10.1071/CH14525_AC

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SUPPLEMENTARY MATERIAL

Synthesis and catalytic applications of chemically grafted SiH-functionalized tripodal Ti-POSS complexes in crosslinked hyperbranched poly(siloxysilane)

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Figure S1. ^{1}HNMR ($CDCl_3$) spectrum of*(ClSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_7$Si$_8$O$_{12}$* ***(1)***

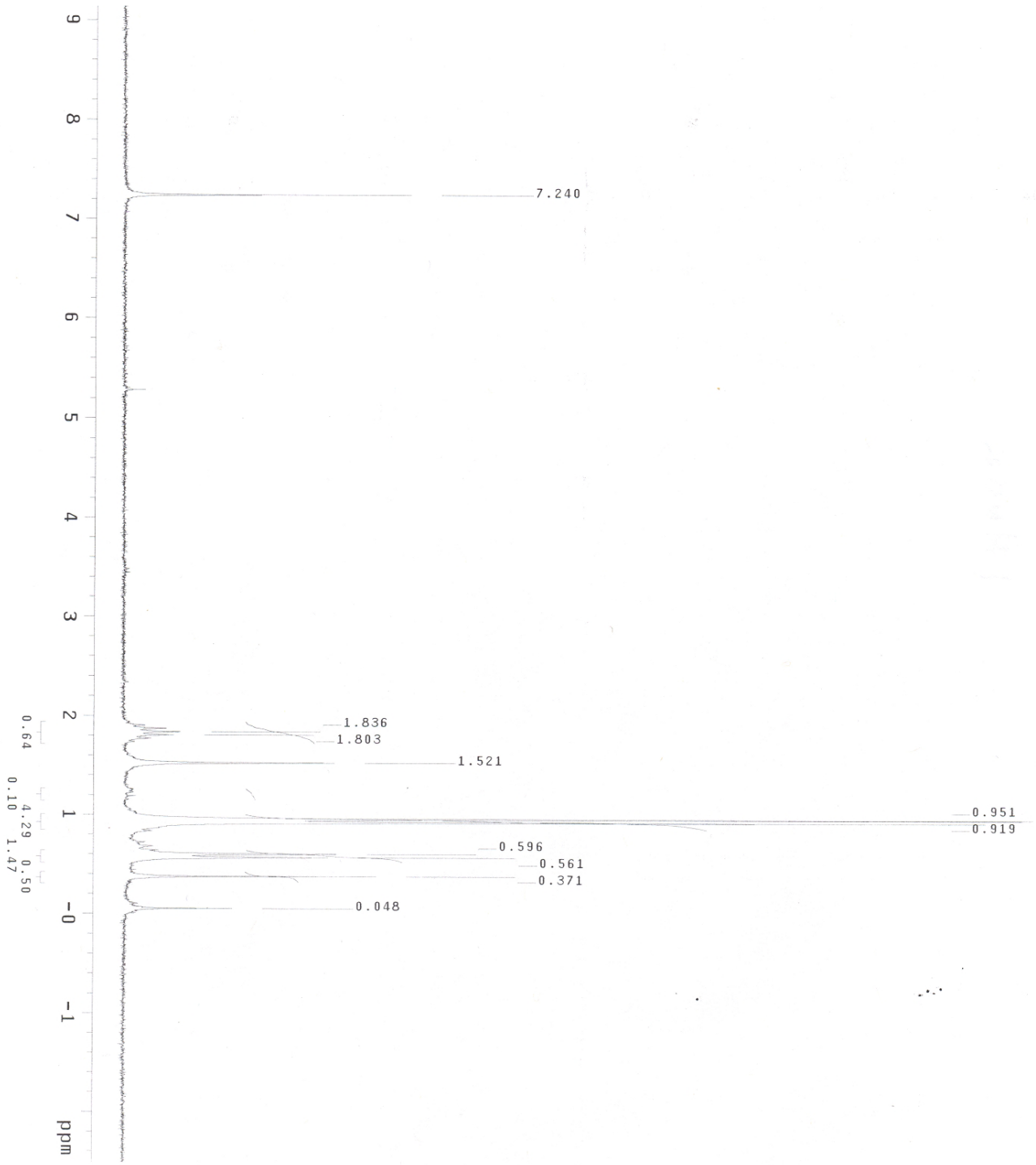


Figure S2. ^{13}C NMR ($CDCl_3$) spectrum of *(ClSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_7$Si$_8$O$_{12}$* ***(1)***

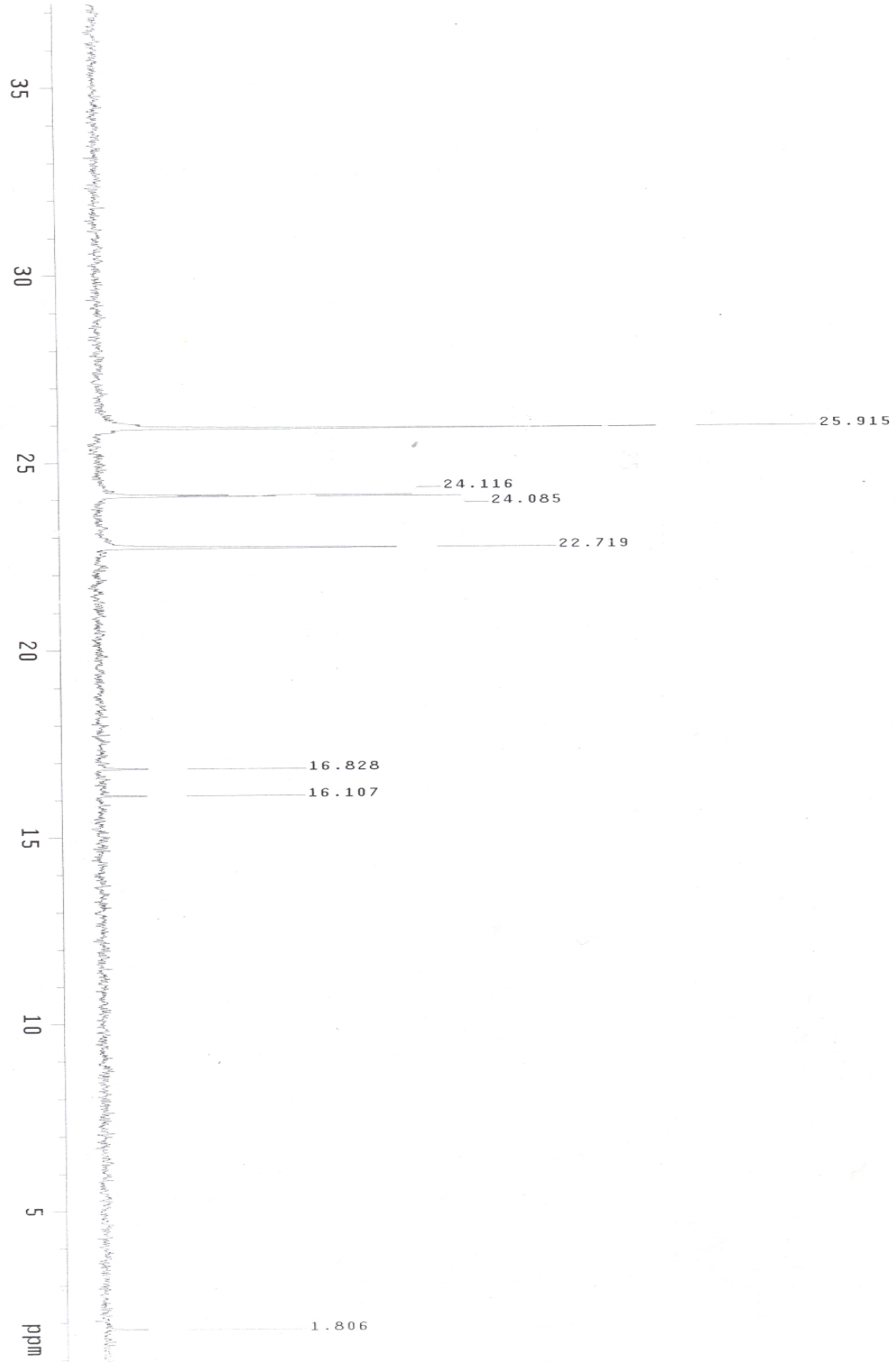
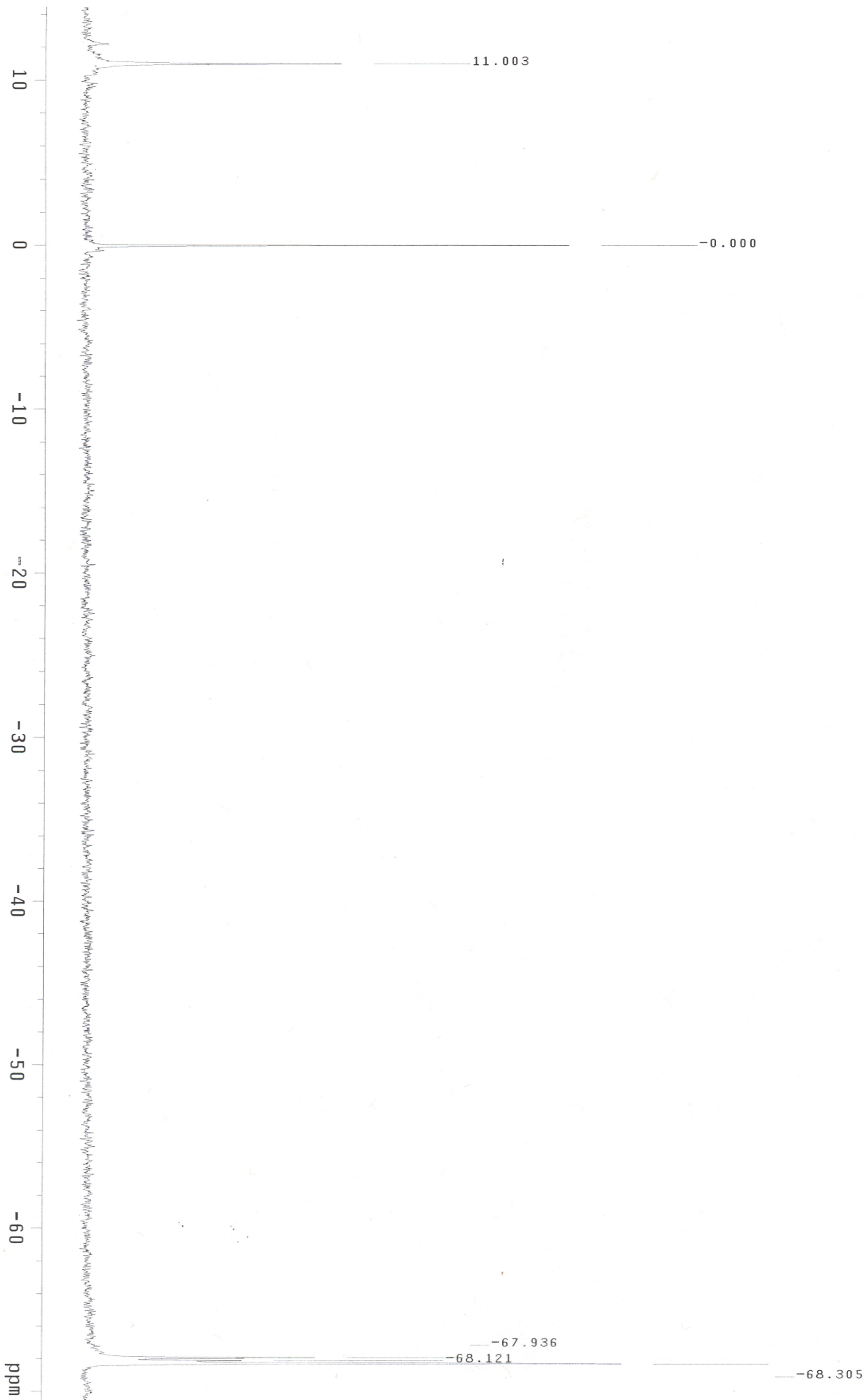


Figure S3. ^{29}SiNMR ($CDCl_3$) spectrum of *(ClSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_7$Si$_8$O$_{12}$* ***(1)***



11.003
-0.000
-67.936
-68.121
-68.305
10
0
-10
-20
-30
-40
-50
-60
ppm

Figure S4. ^{1}HNMR ($CDCl_3$) spectrum of ***(HSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_7$Si$_8$O$_{12}$ (2)***

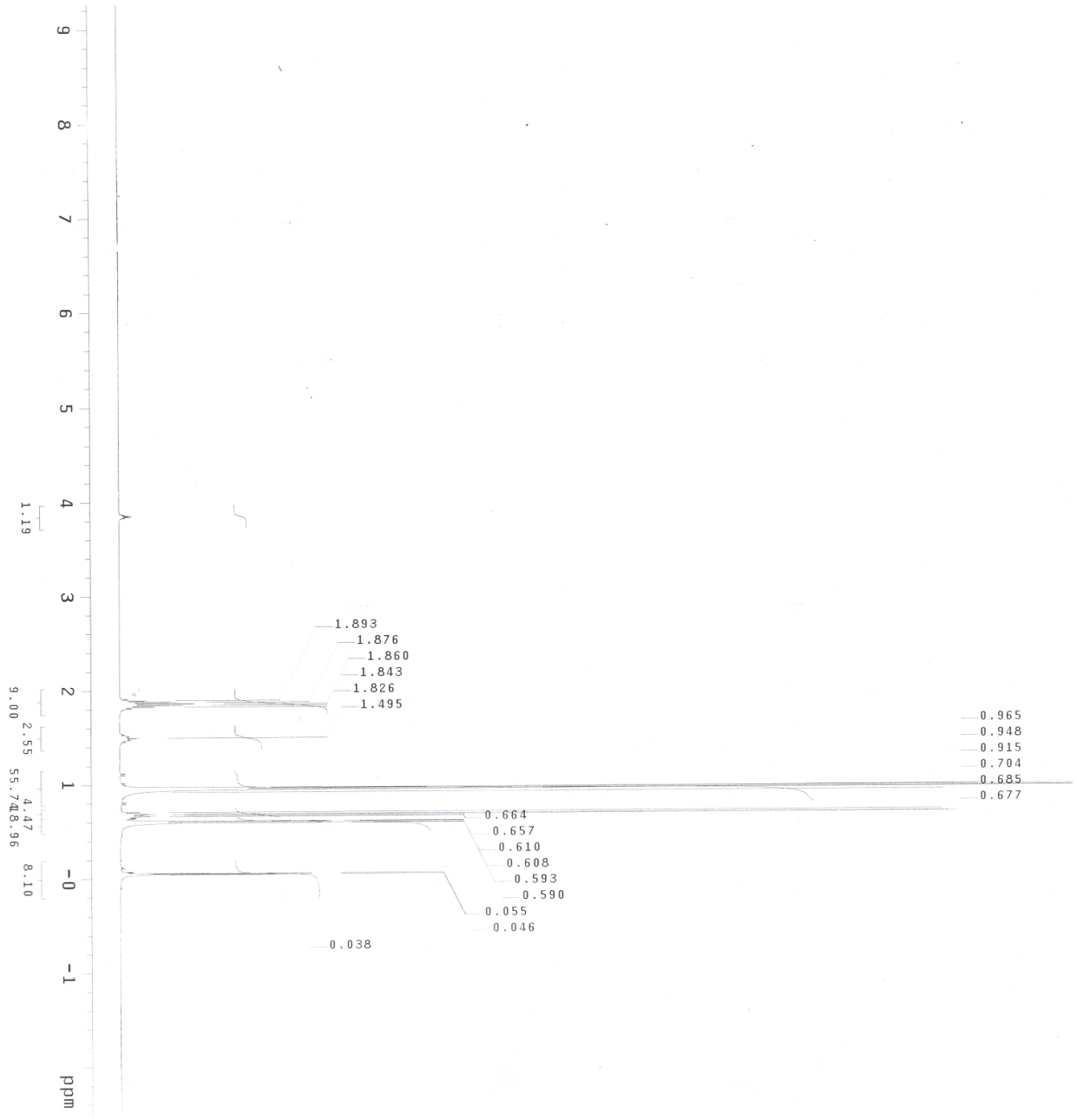


Figure S5. ^{13}C NMR ($CDCl_3$) spectrum of ***(HSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_7$Si$_8$O$_{12}$ (2)***

