

Supporting Information for

Multifunctional thiols from the highly selective reaction of mercaptoalcohols with chlorosilanes

Abby R. Jennings and David Y. Son*

*dson@smu.edu

Table of Contents

Small-scale synthetic procedure used to determine GC yields for 2, 3, 5	2
Synthesis of 1-9	2
¹H, ¹³C, and ²⁹Si NMR Spectra of 2-9	11
Mass Spectra of 2,3,5-7	23
Cyclization Study of 6.....	26
Stability Study of 2.....	29

General Experimental Procedures. All solvents and reagents were obtained commercially. The chlorosilane starting reagents were distilled from magnesium and the triethylamine was distilled from calcium hydride prior to use. Ether and tetrahydrofuran (THF) were dried over activated 4 Å molecular sieves.

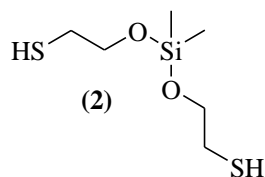
Small-scale synthetic procedure used to determine GC yields for 2, 3, 5.

A 250 mL round-bottomed flask was charged with a magnetic stir bar, ether (100 mL), triethylamine (3.5 mL, 0.025 mol), and 2-mercaptoethanol (1.8 mL, 0.025 mol). The solution was cooled in an ice bath, with stirring, under nitrogen. Using a syringe, the appropriate chlorosilane (**2**, dichlorodimethylsilane (1.6 mL, 0.013 mol); **3**, trichloromethylsilane (1.0 mL, 0.0085 mol); **5**, dichloromethylphenylsilane (2.1 mL, 0.013 mol)) was added slowly to the stirred solution. The suspension was gradually warmed to room temperature and stirred under nitrogen overnight. The suspension was vacuum filtered, using ether as a wash. Rotary evaporation was used to remove all volatiles from the filtrate. The samples were analyzed on an Agilent Technologies 6850 series II network GC system in dichloromethane.

Synthesis of 2-9.

2-Trimethylsilyloxyethanethiol (1). The synthesis of **1** and corresponding spectral data have been reported previously.¹

2-[Dimethyl(2-sulfanylethoxy)silyl]oxyethanethiol (2).



A 3-necked, 1 L, round-bottomed flask was charged with ether (250 mL), triethylamine (10.0 mL, 0.072 mol), and 2-mercaptoethanol (5.0 mL, 0.071 mol). Using an overhead mechanical stirrer, the solution was cooled, with stirring, in an ice bath under nitrogen. Using a syringe, dichlorodimethylsilane (4.4 mL, 0.036 mol) was added slowly to the stirred solution. The suspension was gradually warmed to room temperature and stirred under nitrogen overnight. The suspension was vacuum filtered, using ether as a wash. Rotary evaporation was used to remove all volatiles from the filtrate to give an oil (7.6 g). Compound **2** was purified by distillation under reduced pressure and obtained as a clear, colorless, foul-smelling liquid (6.2 g, 81%, 80% GC yield), bp = 86-87 °C at 1 mmHg.

¹H-NMR (500 MHz, CDCl₃): δ 3.77 (t, -OCH₂CH₂SH, 4H, ³J = 7 Hz), 2.65-2.61 (m, -OCH₂CH₂SH, 4H), 1.50 (t, -OCH₂CH₂SH, 2H, ³J = 8 Hz), 0.13 (s, -Si(CH₃)₃, 6H)

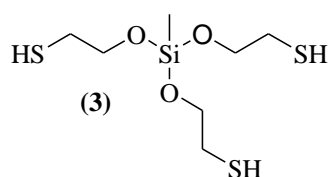
¹³C-NMR (125 MHz, CDCl₃): δ 64.4 (-OCH₂CH₂SH), 26.9 (-OCH₂CH₂SH), -3.1 ((CH₃)₂Si-)

²⁹Si-NMR (99 MHz, CDCl₃): δ -2.0 ((CH₃)₂Si-)

IR (NaCl, liquid film, cm⁻¹): 2962 (m), 2932 (m), 2867 (m), 2733 (w), 2561 (w, -SH), 1381 (w), 1280 (m), 1259 (m), 1090 (s), 957 (m), 854 (s), 801 (s), 715 (w), 473 (s)

EA: Calculated for C₆H₁₆O₂S₂Si, C 33.93, H 7.59, Found C 33.56, H 7.44.

2-[Methyl-bis(2-sulfanylethoxy)silyl]oxyethanethiol (3).



Compound **3** was synthesized according to the same procedure as **2**, using triethylamine (24.8 mL, 0.18 mol), 2-mercaptoethanol (12.5 mL, 0.18 mol), and trichloromethylsilane (7.0 mL, 0.060 mol) in ether (500 mL). Compound **3** was purified by distillation under reduced pressure and obtained as a clear, colorless, foul-smelling liquid (9.9 g, 69%, 88% GC yield), bp = 128-129 °C at 0.25 mmHg.

¹H-NMR (500 MHz, CDCl₃): δ 3.82 (t, -OCH₂CH₂SH, 6H, ³J = 7 Hz), 2.65-2.61 (m, -OCH₂CH₂SH, 6H), 1.50 (t, -OCH₂CH₂SH, 3H, ³J = 8 Hz), 0.14 (s, -SiCH₃, 3H)

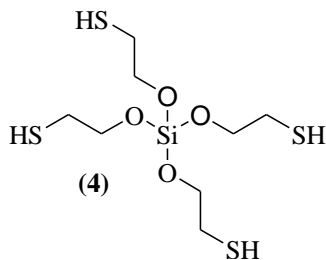
¹³C-NMR (125 MHz, CDCl₃): δ 64.6 (-OCH₂CH₂SH), 26.9 (-OCH₂CH₂SH), -7.1 (CH₃Si-)

²⁹Si-NMR (99 MHz, CDCl₃): δ -42.1 (CH₃Si-)

IR (NaCl, liquid film, cm⁻¹): 2933 (m), 2873 (m), 2735 (w), 2560 (w, -SH), 1416 (m), 1382 (m), 1280 (m), 1267 (m), 1208 (m), 1085 (s), 963 (m), 851 (s), 761 (m), 663 (m), 475 (s)

EA: Calculated for C₇H₁₈O₃S₃Si, C 30.63, H 6.61, Found C 30.25, H 6.50.

Tetrakis(2-sulfanylethyl) silicate (**4**).



A 3-necked 1 L round-bottomed flask was charged with ether (500 mL) and triethylamine (17.3 g, 0.17 mol). Using an overhead mechanical stirrer, the flask was cooled in an ice bath, with stirring, under nitrogen. Tetrachlorosilane (7.3 g, 0.043 mol) was added to this stirred solution followed by 2-mercaptoethanol (13.3 g, 0.17 mol). The suspension was gradually warmed to room temperature and stirred under nitrogen overnight. The suspension was vacuum

filtered using ether as a wash. Rotary evaporation was used to remove all volatiles from the filtrate to give an oil (13.6 g). Compound **4** was purified by distillation under reduced pressure and obtained as a clear, colorless liquid (8.4 g, 60%), bp = 143-145 °C at 0.05 mmHg.

¹H-NMR (500 MHz, CDCl₃): δ 3.83 (t, -OCH₂CH₂SH, 8H, ³J = 6 Hz), 2.63- 2.59 (m, -OCH₂CH₂SH, 8H), 1.48 (t, -OCH₂CH₂SH, 4H, ³J = 9 Hz)

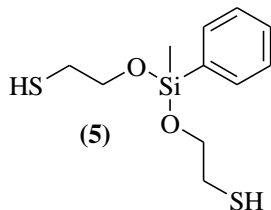
¹³C-NMR (125 MHz, CDCl₃): δ 65.5 (-OCH₂CH₂SH), 26.7 (-OCH₂CH₂SH)

²⁹Si-NMR (99 MHz, CDCl₃): δ -83.1 ((SHCH₂CH₂O)₄Si)

IR (NaCl, liquid film, cm⁻¹): 2935 (m), 2878 (m), 2739 (w), 2560 (w, -SH), 1466 (w), 1416 (w), 1300 (m), 1209 (m), 1097 (s), 970 (m), 846 (m), 738 (m), 465 (s)

EA: Calculated for C₈H₂₀O₄S₄Si, C 28.55, H 5.99, Found C 28.24, H 5.88.

2-[Methyl-phenyl-(2-sulfanylethoxy)silyl]oxyethanethiol (**5**).



Compound **5** was synthesized according to the same procedure as **4**, using triethylamine (5.0 g, 0.049 mol), dichloromethylphenylsilane (4.7 g, 0.025 mol), and 2-mercaptoethanol (3.9 g, 0.050 mol) in ether (150 mL). Compound **5** was purified by distillation under reduced pressure and obtained as a clear, colorless, foul-smelling liquid (3.6 g, 54%, 76% GC yield), bp = 140-142 °C at 0.50 mmHg.

¹H-NMR (500 MHz, CDCl₃): δ 7.67-7.64 (m, aromatic, 2H), 7.46-7.38 (m, aromatic, 3H), 3.87 (td, -OCH₂CH₂SH, 4H, ³J = 6 Hz, ⁴J = 1 Hz), 2.71- 2.67 (m, -OCH₂CH₂SH, 4H), 1.56 (t, -OCH₂CH₂SH, 2H, ³J = 8 Hz), 0.43 (s, -SiCH₃, 3H)

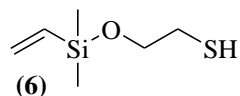
¹³C-NMR (125 MHz, CDCl₃): δ 134.2 (aromatic), 134.0 (aromatic), 130.6 (aromatic), 128.2 (aromatic), 65.0 (-OCH₂CH₂SH), 27.2 (-OCH₂CH₂SH), -3.9 (CH₃Si-)

²⁹Si-NMR (99 MHz, CDCl₃): δ -16.2 (CH₃Si-)

IR (NaCl, liquid film, cm⁻¹): 3069 (m), 3049 (m), 3024 (m), 3003 (m), 2963 (m), 2932 (m), 2869 (m), 2733 (w), 2565 (w, -SH), 1591 (m), 1429 (m), 1381 (m), 1299 (m), 1260 (m), 1207 (m), 1089 (m), 959 (m), 818 (m), 785 (m), 758 (m), 736 (m), 701 (m), 484 (s)

EA: Calculated for C₁₁H₁₈O₂S₂Si, C 48.13, H 6.61, Found 48.20 C, 6.63.

2-[Dimethyl(vinyl)silyl]oxyethanol (**6**).



Compound **6** was synthesized according to the same procedure as **2**, using triethylamine (6.1 mL, 0.044 mol), 2-mercaptoethanol (3.1 mL, 0.044 mmol), and chlorodimethylvinylsilane (6.0 mL, 0.044 mol) in ether (150 mL). Compound **6** was obtained as a clear, colorless, and foul-smelling liquid (7.0 g, 99% crude yield). The crude product could be distilled to give pure **6**, but it quickly undergoes cyclization reactions (bp = 60-64 °C at 10.5 mmHg).

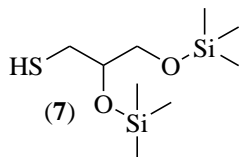
¹H-NMR (500 MHz, CDCl₃): δ 6.10 (dd, CH₂CHSi-, 1H, ³J = 20 Hz, ³J = 15 Hz), 6.00 (dd, CH₂CHSi-, 1H, ³J = 15 Hz, ²J = 4 Hz), 5.77 (dd, CH₂CHSi-, 1H, ³J = 20, ²J = 4 Hz), 3.68 (t, -OCH₂CH₂SH, 2H, ³J = 7 Hz), 2.63-2.59 (m, -OCH₂CH₂SH, 2H), 1.49 (t, -OCH₂CH₂SH, 1H, ³J = 8 Hz), 0.19 (s, -Si(CH₃)₂, 6H)

¹³C-NMR (125 MHz, CDCl₃): δ 137.1 (vinyl C), 133.7 (vinyl C), 64.9 (-OCH₂CH₂SH), 27.1 (-OCH₂CH₂SH), -2.1(-Si(CH₃)₂)

²⁹Si-NMR (99 MHz, CDCl₃): δ 7.2 (-Si(CH₃)₂)

IR (NaCl, liquid film, cm^{-1}): 3050 (m), 2959 (m), 2902 (m), 2863 (m), 2730 (w), 2563 (w, -SH), 1920 (w), 1594 (m), 1407 (m), 1380 (m), 1298 (m), 1252 (m), 1206 (w), 1090 (m), 1009 (m), 957 (m), 836 (m), 715 (m), 693 (m), 437 (m)

2,3-Bis(trimethylsilyloxy)propane-1-thiol (7).



