Supporting Information

for

On the Primary Structure of Polysilenes and Polygermenes

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Contents

Figure S1. ESI-TOF MS of oligosilene 3-2K

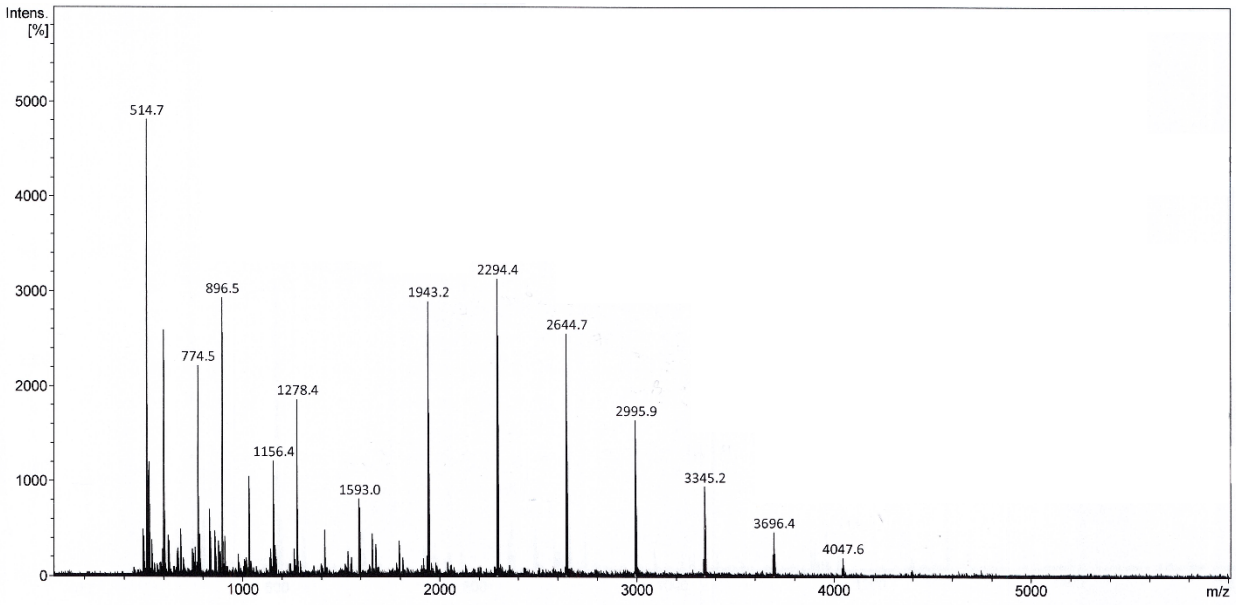


Table S1. Signal assignment for the mass spectrum of oligosilene 3-2K

Ion assignment[a]	*m/z* calculated[b]	*m/z* observed[b]
[*t*-Bu-S_4-H+Cs]$^+$	1593.0	1593.0
[*t*-Bu-S_5-H+Cs]$^+$	1943.2	1943.2
[*t*-Bu-S_6-H+Cs]$^+$	2294.4	2294.4
[*t*-Bu-S_7-H+Cs]$^+$	2644.7	2644.7
[*t*-Bu-S_8-H+Cs]$^+$	2994.9	2995.9
[*t*-Bu-S_9-H+Cs]$^+$	3346.2	3345.2
[*t*-Bu-S_{10}-H+Cs]$^+$	3696.4	3696.4
[*t*-Bu-S_{11}-H+Cs]$^+$	4046.7	4047.6

[a]S = $SiMes_2CHCH_2$t-Bu; [b]For the most intense signal within the isotopic cluster

Figure S2. ESI-TOF MS of oligosilene PSBu-4K (a) from *m/z* 1450 to 2300, (b) from *m/z* 2300 to 3500

