Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

$Mn_2(CO)_{10}$ and UV light: a promising combination for regioselective alkene hydrosilylation at low temperature

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Equipment and methods

Unless otherwise noted, all reactions were conducted in oven-dried vials with a magnetic stirring bar under an argon atmosphere. Toluene and mesitylene were distilled from sodium benzophenone ketyl radical and stored under argon in a glovebox. $Mn_2(CO)_{10}$ was used as received and stored under argon in a glovebox. Alkenes were stirred overnight on activated alumina, degassed by freeze-pump-thaw cycles, and stored under argon in a glovebox. Short-plug column chromatography was performed with Macherey-Nagel Silica 60 M silica gel (0.04−0.063 mm).

For all of the UV experiments, Asahi spectra xenon light source 300 W (Max303) instrument was used without any filters unless stated otherwise. The wavelength of the light was ca. 250-420 nm, and the reaction mixture could warm up to 45 °C maximum during the irradiation. At the end of the thermal or UV reaction, the mixture was passed through a short plug of silica (pentane was used as eluent) to remove the catalyst, and volatiles (remaining starting materials) were removed under reduced pressure to give a clear liquid product.

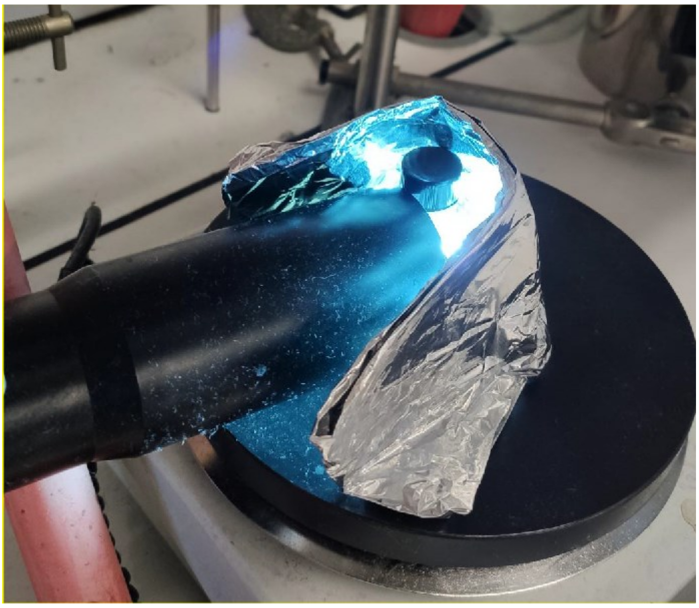
^{1}H NMR spectra were recorded on a Bruker AC 300 MHz instrument. Chemical shifts (δ) are given in parts per million (ppm) referenced to the appropriate solvent peak (^{1}H NMR: $CDCl_3$ at 7.26 ppm). The data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, t = triplet, dd = doublet of doublets, nfom = non-first order multiplet, br. s = broad singlet, m = multiplet), coupling constant *J* (Hz), and integration.

Gas chromatography analysis was performed on an Agilent 8890 chromatograph with an HP5 (5% of phenylmethylsiloxane) column (30 m length, 320 µm of diameter, 0.25 nm of thickness) equipped with a flame ionization detector (FID). Throughout the study, mesitylene was used as GC internal standard to obtain the GC yield for products **3a-i**.

Experimental procedures and spectral data

General procedure for alkene hydrosilylations

In an argon-filled glovebox, a 4 mL vial was charged with the appropriate alkene (0.47 mmol, 1 equiv.), MD^HM (256 µL, 0.94 mmol, 2 equiv.), mesitylene (46 µL, 0.335 mmol, GC standard), $Mn_2(CO)_{10}$ catalyst solution (47 mM, 100 µL, 4.7 µmol, 1 mol%), and a stirring bar. The reaction volume was adjusted by adding the corresponding amount of toluene to reach a total volume of 571 µL. The vials were placed against the collimator and wrapped with aluminum foil for the reaction duration then quenched with a mixture of water and pentane (1:2) and filtrated through a pad of $MgSO_4$ and silica. The catalytic reactions were monitored by GC using mesitylene as internal standard.



Experimental setup for alkene hydrosilylation under UV light

General Procedure for 1-octene hydrosilylation with various silanes

In an argon-filled glovebox, a 4 mL vial was charged with 1-octene (74 µL, 0.47 mmol, 1 equiv.), the chosen silane (0.94 mmol, 2 equiv.), mesitylene (46 µL, 0.335 mmol, GC standard), $Mn_2(CO)_{10}$ catalyst solution (47 mM, 100 µL, 4.7 µmol, 1 mol%), and a stirring bar. The reaction volume was adjusted by adding the corresponding amount of toluene to reach a total volume of 571 µL. The vials were placed against the collimator and wrapped with aluminum foil for the reaction duration then quenched with a mixture of water and pentane (1:2) and filtrated through a pad of $MgSO_4$ and silica. The catalytic reactions were monitored by GC using mesitylene as internal standard.

Table S1. Mn-catalyzed hydrosilylation of 1-octene with different silanes

Silanes	Yield after 4 hours	Yield after 16 hours
$(EtO)_3SiH$	9% (4% isomerization)	20% (15% isomerization)
Et_3SiH	32% (9% isomerization)	46% (10% isomerization)
$PhSiH_3$	0%	< 1%

GC method used for the catalytic tests

For GC analysis, an Agilent 8890 chromatograph with a HP5 (5% of phenylmethylsiloxane) column was used (30 m length, 320 µm of diameter, 0.25 nm of thickness, and 1.08 nm of deadtime) throughout the project for the characterization of alkene hydrosilylation tests. Initial oven temperature 70 °C (hold 1 min) and then two ramps were applied: first ramp - 10 °C/min, next temperature 120 °C, second ramp - 10 °C/min, next temperature 300 °C (hold 3 min). The flame ionization detector (FID) was set at 300 °C, with a H_2 flow of 40 mL/min, air flow of 450 mL/min and a makeup flow of N_2 of 450 mL/min. The calibration was made with 1-octene,

MD^HM, 1,1,1,3,5,5,5-heptamethyl-3-octyltrisiloxane (previously synthesized in the lab) and compared with mesitylene, which was used as GC internal standard to obtain the response factors of all the reagents in the reaction medium.

Radical trapping experiment

In an argon-filled glovebox, a 4 mL vial was charged with *n*-octene (0.47 mmol, 1 equiv.), MD^HM (256 µL, 0.94 mmol, 2 equiv.), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (5.9 mg, 0.038 mmoles, 16 equiv./Mn), mesitylene (46 µL, 0.335 mmol, GC standard), $Mn_2(CO)_{10}$ catalyst solution (47 mM, 100 µL, 4.7 µmol, 1 mol%), 95 µL of toluene and a stirring bar. The vial was placed against the collimator and wrapped with aluminum foil for the reaction duration then quenched with a mixture of water and pentane (1:2) and filtrated through a pad of $MgSO_4$ and silica. The catalytic reactions were monitored by GC using mesitylene as internal standard.

