

Supporting Information for

Polysiloxanes grafted with Mono(alkenyl)Silsesquioxanes – Particular Concept for their Connection[‡]

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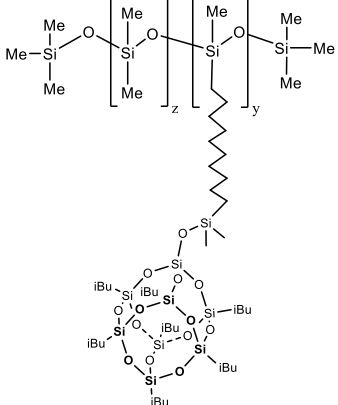
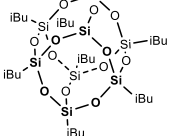
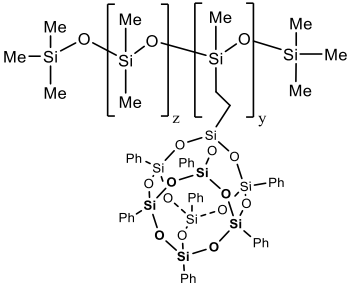
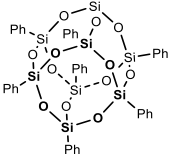
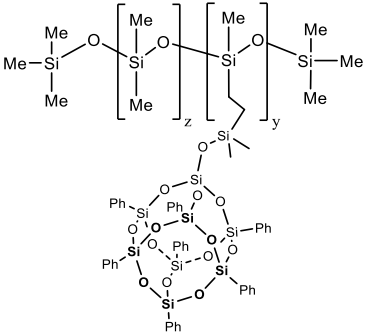
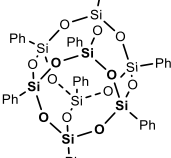
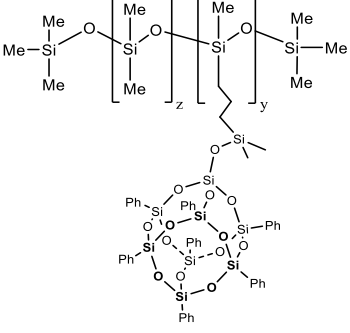
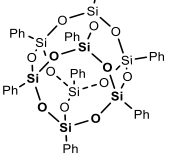
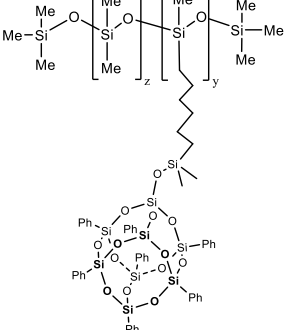
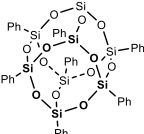
[‡]Dedicated to Professor Bogdan Marciniak on the occasion of his forthcoming 80th birthday.

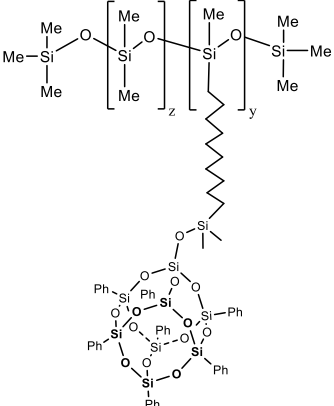
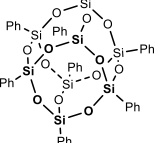
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1. Table S1 of compounds

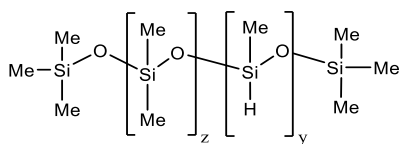
Structure	Compound Abbrev.	NMR spectra page:
<p>Me-Si(Me)₂-O-[Si(Me)₂]_z-[Si(Me)(H)]_y-Si(Me)₂-Me</p>	PS1	S 5
	PS2	S 7
<p>Me-Si(Me)₂-O-[Si(Me)₂]_z-[Si(Me)(tBu)]_y-Si(Me)₂-Me</p> <p> 1-iBuT₈ </p>	1-iBuT₈@PS1	S 9
	1-iBuT₈@PS2	S 11
<p>Me-Si(Me)₂-O-[Si(Me)₂]_z-[Si(Me)(OSiMe₂)]_y-Si(Me)₂-Me</p> <p> 2-iBuT₈ </p>	2-iBuT₈@PS1	S 13
	2-iBuT₈@PS2	S15
<p>Me-Si(Me)₂-O-[Si(Me)₂]_z-[Si(Me)(CH₂CH₂CH₃)]_y-Si(Me)₂-Me</p> <p> 3-iBuT₈ </p>	3-iBuT₈@PS1	S 17
	3-iBuT₈@PS2	S 19
<p>Me-Si(Me)₂-O-[Si(Me)₂]_z-[Si(Me)(CH₂CH₂CH₂CH₂CH₂CH₃)]_y-Si(Me)₂-Me</p> <p> 4-iBuT₈ </p>	4-iBuT₈@PS1	S 21
	4-iBuT₈@PS2	S 23

	5-iBuT₈@PS1	S 25
	5-iBuT₈@PS2	S 27
	1-PhT₈@PS1	S 29
	1-PhT₈@PS2	S 31
	2-PhT₈@PS1	S 33
	2-PhT₈@PS2	S 35
	3-PhT₈@PS1	S 37
	3-PhT₈@PS2	S 39
	4-PhT₈@PS1	S 41
	4-PhT₈@PS2	S 43

 <p>The structure shows a linear polysiloxane chain. It starts with a dimethylsilyloxy group, followed by a repeating unit of dimethylsilyloxy groups enclosed in brackets with subscript 'z'. This is followed by another repeating unit of dimethylsilyloxy groups enclosed in brackets with subscript 'y'. The chain ends with a dimethylsilyloxy group. A long zigzag line representing a polymer backbone connects the terminal dimethylsilyloxy group to a cage structure.</p>	<p>5-PhT₈@PS1</p>	<p>S 45</p>
 <p>The structure shows a cage-like structure consisting of eight silicon atoms and eight oxygen atoms. Each silicon atom is bonded to two oxygen atoms, and each oxygen atom is bonded to two silicon atoms, forming a closed cage. Each silicon atom is also bonded to a phenyl group (Ph).</p>	<p>5-PhT₈@PS2</p>	<p>S 47</p>

2. Data characterizing PS1-2 and obtained products 1-5-RT₈@PS1-2 (copies of ¹H, ¹³C, and ²⁹Si NMR spectra)

PS1 (4.3 mmol/g Si-H)

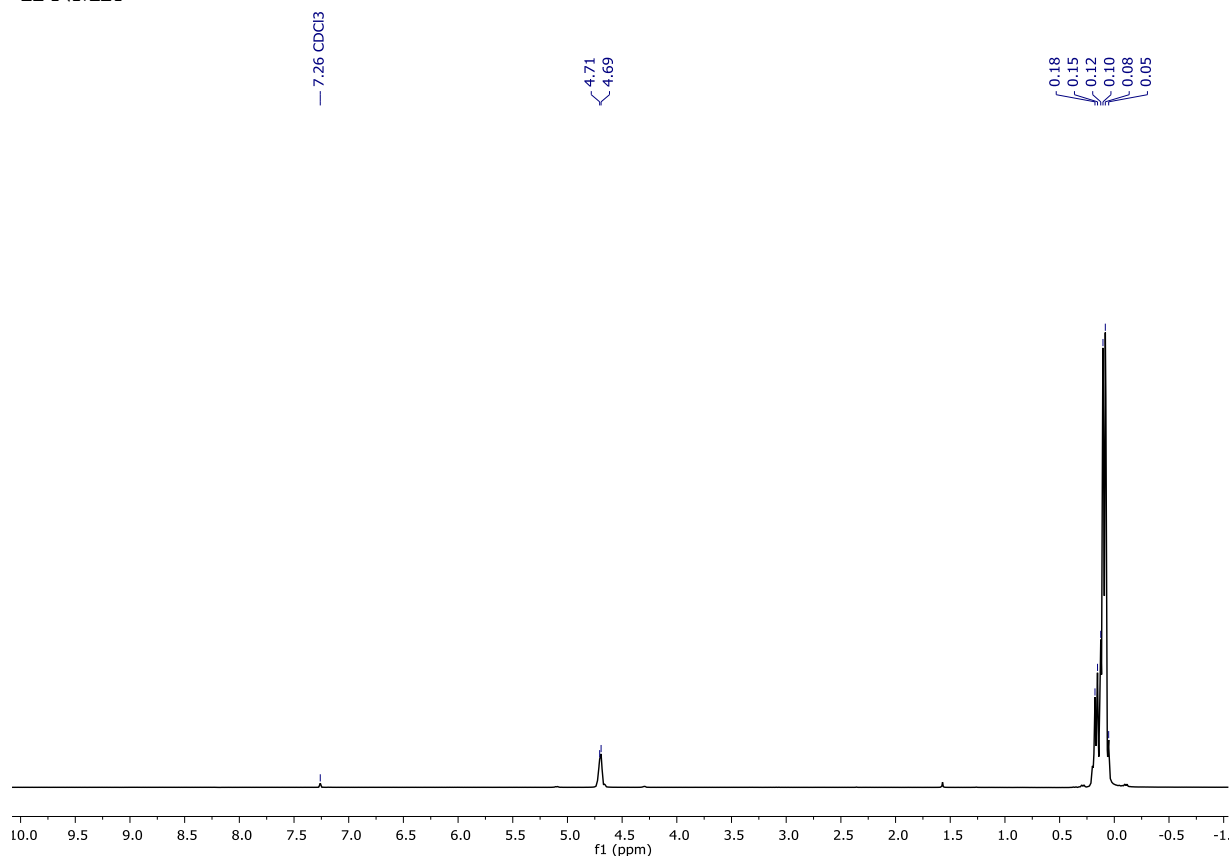


¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.05-0.18 (m, -SiCH₃), 4.69-4.71 (s, -Si-H). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): 1.04-1.34, 1.53, 1.86, 1.99 (-SiCH₃). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 9.50-9.39, 7.57-7.15, -18.92, -19.21, -20.36, -20.64, -21.66, -22.02 (-Si-CH₃), -35.11, -35.38, -36.03, -36.51, -37.11, -37.34, -37.58 (-Si-H).

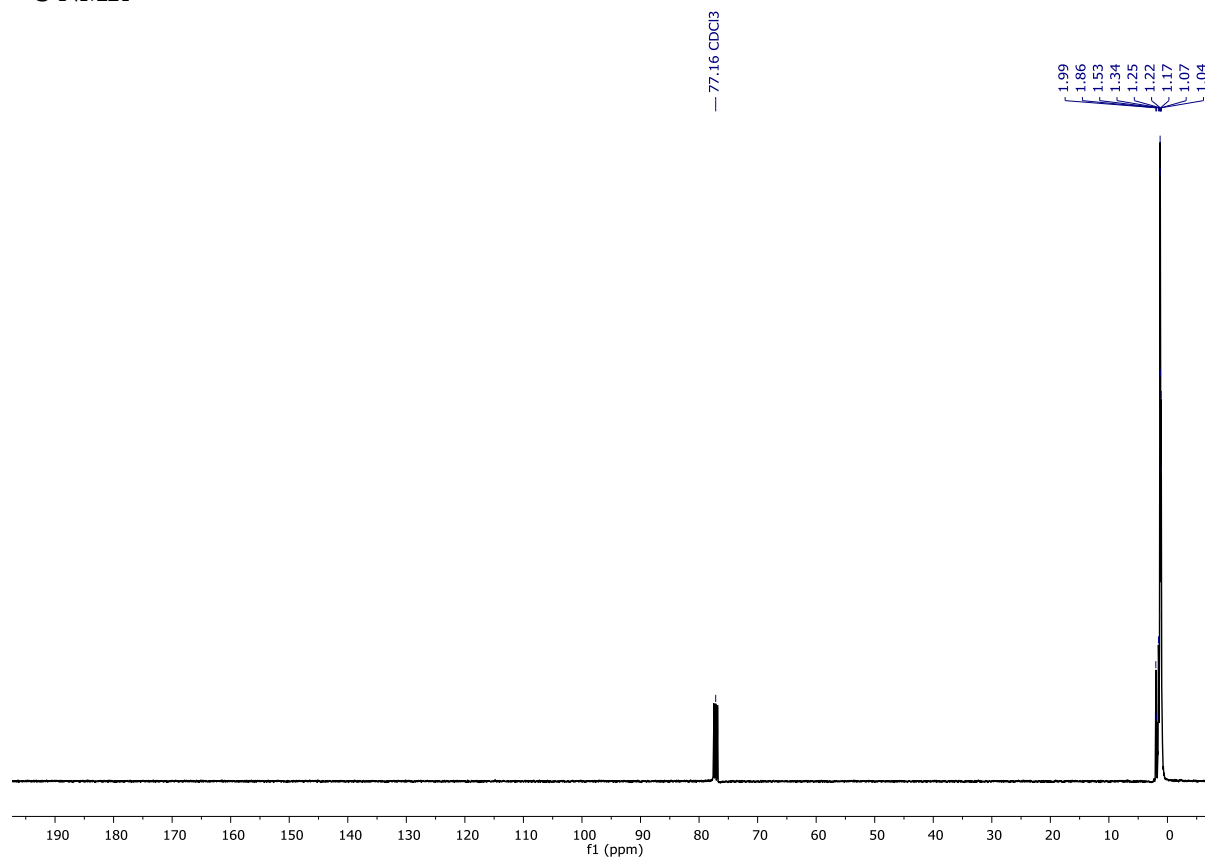
FT-IR (cm⁻¹): 2962.21, 2904.18 (-CH₃), 2156.57 (Si-H), 1411.40 (-C-H), 1257.63 (Si-C), 1015.81 (Si-O), 908.42 (Si-H).

The assignments are consistent with those in the literature.[1-3]

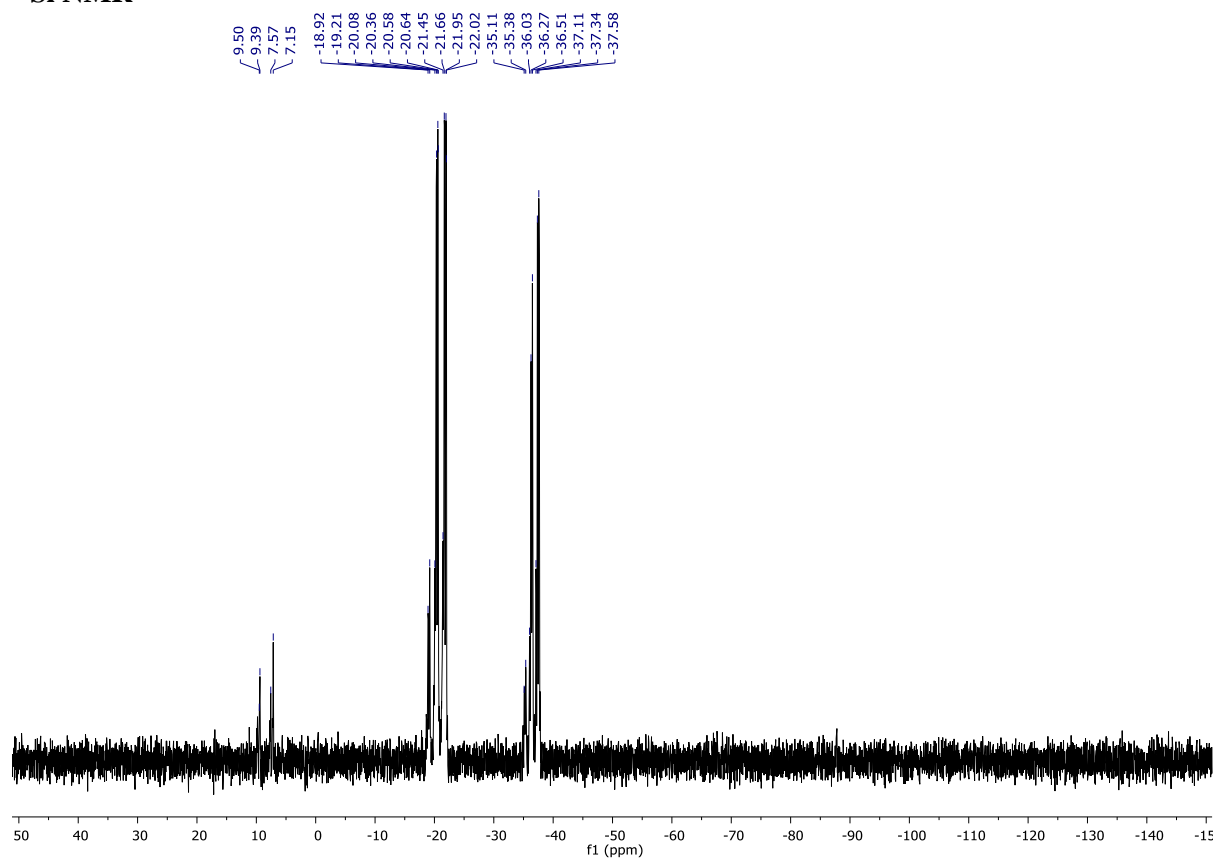
¹H NMR



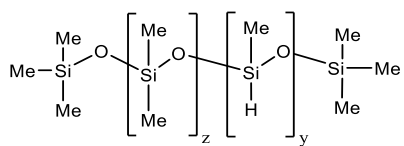
¹³C NMR



²⁹Si NMR



PS2 (1.1 mmol/g Si-H)

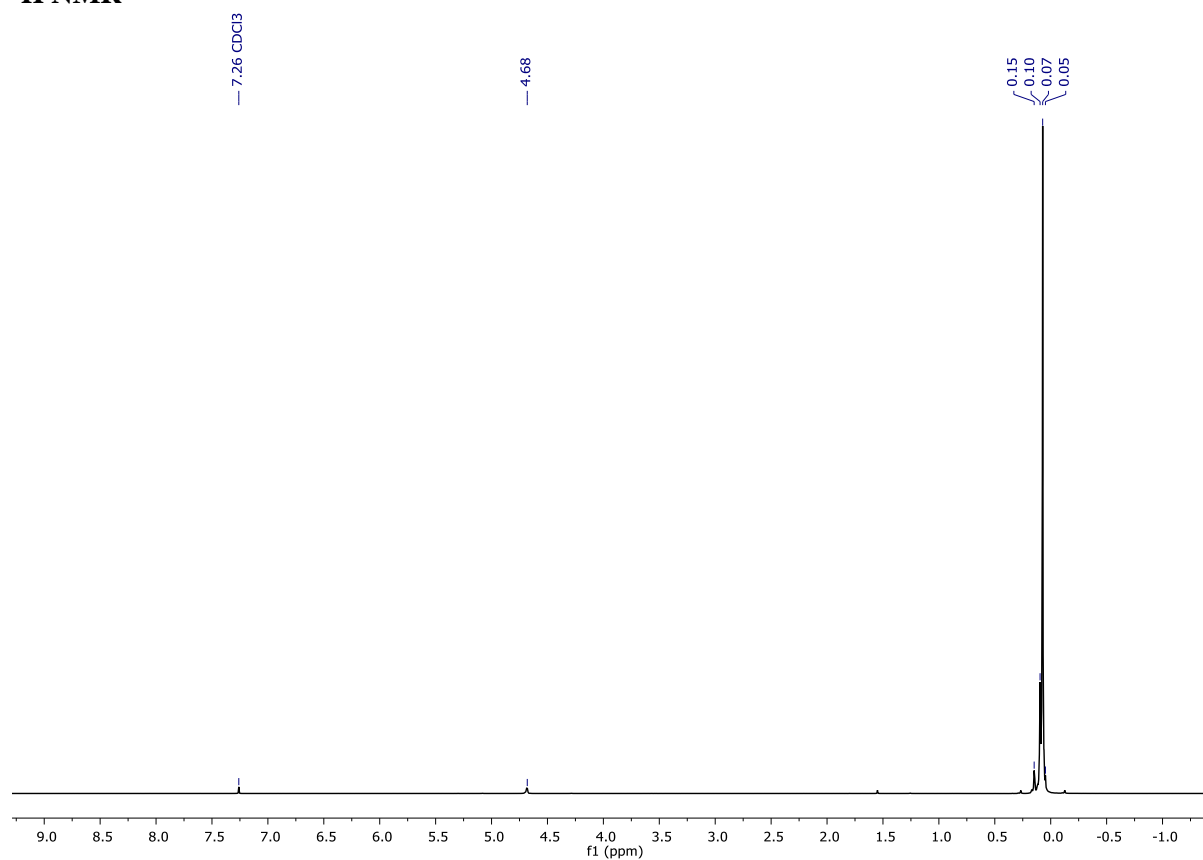


¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.05-0.15 (m, -SiCH₃), 4.68 (s, -Si-H). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): 0.97, 1.03, 1.14-1.21, 1.49, 1.96 (-SiCH₃). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 7.24, -20.27, -20.56, -21.65, -21.86, -21.94 (-Si-CH₃), -37.58 (-Si-H).

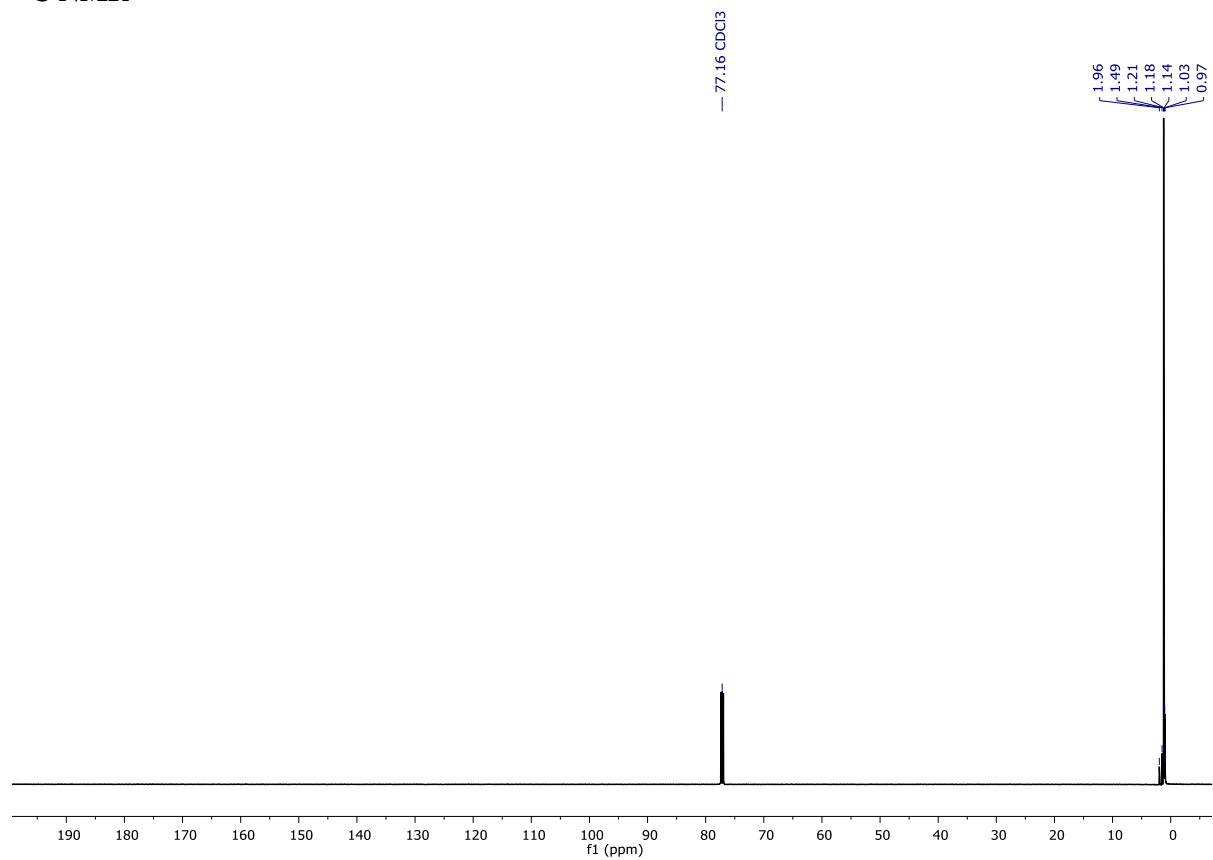
FT-IR (cm⁻¹): 2962.21, 2904.18 (-CH₃), 2152.80 (Si-H), 1411.76 (-C-H), 1257.21 (Si-CH₃), 1078.08, 1009.60 (Si-O), 910.77 (Si-H).

The assignments are consistent with those in the literature.[1-3]

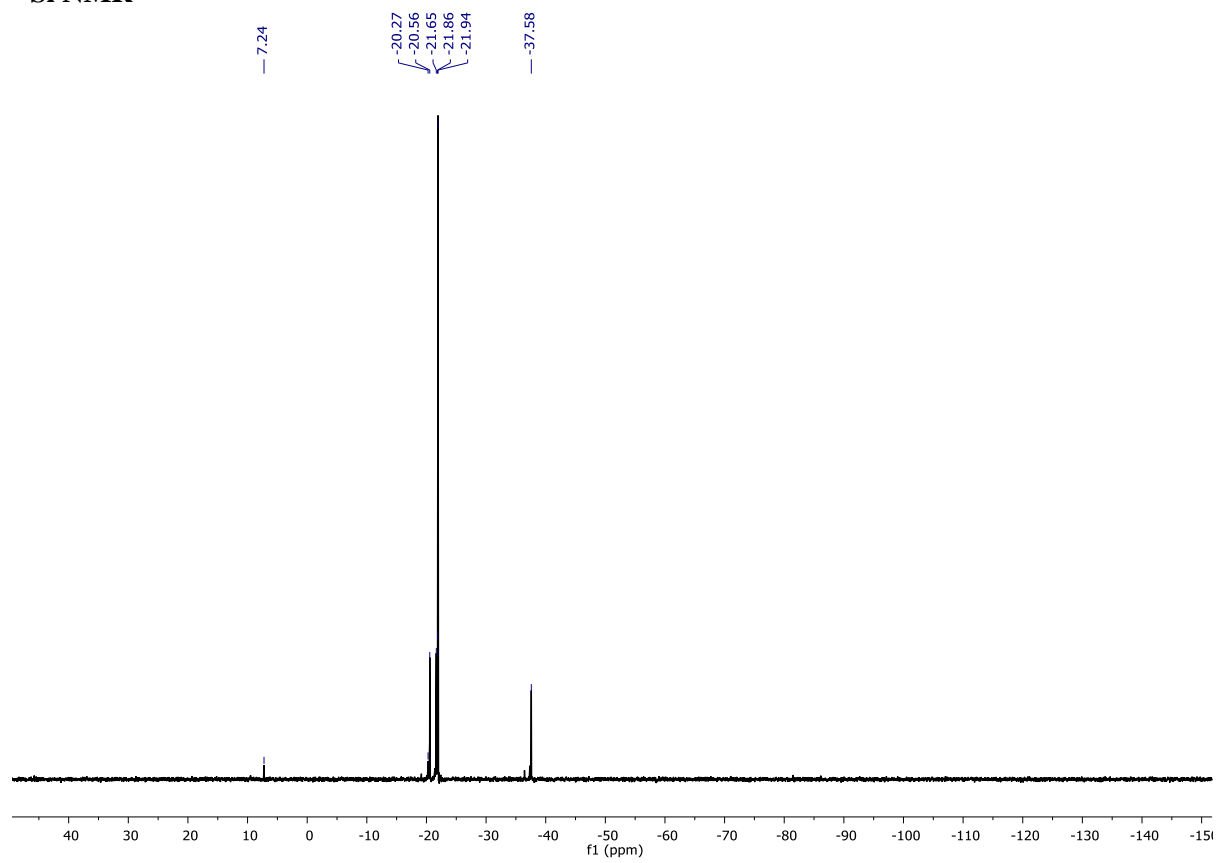
¹H NMR



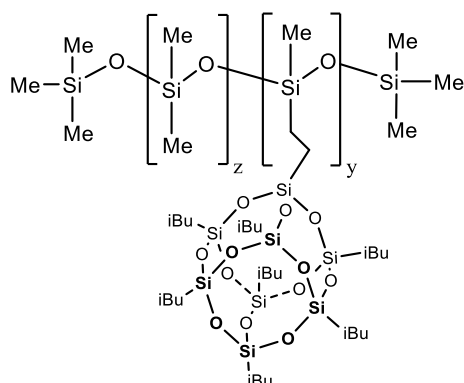
^{13}C NMR



^{29}Si NMR



1-iBuT₈@PS

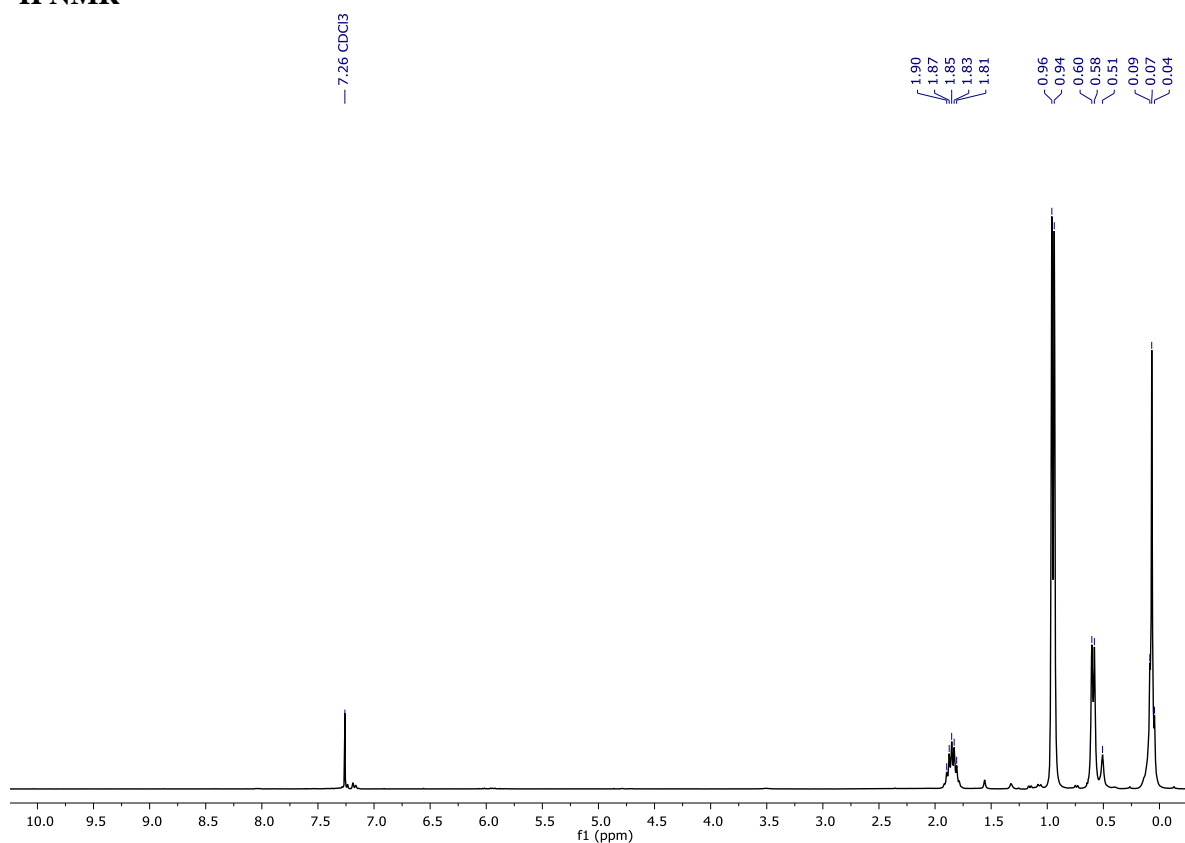


1-iBuT₈@PS1

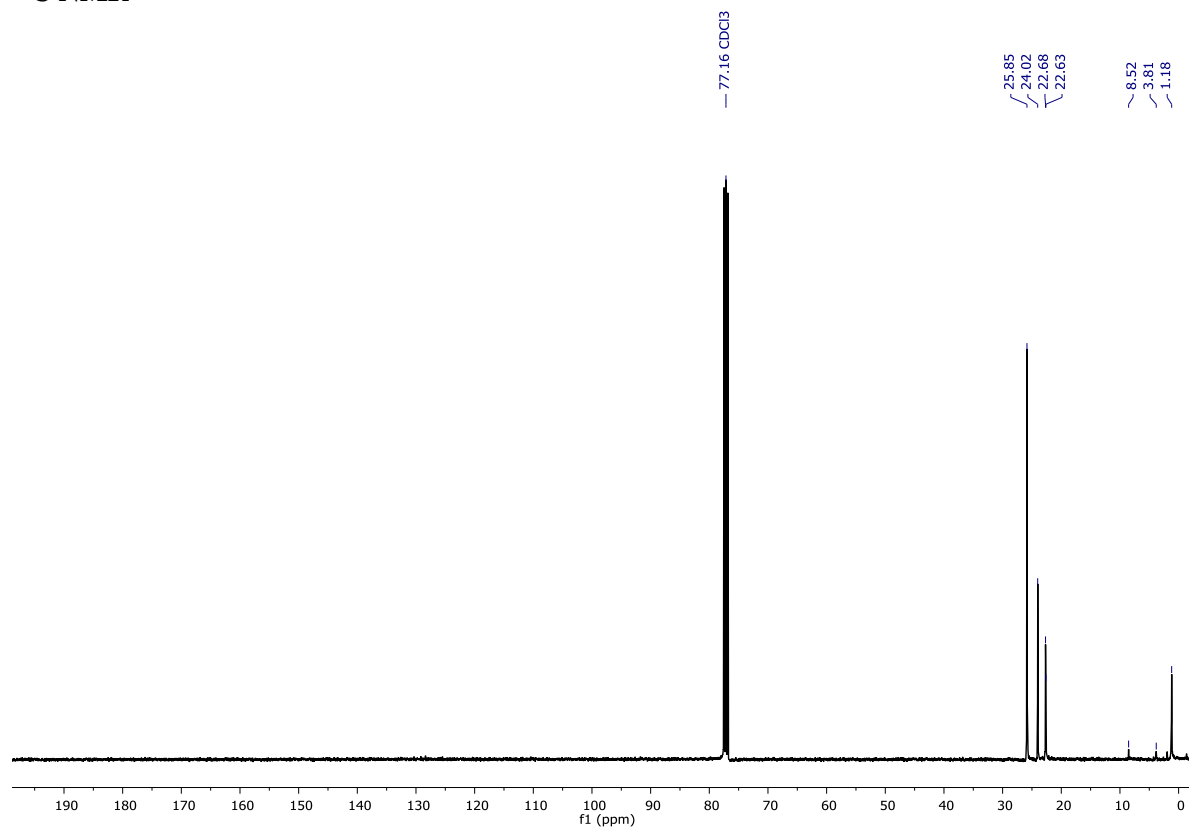
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.04-0.09 (m, -SiCH₃), 0.51, 0.58-0.60 (m, -CH₂-, -CH₂- (iBu)), 0.94-0.96 (m, -CH₃ (iBu)), 1.81-1.90 (m, -CH- (iBu)). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): 1.18 (-SiCH₃), 3.81, 8.52 (-CH₂-), 22.63-22.68, 24.02, 25.85 (iBu). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): -21.69, -21.94, -22.06, -22.28 (-SiCH₃), -66.87 (-Si-CH₂-CH₂-Si-), -67.42, -67.65, -67.94.