A 250 mL round-bottomed flask was charged with a stir bar, THF (100 mL), and triethylamine (4.4 g, 0.043 mol). The solution was cooled in an ice bath, with stirring, under nitrogen. Trimethylchlorosilane (4.7 g, 0.043 mol) was added to this stirred solution, followed by α -thioglycerol (2.2 g, 0.020 mol). The suspension was stirred in an ice bath, under nitrogen, for five minutes. The round-bottomed flask was then equipped with a reflux condenser and the suspension was heated (~ 70 °C) in an oil bath under nitrogen overnight. The suspension was cooled to room temperature and vacuum filtered using THF as a wash. Rotary evaporation was used to remove all volatiles from the filtrate to give an oil (5.0 g). Compound **7** was purified by distillation under reduced pressure and obtained as a clear, colorless, and foul-smelling liquid (1.6 g, 42%), bp = 61-63 °C at 0.50 mmHg.

Small-scale procedure to obtain GC yield of (7).

A 250 mL round-bottomed flask was charged with a magnetic stir bar, THF (100 mL), triethylamine (3.5 mL, 0.025 mol), and α -thioglycerol (1.1 mL, 0.013 mol). The solution was cooled in an ice bath under nitrogen. Using a syringe, trimethylchlorosilane (3.2 mL, 0.025 mol) was added dropwise to this cooled, stirred solution. The suspension was stirred in the ice bath for five minutes. The round bottom flask was then equipped with a reflux condenser and the

suspension was heated in an oil bath (~70 °C) under nitrogen overnight. The suspension was cooled to room temperature and vacuum filtered using THF as a wash. Rotary evaporation was used to remove all volatiles from the filtrate. The product was obtained as a clear, pink, smelly liquid (78% GC yield).

¹H-NMR (500 MHz, CDCl₃): δ 3.74 (p, -CHCH₂OSi(CH₃)₃, 1H, ³J= 6 Hz), 3.52 (d, -CHCH₂OSi(CH₃)₃, 2H, ³J= 6 Hz), 2.71-2.66 (m, -CHCH₂SH, 1H), 2.56-2.51 (m, -CHCH₂SH, 1H), 1.46 (t, -CHCH₂SH, 1H, ³J = 8 Hz), 0.14 (s, -OSi(CH₃)₃, 9H), 0.10 (s, -OSi(CH₃)₃, 9H)

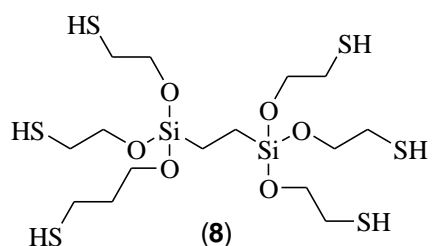
¹³C-NMR (125 MHz, CDCl₃): δ 74.1 (-CHCH₂OSi(CH₃)₃), 64.9 (-CHCH₂OSi(CH₃)₃), 28.4 (-CHCH₂SH), 0.4 (-OSi(CH₃)₃), -0.5 (-OSi(CH₃)₃)

²⁹Si-NMR (99 MHz, CDCl₃): δ 18.8 (-OSi(CH₃)₃), 17.9 (-OSi(CH₃)₃)

IR (NaCl, liquid film, cm⁻¹): 2957 (s), 2903 (m), 2869 (m), 2584 (w), 1458 (w), 1415 (w), 1348 (w), 1198 (s), 1120 (s), 1078 (s), 987 (m), 842 (s), 748 (m), 685 (m), 665 (m), 448 (s)

EA: Calculated for C₉H₂₄O₂SSi₂, C 42.81, H 9.58, Found 43.01 C, 9.65 H.

2-[Bis(2-sulfanylethoxy)-[2-[tris(2-sulfanylethoxy)silyl]ethyl]silyl]oxyethanethiol (**8**).



Compound **8** was synthesized according to the same procedure as **2**, using triethylamine (2.6 mL, 0.019 mol) 2-mercaptoethanol (1.3 mL, 0.019 mol), and trichloro(2-trichlorosilylethyl)silane (0.9 g, 0.0030 mol) in ether (75 mL). The trichloro(2-trichlorosilylethyl)silane was synthesized in house via a hydrosilylation reaction between vinyltrichlorosilane and trichlorosilane.² Compound **8** was obtained as a clear and colorless, foul-

smelling liquid (1.7 g). The product was purified by heating (~100 °C) in an oil bath under reduced pressure (0.050 mmHg) to remove any unreacted 2-mercaptoethanol and other impurities. The product was obtained as a clear and colorless, foul-smelling viscous liquid (0.9 g, 85%).

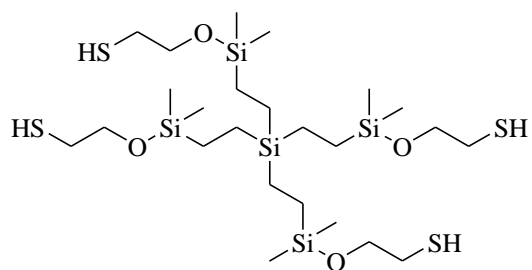
¹H-NMR (500 MHz, CDCl₃): δ 3.85 (t, -OCH₂CH₂SH, 12H, ³J = 6 Hz), 2.67- 2.62 (m, -OCH₂CH₂SH, 12H), 1.51 (t, -OCH₂CH₂SH, 6H, ³J = 8 Hz), 0.69 (s, -SiCH₂CH₂Si-, 4H)

¹³C-NMR (125 MHz, CDCl₃): δ 64.9 (-OCH₂CH₂SH), 27.0 (-OCH₂CH₂SH), 1.5 (-SiCH₂CH₂Si-)

²⁹Si-NMR (99 MHz, CDCl₃): δ -45.3 (-SiCH₂CH₂Si-)

IR (NaCl, liquid film, cm⁻¹): 2931 (s), 2873 (s), 2735 (w), 2558 (m, -SH), 1465 (m), 1414 (m), 1381 (m), 1299 (s), 1248 (m), 1207 (m), 1089 (s), 962 (m), 835 (s), 754 (m), 663 (m), 464 (s)

2-[Dimethyl-[2-[tris[2-[dimethyl(2-sulfanylethoxy)silyl]ethyl]silyl]ethyl]silyl]oxyethanethiol (9).



(9)

Compound **9** was synthesized according to the same procedure as **2**, using triethylamine (1.0 mL, 7.2 mmol) 2-mercaptoethanol (0.5 mL, 7.1 mmol), and tetrakis[2-[chloro(dimethyl)silyl]ethyl]silane (0.9 g, 1.7 mmol) in ether (30 mL). Tetrakis[2-[chloro(dimethyl)silyl]ethyl]silane was synthesized in house via a hydrosilylation reaction

between tetravinylsilane and chlorodimethylsilane (1.1 g).³ The product was purified by heating (~100 °C) in an oil bath under reduced pressure (0.025 mmHg) to remove any unreacted 2-mercaptoethanol and other impurities. The product was obtained as a clear and colorless, foul-smelling viscous liquid (0.8 g, 86%).

¹H-NMR (500 MHz, CDCl₃): δ 3.67 (t, -OCH₂CH₂SH, 8H, ³J = 7 Hz), 2.62- 2.58 (m, -OCH₂CH₂SH, 8H), 1.49 (t, -OCH₂CH₂SH, 4H, ³J = 8 Hz), 0.43 (s, -SiCH₂CH₂Si-, 16H), 0.09 (s, -CH₂Si(CH₃)₂O-, 24 H)

¹³C-NMR (125 MHz, CDCl₃): δ 64.7(-OCH₂CH₂SH), 27.2 (-OCH₂CH₂SH), 8.3(-SiCH₂CH₂Si-), 2.0 (-SiCH₂CH₂Si-), -2.7 (-CH₂Si(CH₃)₂O-)

²⁹Si-NMR (99 MHz, CDCl₃): δ 19.5 (-SiCH₂CH₂Si-), 0.1 (-CH₂Si(CH₃)₂O-)

IR (NaCl, liquid film, cm⁻¹): 2954 (s), 2905 (m), 2729 (w), 2557 (w, -SH), 1463 (m), 1409 (m), 1379 (m), 1298 (m), 1250 (s), 1204 (m), 1093 (s), 952 (m), 840 (s), 769 (s), 662 (w), 440 (s)

EA: Calculated for C₂₄H₆₀O₄S₄Si₅, C 42.30, H 8.88, Found C 42.77, H 8.77.

^1H , ^{13}C , and ^{29}Si NMR Spectra of 2-9.

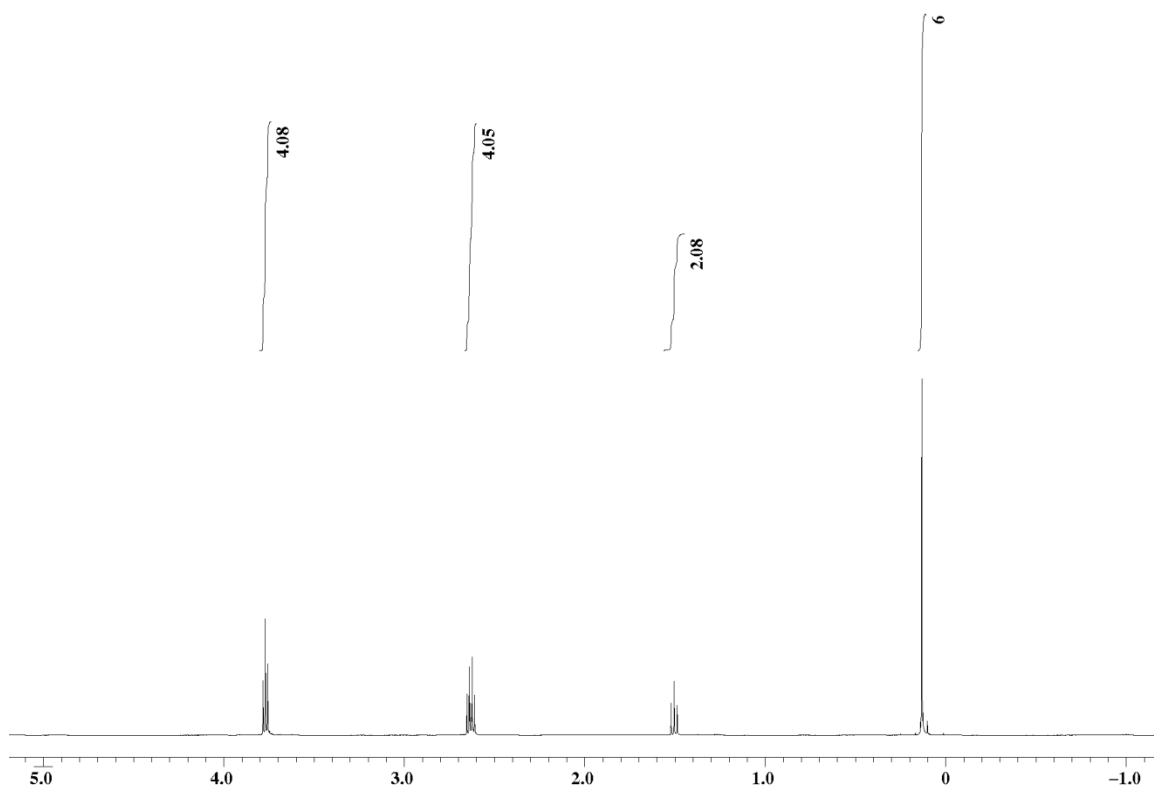


Figure SI 1. ^1H NMR (500 MHz, CDCl_3) compound **2**.