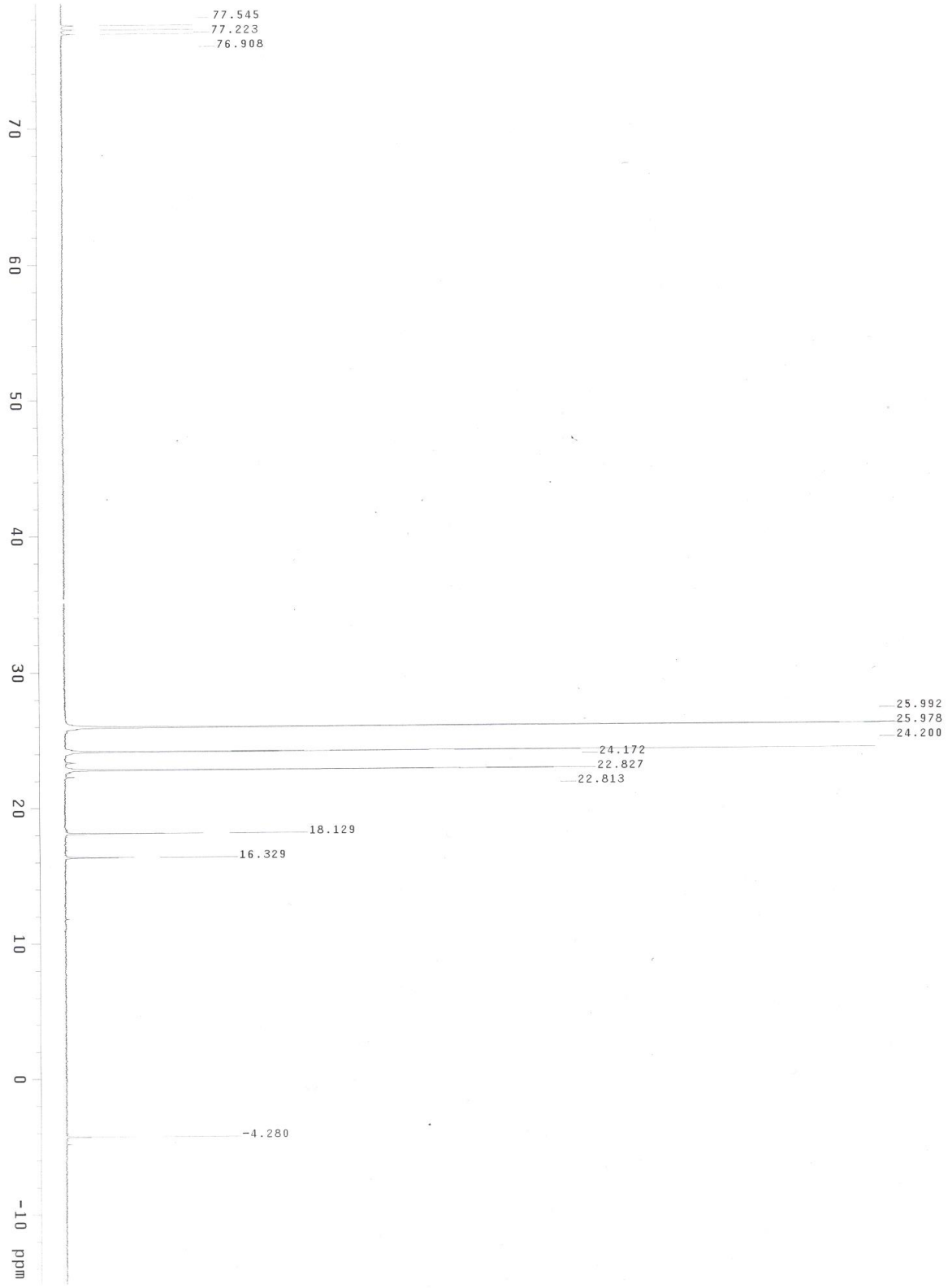


Figure S6. ^{29}SiNMR ($CDCl_3$) spectrum of *(HSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_7$Si$_8$O$_{12}$* ***(2)***

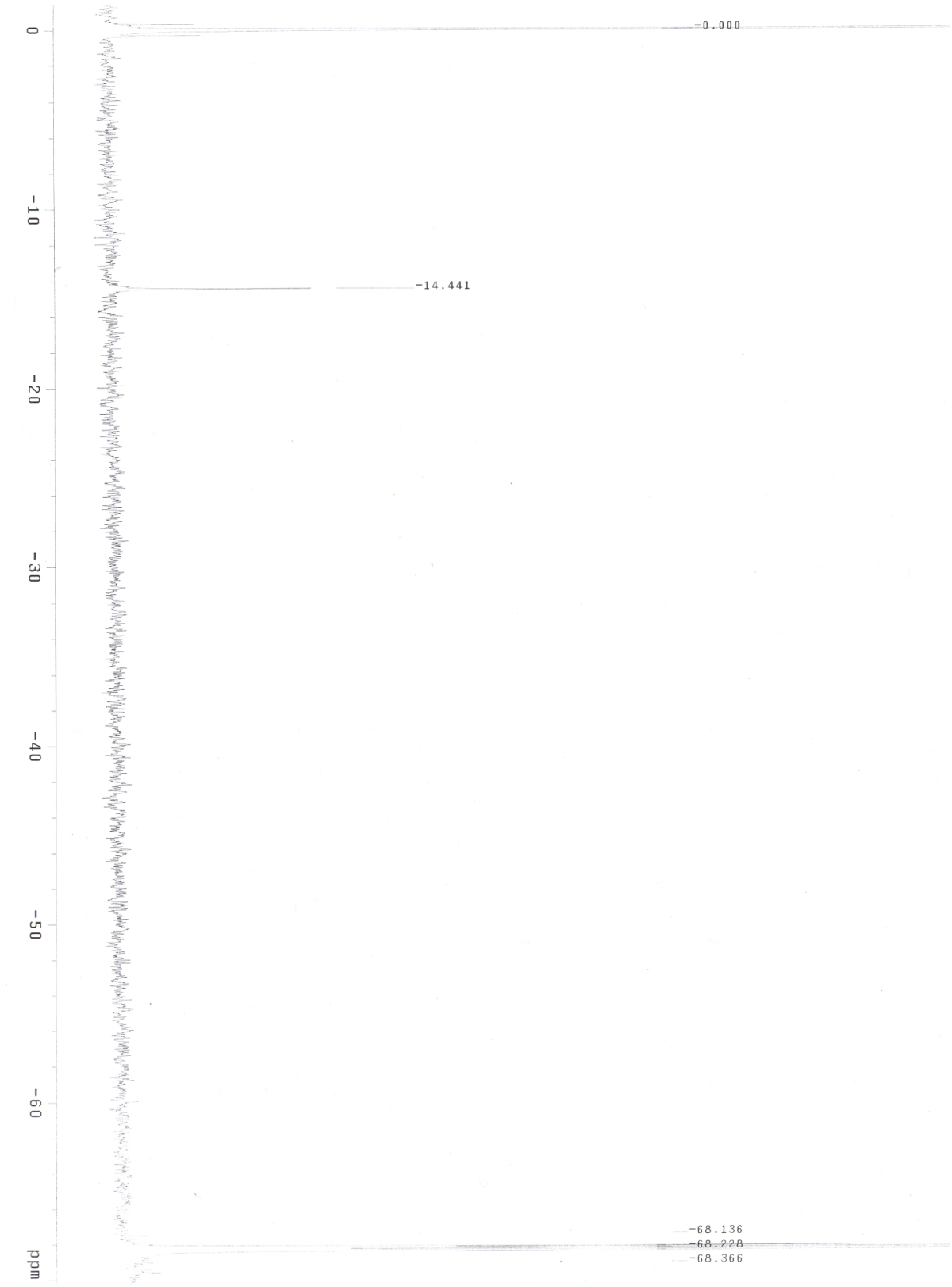


Figure S7. ^{1}HNMR ($CDCl_3$) spectrum of *{(HSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_6$Si$_7$O$_9$(OH)$_3$}* ***(3)***

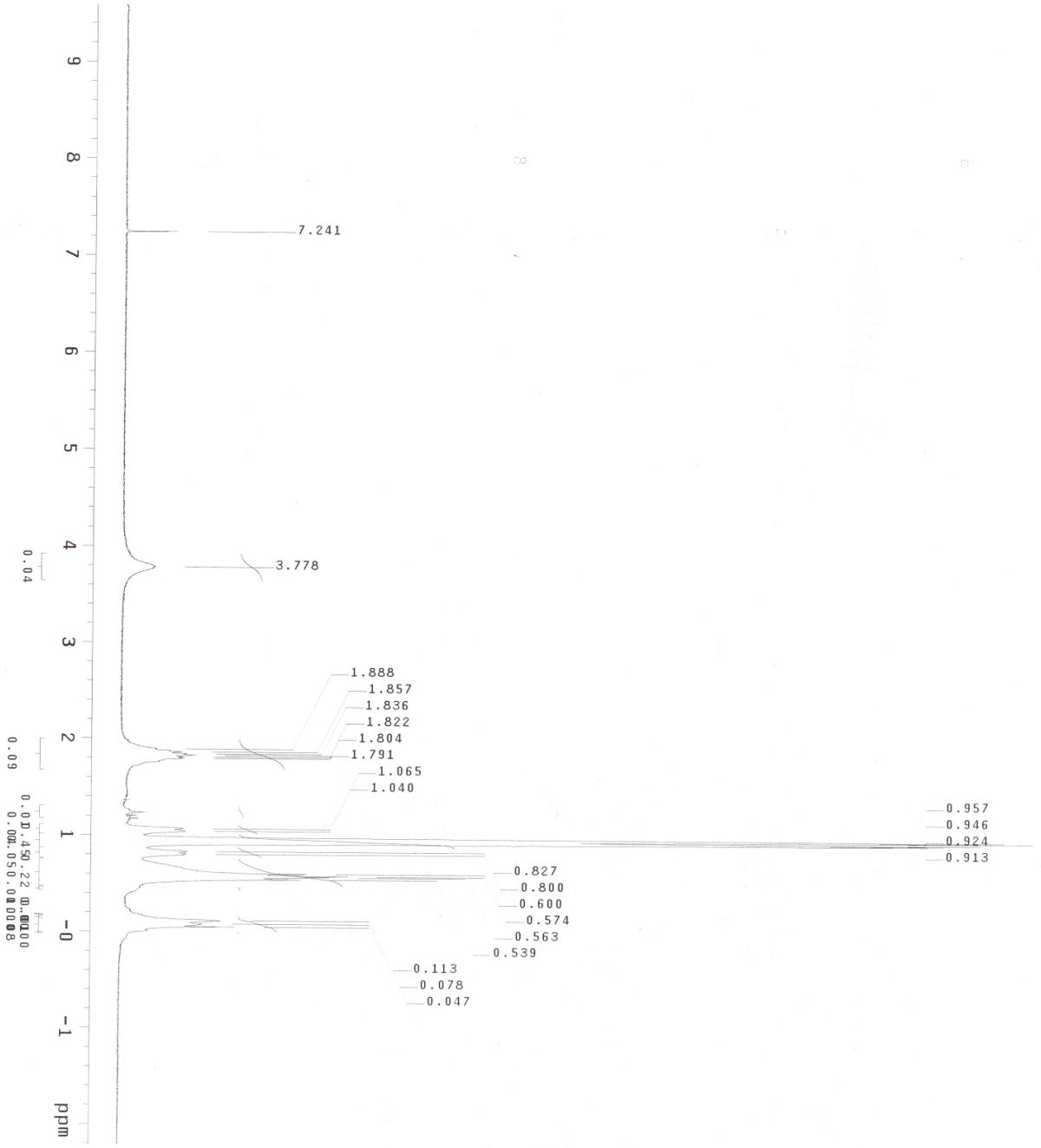


Figure S8. ^{13}C NMR ($CDCl_3$) spectrum of *{(HSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_6$Si$_7$O$_9$(OH)$_3$}* ***(3)***

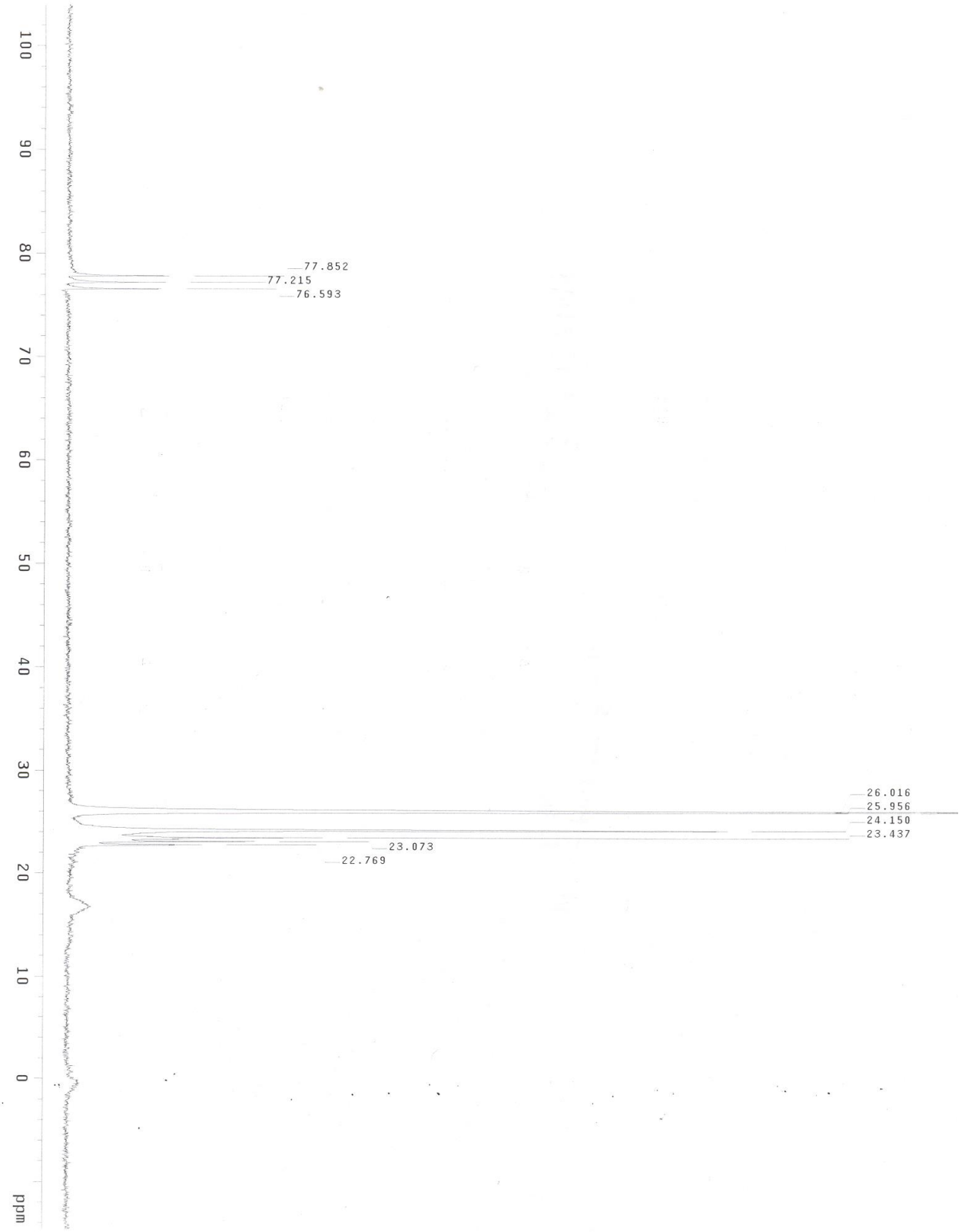


Figure S9. ^{29}SiNMR ($CDCl_3$) spectrum of *{(HSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_6$Si$_7$O$_9$(OH)$_3$}* ***(3)***