FT-IR (cm⁻¹): 2953.20, 2905.52, 2869.27 (-C-H), 1464.62 (-C-H), 1259.49, 1228.75 (Si-C), 1084.86 (Si-O).

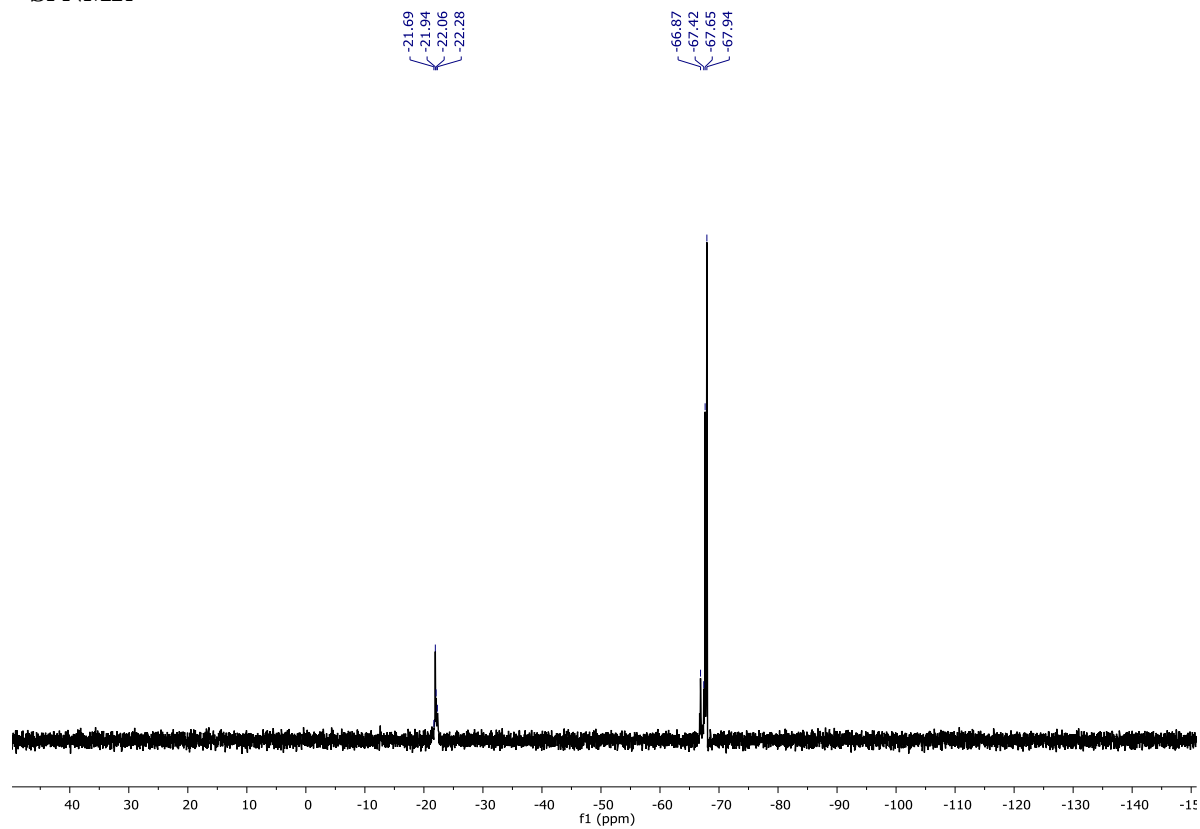
¹H NMR



¹³C NMR



²⁹Si NMR

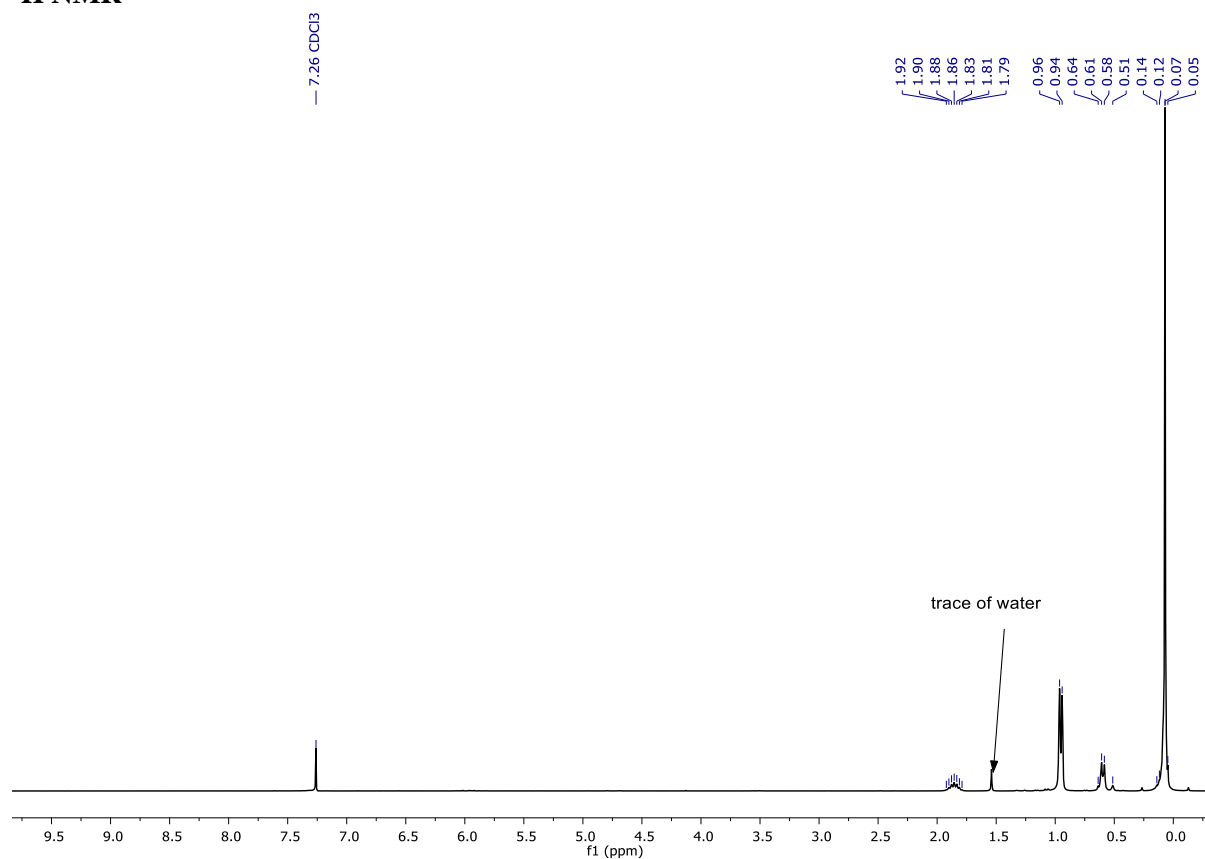


1-iBuT₈@PS2

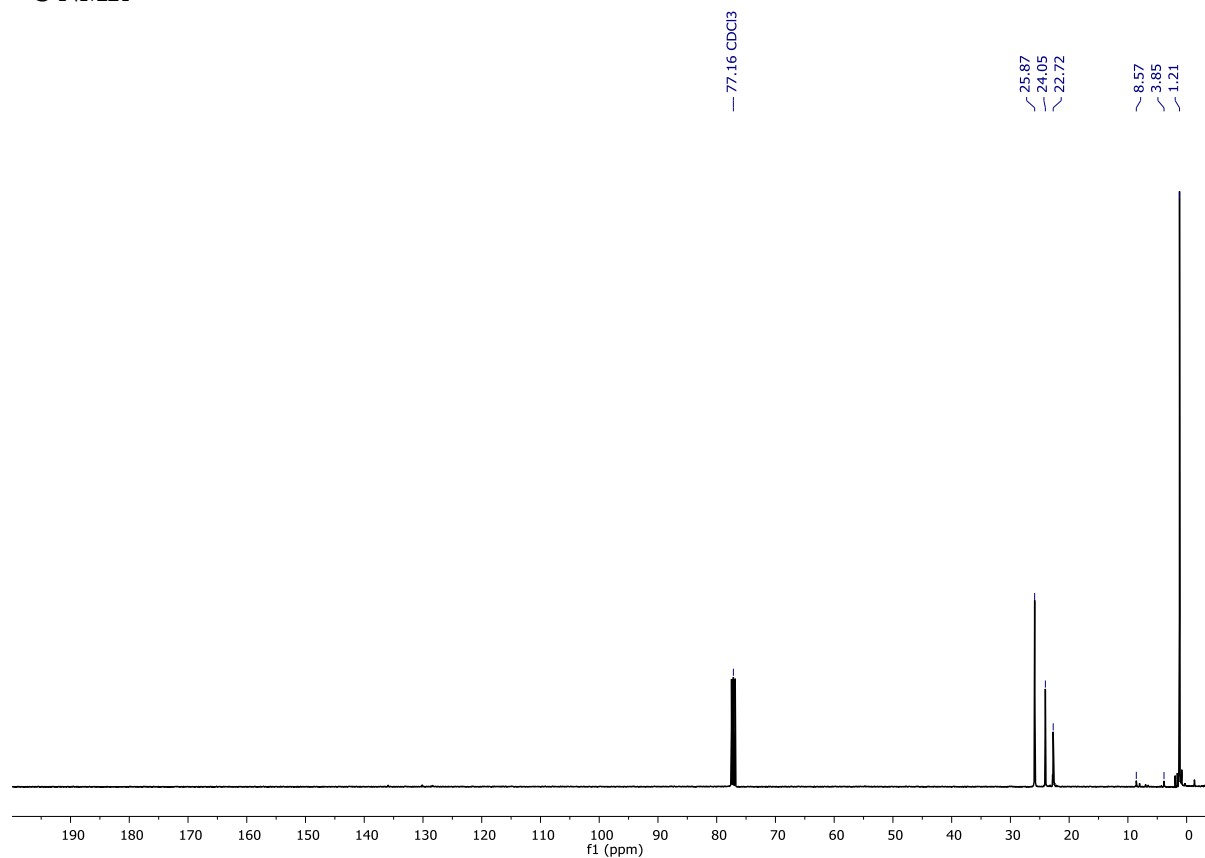
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.05-0.14 (m, -SiCH₃), 0.51, 0.58-0.64 (m, -CH₂-, -CH₂- (iBu)), 0.94-0.96 (m, -CH₃ (iBu)), 1.79-1.92 (m, -CH- (iBu)). ¹³C NMR (100.6 MHz, CDCl₃, δ, ppm): 1.21 (-SiCH₃), 3.85, 8.57 (-CH₂-), 22.62, 24.05, 25.87 (iBu). ²⁹Si NMR (79.5 MHz, CDCl₃, δ, ppm): -21.94, -22.33 (-SiCH₃), -66.84 (-Si-CH₂-CH₂-Si-), -67.41, -67.63, -67.93.

FT-IR (cm⁻¹): 2957.69, 2905.43, 2870.93 (-C-H), 1465.31 (-C-H), 1258.18, 1228.59 (Si-C), 1084.43, 1009.79 (Si-O).

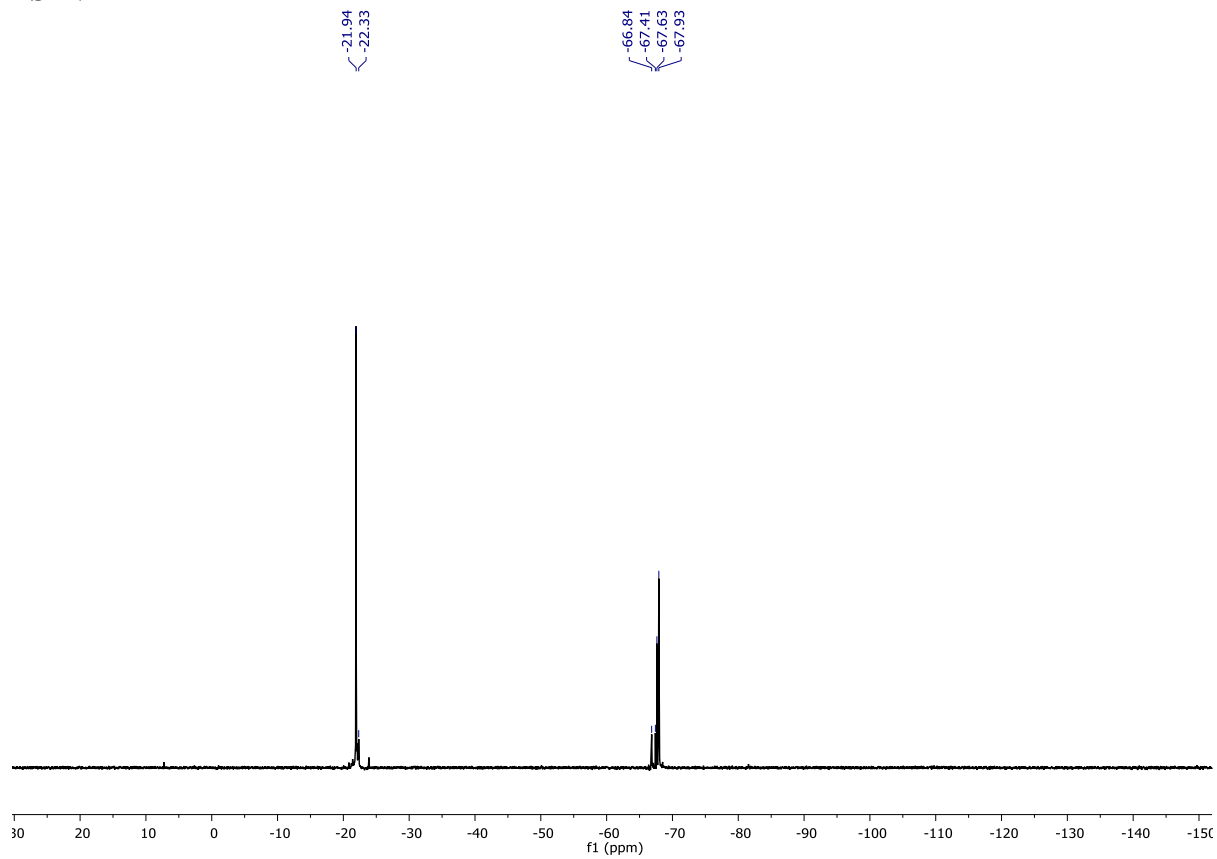
¹H NMR



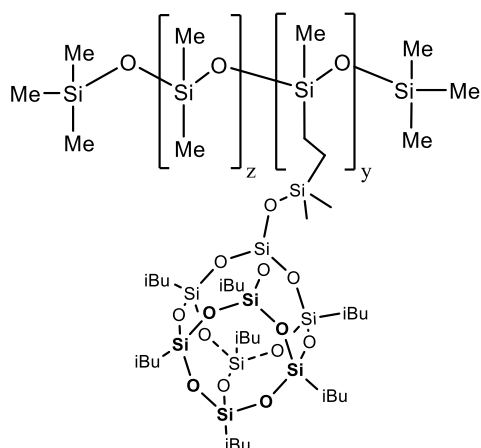
¹³C NMR



²⁹Si NMR



2-iBuT₈@PS

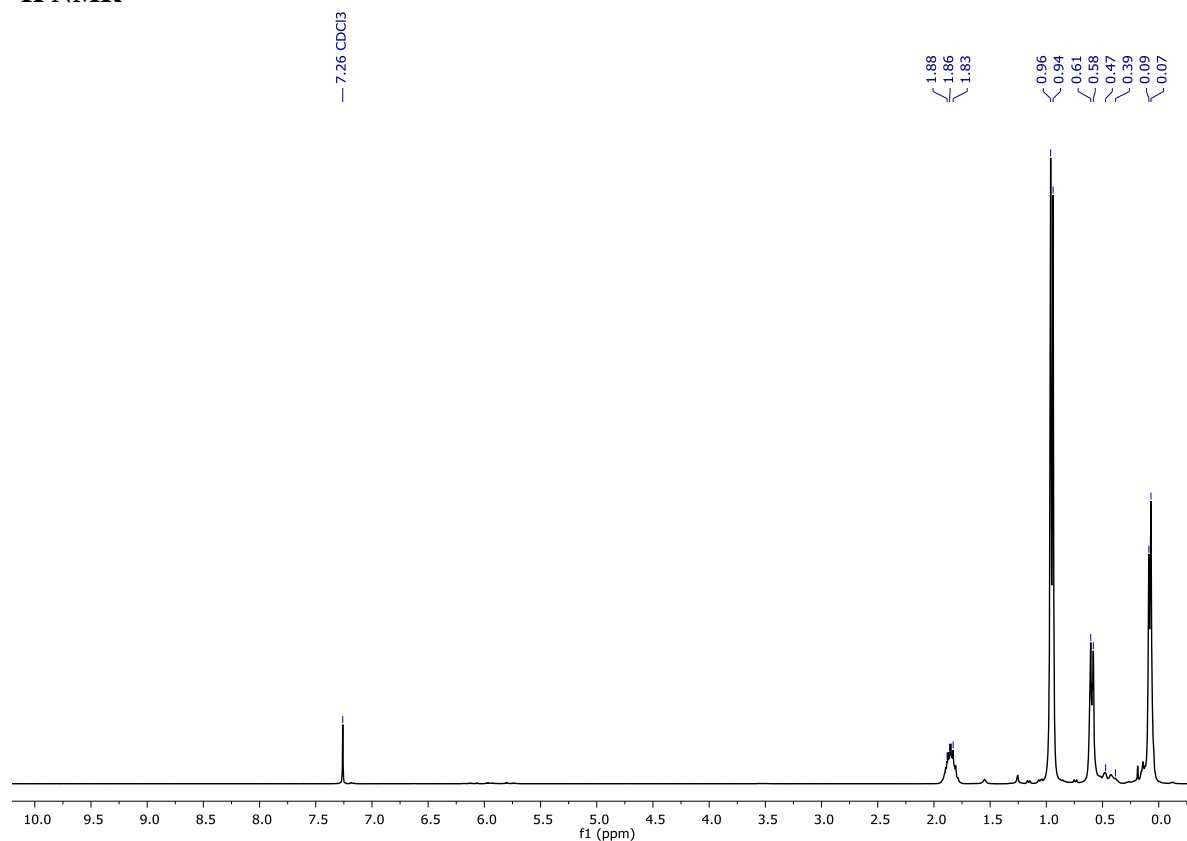


2-iBuT₈@PS1

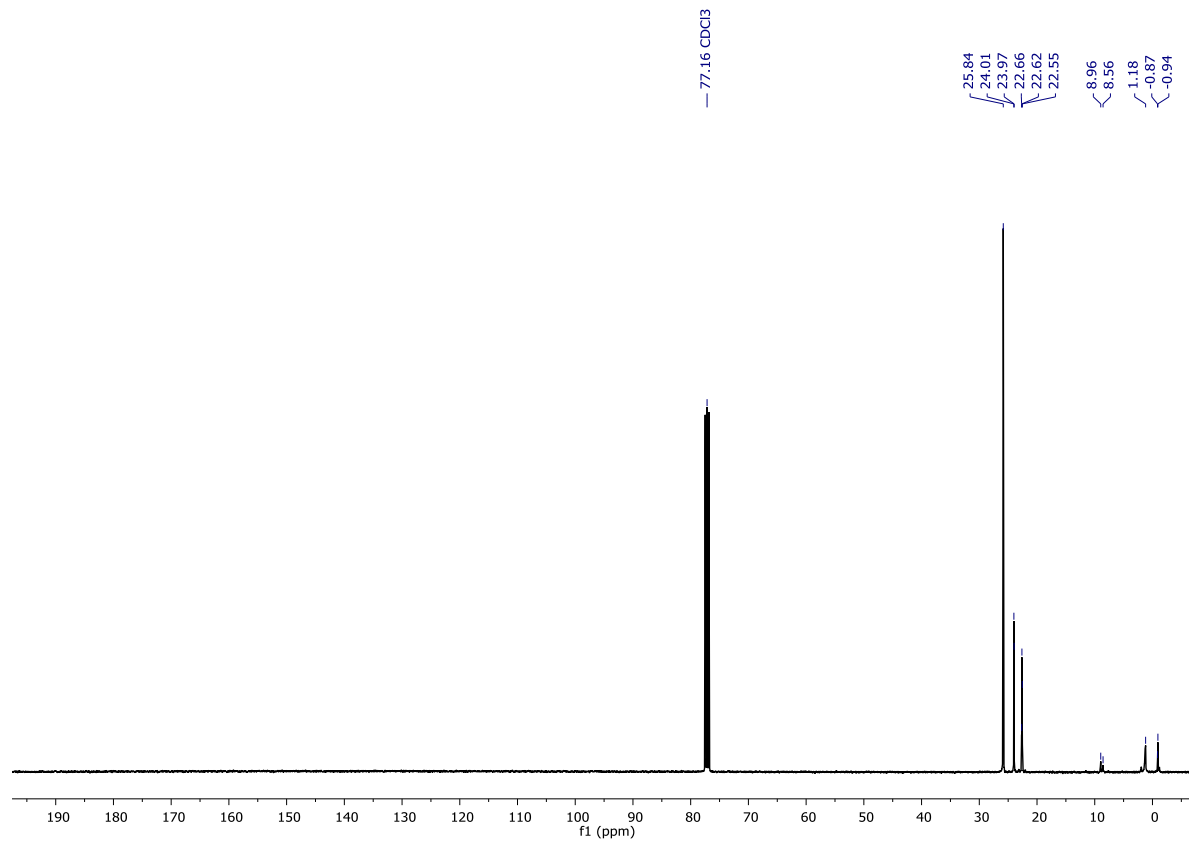
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.07-0.09 (m, -SiCH₃), 0.39-0.41, 0.58-0.61 (m, -CH₂-, -CH₂- (iBu)), 0.94-0.96 (m, -CH₃ (iBu)), 1.83-1.88 (m, -CH- (iBu)). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -0.94, -0.87, 1.18 (-SiCH₃), 8.56, 8.95 (-CH₂-), 22.55-22.66, 23.97-24.01, 25.84 (iBu). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 11.91(-Si-CH₂-CH₂-Si-), -22.03, -22.21, -22.60, (-SiCH₃), -67.11, -67.90, -109.66 (-SiO₄).

FT-IR (cm⁻¹): 2953.38, 2905.92, 2869.69 (-C-H), 1464.83 (-C-H), 1258.87, 1228.58 (Si-C), 1076.60 (Si-O).

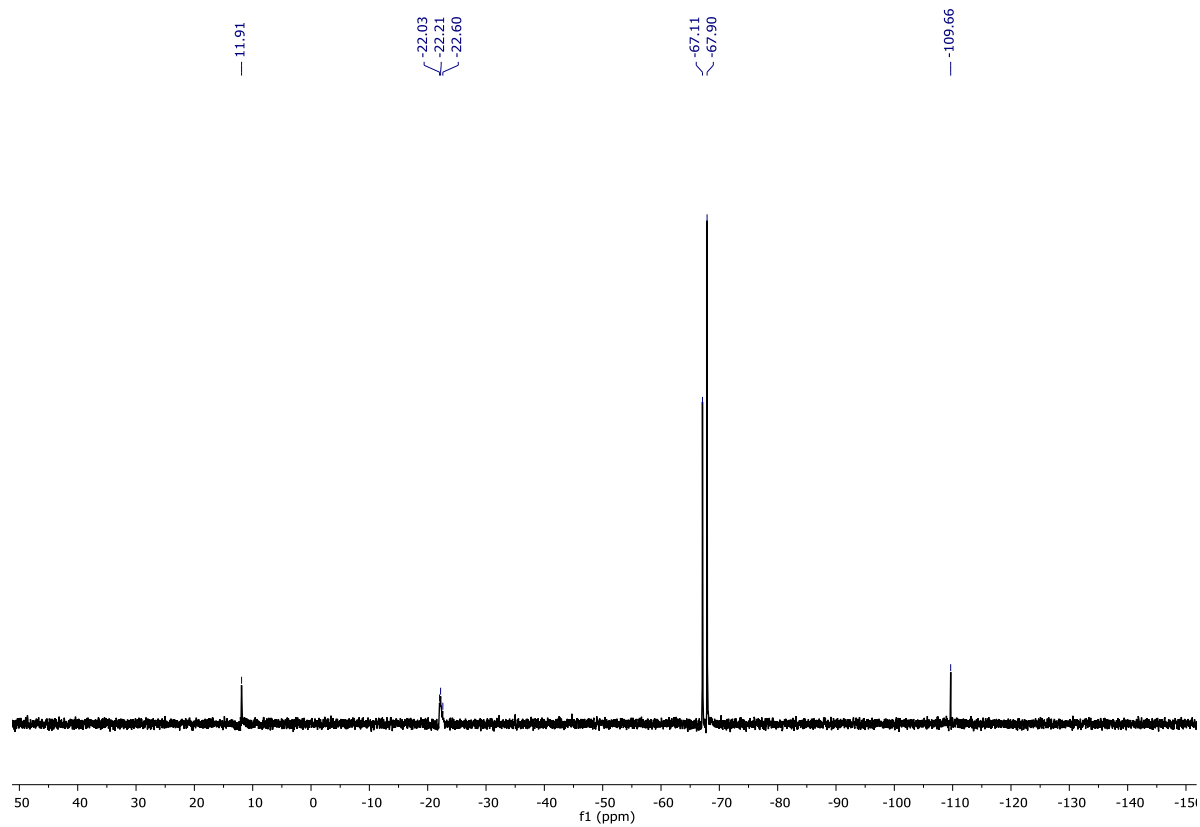
¹H NMR



¹³C NMR



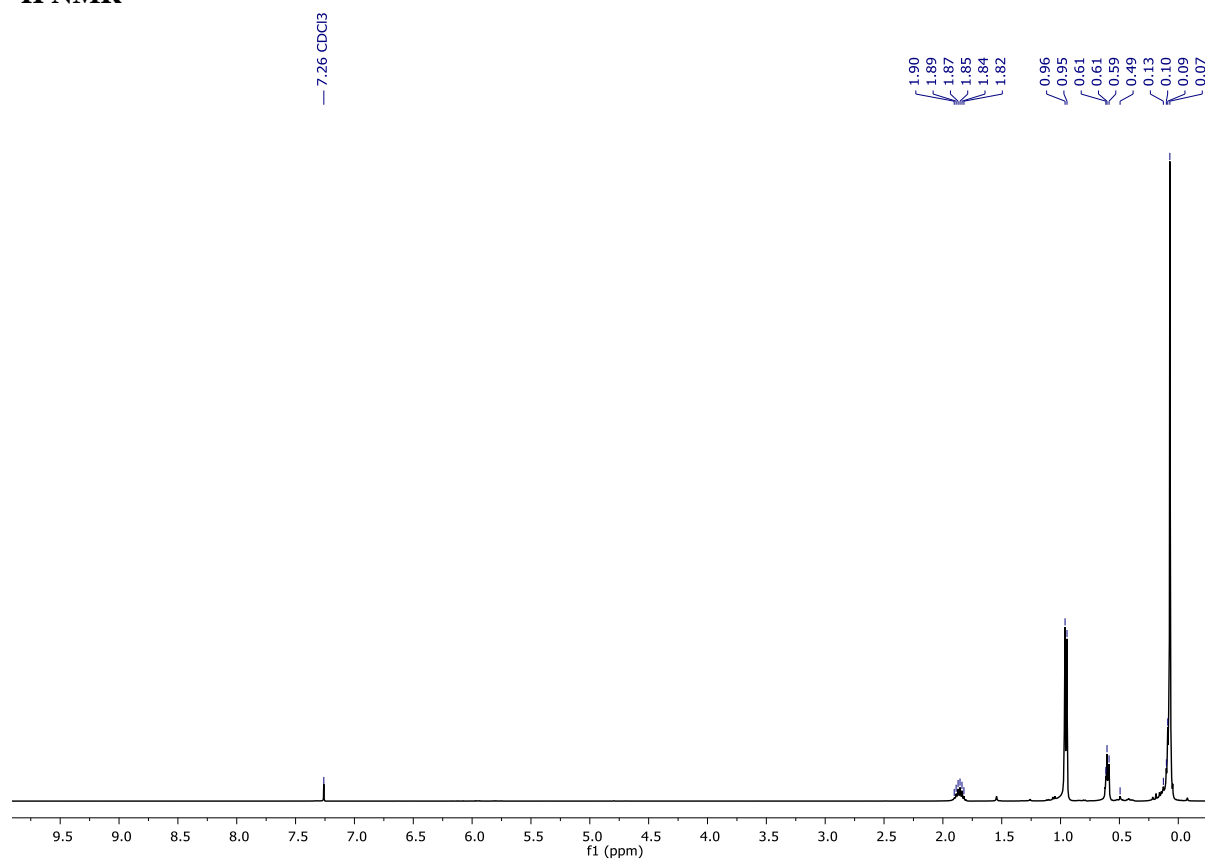
²⁹Si NMR



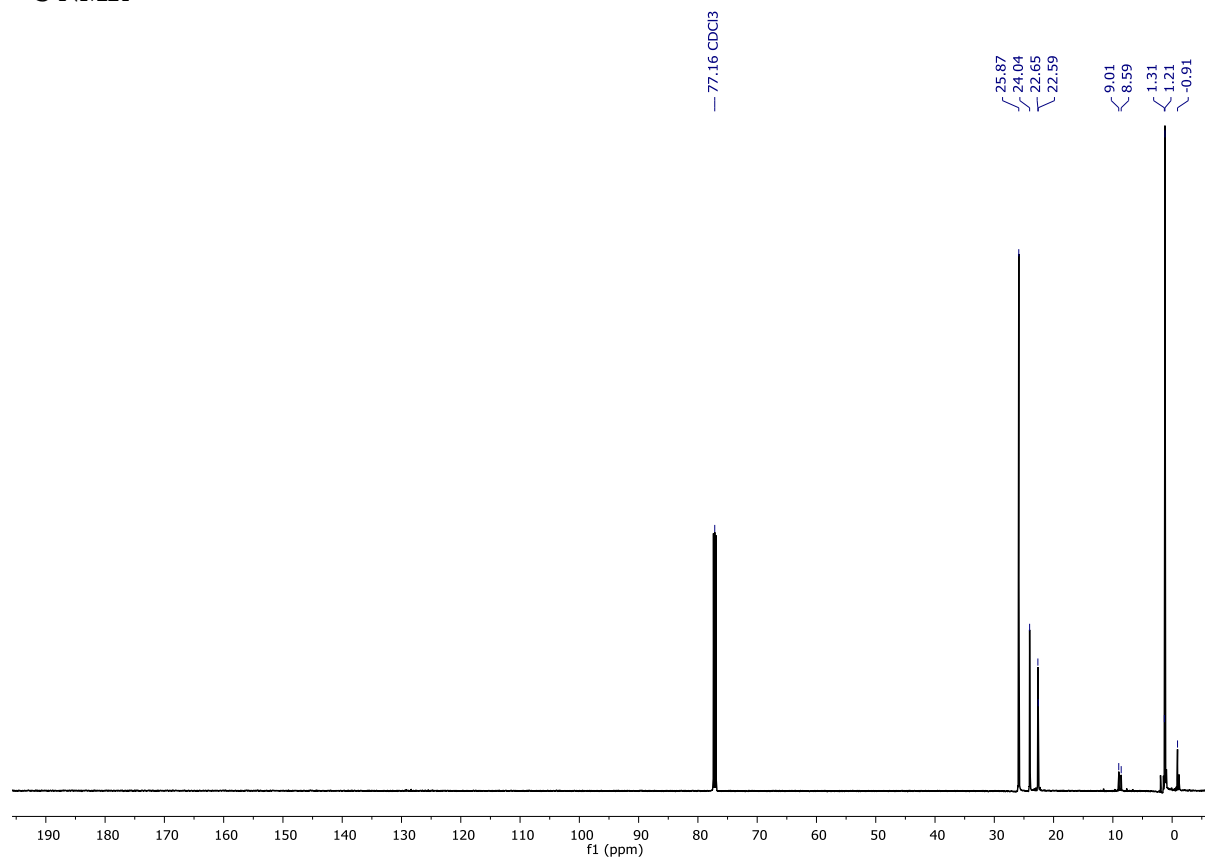
2-iBuT₈@PS2

¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.07-0.13 (m, -SiCH₃), 0.49, 0.59-0.61 (m, -CH₂-, -CH₂- (iBu)), 0.95-0.96 (m, -CH₃ (iBu)), 1.82-1.90 (m, -CH- (iBu)). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -0.91, 1.21, 1.31 (-SiCH₃), 8.59, 9.01 (-CH₂-), 22.59-22.65, 24.04, 25.87 (iBu). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 11.96 (-Si-CH₂-CH₂-Si-), -21.94, -22.16 (-SiCH₃), -67.10, -67.89, -109.66 (-SiO₄). **FT-IR** (cm⁻¹): 2955.38, 2924.79, 2869.81 (C-H), 1464.98 (C-H), 1259.06, 1229.16 (Si-C), 1089.76, 1017.18 (Si-O).