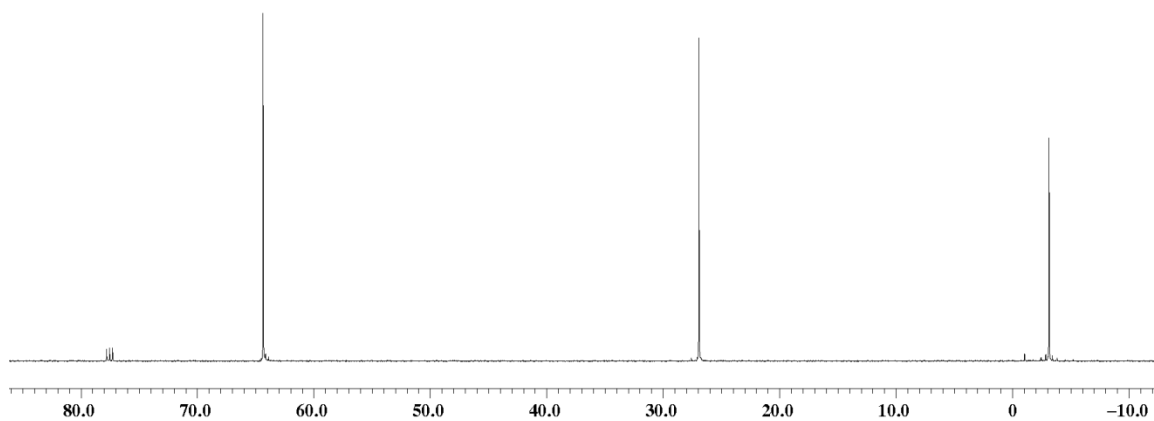


Figure SI 2. ^{13}C NMR (125 MHz, CDCl_3) compound **2**.

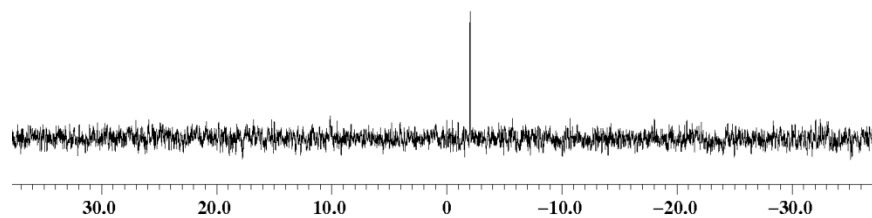


Figure SI 3. ^{29}Si NMR (99 MHz, CDCl_3) compound **2**.

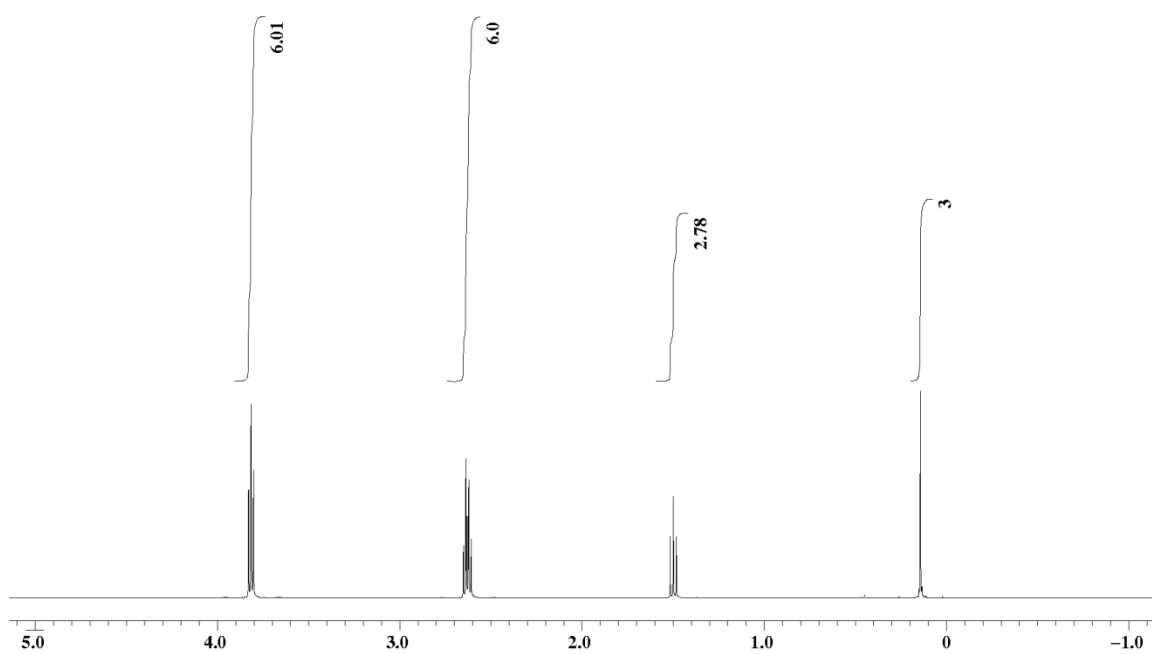


Figure SI 4. ^1H NMR (500 MHz, CDCl_3) compound **3**.

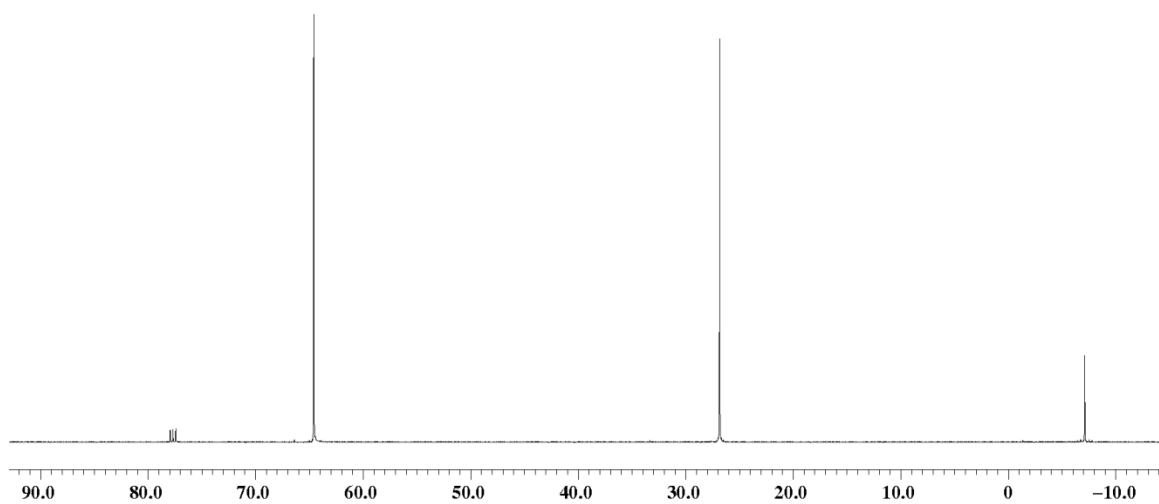


Figure SI 5. ^{13}C NMR (125 MHz, CDCl_3) compound **3**.

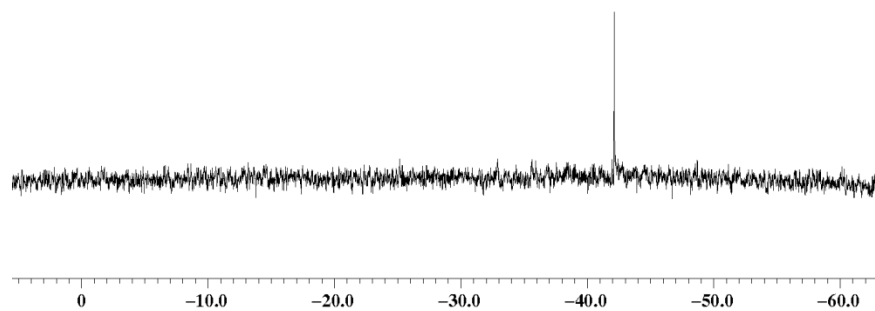


Figure SI 6. ^{29}Si NMR (99 MHz, CDCl_3) compound **3**.

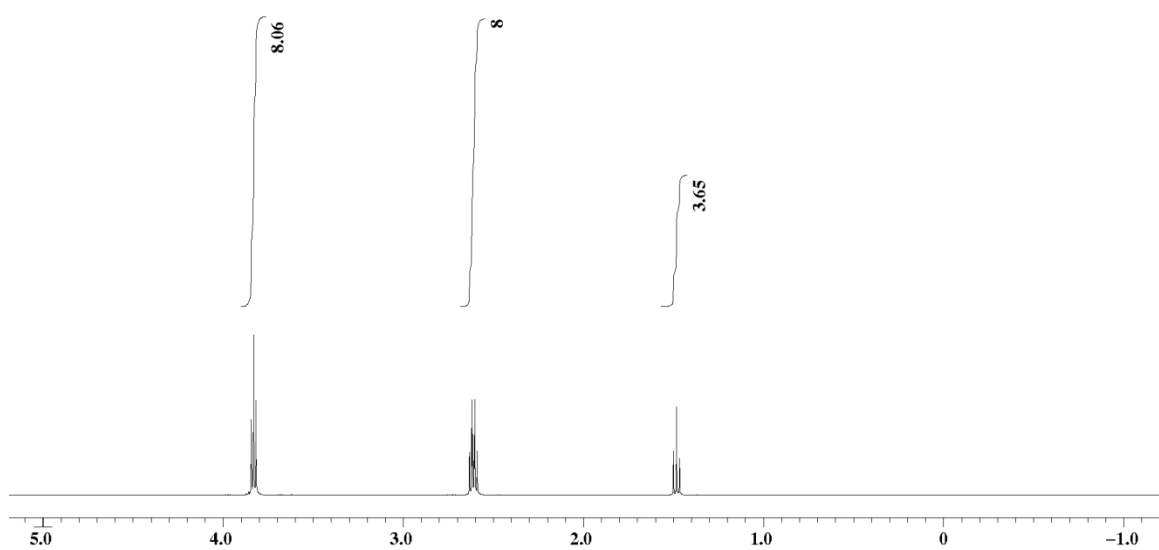


Figure SI 7. ^1H NMR (500 MHz, CDCl_3) compound 4.

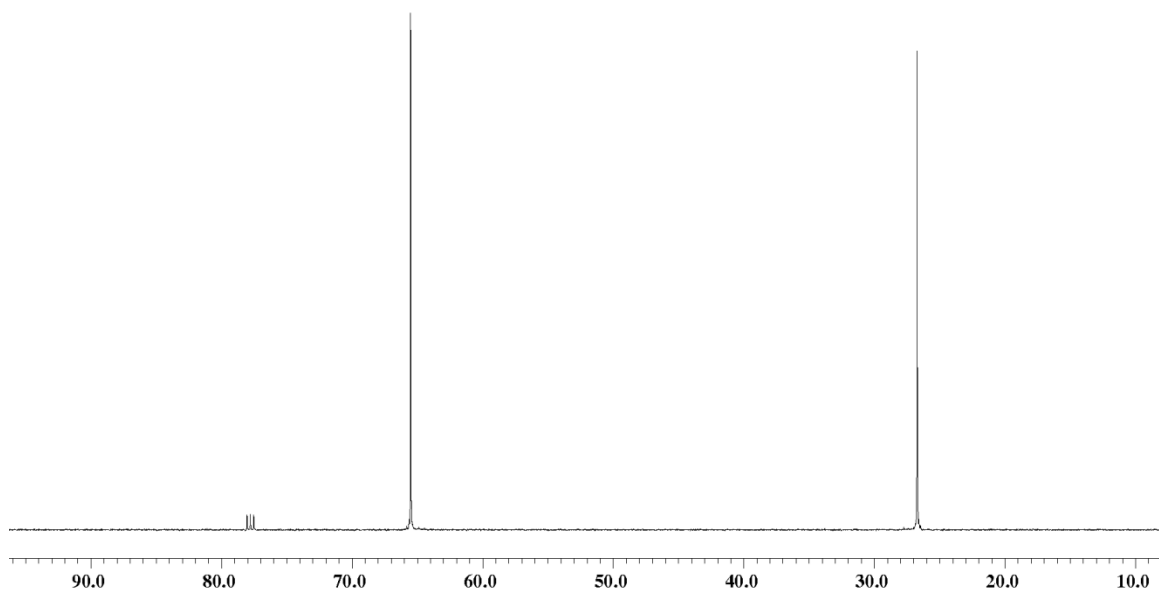


Figure SI 8. ^{13}C NMR (125 MHz, CDCl_3) compound 4.

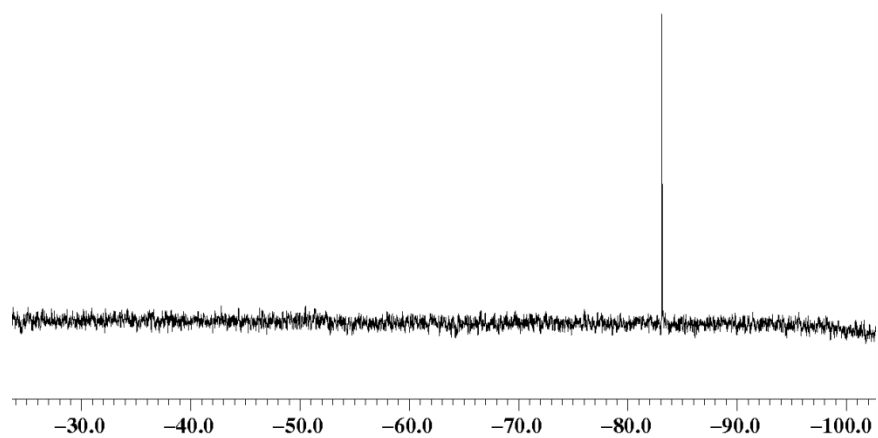


Figure SI 9. ^{29}Si NMR (99 MHz, CDCl_3) compound **4**.

