Reductive Haloyclosilazane Polymerization

Supporting Information

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1. Supplemental Figures and Tables

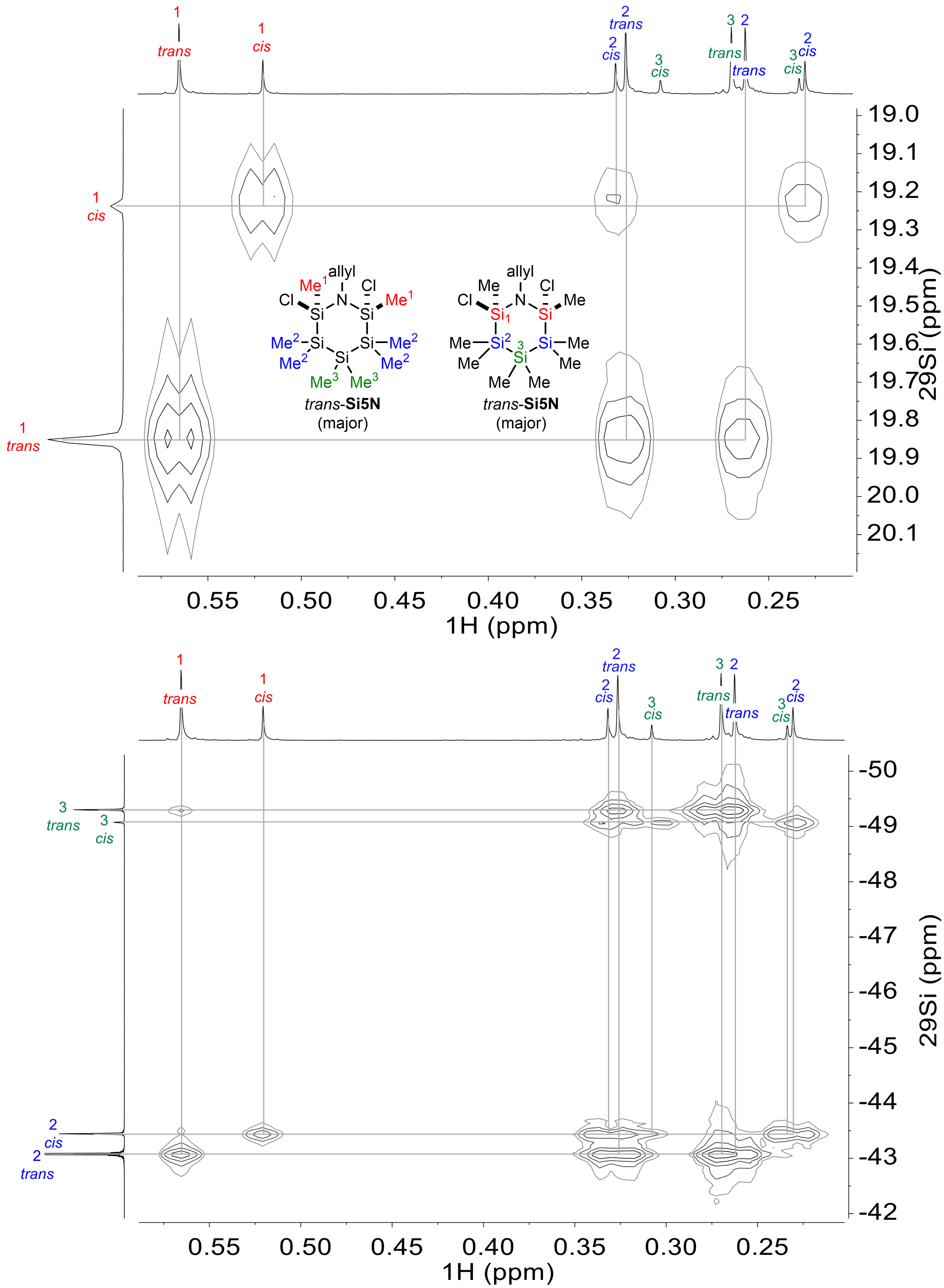


Figure S1. Cropped ^{1}H-^{29}Si HMBC spectra of **Si5N** (400 MHz, $CDCl_3$).

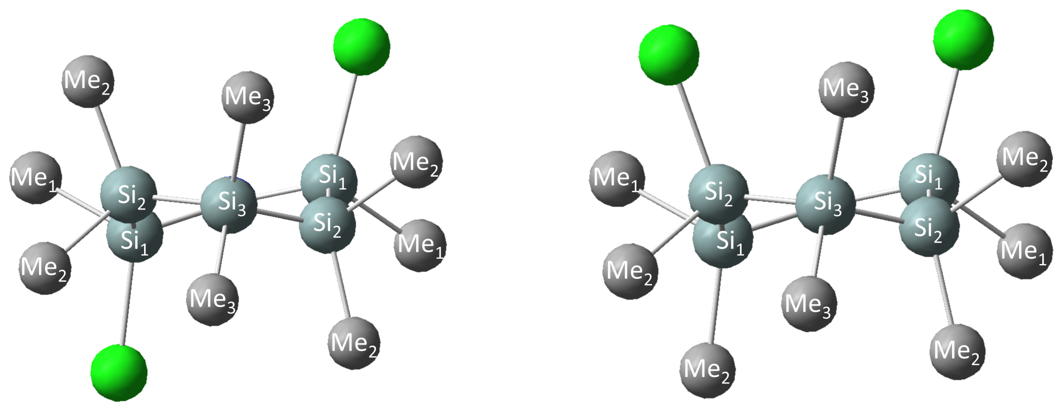


Figure S2. Twist-boat configurations for *trans*- and *cis*-**Si5N** looking through Si_3-N axis drawn in GaussView to help visualize the C_2 axis in *trans*-**Si5N**. Hydrogens and allyl group omitted for clarity. Teal = Si, grey = C, green = Cl.

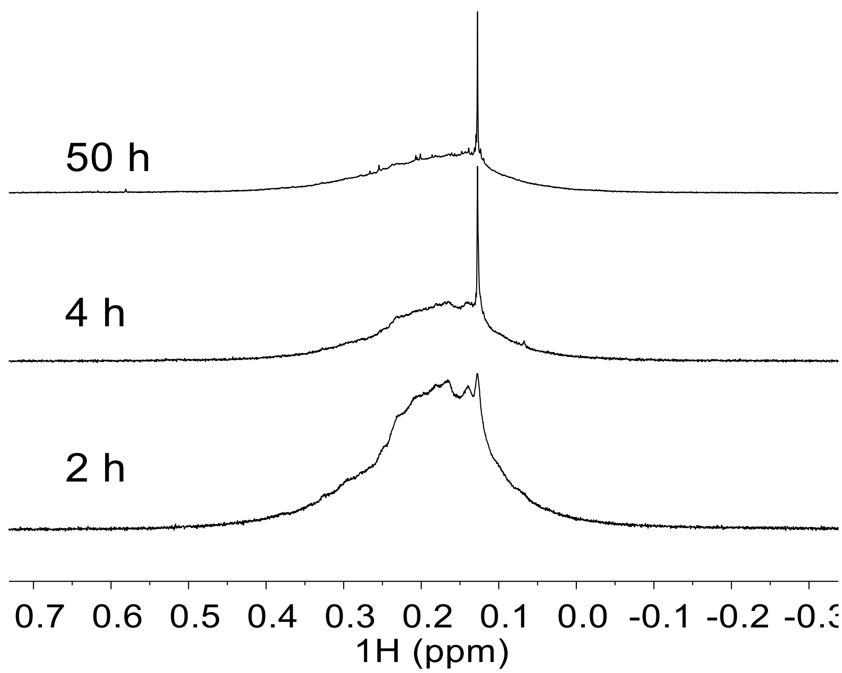


Figure S3. Stacked ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of poly(**Si5N**) from Table 2 entries 2 (2 h), 3 (4 h), and 4 (50 h).

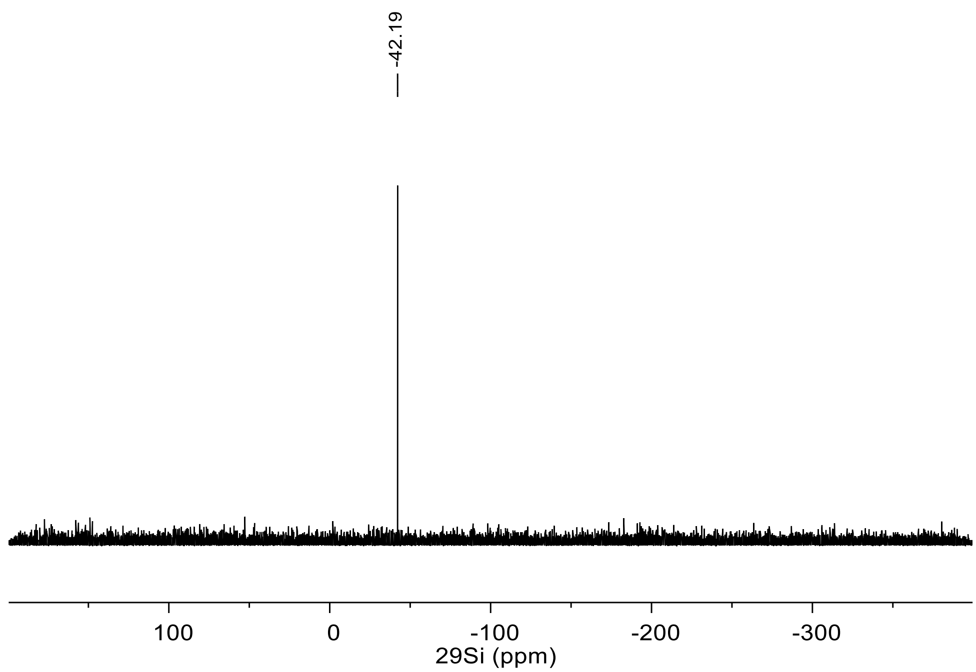


Figure S4. $^{29}Si\{^1H\}$ DEPT NMR spectrum of poly(**Si5N**) from Table 2, entry 5.

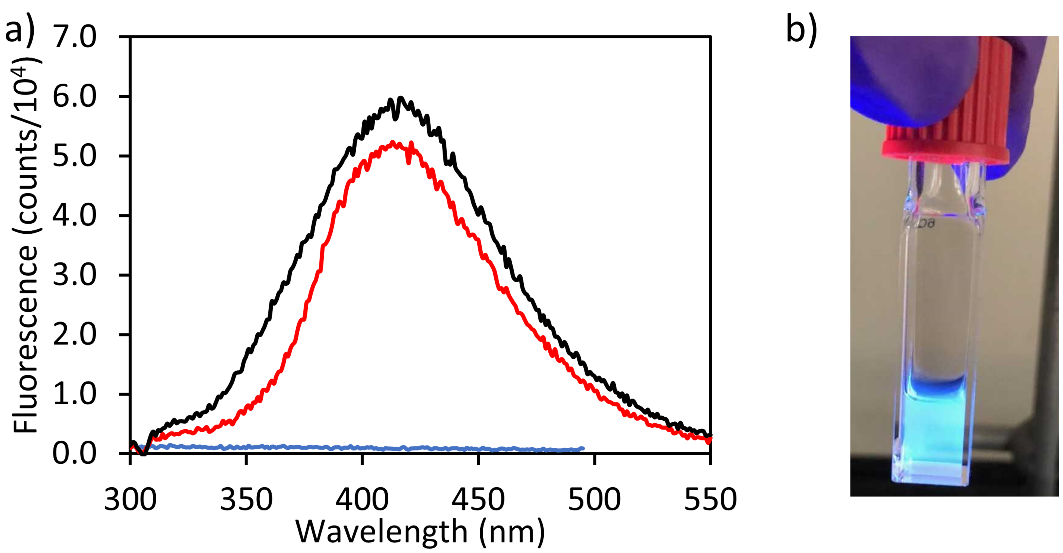


Figure S5. a) Emission spectra of **Si5N** (blue), **P1** (red), and **P2** (black) in THF. **Si5N** excitation wavelength = 250 nm. **P1** and **P2** excitation wavelength = 280 nm. [**Si5N**] = 1.25x10^{-5} M, [polymer = 0.0124 g/L. b) **P2** blue emission in THF; concentration of pictured sample = 0.1 g/L in THF.

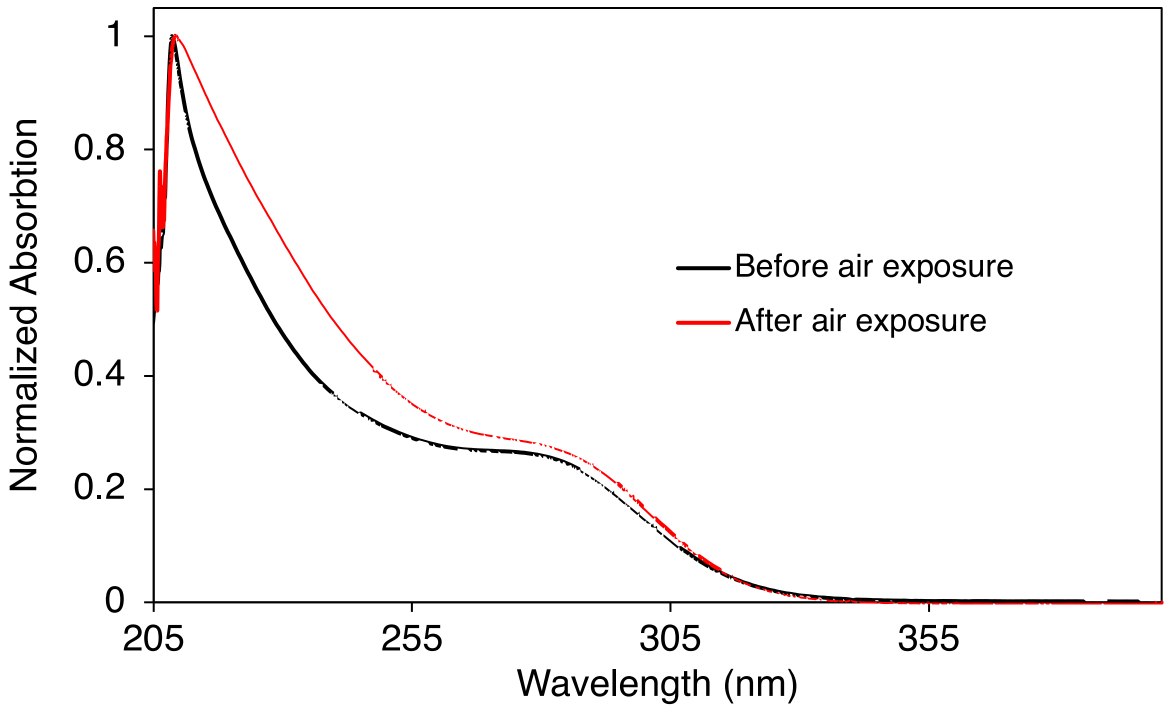


Figure S6. UV-Vis absorption spectrum of **P2** before and after exposure to air for one day. Concentrations were 0.0124 g/L in THF for each sample.