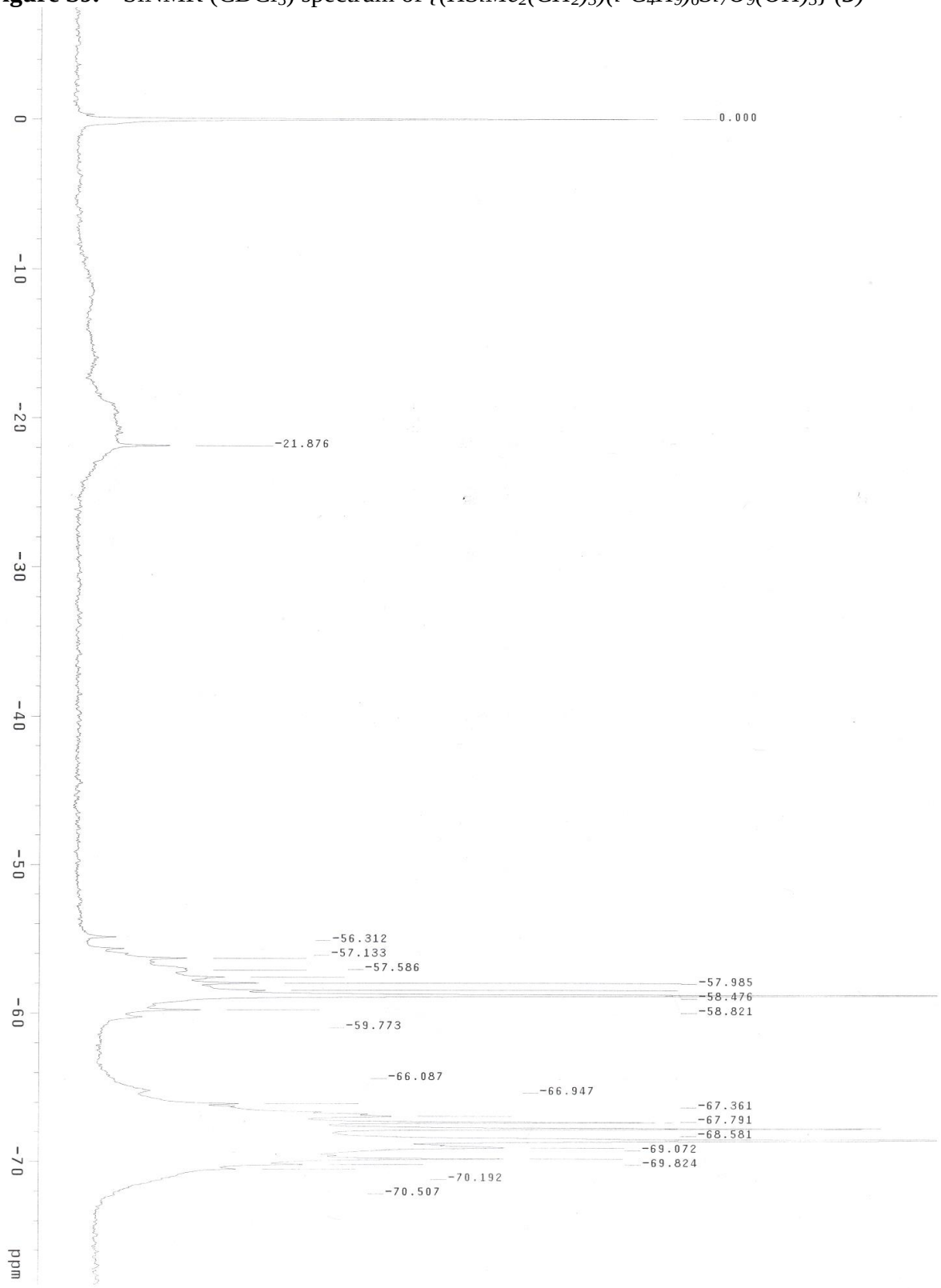


Figure S10. ^{29}SiNMR ($CDCl_3$) spectrum of *(p-ClSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$)(c-C$_6$H$_{11}$)$_7$Si$_8$O$_{12}$* ***(4)***

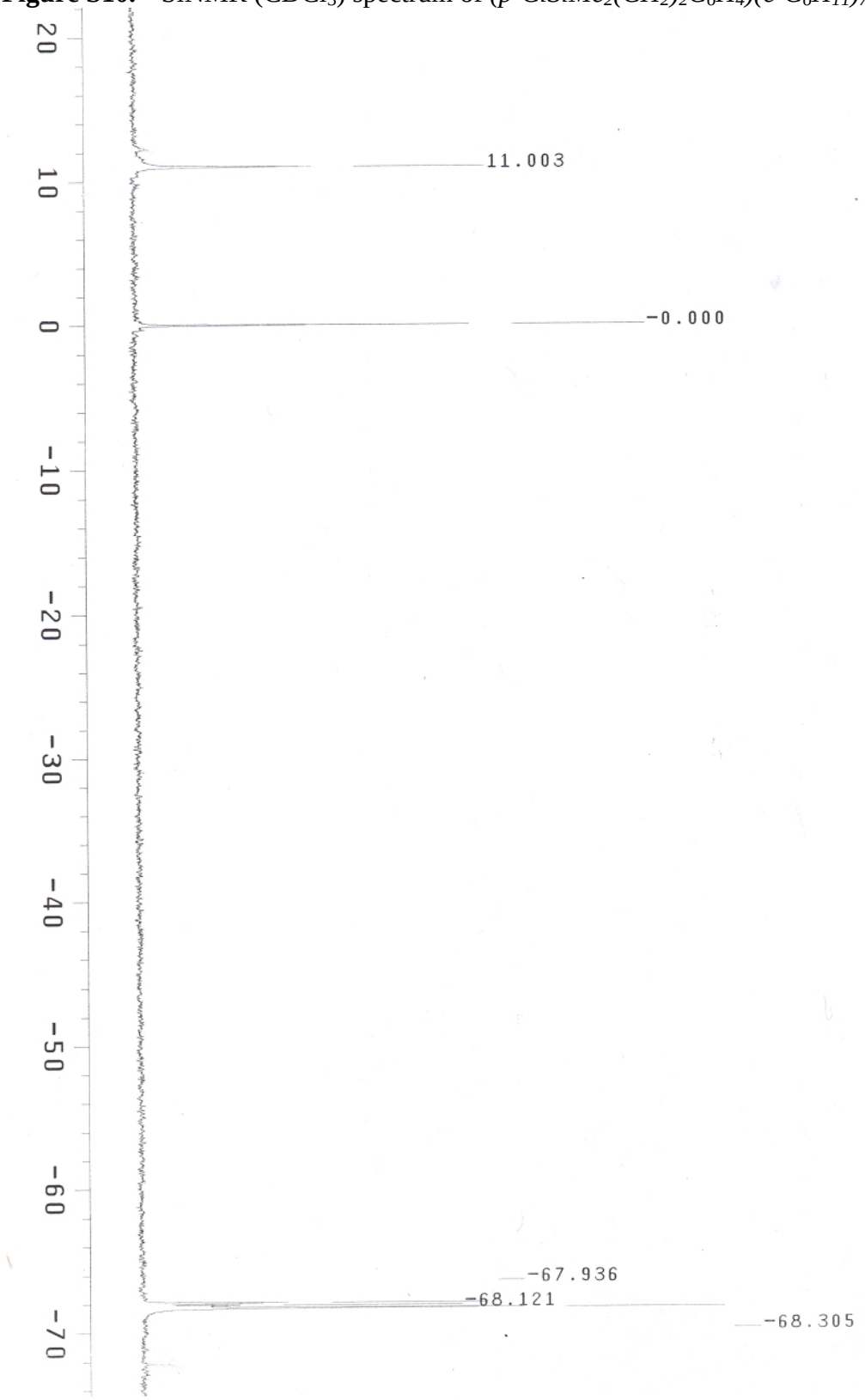


Figure S11. ^{1}HNMR ($CDCl_3$) spectrum of *(p-$HSiMe_2(CH_2)_2C_6H_4$)(c-$C_6H_{11})_7Si_8O_{12}$* ***(5)***

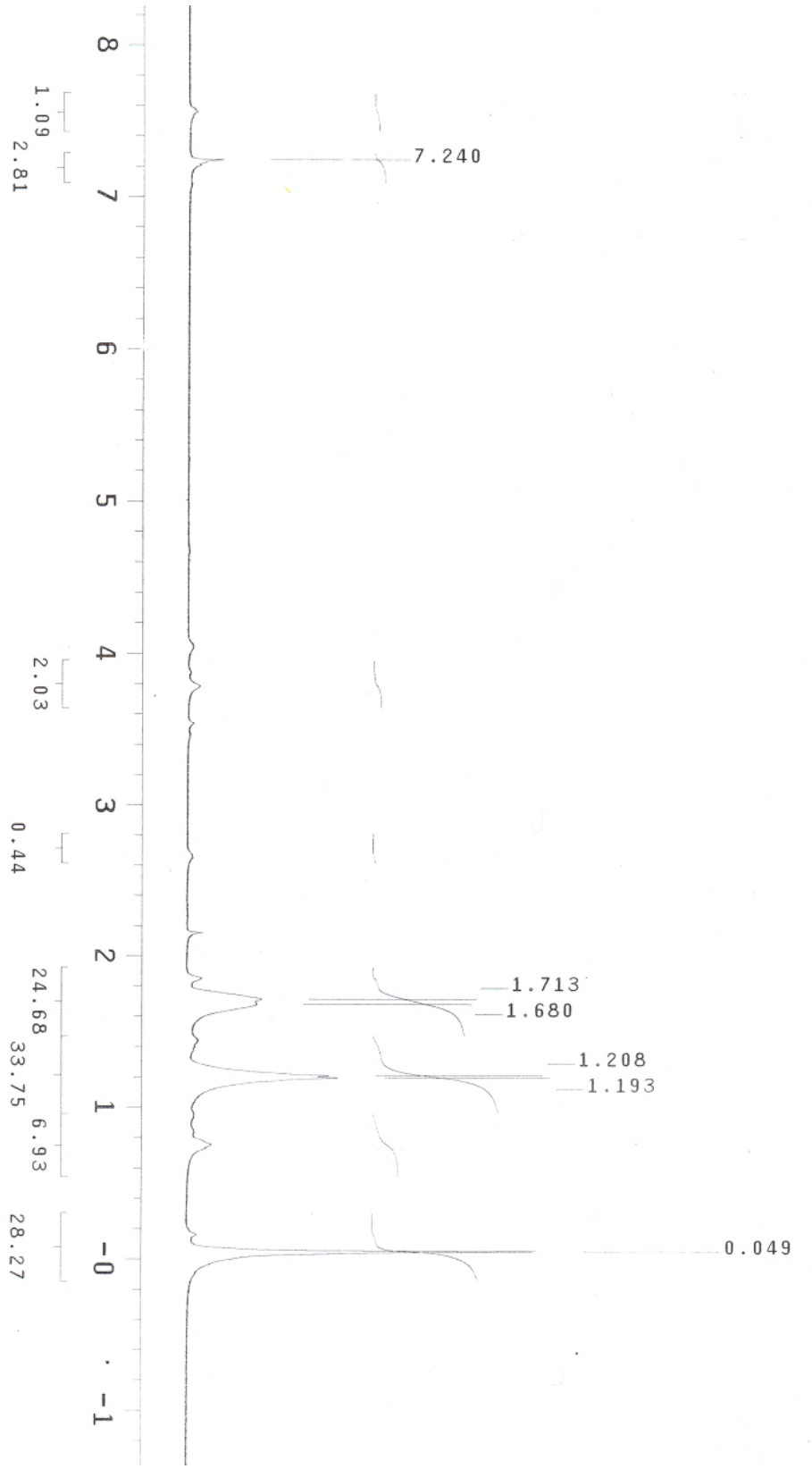


Figure S12. ^{29}SiNMR ($CDCl_3$) spectrum of *(p-HSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$)(c-C$_6$H$_{11}$)$_7$Si$_8$O$_{12}$* ***(5)***

Figure S13. ^{1}HNMR ($CDCl_3$) spectrum of *(p-$HSiMe_2(CH_2)_2C_6H_4$)(c-$C_6H_{11})_6Si_7O_9(OH)_3$* ***(6)***

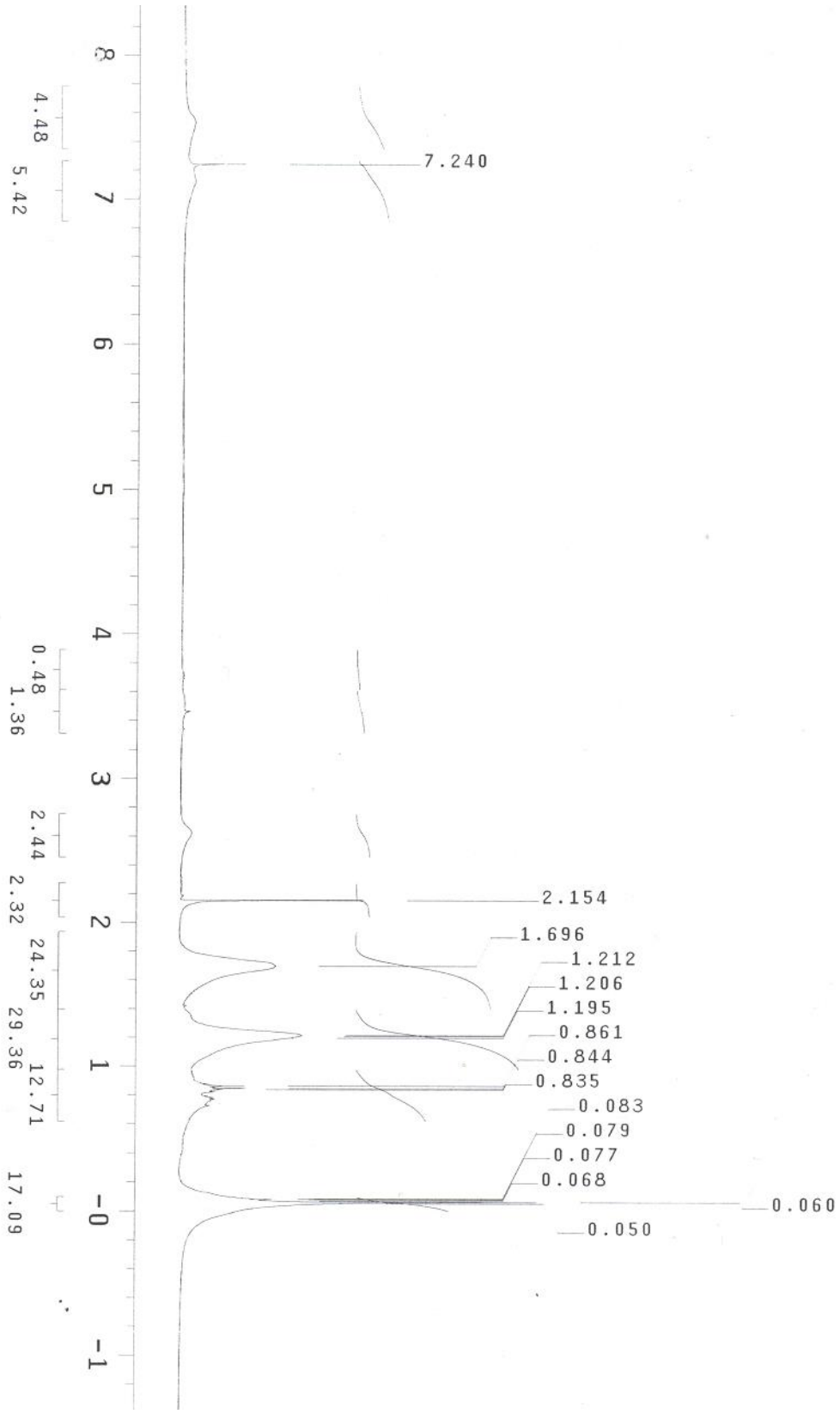


Figure S14. ^{13}C NMR ($CDCl_3$) spectrum of *(p-HSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$)(c-C$_6$H$_{11}$)$_6$Si$_7$O$_9$(OH)$_3$* ***(6)***

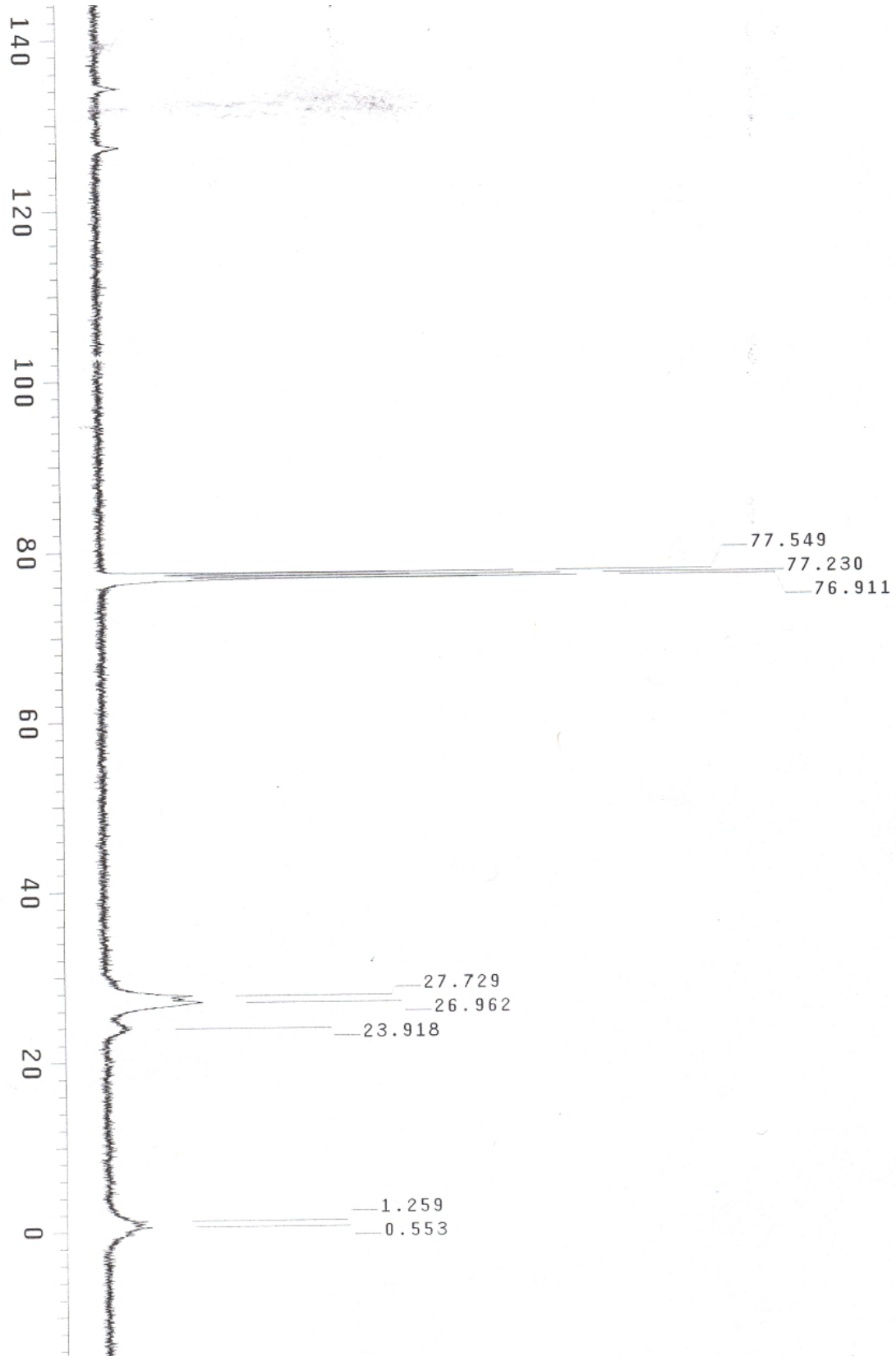


Figure S15. ^{1}HNMR ($CDCl_3$) spectrum of *[{(HSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_6$Si$_7$O$_{12}$}Ti(OPr^i)] (7)*