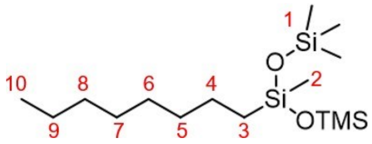
Mercury test

In an argon-filled glovebox, a 4 mL vial was charged with *n*-octene (0.47 mmol, 1 equiv.), MD^HM (256 µL, 0.94 mmol, 2 equiv.), Hg (14 µL, 0.94 mmoles, 400 equiv./Mn), mesitylene (46 µL, 0.335 mmol, GC standard), the toluene solution of $Mn_2(CO)_{10}$ (47 mM, 100 µL, 4.7 µmol, 1 mol%), 81 µL of toluene and a stirring bar. The vial was placed against the collimator and wrapped with aluminum foil for the reaction duration then quenched with a mixture of water and pentane (1:2) and filtrated through a pad of $MgSO_4$ and silica. The catalytic reactions were monitored by GC using mesitylene as internal standard.

Isolation and characterization of the hydrosilylated products

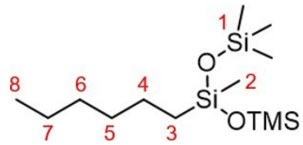
After the designated reaction time, the crude mixtures (color variation from pale orange-brown to almost colorless) were passed through a neutral silica column (3 cm in height in a Pasteur pipette) and eluted with pentane. The collected solution was put under vacuum to remove the solvent. Resulting products were colorless or slightly yellow liquids.

1,1,1,3,5,5,5-heptamethyl-3-octyltrisiloxane (3a)



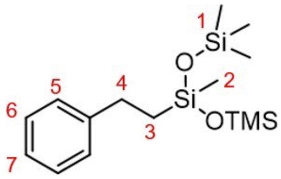
^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.34-1.24 (br. s, 12H, *H4-H9*), 0.88 (br. s, 3H, *H1*), 0.48-0.42 (br. s, 2H, *H3*), 0.09 (s, 18H, *H1*), -0.01 (s, 3H, *H2*). The spectroscopic data correspond to the reported data.[1]

1,1,1,3,5,5,5-heptamethyl-3-hexyltrisiloxane (3b)



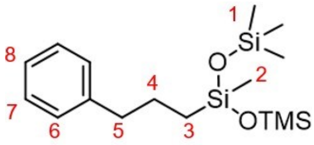
^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.29 (br. s, 8H, *H4-H7*), 0.89 (br. s, 3H, *H8*), 0.45 (br. s, 2H, *H3*), 0.09 (s, 18H, *H1*), 0.00 (s, 3H, *H2*). The spectroscopic data correspond to the reported data.[1]

1,1,1,3,5,5,5-heptamethyl-3-phenethyltrisiloxane (3c)



^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.31-7.25 (m, 2H, *H6*), 7.19-7.13 (m, 3H, *H5+H7*), 2.67-2.61 (m, 2H, *H4*), 0.88-0.80 (m, 2H, *H3*), 0.11 (s, 18H, *H1*), 0.03 (s, 3H, *H2*). The spectroscopic data correspond to the reported data.[2]

1,1,1,3,5,5,5-heptamethyl-3-(4-phenylbutyl)trisiloxane (3d)



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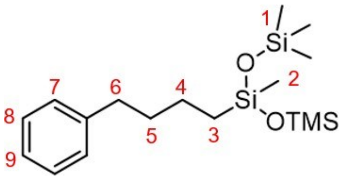
[1] X. Jia, Z. Huang, *Nature Chemistry* **2015**, *8*, 157.

[2] A. Bokka, J. Jeon, *Organic Letters* **2016**, *18*, 5324.

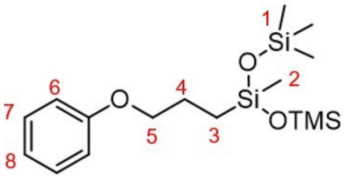
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29-7.23 (m, 2H, *H7*), 7.20-7.14 (m, 3H, *H6*+*H8*), 2.62 (t, *J* = 7.7 Hz, 2H, *H5*), 1.67-1.59 (m, 2H, *H4*), 0.55-0.49 (m, 2H, *H3*), 0.08 (s, 18H, *H1*), 0.00 (s, 3H, *H2*). The spectroscopic data correspond to the reported data.[3]

1,1,1,3,5,5,5-heptamethyl-3-(4-phenylbutyl)trisiloxane (3e)



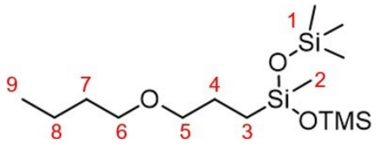
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29-7.20 (m, 2H, *H8*), 7.22-7.15 (m, 3H, *H6*+*H8*), 2.61 (t, *J* = 7,7 Hz, 2H, *H5*), 1.65-1.60 (m, 2H, *H5*), 1.41-1.35 (m, 2H, *H4*), 0.53-0.46 (m, 2H, *H3*), 0.08 (s, 18H, *H1*), -0.01 (s, 3H, *H2*). The spectroscopic data correspond to the reported data.[4]

1,1,1,3,5,5,5-heptamethyl-3-(3-(benzyloxy)propyl)trisiloxane (3f)



^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29-7.22 (m, 2H, *H7*), 6.95-6.89 (m, 3H, *H6*+*H8*), 3.91 (t, 2H, *H5*), 1.85-1.79 (m, 2H, *H4*), 0.61-0.55 (m, 2H, *H3*), 0.14 (s, 18H, *H1*), 0.04 (s, 3H, *H2*). The spectroscopic data correspond to the reported data.[5]

1,1,1,3,5,5,5-heptamethyl-3-(3-Butoxypropyl)trisiloxane (3g)



^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.42-3.36 (m, 4H, *H5*+*H6*), 1.59-1.51 (m, 4H, *H4*+*H7*), 1.41-1.35 (m, 2H, *H8*), 0.92 (t, *J* = 7.0 Hz, 3H, *H8*), 0.47-0.41 (m, 2H, *H3*), 0.08 (s, 18H, *H1*), 0.01 (s, 3H, *H2*). The spectroscopic data correspond to the reported data.[6]

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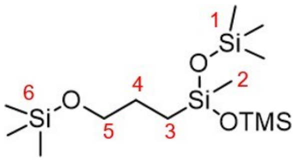
[3] Iimura, T.; Akasaka, N.; Kosai, T.; Iwamoto, T. Dalton Trans. **2017**, *46*, 8868.

[4] R. Srivastava, M. Jakoobi, C. Thieuleux, E. A. Quadrelli, C. Camp, *Dalton Trans*., **2021**, *50*, 869.

[5] M. Jakoobi, V. Dardun, L. Veyre, V. Meille, C. Camp, C. Thieuleux, *J. Org. Chem*. **2020**, *85*, 11732.