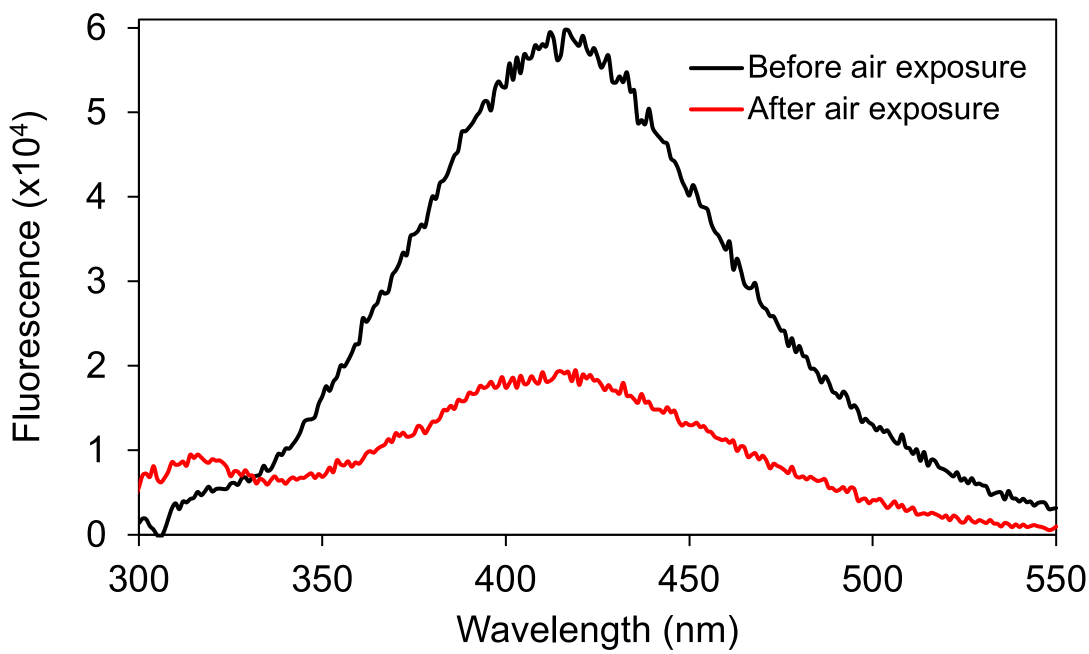


Figure S7. Emission spectra of **P2** before (black) and after (red) exposing to air for one day. Excitation wavelength = 280 nm. Concentrations were 0.0124 g/L in THF for each sample.

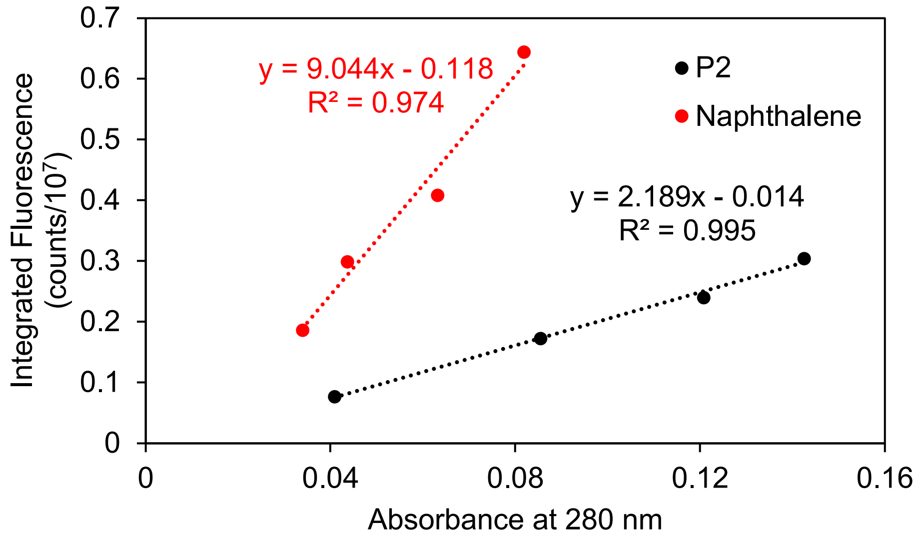


Figure S8. Linear fits to determine the fluorescence quantum yield for **P2** in THF relative to a naphthalene standard in cyclohexane.

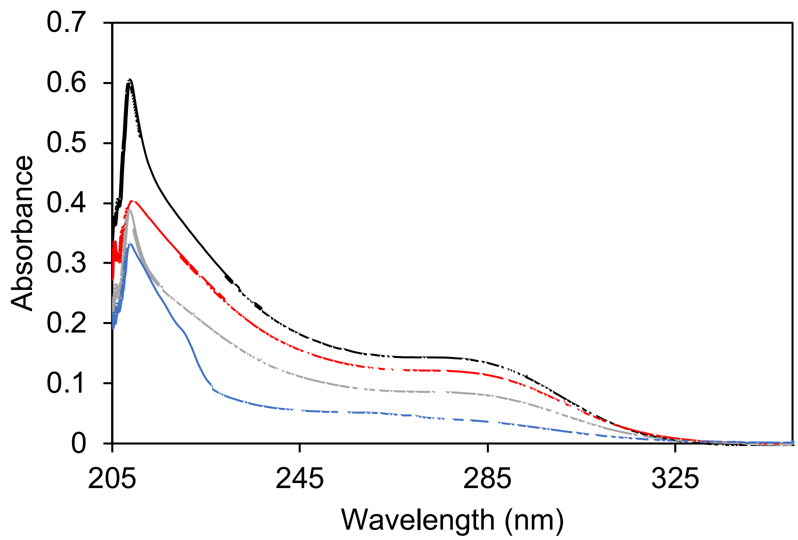


Figure S9. Absorption spectra of **P2** in THF (black = 6.20x10^{-3} g/L, red = 7.43x10^{-3} g/L, grey = 4.96x10^{-3} g/L, blue = 1.24x10^{-3} g/L) used to obtain the linear fit in Figure S7.

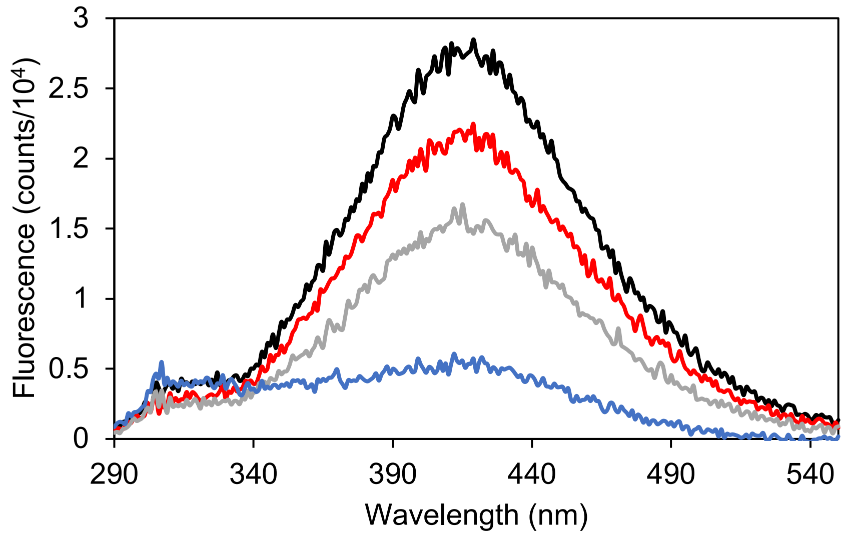


Figure S10. Emission spectra of **P2** in THF excited at 280 nm (black = 6.20x10^{-3} g/L, red = 7.43x10^{-3} g/L, grey = 4.96x10^{-3} g/L, blue = 1.24x10^{-3} g/L) used to obtain the linear fit in Figure S7.

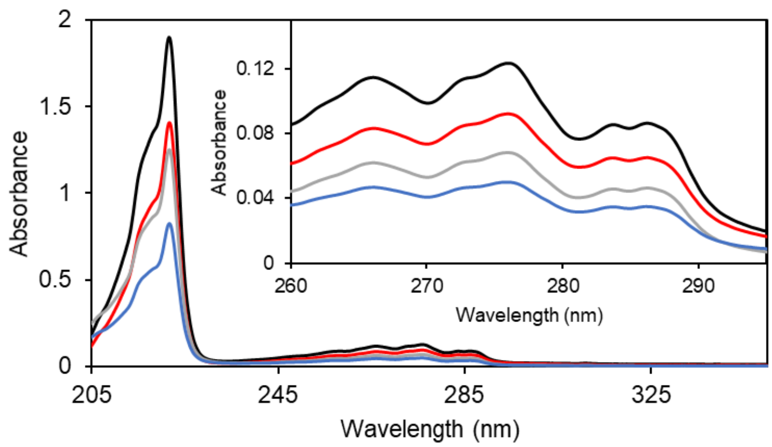


Figure S11. Absorption spectra of naphthalene in cyclohexane (black = 1.72x10^{-5} M, red = 1.17x10 M, grey = 1.01x10^{-5} M, blue 6.24x10^{-6} M) used to obtain the linear fit in Figure S7.

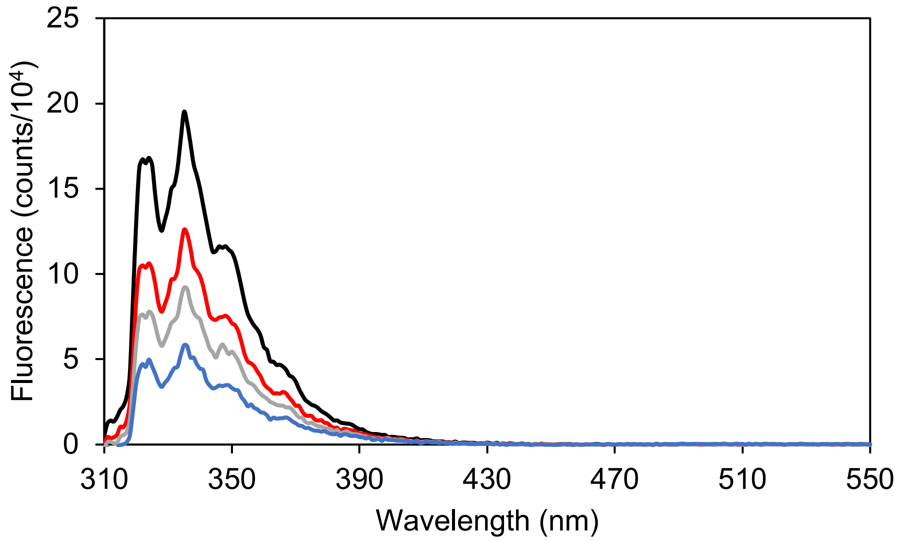


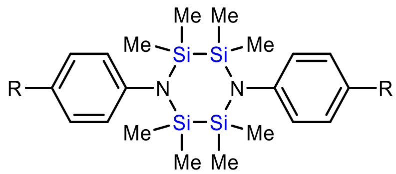
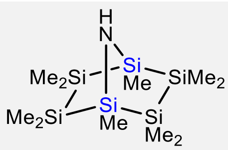
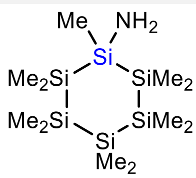
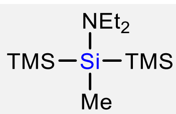
Figure S12. Emission spectra of naphthalene excited at 280 nm in cyclohexane (black = 1.72×10^{-5} M, red = 1.17x10 M, grey = 1.01×10^{-5} M, blue 6.24×10^{-6} M) used to obtain the linear fit in Figure S7.

Table S1. Symmetry elements of *cis*- and *trans*-**Si5N** in boat and twist-boat conformations.

Compound	Boat symmetry elements[a]	Twist-boat symmetry elements[a]
trans-**Si5N**	None	C_2
cis-**Si5N**	σ	none

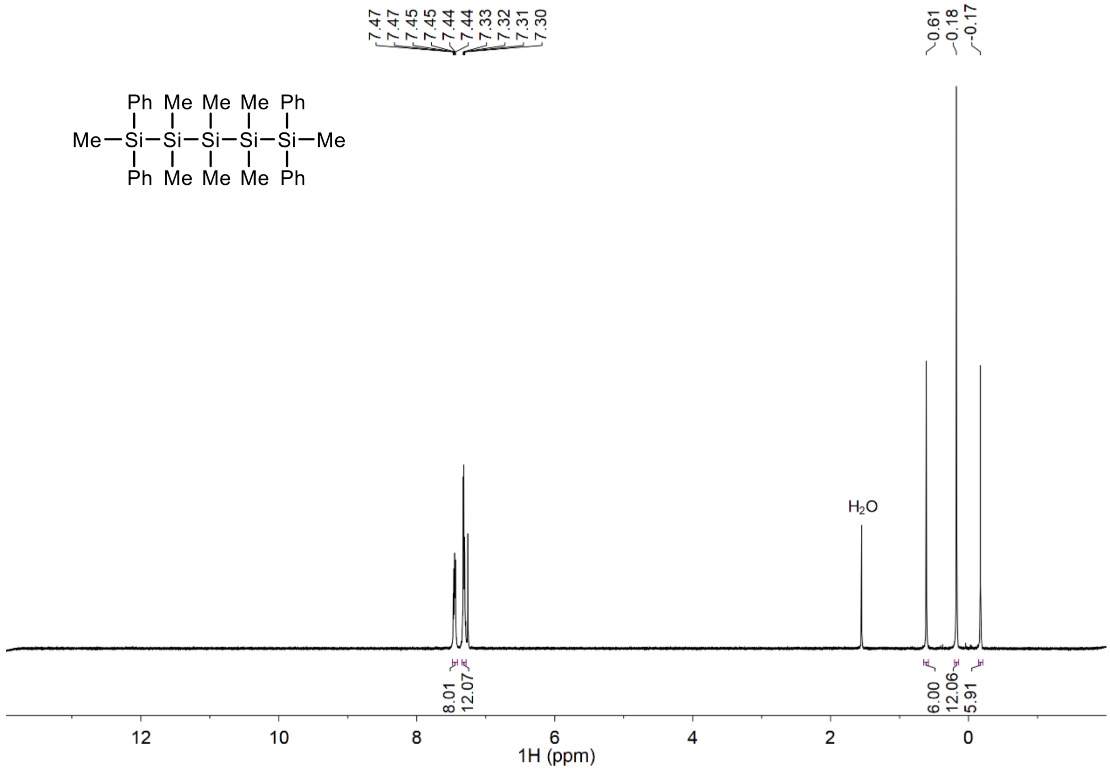
[a] Identity not included.

Table S2. ^{29}Si NMR *Si*-N resonances of relevant compounds from the literature. Selected *Si* resonance is highlighted in blue.