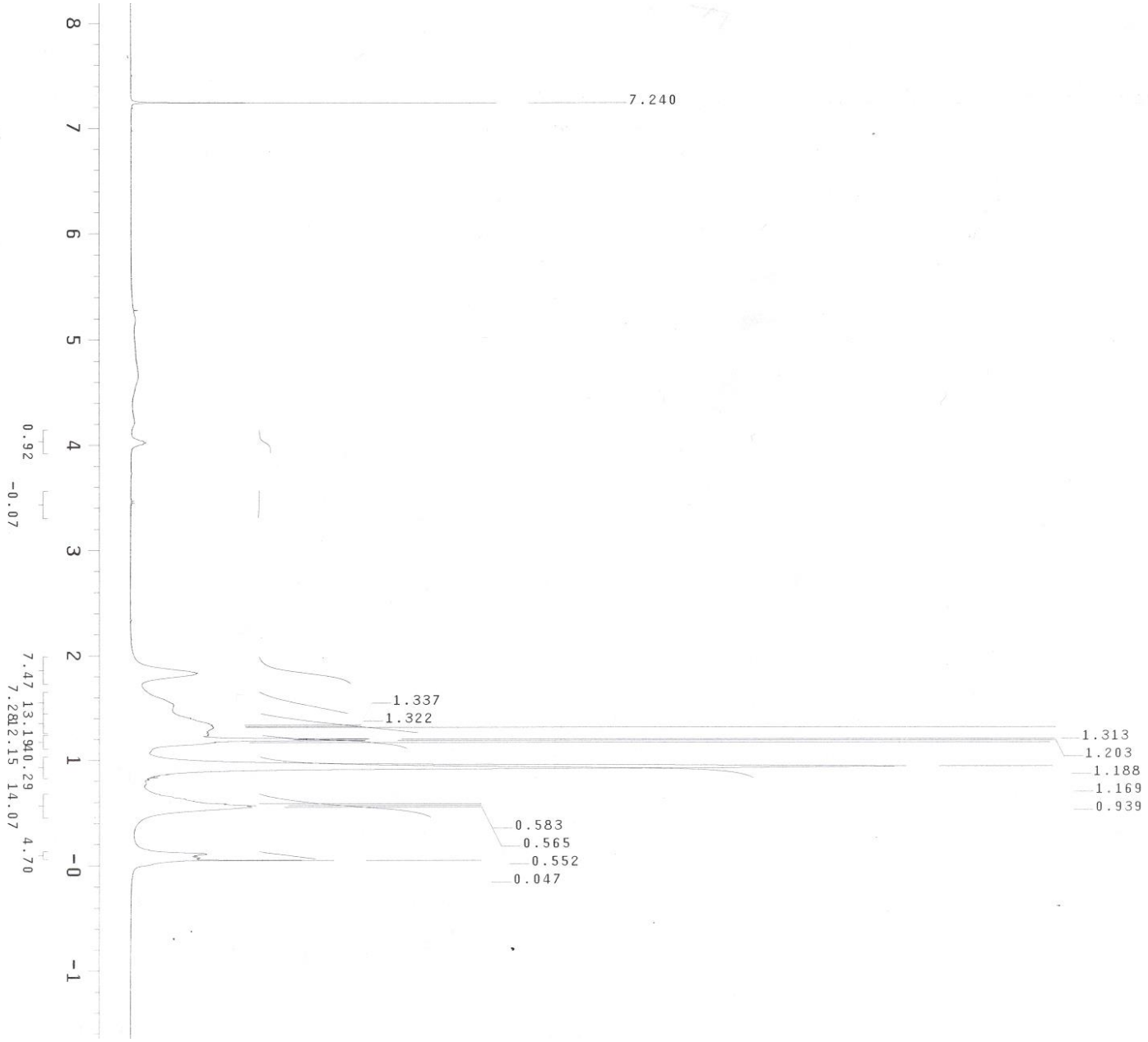


Figure S16. ^{29}SiNMR ($CDCl_3$) spectrum of *[{(HSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_6$Si$_7$O$_{12}$}Ti(OPr^i)] (**7**)*

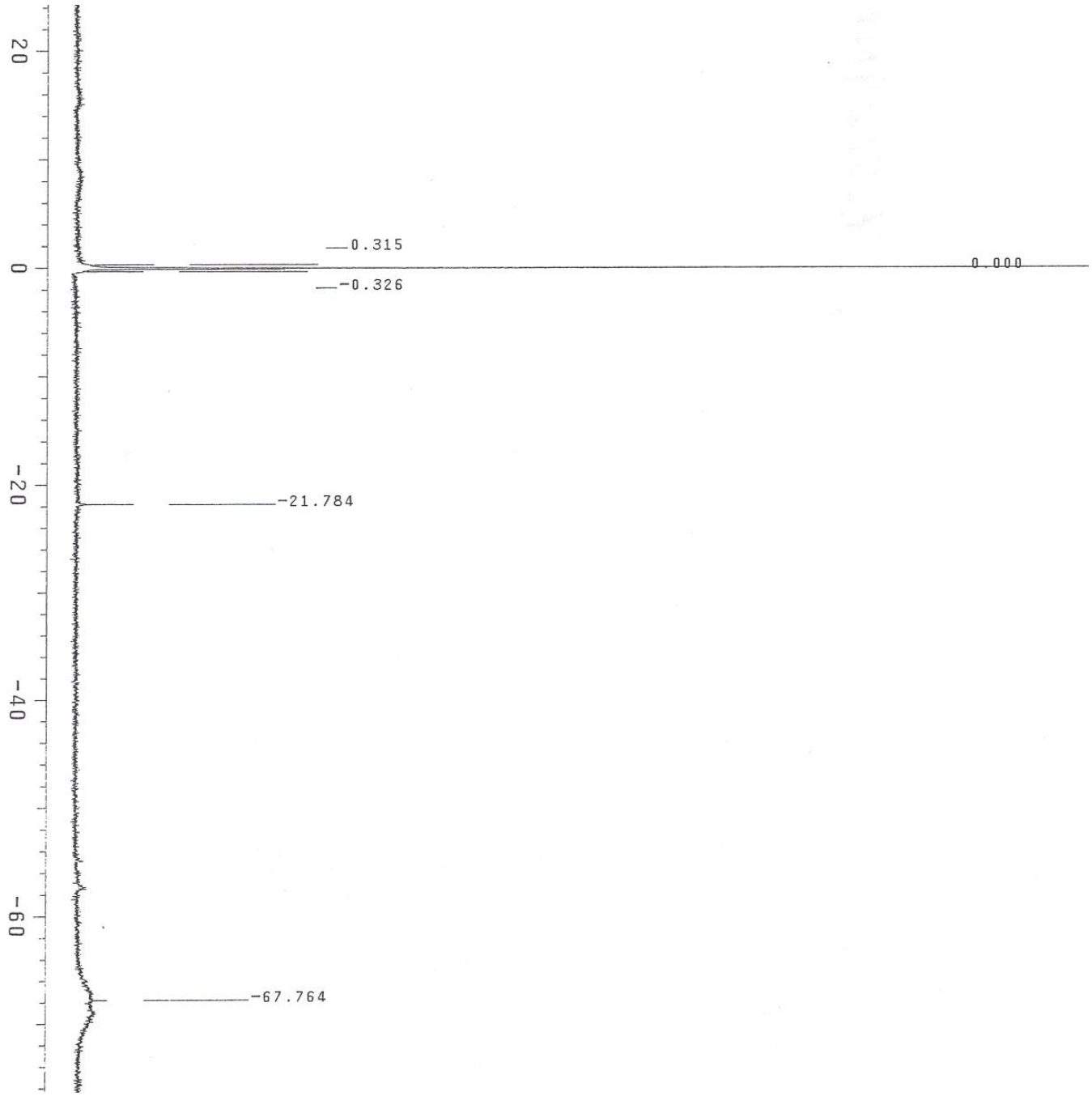


Figure S17. ^{1}HNMR ($CDCl_3$) spectrum of *[{(HSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)]* ***(8)***

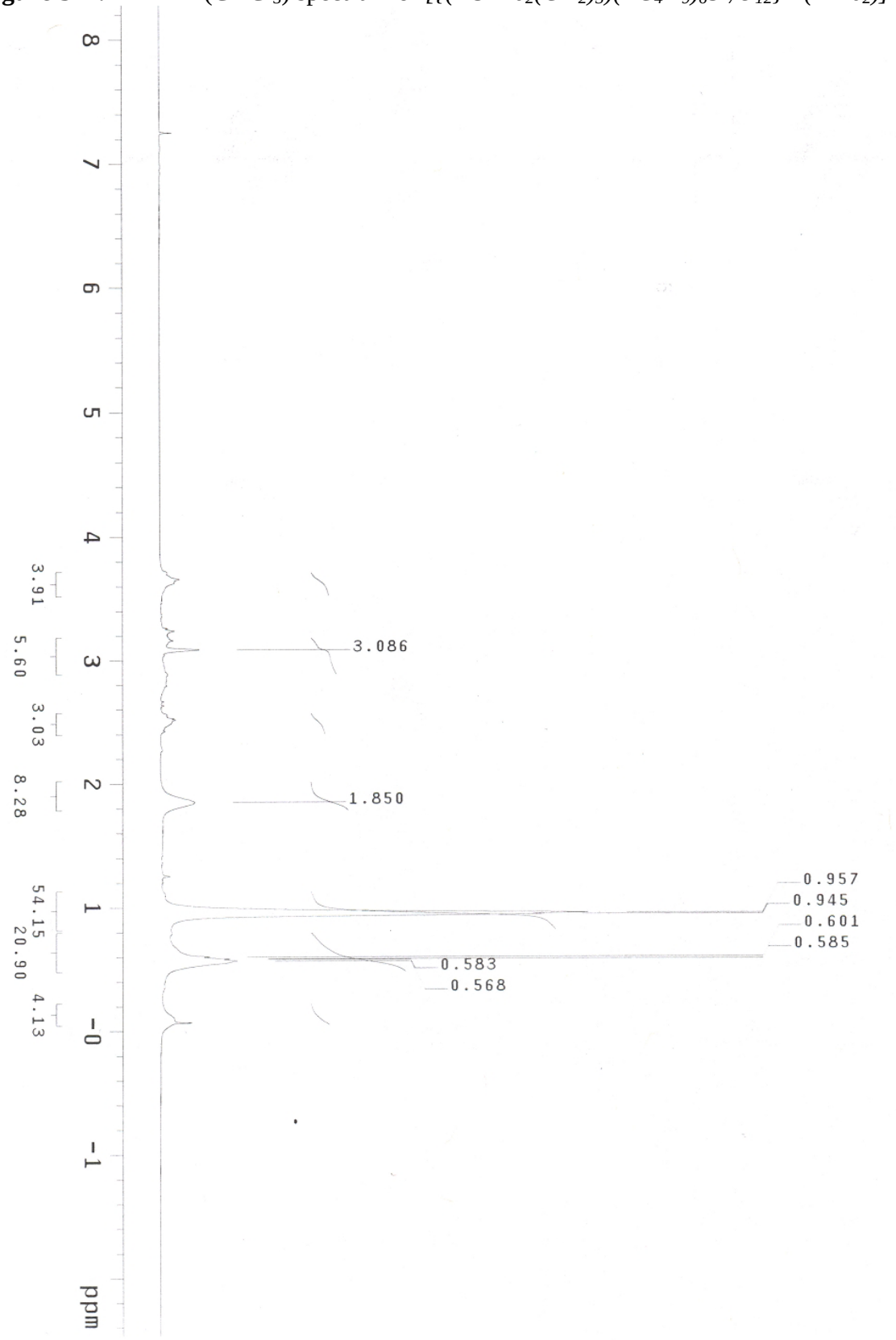


Figure S18. ^{13}C NMR ($CDCl_3$) spectrum of *[{(HSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)]* ***(8)***

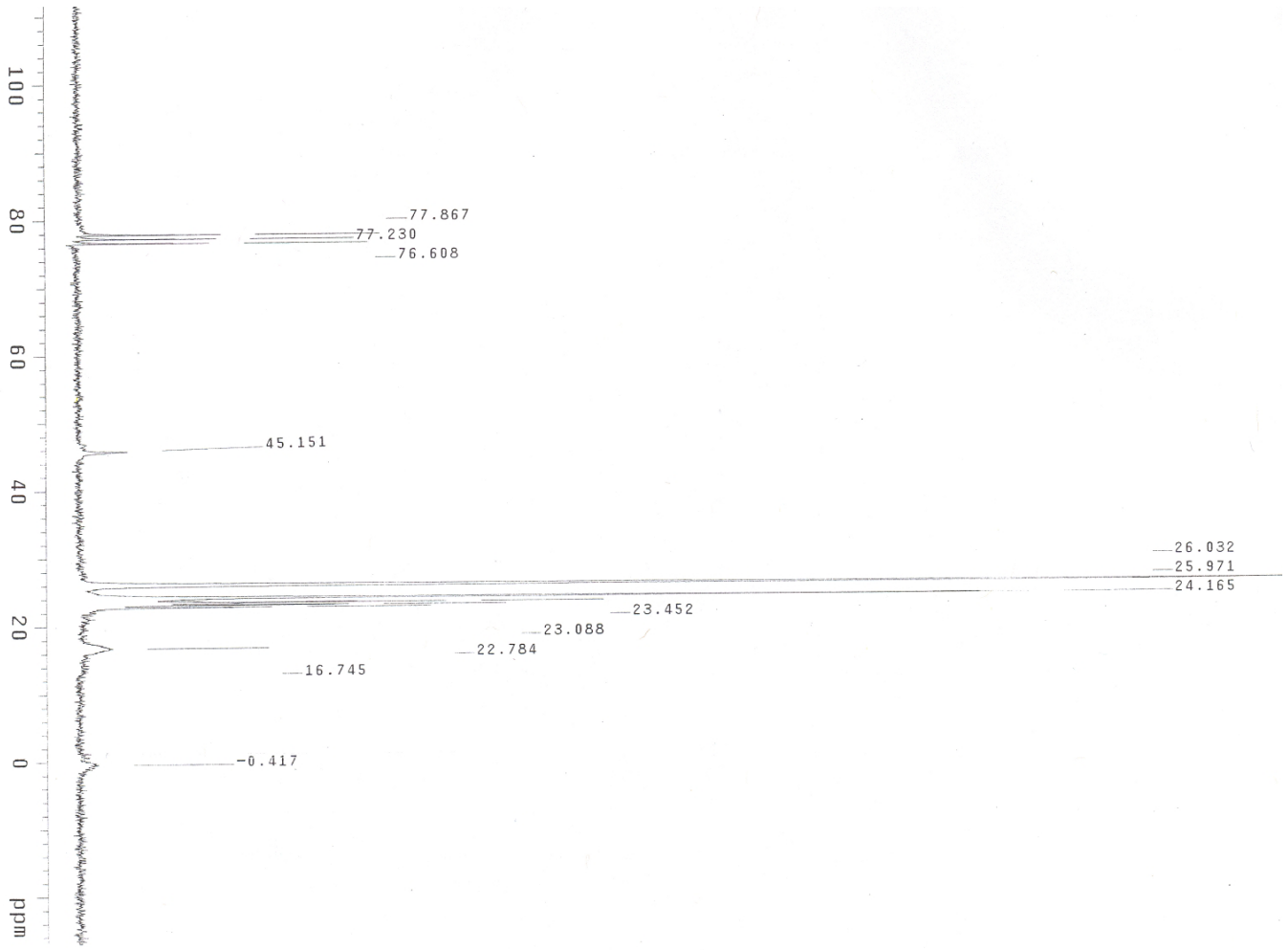


Figure S19. ^{29}SiNMR ($CDCl_3$) spectrum of *[{(HSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)]* ***(8)***