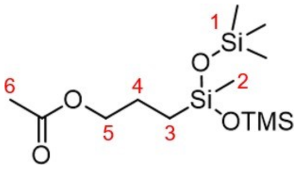
[6] H. Maciejewski, K. Szubert, B. Marciniec, J. Pernak, *Green Chem.,* **2009**, *11*, 1045.

1,1,1,3,5,5,5-heptamethyl-3-(3-(trimethylsilyloxy)propyl)trisiloxane (3h)



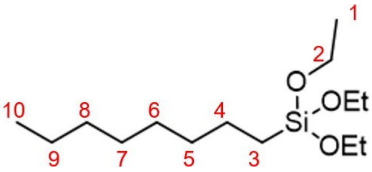
^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.51 (dd, 2H, *H5*), 1.58-1.52 (m, 2H, *H4*), 0.46-0.40 (m, 2H, *H3*), 0.11 (s, 9H, *H6*), 0.09 (s, 18H, *H1*), 0.01 (s, 3H, *H2*). The spectroscopic data correspond to the reported data.[5]

1,1,1,3,5,5,5-heptamethyl-3-(3-acetoxypropyl)trisiloxane (3i)



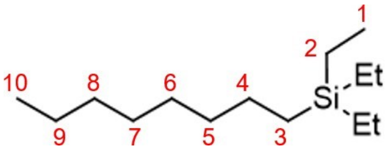
^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.91 (t, 2H, *H5*), 1.96 (s, 3H, *H6*), 1.59−1.49 (m, 2H, *H4*), 0.40−0.35 (m, 2H, *H3*), 0.00 (s, 18H, *H1*), -0.07 (s, 3H, *H2*). The spectroscopic data correspond to the reported data.[5]

Triethoxy(octyl)silane (4)



^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.83 (m, 2H, *H2*), 1.29−1.20 (m, 21H, *H1+H3-H8*), 0.87 (m, 3H, *H10*), 0.63 (s, 2H, *H9*). The spectroscopic data correspond to the reported data.[7]

Triethyloctylsilane (5)



^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.26 (brs, 12H, *H3-H8*), 0.91 (m, 12H, *H1+H10*), 0.63 (m, 8H, *H2+H9*). The spectroscopic data correspond to the reported data.[7]

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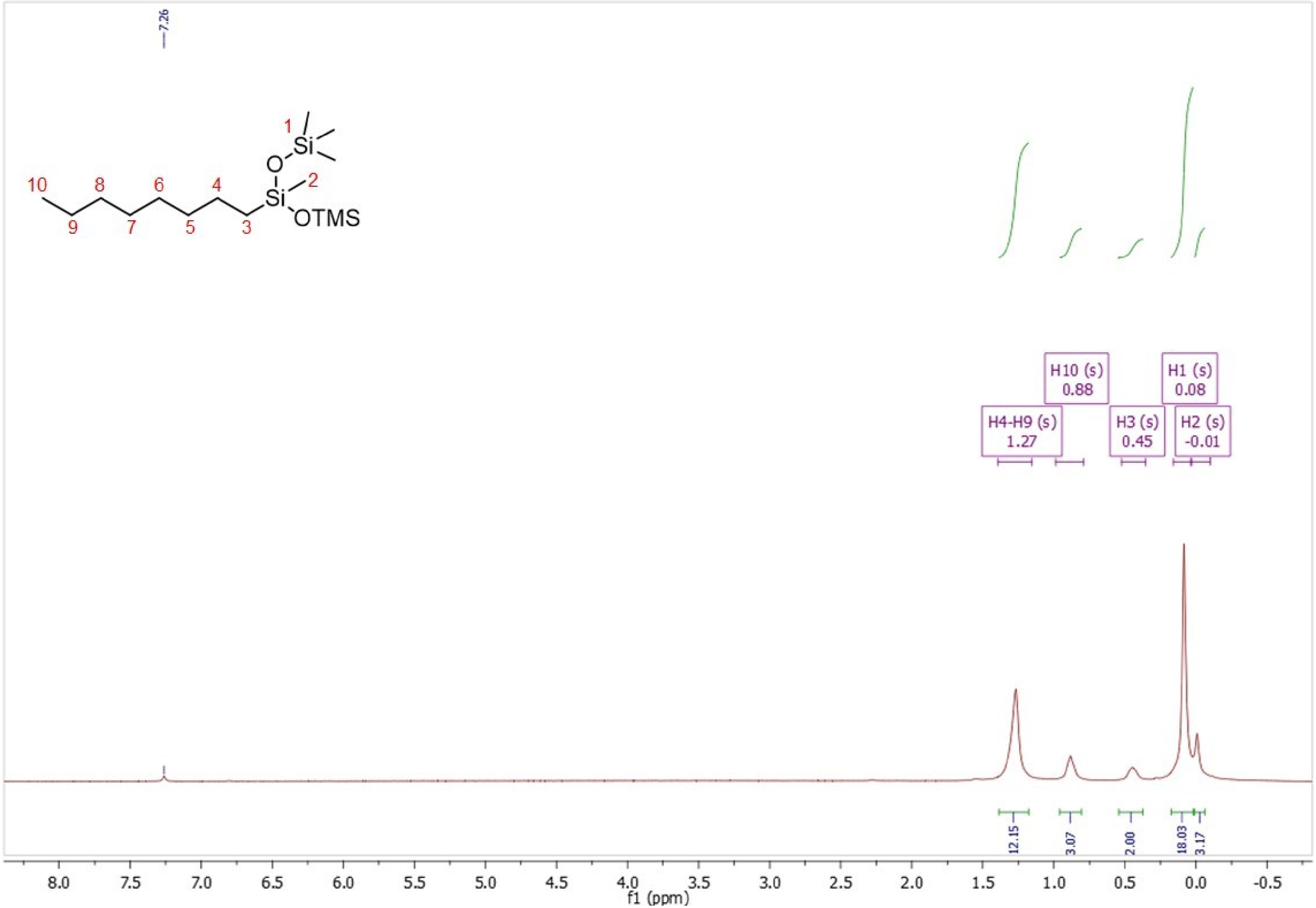
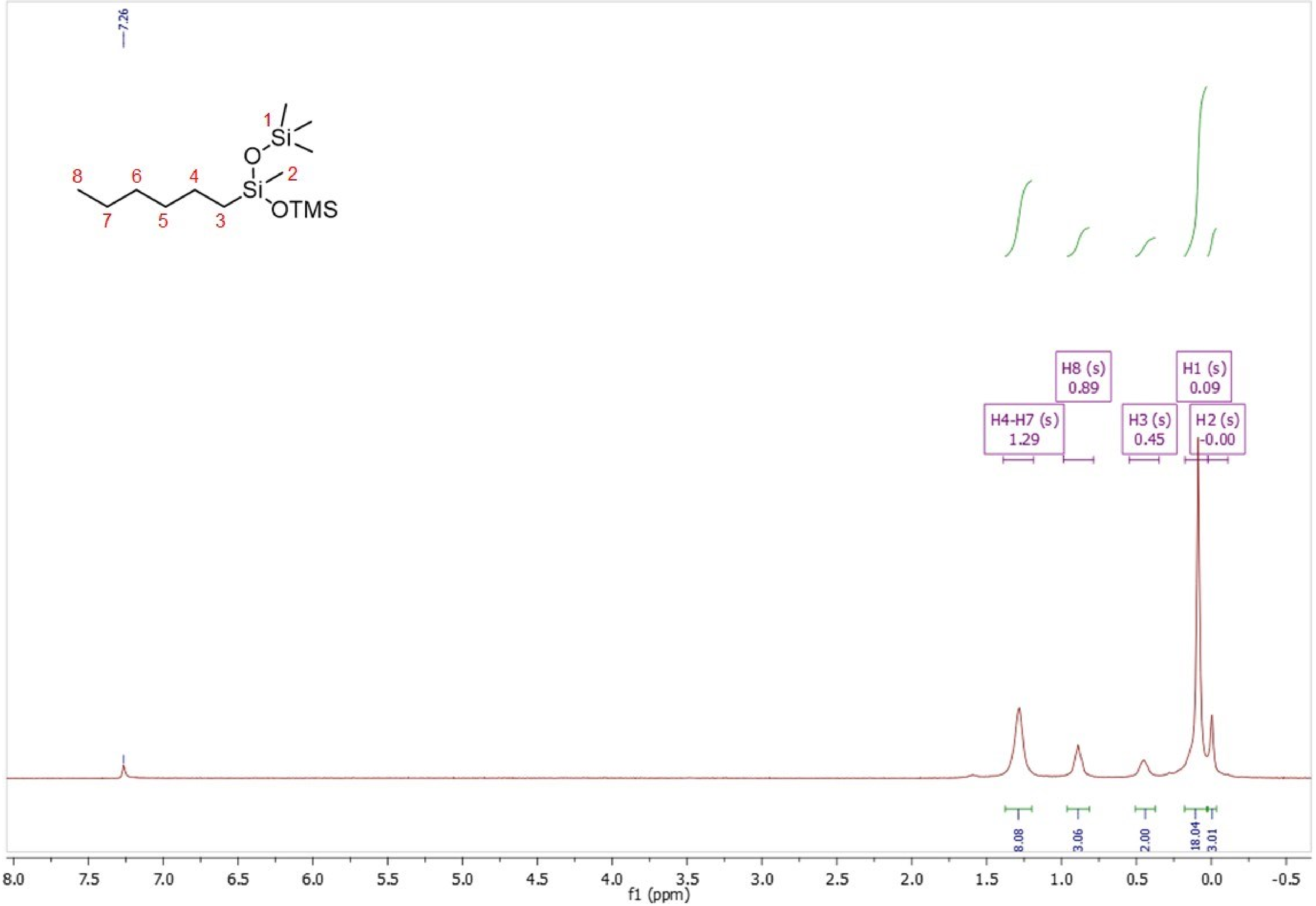
[7] A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, P. J. Chirik, *Science*, 2012, **335**, 567.

