65 2.63 2.62 2.61 2.59 2.59 2.56 2.55 2.54 2.53 2.52 2.52 2.50 2.50 2.10 2.07 2.04
1.70 1.68
0.82 0.80
HO
CH3
CH3
1.00 2.83 1.06 1.00 0.79 1.02 1.17 1.05 0.92 1.13 3.01 2.75
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

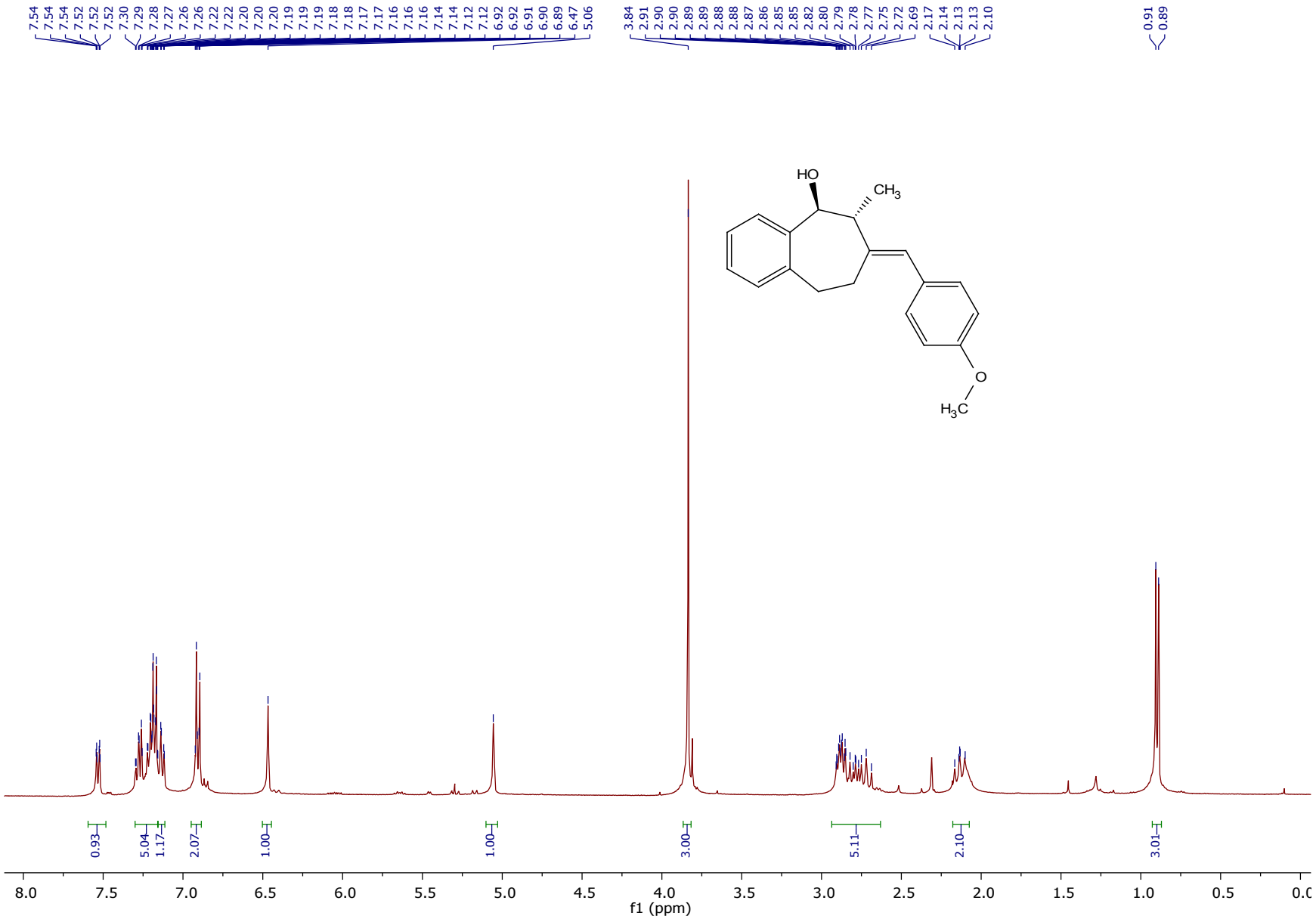

143.03
141.51
139.78
129.33
127.03
126.24
126.21
119.89
77.48
77.16
76.84
76.08
49.28
35.08
26.32
14.33
12.92
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

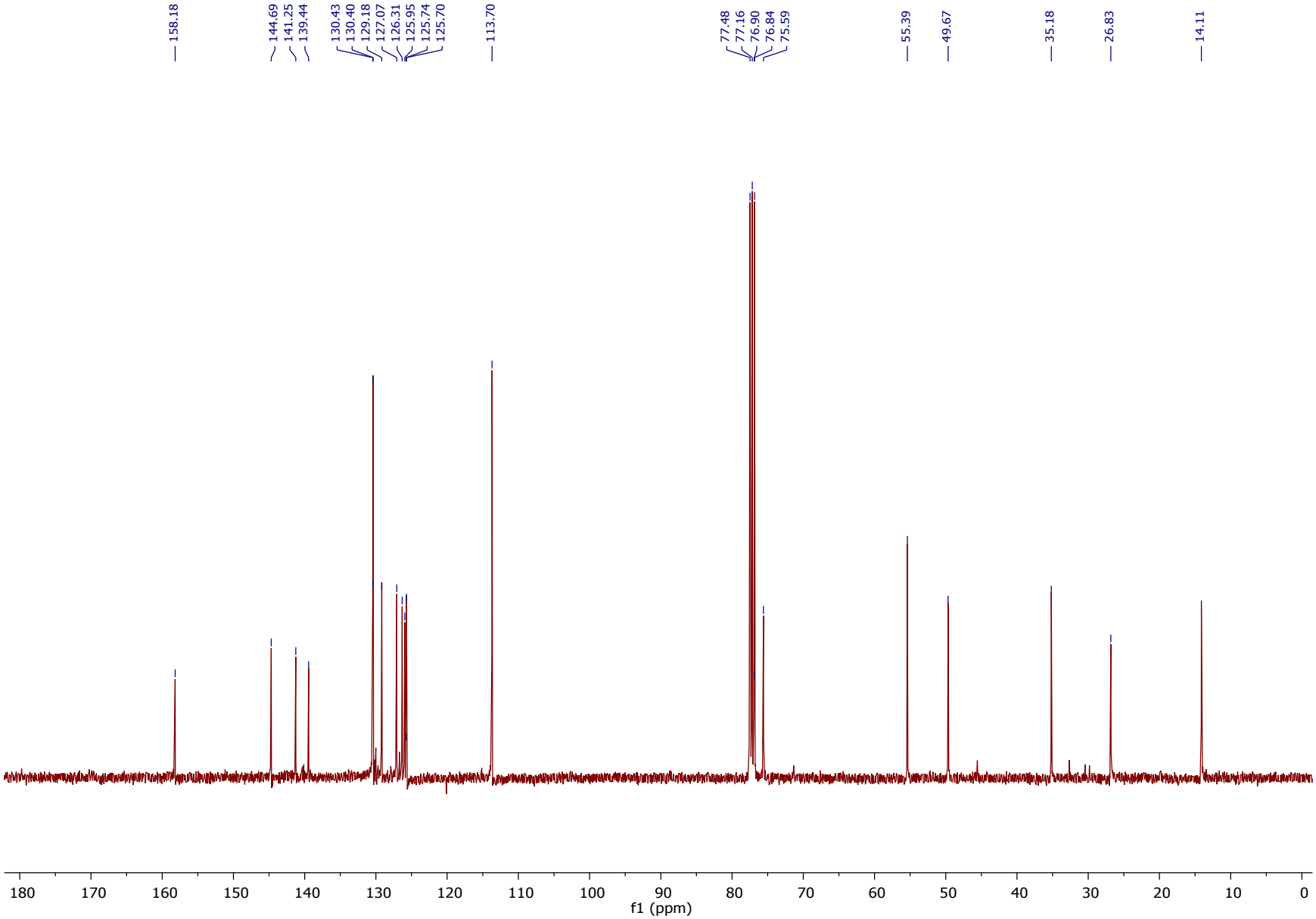

7.51 7.51 7.50 7.49 7.49 7.48 7.26 7.25 7.24 7.23 7.22 7.21 7.21 7.18 7.18 7.16 7.16 7.15 7.14 7.10 7.10 7.08 7.08 5.55 5.50 4.92 4.09 4.07 4.07 4.07 4.06 4.06 4.06 4.06 4.05 4.05 4.05 4.04 4.04 4.04 4.04 4.03 4.03 4.02 4.02 4.01 4.00 3.19 3.17 3.15 3.13 2.92 2.92 2.90 2.89 2.88 2.87 2.86 2.85 2.85 2.85 2.84 2.83 2.83 2.83 2.68 2.68 2.65 2.65 2.64 2.62 2.61 2.30 2.29 1.32 1.32 1.31 1.31 1.31 1.30 1.30 1.30 1.29 1.29 1.29 1.28 0.82 0.81
HO
CH3
CH3
O
O
P
O
H3C
O
0.99
1.08
1.18
1.05
1.06
1.00
4.97
1.93
2.23
1.18
1.09
7.64
3.12
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

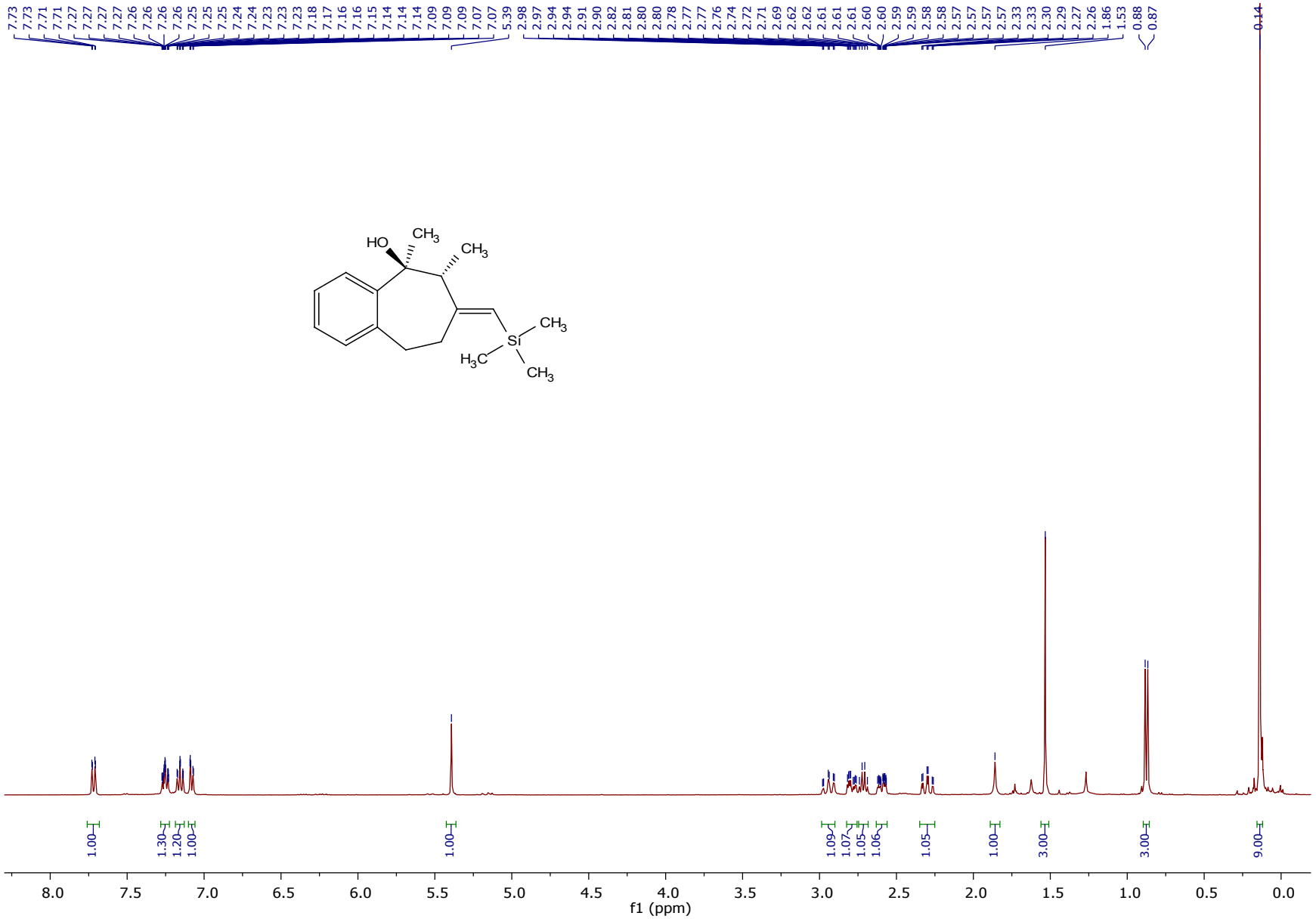

168.60
168.54
140.74
138.81
129.10
127.20
126.42
126.22
113.75
111.90
77.48
77.16
76.84
74.03
61.64
61.58
61.53
61.50
61.47
51.14
50.92
33.66
33.63
29.74
29.67
16.51
16.48
16.44
16.41
14.06
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