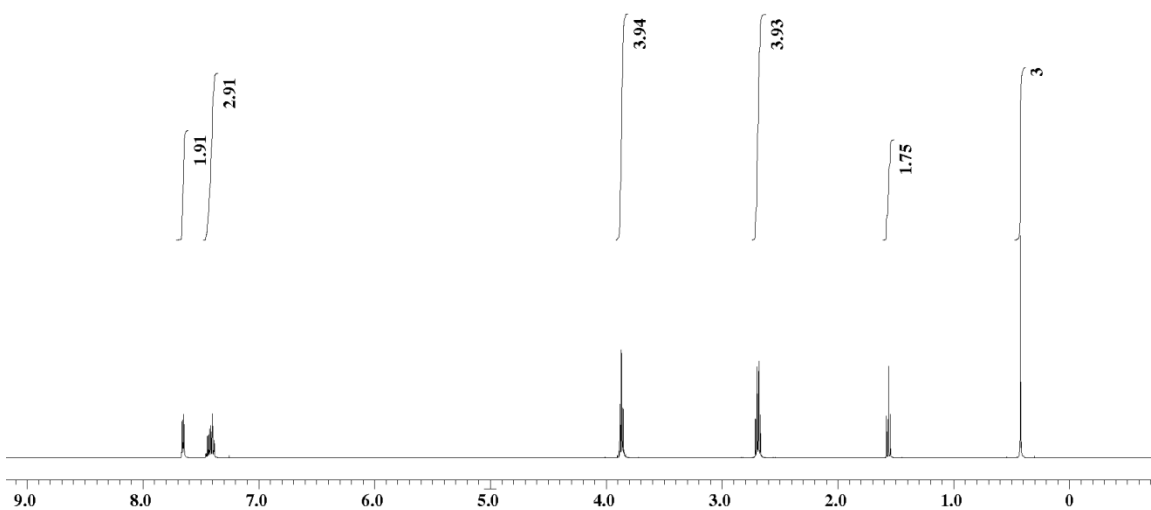


Figure SI 10. ^1H NMR (500 MHz, CDCl_3) compound **5**.

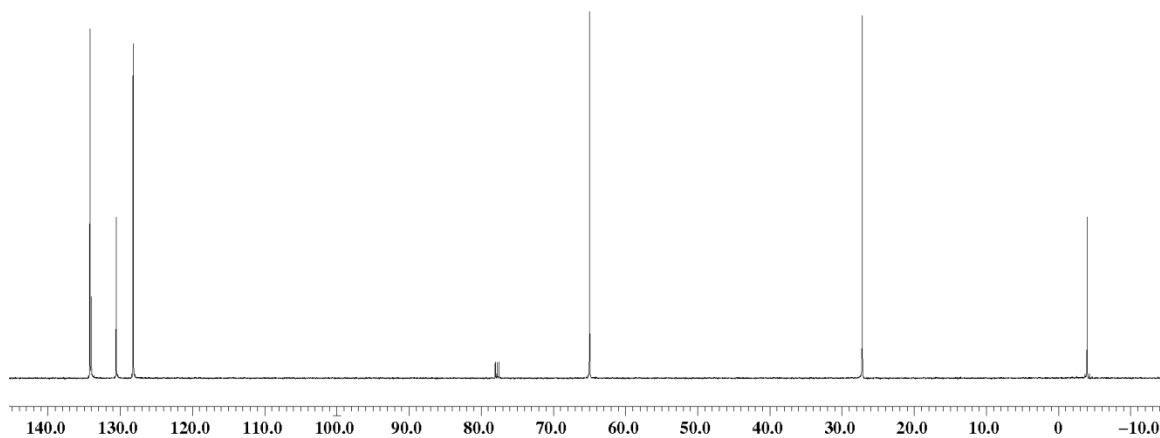


Figure SI 11. ^{13}C NMR (125 MHz, CDCl_3) compound **5**.

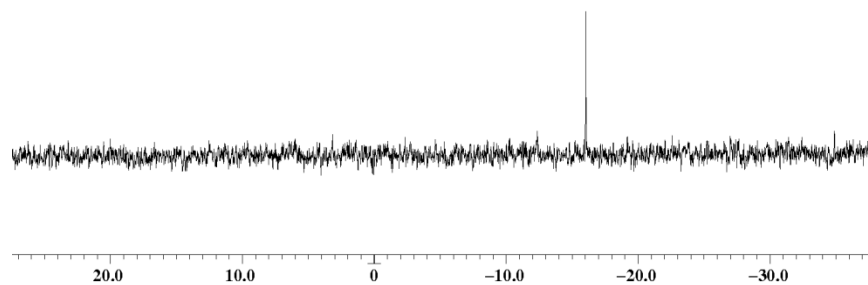


Figure SI 12. ^{29}Si NMR (99 MHz, CDCl_3) compound **5**.

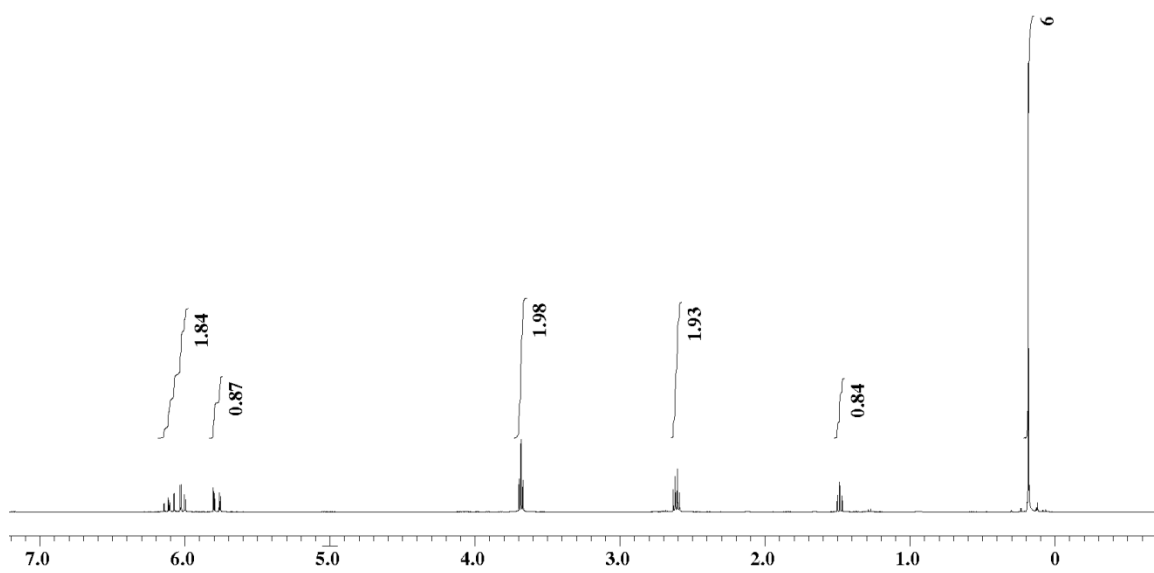


Figure SI 13. ^1H NMR (500 MHz, CDCl_3) compound **6**.

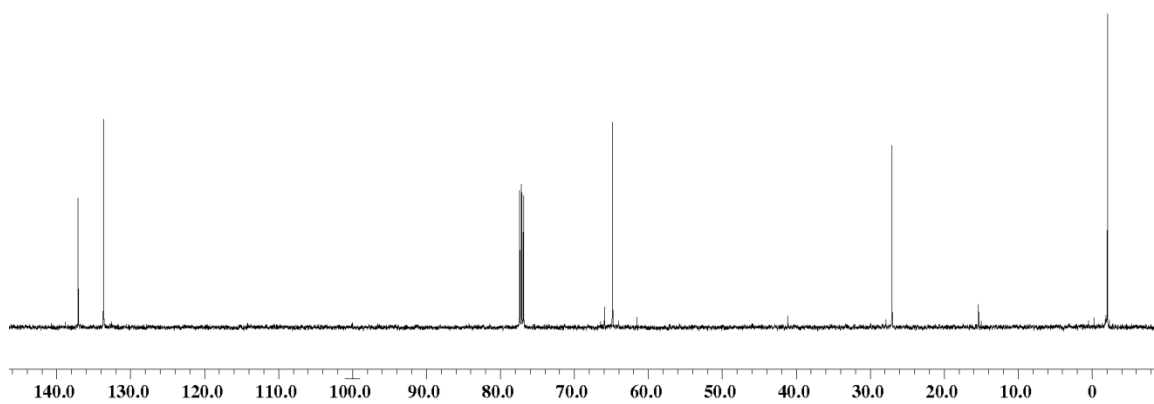


Figure SI 14. ^{13}C NMR (125 MHz, CDCl_3) compound **6**.

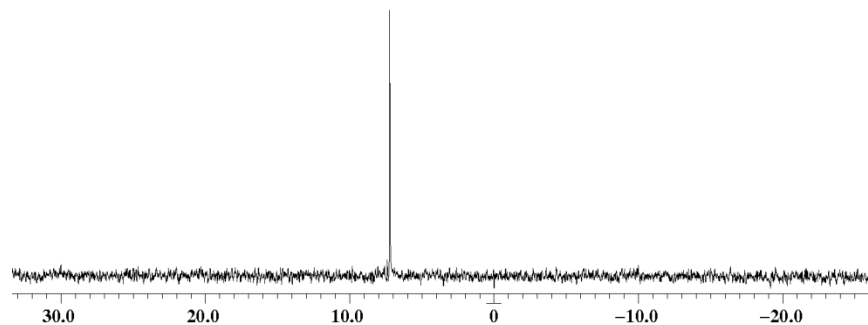


Figure SI 15. ^{29}Si NMR (99 MHz, CDCl_3) compound **6**.

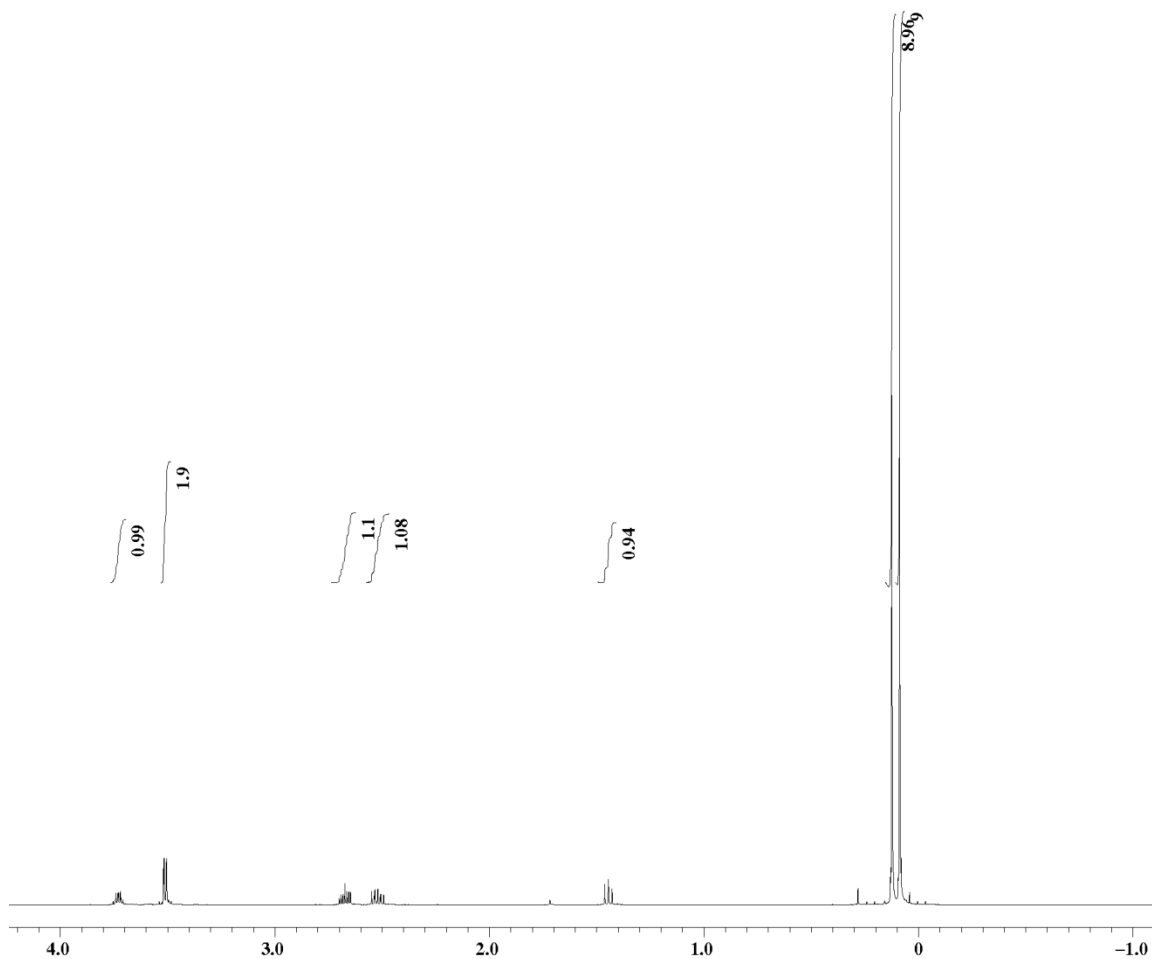


Figure SI 16. ^1H NMR (500 MHz, CDCl_3) compound **7**.