NMR spectra

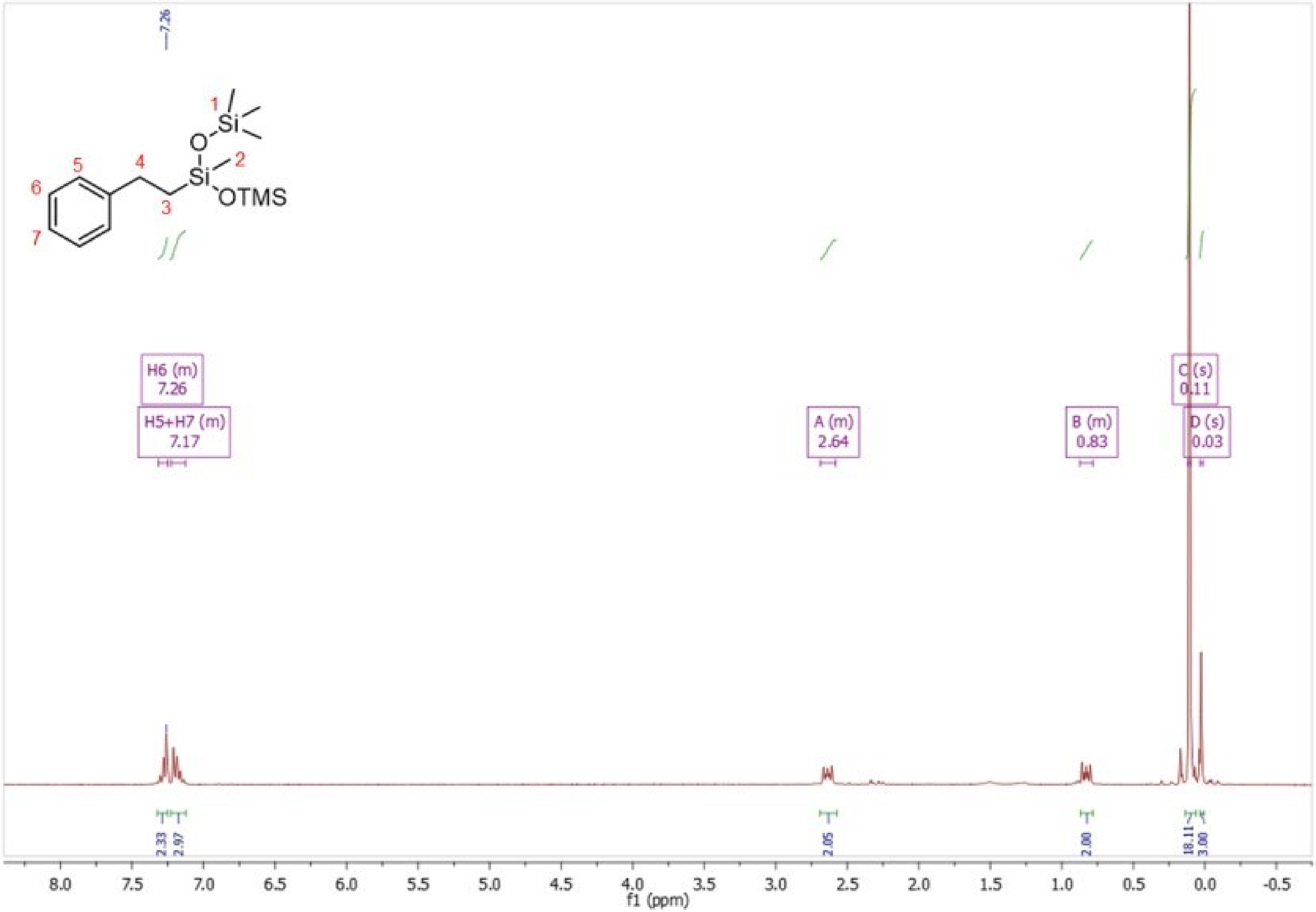
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of functionalization of MD^HM with 1-octene