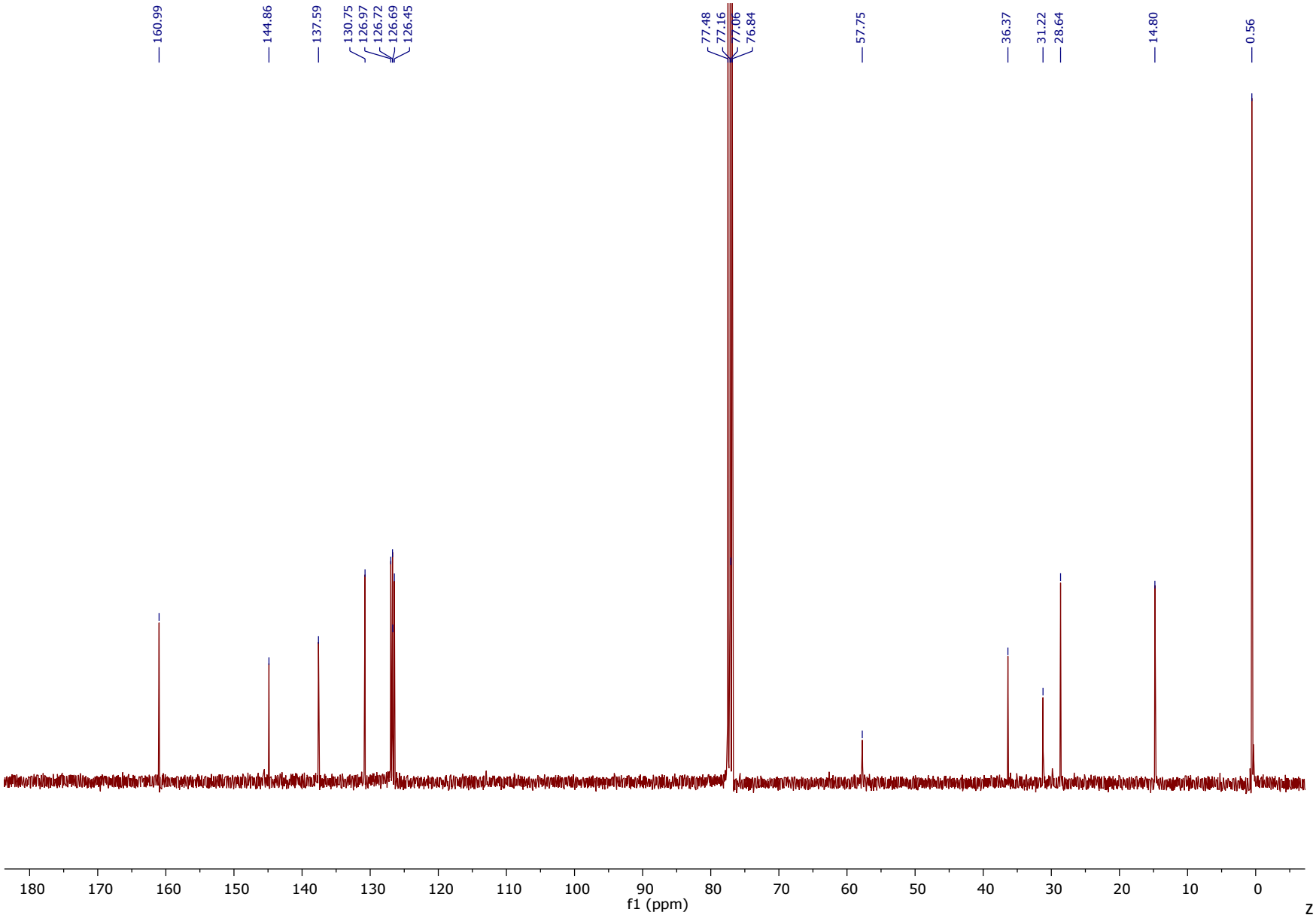

7.55
7.53
7.39
7.37
7.35
7.29
7.29
7.27
7.26
7.26
7.24
7.23
7.23
7.21
7.21
7.14
7.14
7.13
6.54
5.08
5.07
2.92
2.92
2.90
2.90
2.89
2.89
2.87
2.86
2.85
2.84
2.80
2.80
2.78
2.76
2.73
2.70
2.17
2.14
2.10
0.92
0.90
HO
CH3
1.00
2.05
5.67
1.06
0.98
0.98
2.07
1.08
1.06
1.67
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

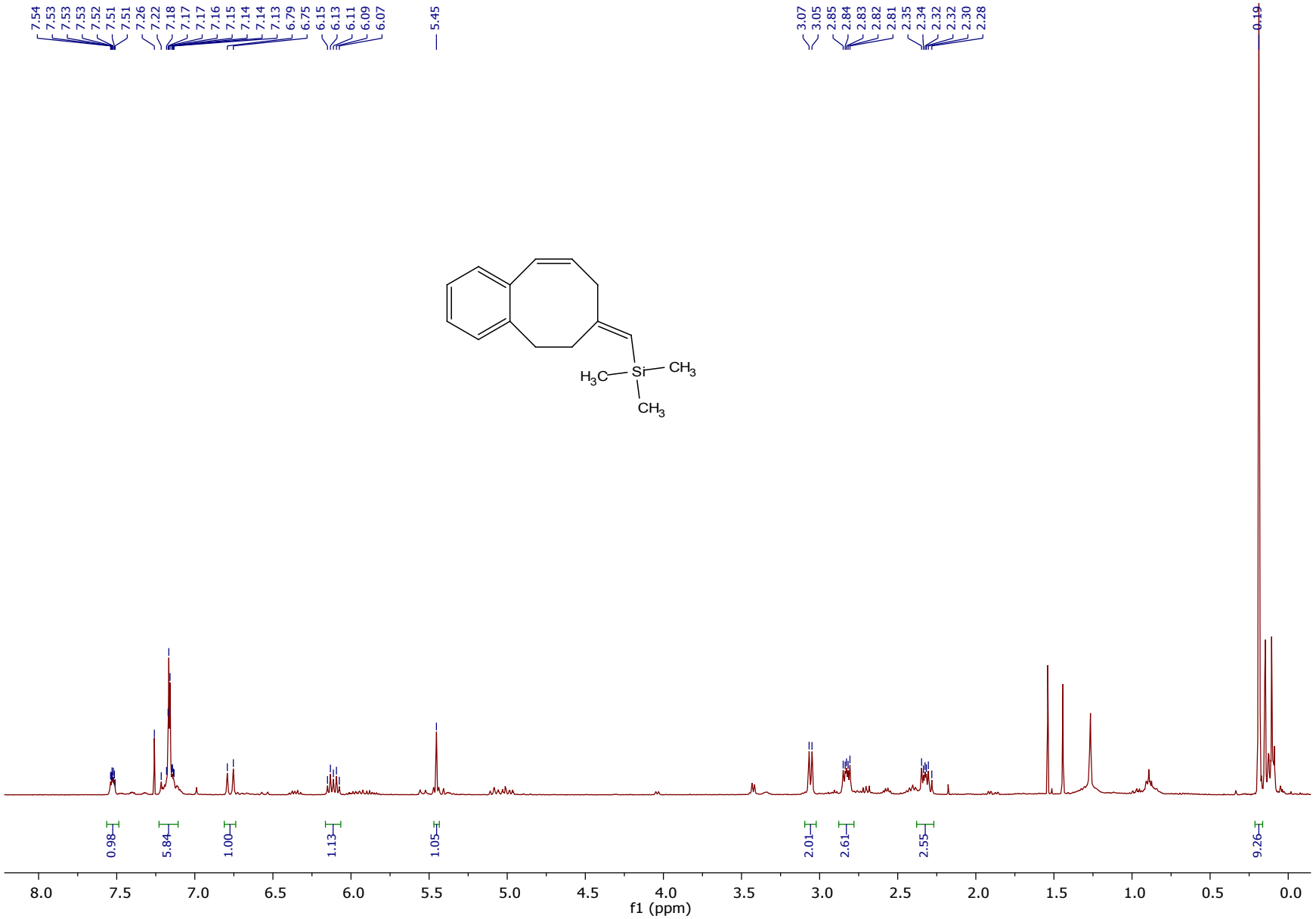

145.77
141.16
139.38
137.96
129.28
129.18
128.25
127.10
126.44
126.34
126.25
125.89
77.48
77.16
76.84
75.48
49.70
35.11
26.81
14.09
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

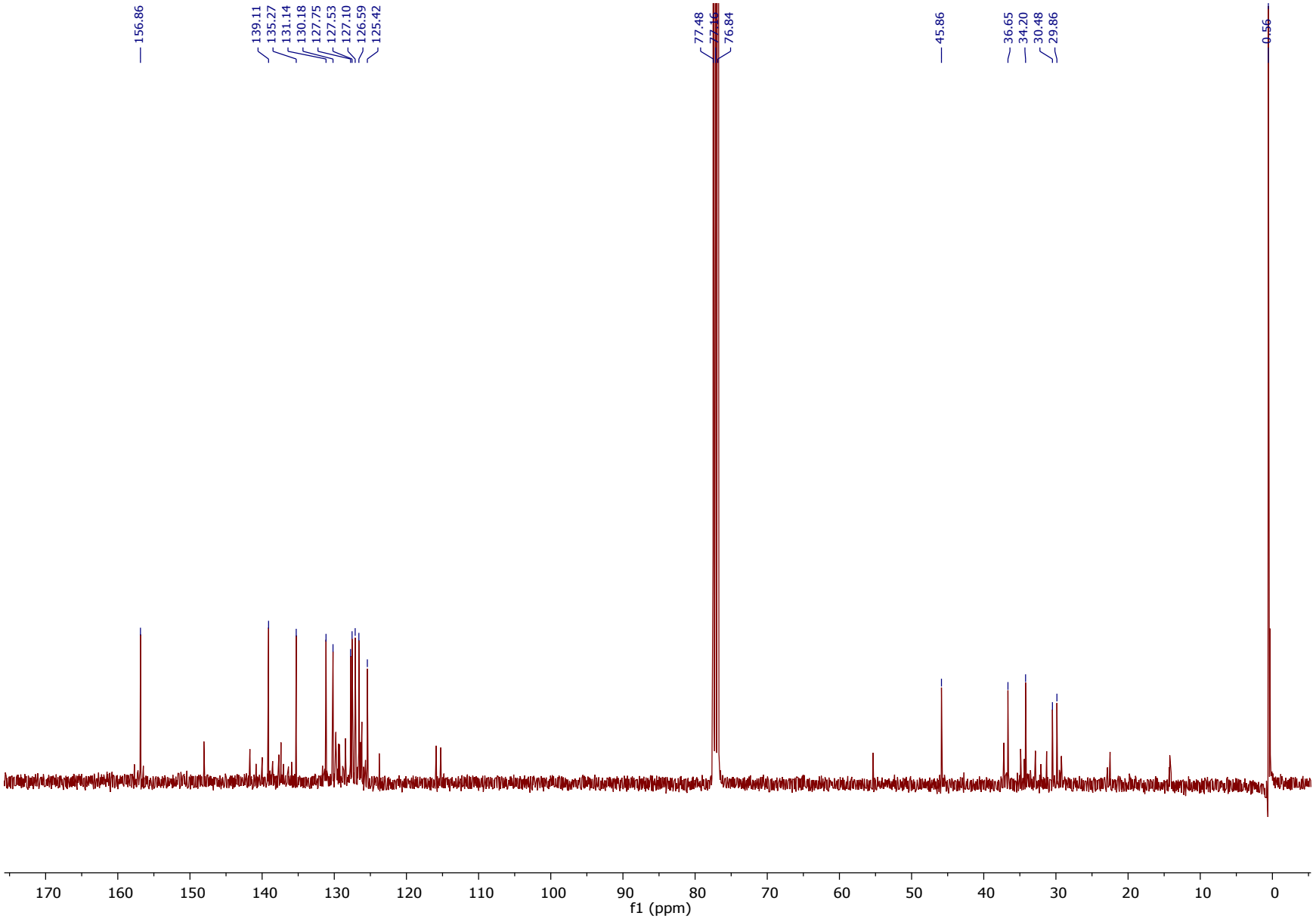

7.54 7.54 7.54 7.52 7.52 7.52 7.30 7.29 7.28 7.27 7.26 7.26 7.22 7.22 7.20 7.20 7.20 7.19 7.19 7.19 7.18 7.18 7.17 7.17 7.16 7.16 7.16 7.14 7.14 7.12 7.12 6.92 6.92 6.91 6.90 6.89 6.47 5.06
3.84 2.91 2.90 2.90 2.89 2.89 2.88 2.88 2.87 2.86 2.85 2.85 2.82 2.80 2.79 2.78 2.77 2.75 2.72 2.69 2.17 2.14 2.13 2.13 2.10
0.91 0.89
HO
CH3
O
H3C
0.93 5.04 1.17 2.07 1.00 1.00 3.00 5.11 2.10 3.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

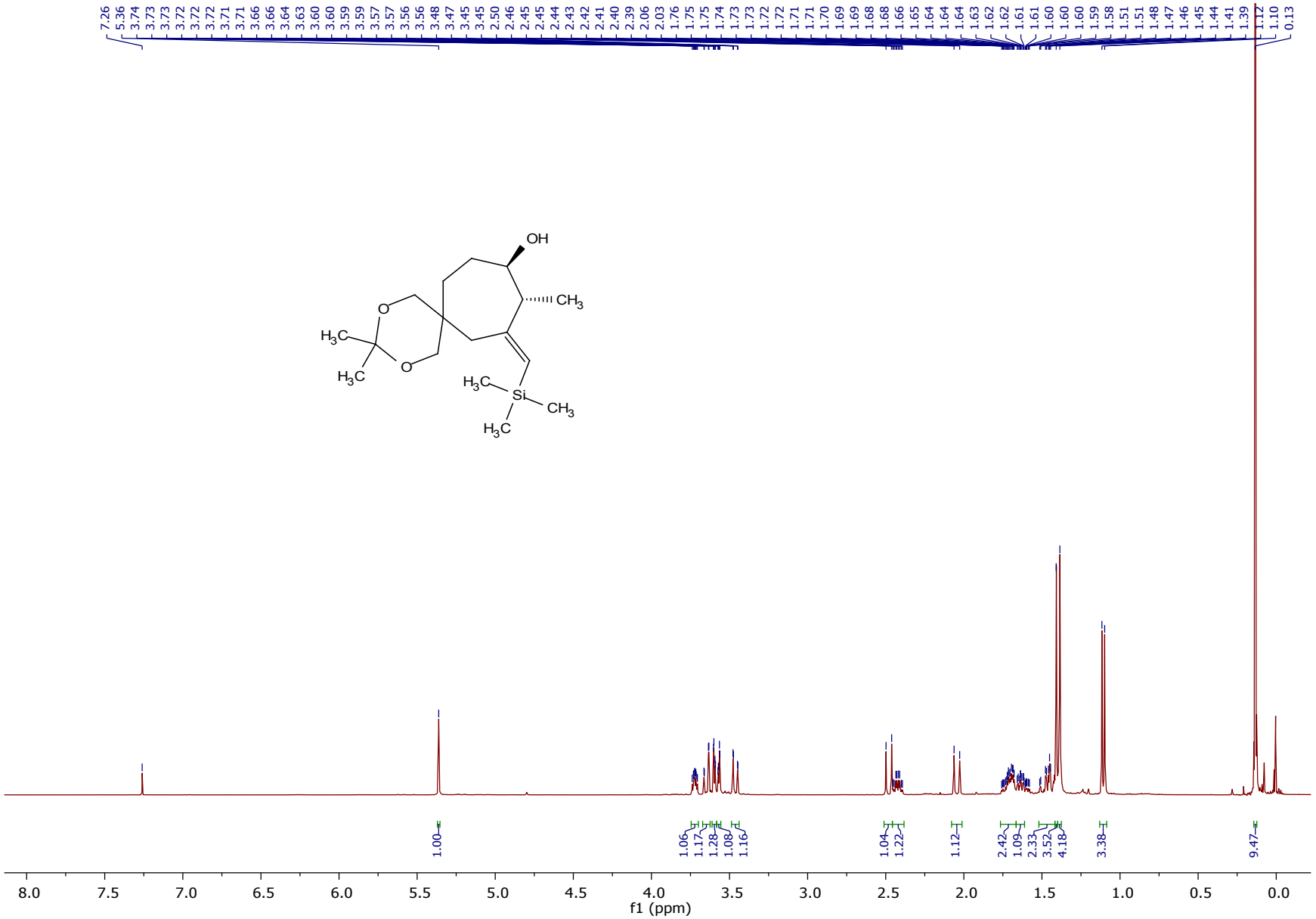

158.18
144.69
141.25
139.44
130.43
130.40
129.18
127.07
126.31
125.95
125.74
125.70
113.70
77.48
77.16
76.90
76.84
75.59
55.39
49.67
35.18
26.83
14.11
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