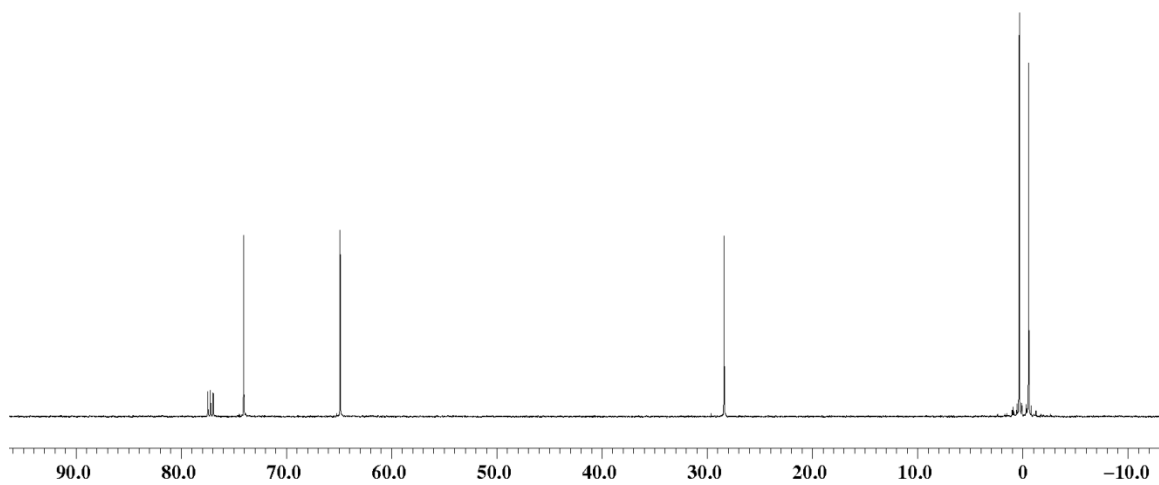


Figure SI 17. ^{13}C NMR (125 MHz, CDCl_3) compound **7**.

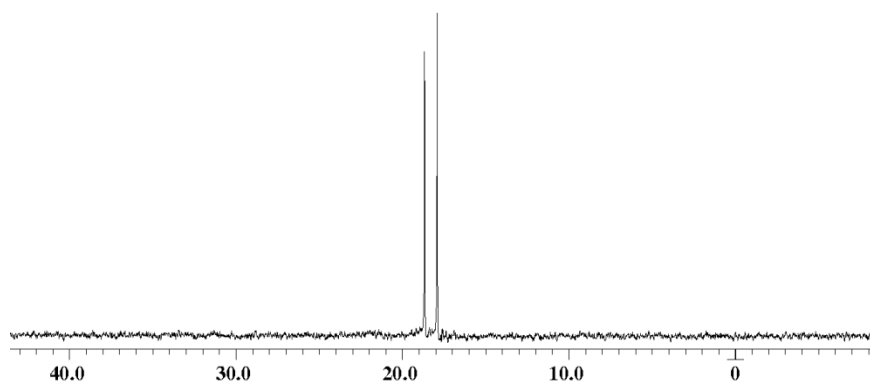


Figure SI 18. ^{29}Si NMR (99 MHz, CDCl_3) compound **7**.

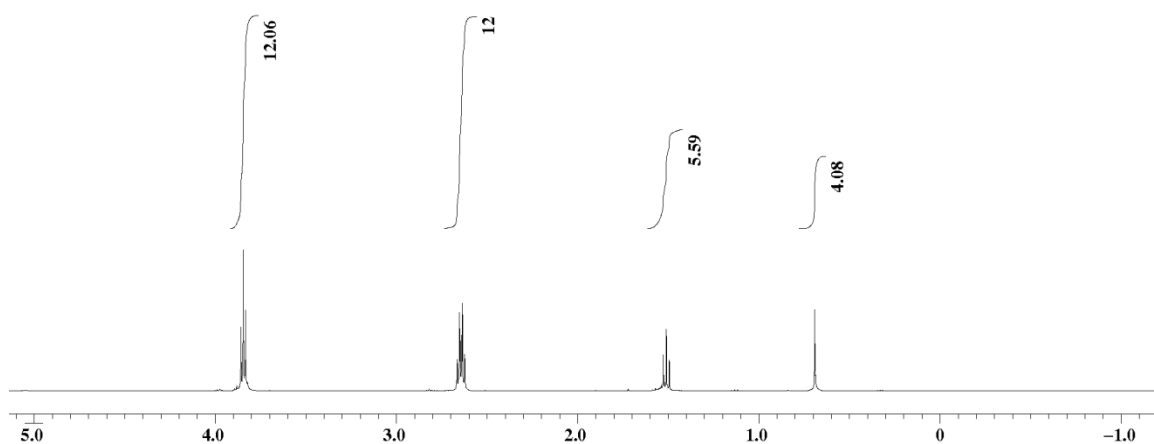


Figure SI 19. ¹H NMR (500 MHz, CDCl₃) compound **8**.

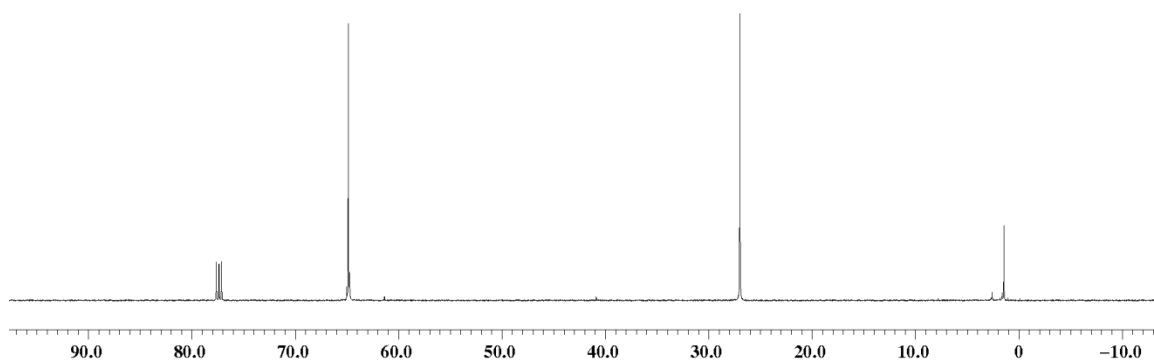


Figure SI 20. ¹³C NMR (125 MHz, CDCl₃) compound **8**.

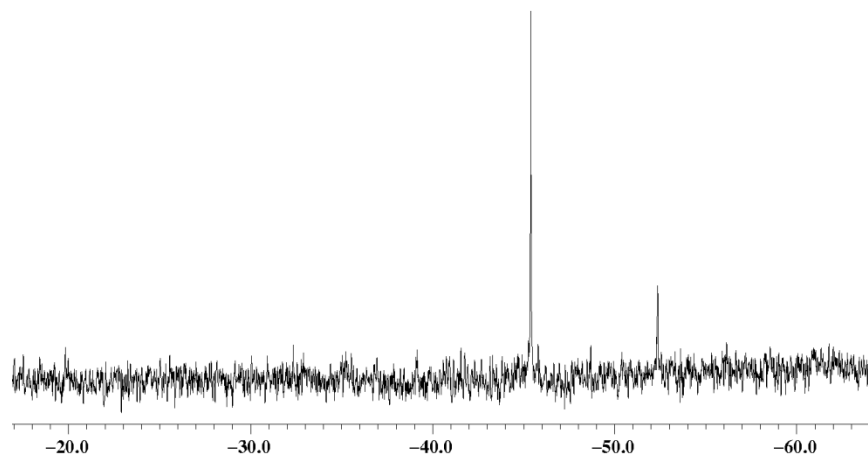


Figure SI 21. ^{29}Si NMR (99 MHz, CDCl_3) compound **8**.

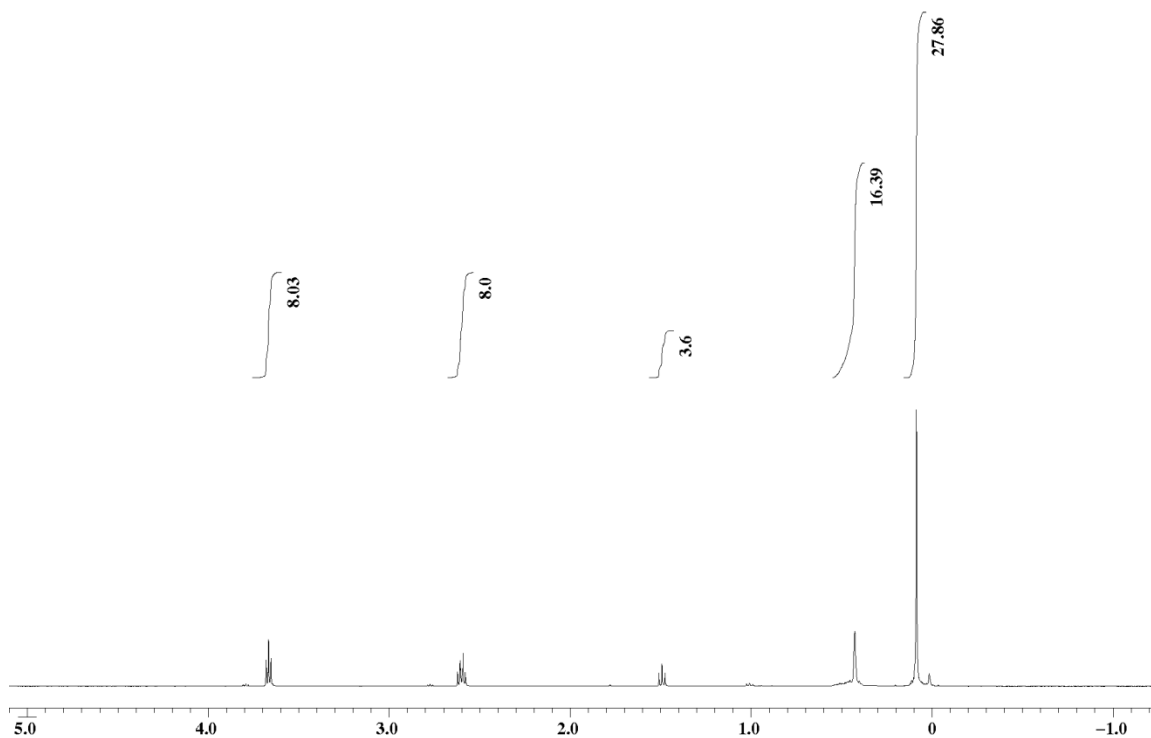


Figure SI 22. ^1H NMR (500 MHz, CDCl_3) compound **9**.