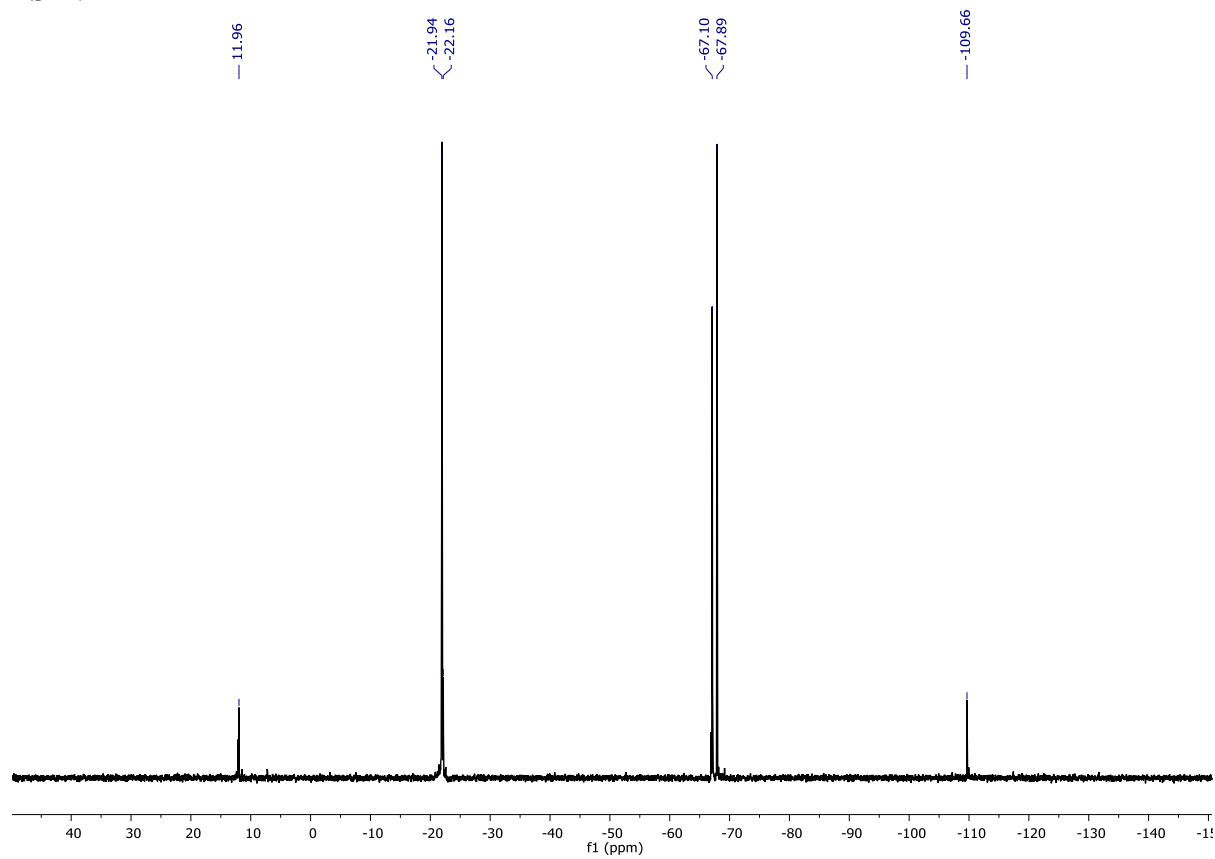
¹H NMR



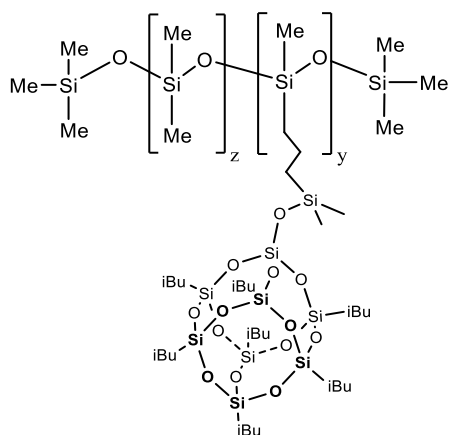
¹³C NMR



²⁹Si NMR



3-iBuT₈@PS

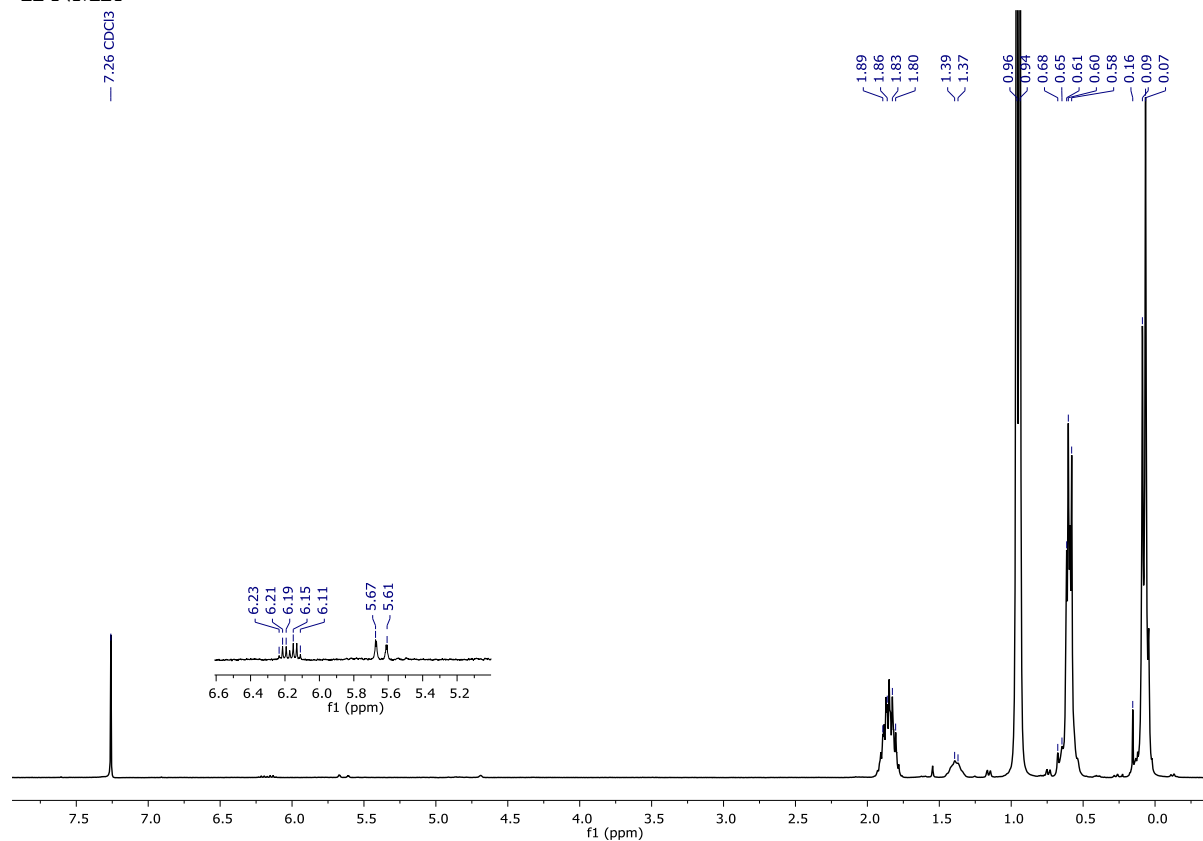


3-iBuT₈@PS1

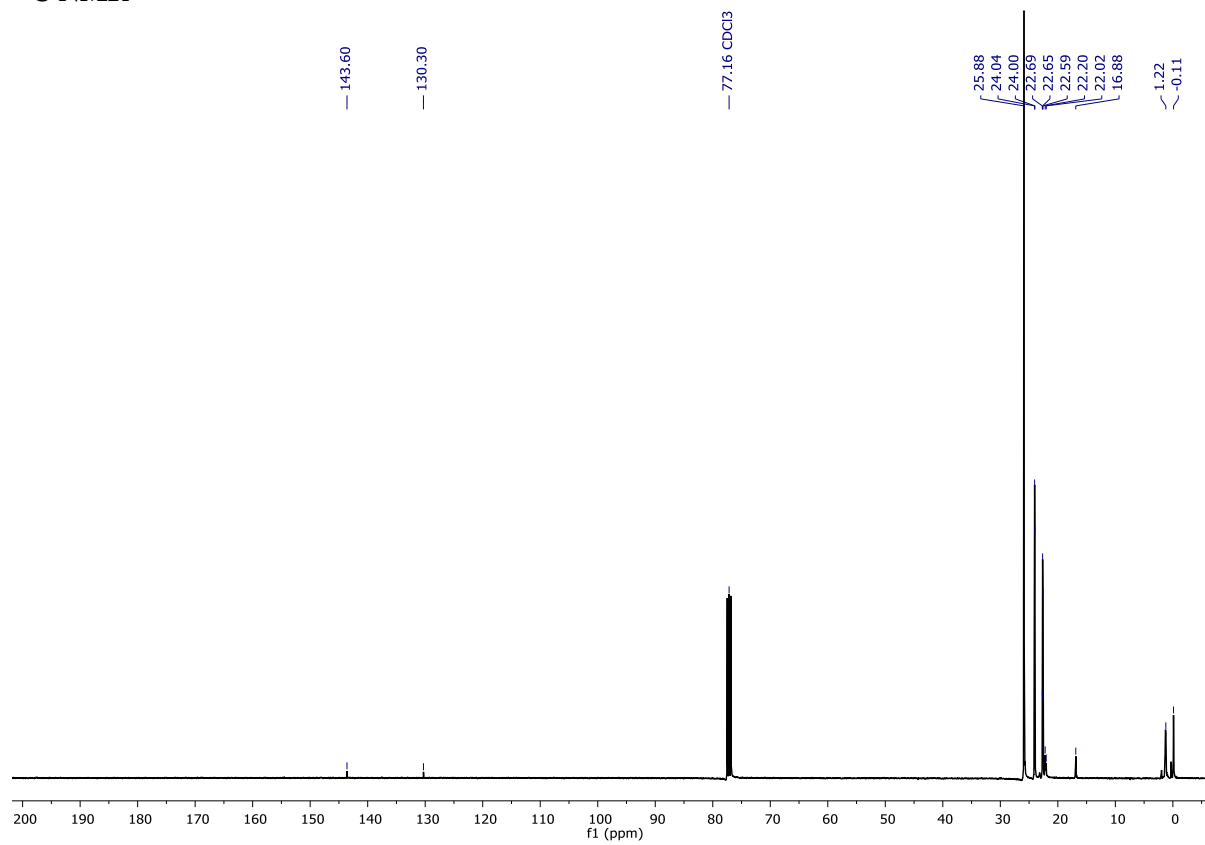
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.07-0.09 (m, -SiCH₃), 0.58-0.68 (m, -CH₂-, -CH₂- (iBu)), 0.94-0.96 (m, -CH₃ (iBu)), 1.37-1.39 (m, -CH₂-), 1.80-1.89 (m, -CH- (iBu)), 5.61-5.67 and 6.11-6.23 (m, -CH=CH- from dehydrogenative silylation by-product). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -0.11, 1.22 (-SiCH₃), 16.88, 22.02, 22.20 (-CH₂-), 22.59-22.69, 24.00-24.04, 25.88 (iBu), 130.30 and 143.60 (-CH=CH- from dehydrogenative silylation by-product). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 10.87 (-Si-CH₂-CH₂-CH₂-Si-), -21.94, -22.21, -23.00, (-SiCH₃), -67.11, -67.90, -109.66 (-SiO₄).

FT-IR (cm⁻¹): 2953.32, 2924.65, 2869.56 (-C-H), 1464.78 (-C-H), 1259.04, 1228.62 (Si-C), 1077.49 (Si-O).

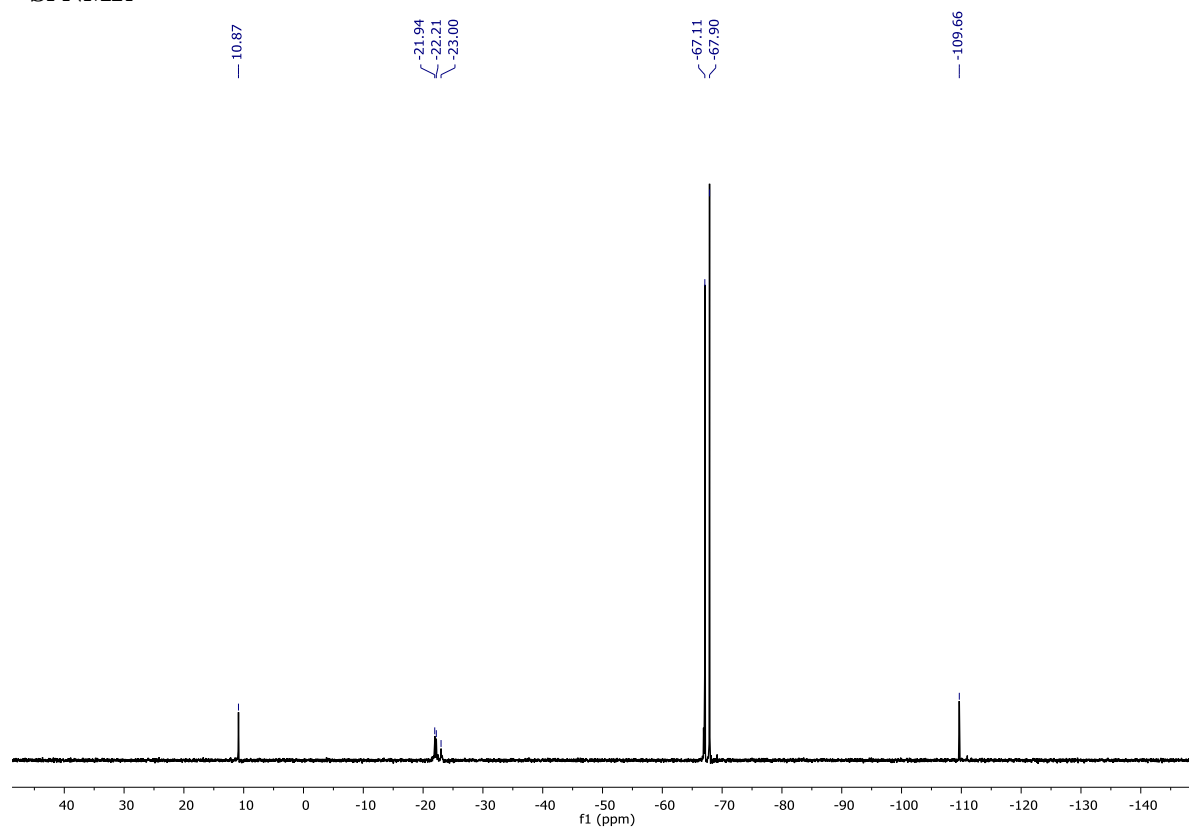
¹H NMR



¹³C NMR



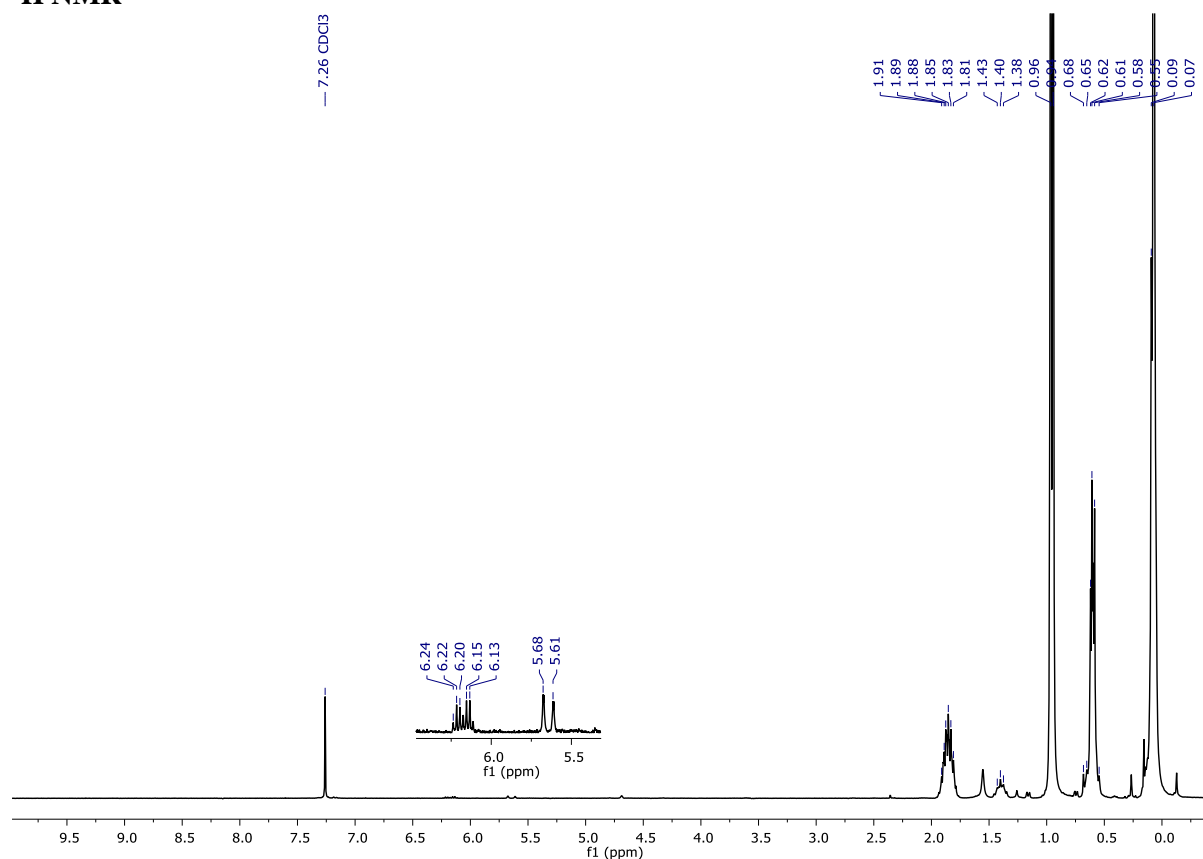
²⁹Si NMR



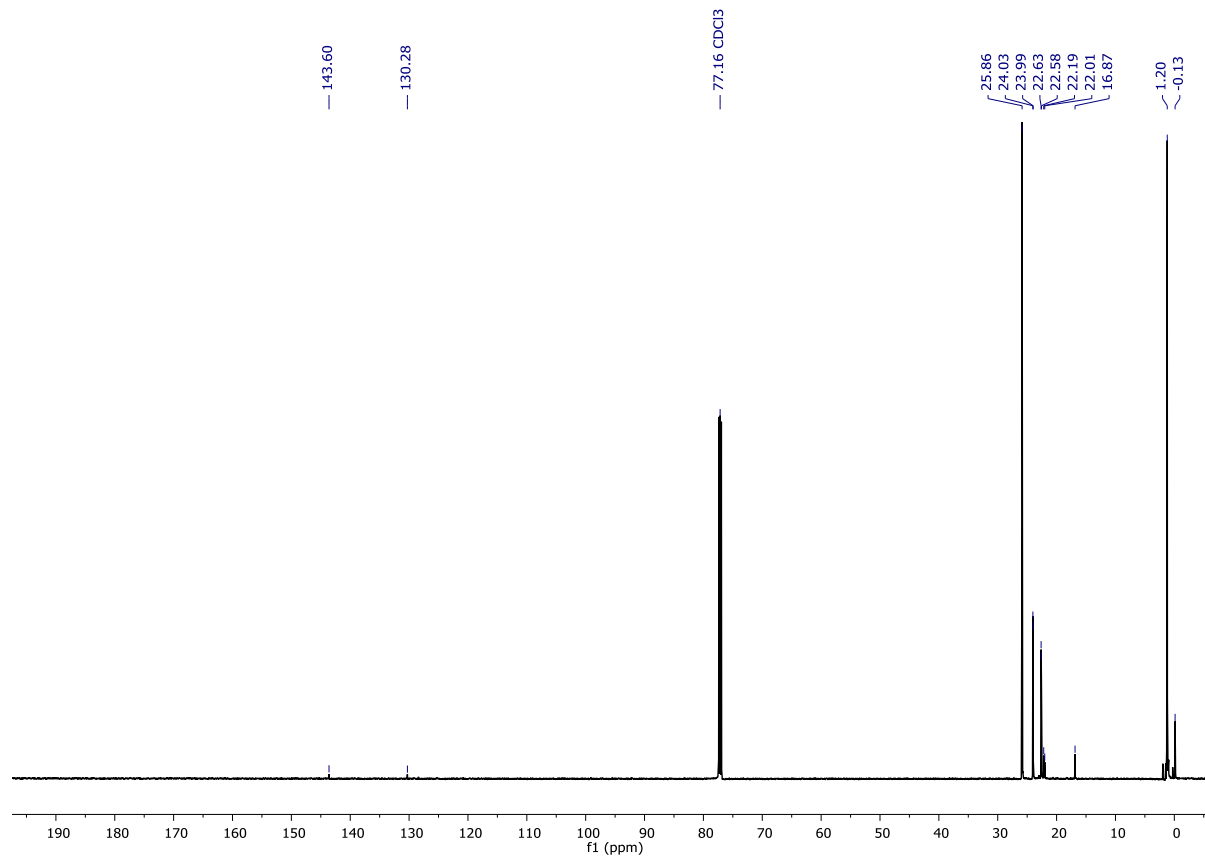
3-iBuT₈@PS2

¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.07-0.09 (m, -SiCH₃), 0.55-0.68 (m, -CH₂-, -CH₂- (iBu)), 0.94-0.96 (m, -CH₃ (iBu)), 1.38-1.43 (m, -CH₂-), 1.81-1.91 (m, -CH- (iBu)), 5.61-5.68 and 6.13-6.24 (m, -CH=CH- from dehydrogenative silylation by-product). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -0.13, 1.20 (-SiCH₃), 16.87, 22.01, 22.19 (-CH₂-), 22.58-22.63, 23.99-24.03, 25.86 (iBu), 130.28 and 143.60 (-CH=CH- from dehydrogenative silylation by-product). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 10.89 (-Si-CH₂-CH₂-CH₂-Si-), -21.94, -22.21, -22.98, (-SiCH₃), -67.10, -67.89, -109.65 (-SiO₄). **FT-IR** (cm⁻¹): 2955.84, 2925.46, 2870.51 (-C-H), 1465.15 (-C-H), 1258.63, 1228.71 (Si-C), 1083.40, 1012.74 (Si-O).