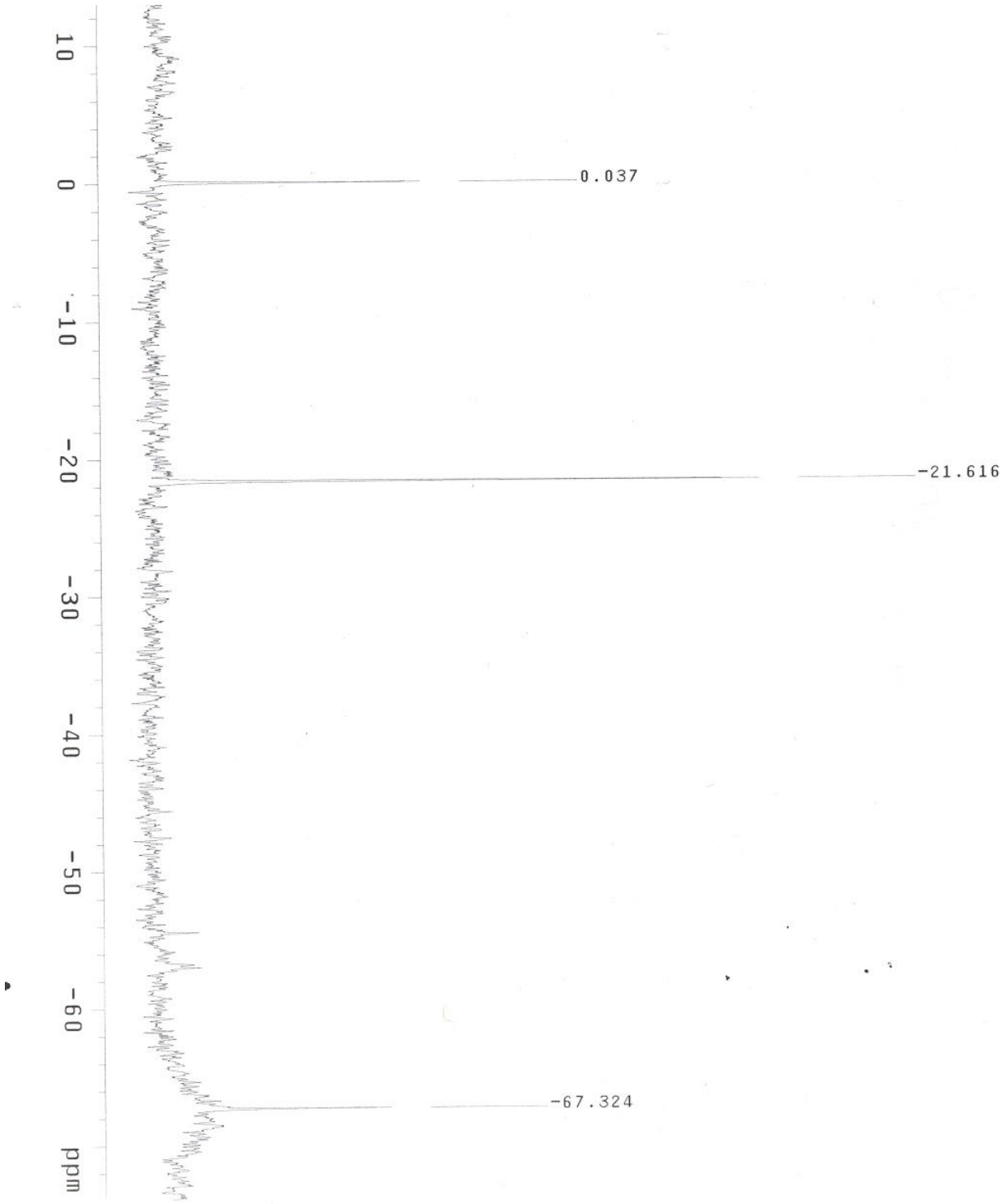
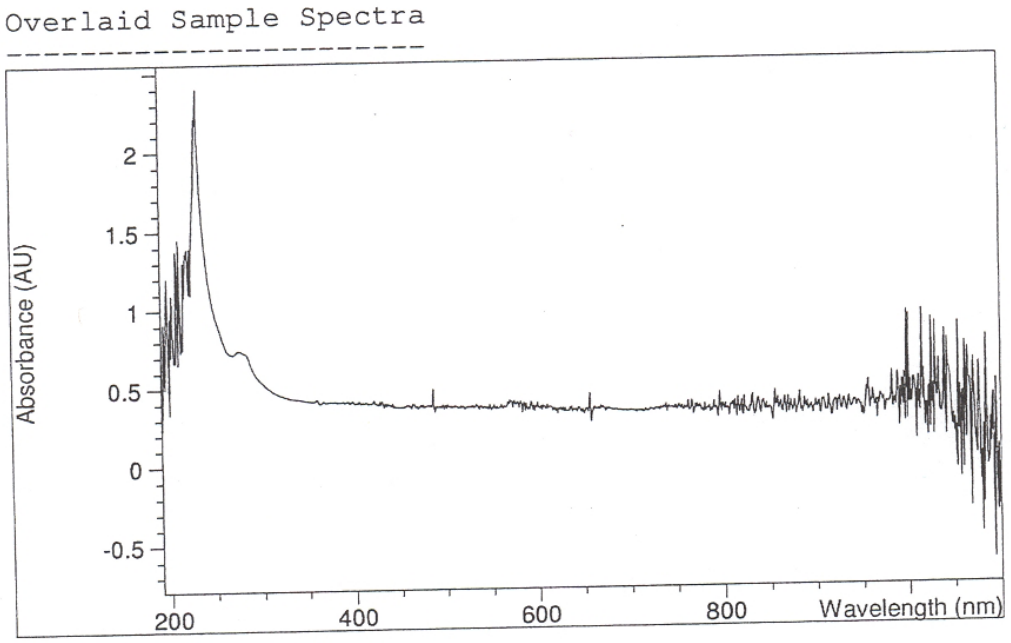


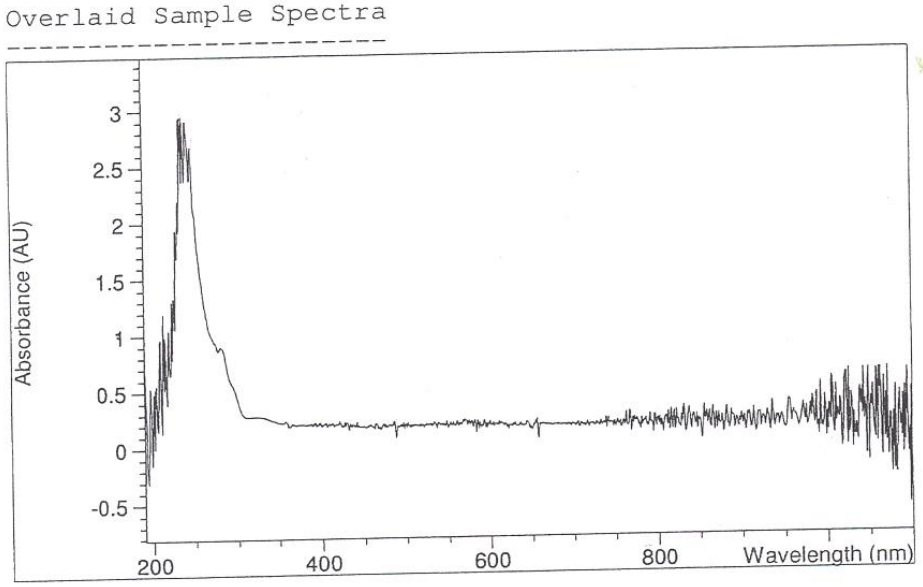
Figure S20. UV-vis spectrum of *[{(HSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)]* ***(8)***



Sample/Result Table

#	Name	Abs<230nm>
1		2.29060

Figure S21. UV-vis spectrum of *[{(p-HSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$)(c-C$_6$H$_{11}$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)]* ***(9)***



Sample/Result Table

#	Name	Abs<235nm>
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Figure S22. ^{1}HNMR ($CDCl_3$) spectrum of *[{(p-HSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$)(c-C$_6$H$_{11}$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)] (**9**)*

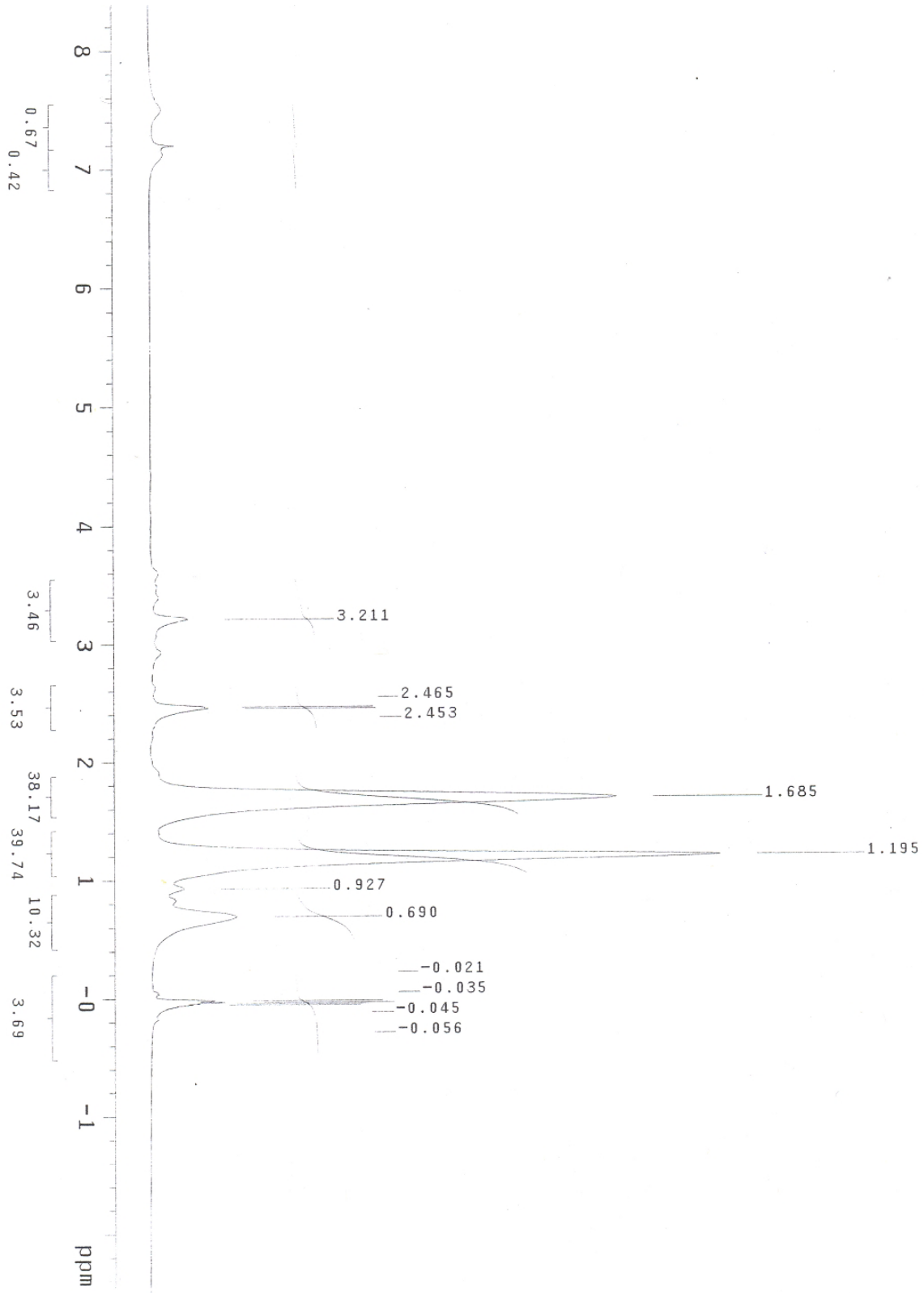


Figure S23. ^{13}C NMR ($CDCl_3$) spectrum of *[{(p-HSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$)(c-$_6$H$_{11}$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)] (**9**)*

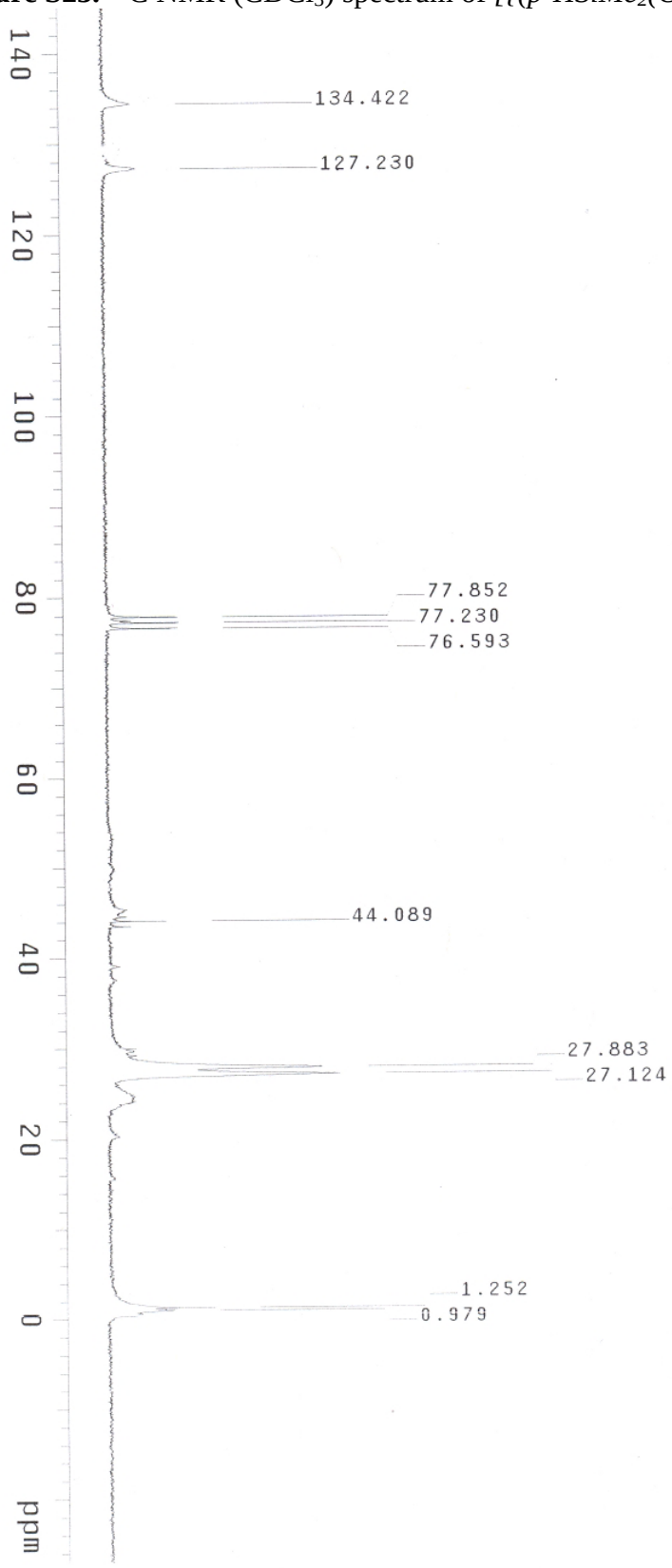
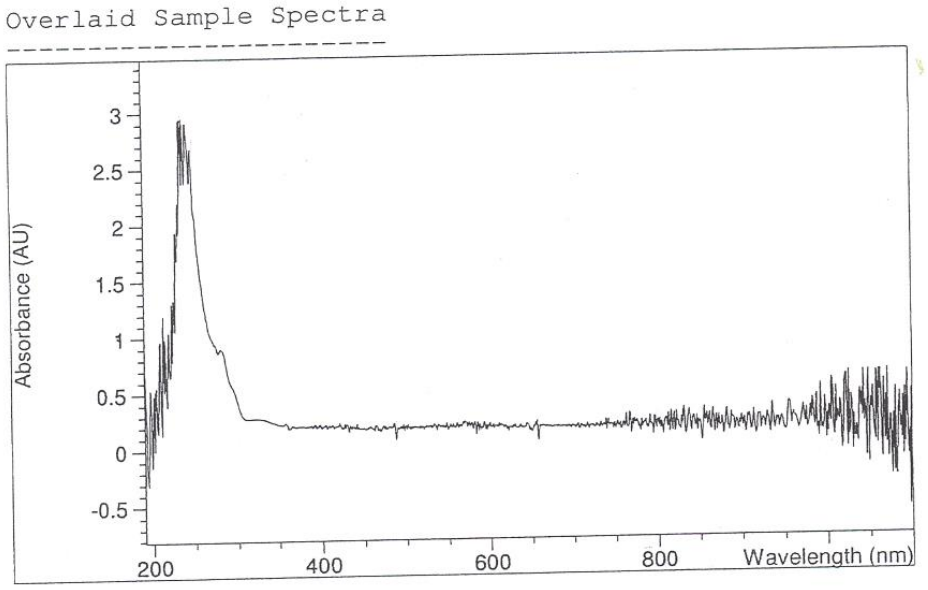