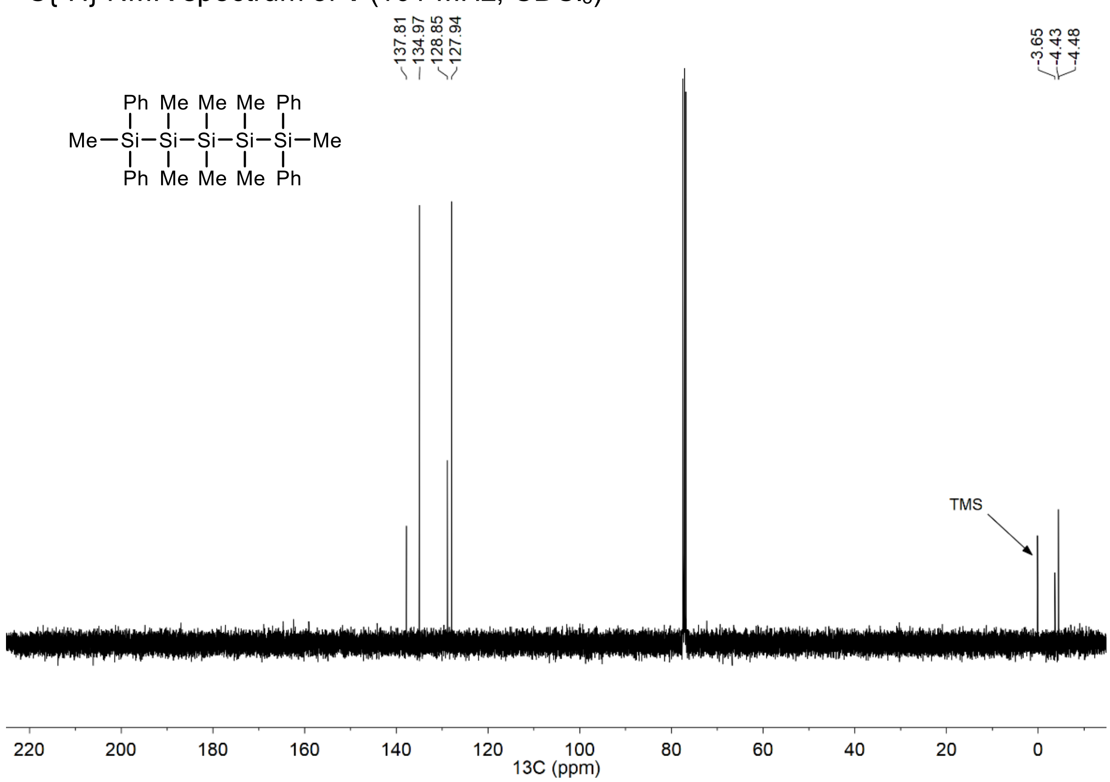
Compound	*Si*-N resonance (ppm)	Solvent[ref]
	-5.0 to -6.8	$CDCl_3$[1]
	-9.5	C_6D_6[2]
	-15.3	C_6D_6[2]
	-13.4	$CDCl_3$[3]

2. NMR Spectra

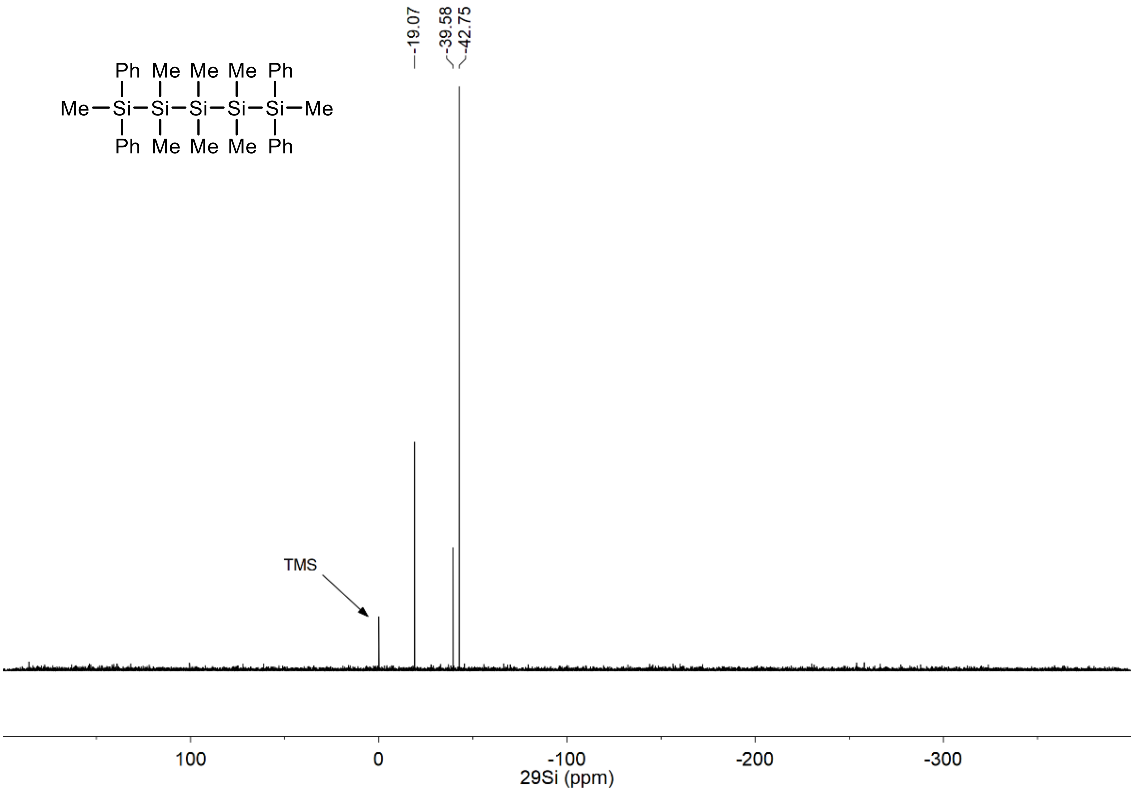
^{1}H NMR spectrum of **1** (300 MHz, $CDCl_3$)



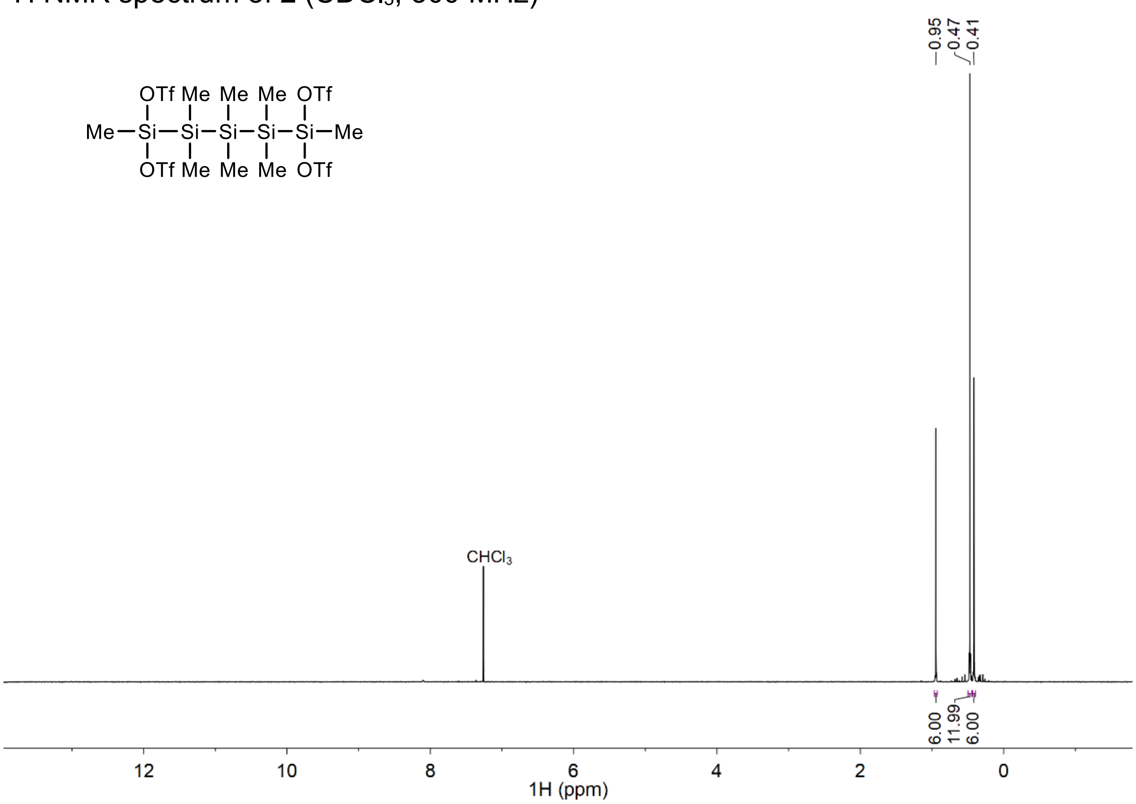
$^{13}C\{^{1}H\}$ NMR spectrum of **1** (101 MHz, $CDCl_3$)



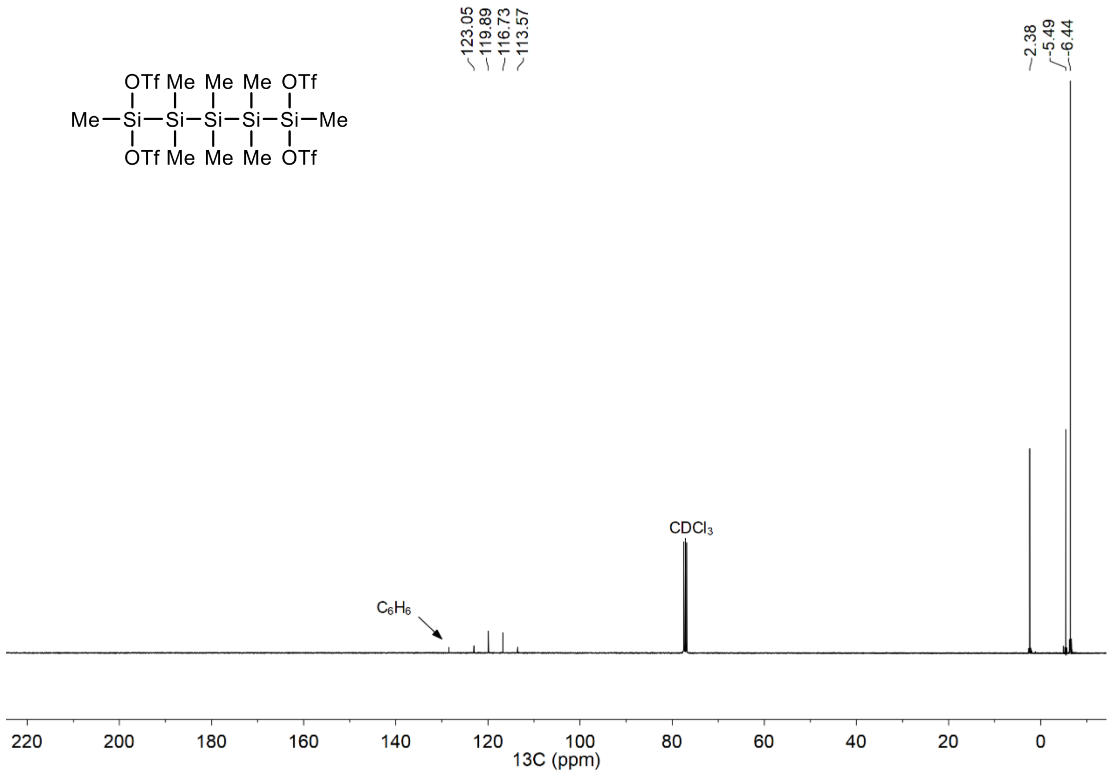
$^{29}Si\{^{1}H\}$ DEPT NMR spectrum of **1** (79 MHz, $CDCl_3$)



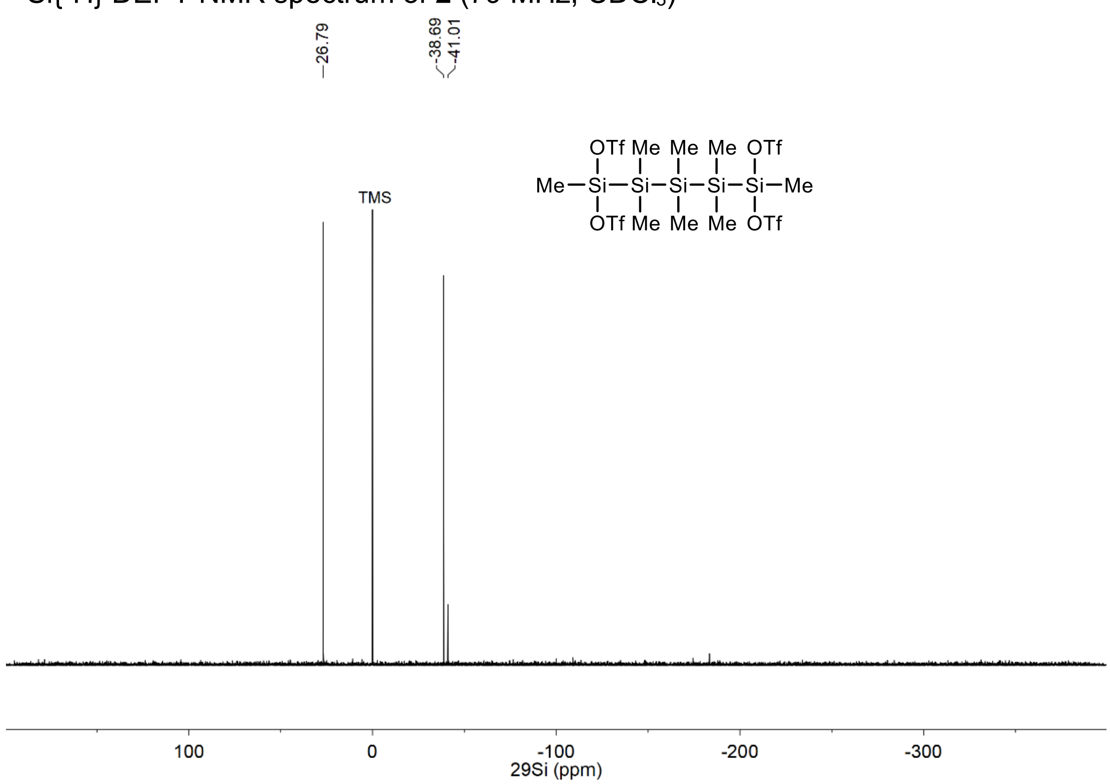
^{1}H NMR spectrum of **2** ($CDCl_3$, 300 MHz)



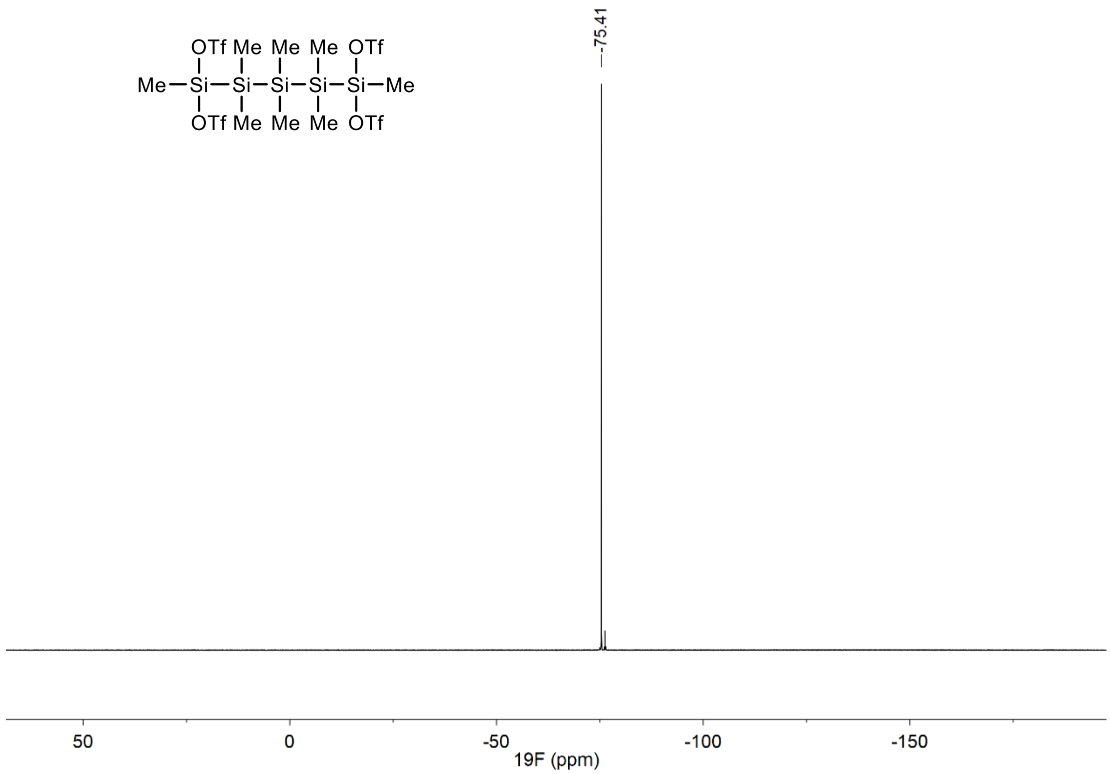
$^{13}C\{^1H\}$ NMR spectrum of **2** (101 MHz, $CDCl_3$)