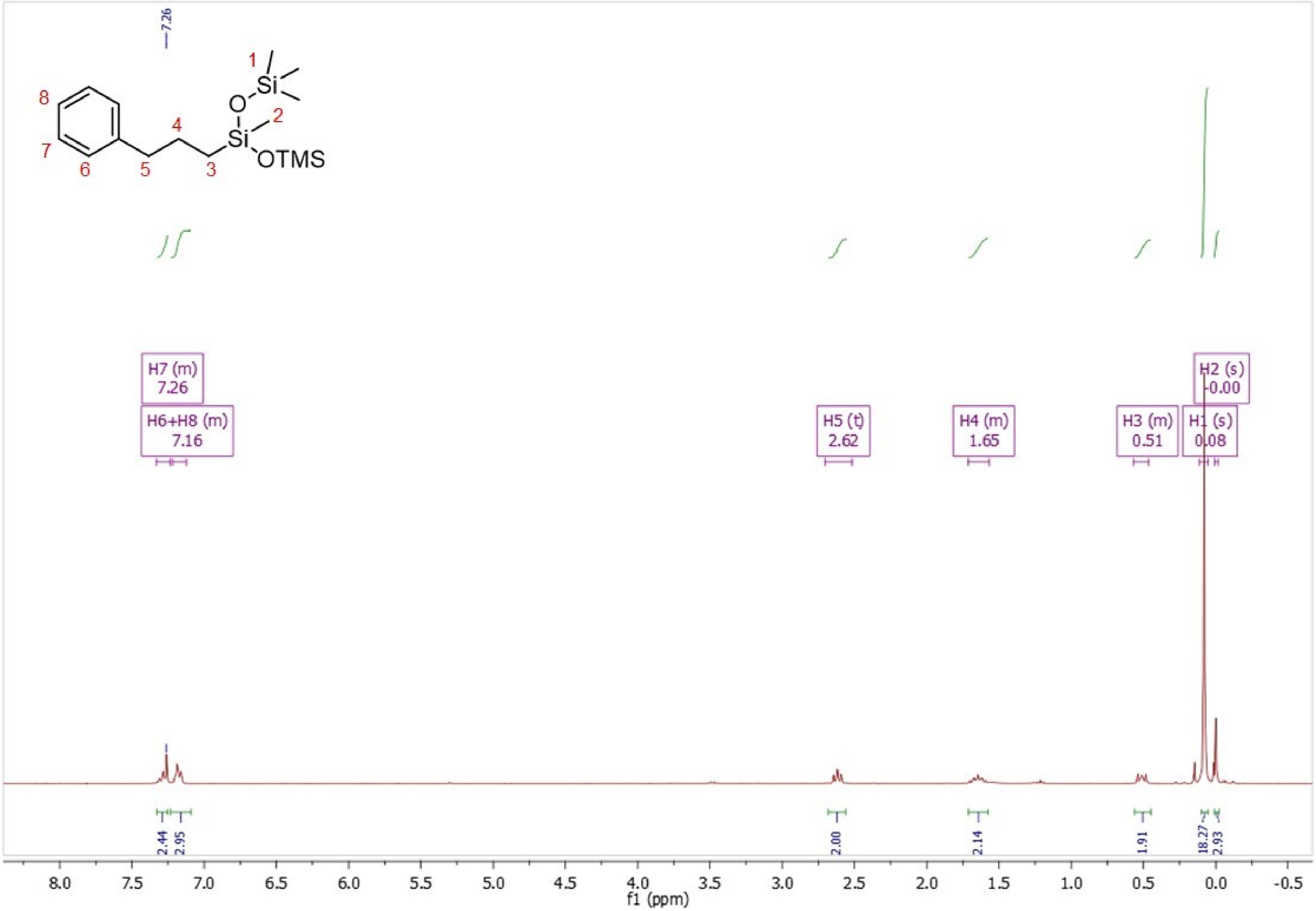
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of functionalization of MD^HM with 1-hexene



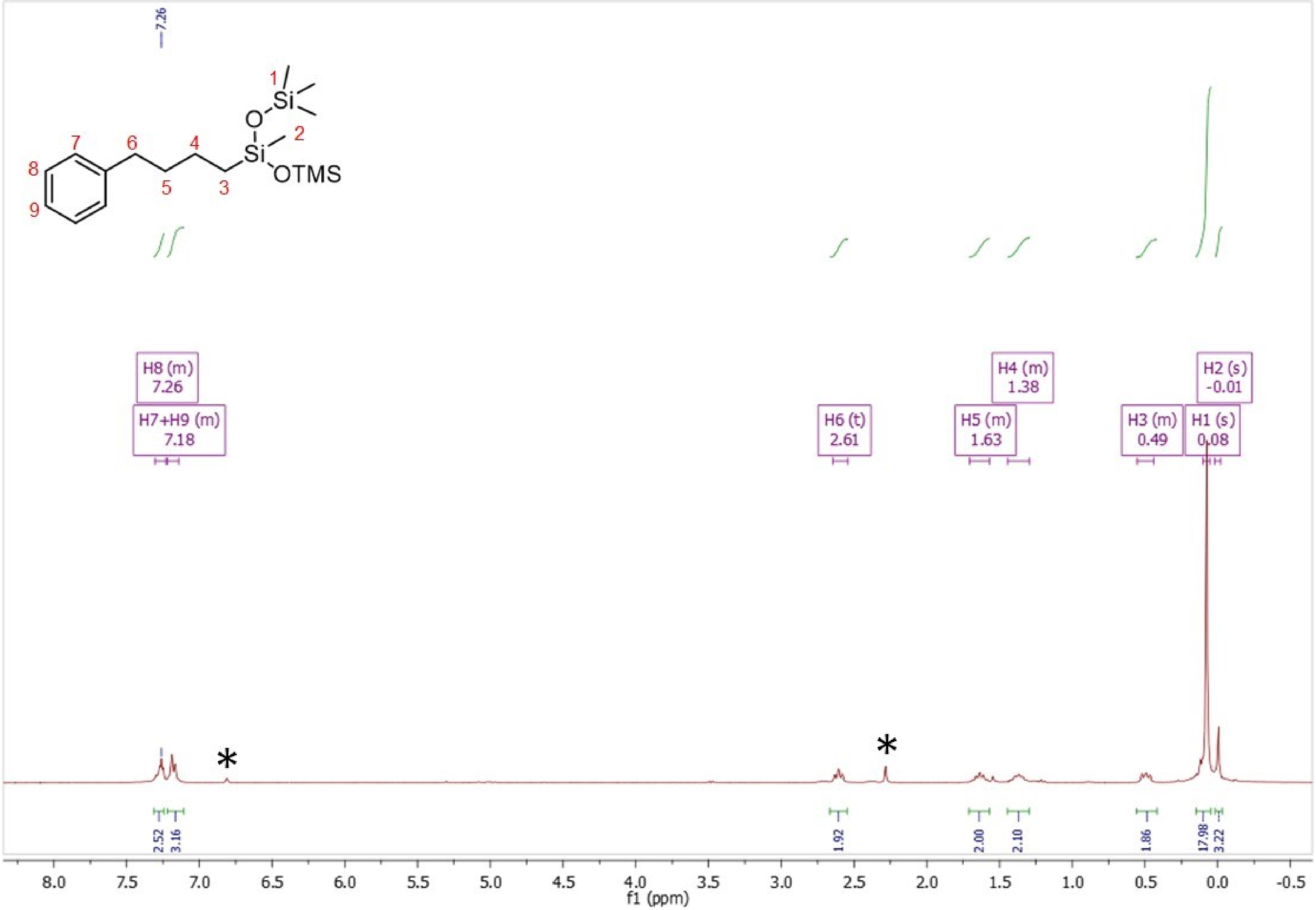
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of functionalization of MD^{H}M with styrene