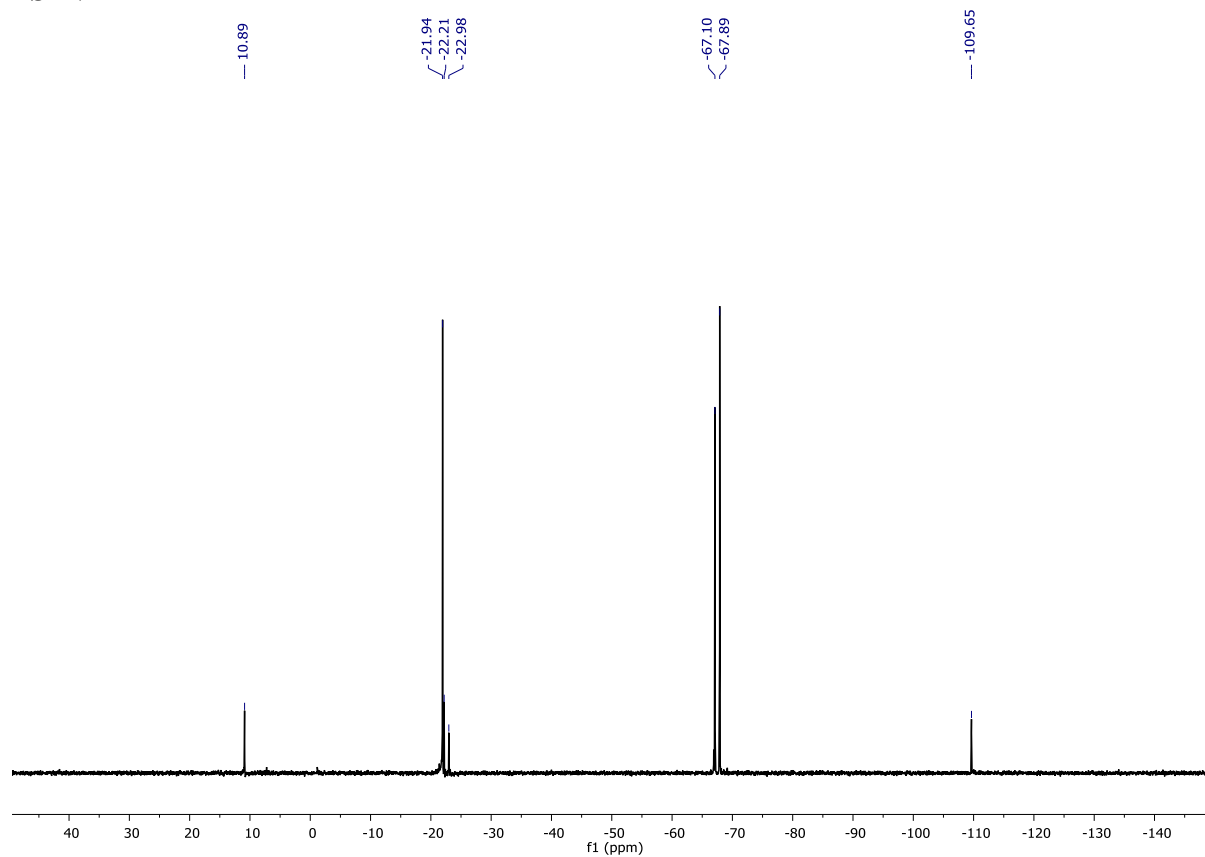
¹H NMR



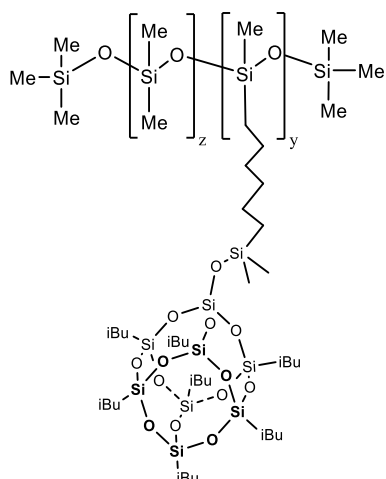
¹³C NMR



²⁹Si NMR



4-iBuT₈@PS

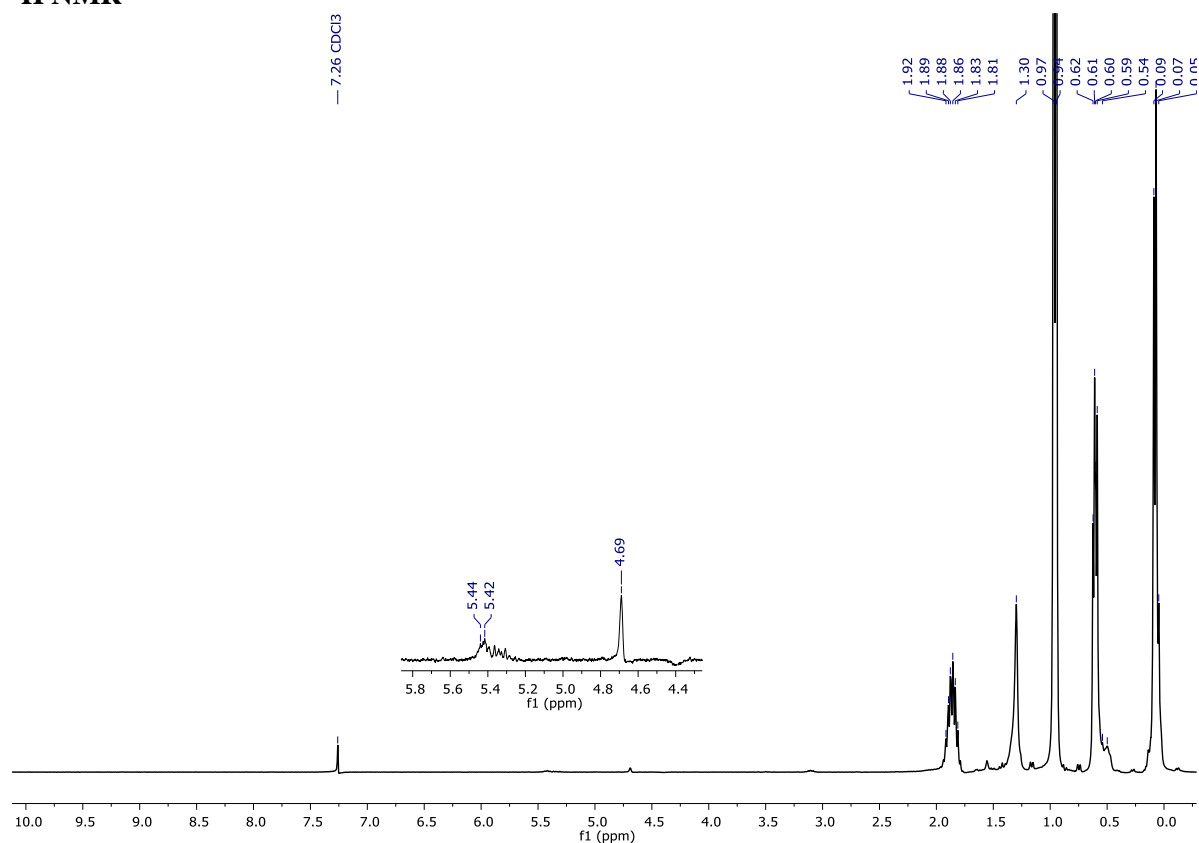


4-iBuT₈@PS1

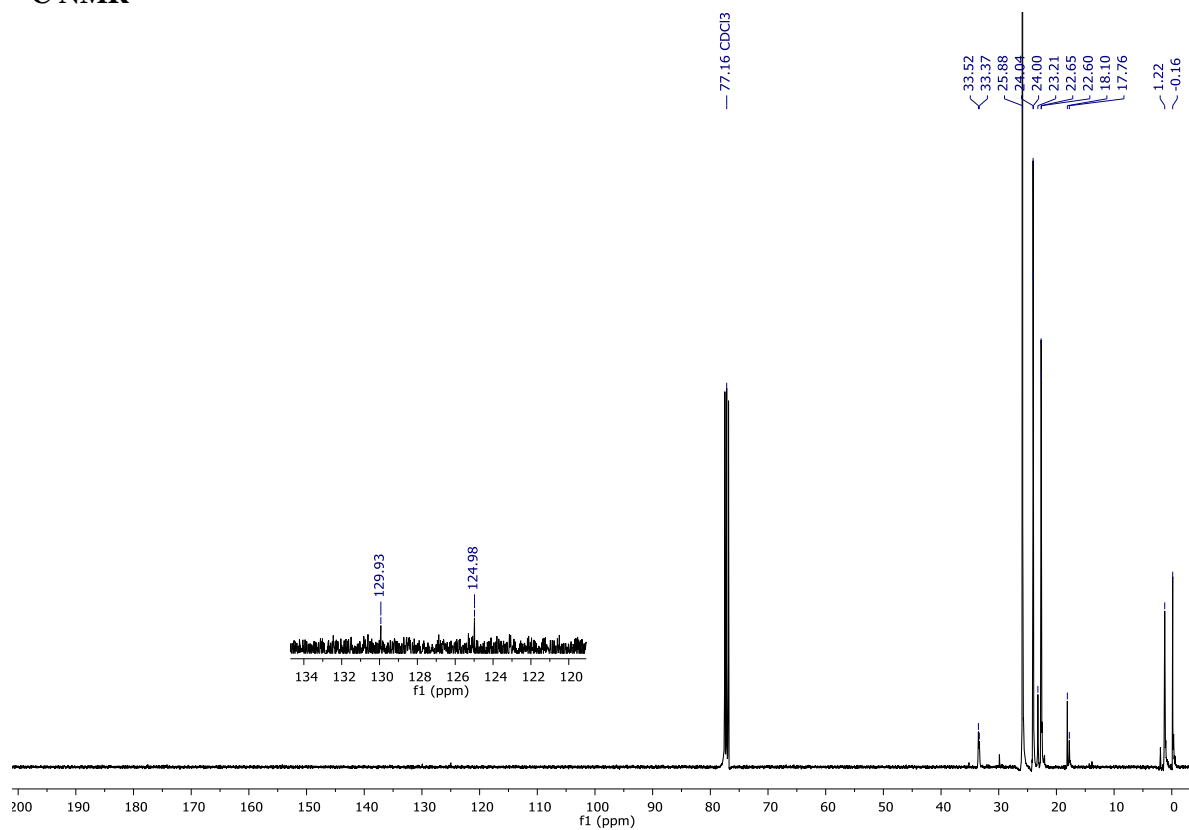
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.05-0.09 (m, -SiCH₃), 0.50-0.62 (m, -CH₂-, -CH₂- (iBu)), 0.94-0.97 (m, -CH₃ (iBu)), 1.30 (m, -CH₂-), 1.81-1.92 (m, -CH- (iBu)), 4.69 (s, -Si-H), 5.42-5.44 (m, -CH=CH- from by-product of bond isomerization). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -0.16, 1.22 (-SiCH₃), 17.76, 18.10, 23.21, 33.37, 33.52 (-CH₂-), 22.60-22.65, 24.00-24.04, 25.88 (iBu), 124.98 and 129.93 (-CH=CH- from by-product of bond isomerization). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 11.36 (-Si-(CH₂)₆-Si-), -21.96, -22.23, -22.36 (-SiCH₃), -67.10, -67.89, -109.70 (-SiO₄).

FT-IR (cm⁻¹): 2953.14, 2923.48, 2868.95 (-C-H), 1464.53 (-C-H), 1258.85, 1228.75 (Si-C), 1077.23 (Si-O).

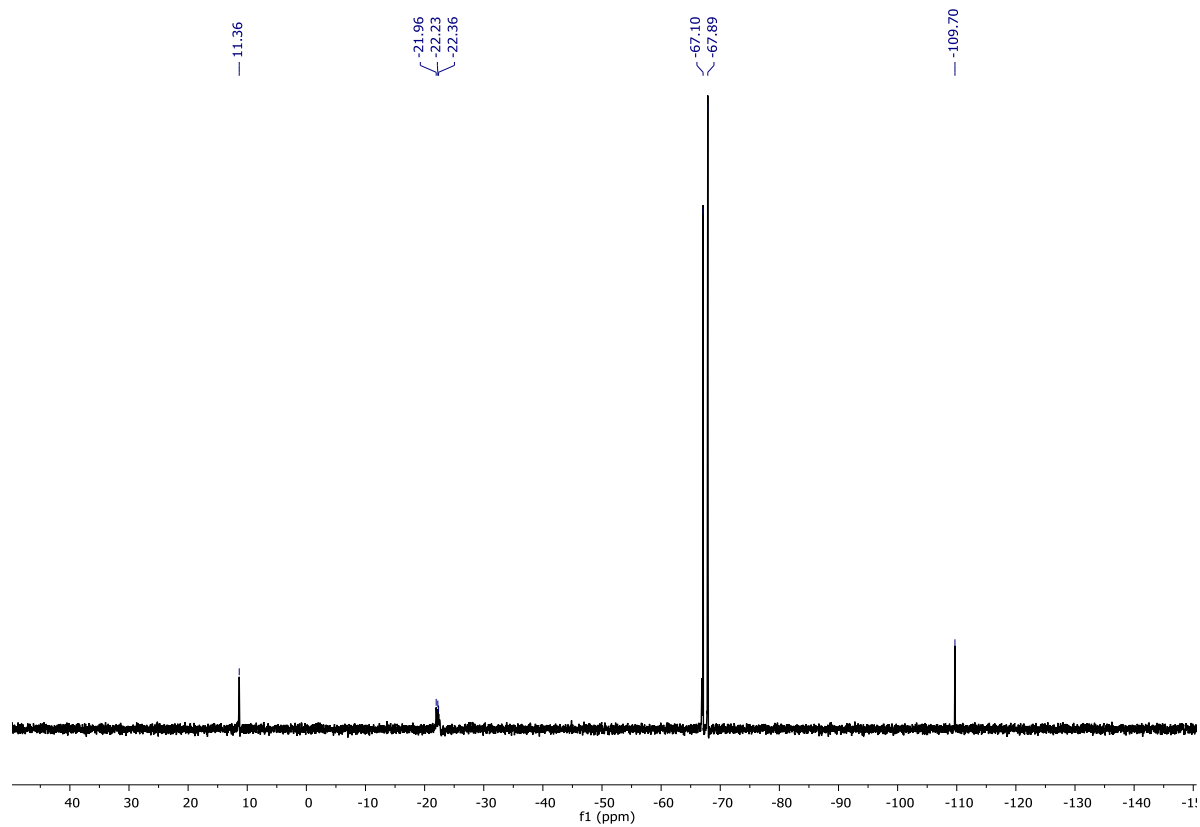
¹H NMR



¹³C NMR



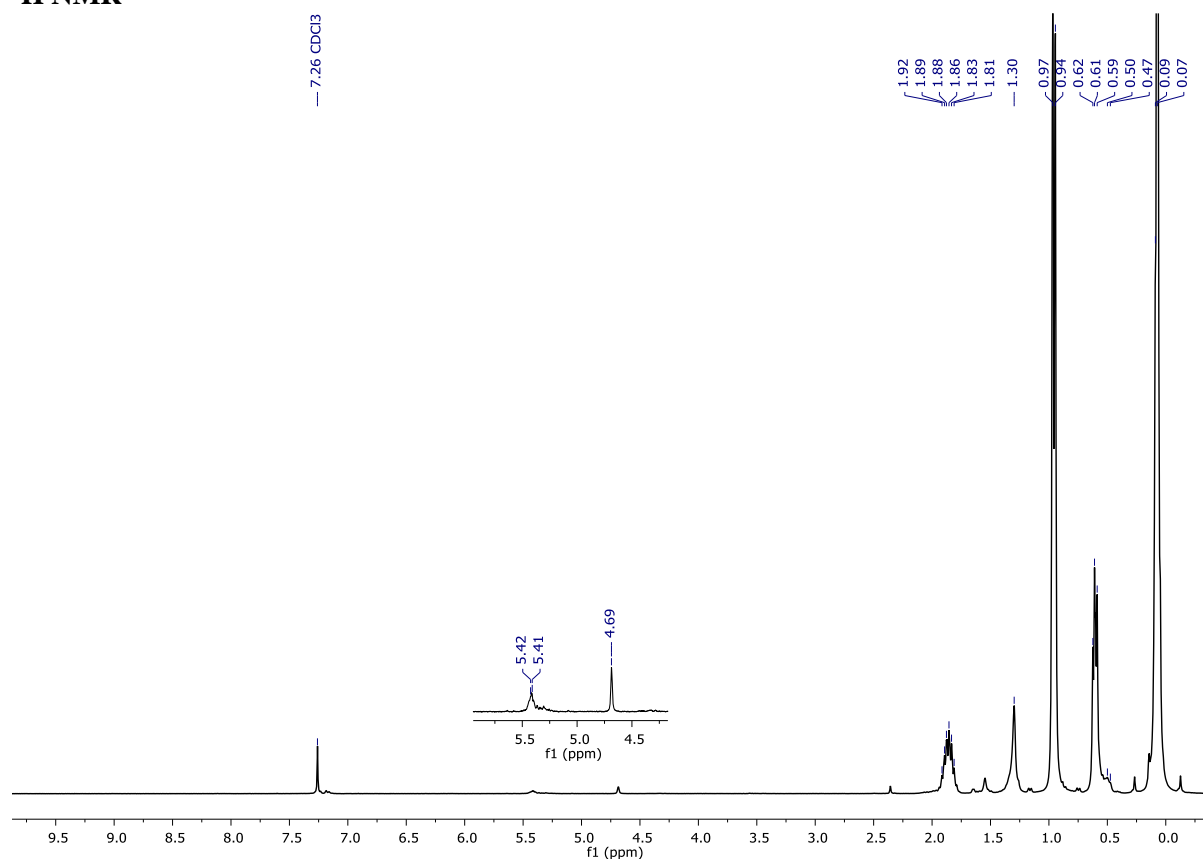
²⁹Si NMR



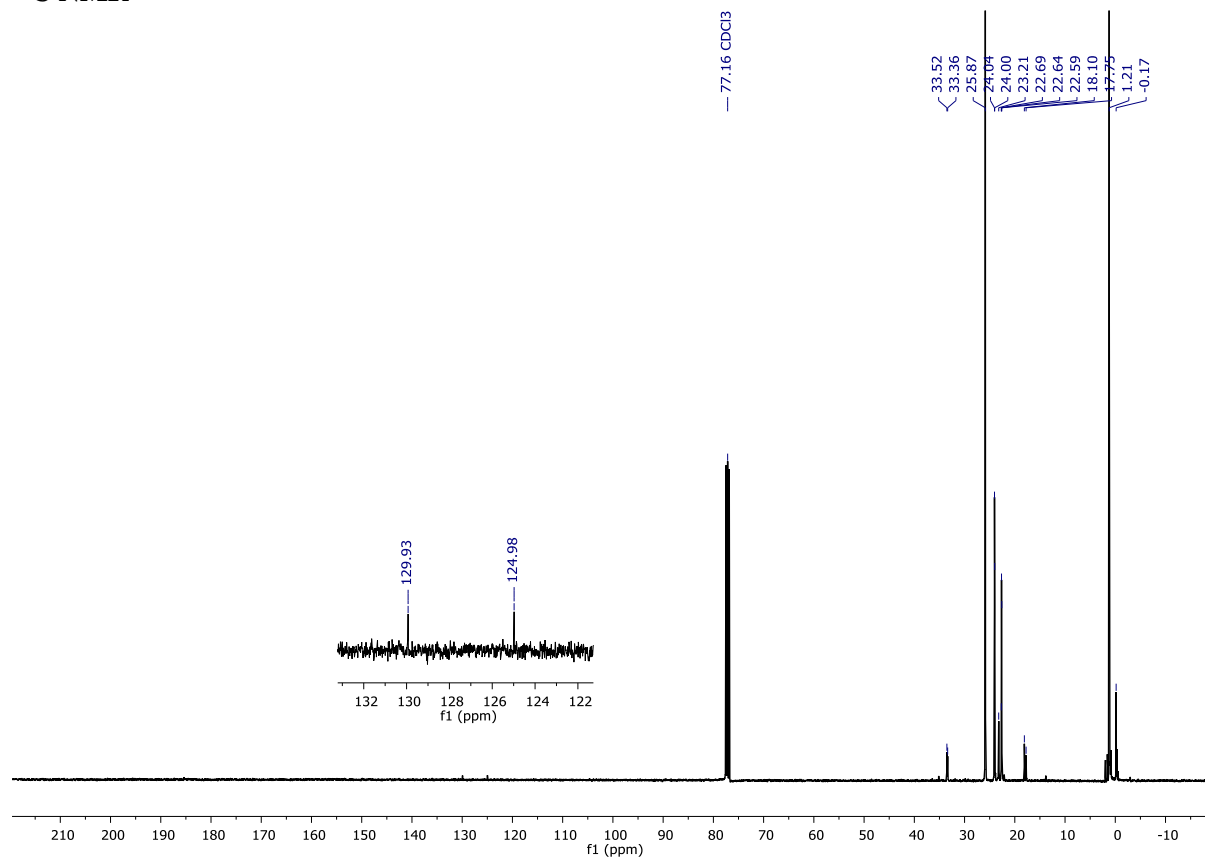
4-iBuT₈@PS2

¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.07-0.09 (m, -SiCH₃), 0.47-0.62 (m, -CH₂, -CH₂- (iBu)), 0.94-0.97 (m, -CH₃ (iBu)), 1.30 (m, -CH₂-), 1.81-1.92 (m, -CH- (iBu)), 4.69 (s, -Si-H), 5.41-5.42 (m, -CH=CH- from by-product of bond isomerization). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -0.17, 1.21 (-SiCH₃), 17.75, 18.10, 23.21, 33.36, 33.52 (-CH₂-), 22.64-22.69, 24.00-24.04, 25.87 (iBu), 124.98 and 129.93 (-CH=CH- from by-product of bond isomerization). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 11.37 (-Si-(CH₂)₆-Si-), -21.95, -22.01, -22.24, -22.37 (-SiCH₃), -67.09, -67.89, -109.69 (-SiO₄). **FT-IR** (cm⁻¹): 2955.88, 2924.57, 2870.22 (-C-H), 1465.08 (-C-H), 1258.60, 1228.59 (Si-C), 1081.19, 1013.48 (Si-O).

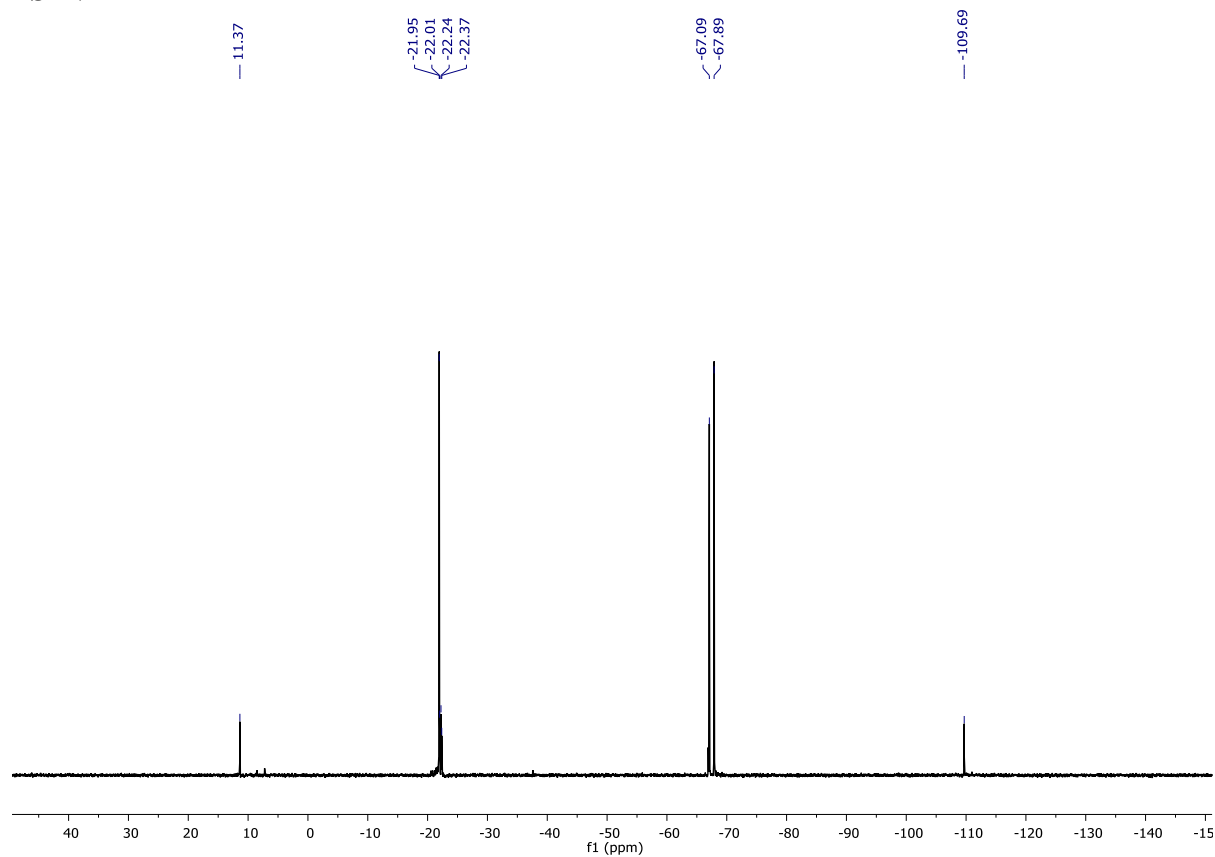
¹H NMR



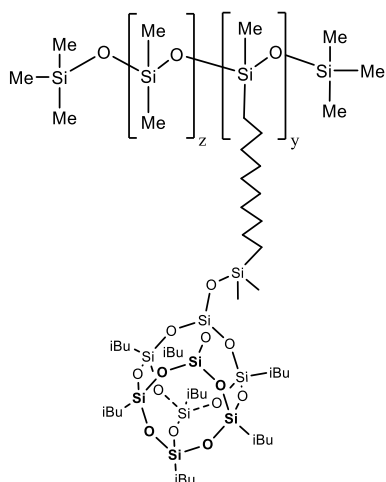
¹³C NMR



²⁹Si NMR



5-iBuT₈@PS

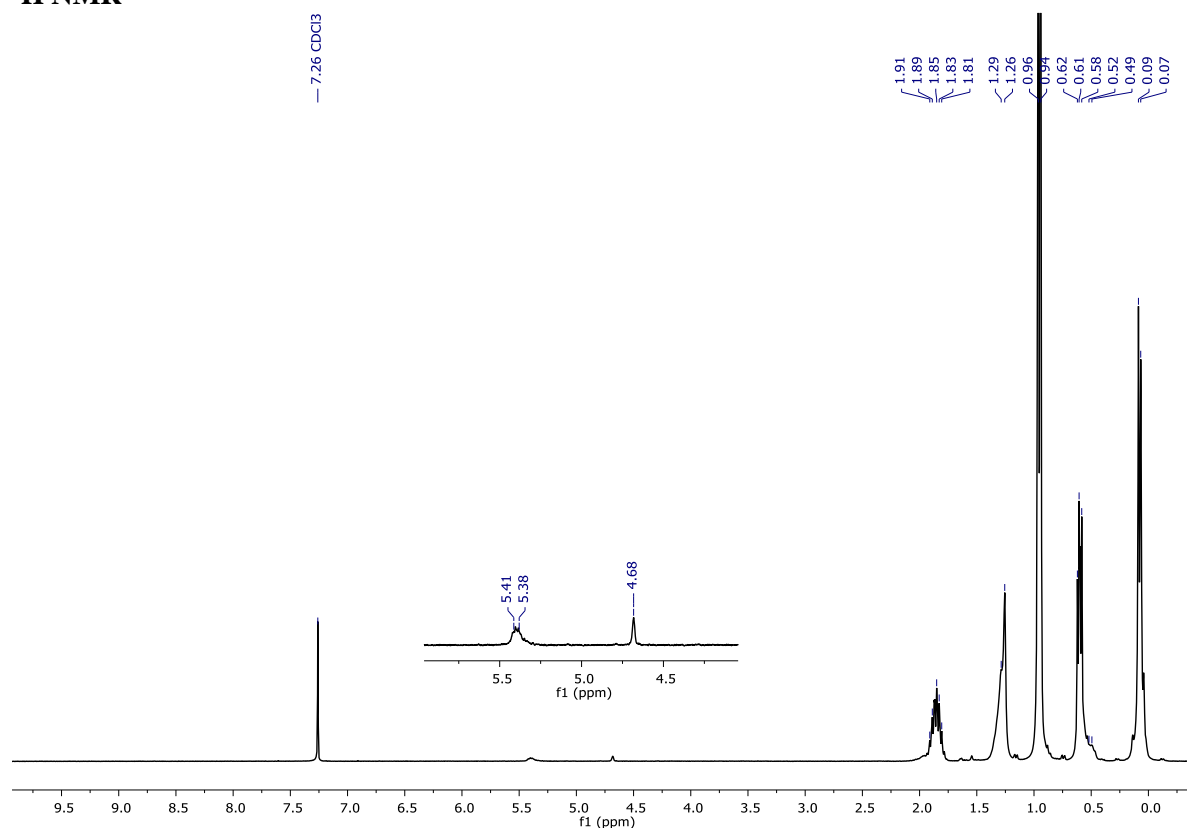


5-iBuT₈@PS1

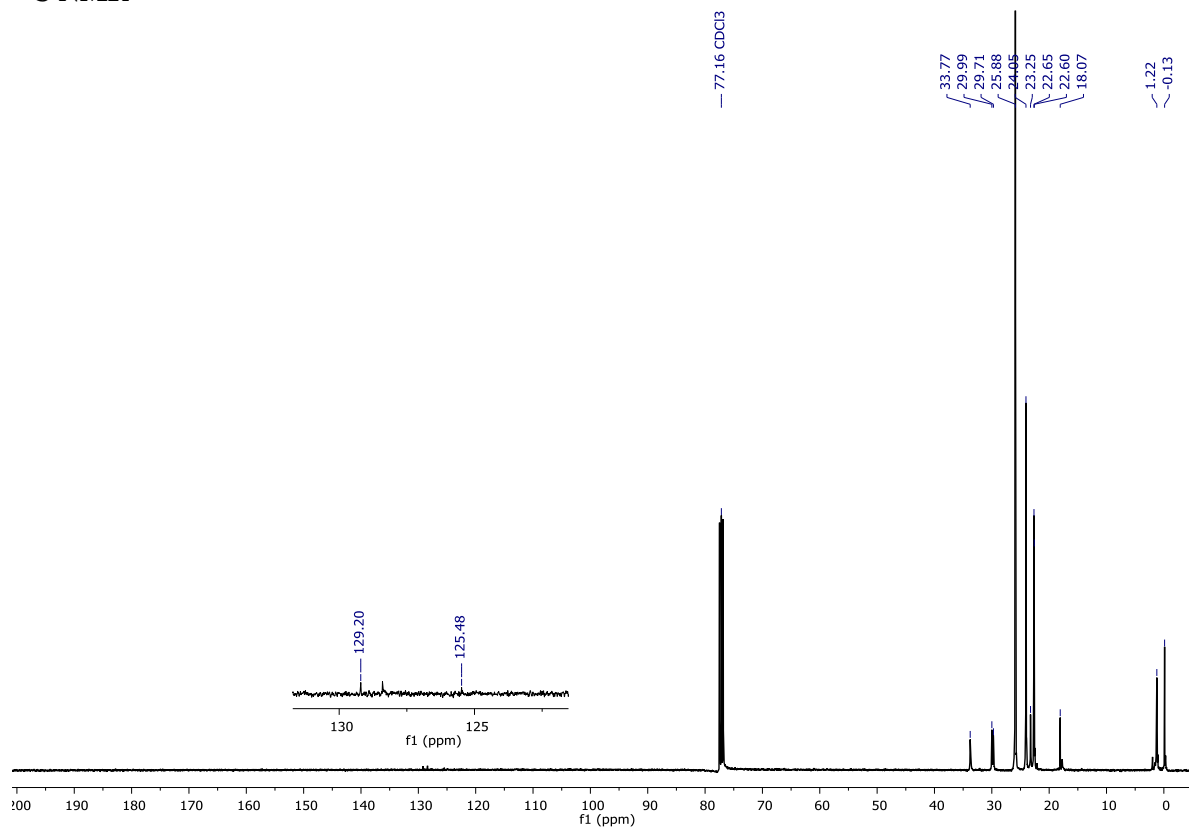
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.07-0.09 (m, -SiCH₃), 0.49-0.62 (m, -CH₂-, -CH₂- (iBu)), 0.94-0.96 (m, -CH₃ (iBu)), 1.26-1.29 (m, -CH₂-), 1.81-1.91 (m, -CH- (iBu)), 4.68 (s, -Si-H), 5.38- 5.41 (m, -CH=CH- from by-product of bond isomerization). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -0.13, 1.22 (-SiCH₃), 18.07, 23.25, 29.99, 33.77 (-CH₂-), 22.60-22.65, 24.05, 25.88 (iBu), 125.48 and 129.20 (-CH=CH- from by-product of bond isomerization). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 11.38 (-Si-(CH₂)₁₀-Si-), -21.94, -22.29, (-SiCH₃), -67.10, -67.89, -109.70 (-SiO₄).

FT-IR (cm⁻¹): 2953.13, 2923.21, 2868.37 (-C-H), 1464.53 (-C-H), 1258.84, 1228.88 (Si-C), 1081.40 (Si-O).