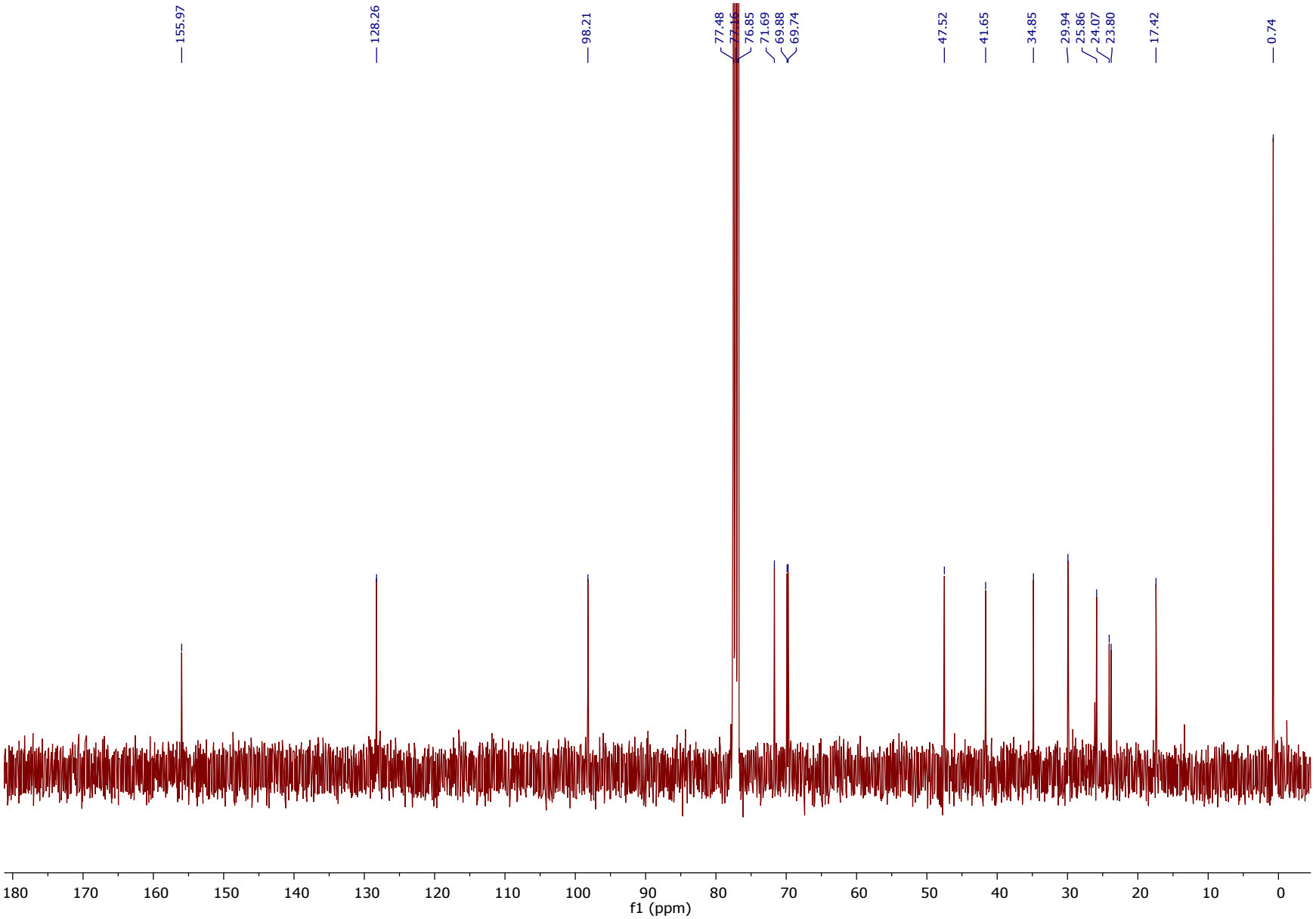

7.73 7.73 7.71 7.71 7.27 7.27 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.25 7.24 7.24 7.23 7.23 7.23 7.18 7.17 7.16 7.16 7.15 7.14 7.14 7.14 7.09 7.09 7.09 7.07 7.07 5.39 2.98 2.97 2.94 2.94 2.91 2.90 2.82 2.81 2.80 2.80 2.78 2.77 2.77 2.76 2.74 2.72 2.71 2.69 2.62 2.62 2.61 2.61 2.61 2.60 2.60 2.59 2.59 2.58 2.58 2.57 2.57 2.57 2.57 2.33 2.33 2.30 2.29 2.27 2.26 1.86 1.53 0.88 0.87 0.14
HO
CH3
CH3
CH3
Si
H3C
CH3
1.00 1.30 1.20 1.00 1.00 1.09 1.07 1.05 1.06 1.05 1.00 3.00 3.00 9.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

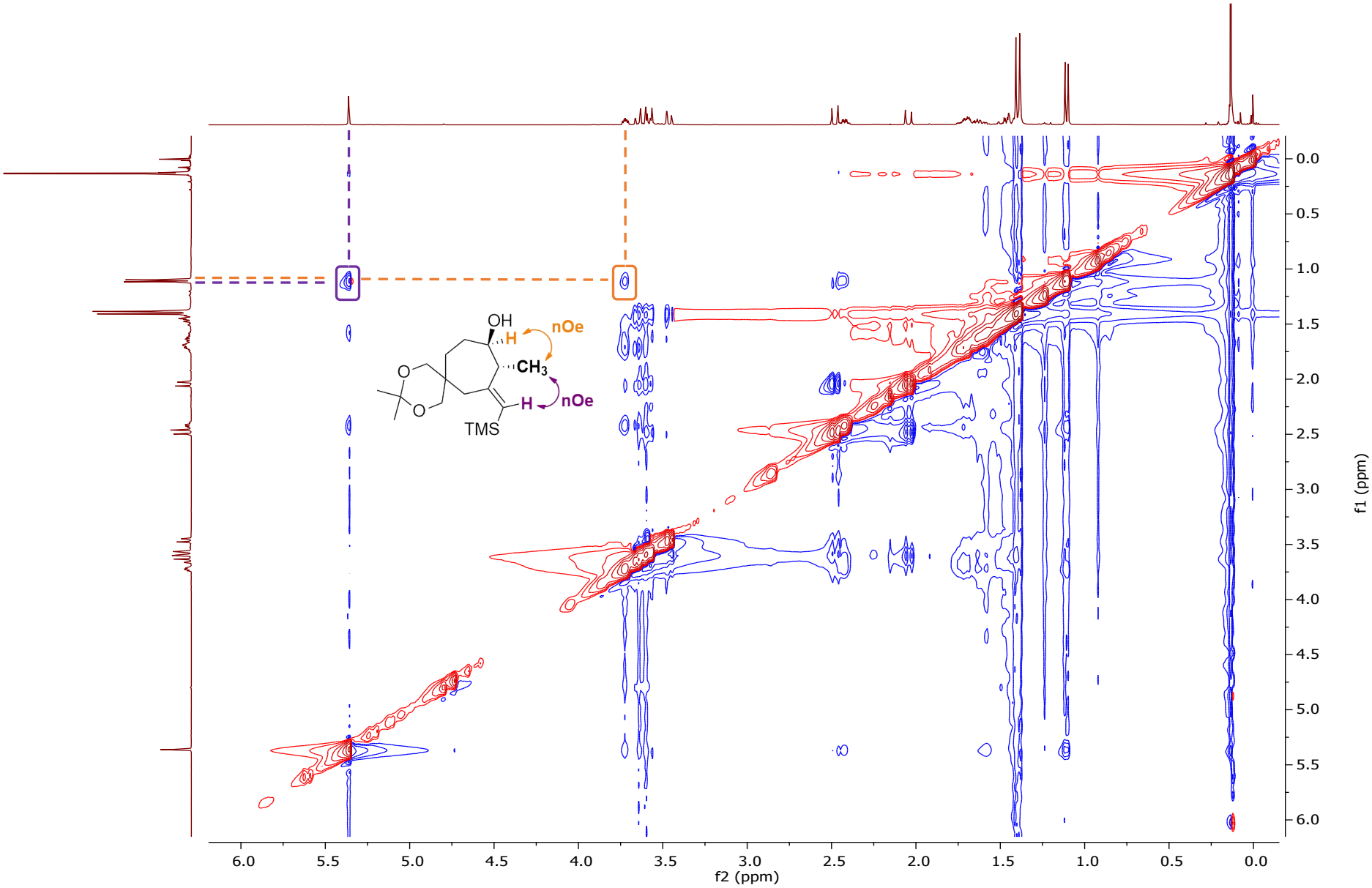

160.99
144.86
137.59
130.75
126.97
126.72
126.69
126.45
77.48
77.16
77.06
76.84
57.75
36.37
31.22
28.64
14.80
0.56
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

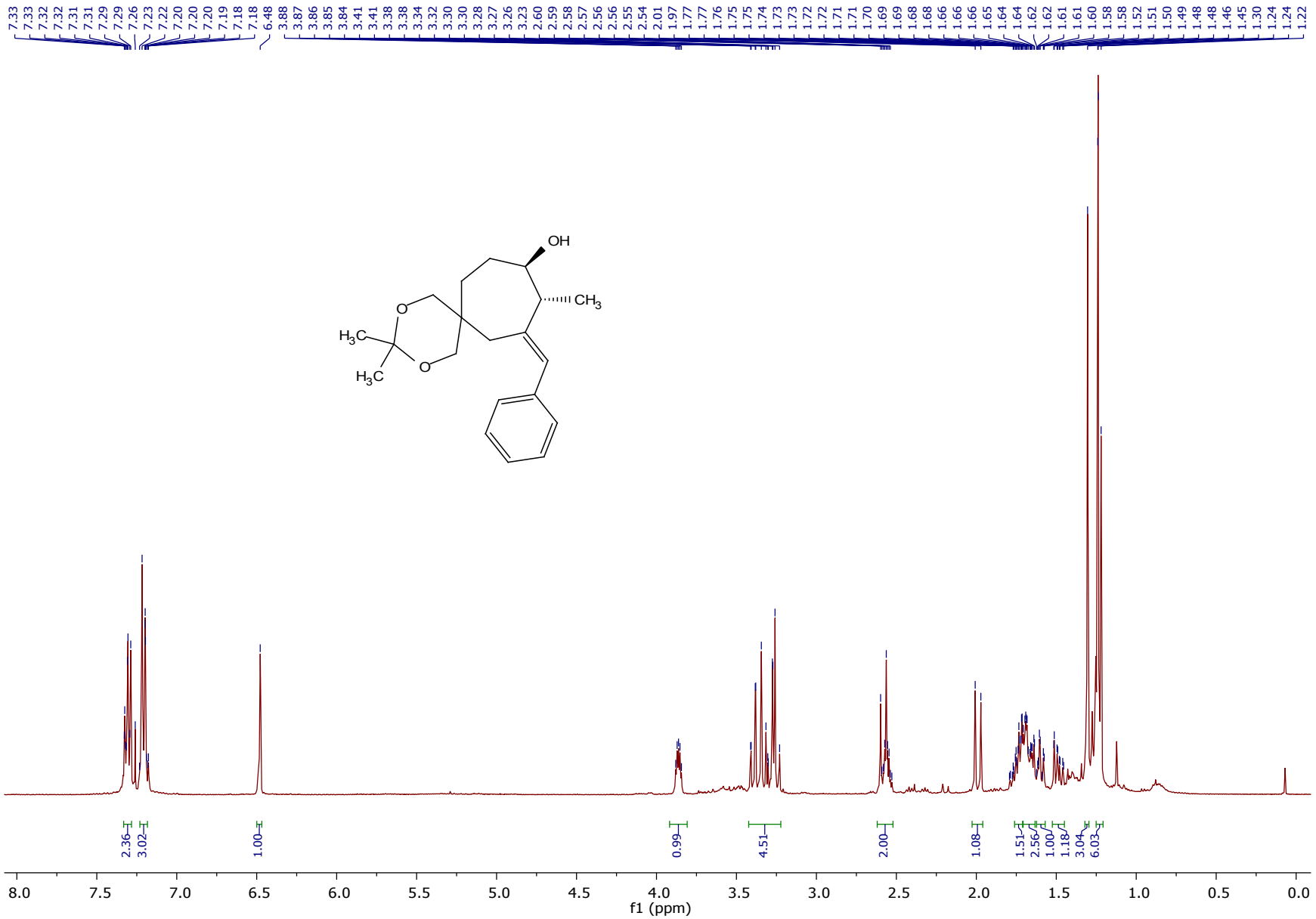

7.54
7.53
7.53
7.53
7.52
7.51
7.51
7.26
7.22
7.18
7.17
7.17
7.16
7.15
7.14
7.14
7.13
6.79
6.75
6.15
6.13
6.11
6.09
6.07
5.45
3.07
3.05
2.85
2.84
2.83
2.82
2.81
2.35
2.34
2.32
2.32
2.30
2.28
0.19
H3C
Si
CH3
CH3
0.98
5.84
1.00
1.13
1.05
2.01
2.61
2.55
9.26
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