^{1}H NMR spectrum (300 MHz, $CDCl_3$) of functionalization of MD^HM with allylbenzene

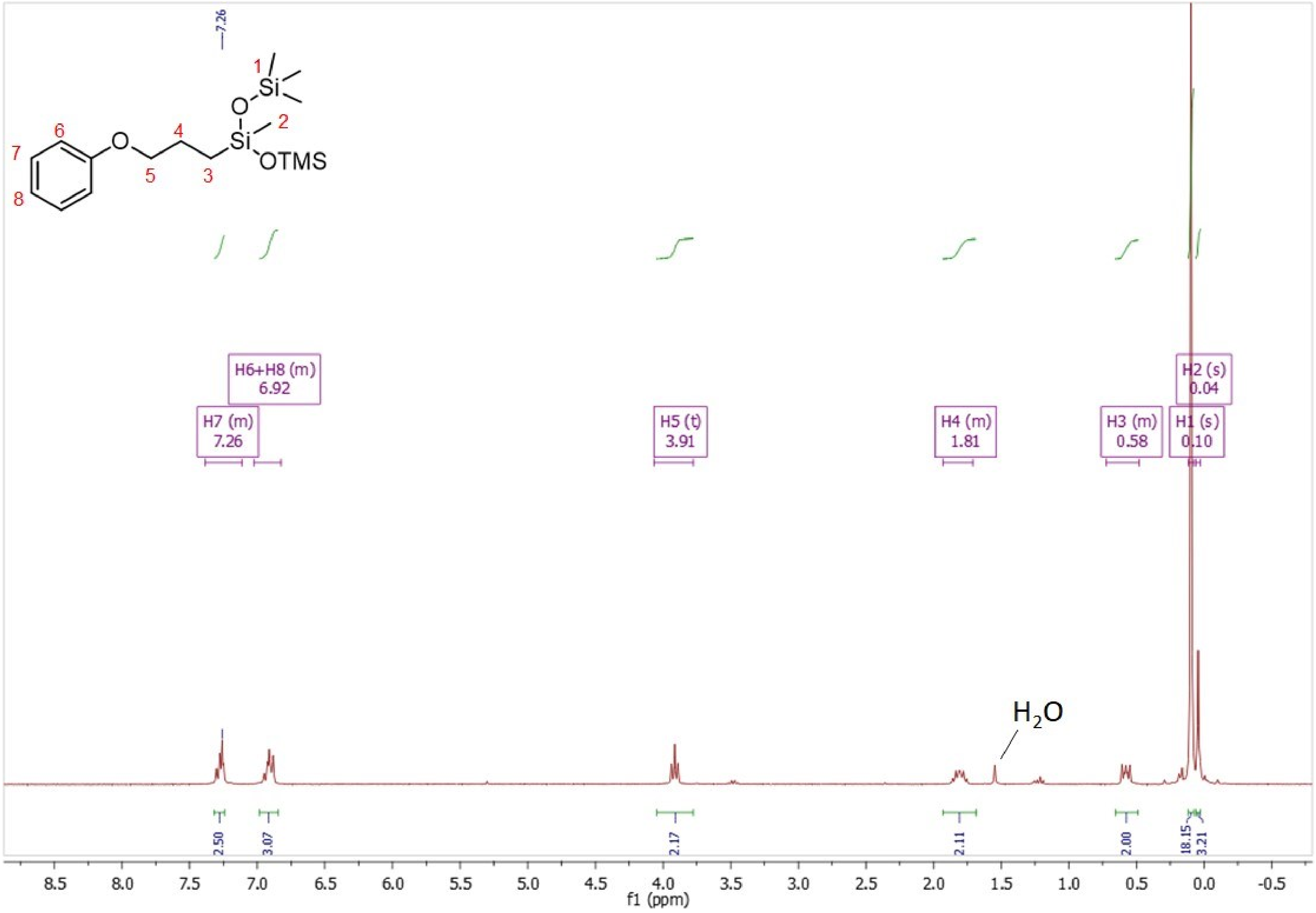


^{1}H NMR spectrum (300 MHz, CDCl$_3$) of functionalization of MD^{H}M with 4-phenyl-1-butene



* Mesitylene
(GC
Standard)

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of functionalization of MD^HM with allyl phenyl ether