Figure S24. UV-vis spectrum of *[{(p-HSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$)(c-C$_6$H$_{11}$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)] (**9**)*



Sample/Result Table

#	Name	Abs<235nm>
1		2.83540

Figure S25. ^{1}HNMR (d8-toluene) spectrum of *crosslinked hyperbranched poly(siloxysilane)-bound [{(p-HSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$)(c-C$_6$H$_{11}$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)]* ***(11)***

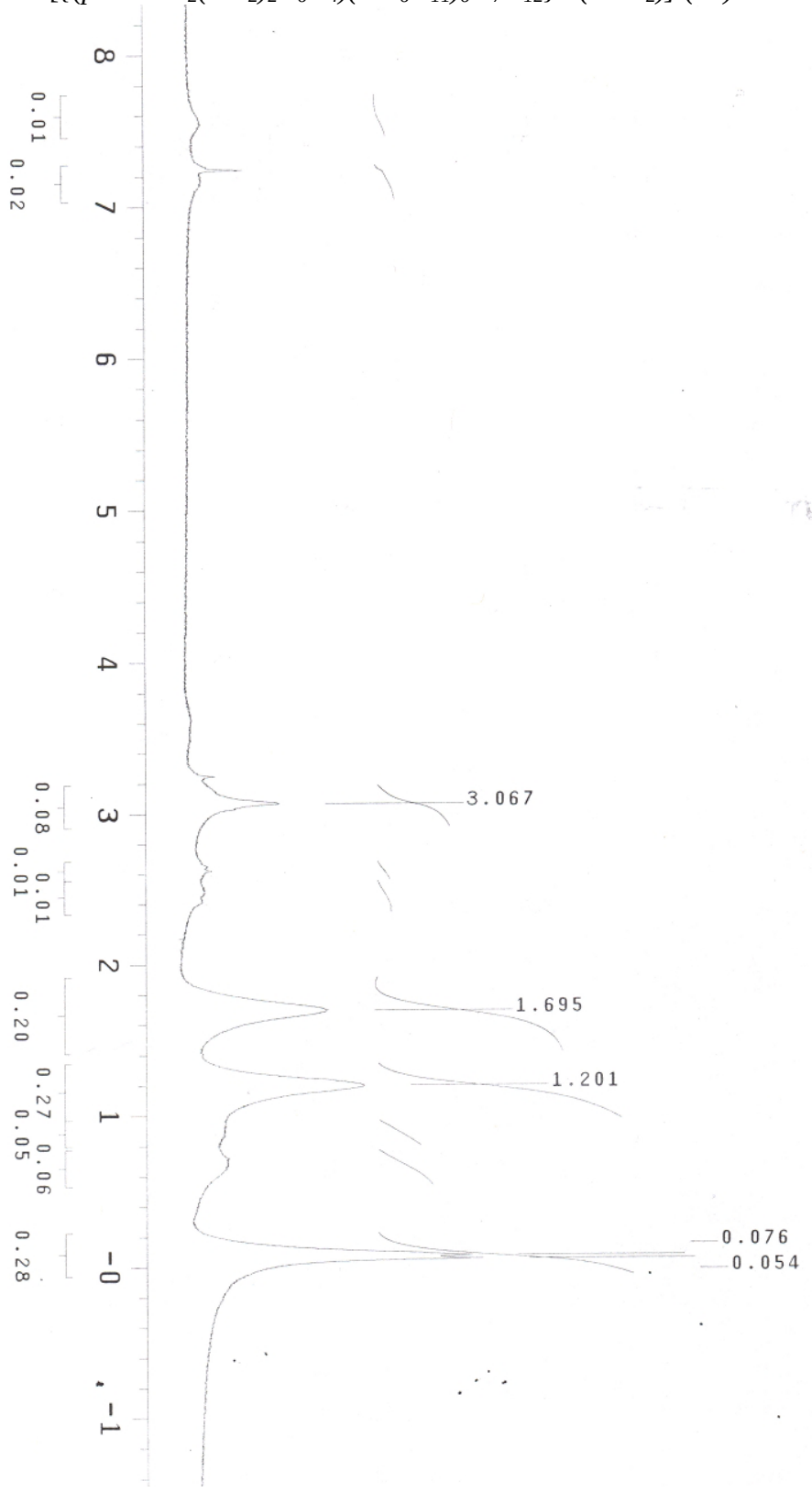


Figure S26. ^{13}C NMR (d_8-toluene) spectrum of *crosslinked hyperbranched poly(siloxysilane)-bound [{(p-HSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$)(c-C$_6$H$_{11}$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)]* (***11***)

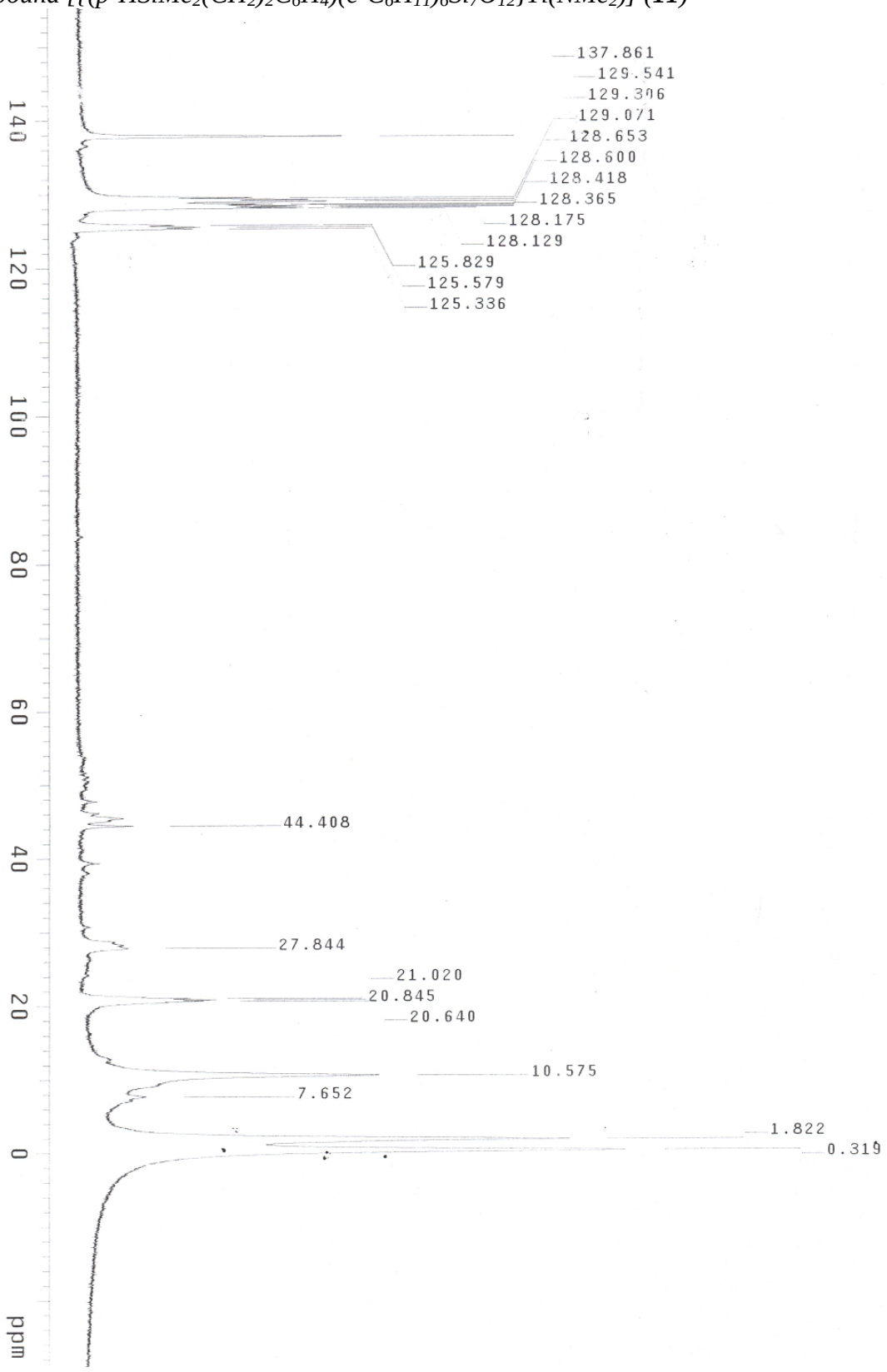
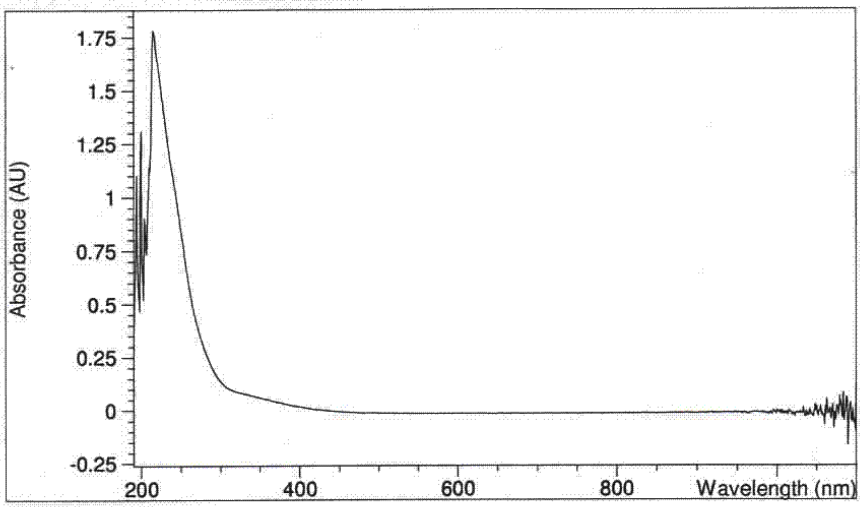


Figure S27. UV-vis spectrum of *crosslinked hyperbranched poly(siloxysilane)-bound [{(p-HSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$)(c-C$_6$H$_{11}$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)] (**11**)*

Overlaid Sample Spectra

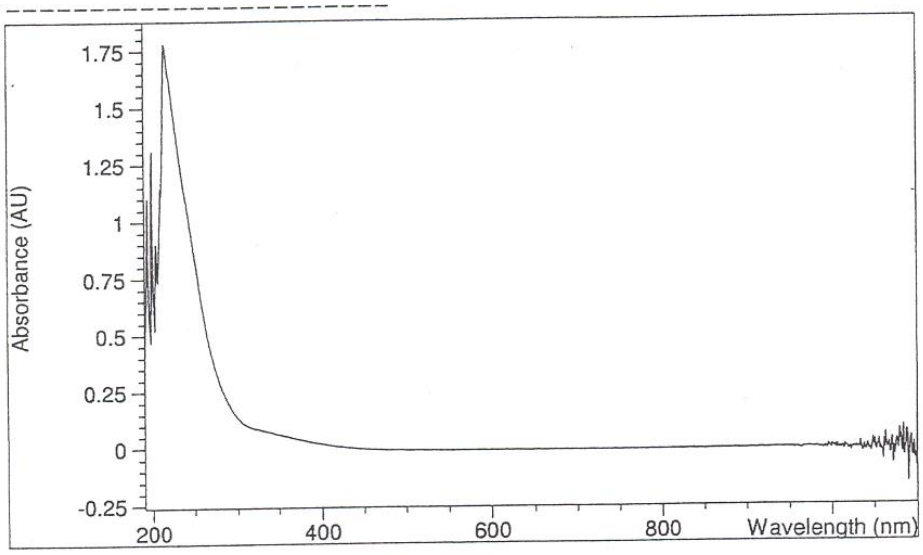


Sample/Result Table

#	Name	Abs<235nm>
1		1.76860

Figure S28. UV-vis spectrum of used *crosslinked hyperbranched poly(siloxysilane)-bound [{(p-HSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$)(c-C$_6$H$_{11}$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)] (**11**)*

Overlaid Sample Spectra



Sample/Result Table

#	Name	Abs<235nm>
1		1.76540

Figure S29. ^{1}H NMR ($CDCl_3$) spectrum of *crosslinked hyperbranched poly(siloxysilane)-bound* $[\{(HSiMe_2(CH_2)_3)(i\text{-}C_4H_9)_6Si_7O_{12}\}Ti(NMe_2)]$ ***(12)***

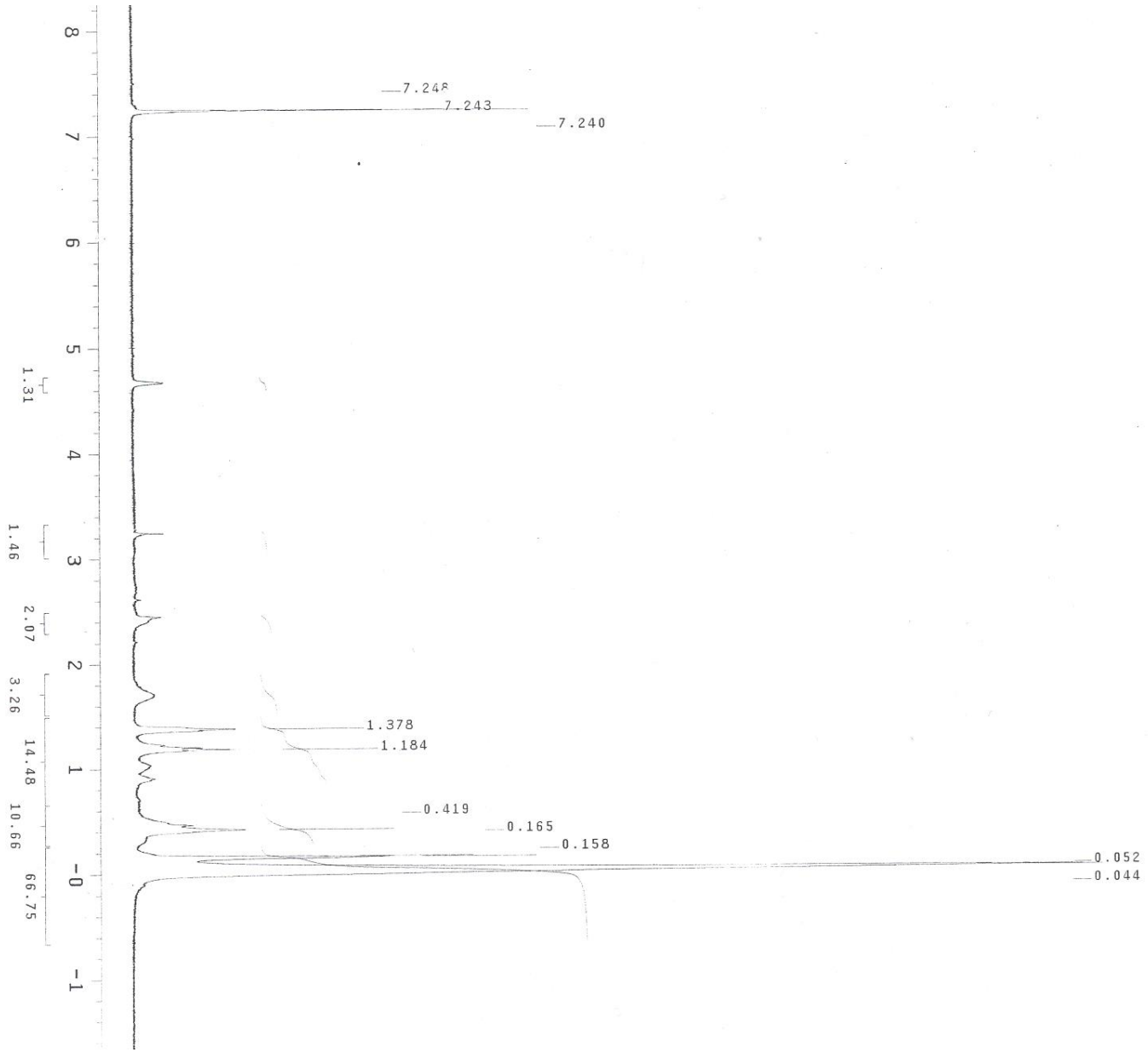


Figure S30. ^{29}SiNMR ($CDCl_3$) spectrum of *crosslinked hyperbranched poly(siloxysilane)-bound* $[\{(HSiMe_2(CH_2)_3)(i\text{-}C_4H_9)_6Si_7O_{12}\}Ti(NMe_2)]$ ***(12)***