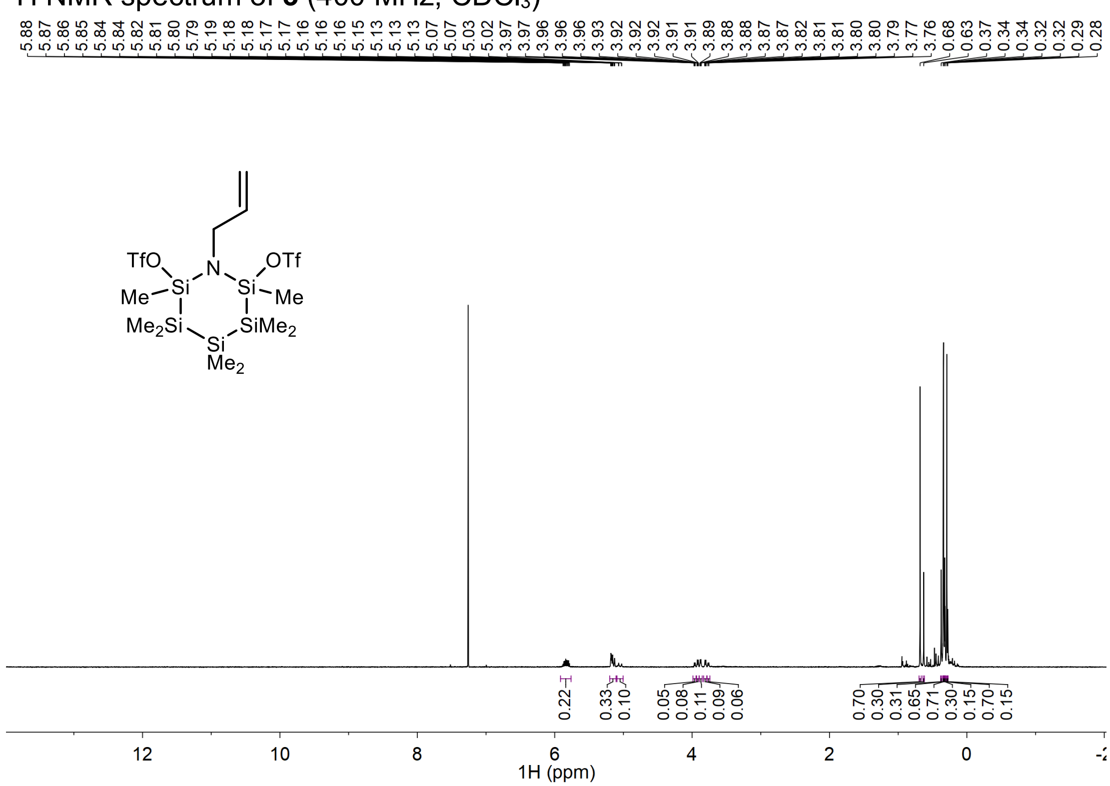
$^{29}Si\{^1H\}$ DEPT NMR spectrum of **2** (79 MHz, $CDCl_3$)



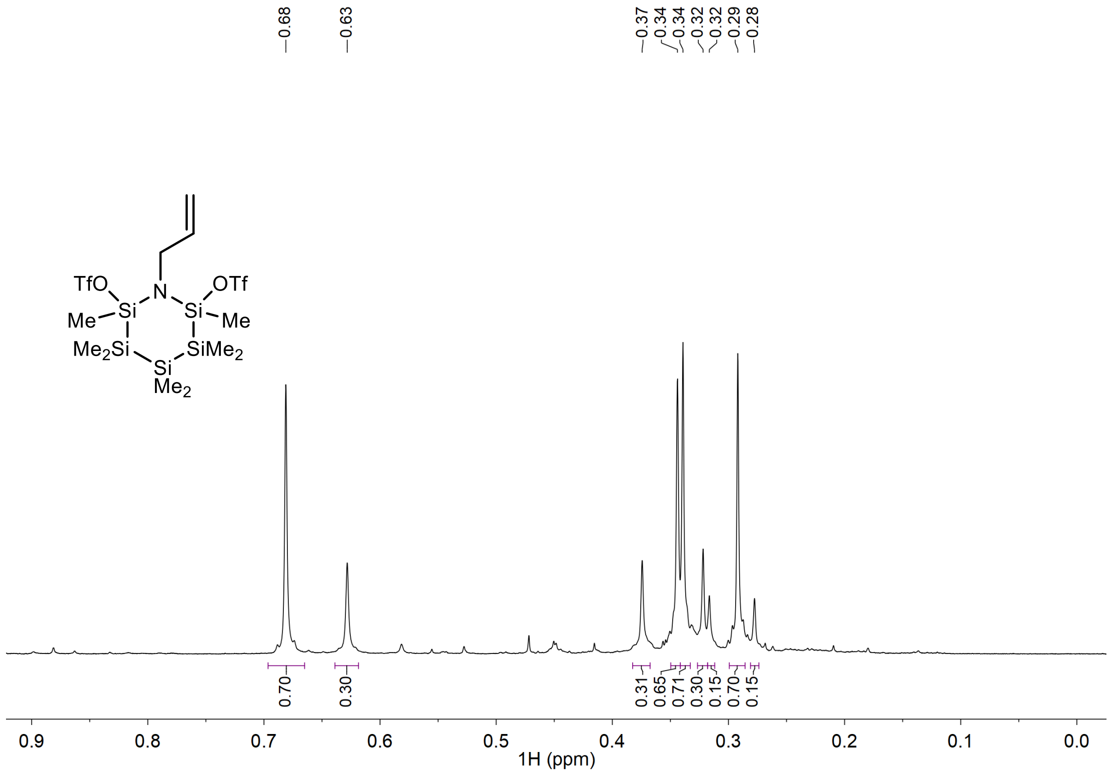
$^{19}F\{^1H\}$ NMR spectrum of **2** (282 MHz, $CDCl_3$)



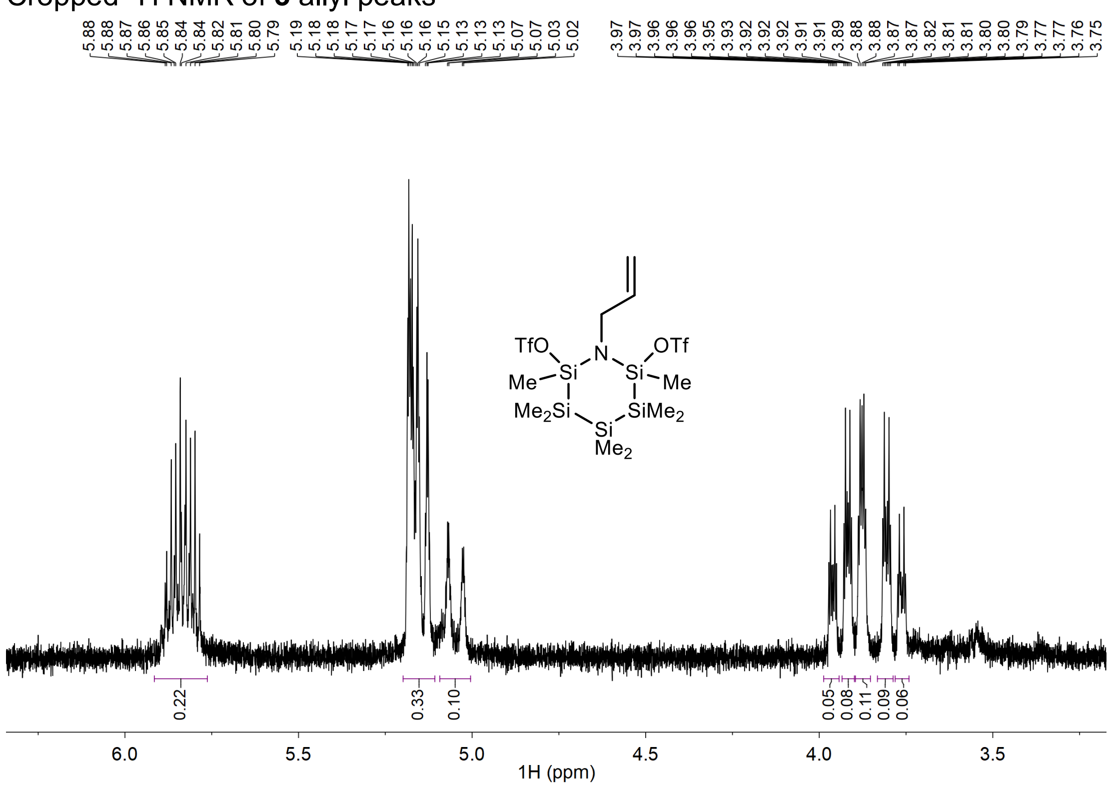
^1H NMR spectrum of **3** (400 MHz, $CDCl_3$)



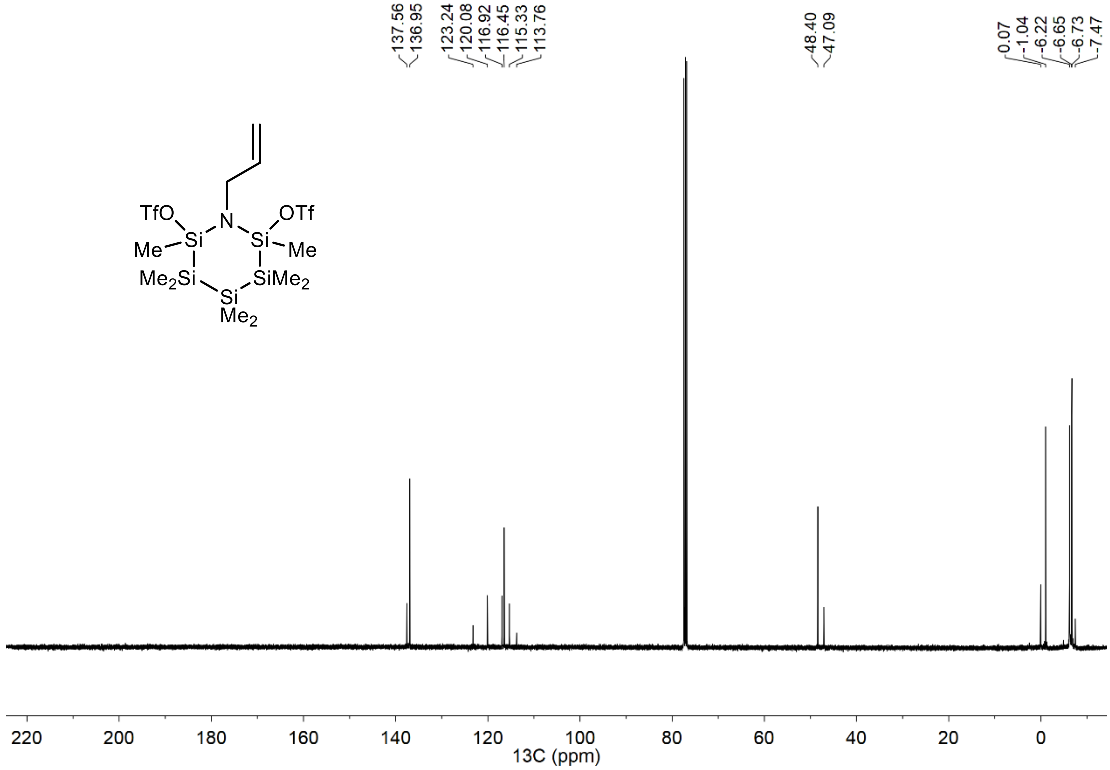
Cropped ^{1}H NMR of **3** alkyl peaks



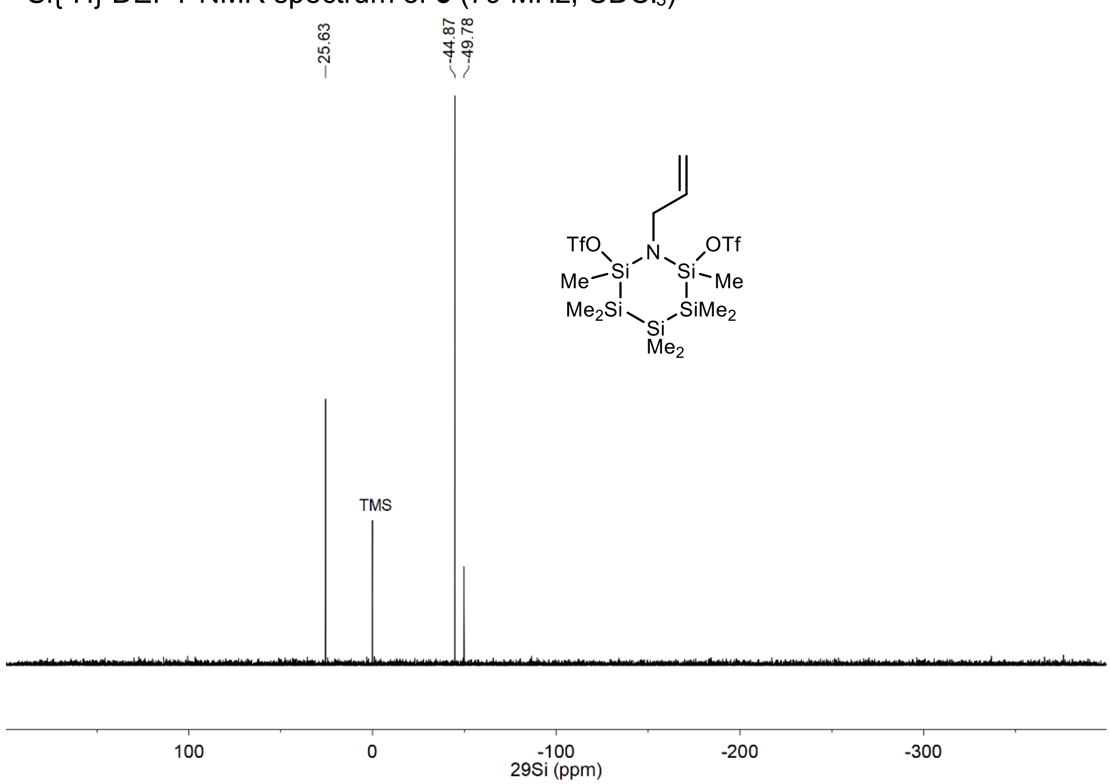
Cropped ^{1}H NMR of **3** allyl peaks



$^{13}C\{^{1}H\}$ NMR spectrum of **3** (101 MHz, $CDCl_3$)