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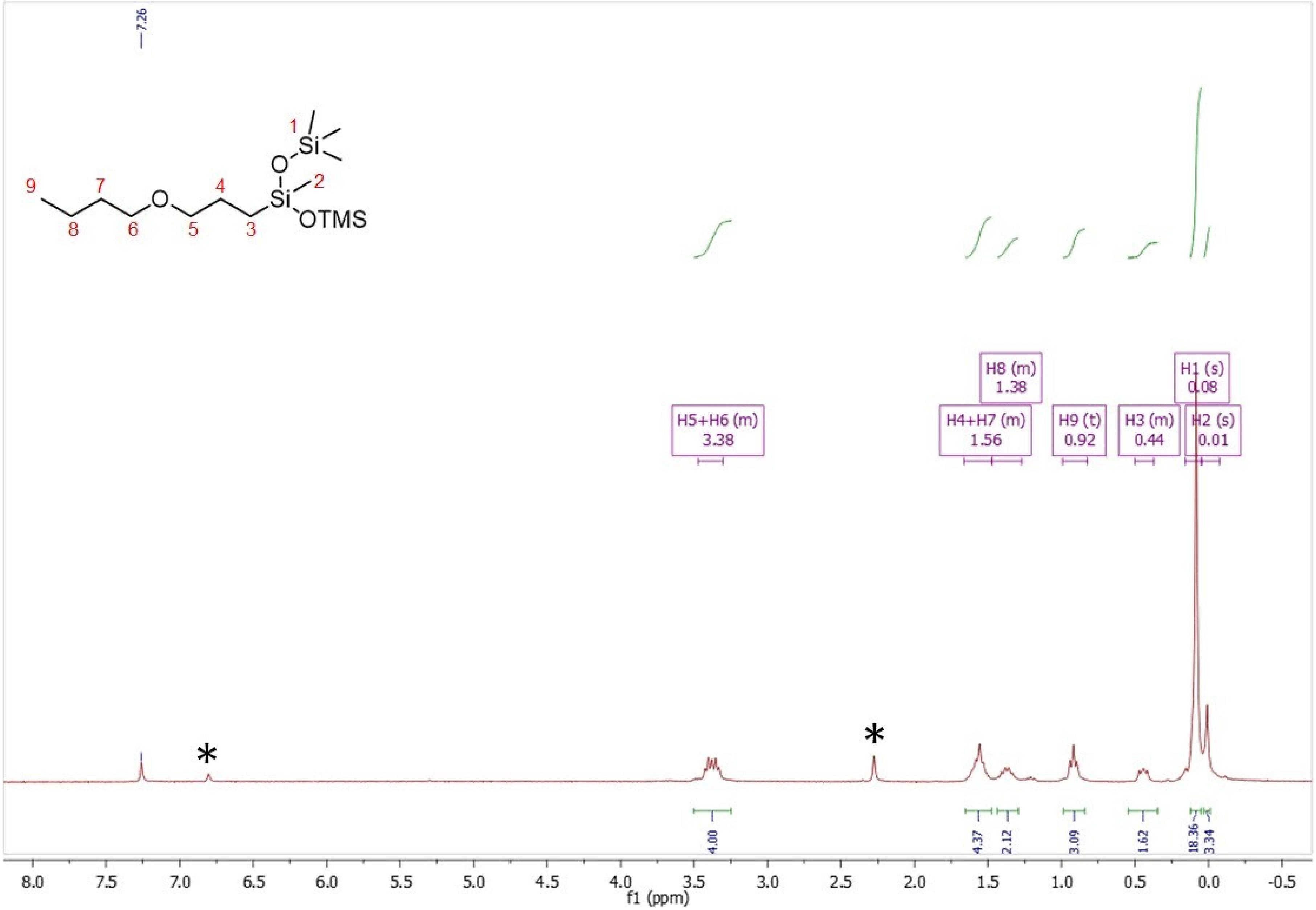
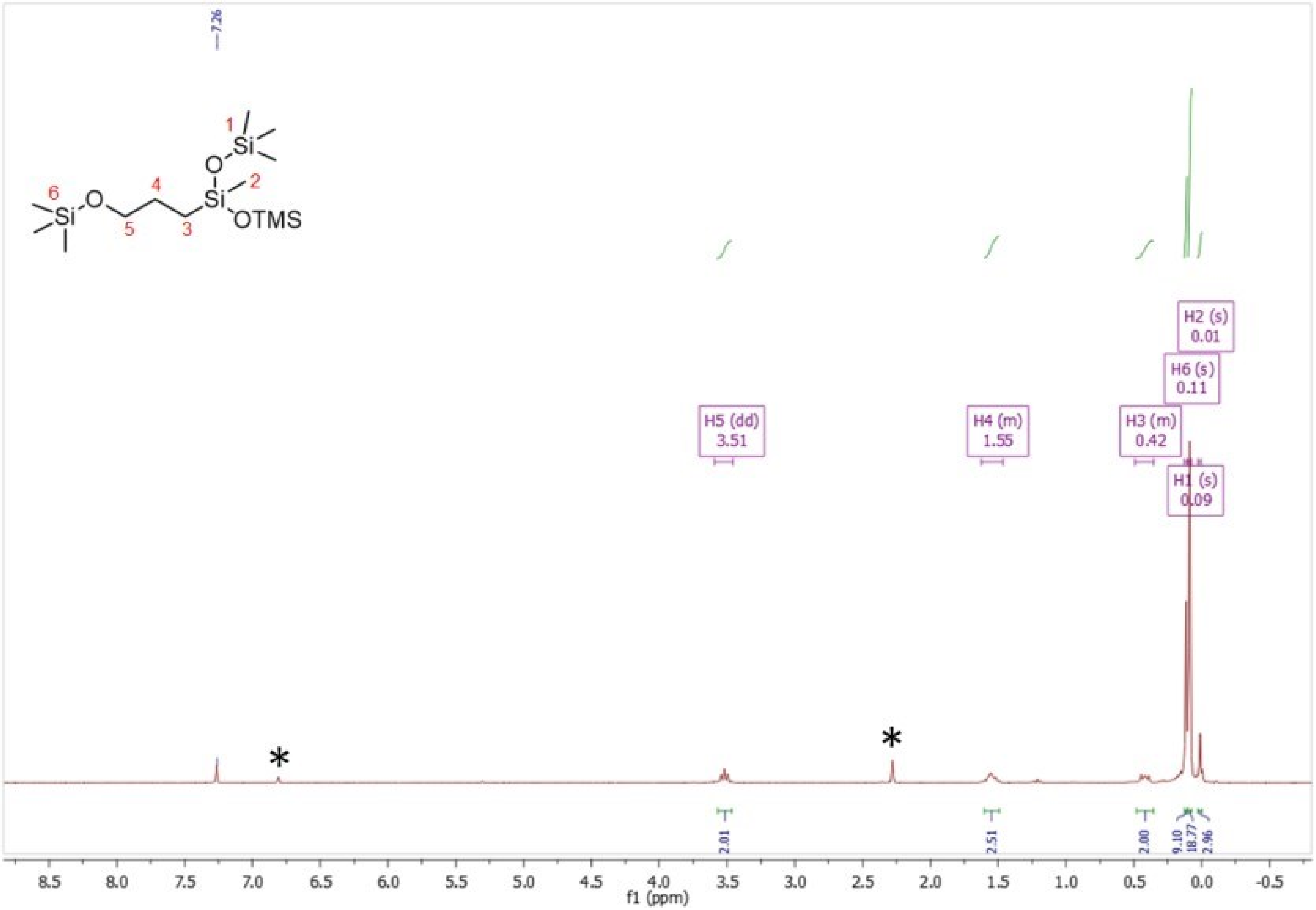