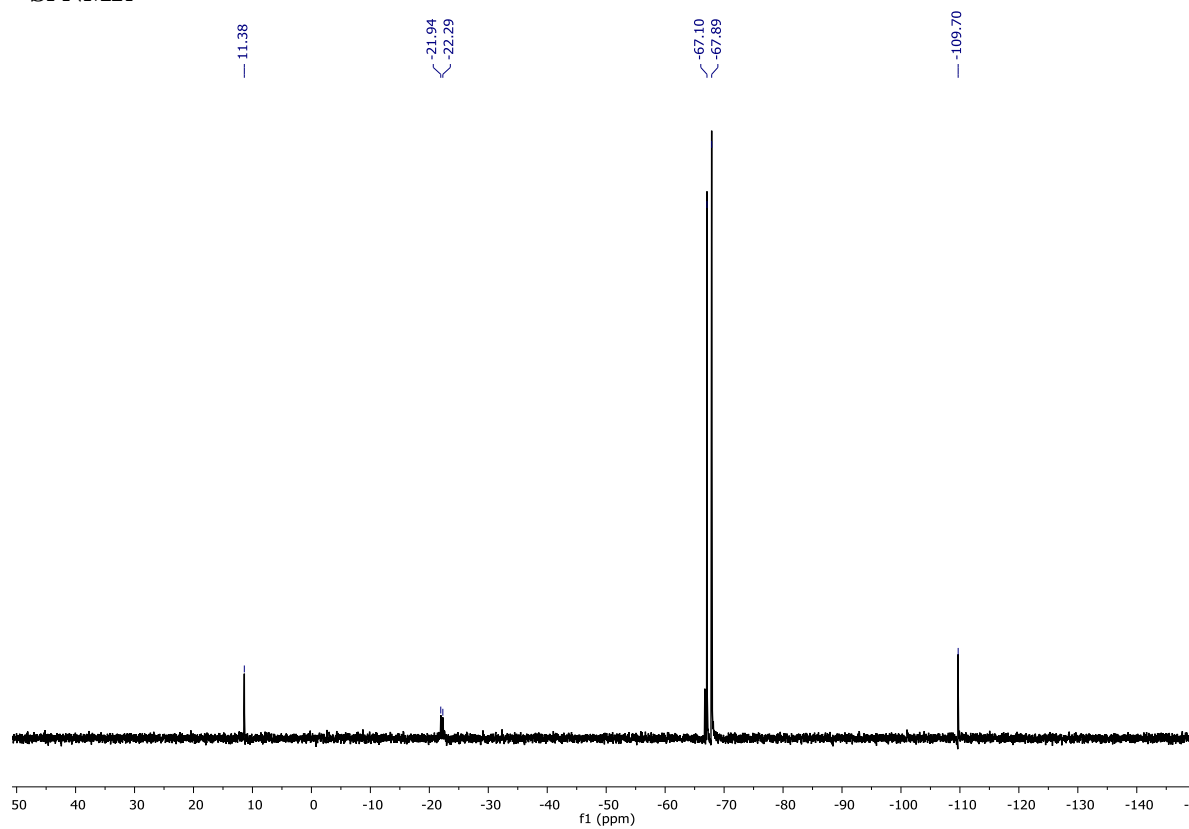
¹H NMR



¹³C NMR



²⁹Si NMR

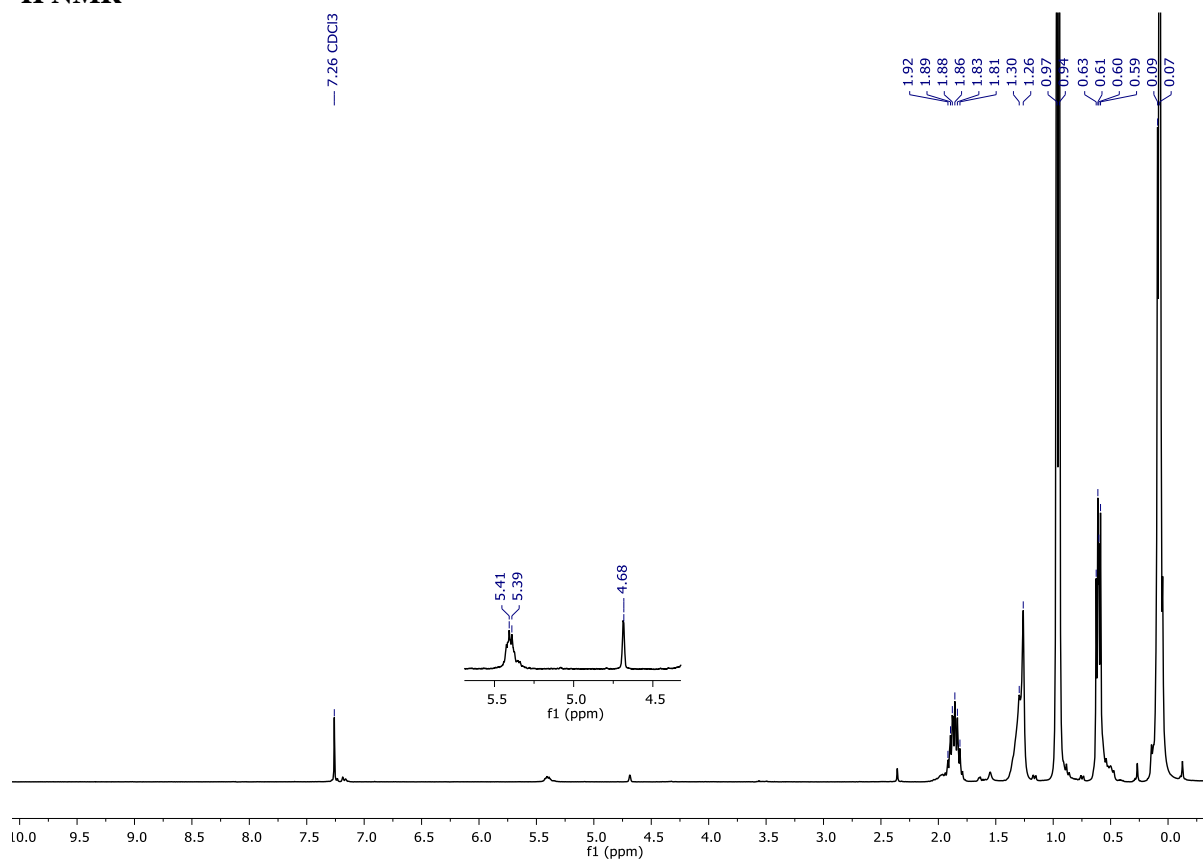


5-iBuT₈@PS2

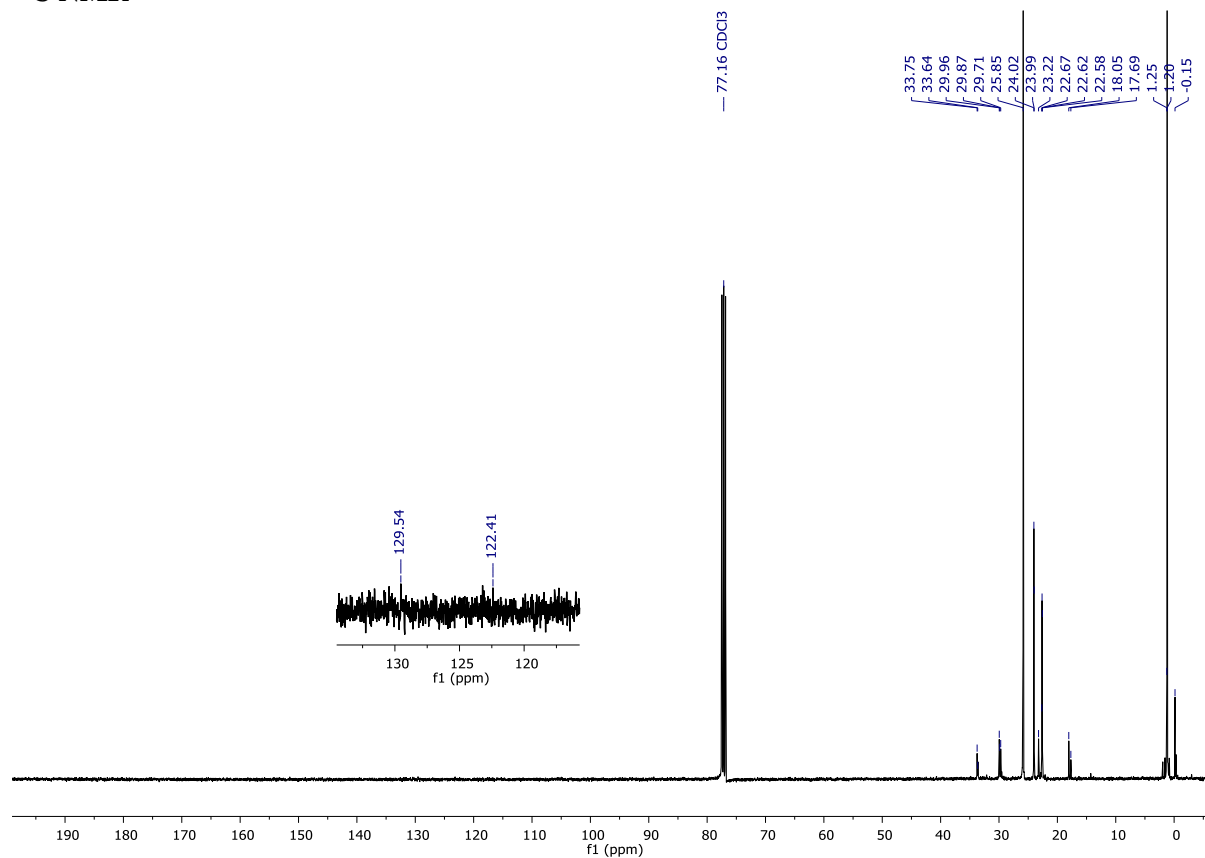
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.07-0.09 (m, -SiCH₃), 0.59-0.63 (m, -CH₂-, -CH₂- (iBu)), 0.94-0.97 (m, -CH₃ (iBu)), 1.26-1.30 (m, -CH₂-), 1.81-1.92 (m, -CH- (iBu)), 4.68 (s, -Si-H), 5.39- 5.41 (m, -CH=CH- from by-product of bond isomerization). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -0.15, 1.20, 1.25 (-SiCH₃), 17.69, 18.05, 23.22, 29.71-29.96, 33.64-33.75 (-CH₂-), 22.58-22.67, 23.99-24.02, 25.85 (iBu), 123.21 and 129.54 (-CH=CH- from by-product of bond isomerization). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 11.40 (-Si-(CH₂)₁₀-Si-), -21.94, -22.24, (-SiCH₃), -67.10, -67.89, -109.70 (-SiO₄).

FT-IR (cm⁻¹): 2955.17, 2923.92, 2855.19 (-C-H), 1464.88 (-C-H), 1258.66, 1228.51 (Si-C), 1083.35, 1012.68 (Si-O).

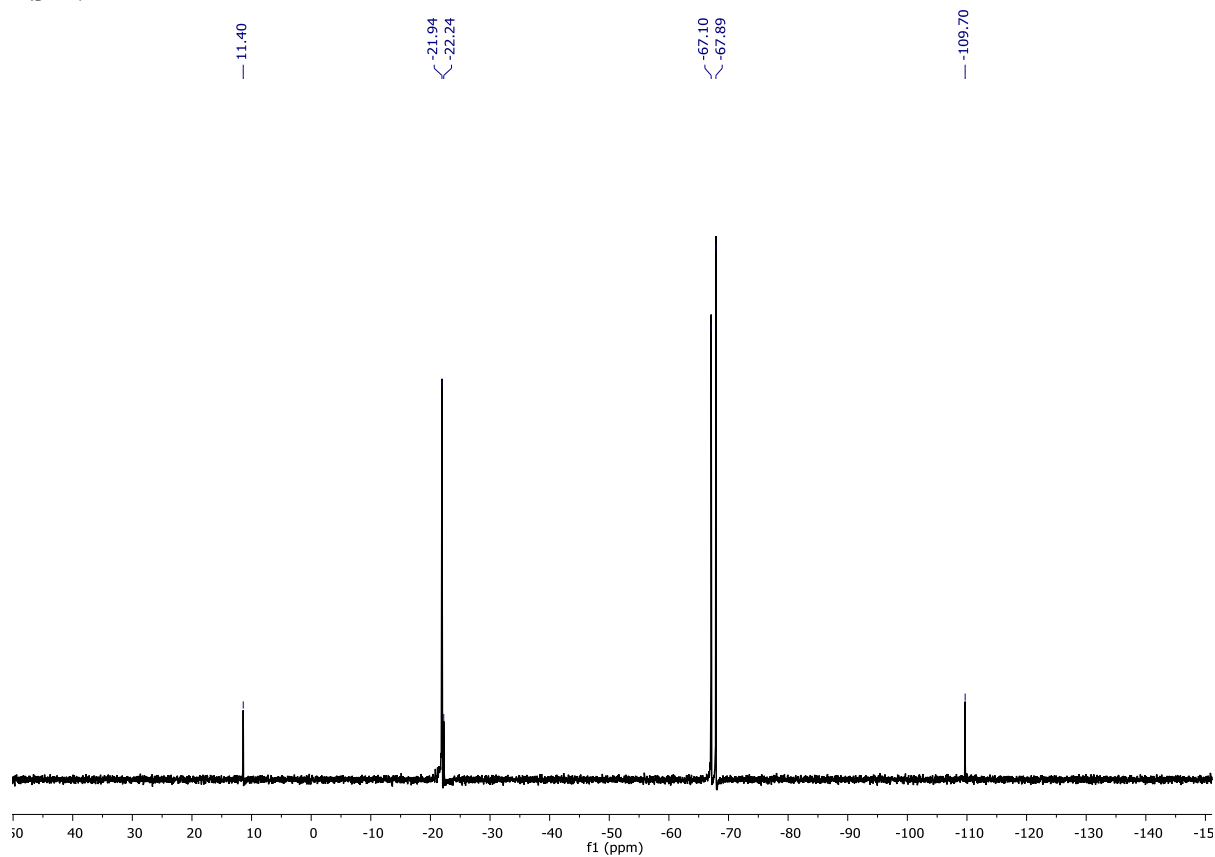
¹H NMR



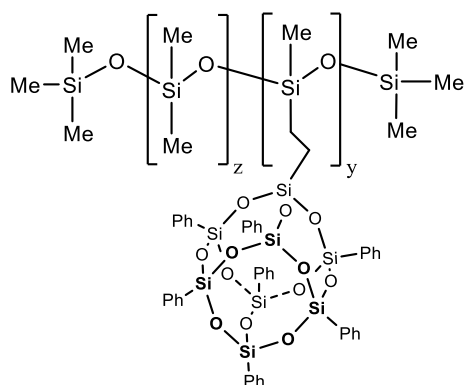
¹³C NMR



²⁹Si NMR



1-PhT₈@PS

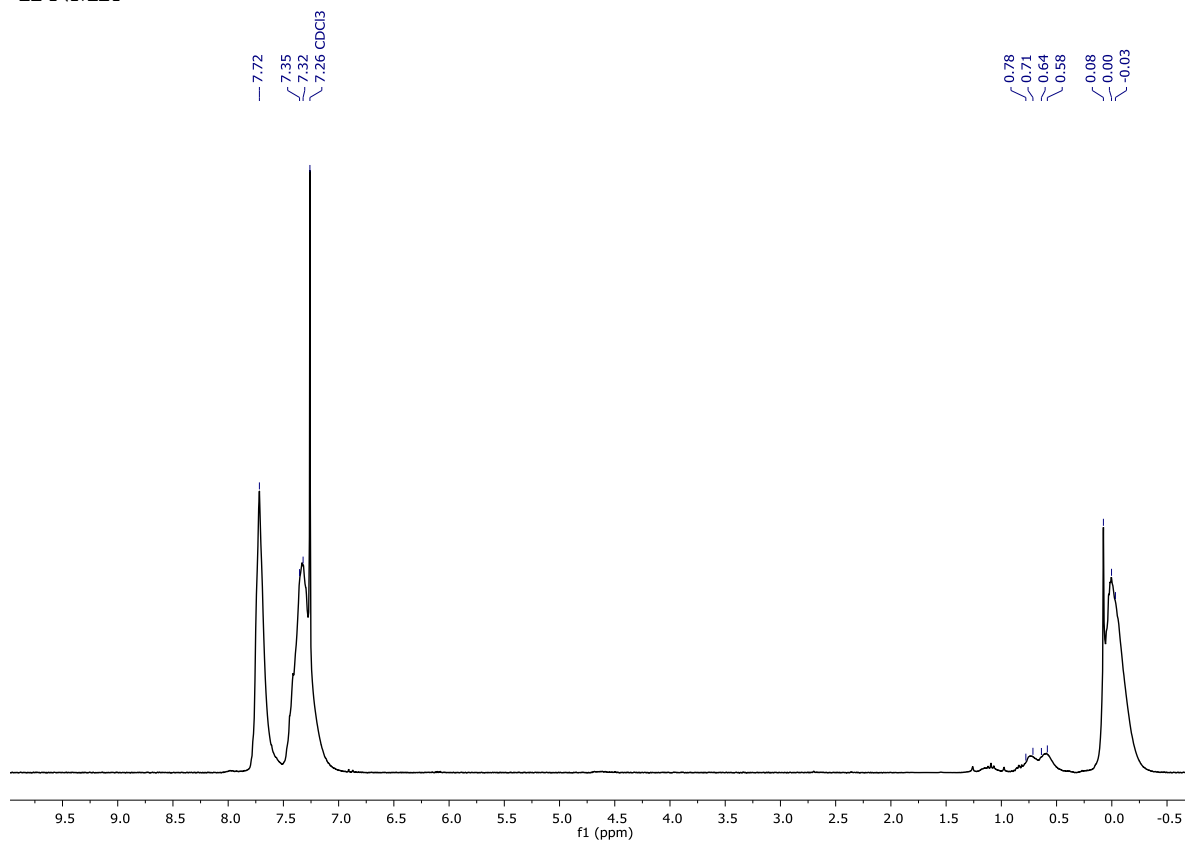


1-PhT₈@PS1

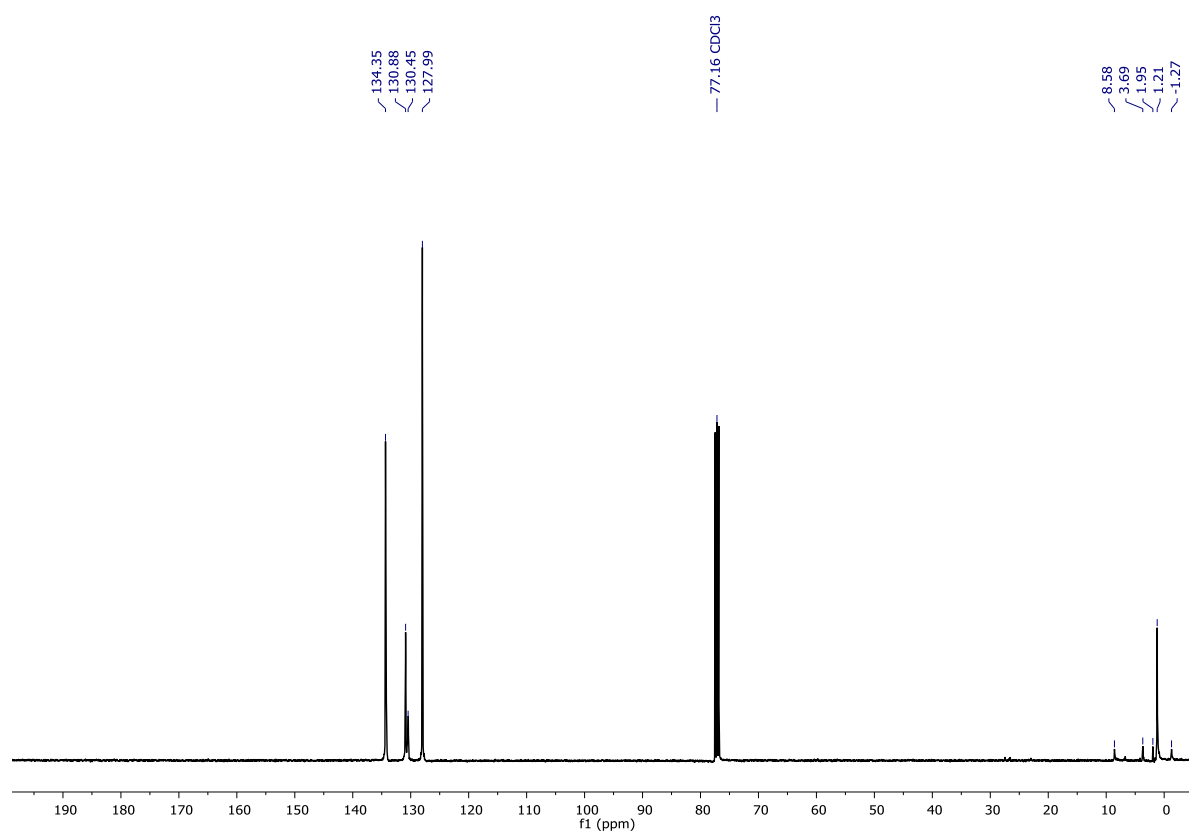
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): -0.03, 0.00 (m, -SiCH₃), 0.58-0.78 (m, -CH₂-), 7.32-7.35, 7.72 (m, Ph). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -1.27, 1.21, 1.95 (-SiCH₃), 3.69, 8.58 (-CH₂-), 127.99, 130.45, 130.88, 134.35 (Ph). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): -21.82, -22.59 (-SiCH₃), -64.50 (-Si-CH₂-CH₂-Si-), -78.29, -78.57, -78.80.

FT-IR (cm⁻¹): 3073.39, 3051.43, 3028.85 (C-H phenyl), 2959.68 (-C-H), 1594.37 (C=C phenyl), 1489.64 (-C-H), 1430.53 (C=C phenyl), 1259.53 (Si-C), 1080.27, 1011.50 (Si-O), 996.80 (C-H phenyl).

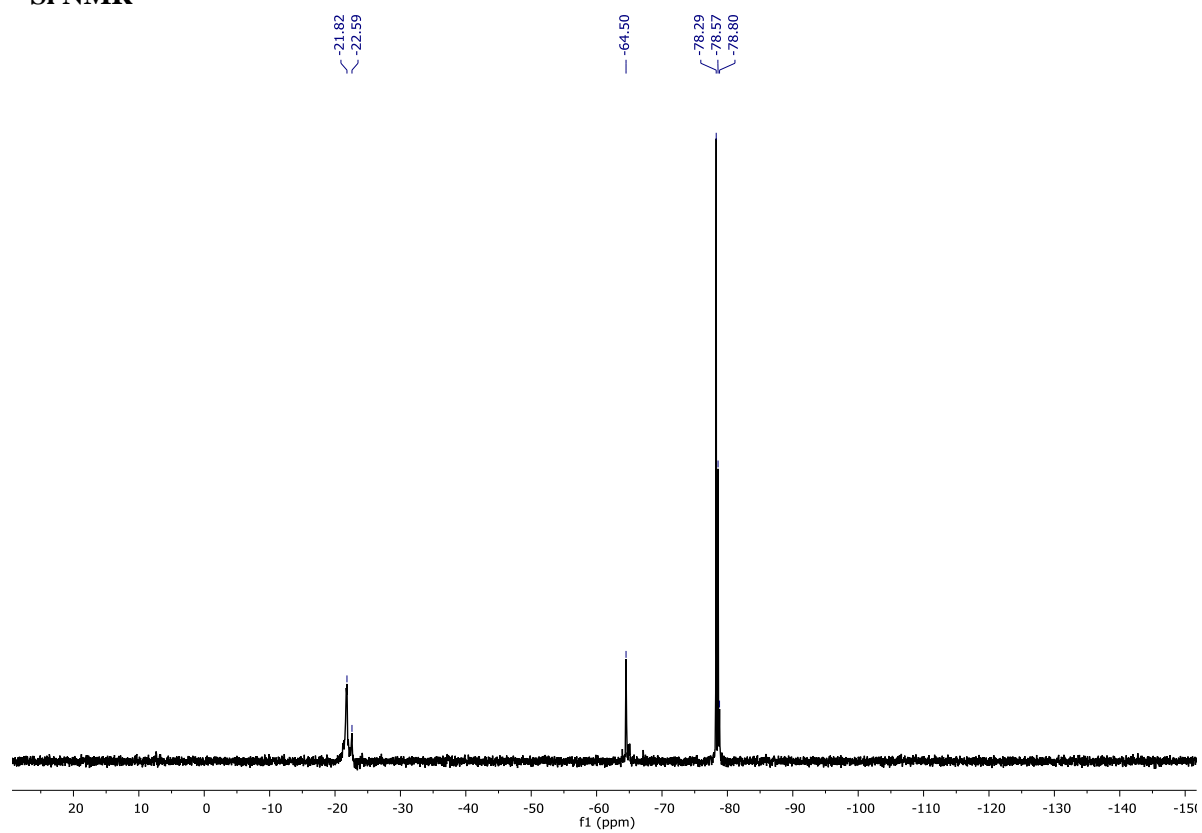
¹H NMR



¹³C NMR



²⁹Si NMR

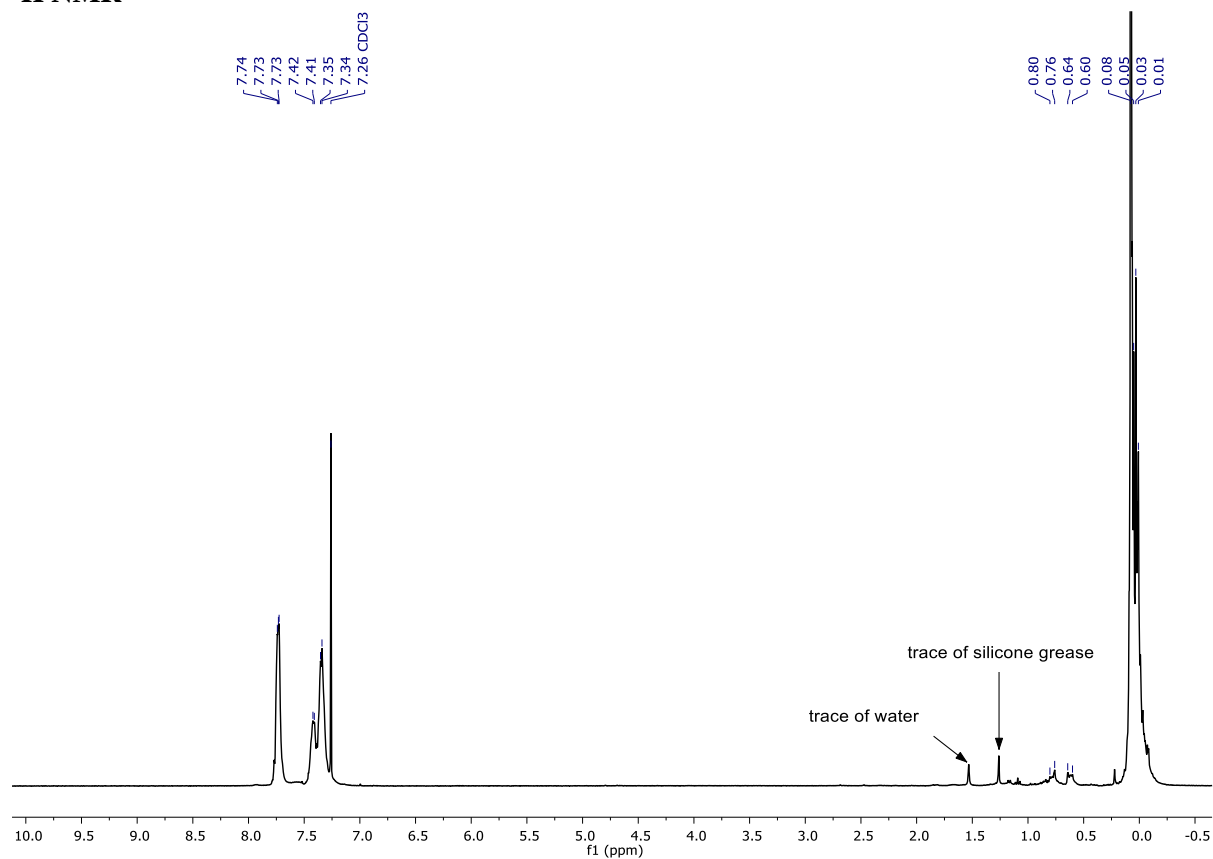


1-PhT₈@PS2

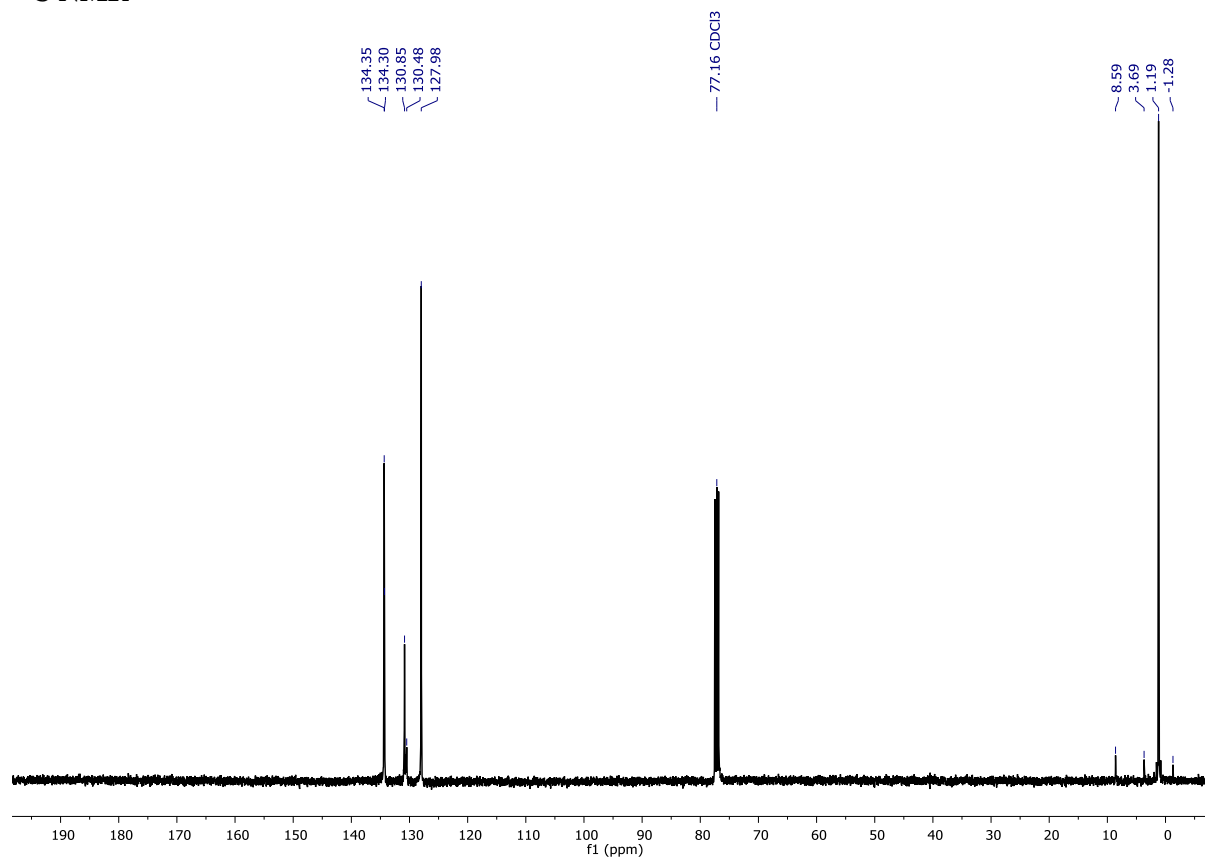
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.01-0.08 (m, -SiCH₃), 0.60-0.80 (m, -CH₂-), 7.34-7.42, 7.73-7.74 (m, Ph). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -1.28, 1.19 (-SiCH₃), 3.69, 8.59 (-CH₂-), 127.98, 130.48, 130.85, 134.30, 134.35 (Ph). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): -21.89 (-SiCH₃), -64.53 (-Si-CH₂-CH₂-Si-), -78.36, -78.67.

FT-IR (cm⁻¹): 3073.78, 3052.14, 3028.97 (C-H phenyl), 2961.02, 2924.80 (-C-H), 1594.64 (C=C phenyl), 1489.55 (-C-H), 1430.86 (C=C phenyl), 1259.35 (Si-C), 1134.63, 1092.26, 1017.15 (Si-O).