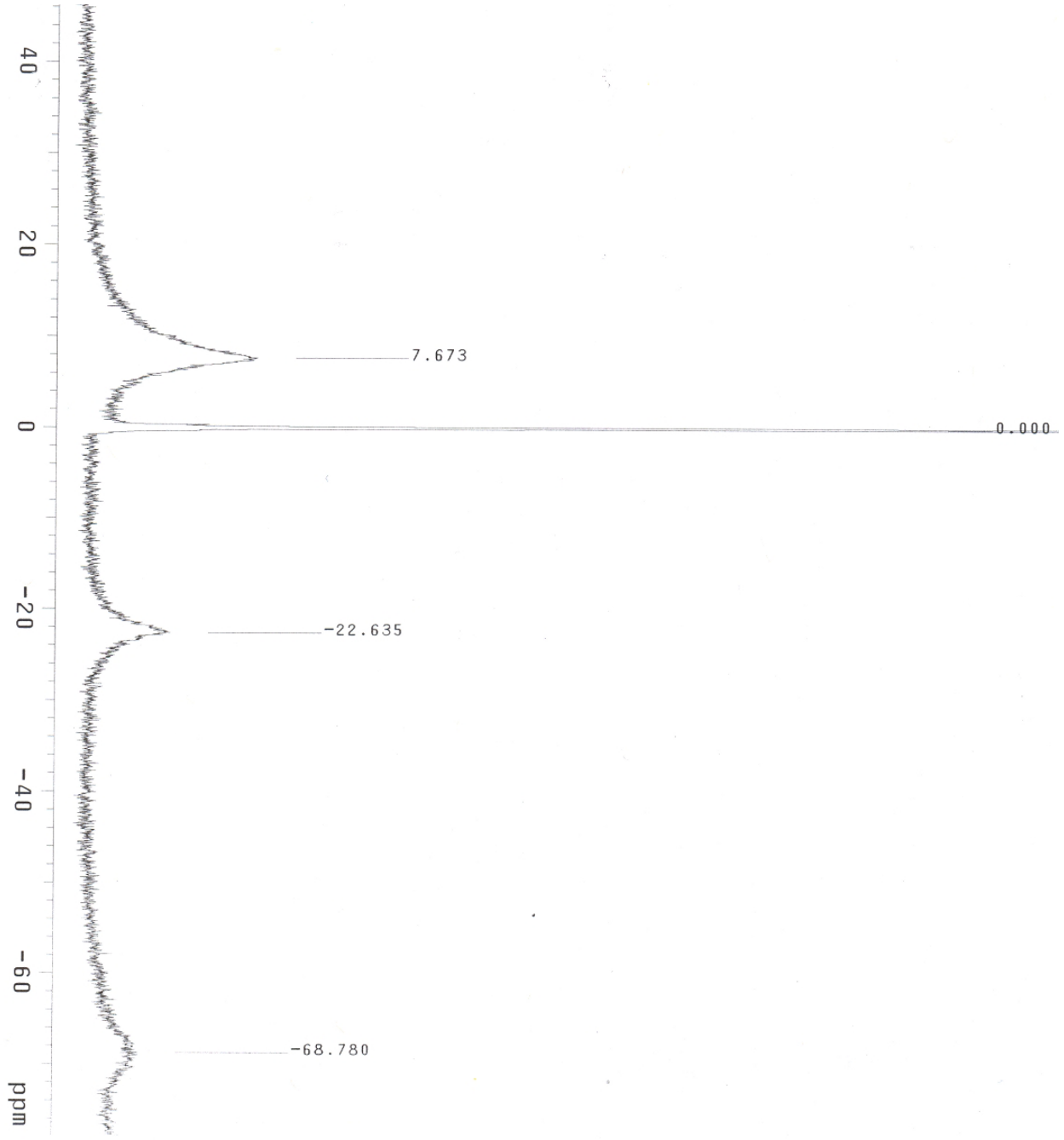
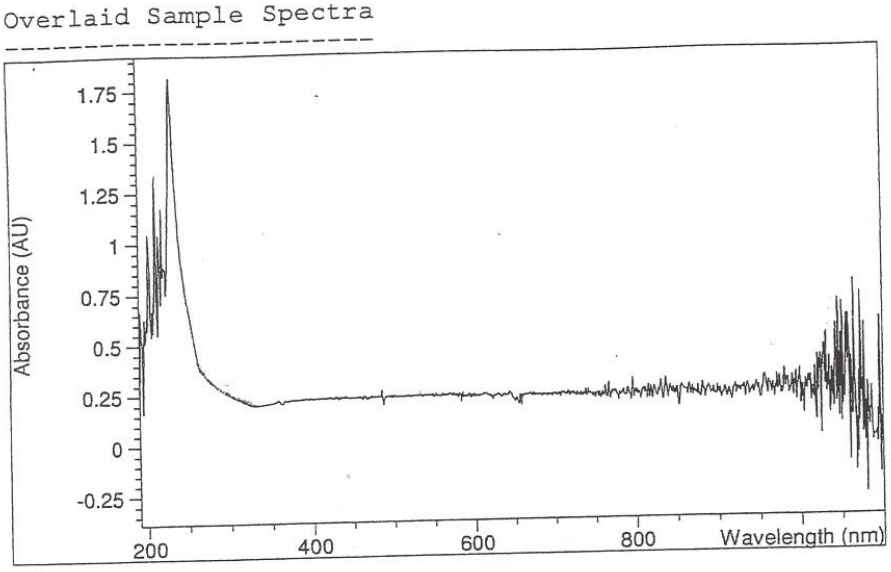


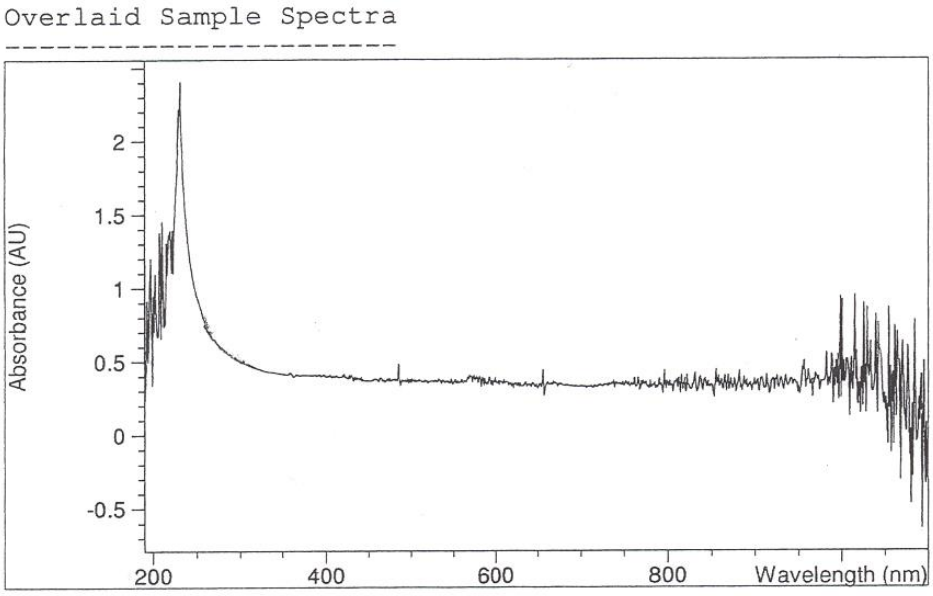
Figure S31. UV-vis spectrum of *crosslinked hyperbranched poly(siloxysilane)-bound* $[\{(HSiMe_2(CH_2)_3)(i\text{-}C_4H_9)_6Si_7O_{12}\}Ti(NMe_2)]$ ***(12)***



Sample/Result Table

#	Name	Abs<230nm>
1		1.80380

Figure S32. UV-vis spectrum of used *crosslinked hyperbranched poly(siloxysilane)-bound* $[\{(HSiMe_2(CH_2)_3)(i\text{-}C_4H_9)_6Si_7O_{12}\}Ti(NMe_2)]$ ***(12)***



Sample/Result Table

#	Name	Abs<230nm>
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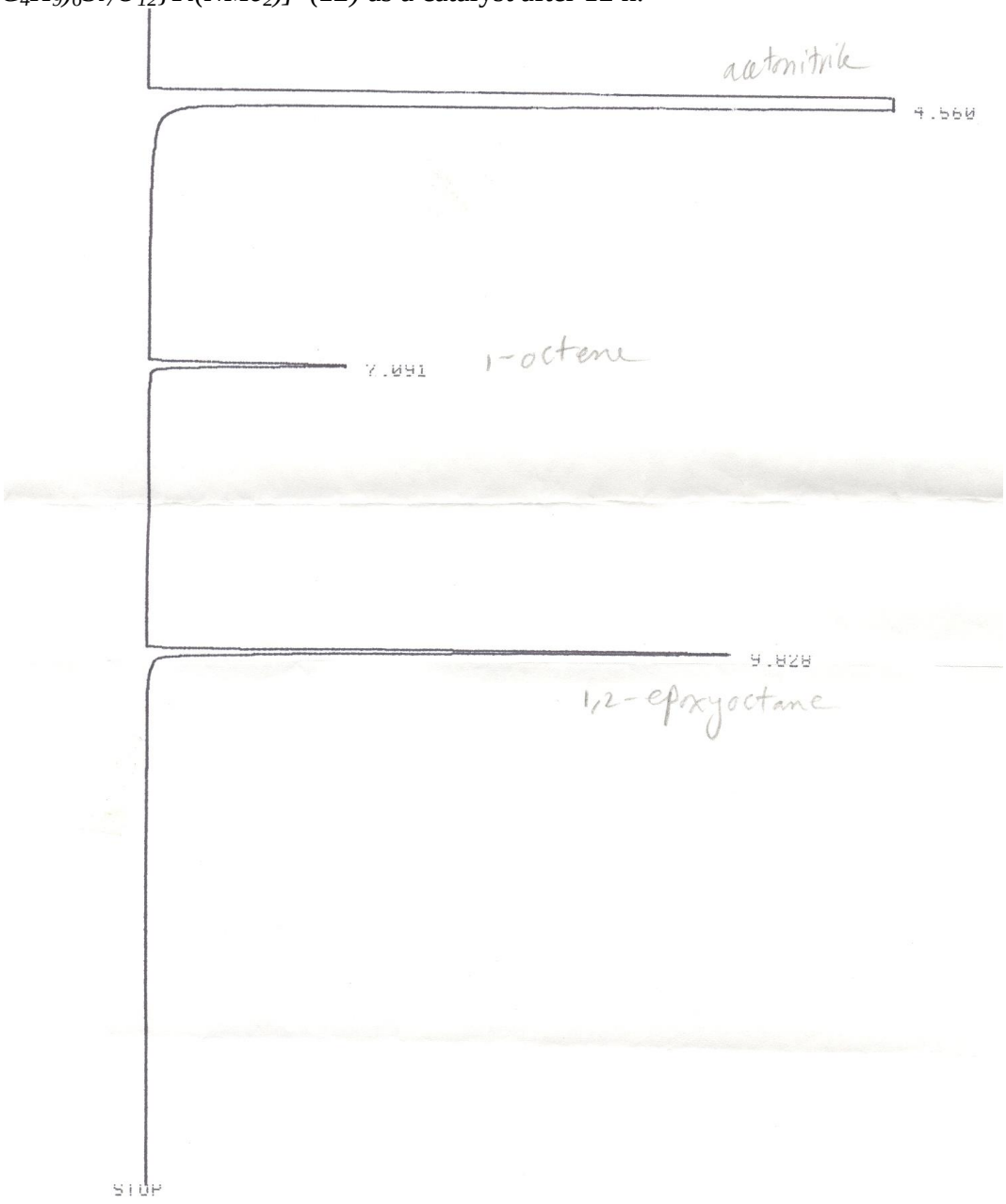
Figure S33. A typical GC chromatograph of 1-octene epoxidation with aq. H_2O_2 using *crosslinked hyperbranched poly(siloxysilane)-grafted [{(HSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)]* ***(12)*** as a catalyst after 12 h.



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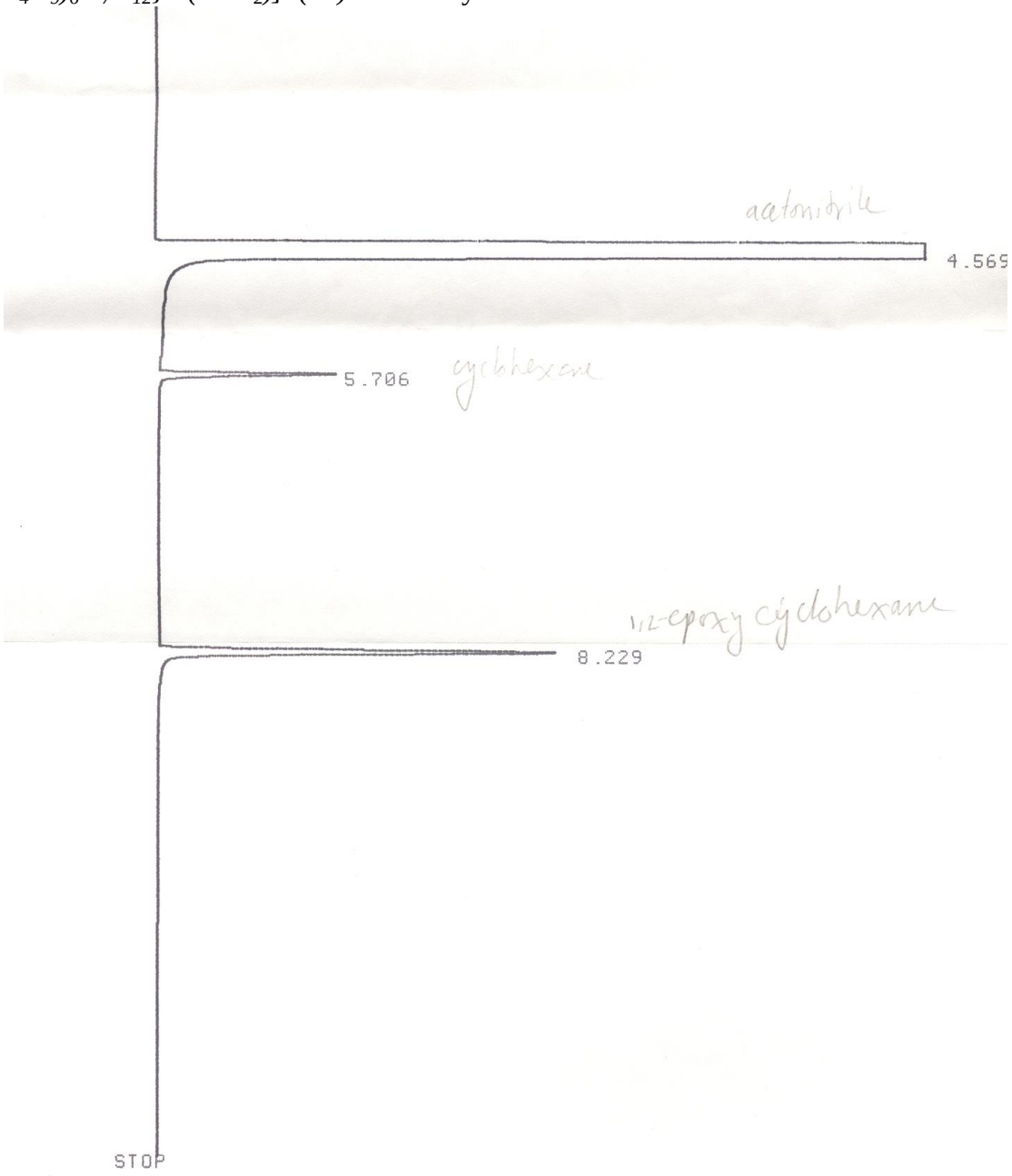
MUL FACTOR=1.000006+00

Figure S34. A typical GC chromatograph of cyclohexene epoxidation with aq. H_2O_2 using *crosslinked hyperbranched poly(siloxysilane)-grafted [{(HSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)]* ***(12)*** as a catalyst after 10 h.



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MUL FACTOR=1.0000E+00

Figure S35. A typical GC chromatograph of 1-octene epoxidation with aq. H_2O_2 using *crosslinked hyperbranched poly(siloxysilane)-grafted [{(p-HSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$)(c-C$_6$H$_{11}$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)] **(11)*** as a catalyst after 15 h.