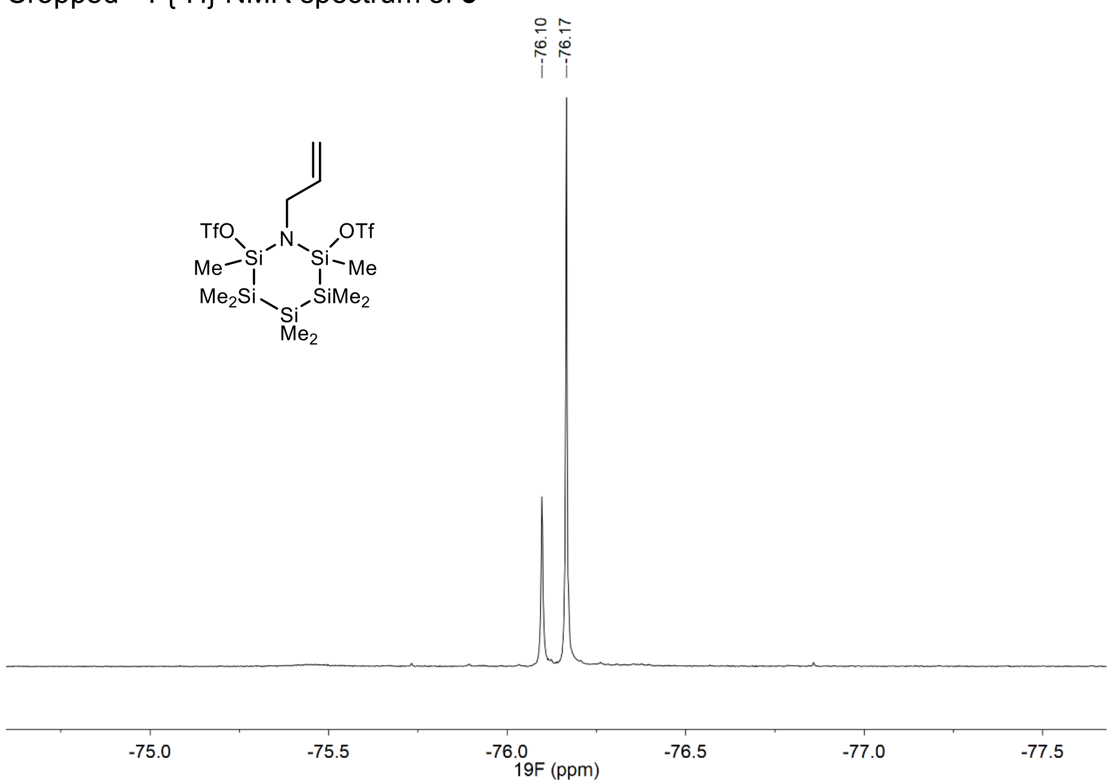


$^{29}Si\{^{1}H\}$ DEPT NMR spectrum of **3** (79 MHz, $CDCl_3$)

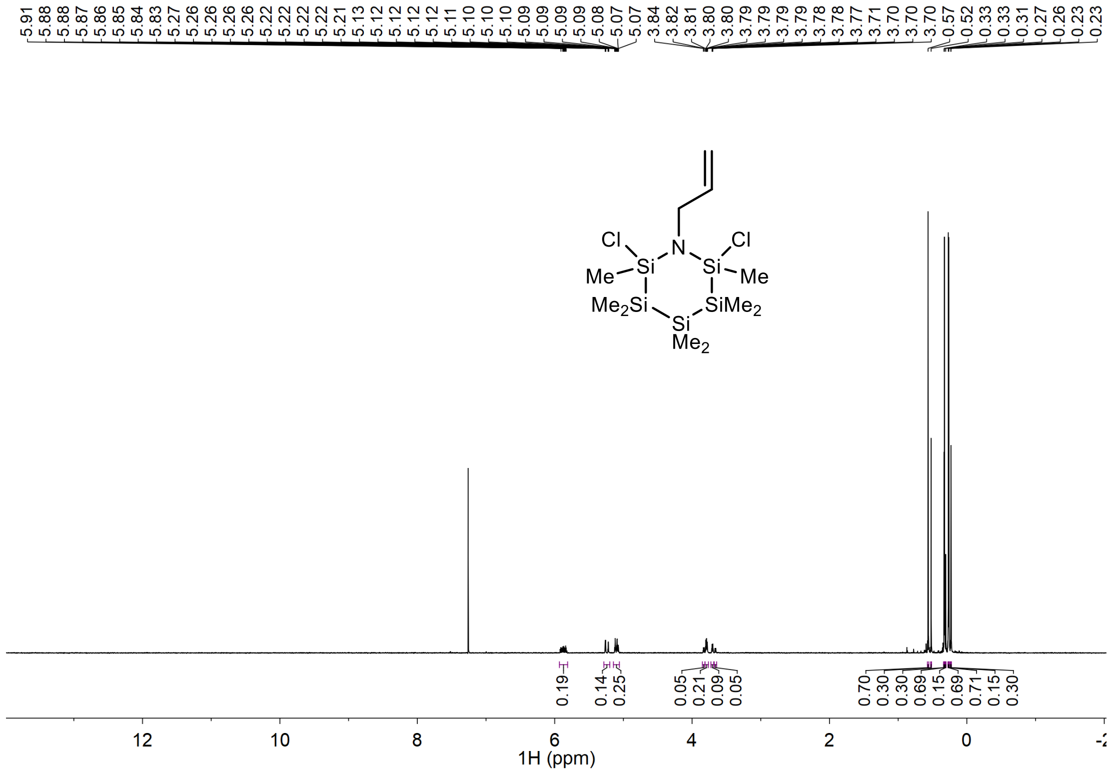


$^{19}F\{^{1}H\}$ NMR spectrum of **3** (282 MHz, $CDCl_3$)

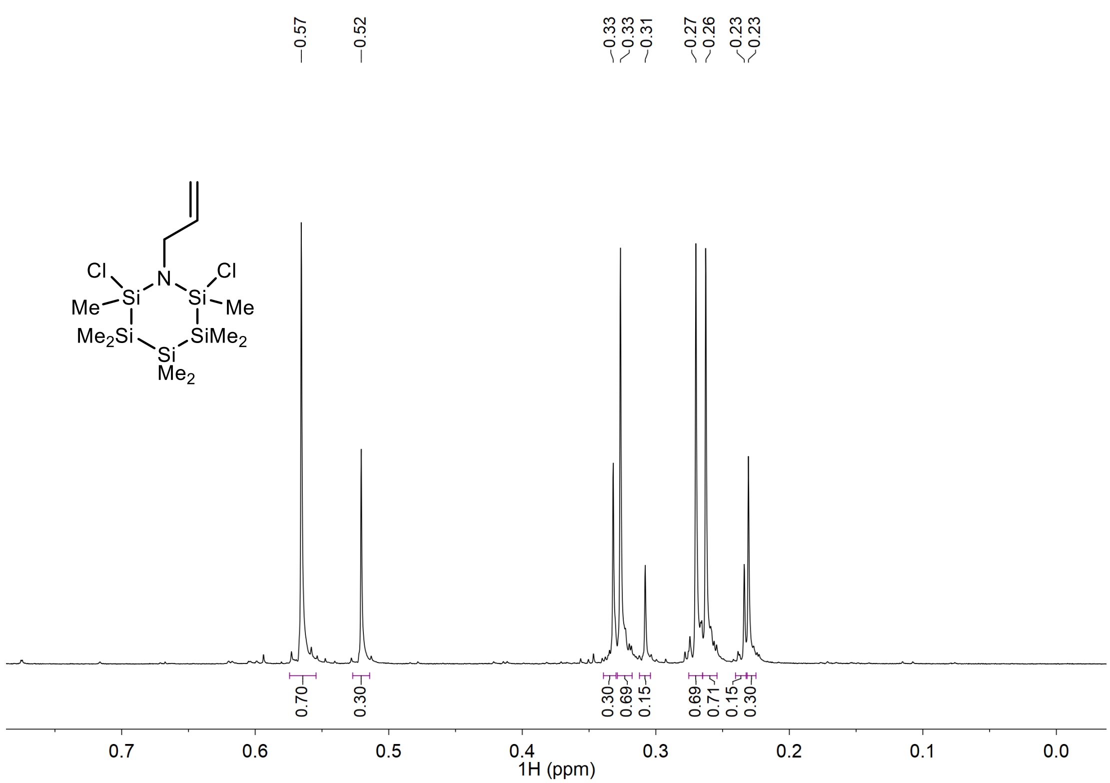
Cropped $^{19}F\{^{1}H\}$ NMR spectrum of **3**



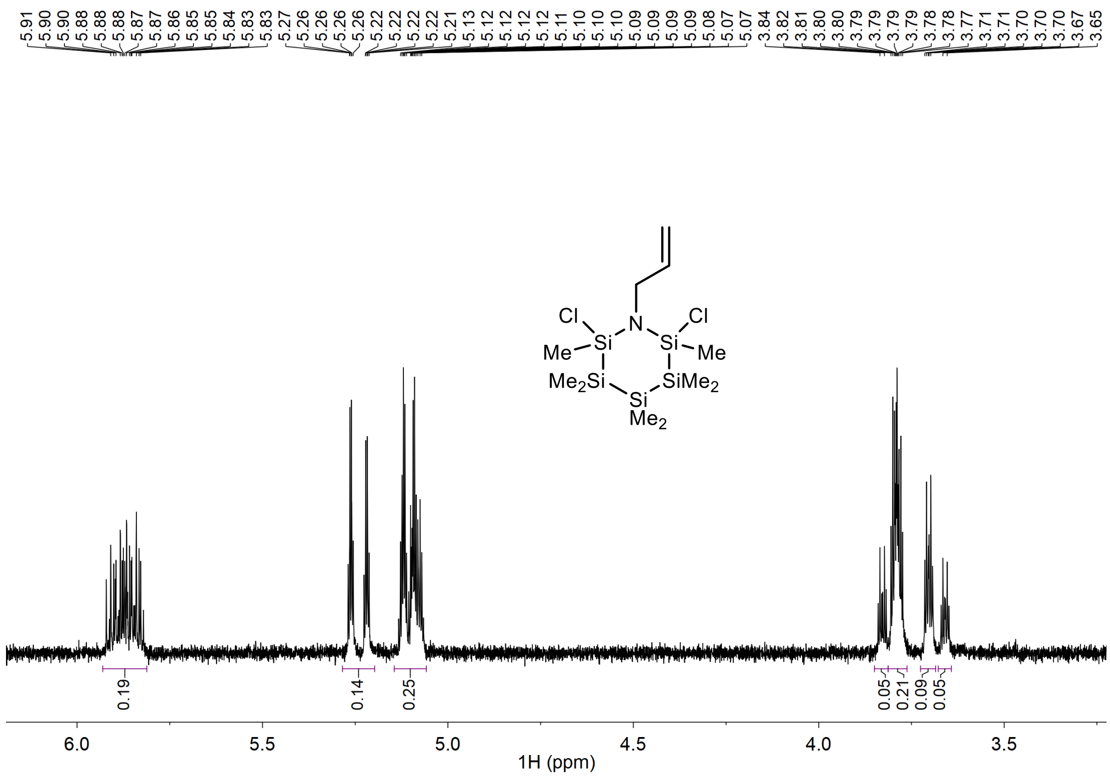
[1]H NMR spectrum of **Si5N** (400 MHz, $CDCl_3$)



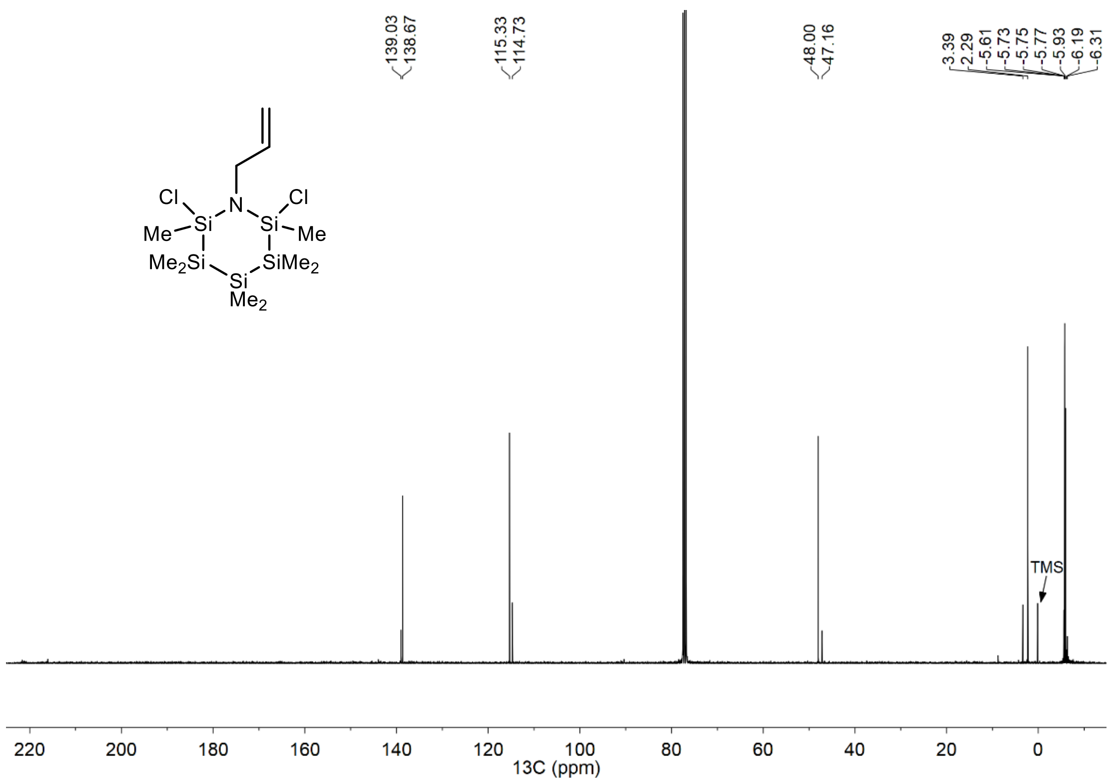
Cropped [1]H NMR of **Si5N** alkyl region