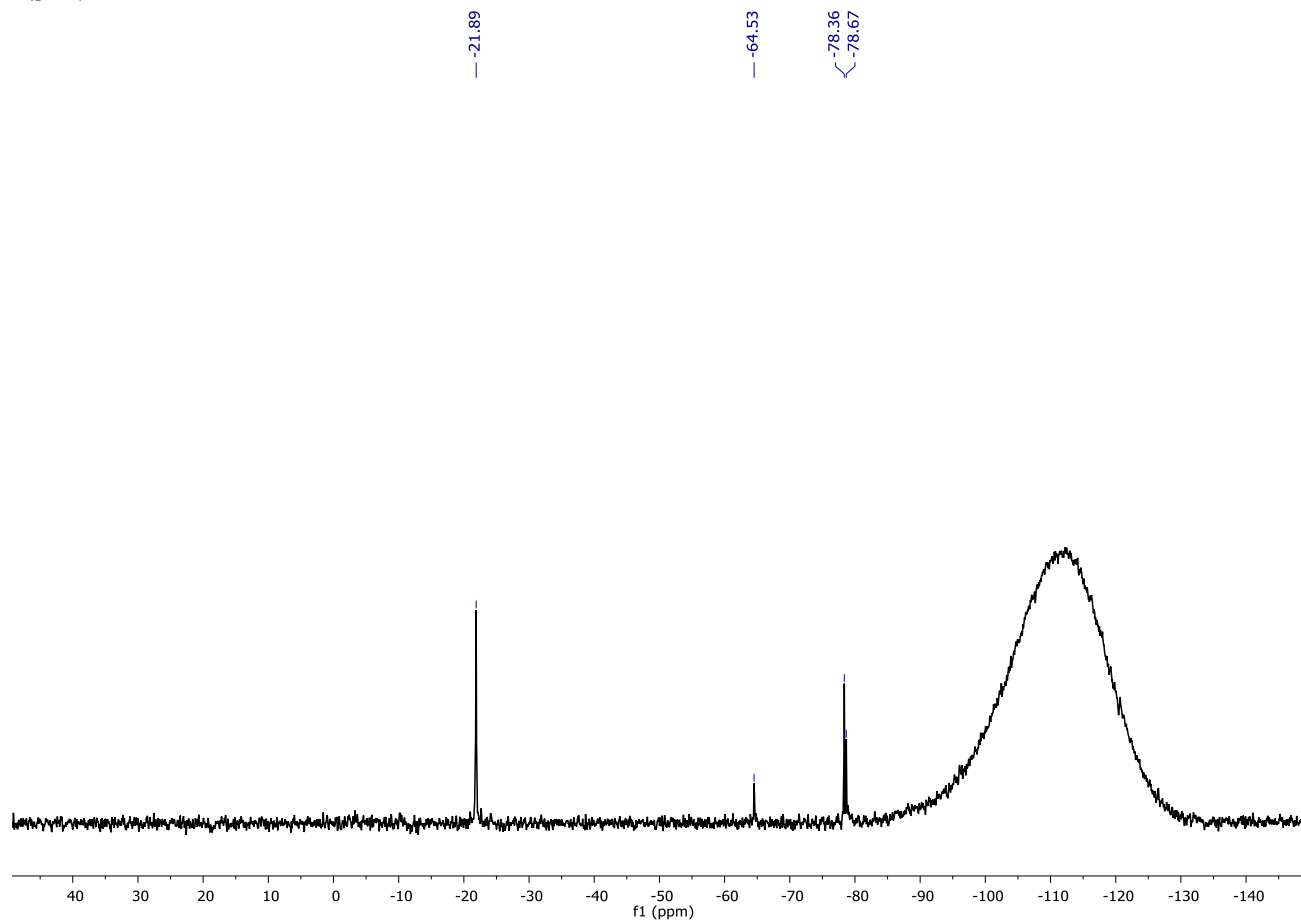
¹H NMR



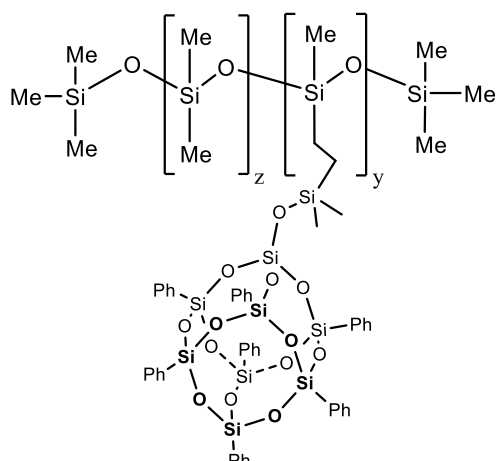
¹³C NMR



²⁹Si NMR



2-PhT₈@PS

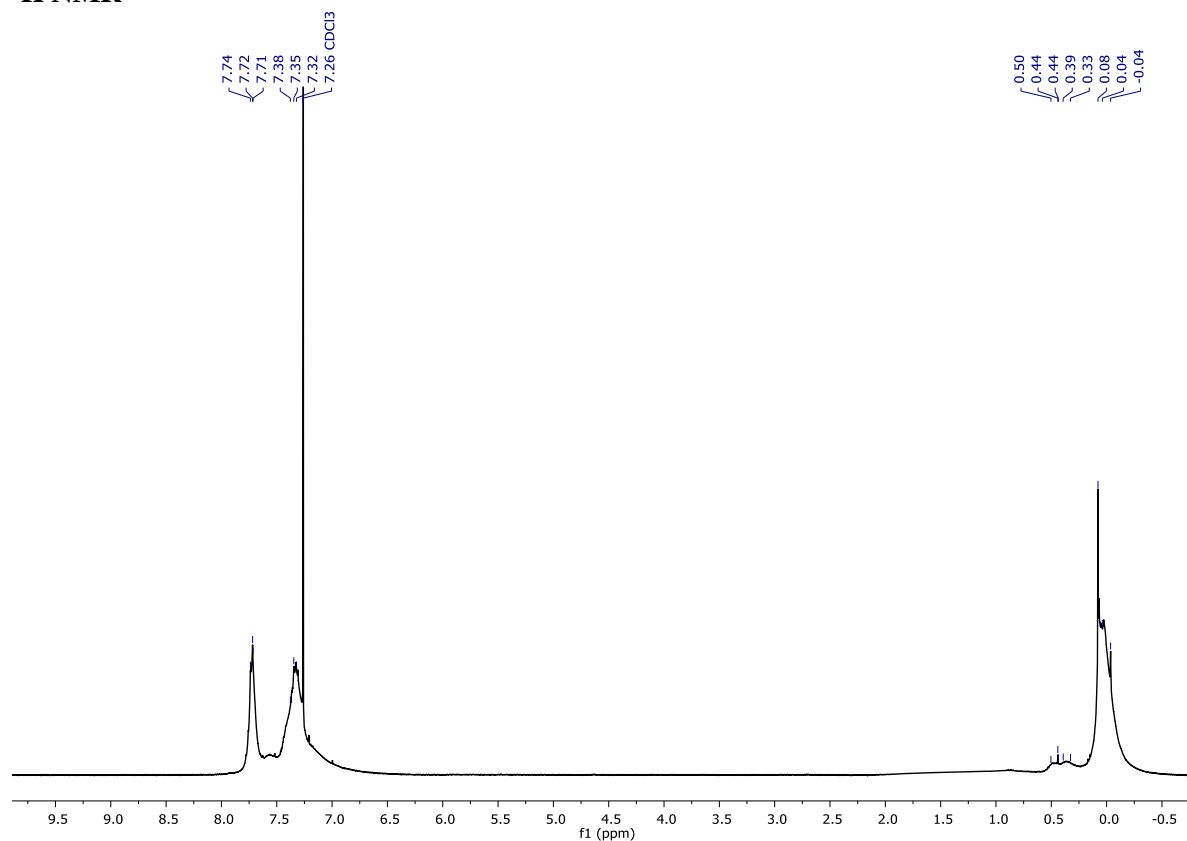


2-PhT₈@PS1

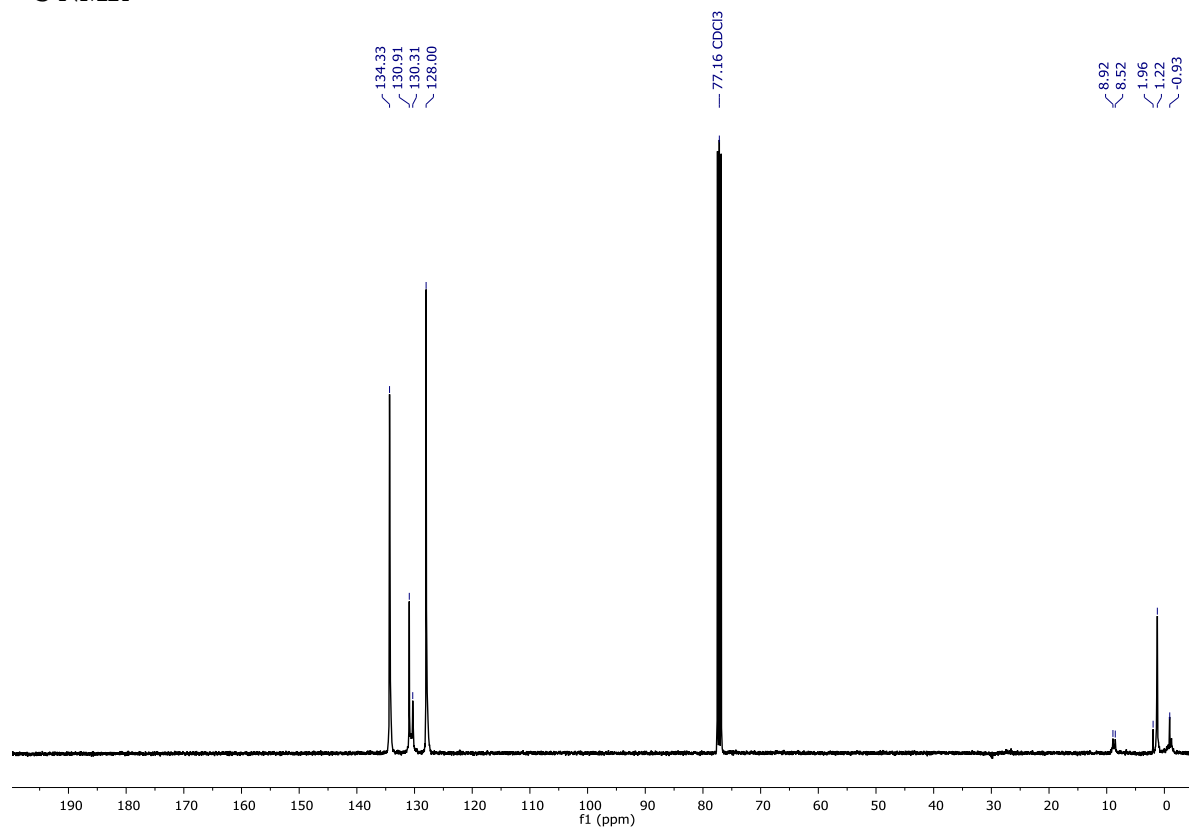
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): -0.04-0.08 (m, -SiCH₃), 0.33-0.50 (m, -CH₂-), 7.32-7.38, 7.71-7.74 (m, Ph). ¹³C NMR (100.6 MHz, CDCl₃, δ, ppm): -0.93, 1.22, 1.96 (-SiCH₃), 8.58, 8.92 (-CH₂-), 128.00, 130.31, 130.91, 134.33 (Ph). ²⁹Si NMR (79.5 MHz, CDCl₃, δ, ppm): 13.68 (-Si-CH₂-CH₂-Si-), -21.59, -21.87, -22.65 (-SiCH₃), -78.09, -78.26, -78.32, 108.82 (-SiO₄).

FT-IR (cm⁻¹): 3073.50, 3051.33 (C-H phenyl), 2959.22 (-C-H), 1594.37 (C=C phenyl), 1489.75 (-C-H), 1430.49 (C=C phenyl), 1258.99 (Si-C), 1131.72, 1079.97, 1026.73 (Si-O), 997.06 (C-H phenyl).

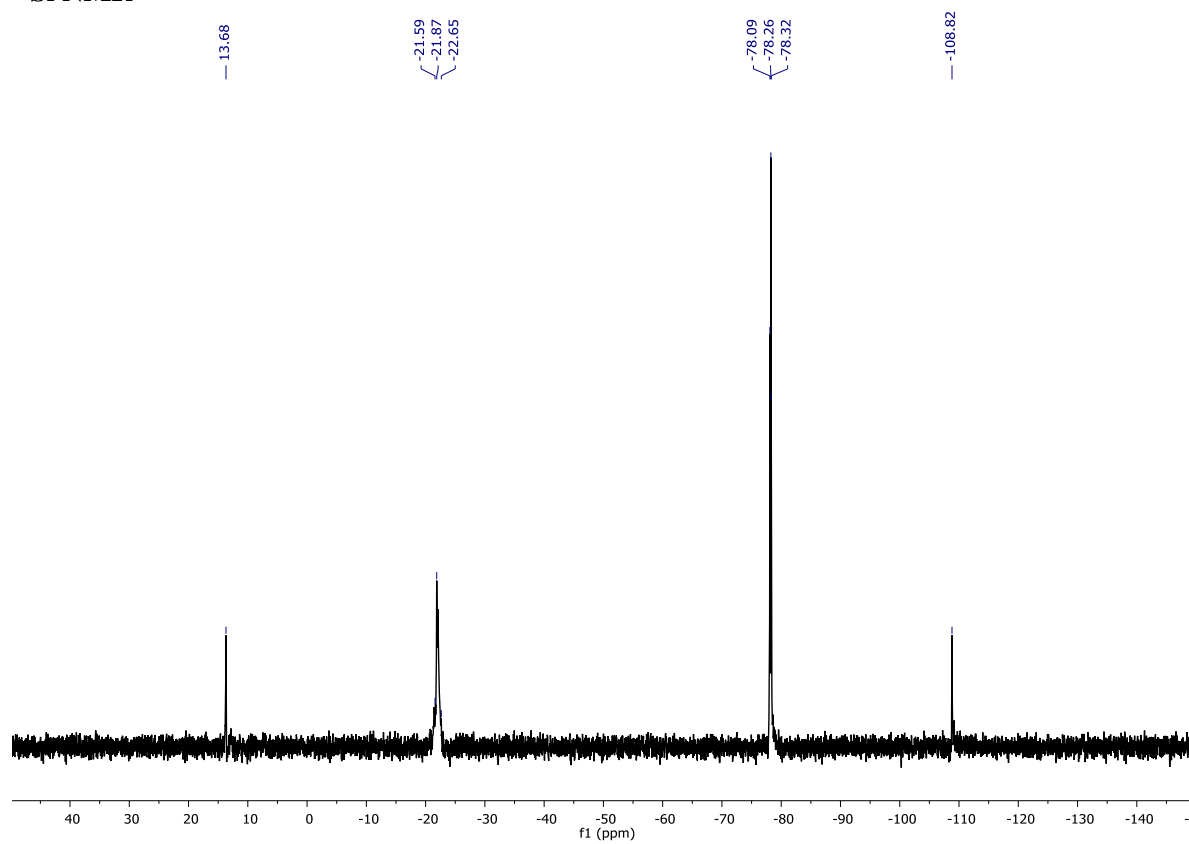
¹H NMR



¹³C NMR



²⁹Si NMR

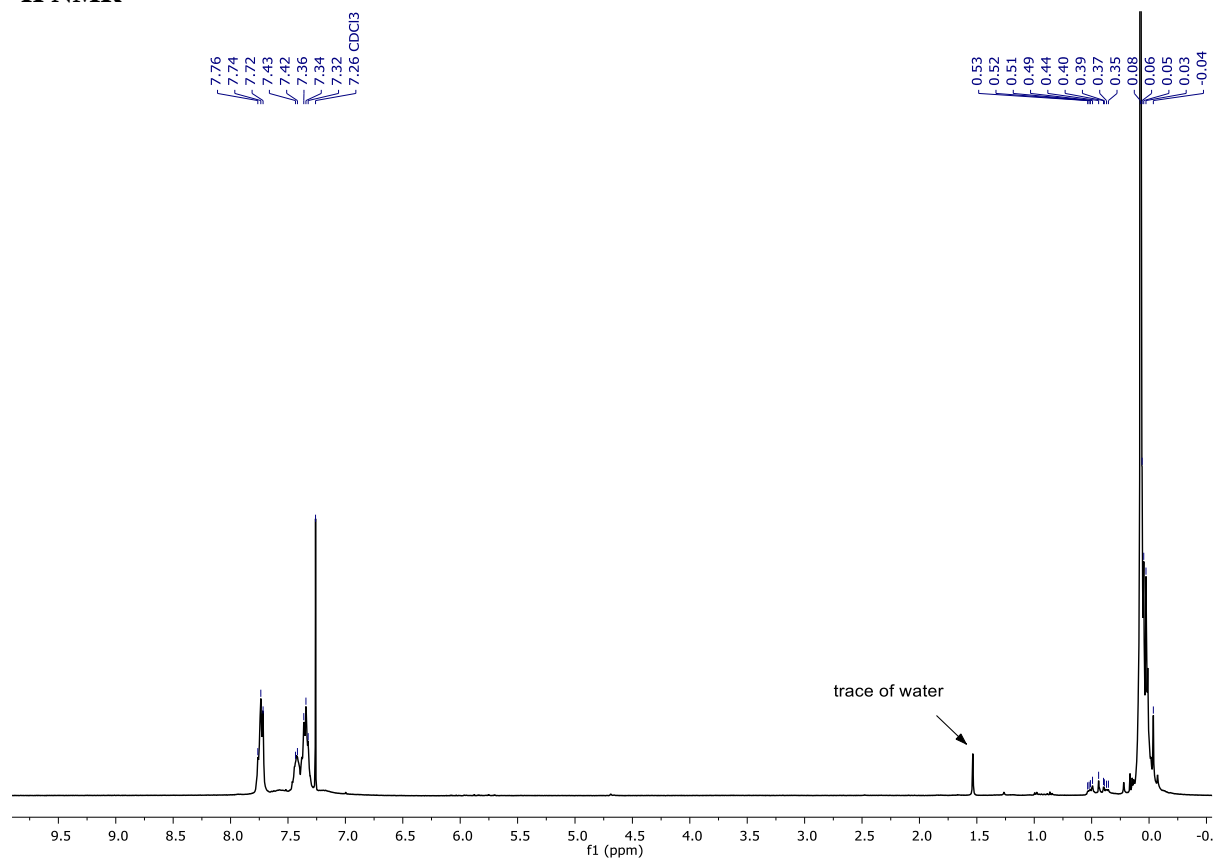


2-PhT₈@PS2

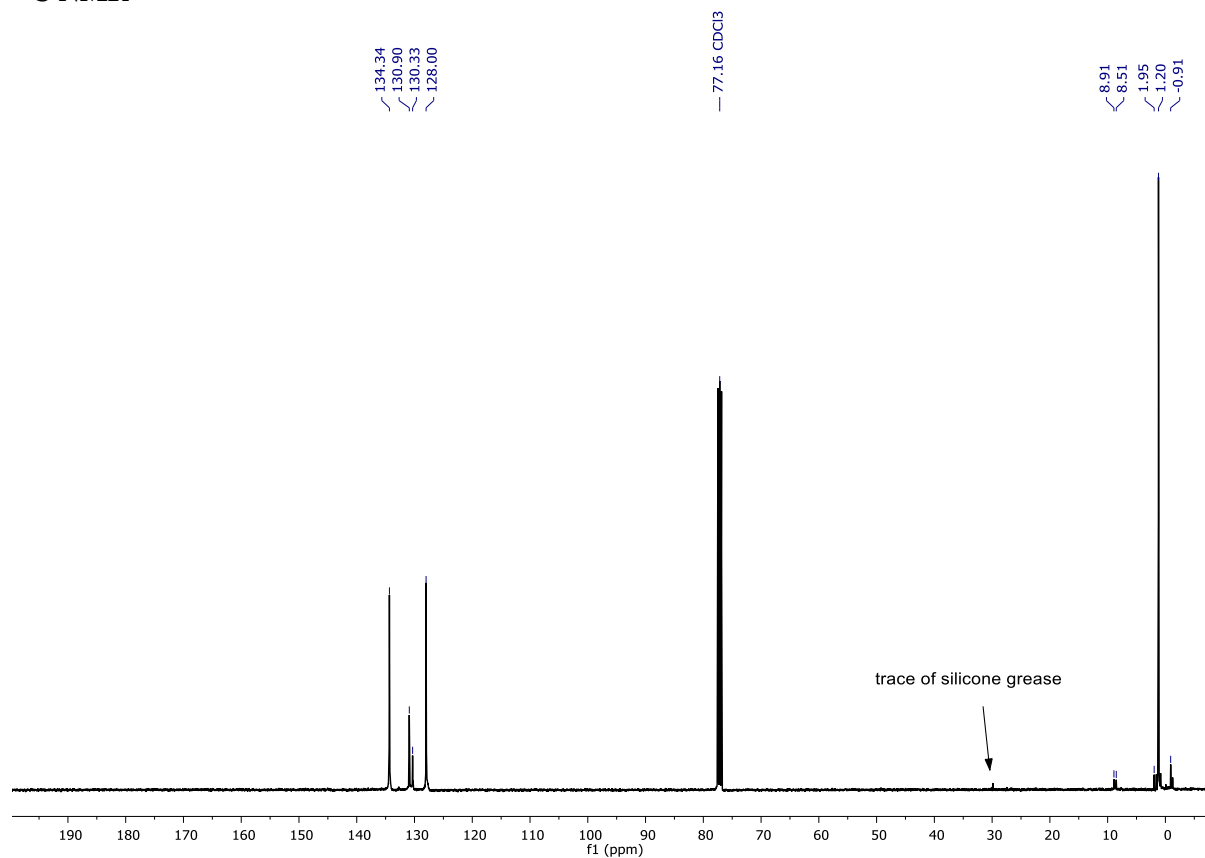
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): -0.04-0.08 (m, -SiCH₃), 0.35-0.53 (m, -CH₂-), 7.32-7.43, 7.72-7.76 (m, Ph). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -0.91, 1.20, 1.95 (-SiCH₃), 8.51, 8.91 (-CH₂-), 128.00, 130.33, 130.90, 134.34 (Ph). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 13.66 (-Si-CH₂-CH₂-Si-), -21.90, -22.06 (-SiCH₃), -78.14, -78.31, -78.36, 108.87 (-SiO₄).

FT-IR (cm⁻¹): 3073.90, 3051.76 (C-H phenyl), 2961.02 (-C-H), 1594.59 (C=C phenyl), 1430.90 (C=C phenyl), 1259.67 (Si-C), 1134.91, 1091.72, 1019.75 (Si-O).

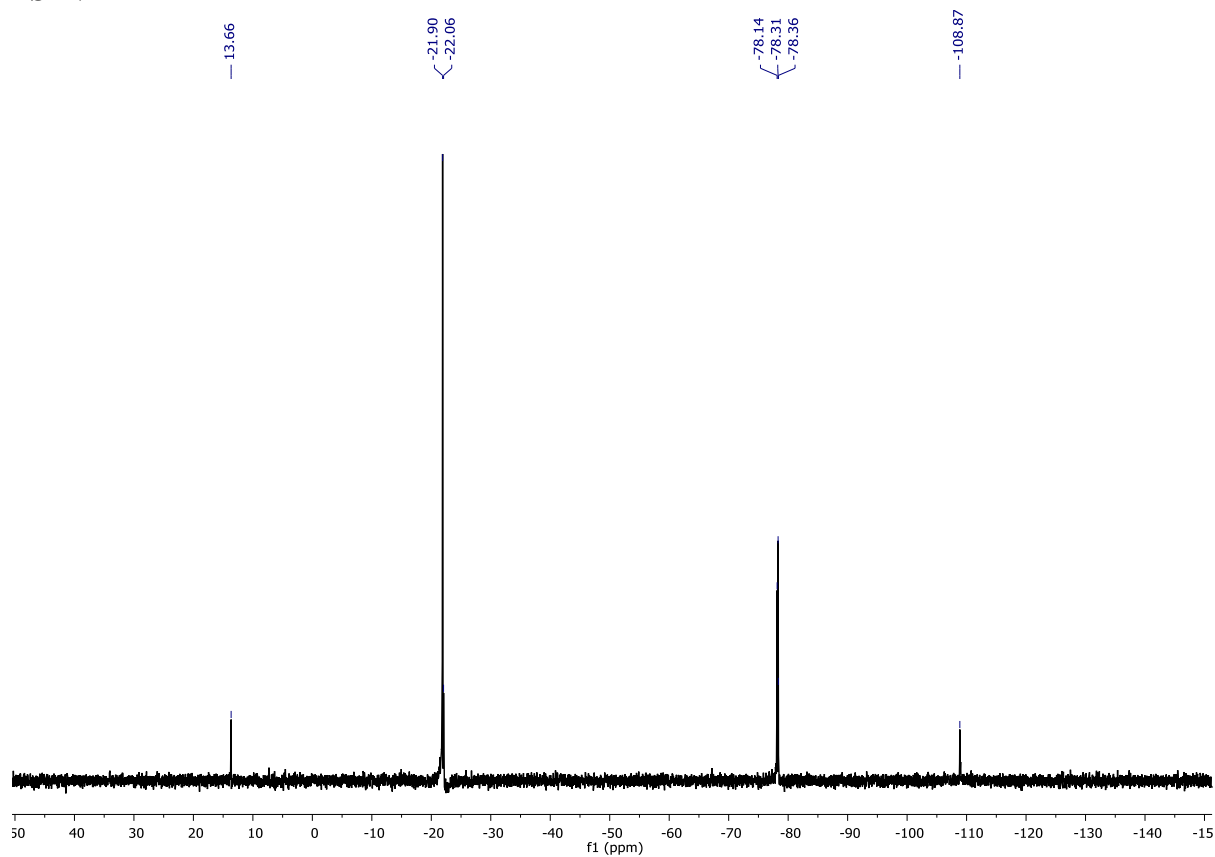
¹H NMR



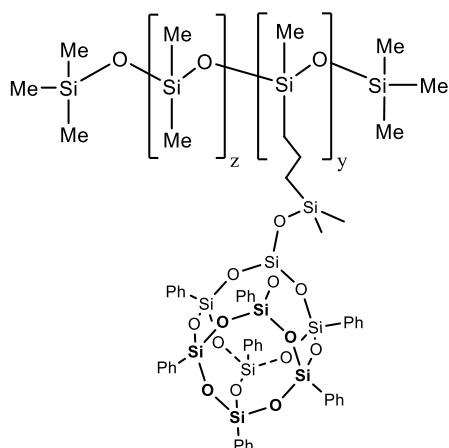
¹³C NMR



²⁹Si NMR



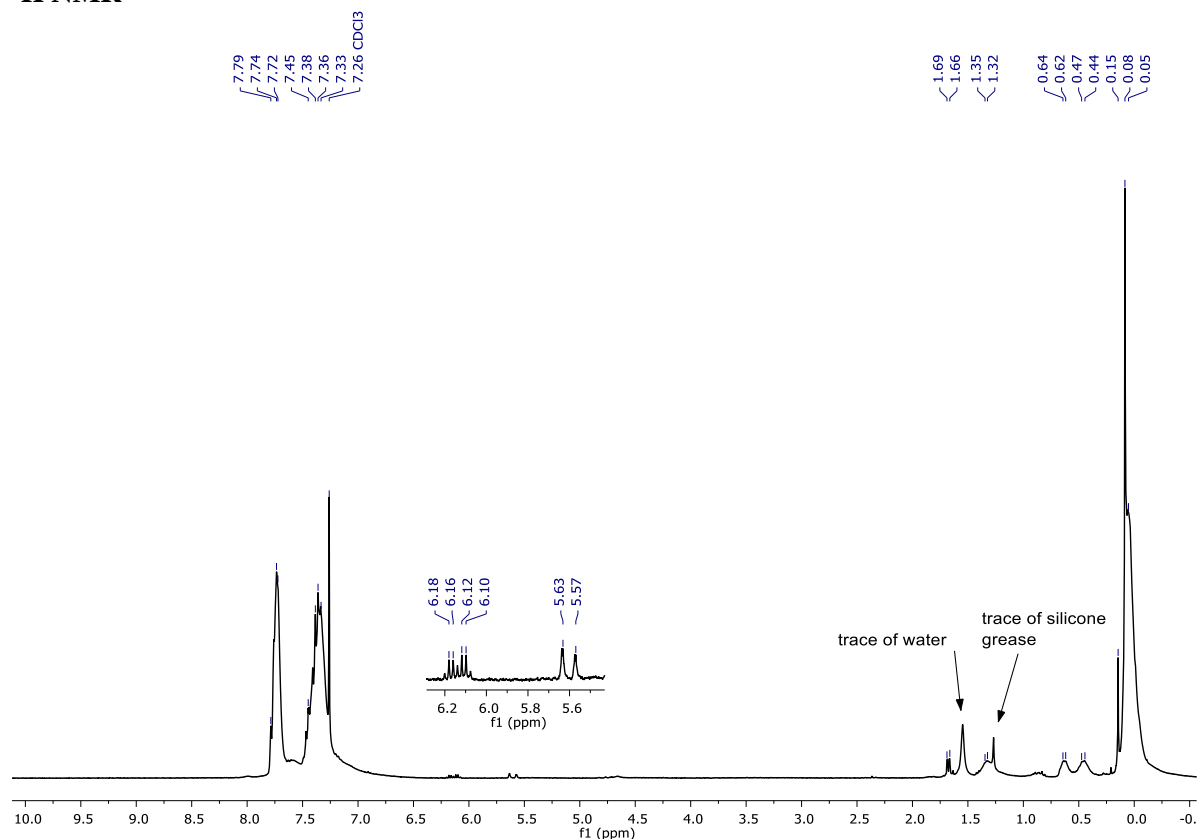
3-PhT₈@PS



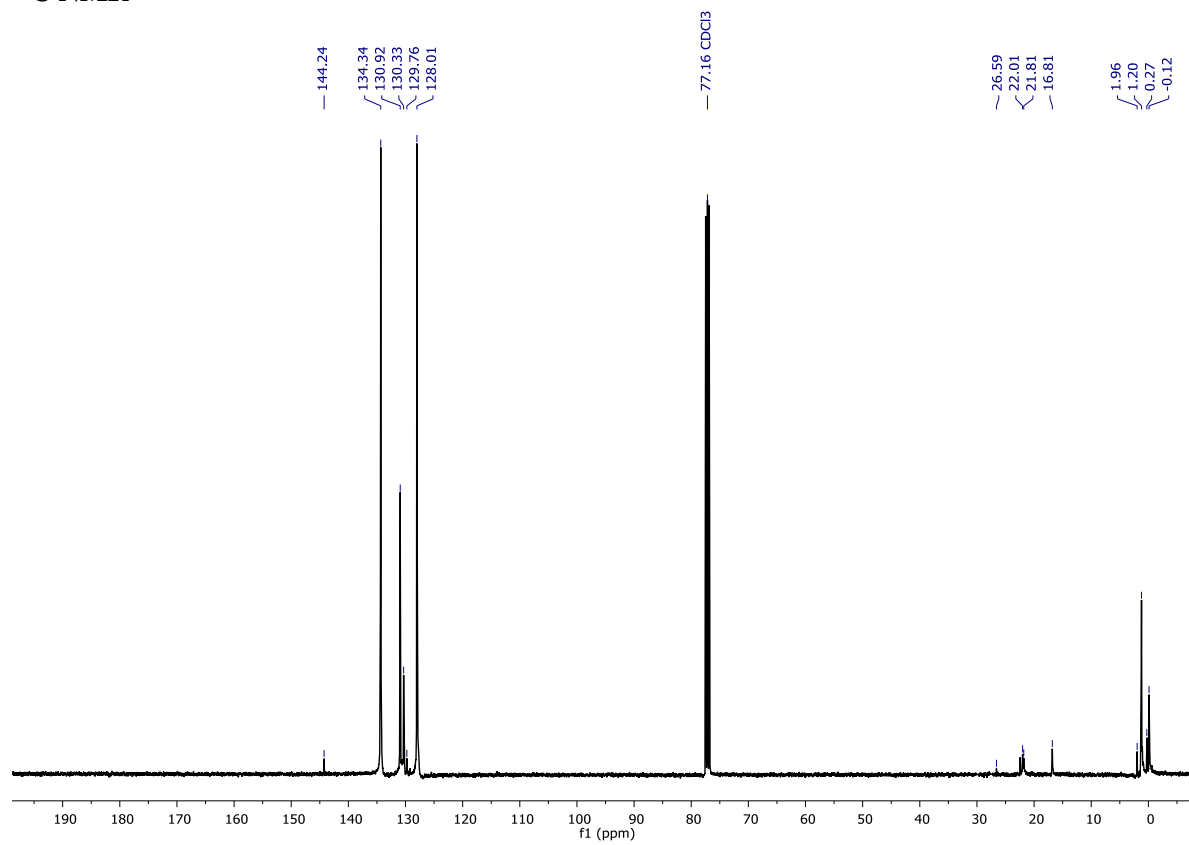
3-PhT₈@PS1

¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.05-0.15 (m, -SiCH₃), 0.44-0.47, 0.62-0.64, 1.32-1.35 (m, -CH₂-), 1.66-1.69, 5.57-5.63 and 6.10-6.18 (m, -CH₂-CH=CH- from dehydrogenative silylation by-product), 7.33-7.45, 7.72-7.79 (m, Ph). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -0.12, 0.27, 1.20, 1.96 (-SiCH₃), 16.81, 21.81, 22.01 (-CH₂-), 128.01, 130.30, 130.92, 134.34 (Ph), 26.86, 129.76 and 144.24 (-CH₂-CH=CH- from dehydrogenative silylation by-product). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 12.64 (-Si-CH₂-CH₂-CH₂-Si-), -21.89, -21.16, -22.65 (-SiCH₃), -78.13, -78.29, -78.35, 108.88 (-SiO₄). **FT-IR** (cm⁻¹): 3073.49, 3051.39 (C-H phenyl), 2959.76, 2919.00 (-C-H), 1594.29 (C=C phenyl), 1489.68 (-C-H), 1430.59 (C=C phenyl), 1259.11 (Si-C), 1132.30, 1081.01, 1026.41 (Si-O), 997.01 (C-H phenyl).