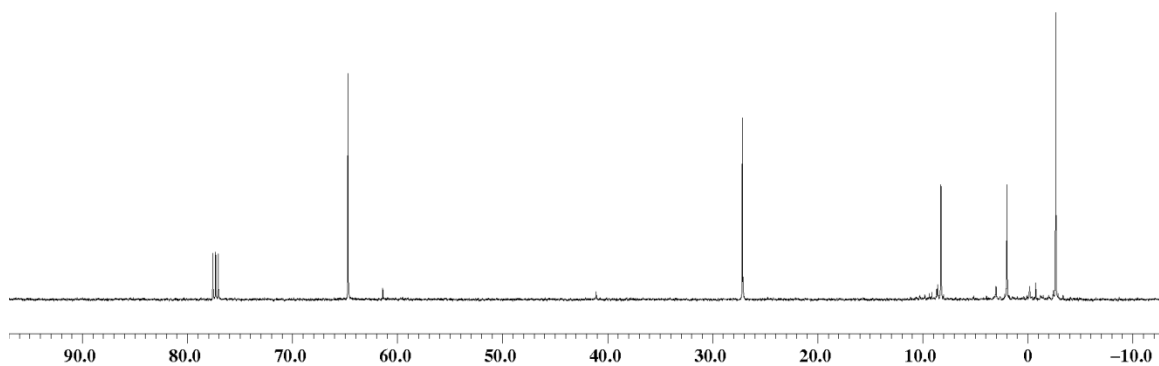


Figure SI 23. ^{13}C NMR (125 MHz, CDCl_3) compound **9**.

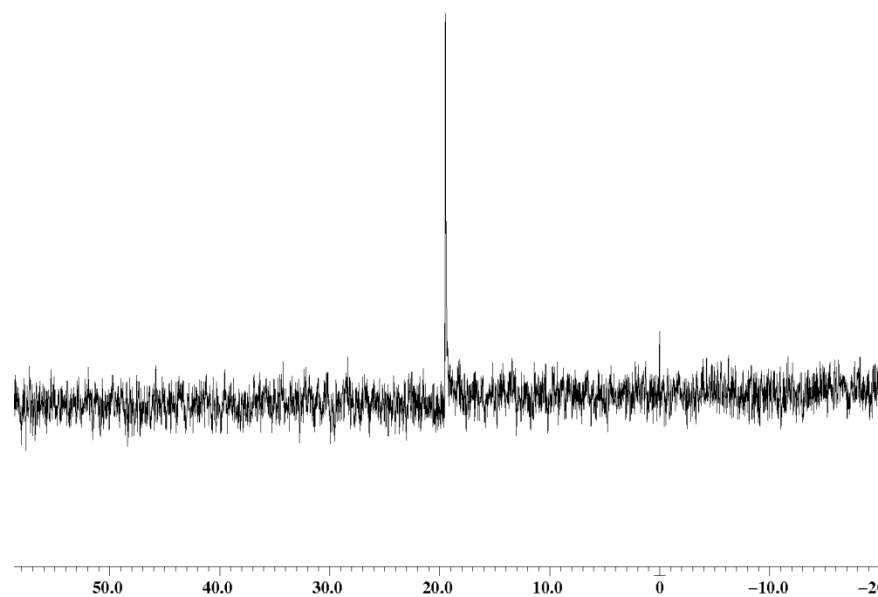


Figure SI 24. ^{29}Si NMR (99 MHz, CDCl_3) compound **9**.

Mass Spectra of 2,3,5-7.

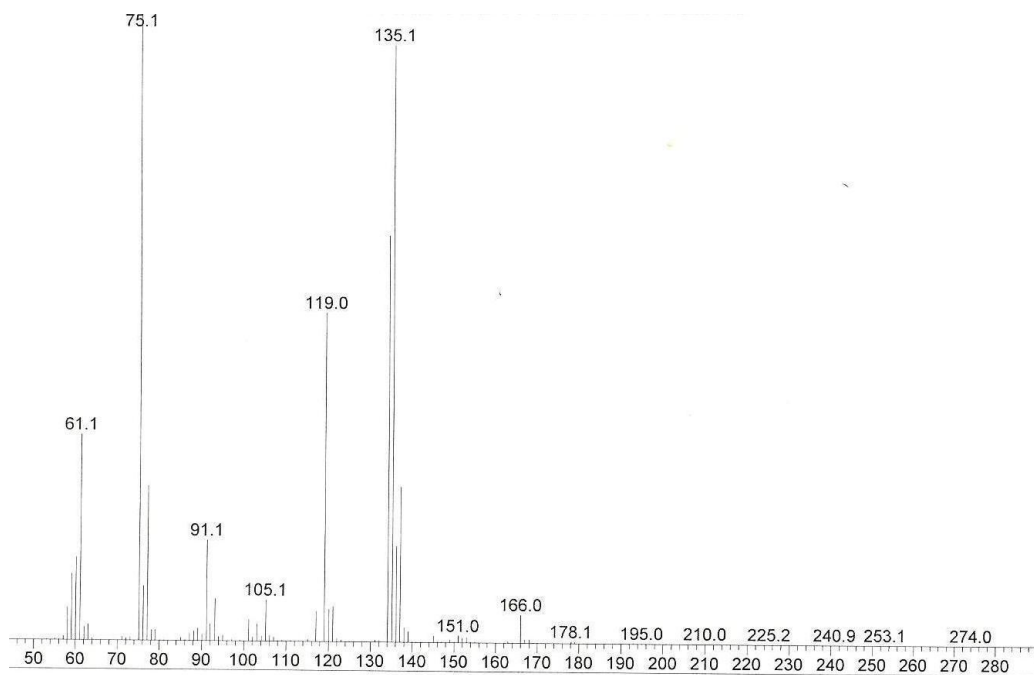


Figure SI 25. Mass Spectrum (DCM) compound 2.

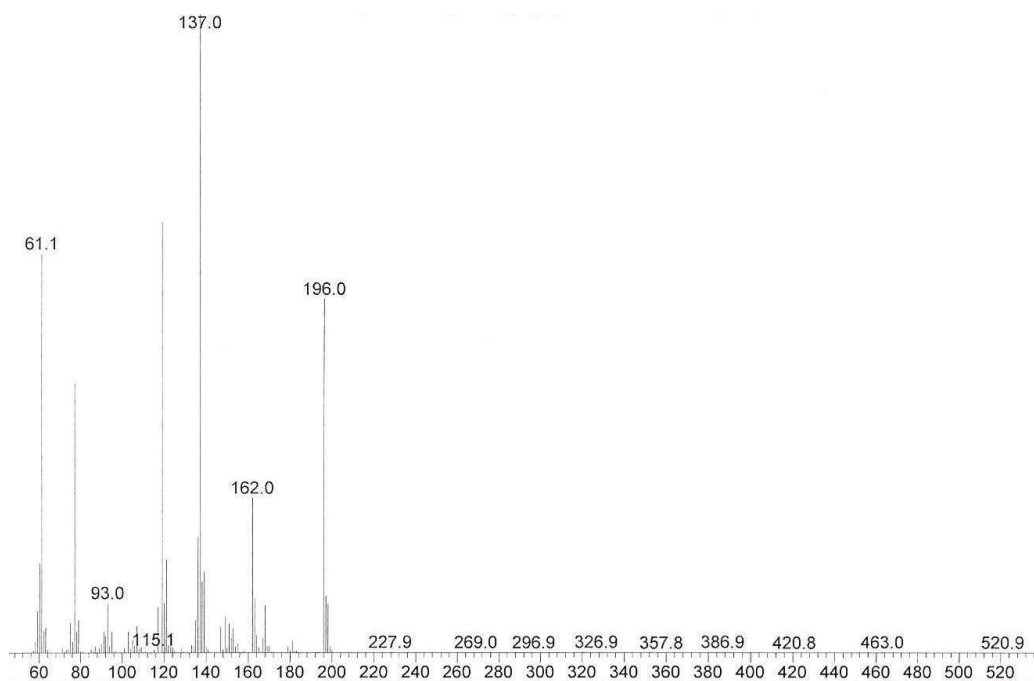


Figure SI 26. Mass Spectrum (DCM) compound 3.

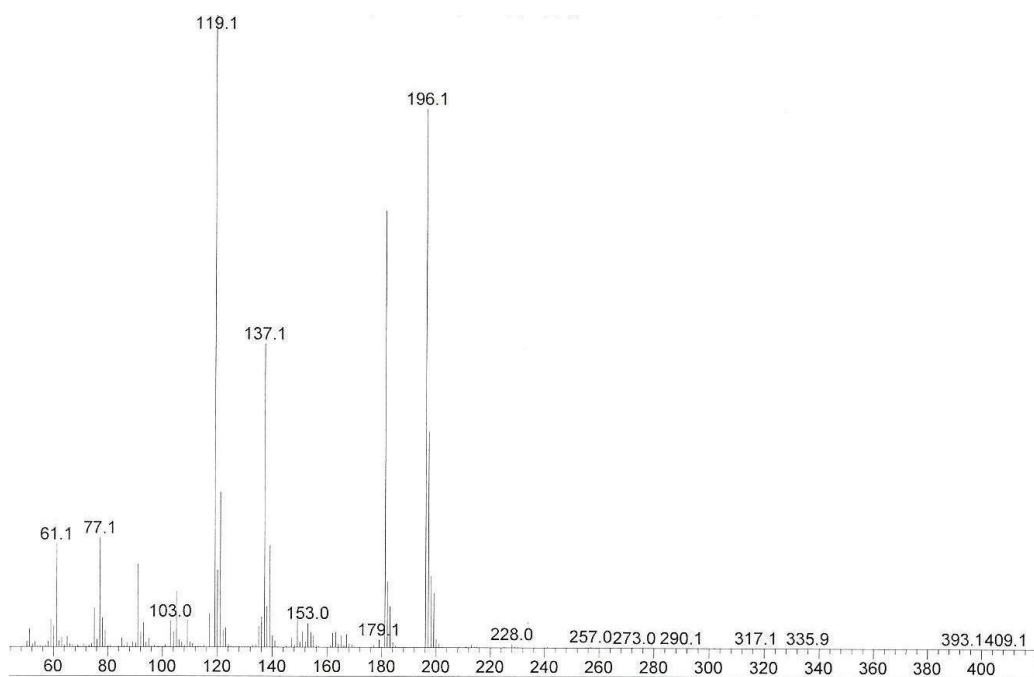


Figure SI 27. Mass Spectrum (DCM) compound **5**.

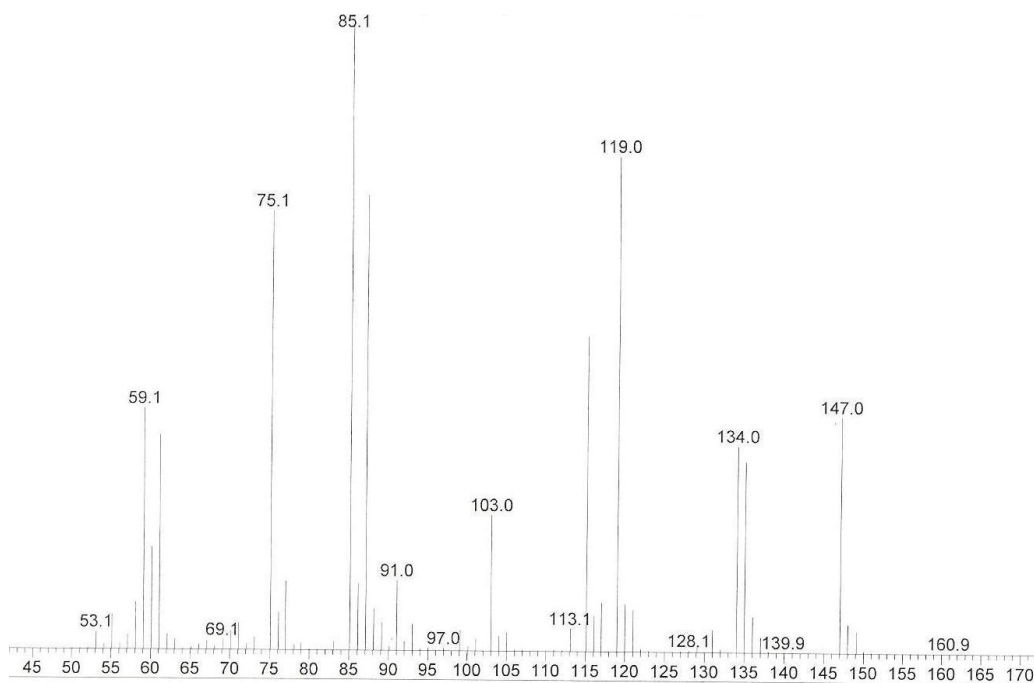


Figure SI 28. Mass Spectrum (DCM) compound **6**.