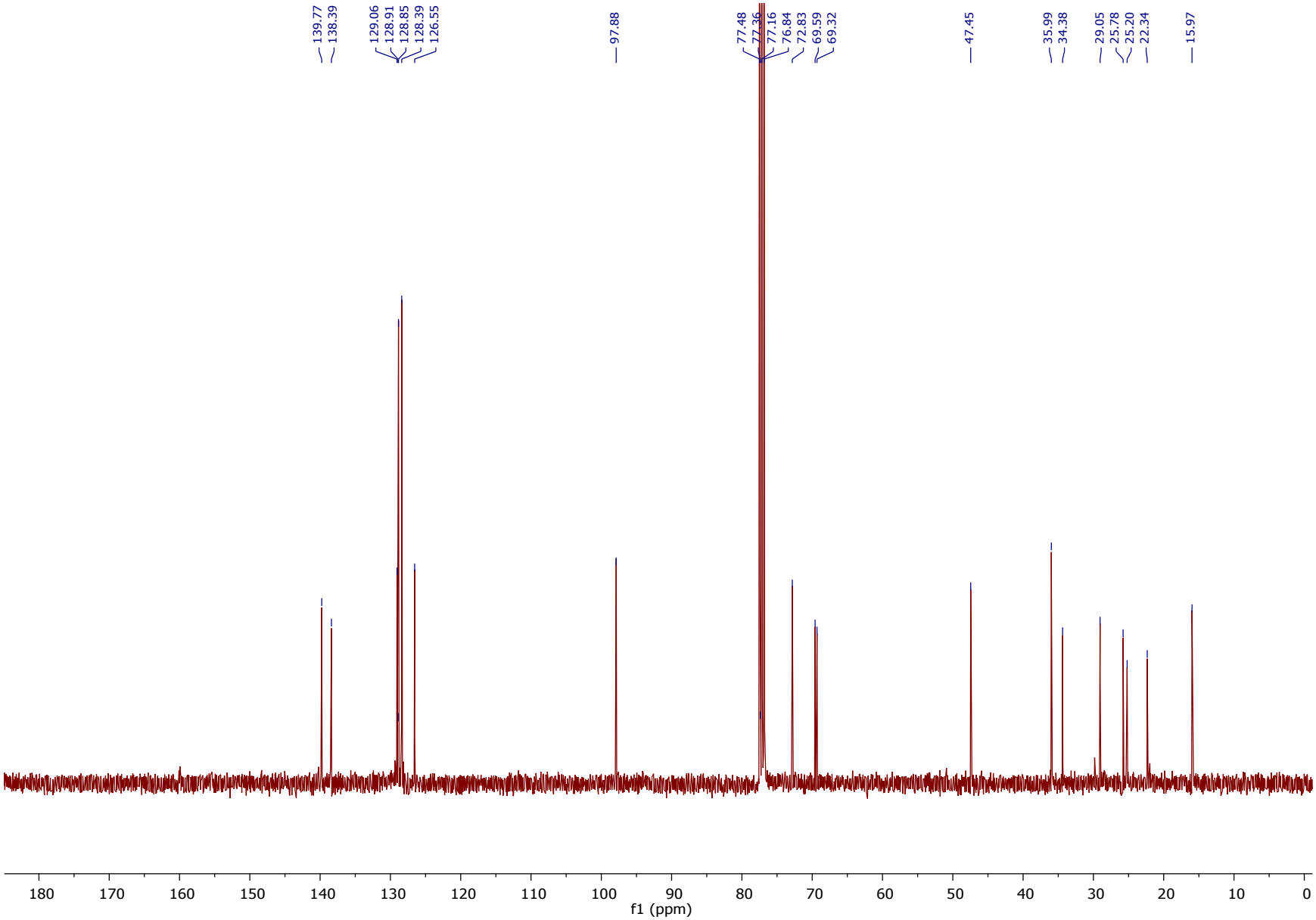

156.86
139.11
135.27
131.14
130.18
127.75
127.53
127.10
126.59
125.42
77.48
77.16
76.84
45.86
36.65
34.20
30.48
29.86
0.56
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

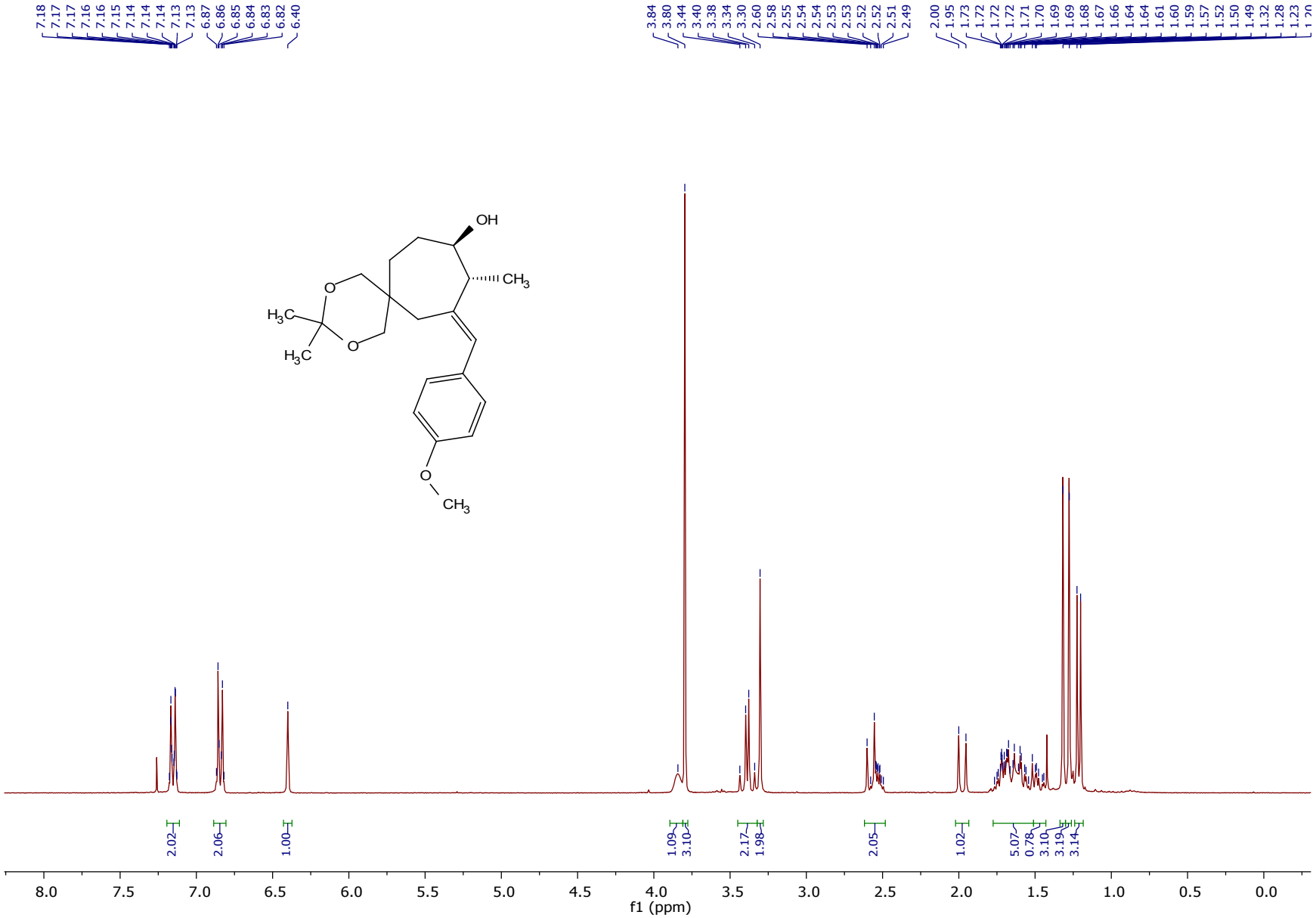

7.26 5.36 3.74 3.73 3.73 3.72 3.72 3.72 3.71 3.71 3.66 3.66 3.64 3.63 3.60 3.60 3.59 3.59 3.57 3.57 3.56 3.56 3.48 3.47 3.45 3.45 2.50 2.46 2.45 2.45 2.44 2.43 2.42 2.41 2.40 2.39 2.06 2.03 1.76 1.75 1.75 1.74 1.73 1.73 1.72 1.72 1.71 1.71 1.70 1.69 1.69 1.68 1.68 1.66 1.65 1.64 1.64 1.64 1.63 1.62 1.62 1.61 1.61 1.60 1.60 1.60 1.59 1.58 1.51 1.51 1.48 1.47 1.46 1.45 1.44 1.41 1.39 1.12 1.10 0.13
OH
CH3
O
H3C
H3C
O
H3C
Si
CH3
H3C
1.00
1.06
1.17
1.28
1.08
1.16
1.04
1.22
1.12
2.42
1.09
2.33
3.52
4.18
3.38
9.47
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

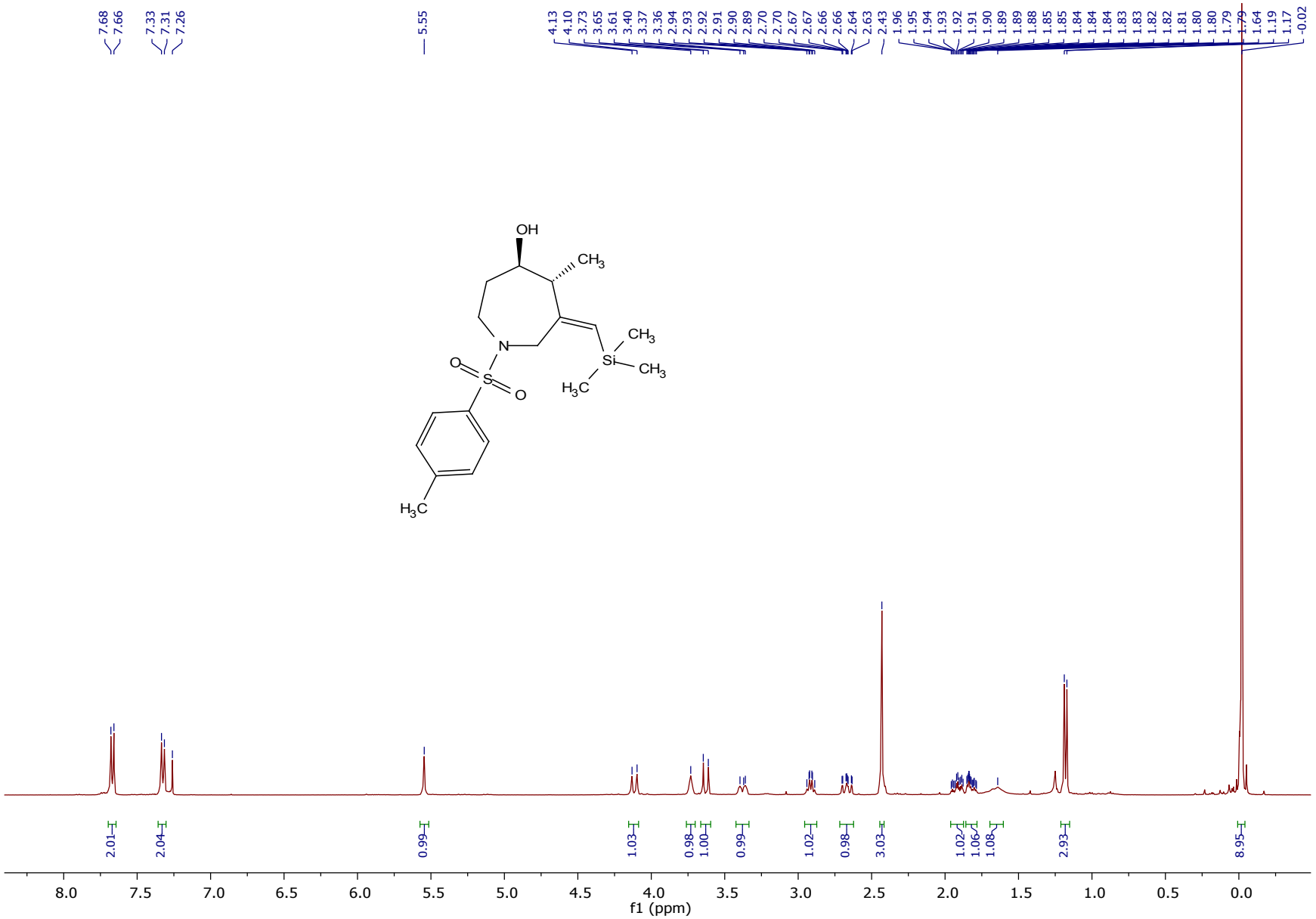

155.97
128.26
98.21
77.48
77.16
76.85
71.69
69.88
69.74
47.52
41.65
34.85
29.94
25.86
24.07
23.80
17.42
0.74
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

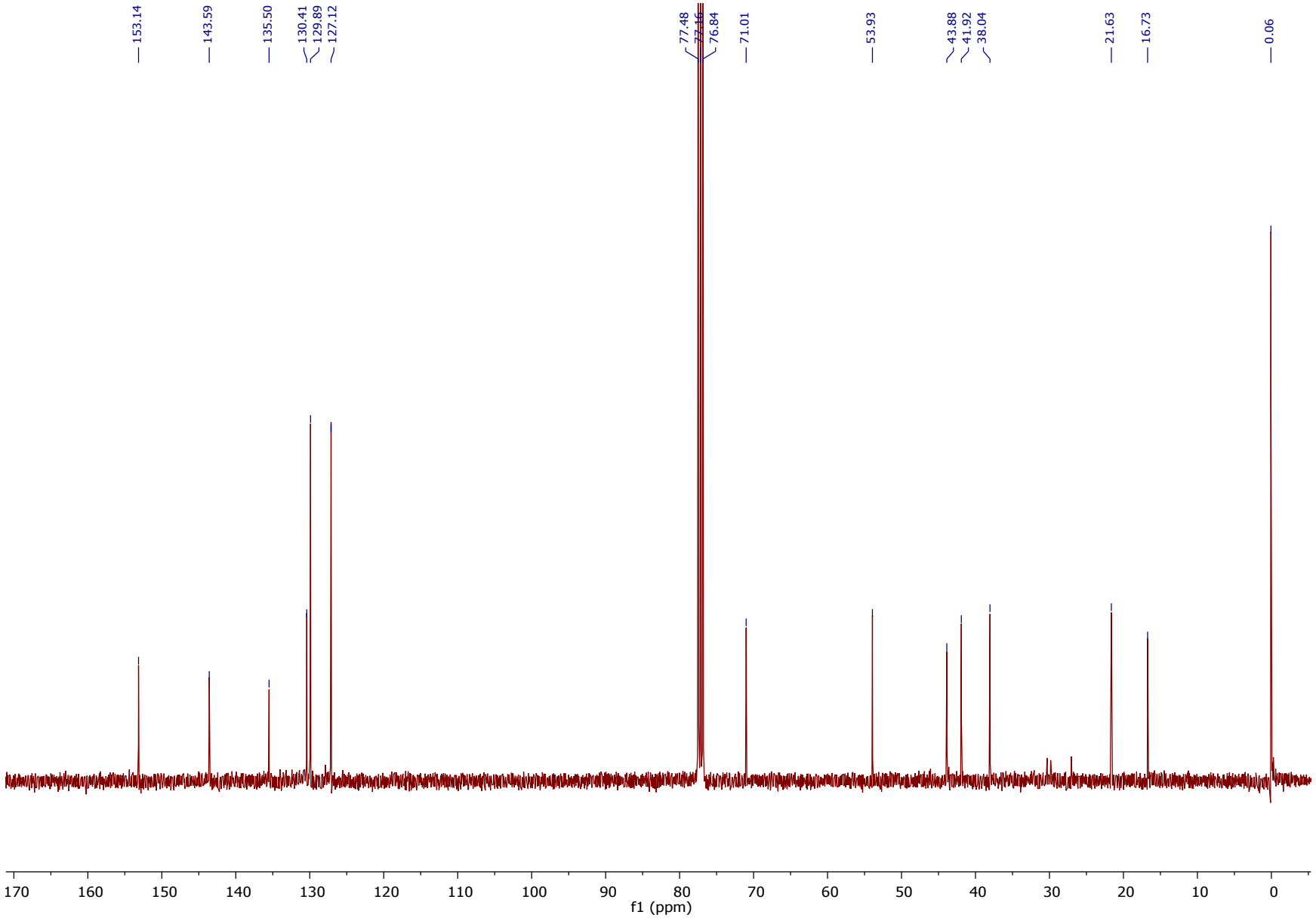

OH
H
nOe
CH3
H
nOe
TMS
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
f1 (ppm)