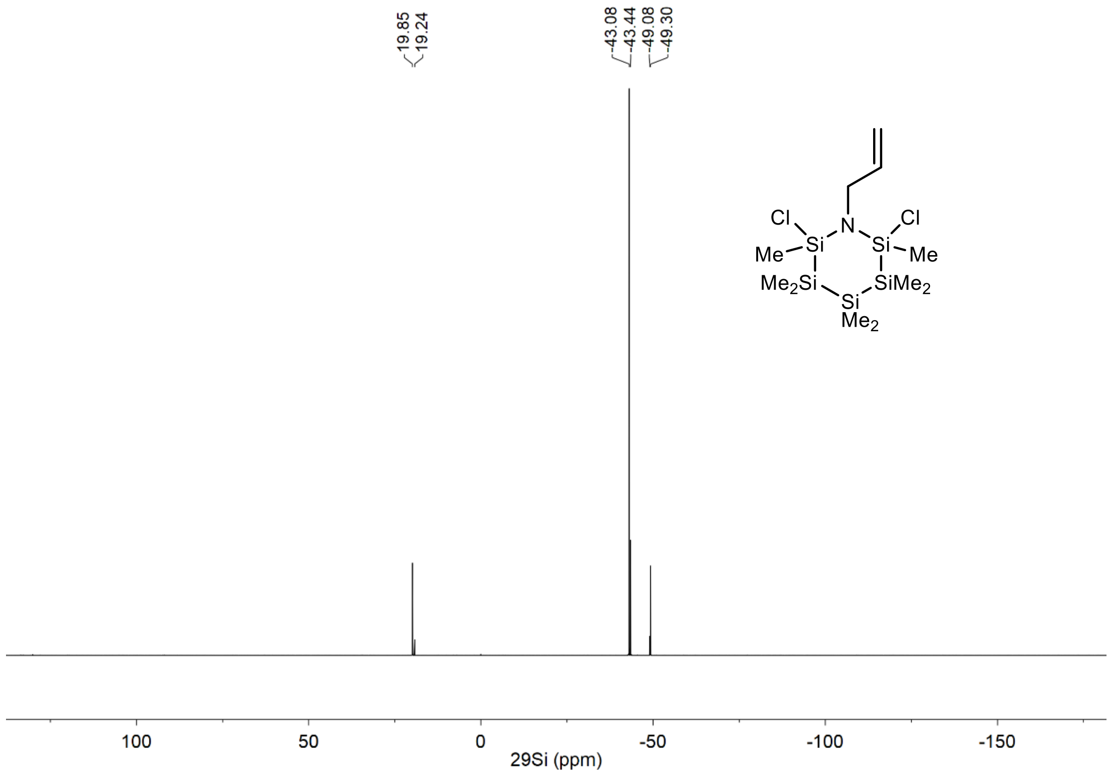
Cropped ^{1}H NMR of **Si5N** allyl region



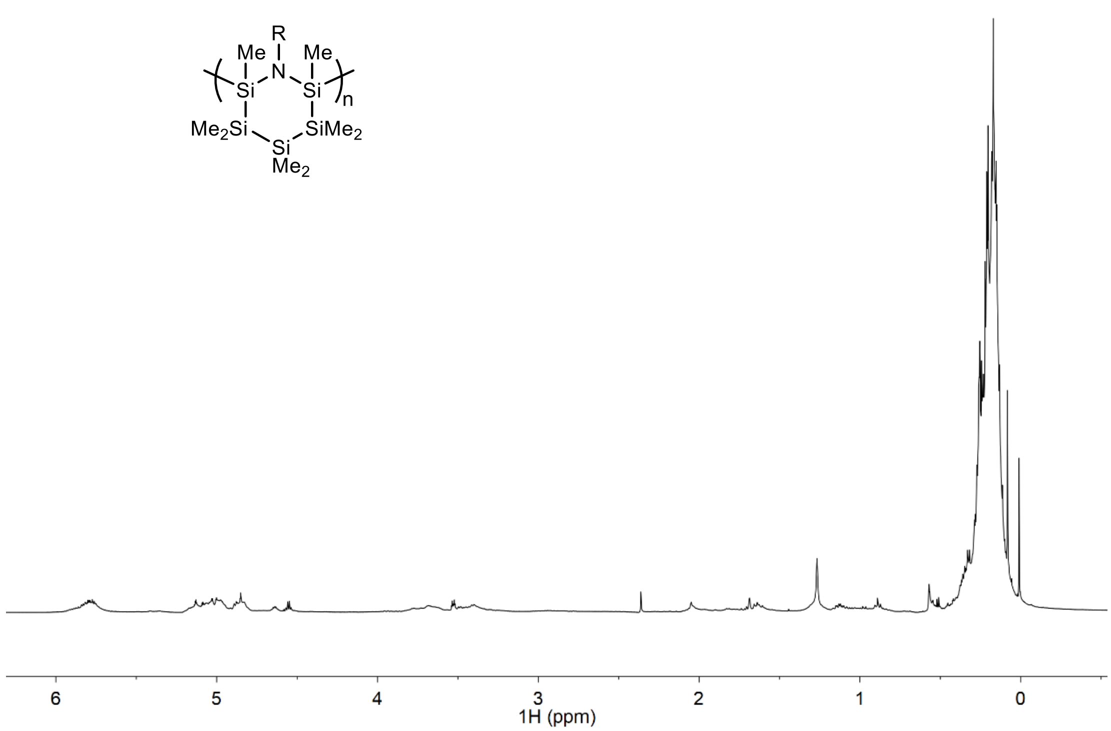
$^{13}C\{^{1}H\}$ NMR spectrum of **Si5N** (101 MHz, $CDCl_3$)



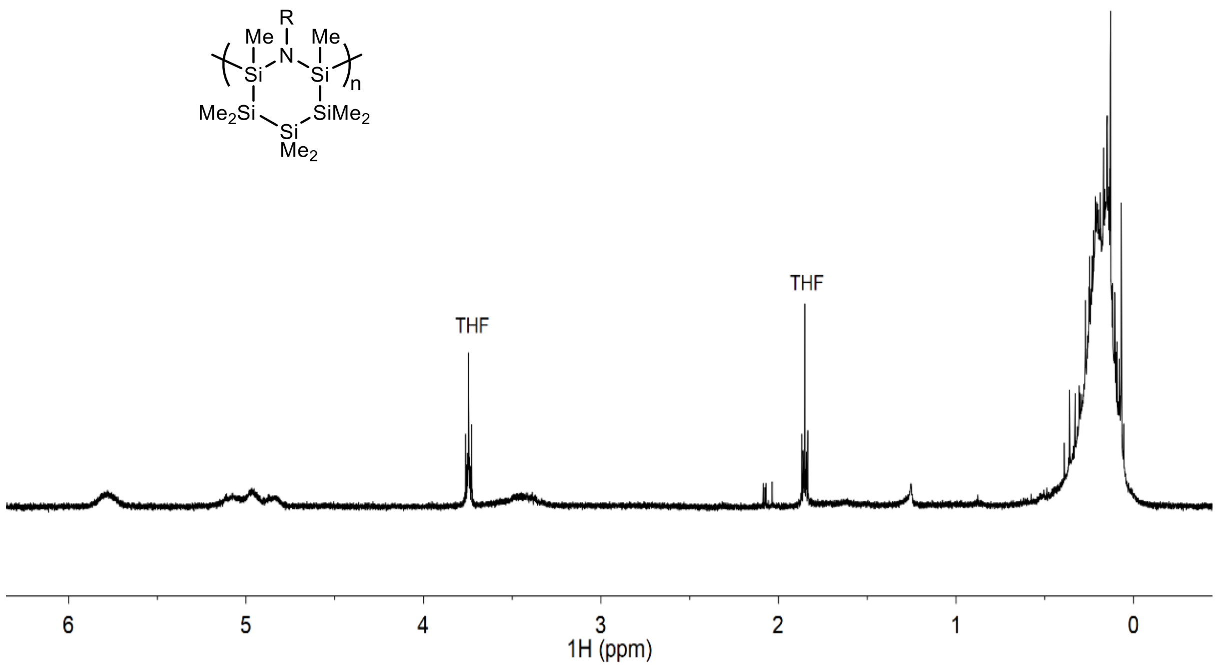
$^{29}Si\{^1H\}$ DEPT NMR spectrum of **Si5N** (79 MHz, $CDCl_3$)



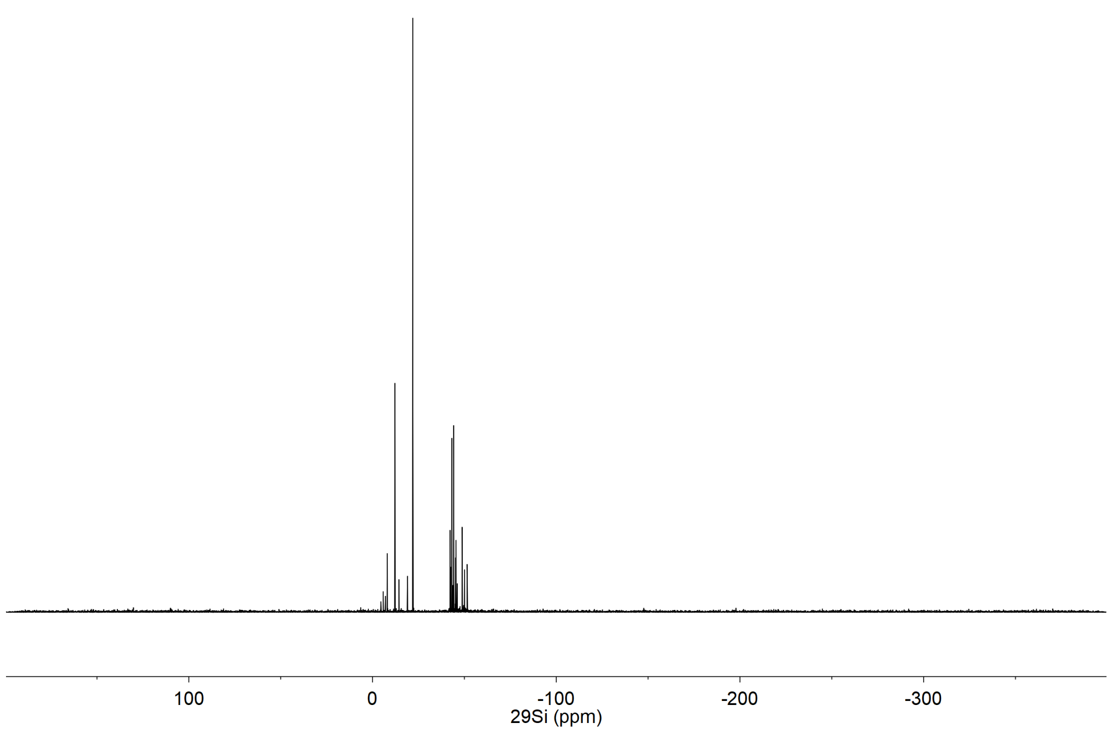
^1H NMR spectrum of poly(**Si5N**) (Table 1, entry 2, 400 MHz, $CDCl_3$)



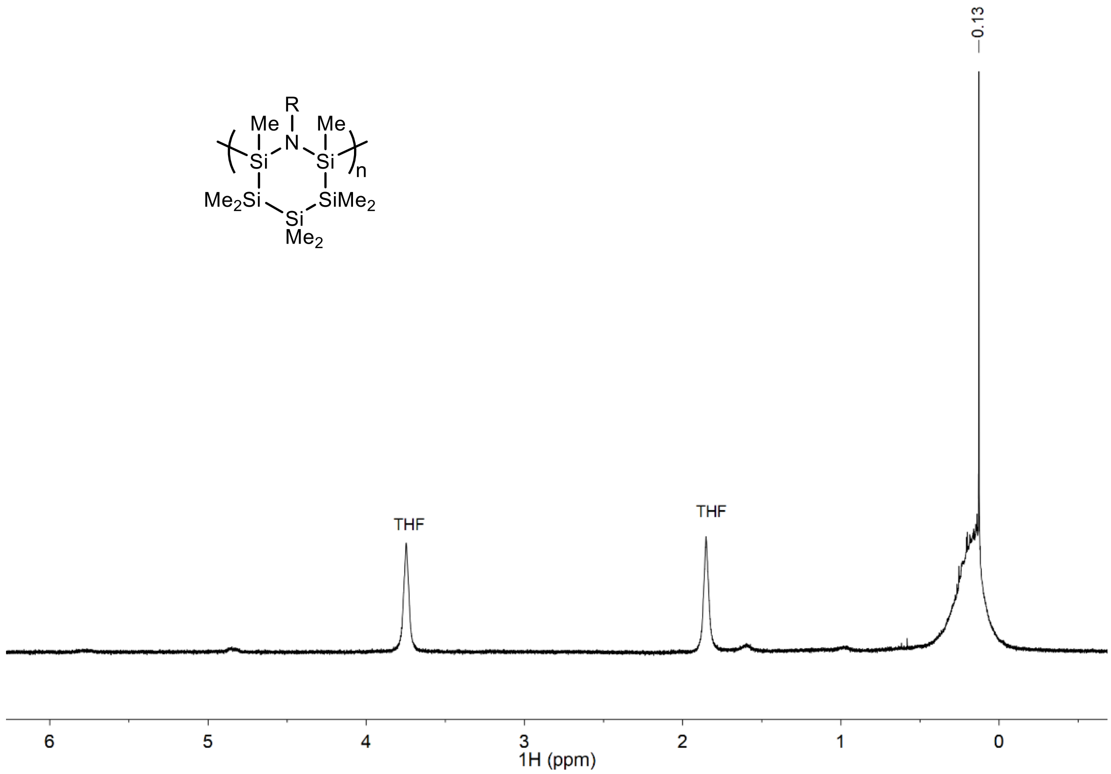
^{1}H NMR spectrum of **P1** (Table 1, entry 5, 400 MHz, $CDCl_3$)



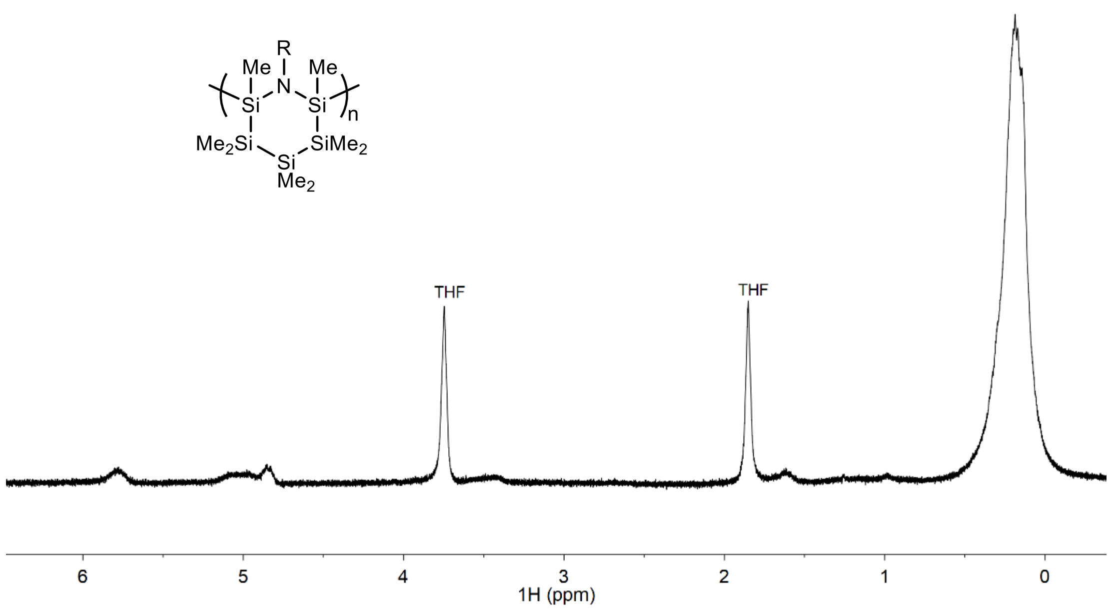
$^{29}Si\{^{1}H\}$ NMR spectrum of **P1** (Table 1, entry 5, 79 MHz, $CDCl_3$)