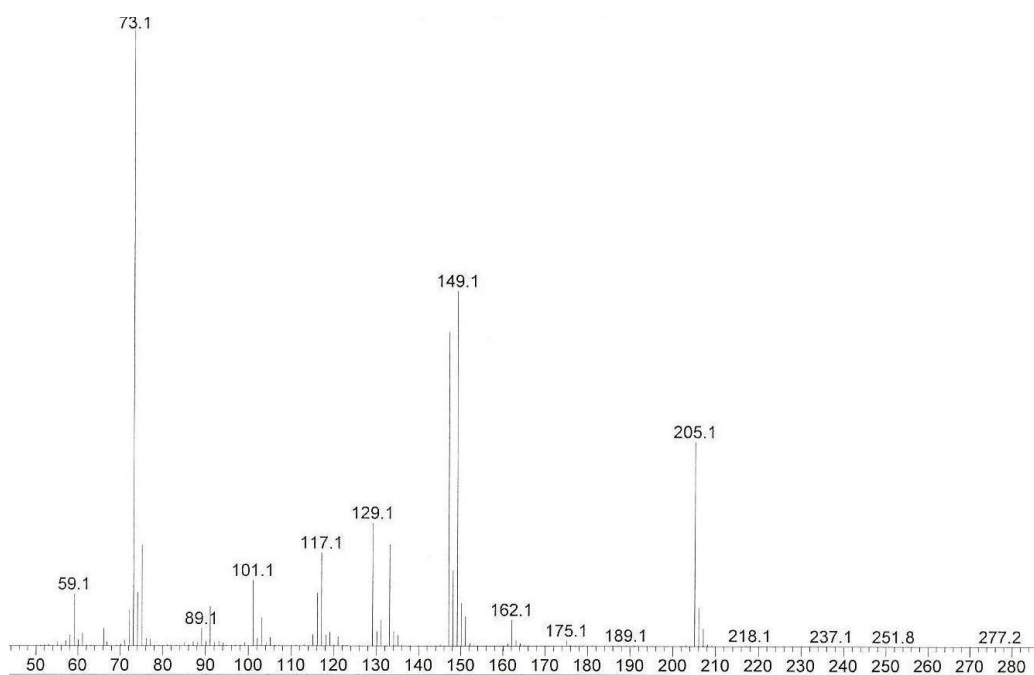


Figure SI 29. Mass Spectrum (DCM) compound **7**.

Cyclization Study of **6**.

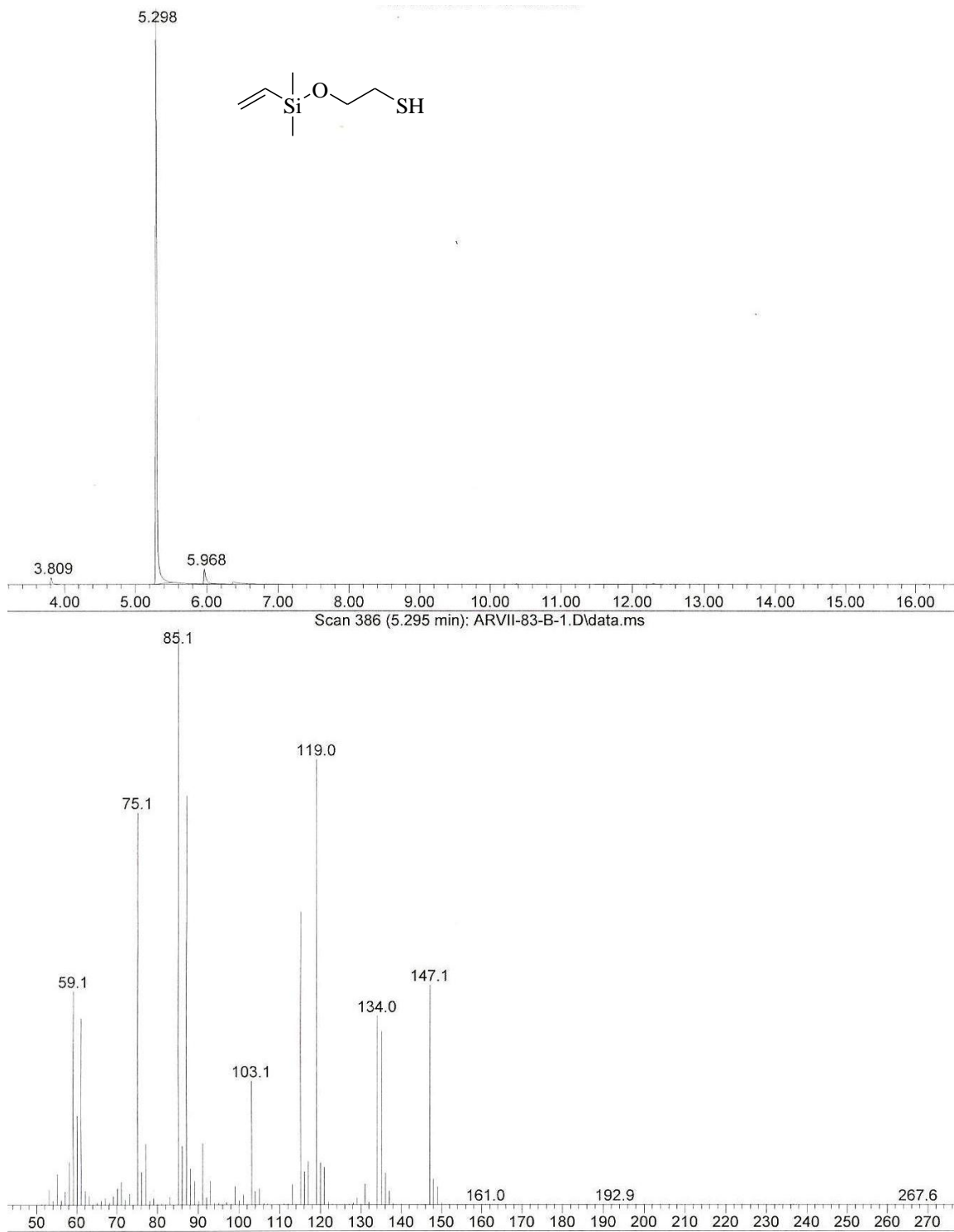


Figure SI 30. GS-MS of **6** (DCM), $t = 0$ h.

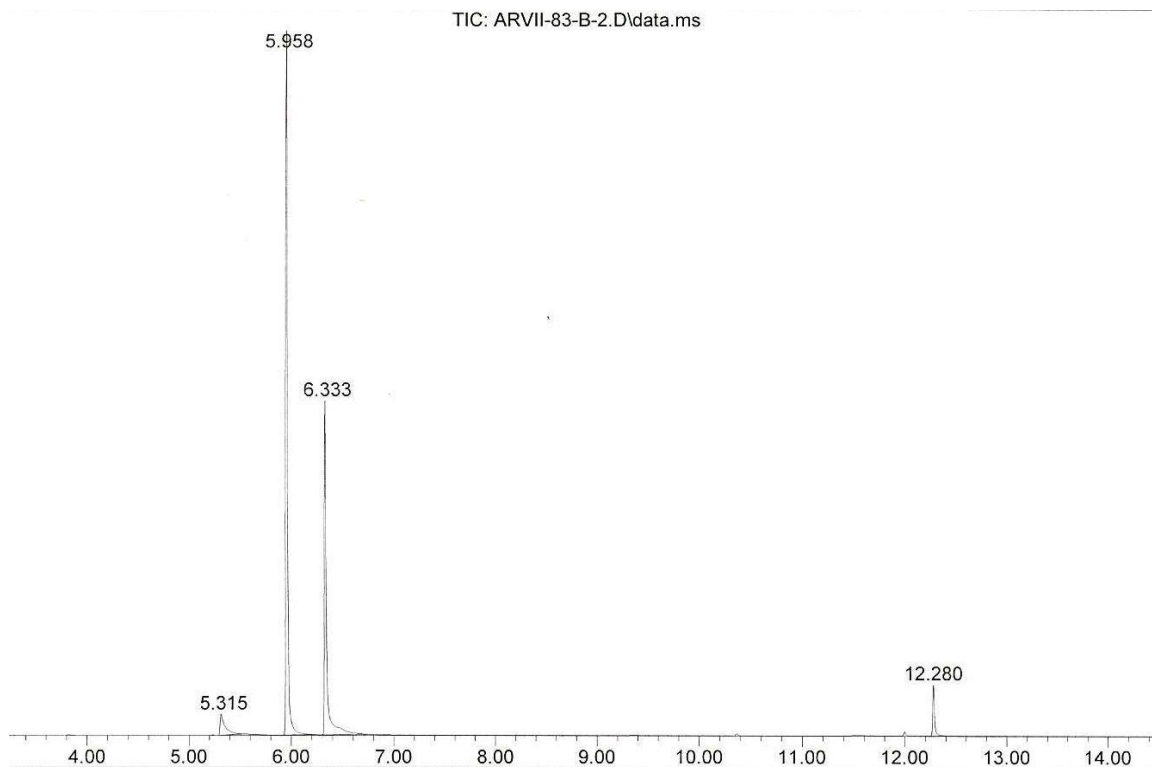


Figure SI 31. GC of **6** (DCM), $t = 1$ h.

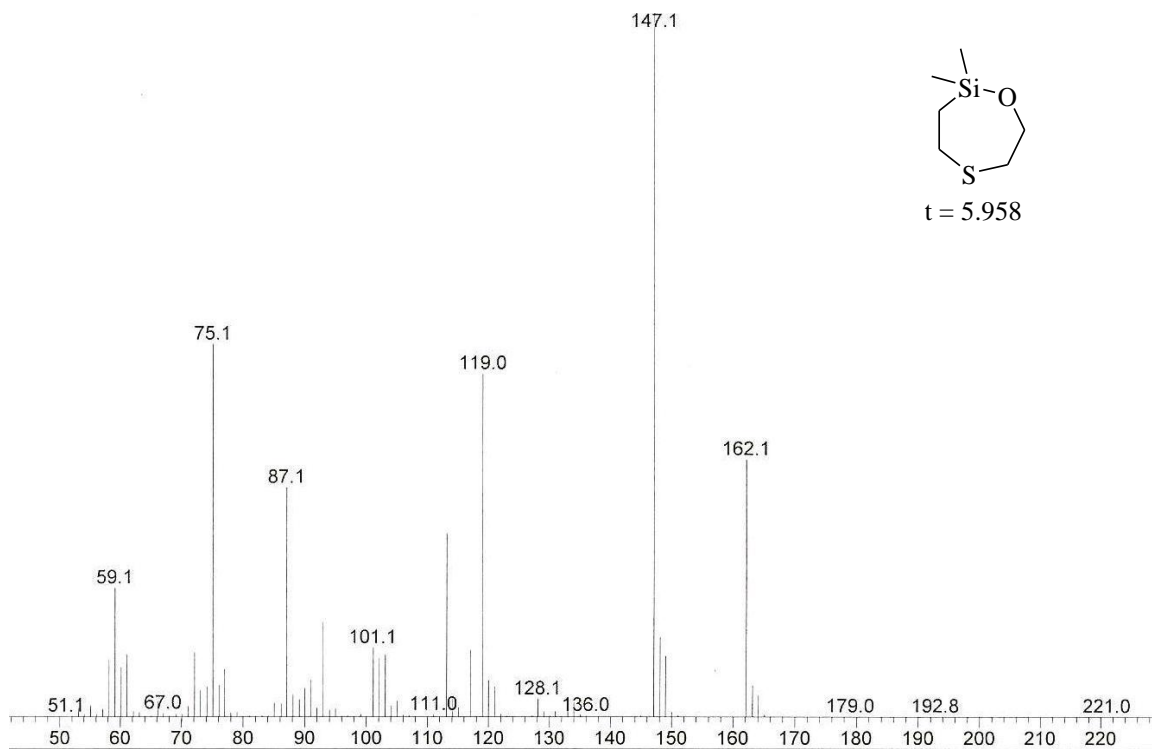


Figure SI 32. Mass Spectrum of cyclized product, retention time = 5.958 min.