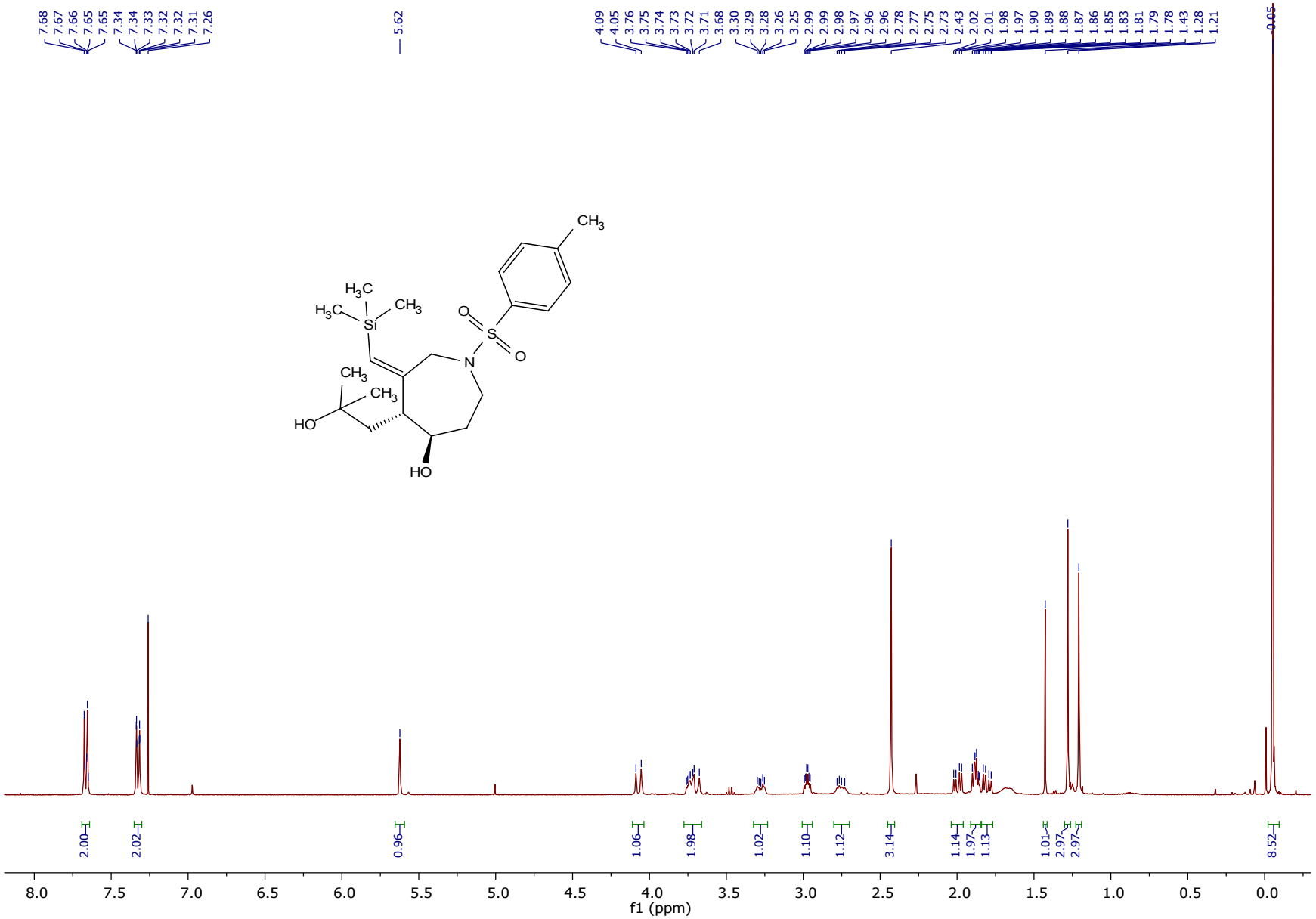

7.33 7.33 7.32 7.32 7.31 7.31 7.29 7.29 7.26 7.23 7.22 7.20 7.20 7.20 7.19 7.18 7.18 6.48
3.88 3.87 3.86 3.85 3.84 3.41 3.41 3.38 3.38 3.34 3.32 3.30 3.30 3.28 3.27 3.26 3.23 2.60 2.59 2.58 2.57 2.56 2.56 2.55 2.54 2.01 1.97 1.77 1.77 1.76 1.75 1.75 1.74 1.73 1.73 1.72 1.72 1.71 1.71 1.70 1.69 1.69 1.68 1.68 1.66 1.66 1.66 1.65 1.64 1.64 1.62 1.62 1.61 1.61 1.60 1.58 1.58 1.52 1.51 1.50 1.49 1.48 1.48 1.46 1.45 1.30 1.24 1.24 1.22
OH
CH3
H3C
H3C
O
O
2.36
3.02
1.00
0.99
4.51
2.00
1.08
1.51
2.56
1.00
1.18
3.04
6.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

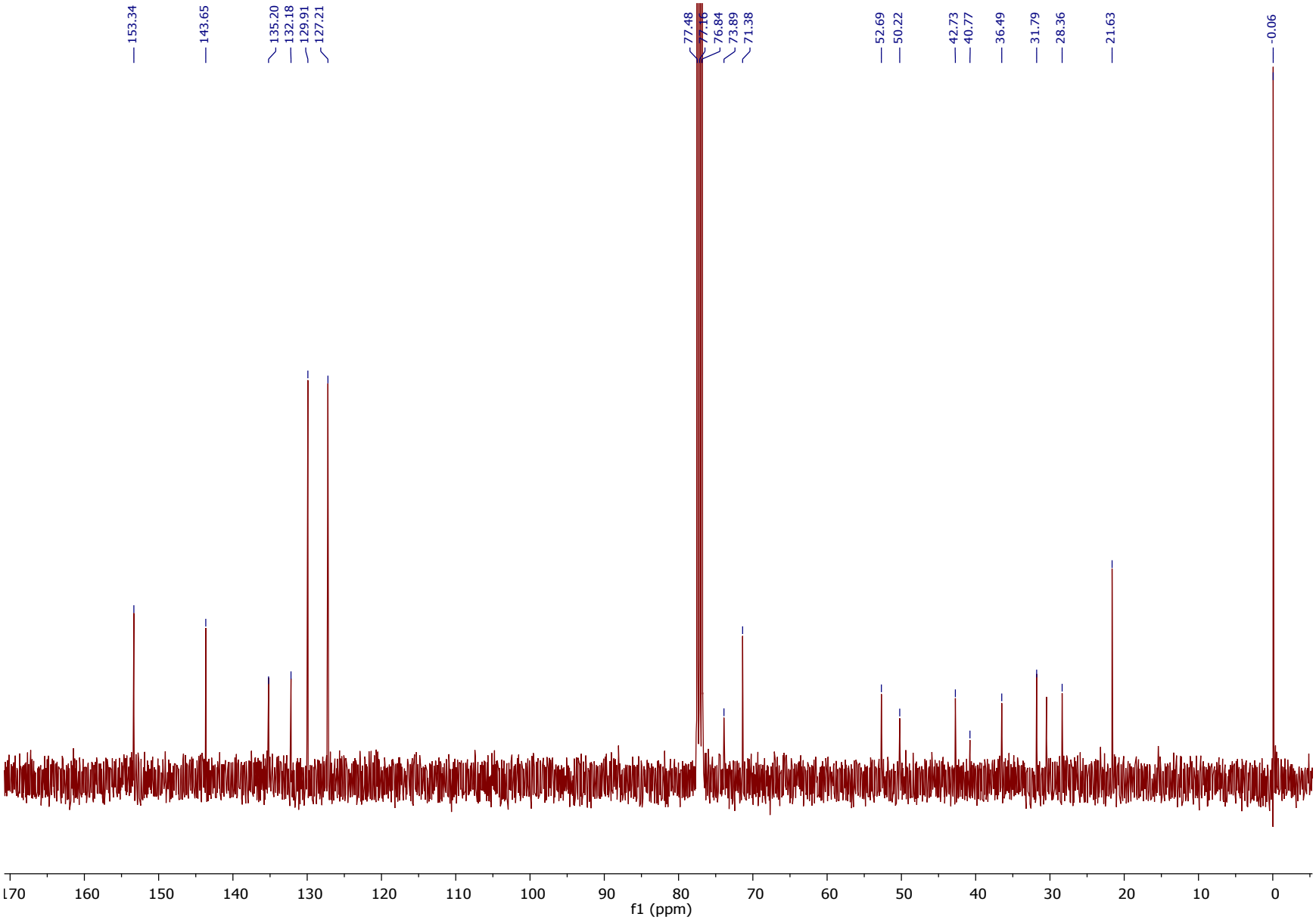

139.77
138.39
129.06
128.91
128.85
128.39
126.55
97.88
77.48
77.36
77.16
76.84
72.83
69.59
69.32
47.45
35.99
34.38
29.05
25.78
25.20
22.34
15.97
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

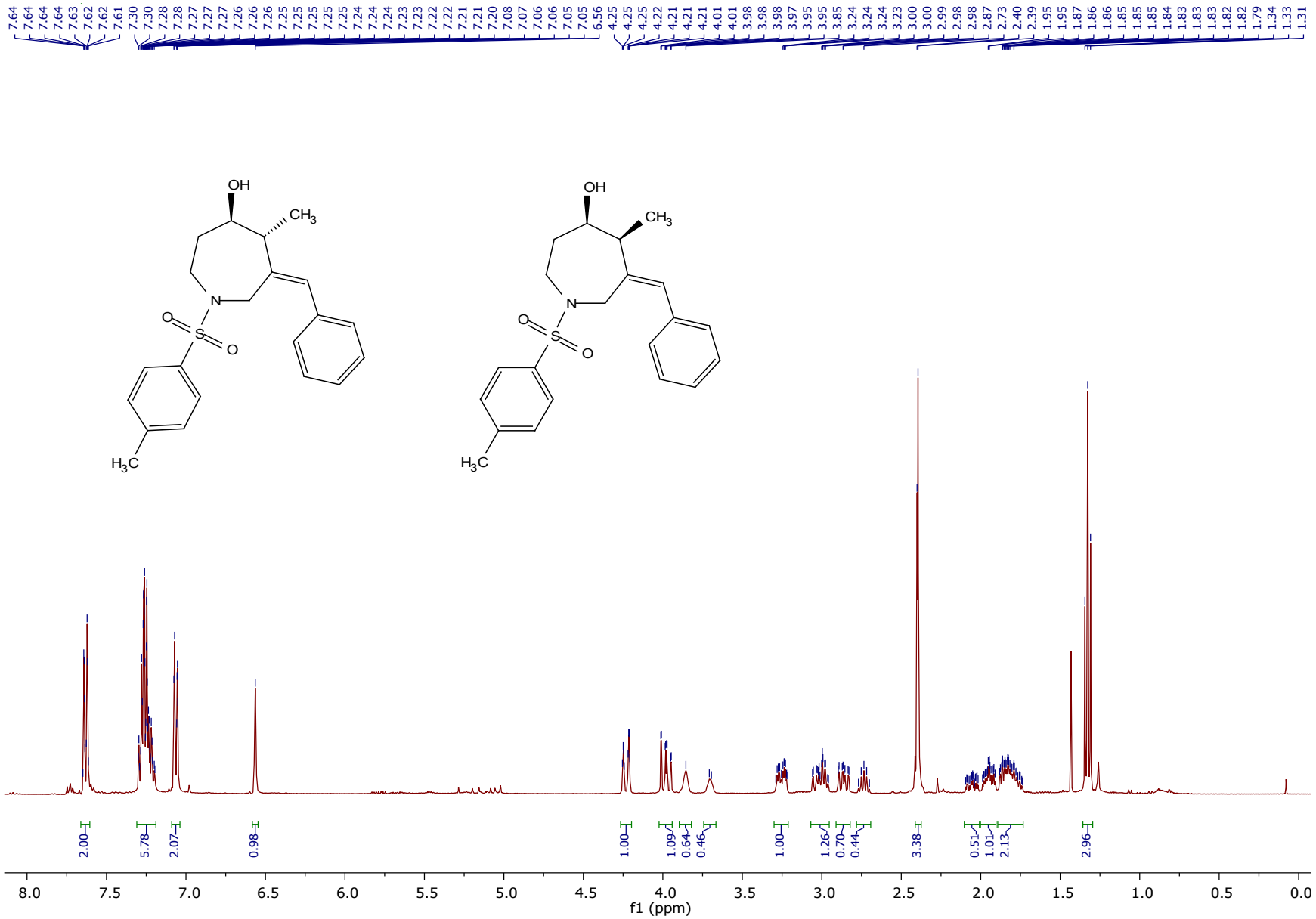

7.18 7.17 7.17 7.16 7.16 7.15 7.14 7.14 7.14 7.13 7.13 6.87 6.86 6.85 6.84 6.83 6.82 6.40
3.84 3.80 3.44 3.40 3.38 3.34 3.30 2.60 2.58 2.55 2.54 2.54 2.53 2.53 2.52 2.52 2.51 2.49
2.00 1.95 1.73 1.72 1.72 1.72 1.71 1.70 1.69 1.69 1.68 1.67 1.66 1.64 1.64 1.61 1.60 1.59 1.57 1.52 1.50 1.49 1.32 1.28 1.23
OH
CH3
O
H3C
H3C
O
O
CH3
2.02 2.06 1.00 1.09 3.10 2.17 1.98 2.05 1.02 5.07 0.78 3.10 3.19 3.14
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