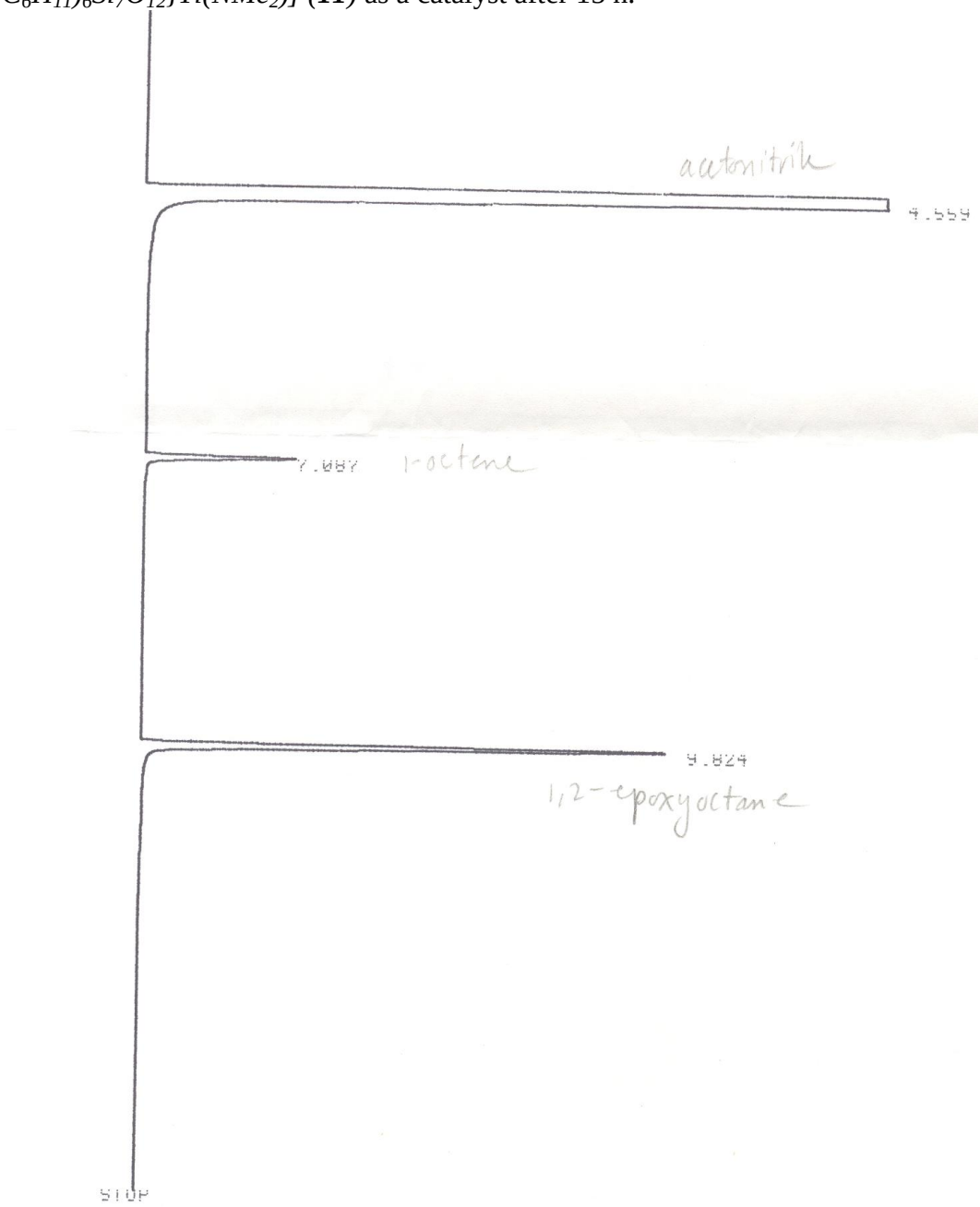

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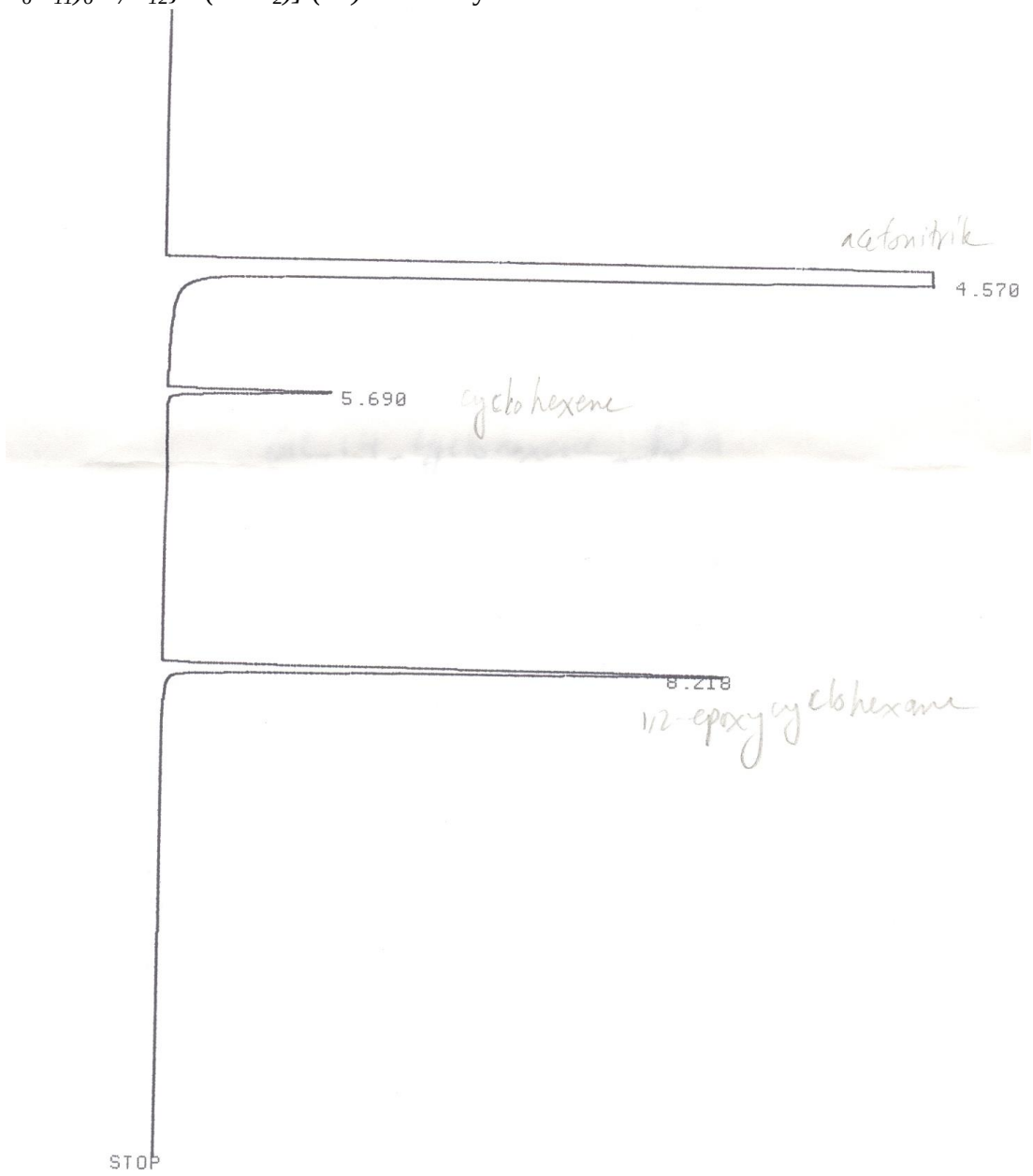
Figure S36. A typical GC chromatograph of cyclohexene epoxidation with aq. H_2O_2 using *crosslinked hyperbranched poly(siloxysilane)-grafted [{(p-HSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$)(c-C$_6$H$_{11}$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)] (**11**)*as a catalyst after 15 h.



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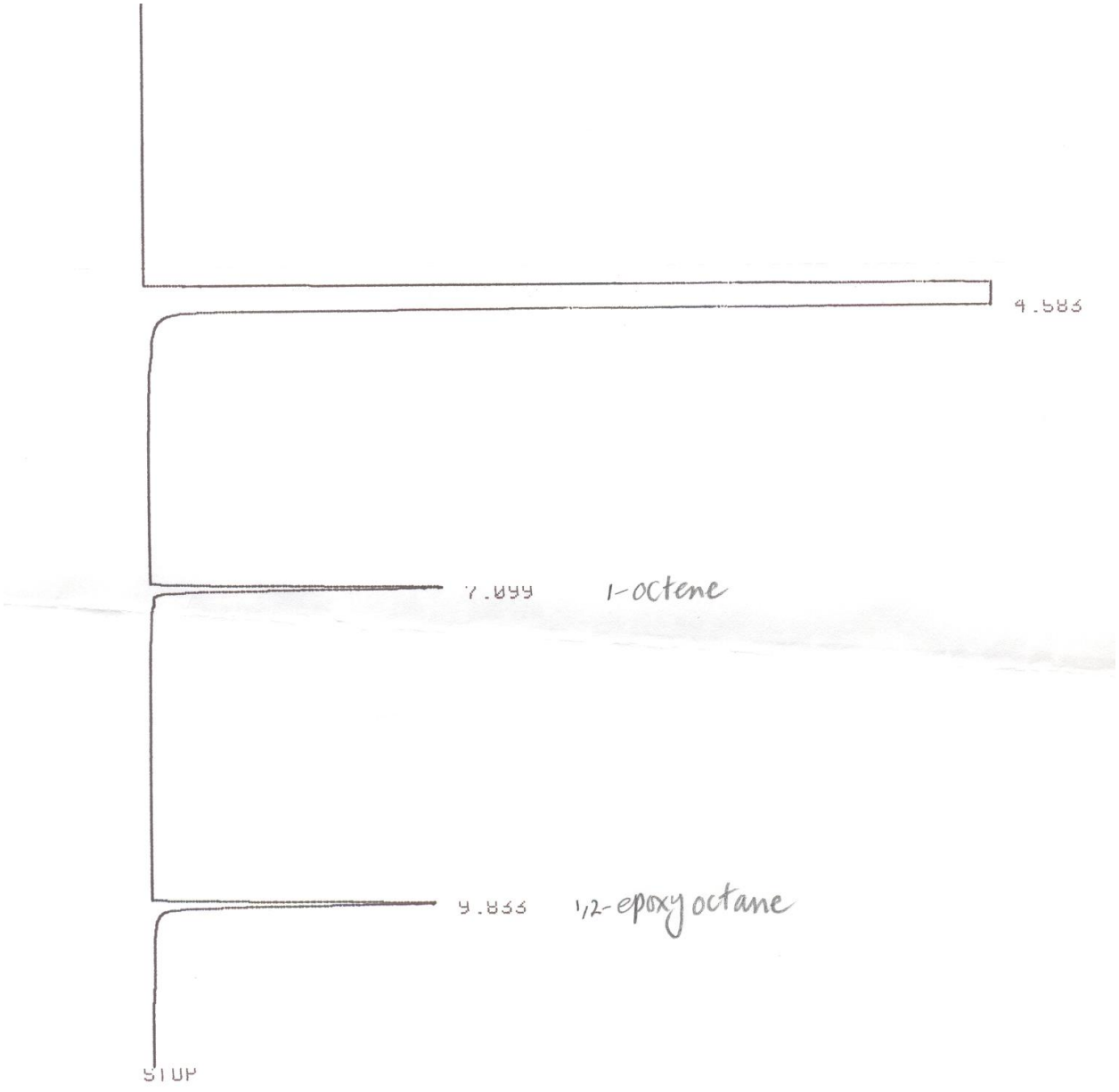
4.570	58504864	SBB	.120	95.69299
5.690	445301	PB	.036	.72835
8.218	2187926	SBB	.052	3.57866

TOTAL AREA=6.1138E+07
MUL FACTOR=1.0000E+00

Figure S37. A typical GC chromatograph of 1-octene epoxidation with aq. H_2O_2 using *crosslinked hyperbranched poly(siloxysilane)-grafted [{(HSiMe$_2$(CH$_2$)$_3$)(i-C$_4$H$_9$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)]* ***(12)*** as a catalyst after 2 h on comparison with TS-1.



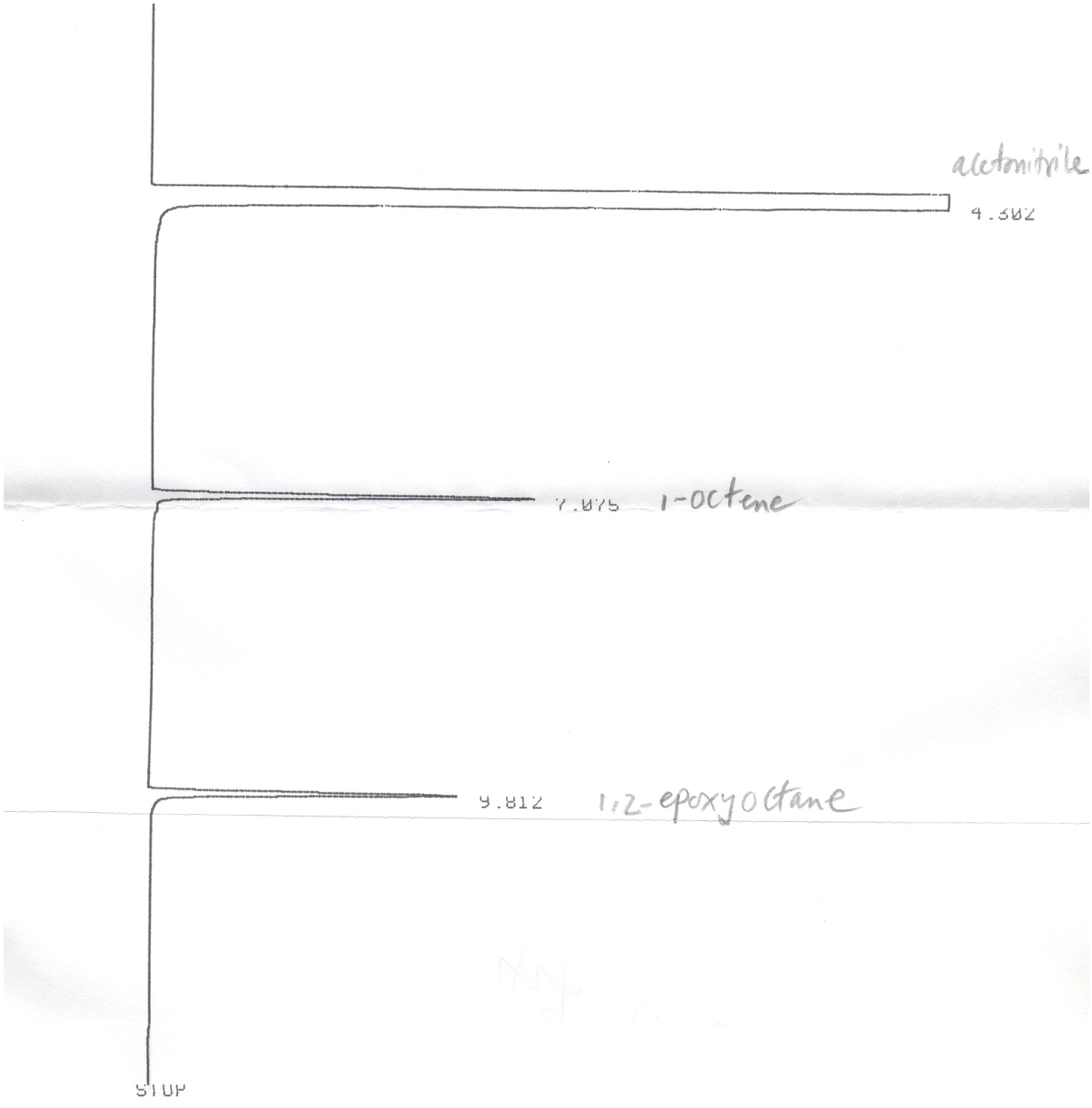
RUN# 141 MAR 4, 1991 13:23:05

AREA%

RT	AREA	TYPE	WIDTH	AREA%
9.583	88660864	BB	.182	98.19875
7.099	860493	PB	.041	.95306
9.833	765812	PB	.038	.84820

TOTAL AREA=9.0287E+07

Figure S38. A typical GC chromatograph of 1-octene epoxidation with aq. H_2O_2 using *crosslinked hyperbranched poly(siloxysilane)-grafted [{(p-HSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$)(c-C$_6$H$_{11}$)$_6$Si$_7$O$_{12}$}Ti(NMe$_2$)] **(11)*** as a catalyst after 2 h on comparison with TS-1.



RUN# 175 MHR 9, 1901 13:18:24

AREA%

RT	AREA	TYPE	WIDTH	AREA%
9.302	65251392	SBB	.154	96.77411
7.075	1250536	SBB	.043	1.85467
9.812	924580	PB	.042	1.37124

TOTAL AREA=6.7426E+07
MUL FACTOR=1.0000E+00