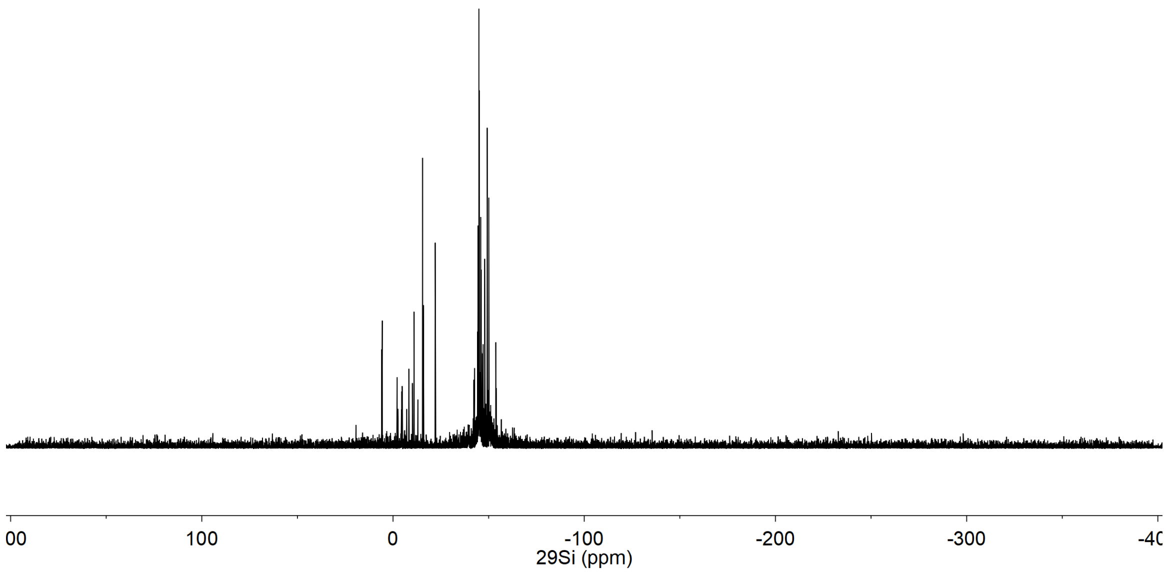
^{1}H NMR spectrum of poly(**Si5N**) (Table 2, entry 5, 400 MHz, $CDCl_3$)



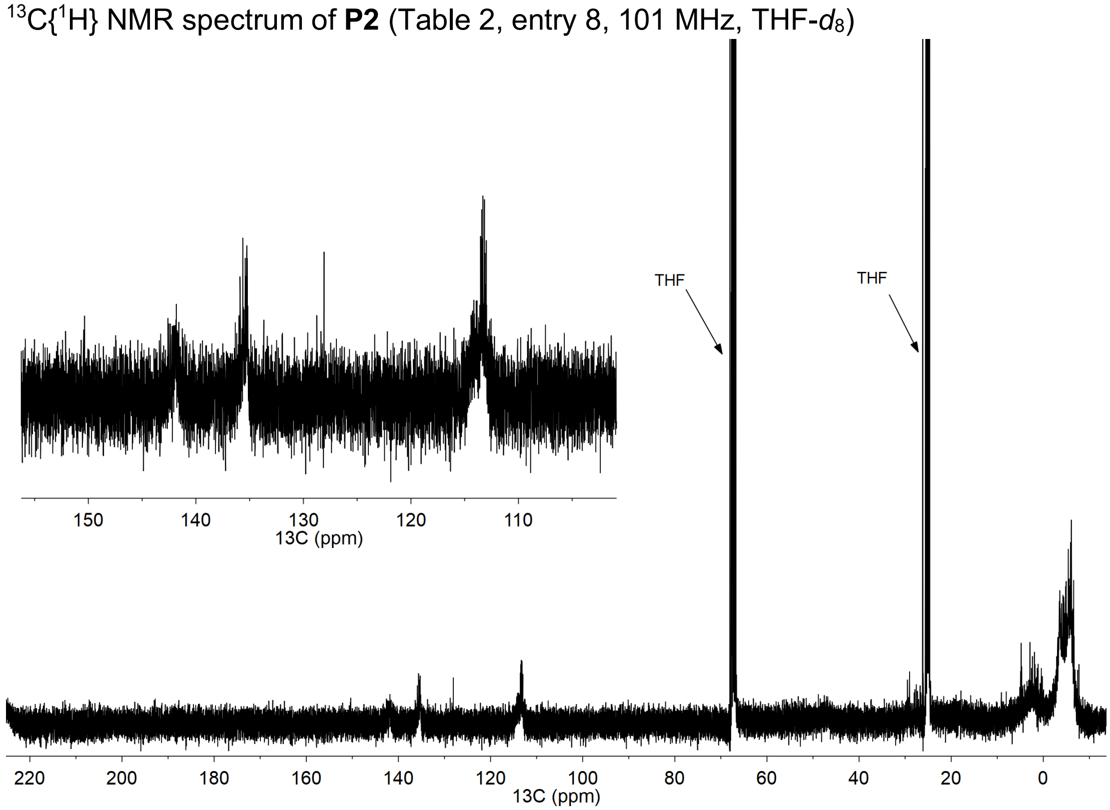
^{1}H NMR spectrum of **P2** (Table 2, entry 8, 400 MHz, THF-d_8)



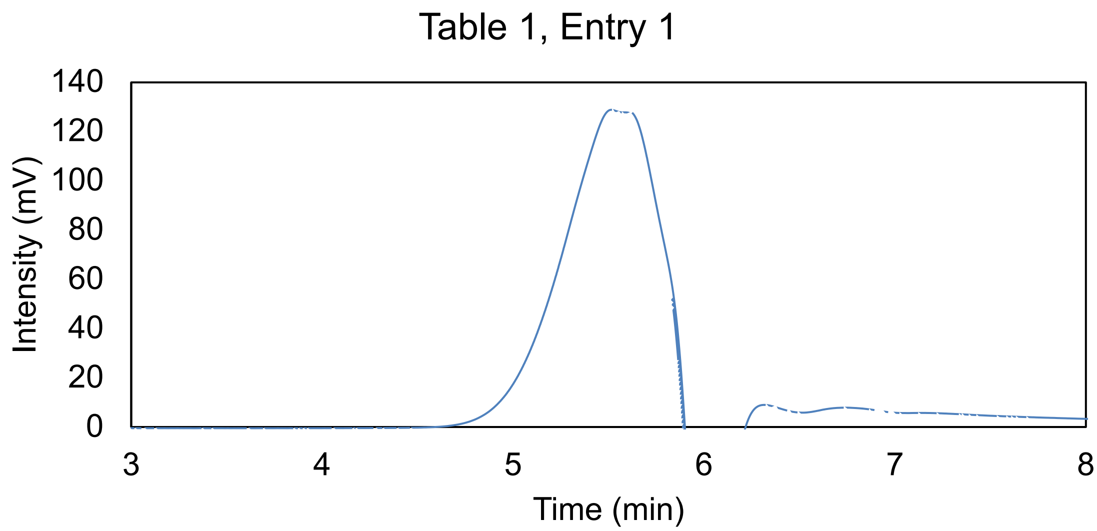
$^{29}Si\{^1H\}$ NMR spectrum of **P2** (Table 2, entry 8, 79 MHz, THF-d_8)



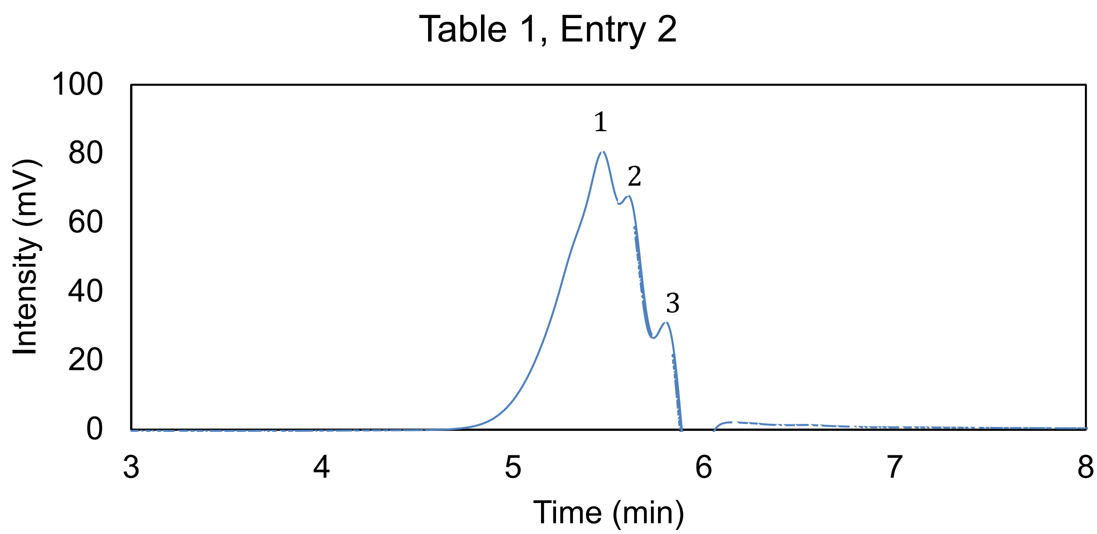
$^{13}C\{^1H\}$ NMR spectrum of **P2** (Table 2, entry 8, 101 MHz, THF-d_8)



3. GPC Spectra

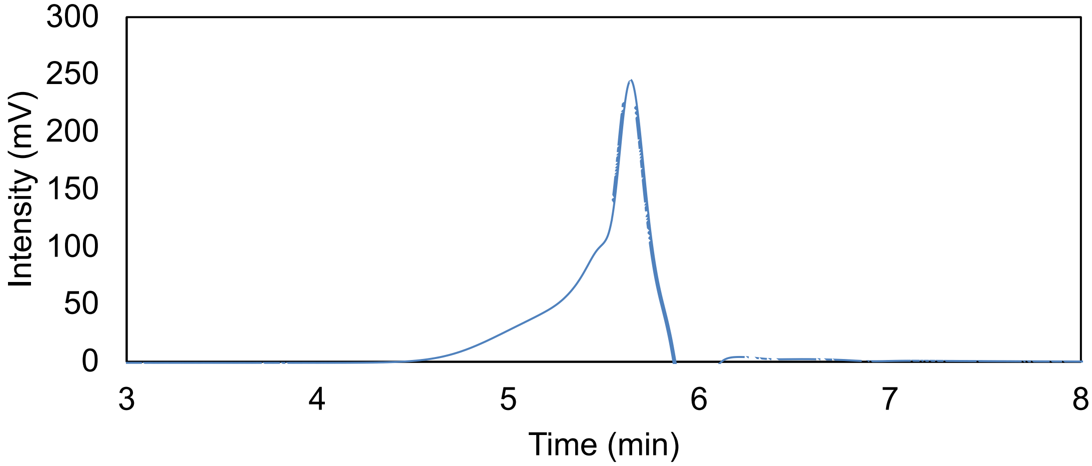


M_n	M_w	Đ
768	1180	1.54



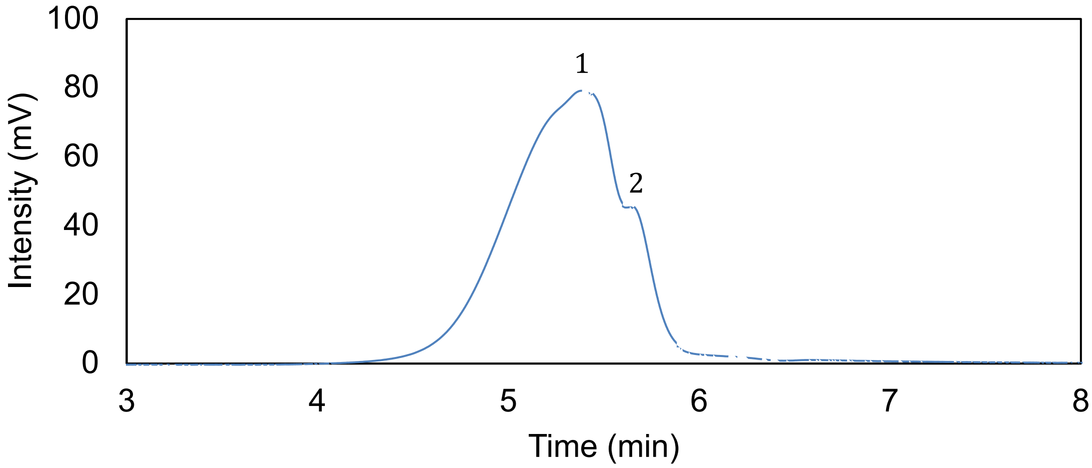
Peak No.	M_n	M_w	Đ
1	1290	1660	1.29
2	588	599	1.02
3	361	365	1.01
ALL	854	1300	1.52

Table 1, Entry 3



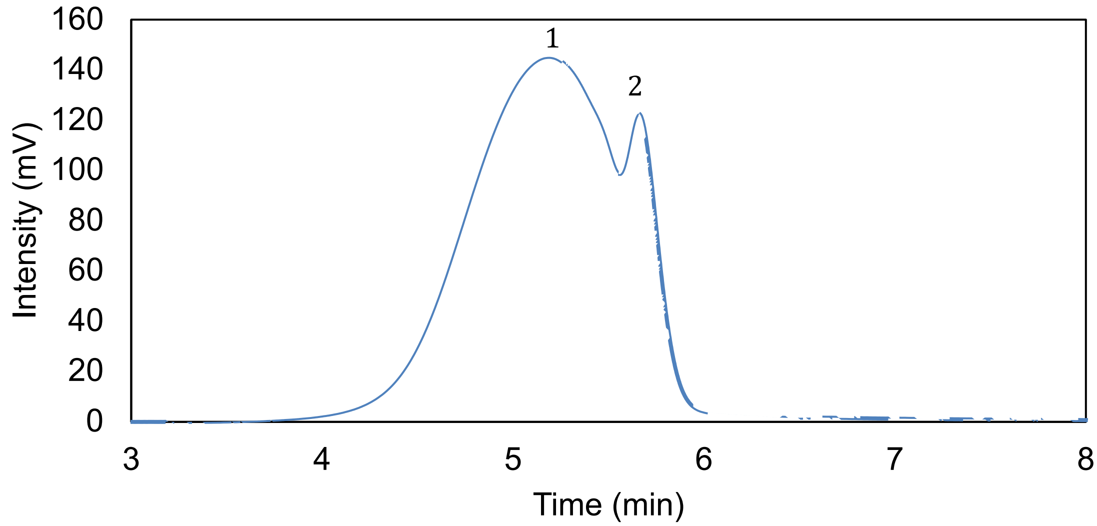
M_n	M_w	Đ
756	1440	1.91

Table 1, Entry 4



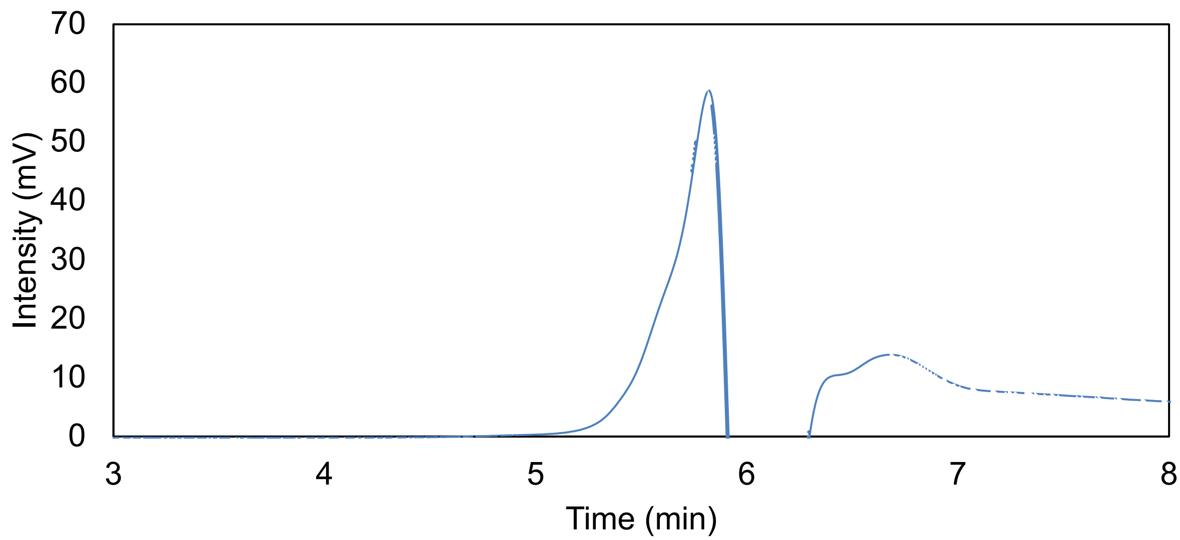
Peak No.	M_n	M_w	Đ
1	1600	2870	1.80
2	335	432	1.29
ALL	1040	2520	2.43