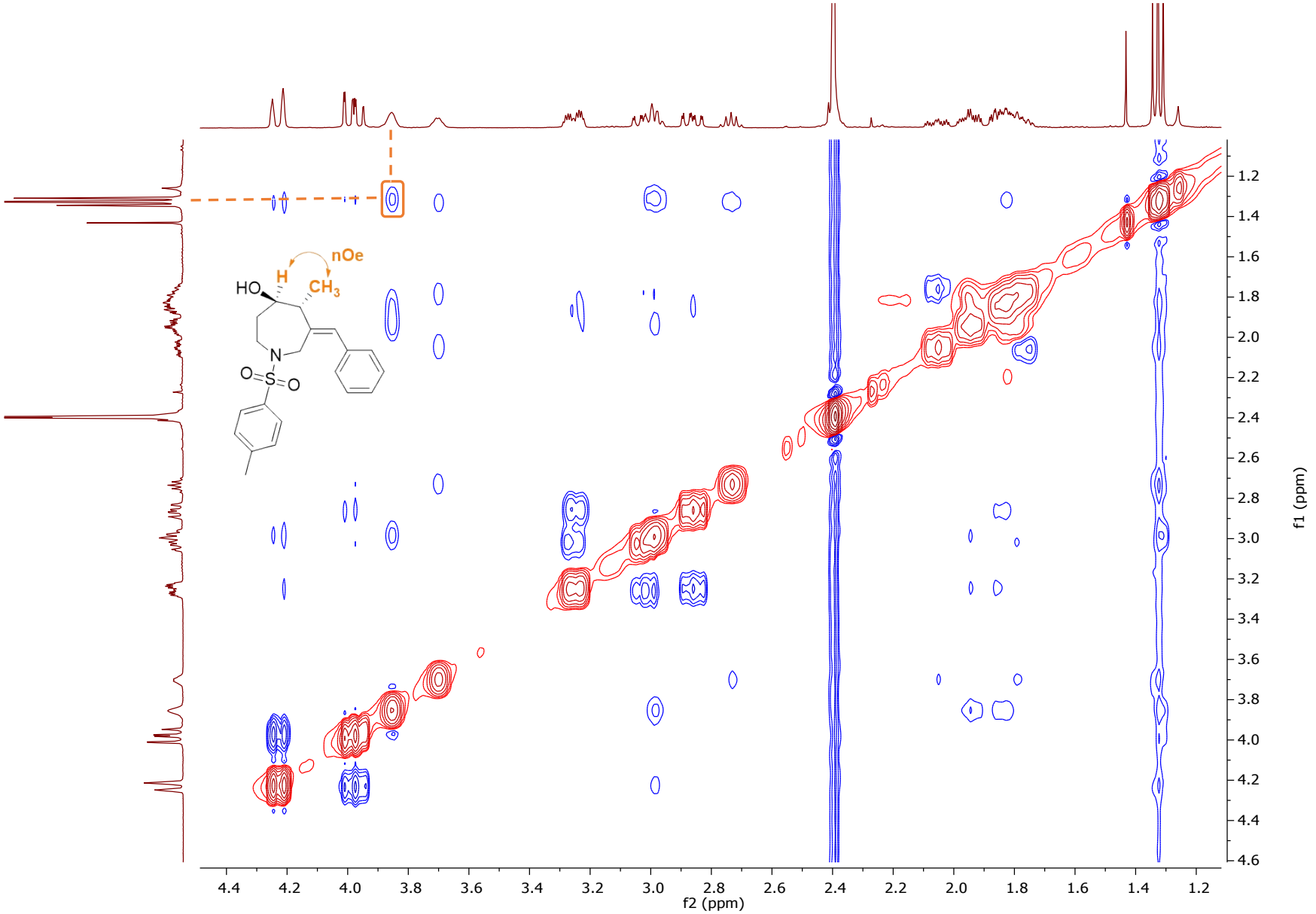

7.68
7.66
7.33
7.31
7.26
5.55
4.13
4.10
3.73
3.65
3.61
3.40
3.37
3.36
2.94
2.93
2.92
2.91
2.90
2.89
2.70
2.70
2.67
2.67
2.66
2.66
2.64
2.63
2.43
1.96
1.95
1.94
1.93
1.92
1.91
1.90
1.89
1.89
1.88
1.85
1.85
1.84
1.84
1.84
1.83
1.83
1.82
1.82
1.81
1.80
1.80
1.79
1.79
1.64
1.19
1.17
-0.02
OH
CH3
N
O
S
O
CH3
Si
CH3
H3C
H3C
2.01
2.04
0.99
1.03
0.98
1.00
0.99
1.02
0.98
3.03
1.02
1.06
1.08
2.93
8.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

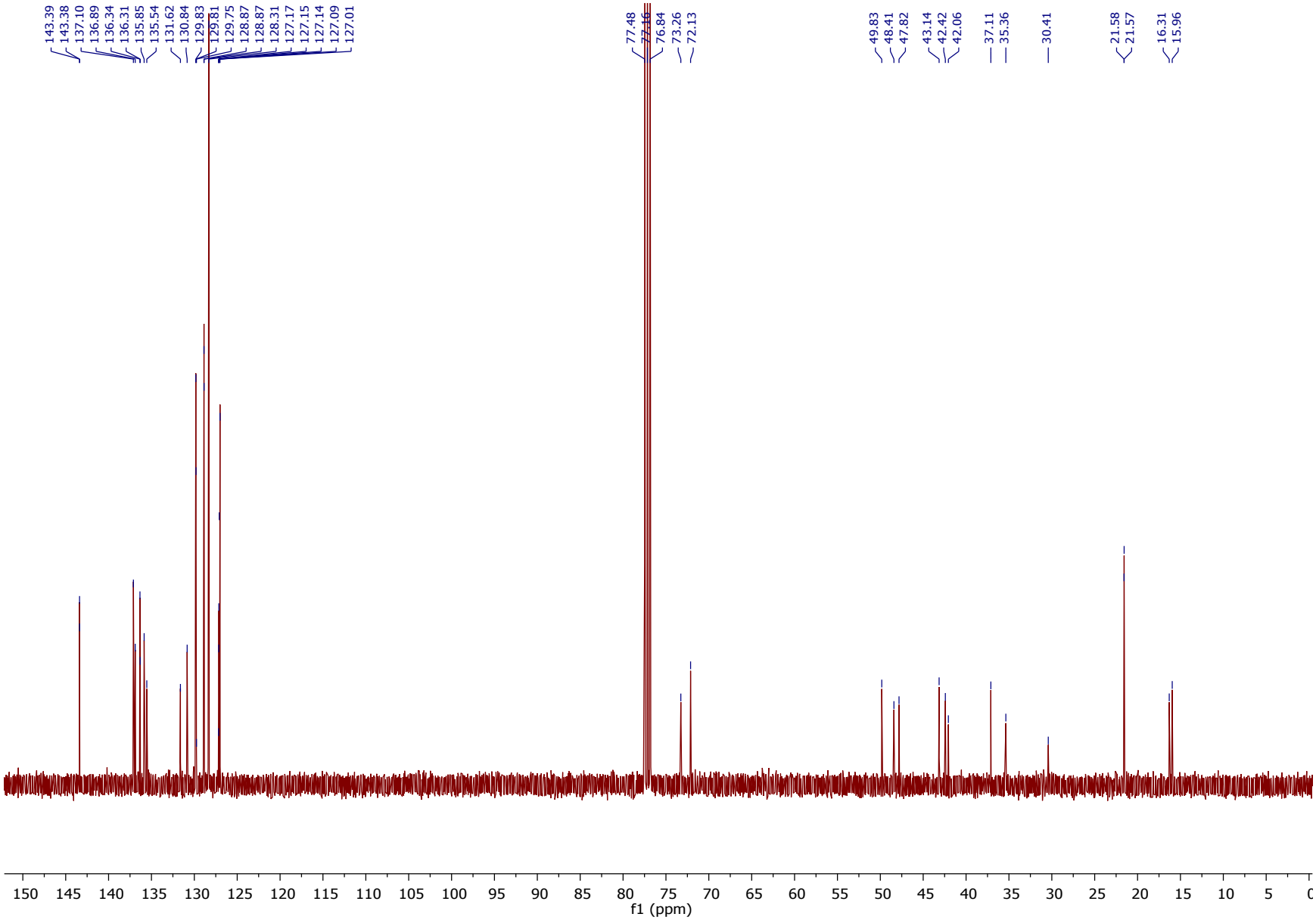

153.14
143.59
135.50
130.41
129.89
127.12
77.48
77.16
76.84
71.01
53.93
43.88
41.92
38.04
21.63
16.73
0.06
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

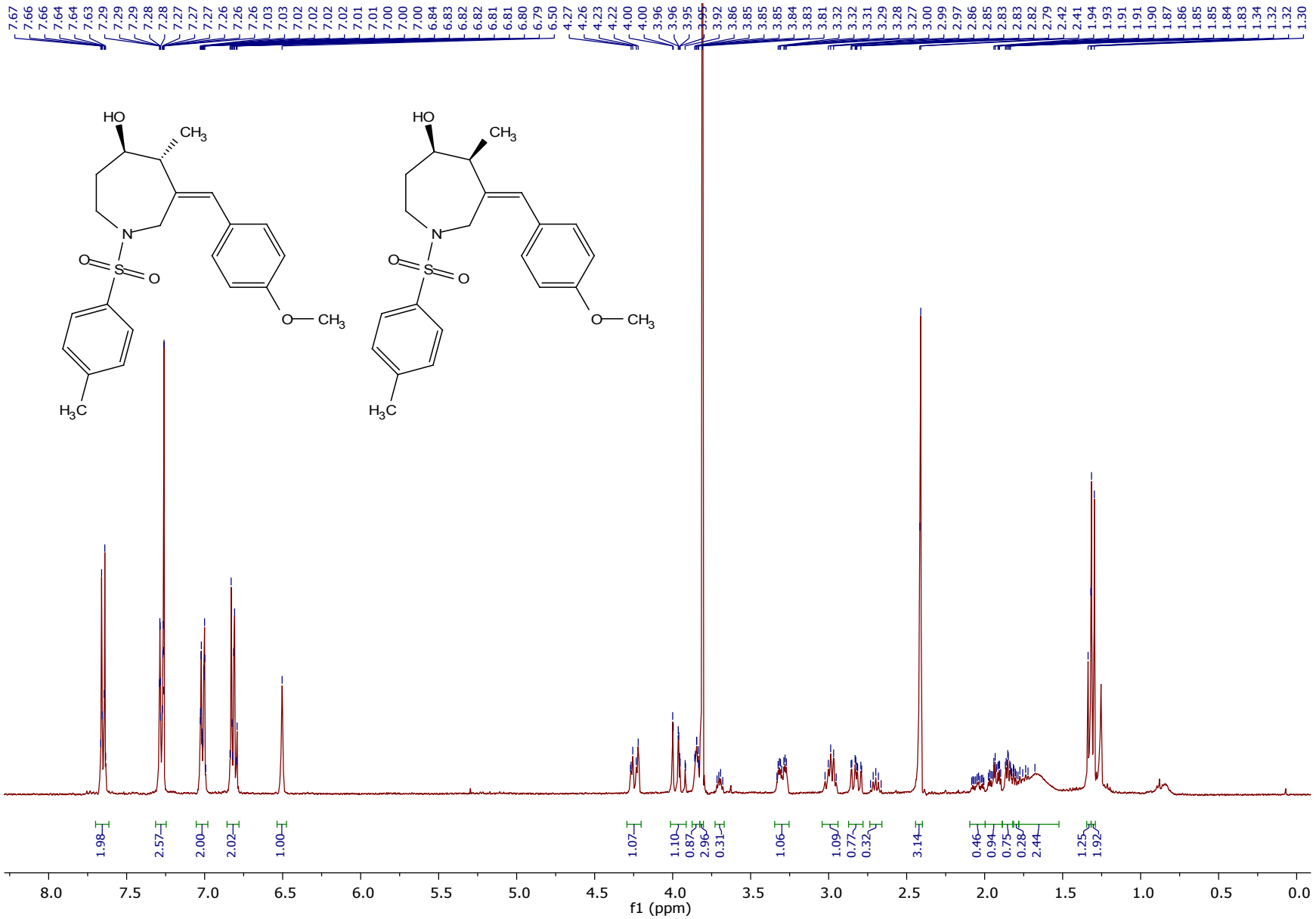

7.68
7.67
7.66
7.65
7.65
7.34
7.34
7.33
7.32
7.32
7.31
7.26
5.62
4.09
4.05
3.76
3.75
3.74
3.73
3.72
3.71
3.68
3.30
3.29
3.28
3.26
3.25
2.99
2.99
2.98
2.97
2.96
2.96
2.78
2.77
2.75
2.73
2.43
2.02
2.01
1.98
1.97
1.90
1.89
1.88
1.87
1.86
1.85
1.83
1.81
1.79
1.78
1.43
1.28
1.21
0.05
CH3
H3C
H3C
Si
CH3
O
S
O
N
CH3
CH3
HO
HO
2.00
2.02
0.96
1.06
1.98
1.02
1.10
1.12
3.14
1.14
1.97
1.13
1.01
2.97
2.97
8.52
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

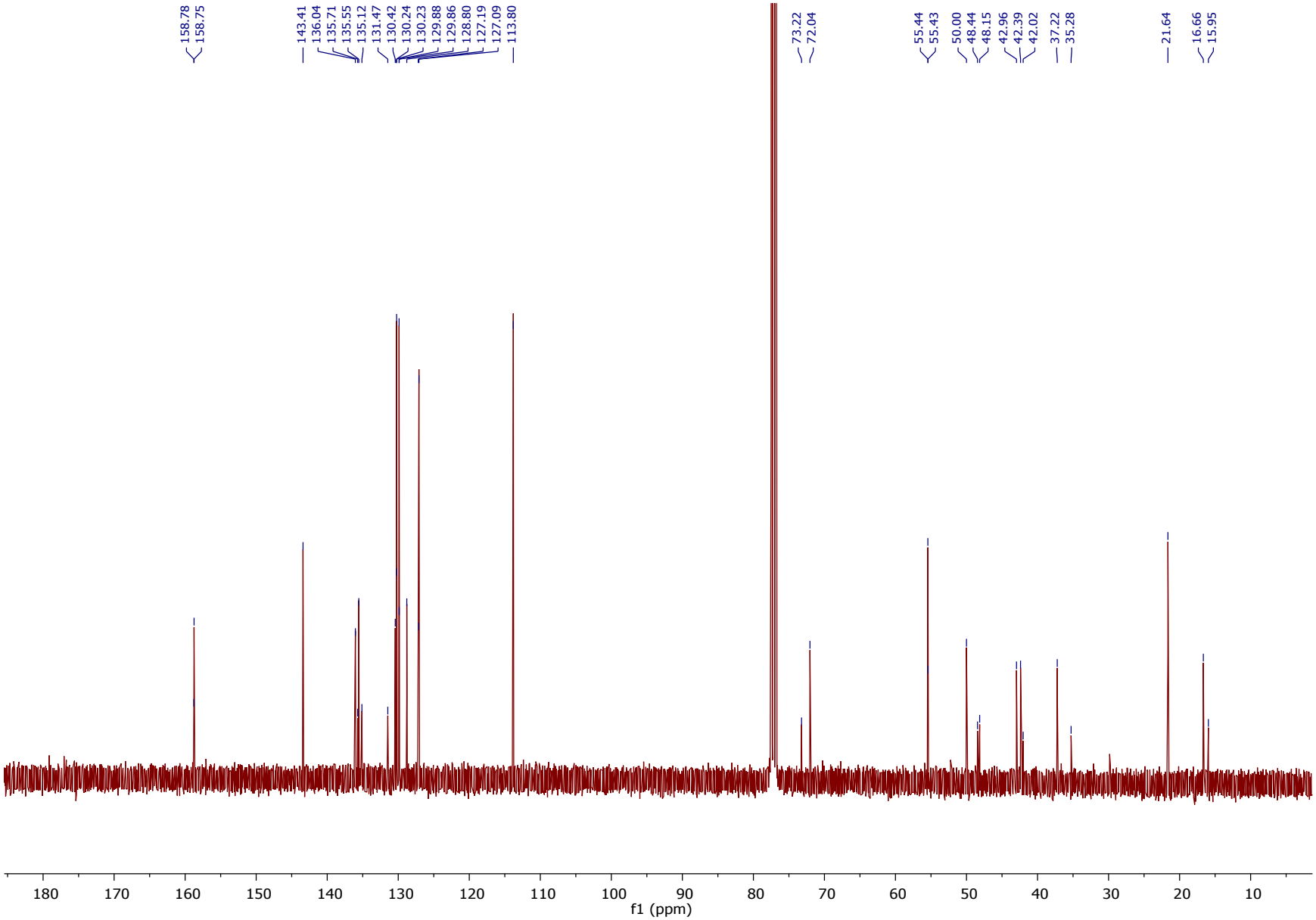

153.34
143.65
135.20
132.18
129.91
127.21
77.48
77.16
76.84
73.89
71.38
52.69
50.22
42.73
40.77
36.49
31.79
28.36
21.63
-0.06
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