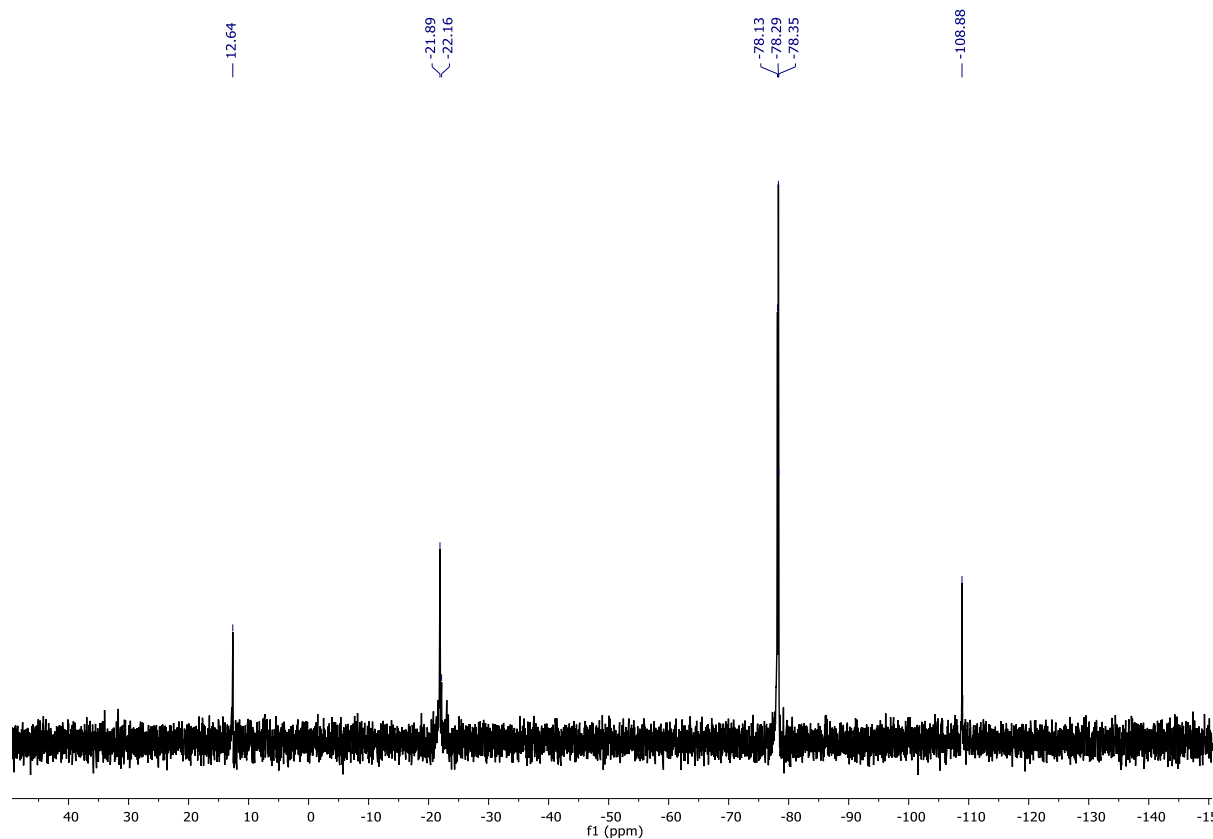
¹H NMR



¹³C NMR



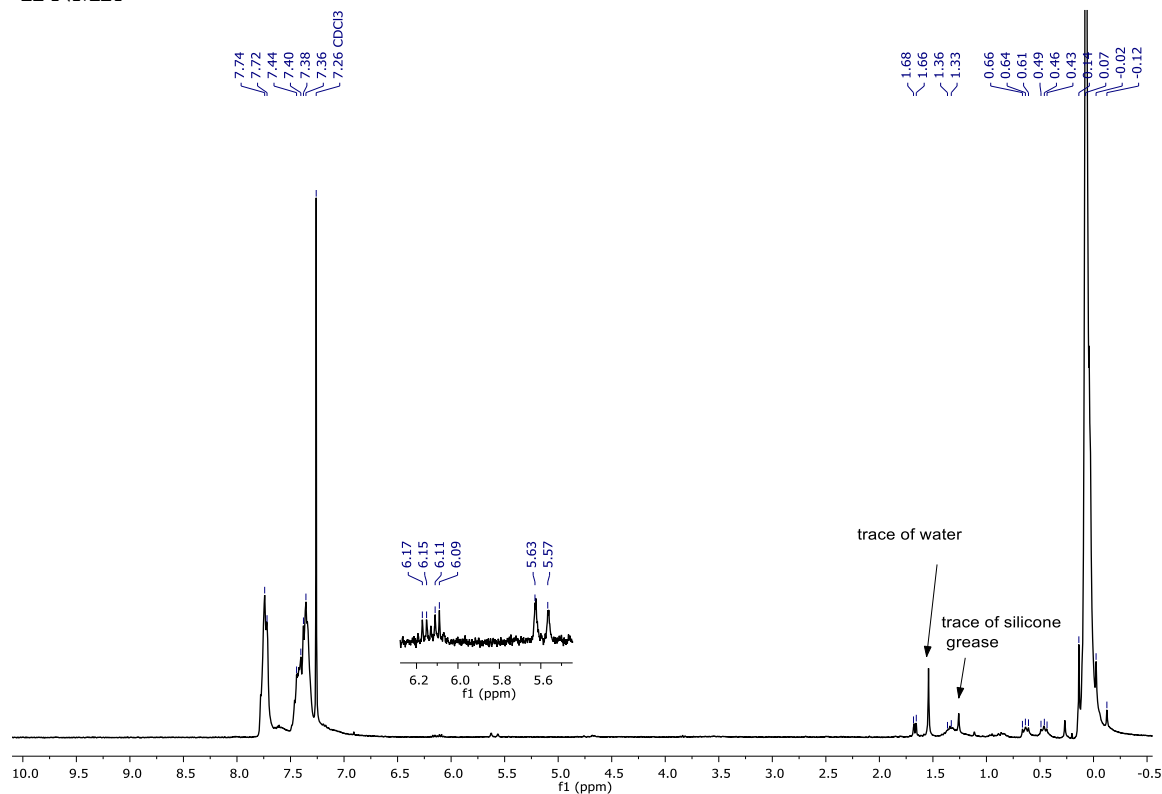
²⁹Si NMR



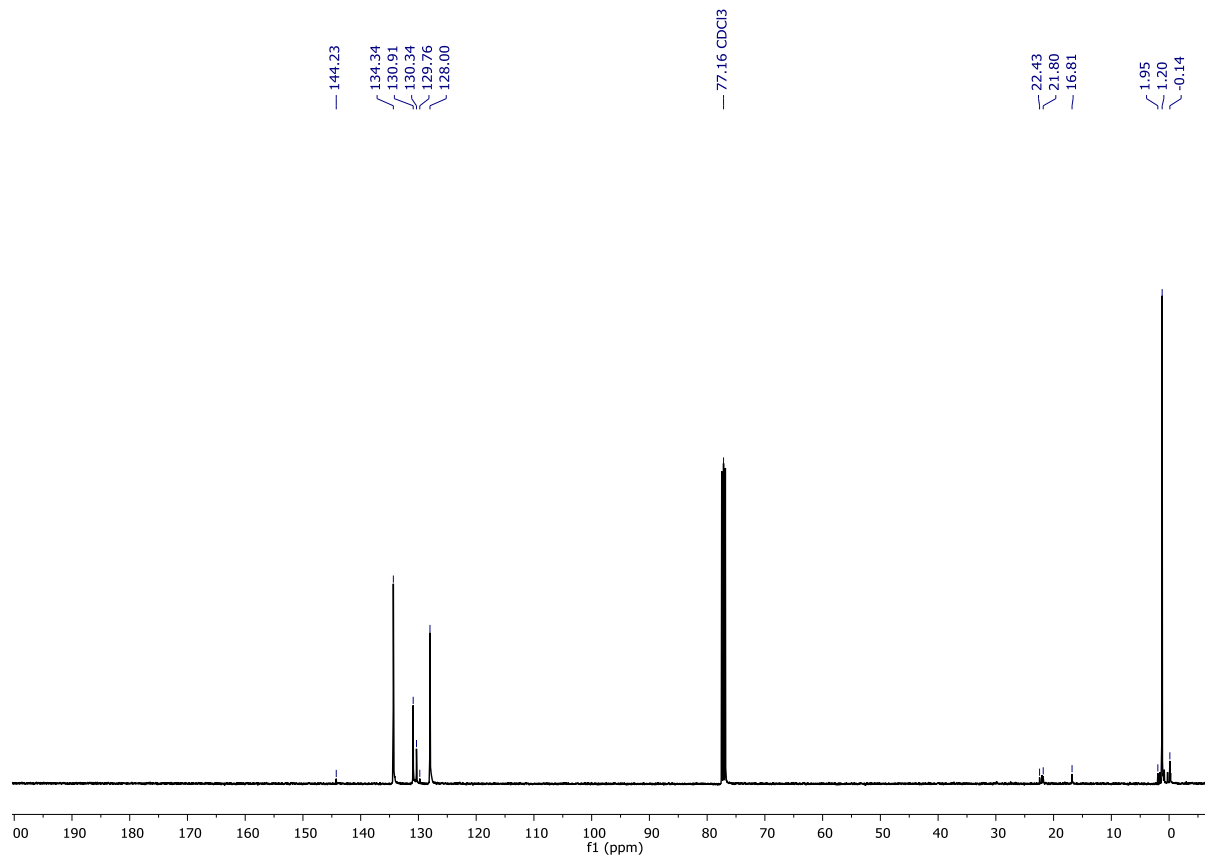
3-PhT₈@PS

¹H NMR (300.2 MHz, CDCl₃, δ, ppm): -0.12-0.14 (m, -SiCH₃), 0.43-0.49, 0.61-0.66, 1.33-1.33 (m, -CH₂-), 1.66-1.68, 5.57-5.63 and 6.09-6.17 (m, -CH₂-CH=CH- from dehydrogenative silylation by-product), 7.36-7.44, 7.72-7.74 (m, Ph). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -0.14, 1.20, 1.95 (-SiCH₃), 16.81, 21.80, 22.43 (-CH₂-), 128.00, 130.34, 130.91, 134.34 (Ph), 129.76 and 144.23 (-CH=CH- from dehydrogenative silylation by-product). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 12.65 (-Si-CH₂-CH₂-CH₂-Si-), -21.90, -23.00 (-SiCH₃), -78.16, -78.30, -78.36, 108.90 (-SiO₄). **FT-IR** (cm⁻¹): 3073.82, 3052.39 (C-H phenyl), 2961.13, 2920.27 (-C-H), 1594.49 (C=C phenyl), 1430.83 (C=C phenyl), 1259.33 (Si-C), 1134.50, 1091.58, 1018.79 (Si-O).

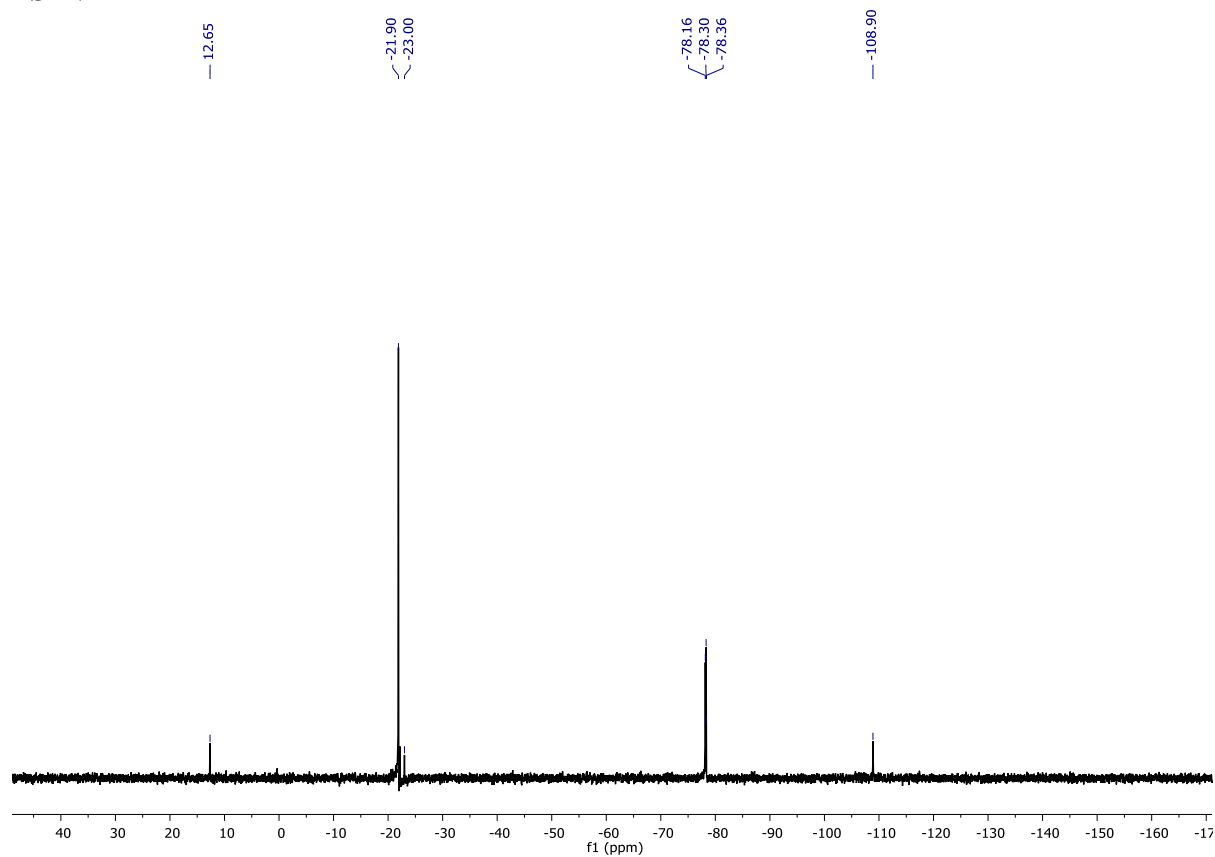
¹H NMR



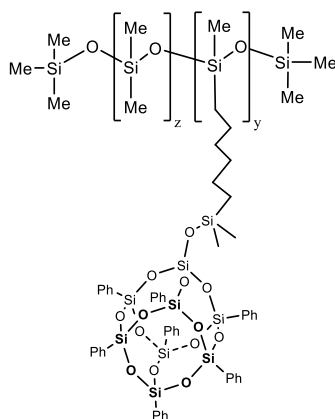
¹³C NMR



²⁹Si NMR



4-PhT₈@PS

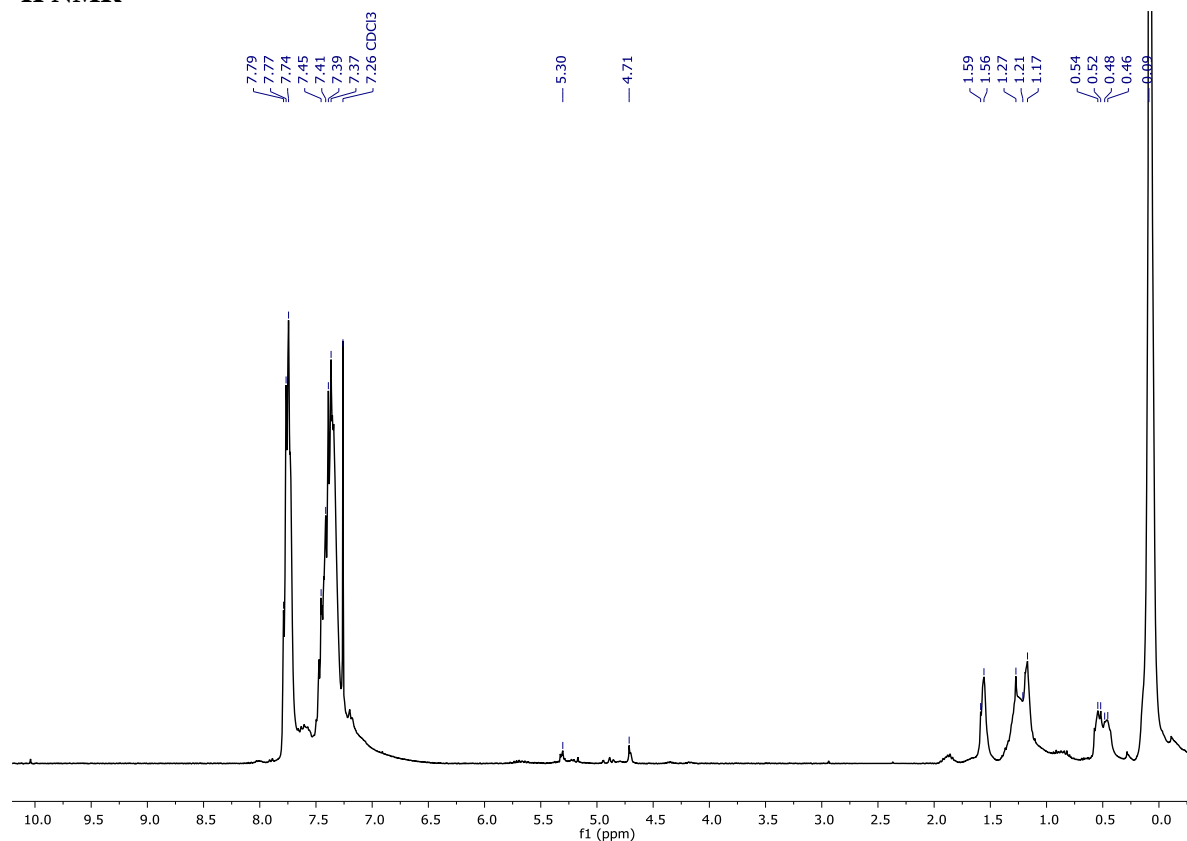


4-PhT₈@PS1

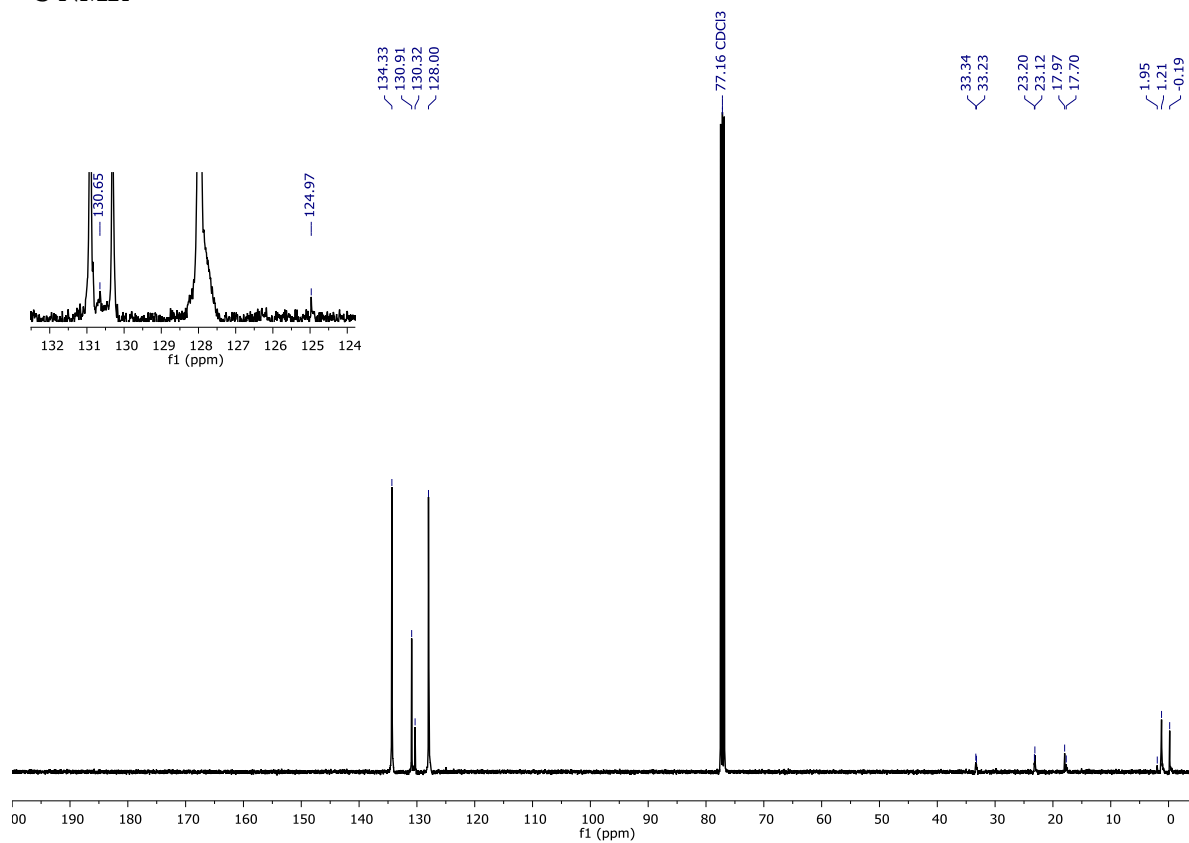
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.09 (m, -SiCH₃), 0.46-0.54, 1.17-1.27, 1.56-1.59 (m, -CH₂-), 4.71 (s, -Si-H), 5.30 (m, -CH=CH- from by-product of bond isomerization), 7.37-7.45, 7.74-7.79 (m, Ph). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -0.19, 1.21, 1.95 (-SiCH₃), 17.70, 17.97, 23.12, 23.20, 33.23, 33.34 (-CH₂-), 128.00, 130.32, 130.91, 134.33 (Ph), 124.97 and 130.65 (-CH=CH- from by-product of bond isomerization). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 13.12 (-Si-(CH₂)₆-Si-), -21.87, -22.15, -22.25 (-SiCH₃), -78.12, -78.26, -78.32, 108.95 (-SiO₄).

FT-IR (cm⁻¹): 3073.46, 3051.35 (C-H phenyl), 2959.22, 2921.80 (-C-H), 1594.38 (C=C phenyl), 1489.81 (-C-H), 1430.55 (C=C phenyl), 1258.86 (Si-C), 1131.73, 1076.04, 1026.74 (Si-O), 997.73 (C-H phenyl).

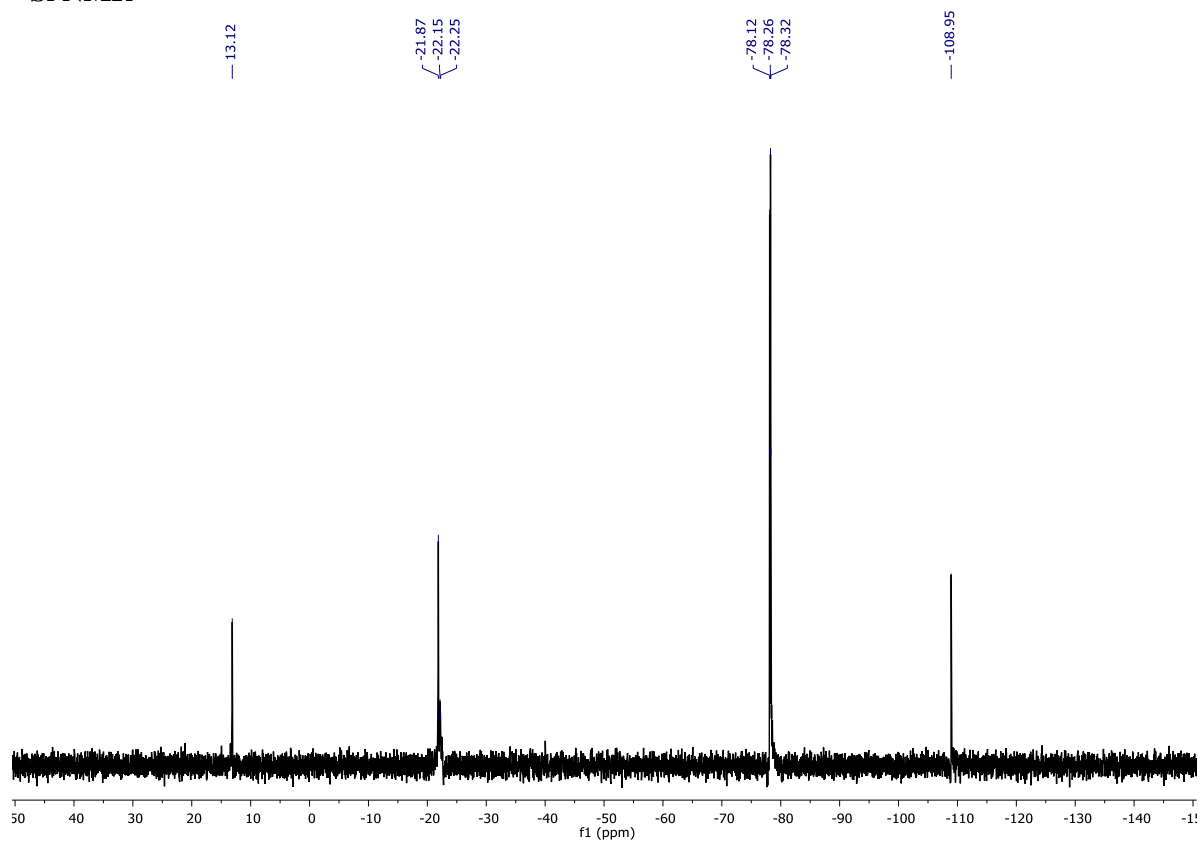
¹H NMR



¹³C NMR



²⁹Si NMR

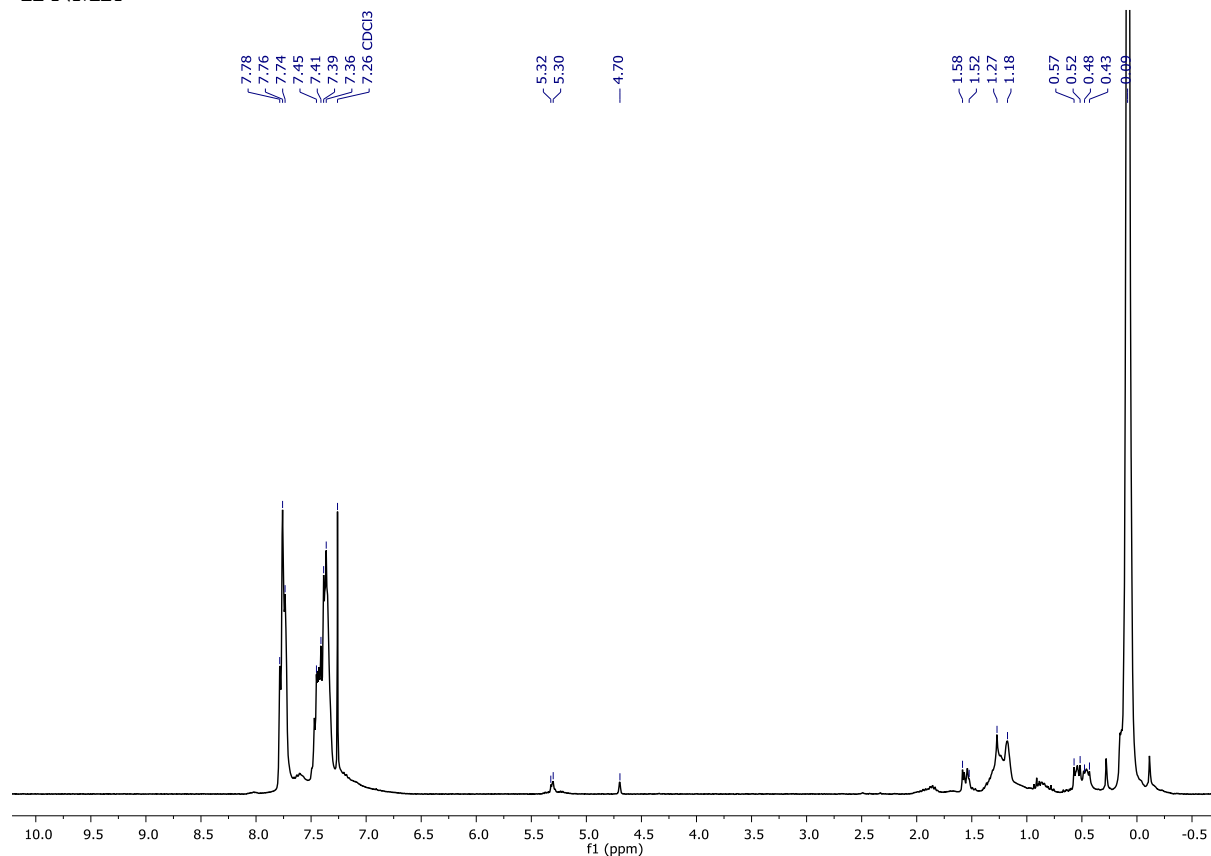


4-PhT₈@PS2

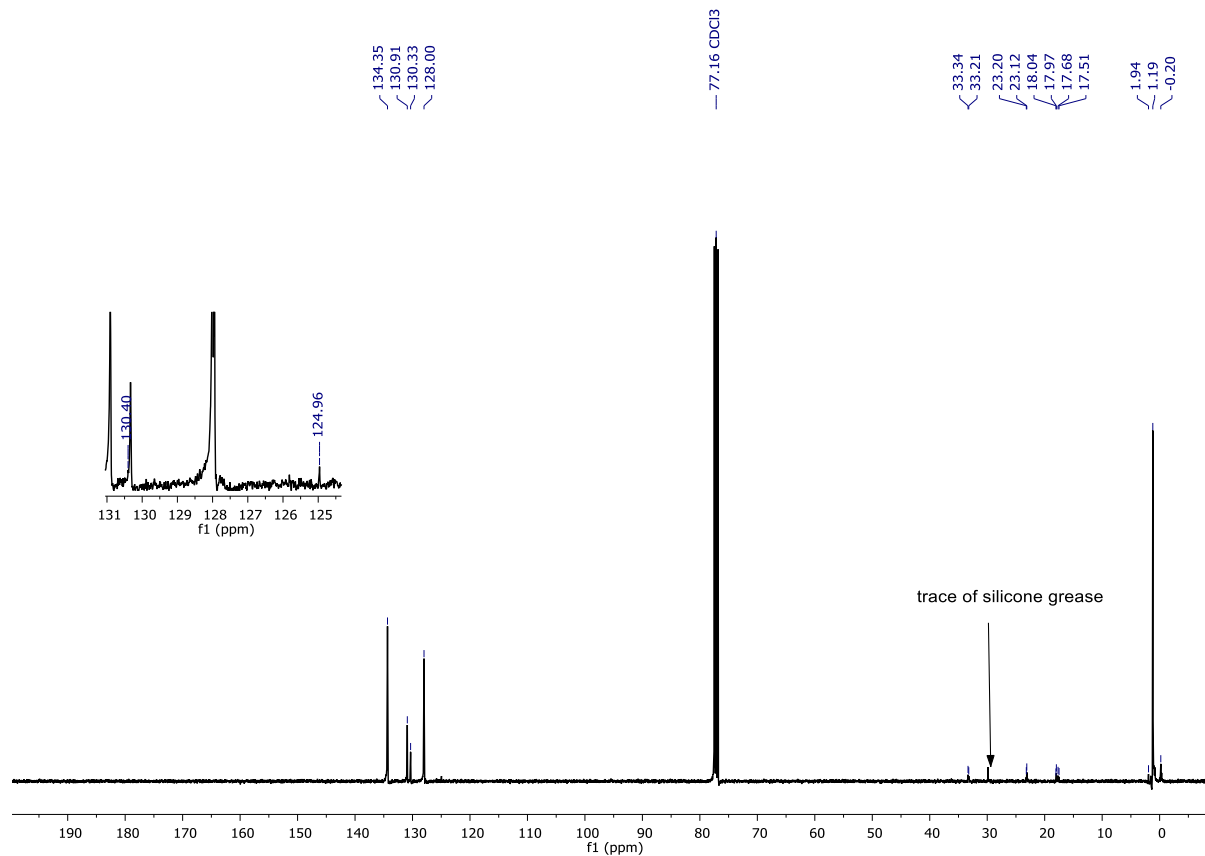
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.09 (m, -SiCH₃), 0.43-0.57, 1.18-1.27, 1.52-1.58 (m, -CH₂-), 4.70 (s, -Si-H), 5.30-5.32 (m, -CH=CH- from by-product of bond isomerization), 7.36-7.45, 7.74-7.78 (m, Ph). **¹³C NMR** (100.6 MHz, CDCl₃, δ, ppm): -0.20, 1.19, 1.94 (-SiCH₃), 17.51, 17.68, 17.97, 18.04, 23.12, 23.20, 33.21, 33.34 (-CH₂-), 128.00, 130.33, 130.91, 134.35 (Ph), 124.96 and 130.40 (-CH=CH- from by-product of bond isomerization). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 13.07 (-Si-(CH₂)₆-Si-), -21.92, -22.21 (-SiCH₃), -78.18, -78.32, -78.38, 109.00 (-SiO₄).