Table 1, Entry 5



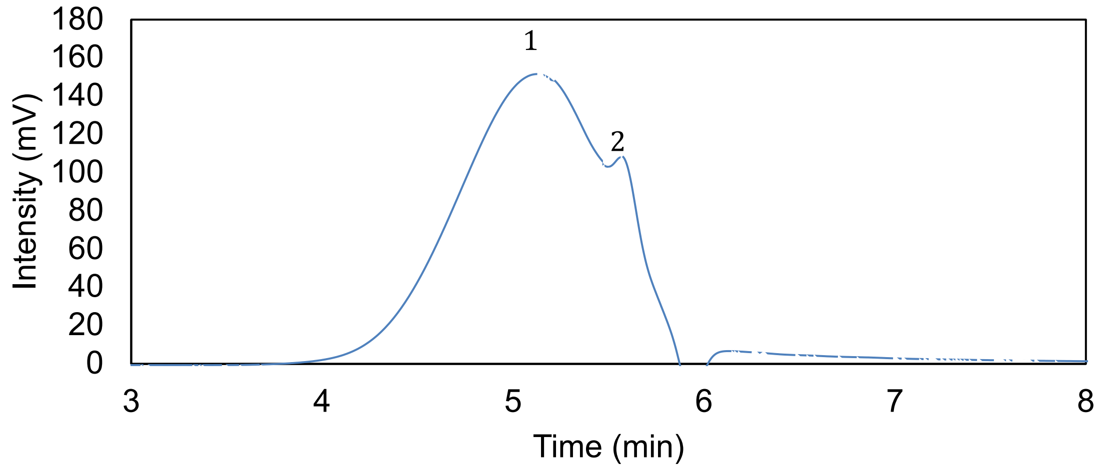
Peak No.	M_n	M_w	Đ
1	2250	5360	2.38
2	459	508	1.11
All	1310	4470	3.41

Table 1, Entry 6 (**Si5N**)



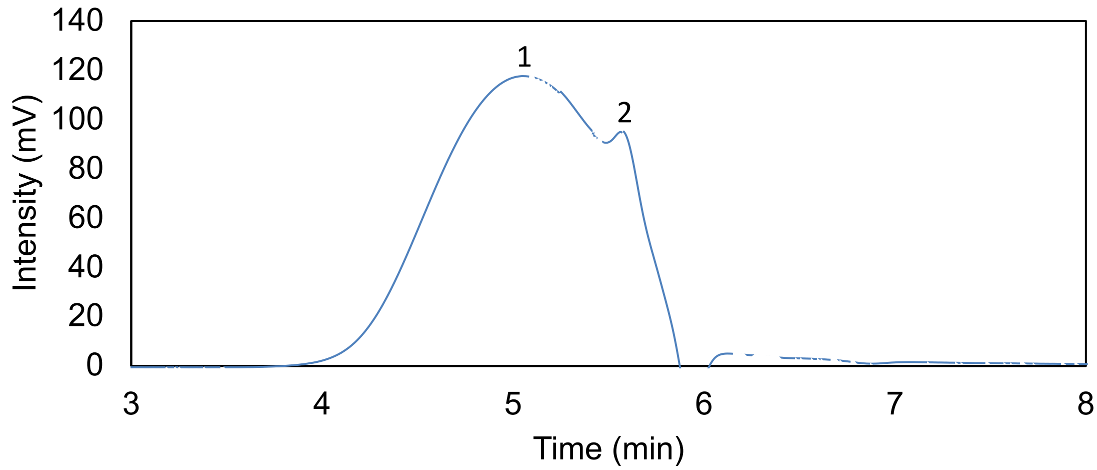
M_n	M_w	Đ
441	523	1.19

Table 2, Entry 1



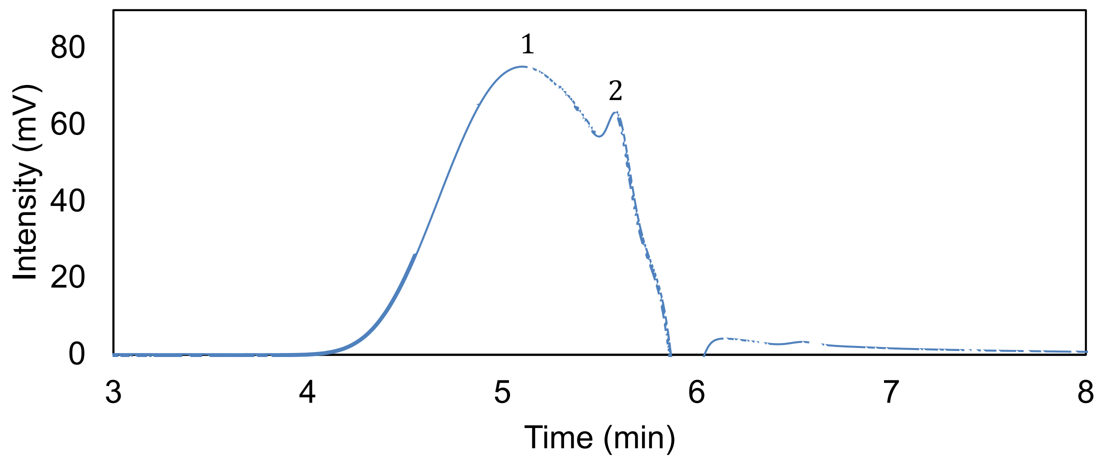
Peak No.	M_n	M_w	Đ
1	2710	6230	2.30
2	588	627	1.07
ALL	1740	5370	3.09

Table 2, Entry 2



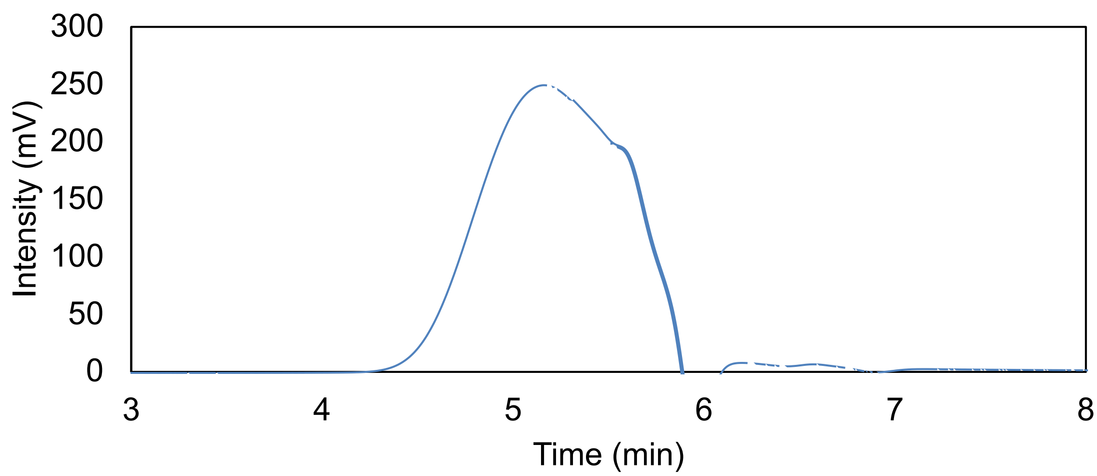
Peak No.	M_n	M_w	Đ
1	2990	7340	2.46
2	583	626	1.07
ALL	1760	6210	3.52

Table 2, Entry 3



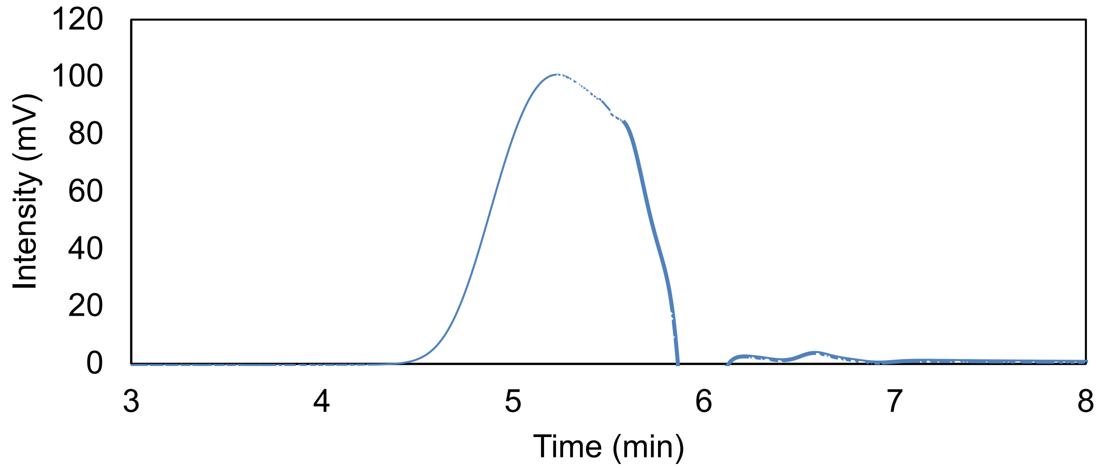
Peak No.	M_n	M_w	Đ
1	2620	5290	2.02
2	574	615	1.07
ALL	1570	4420	2.81

Table 2, Entry 4



M_n	M_w	Đ
1350	3150	2.33

Table 2, Entry 5



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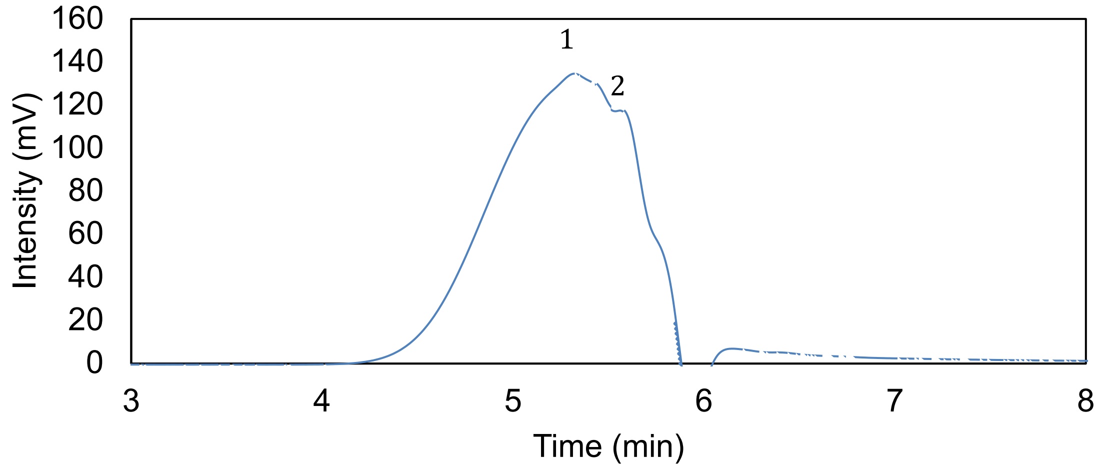
1220	2450	2.00

Table 2, Entry 6



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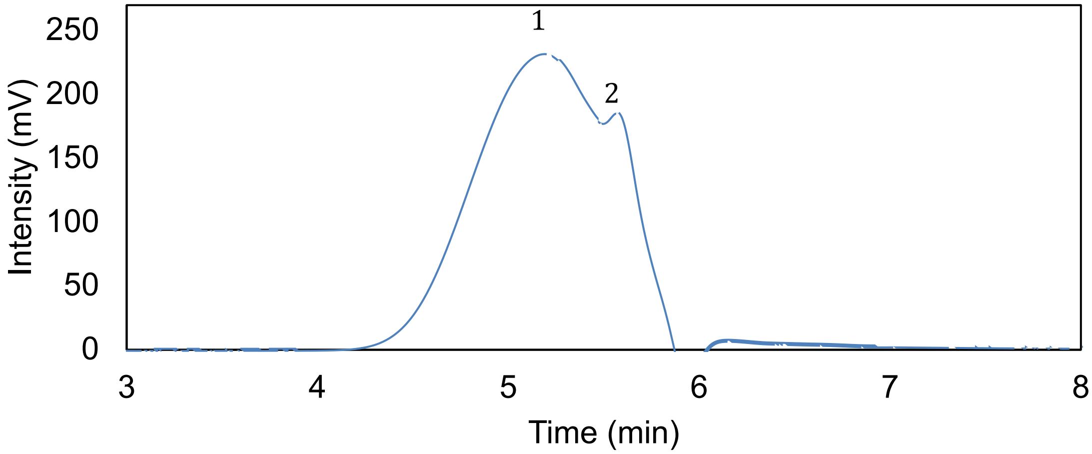
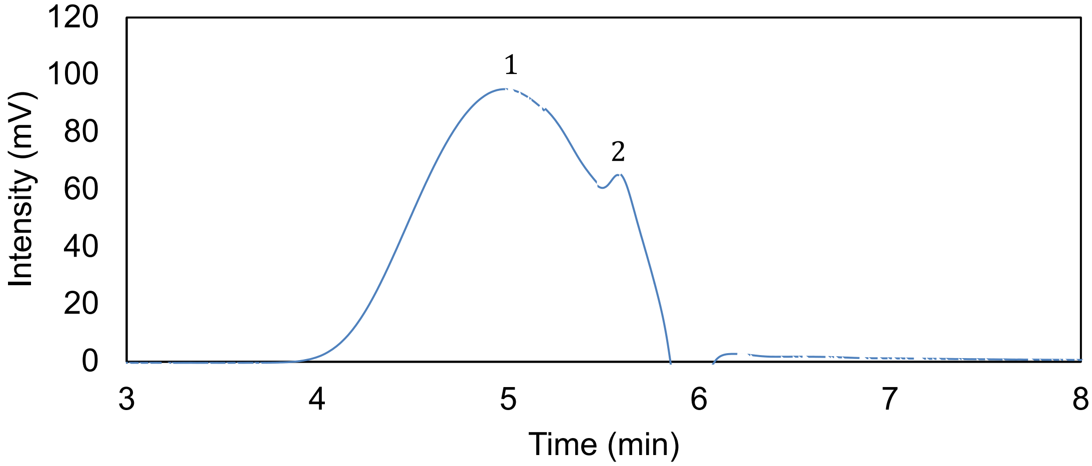
1	2000	3670	1.84
2	526	561	1.07
ALL	1270	3030	2.39

Table 2, Entry 7



Peak No.	M_n	M_w	Đ
1	2360	4210	1.79
2	587	626	1.07
ALL	1470	3500	2.38

Table 2, Entry 8



Peak No.	M_n	M_w	Đ
1	3210	8000	2.49
2	579	618	1.07
ALL	1930	6920	3.59

4. References

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