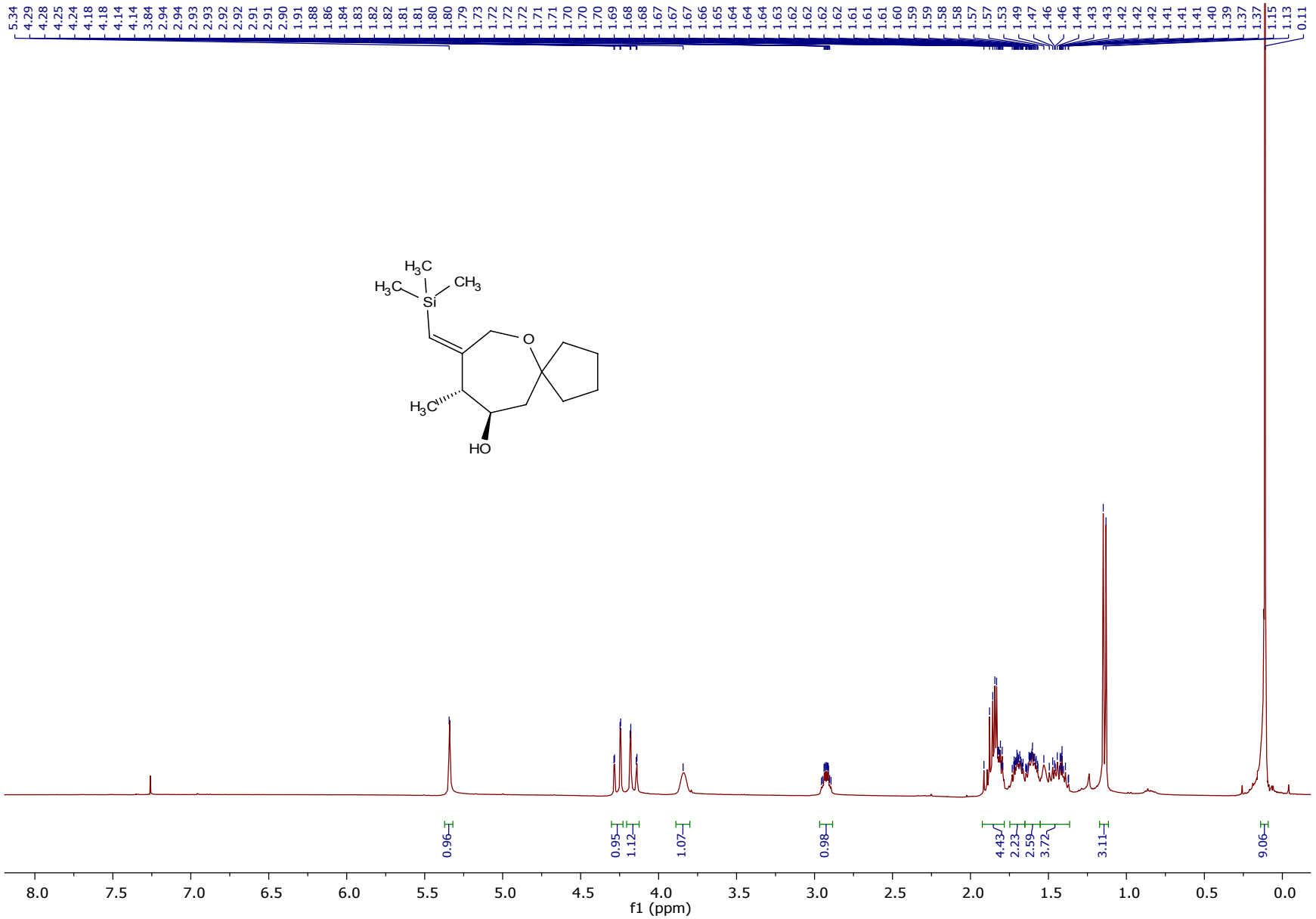

7.64 7.64 7.64 7.64 7.63 7.62 7.62 7.61 7.30 7.30 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.25 7.25 7.25 7.24 7.24 7.24 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.08 7.07 7.06 7.06 7.05 7.05 6.56
4.25 4.25 4.25 4.22 4.21 4.21 4.21 4.01 4.01 3.98 3.98 3.98 3.97 3.95 3.95 3.85 3.24 3.24 3.24 3.23 3.00 3.00 2.99 2.98 2.98 2.87 2.73 2.40 2.39 1.95 1.95 1.87 1.86 1.86 1.85 1.85 1.85 1.84 1.83 1.83 1.83 1.82 1.82 1.79 1.34 1.33 1.31
OH
CH3
N
O
S
O
H3C
OH
CH3
N
O
S
O
H3C
2.00 5.78 2.07 0.98 1.00 1.09 0.64 0.46 1.00 1.26 0.70 0.44 3.38 0.51 1.01 2.13 2.96
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

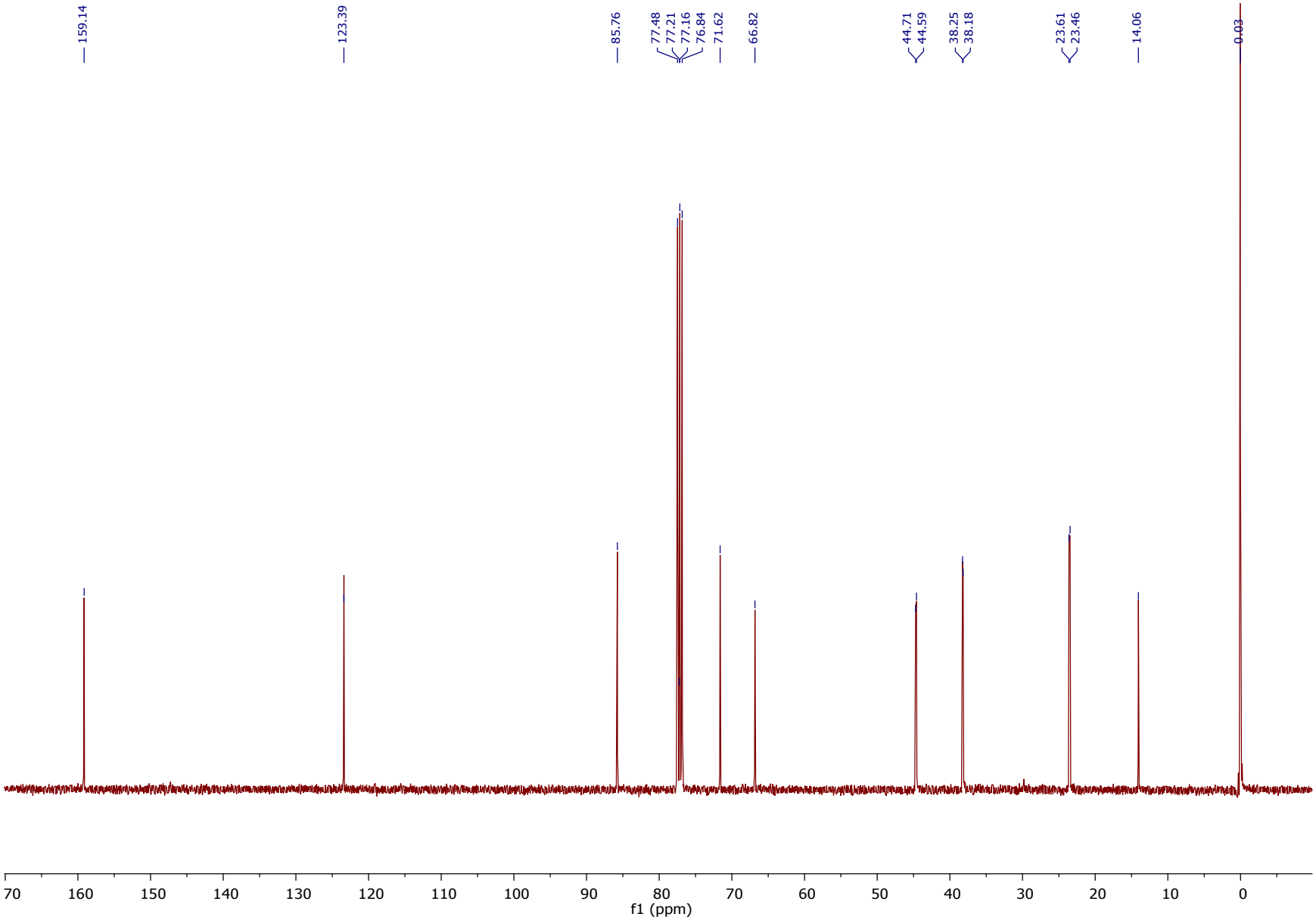

nOe
H
CH3
HO
N
O
S
O
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
f2 (ppm)
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
f1 (ppm)

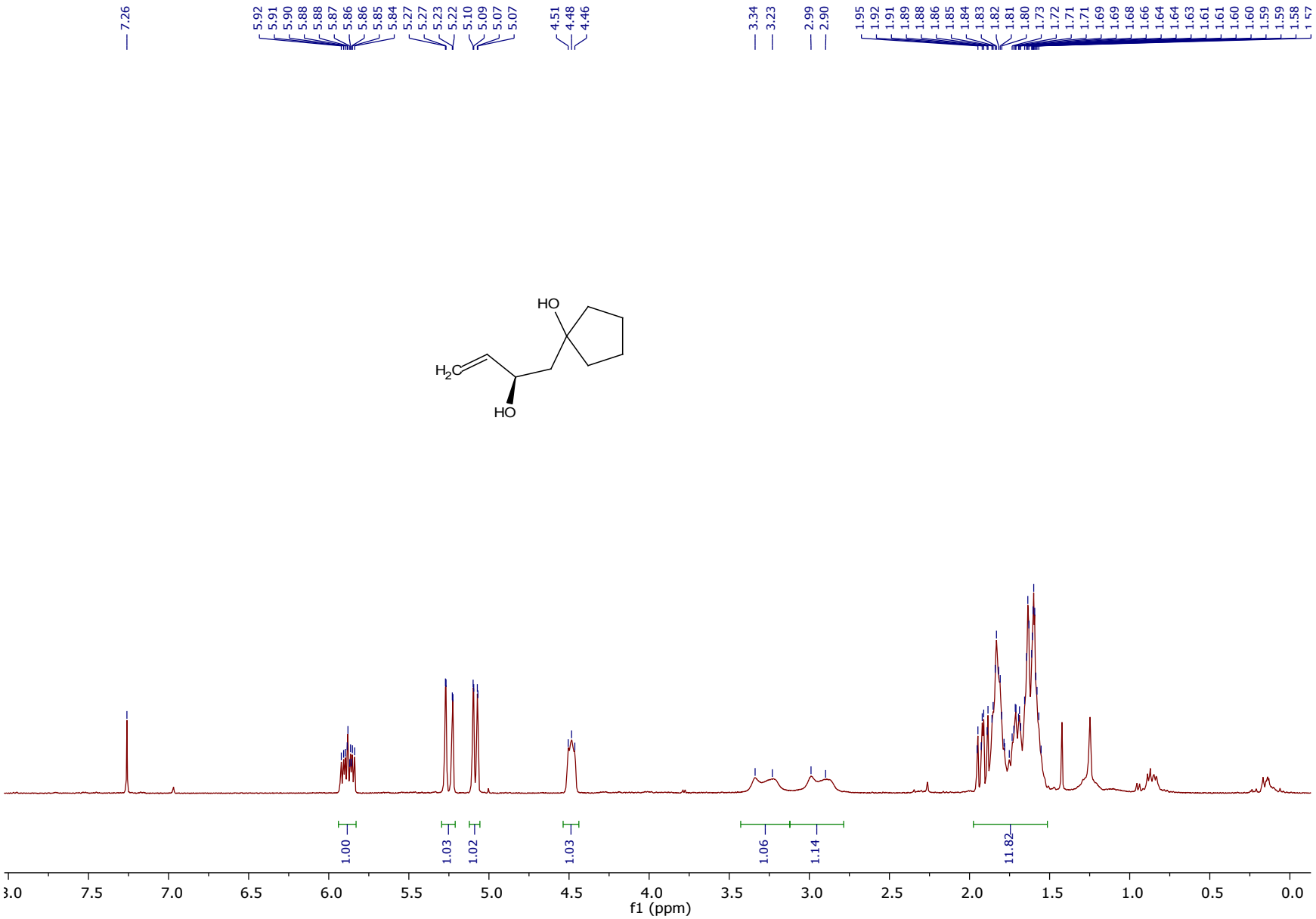

143.39
143.38
137.10
136.89
136.34
136.31
135.85
135.54
131.62
130.84
129.83
129.81
129.75
128.87
128.87
128.31
127.17
127.15
127.14
127.09
127.01
77.48
77.16
76.84
73.26
72.13
49.83
48.41
47.82
43.14
42.42
42.06
37.11
35.36
30.41
21.58
21.57
16.31
15.96
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