FT-IR (cm⁻¹): 3073.56, 3051.52 (C-H phenyl), 2960.80, 2923.08 (-C-H), 1594.29 (C=C phenyl), 1430.64 (C=C phenyl), 1258.86 (Si-C), 1133.70, 1087.75, 1015.68 (Si-O).

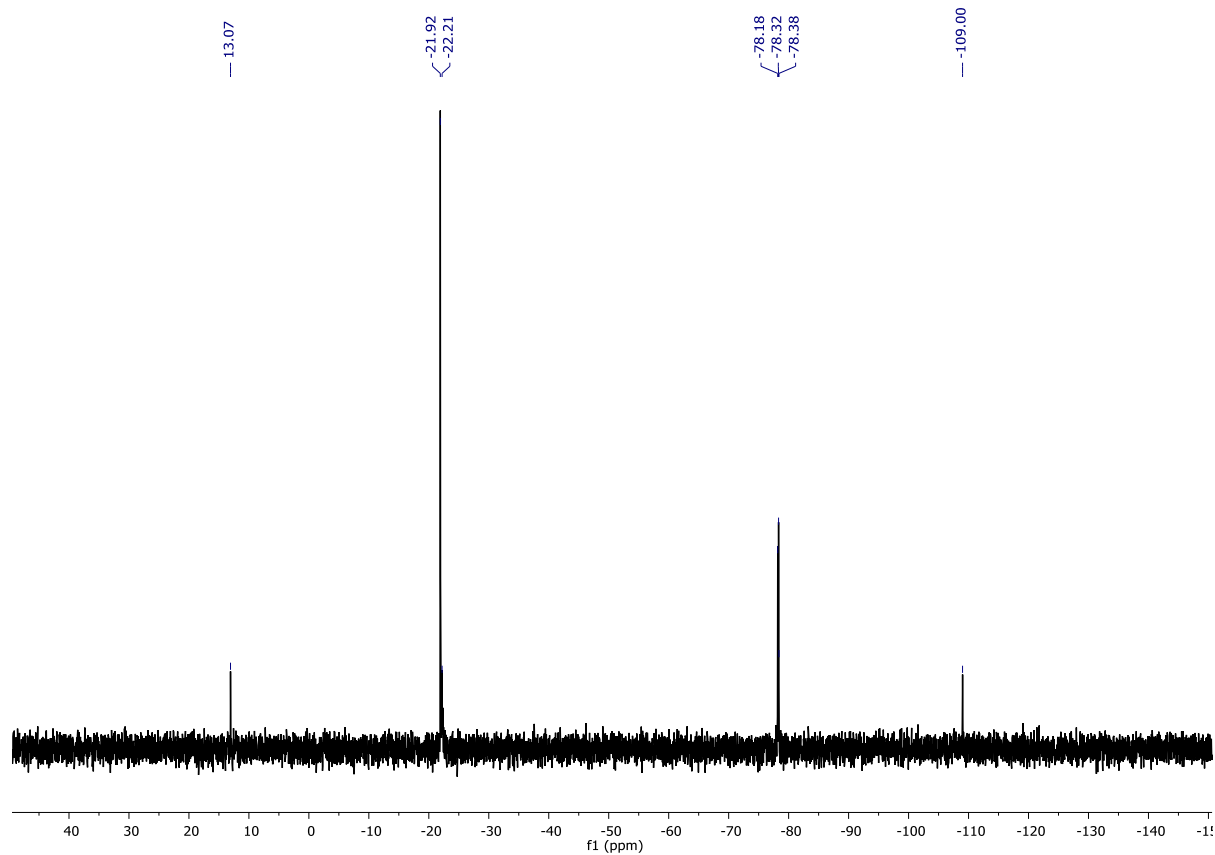
¹H NMR



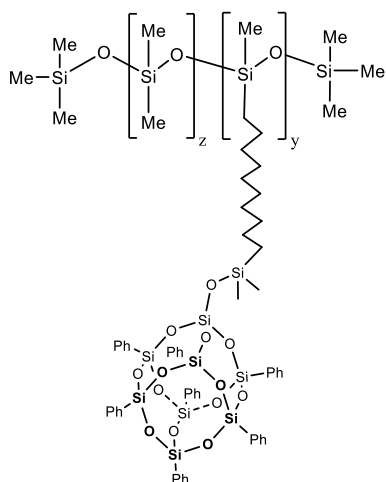
¹³C NMR



²⁹Si NMR



5-PhT₈@PS



5-PhT₈@PS1

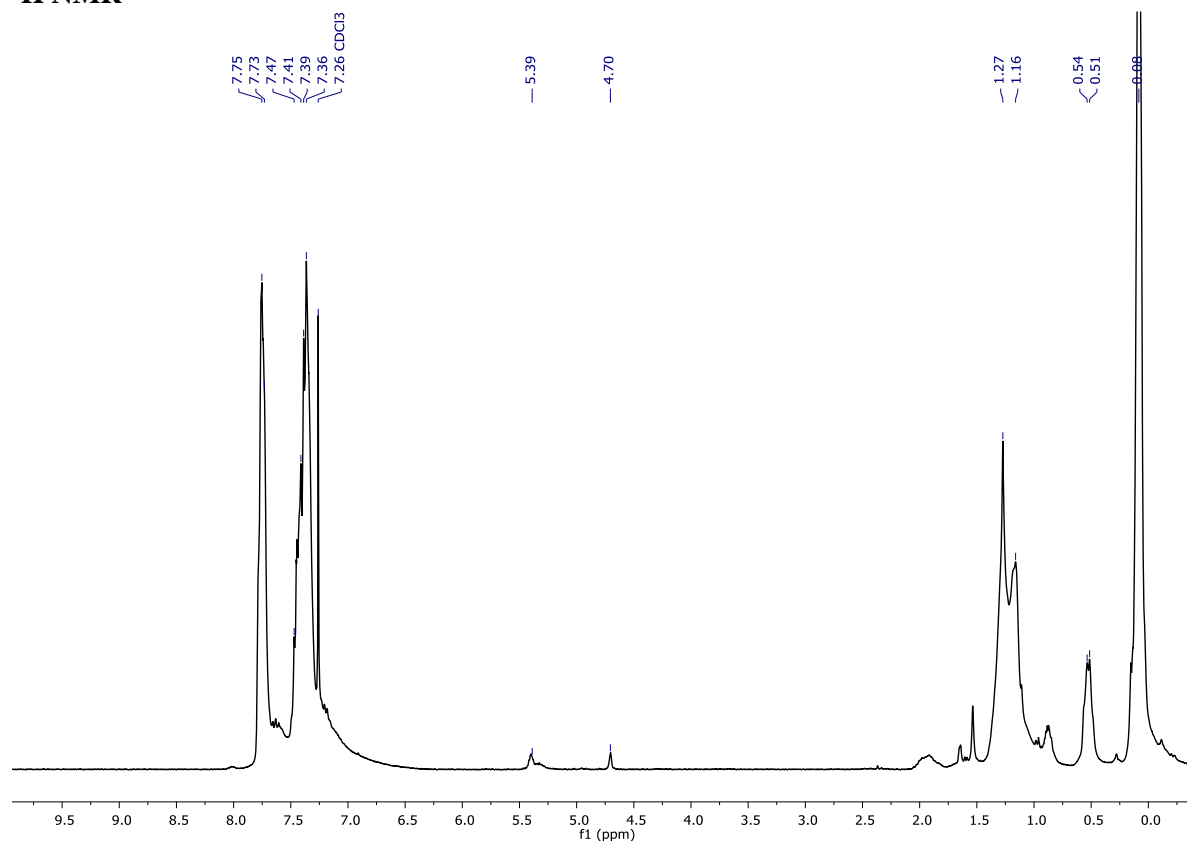
¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.08 (m, -SiCH₃), 0.51-0.54, 1.16-1.27 (m, -CH₂-), 4.70 (m, -Si-H), 5.39 (m, -CH=CH- from by-product of bond isomerization), 7.36-7.47, 7.73-7.75 (m, Ph).

¹³C NMR (100.6 MHz, CDCl₃, δ, ppm): -0.15, 1.22, 1.96 (-SiCH₃), 17.51, 17.95, 23.17, 29.51, 29.93, 33.61 (-CH₂-), 128.00, 130.33, 130.91, 134.35 (Ph).

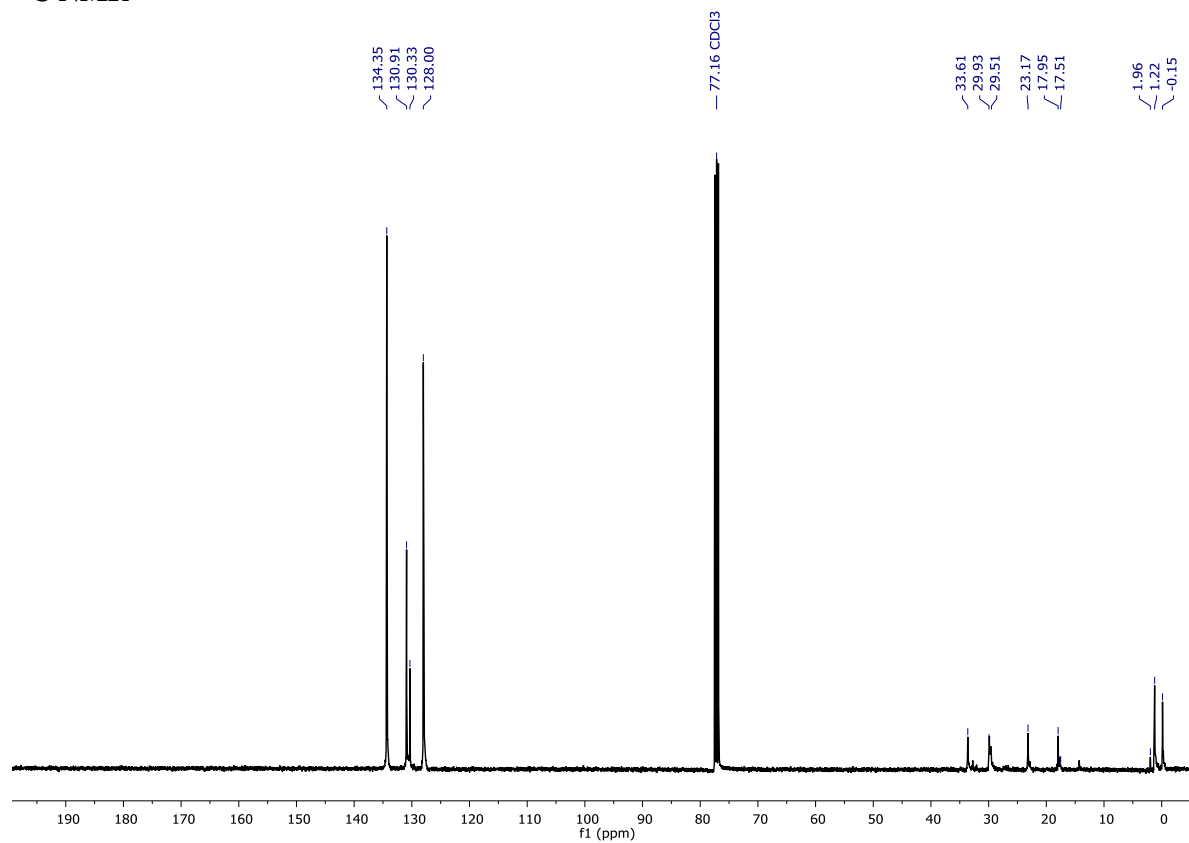
²⁹Si NMR (79.5 MHz, CDCl₃, δ, ppm): 13.15 (-Si-(CH₂)₁₀-Si-), -21.87, -22.26 (-SiCH₃), -78.12, -78.26, -78.32, 108.94 (-SiO₄).

FT-IR (cm⁻¹): 3073.45, 3051.40 (C-H phenyl), 2922.46, 2852.81 (-C-H), 1594.37 (C=C phenyl), 1489.78 (-C-H), 1430.65 (C=C phenyl), 1259.11 (Si-C), 1132.85, 1091.30, 1028.59 (Si-O), 998.07 (C-H phenyl).

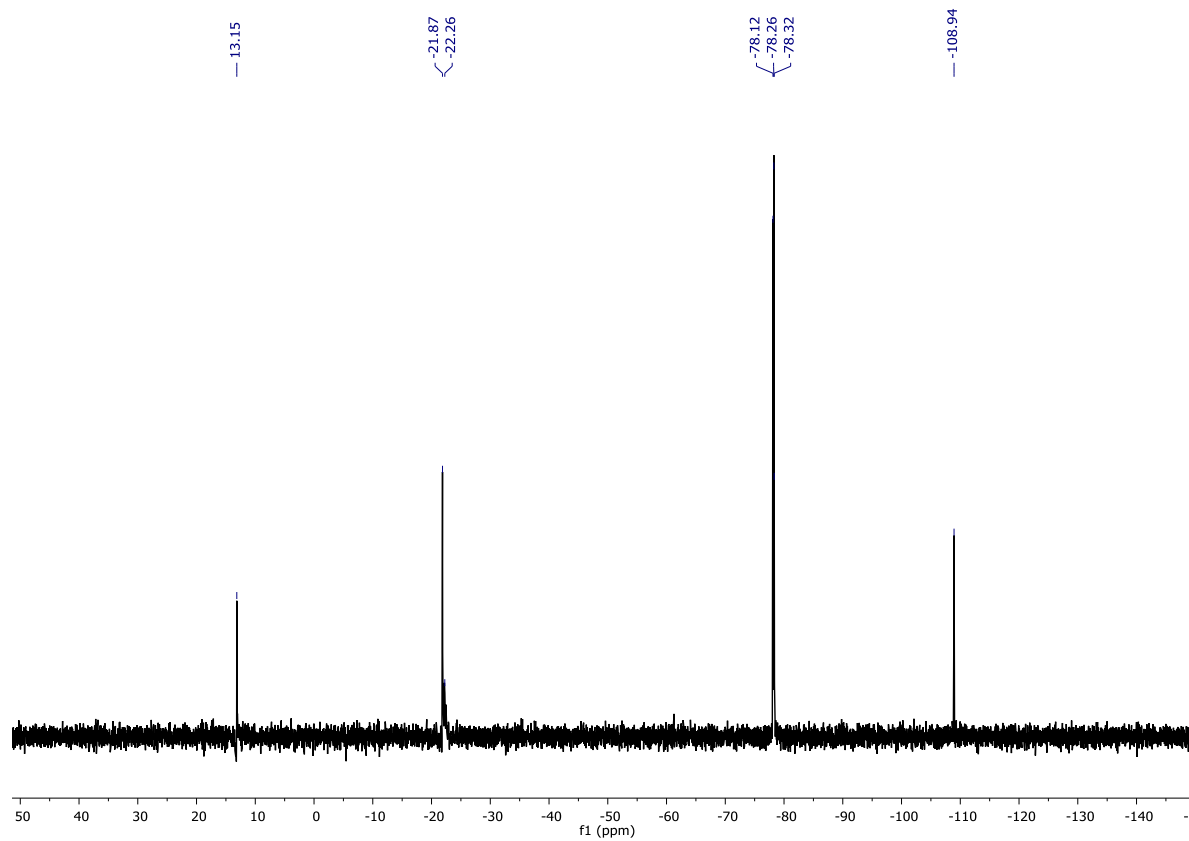
¹H NMR



¹³C NMR



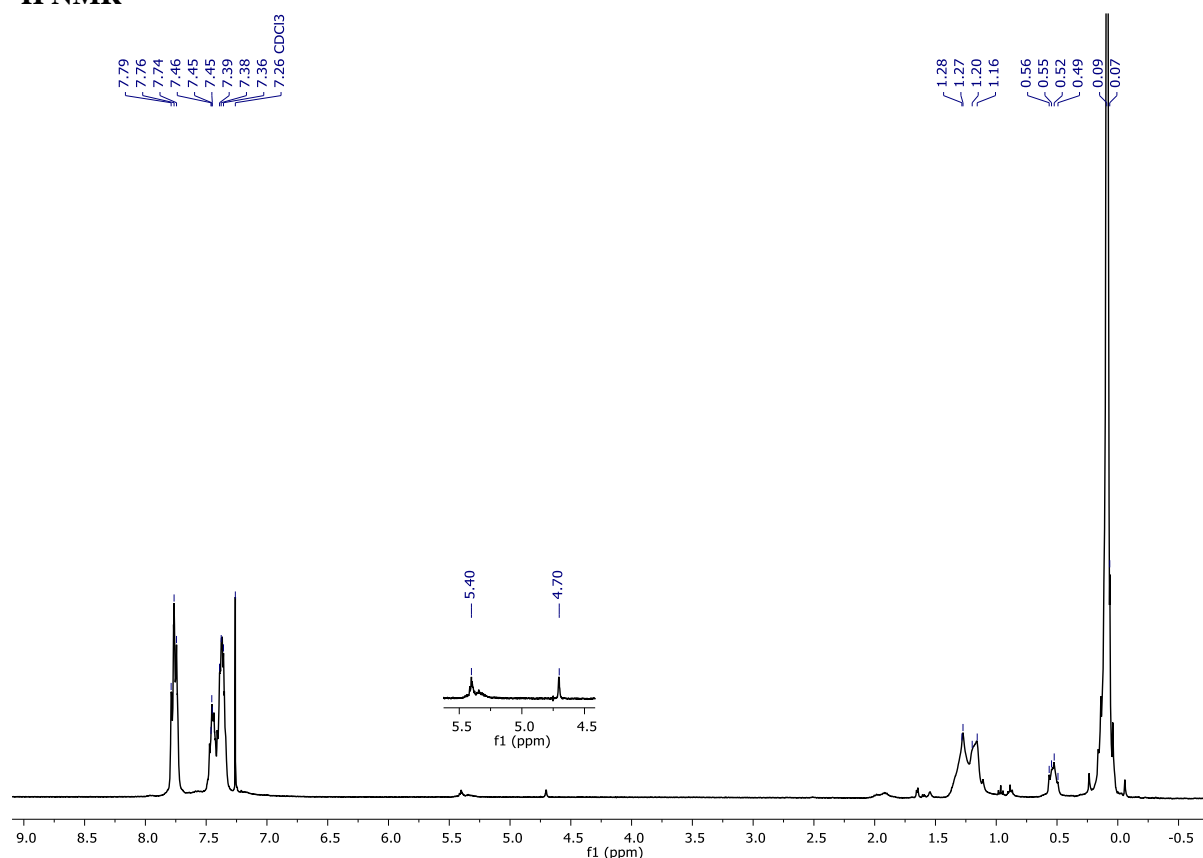
²⁹Si NMR



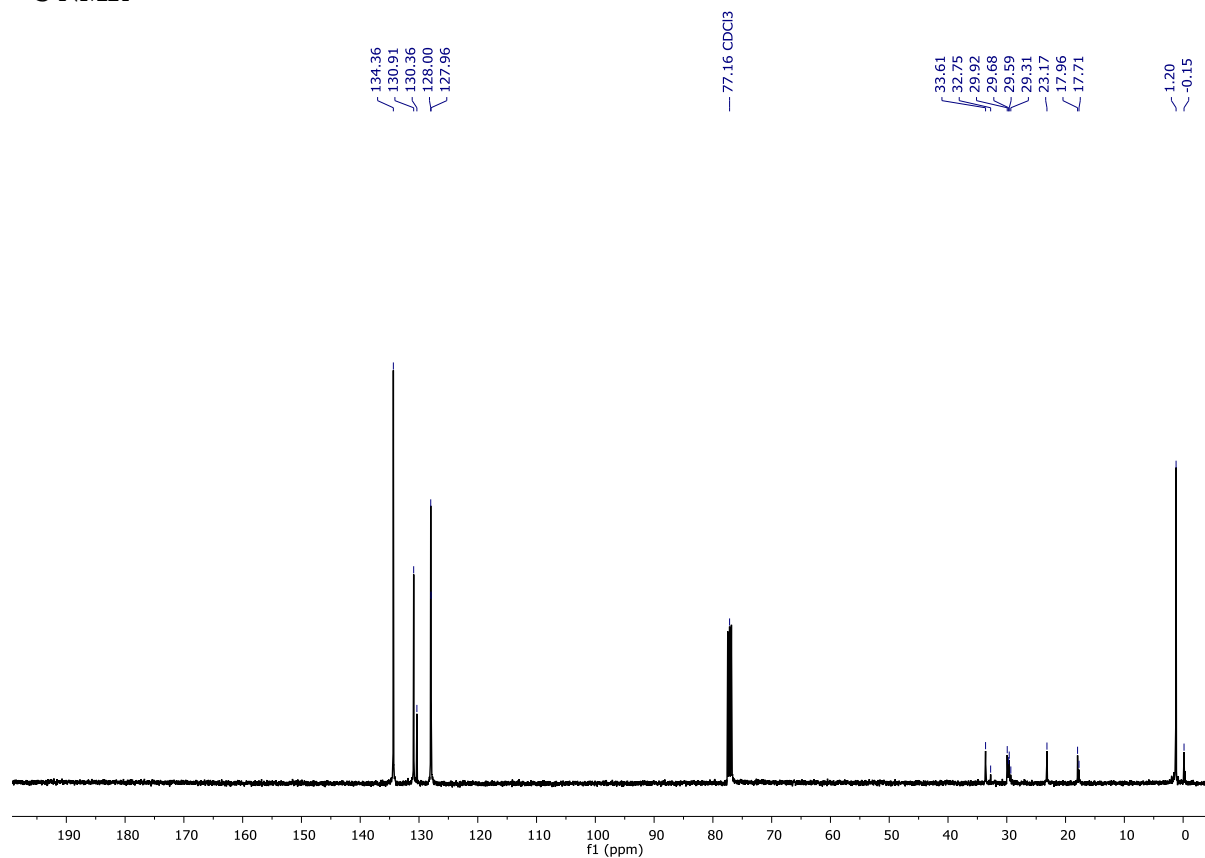
5-PhT₈@PS2

¹H NMR (300.2 MHz, CDCl₃, δ, ppm): 0.07-0.09 (m, -SiCH₃), 0.49-0.56, 1.16-1.28 (m, -CH₂-), 4.70 (m, -Si-H), 5.40 (m, -CH=CH- from by-product of bond isomerization), 7.36-7.46, 7.74-7.79 (m, Ph).
¹³C NMR (100.6 MHz, CDCl₃, δ, ppm): -0.15, 1.20 (-SiCH₃), 17.71, 17.96, 23.17, 29.31, 29.59, 29.68, 29.92, 32.75, 33.61 (-CH₂-), 127.96, 128.00, 130.36, 130.91, 134.36 (Ph). **²⁹Si NMR** (79.5 MHz, CDCl₃, δ, ppm): 13.10 (-Si-(CH₂)₁₀-Si-), -21.96, -22.21, -22.27 (-SiCH₃), -78.19, -78.33, -78.39, 109.00 (-SiO₄).
FT-IR (cm⁻¹): 3073.56, 3052.28 (C-H phenyl), 2960.62, 2823.07 (-C-H), 1594.24 (C=C phenyl), 1489.73 (-C-H), 1430.70 (C=C phenyl), 1259.28 (Si-C), 1133.79, 1087.68, 1015.09 (Si-O), 996.95 (C-H phenyl).

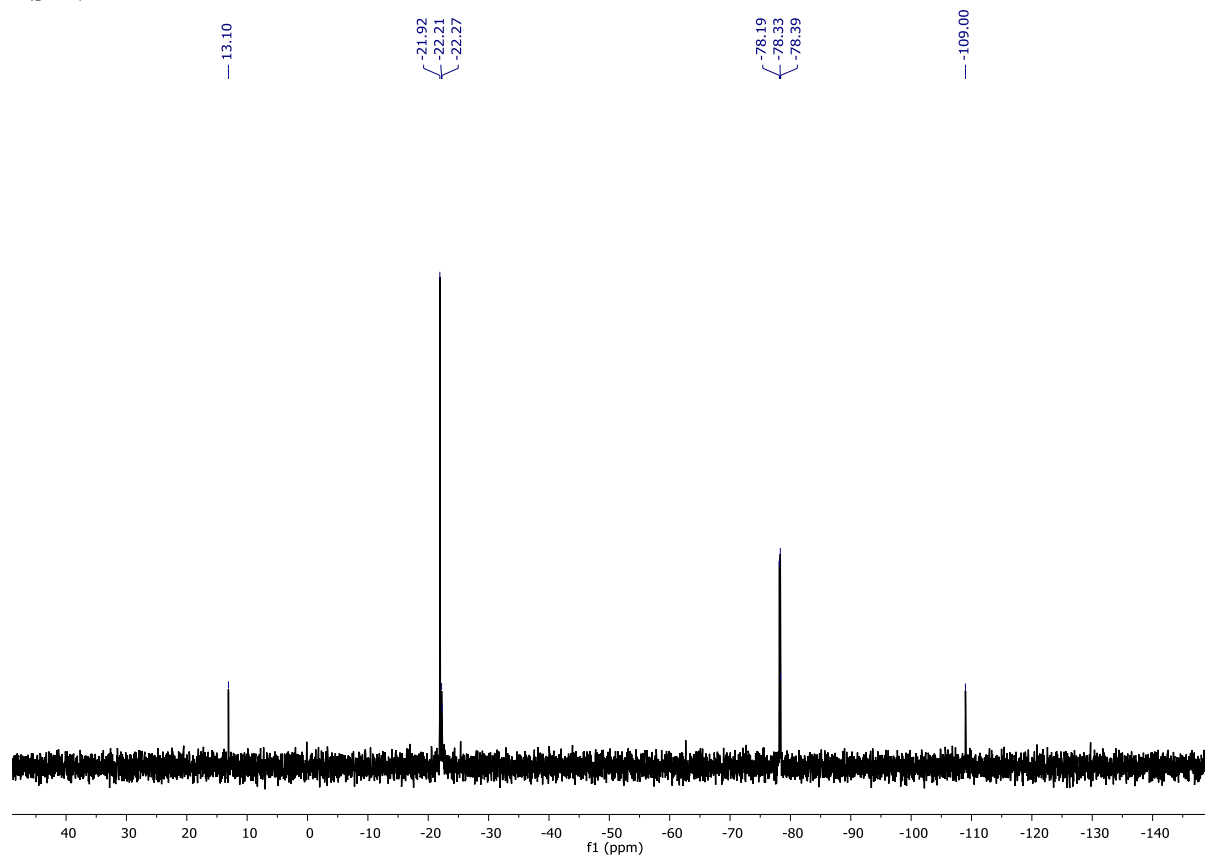
¹H NMR



¹³C NMR



²⁹Si NMR



3. Stacked FT-IR spectra of starting material (PS2), substrates and the resulting products

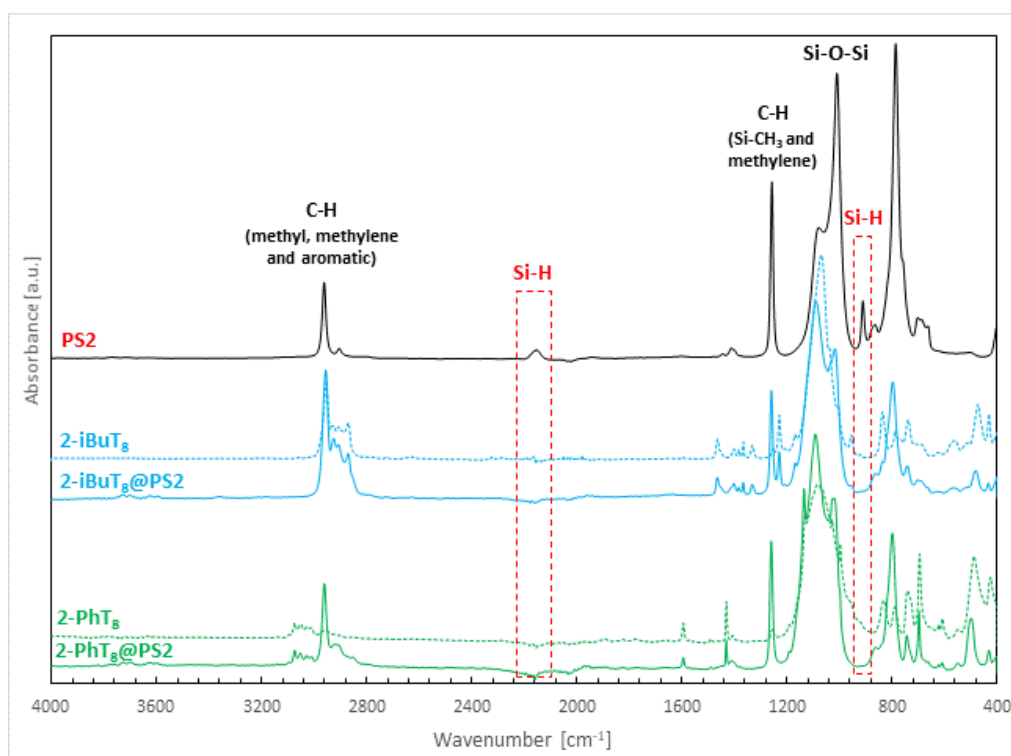


Figure S1. Selected FT-IR spectra of polysiloxane PS2 and mono(vinyl)substituted $i\text{BuT}_8$ (2- $i\text{BuT}_8$), and mono(vinyl)substituted PhT_8 (2- PhT_8) along with the obtained products 2- $i\text{Bu}/\text{PhT}_8@PS2$.

4. References

1. Hou, Z.; Yang, B.; Zhang, D.; Xu, Z.; Kan, C. Polysiloxanes with Quaternary Ammonium and Polyether Groups for Silyl-Terminated Polypropylene Oxide Waterborne Emulsions. *J. Surfactants Deterg.* **2016**, *19*, 739–745, doi:10.1007/s11743-016-1825-8.
2. Guerra-Contreras, A.; Villegas, A.; Ramírez-Oliva, E.; Cervantes, J. Characterization and Study of Properties in a Polar Solvent of a Functionalized and Quaternized Poly(dimethylsiloxane-co-methyl-hydridosiloxane). *Silicon* **2017**, *9*, 525–533, doi:10.1007/s12633-015-9286-7.
3. Chung, D. won; Lim, J.C. Study on the effect of structure of polydimethylsiloxane grafted with polyethyleneoxide on surface activities. *Colloids Surfaces A Physicochem. Eng. Asp.* **2009**, *336*, 35–40, doi:10.1016/j.colsurfa.2008.11.020.