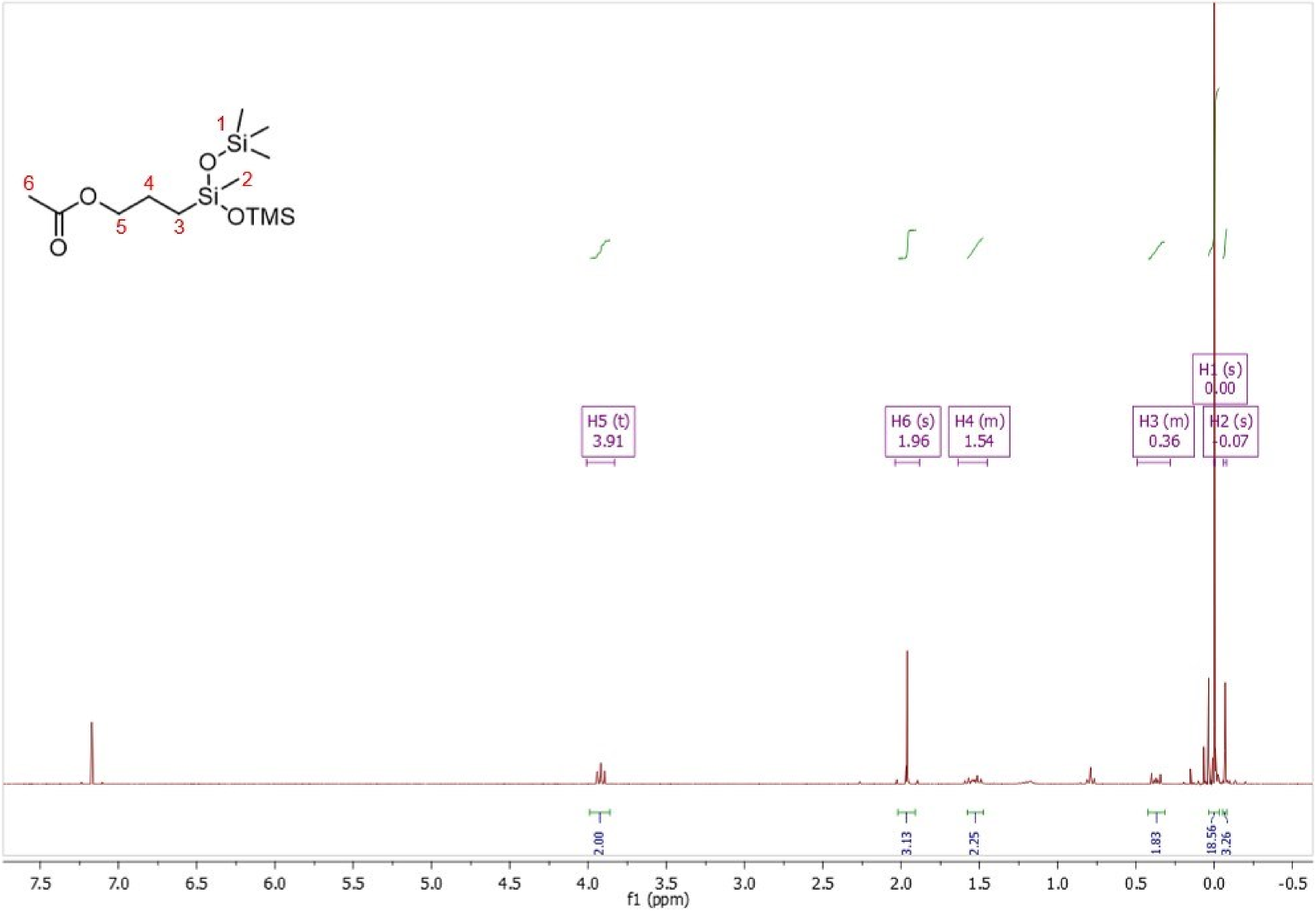
* Mesitylene (GC Standard)

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of functionalization of MD^HM with allyloxytrimethylsilane

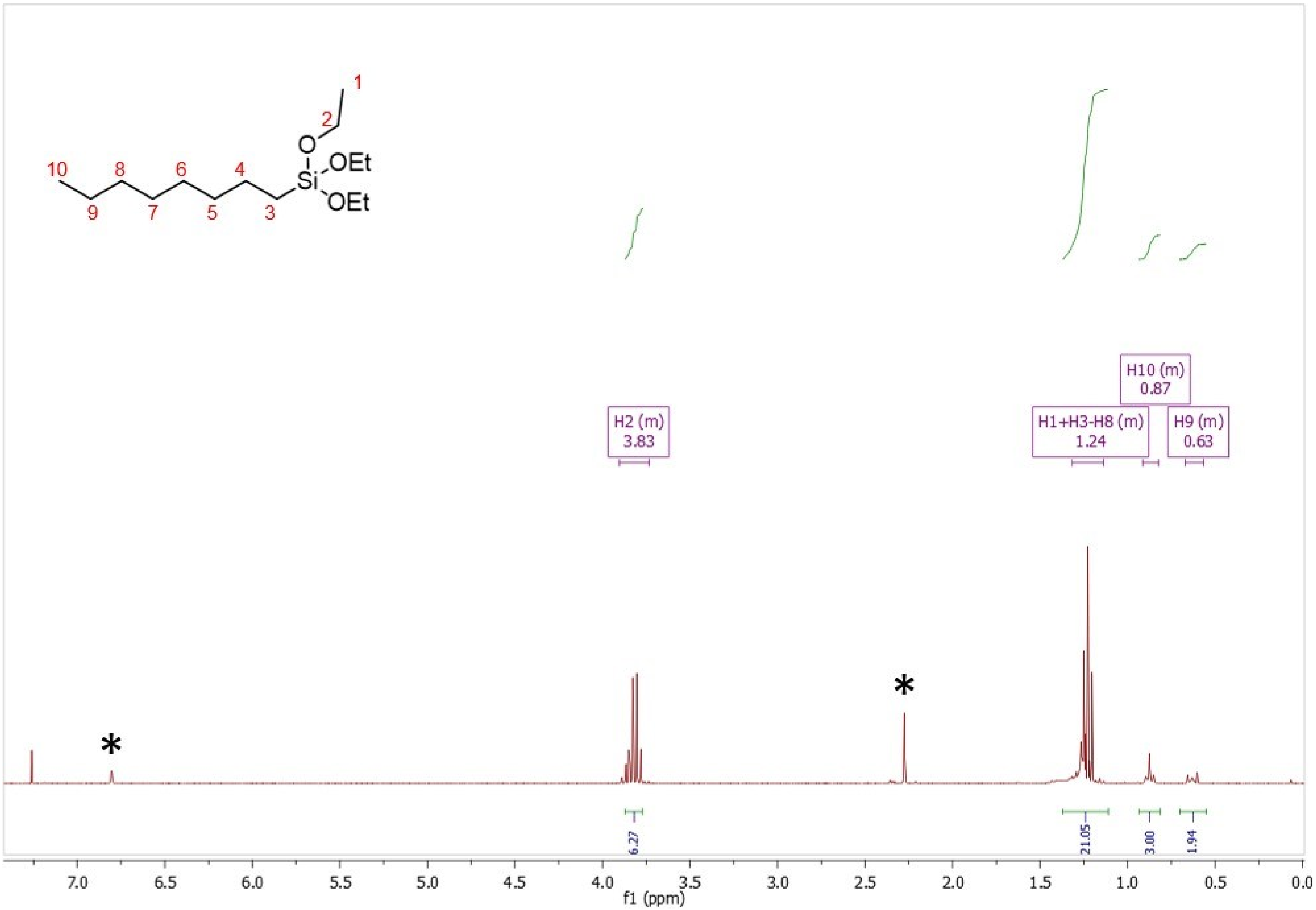


* Mesitylene (GC Standard)

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of functionalization of MD^HM with allyl acetate



^{1}H NMR spectrum (300 MHz, $CDCl_3$) of functionalization of Tri(ethoxy)silane with 1-octene



* Mesitylene
(GC Standard)

^{1}H NMR spectrum (300 MHz, CDCl$_3$) of functionalization of Triethylsilane with 1-octene