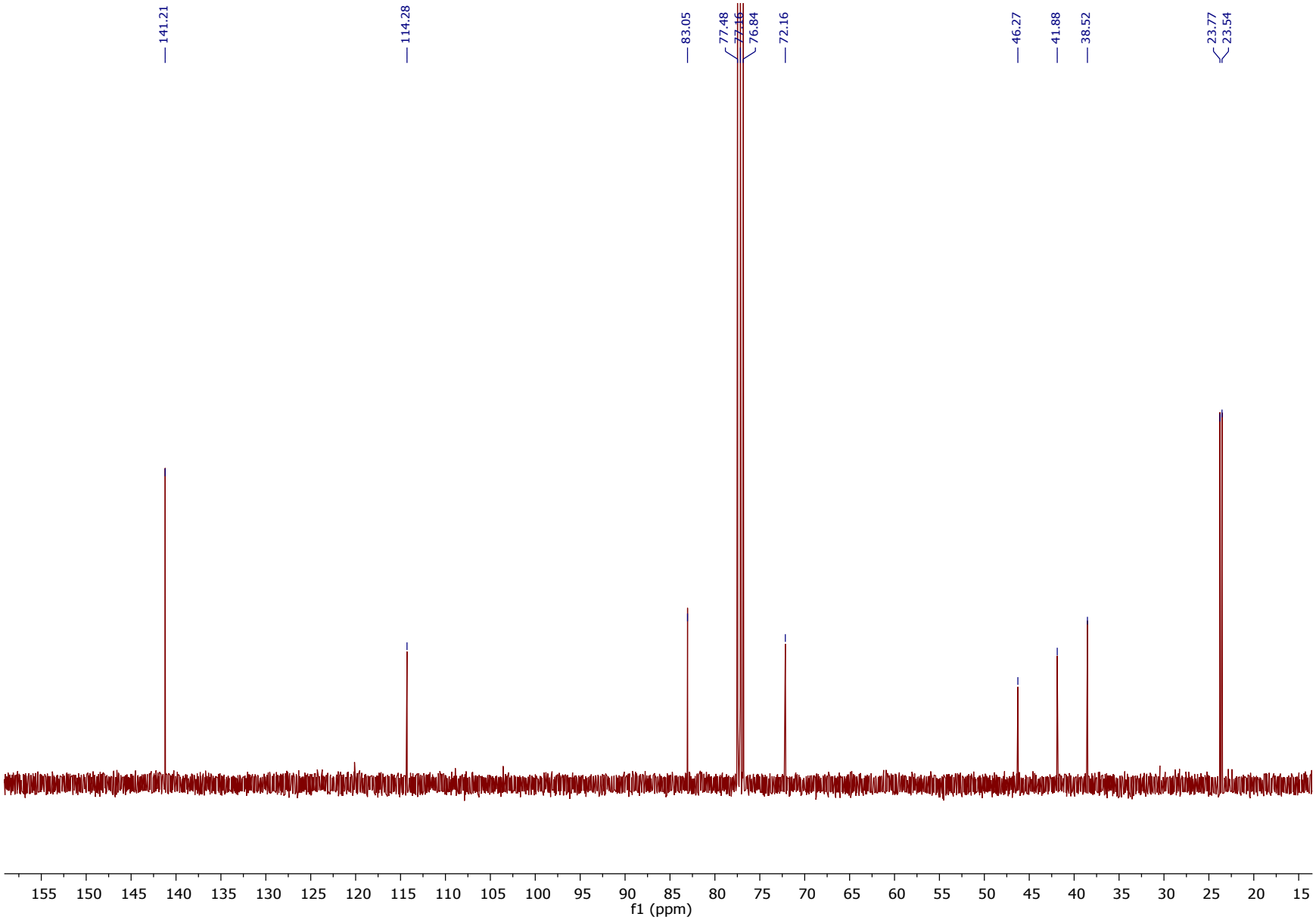

7.67 7.66 7.66 7.64 7.64 7.63 7.29 7.29 7.29 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.03 7.03 7.02 7.02 7.02 7.02 7.01 7.01 7.00 7.00 7.00 6.84 6.83 6.82 6.82 6.81 6.81 6.80 6.79 6.50 4.27 4.26 4.23 4.22 4.00 4.00 3.96 3.96 3.95 3.93 3.92 3.86 3.85 3.85 3.85 3.84 3.83 3.81 3.32 3.32 3.31 3.29 3.28 3.27 3.00 2.99 2.97 2.86 2.85 2.83 2.82 2.79 2.42 2.41 1.94 1.93 1.91 1.91 1.90 1.87 1.86 1.85 1.85 1.84 1.83 1.34 1.32 1.32 1.30
HO
CH3
N
O
S
O
O
CH3
H3C
1.98 2.57 2.00 2.02 1.00 1.07 1.10 0.87 2.96 0.31 1.06 1.09 0.77 0.32 3.14 0.46 0.94 0.75 0.28 2.44 1.25 1.92
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

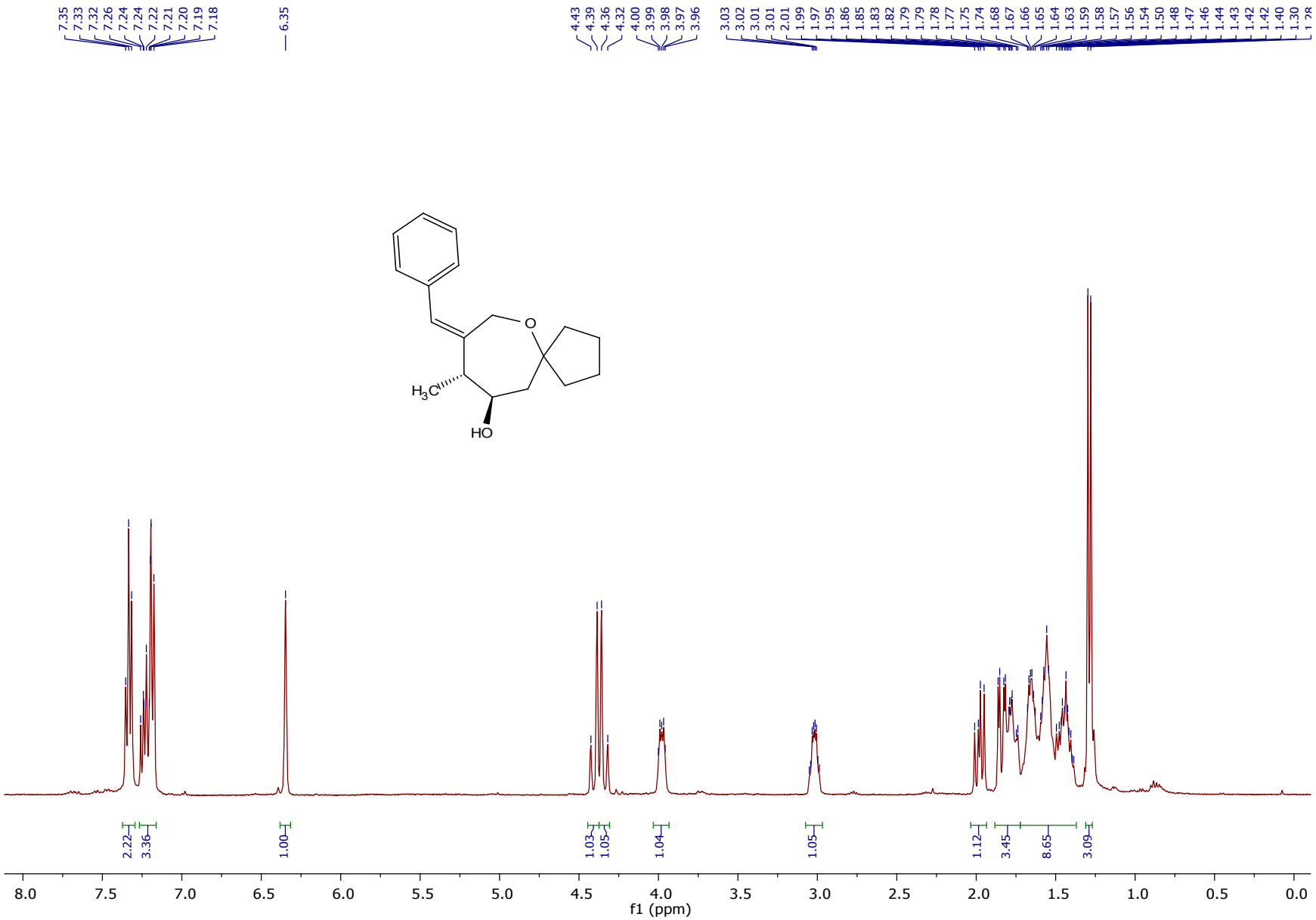

158.78
158.75
143.41
136.04
135.71
135.55
135.12
131.47
130.42
130.24
130.23
129.88
129.86
128.80
127.19
127.09
113.80
73.22
72.04
55.44
55.43
50.00
48.44
48.15
42.96
42.39
42.02
37.22
35.28
21.64
16.66
15.95
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

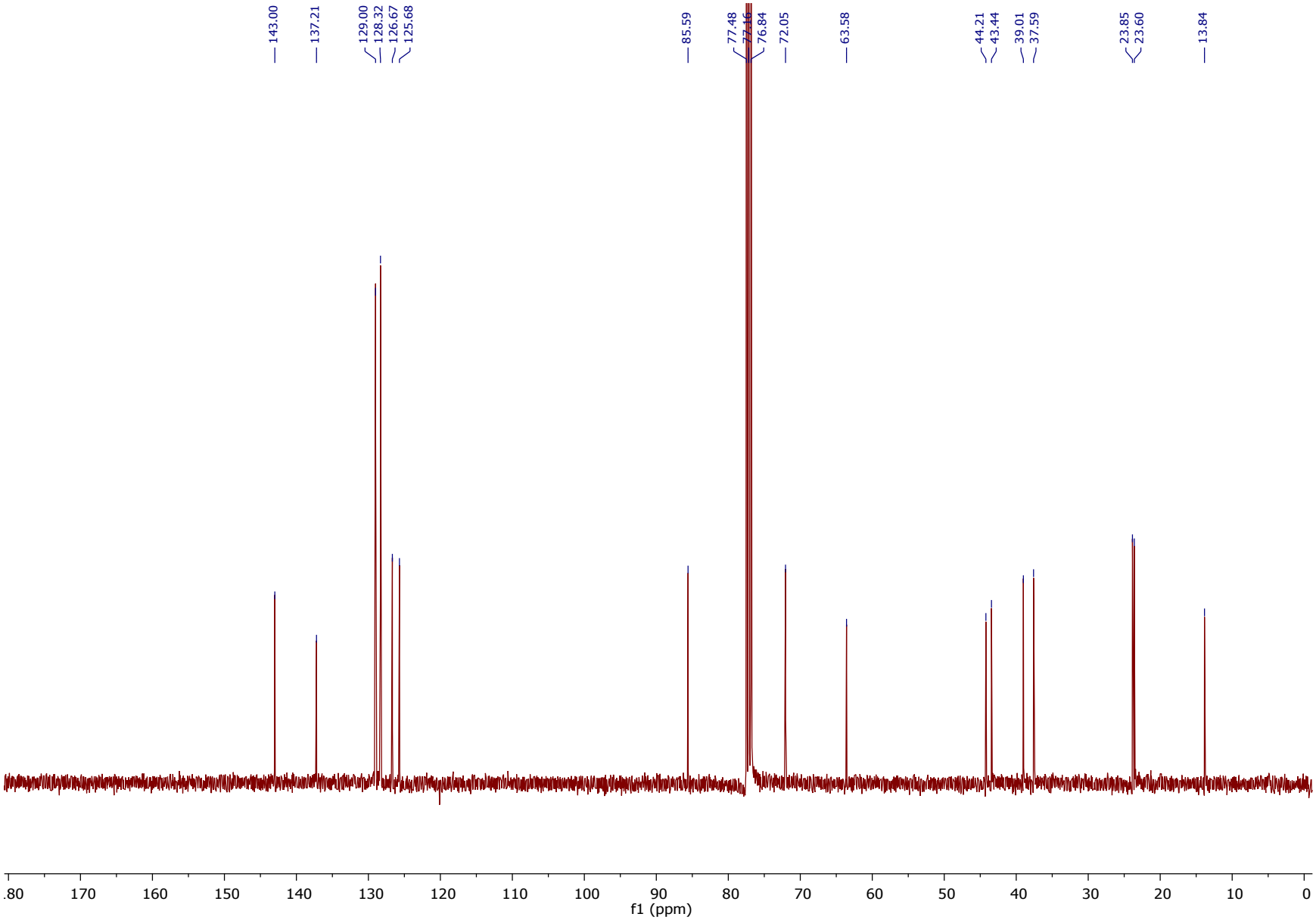

5.34 4.29 4.28 4.25 4.24 4.18 4.18 4.14 4.14 3.84 2.94 2.94 2.93 2.93 2.92 2.92 2.91 2.91 2.90 1.91 1.88 1.86 1.84 1.83 1.82 1.82 1.81 1.81 1.80 1.80 1.79 1.73 1.72 1.72 1.72 1.71 1.71 1.70 1.70 1.70 1.69 1.68 1.68 1.67 1.67 1.67 1.66 1.65 1.64 1.64 1.64 1.63 1.62 1.62 1.62 1.62 1.61 1.61 1.61 1.60 1.59 1.59 1.58 1.58 1.57 1.57 1.53 1.49 1.47 1.46 1.46 1.44 1.43 1.43 1.42 1.42 1.42 1.41 1.41 1.41 1.40 1.39 1.37 1.37 1.15 1.13 0.11
H3C
H3C
CH3
Si
O
H3C
HO
0.96
0.95
1.12
1.07
0.98
4.43
2.23
2.59
3.72
3.11
9.06
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.14
123.39
85.76
77.48
77.21
77.16
76.84
71.62
66.82
44.71
44.59
38.25
38.18
23.61
23.46
14.06
0.03
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26
5.92
5.91
5.90
5.88
5.88
5.87
5.86
5.86
5.85
5.84
5.27
5.27
5.23
5.22
5.10
5.09
5.07
5.07
4.51
4.48
4.46
3.34
3.23
2.99
2.90
1.95
1.92
1.91
1.89
1.88
1.86
1.85
1.84
1.83
1.82
1.81
1.80
1.73
1.72
1.71
1.71
1.69
1.69
1.68
1.66
1.64
1.64
1.63
1.61
1.61
1.60
1.60
1.59
1.59
1.58
HO
H2C
HO
1.00
1.03
1.02
1.03
1.06
1.14
11.82
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


141.21
114.28
83.05
77.48
77.16
76.84
72.16
46.27
41.88
38.52
23.77
23.54
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)


7.35
7.33
7.32
7.26
7.24
7.24
7.22
7.21
7.20
7.19
7.18
6.35
4.43
4.39
4.36
4.32
4.00
3.99
3.98
3.97
3.96
3.03
3.02
3.01
3.01
2.01
1.99
1.97
1.95
1.86
1.85
1.83
1.82
1.79
1.79
1.78
1.77
1.75
1.74
1.68
1.67
1.66
1.65
1.64
1.63
1.59
1.58
1.57
1.56
1.54
1.50
1.48
1.47
1.46
1.44
1.43
1.42
1.42
1.40
1.30
O
H3C
HO
2.22
3.36
1.00
1.03
1.05
1.04
1.05
1.12
3.45
8.65
3.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.00
137.21
129.00
128.32
126.67
125.68
85.59
77.48
77.16
76.84
72.05
63.58
44.21
43.44
39.01
37.59
23.85
23.60
13.84
f1 (ppm)