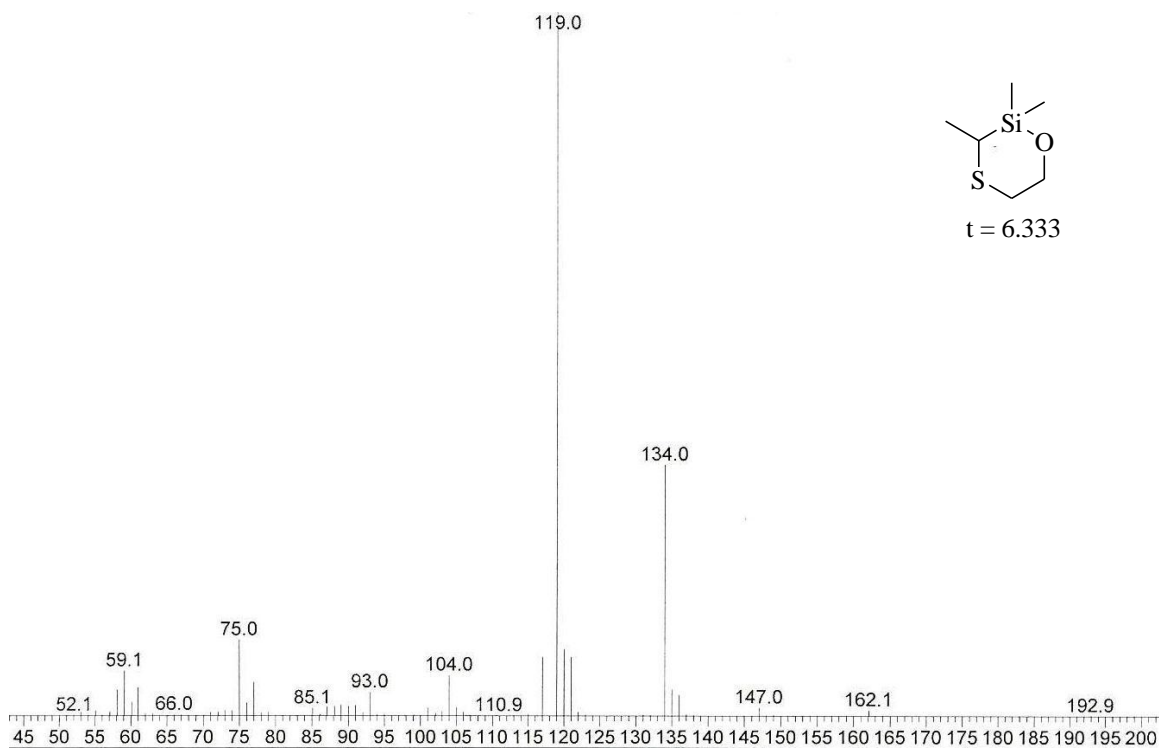


Figure SI 33. Mass Spectrum of cyclized product, retention time = 6.333 min.

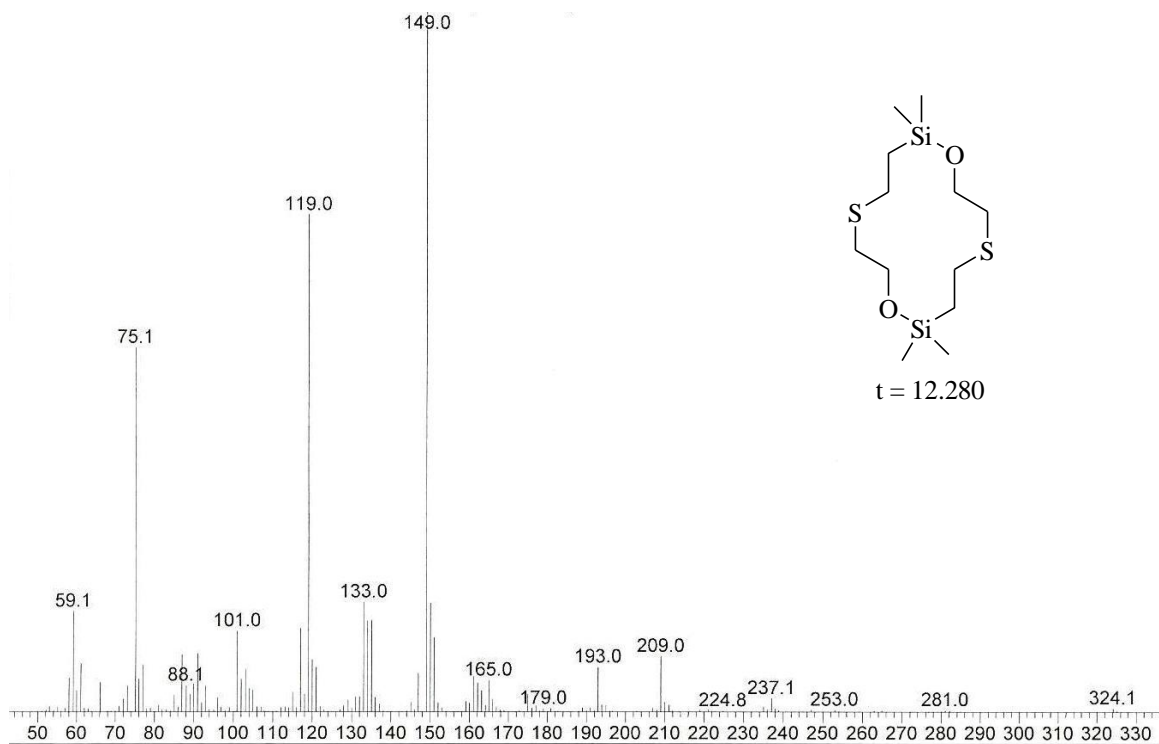


Figure SI 34. Mass Spectrum of cyclized product, retention time = 12.280 min.

Stability Study of **2**.

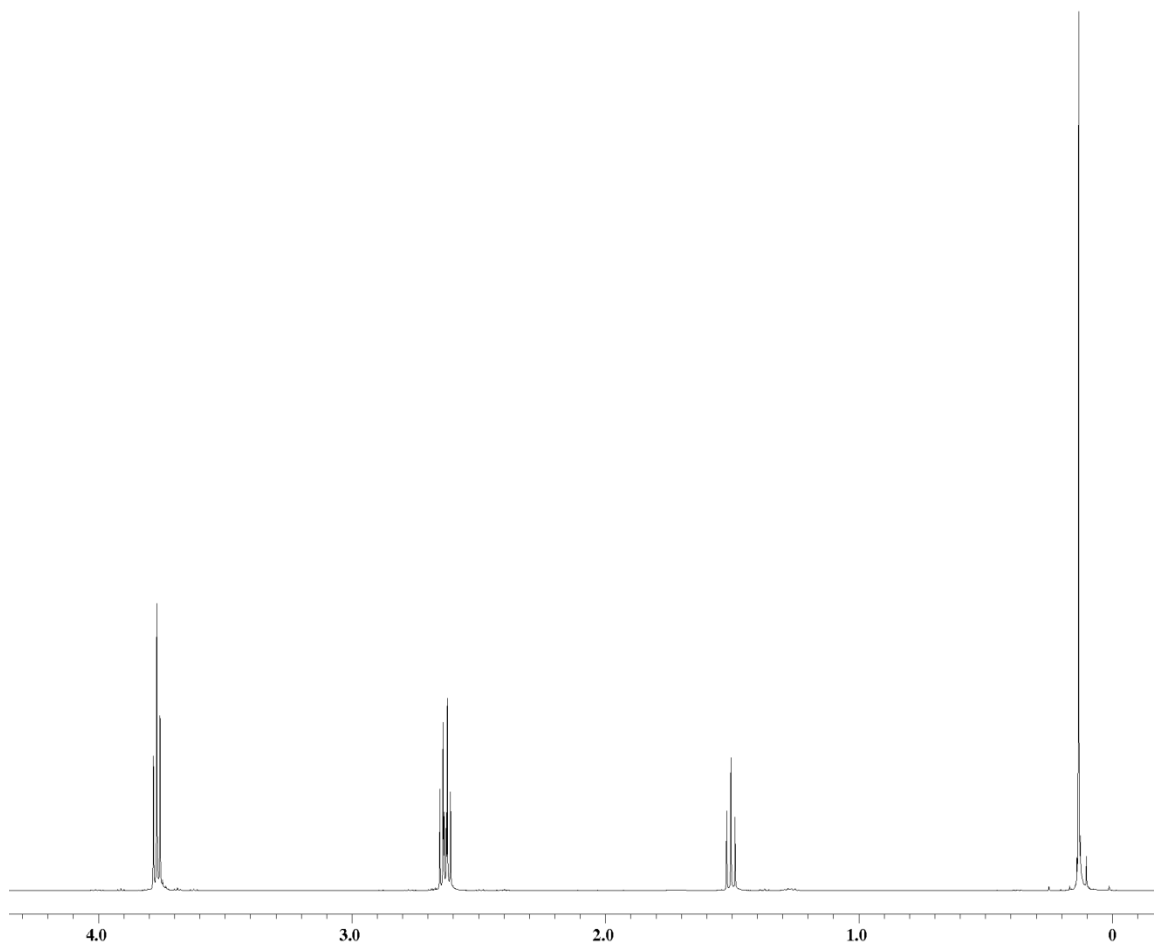


Figure SI 35. ¹H NMR (500 MHz, CDCl₃) compound **2**, t = 0 days.

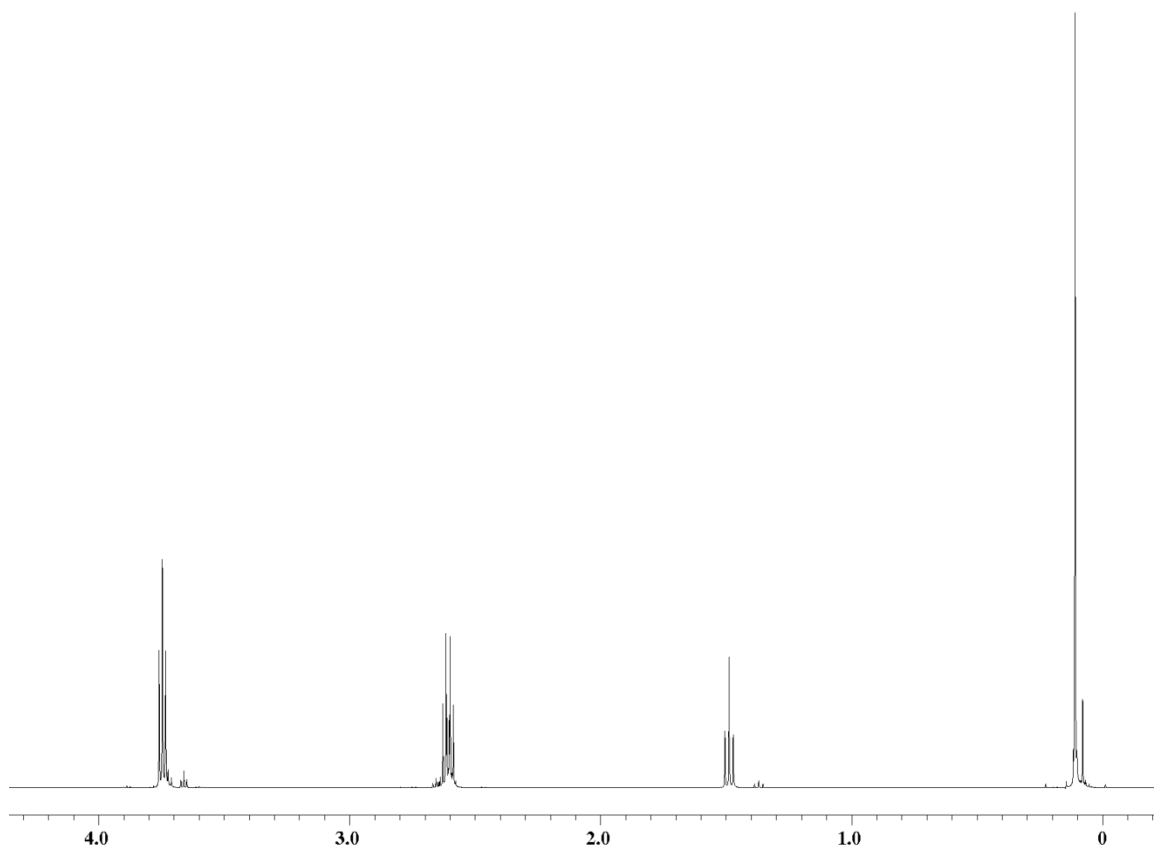


Figure SI 36. ^1H NMR (500 MHz, CDCl_3) compound **2**, $t = 64$ days.

- 1 T. Kniess, H. Spies, I. Santos and A. Zablotska, *J. Labelled Compd. Radiopharm.*, 2002, 45, 629-636.
- 2 D. Seyferth, S. Castellano and J. S. Waugh, *Gazz. Chim. Ital.*, 1958, 88, 1267-1271.
- 3 D. Seyferth, D. Y. Son, A. L. Rheingold and R. L. Ostrander, *Organometallics*, 1994, 13, 2682-2690.