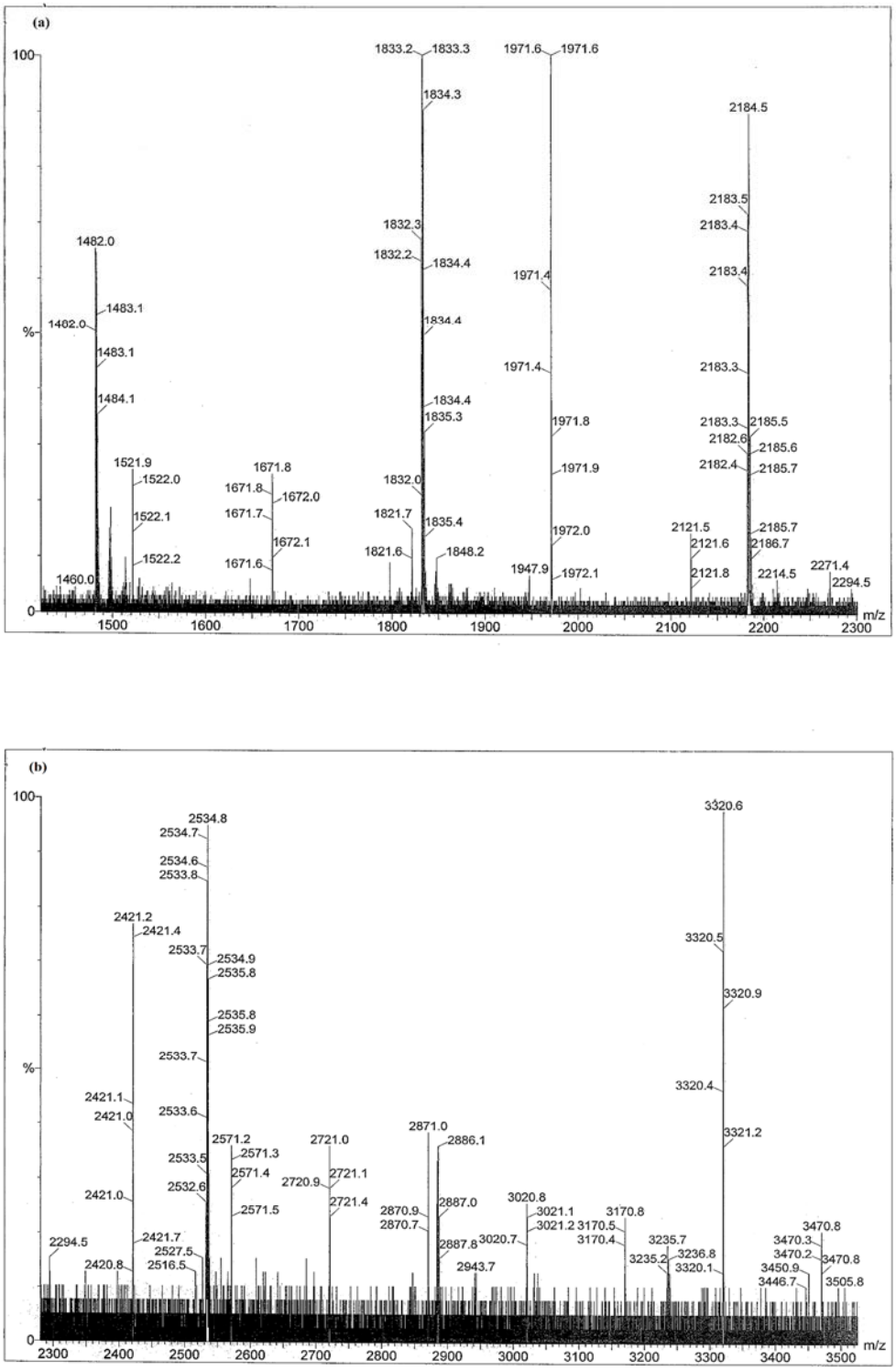


Table S2. Signal assignment for the mass spectrum of PSBu-4K

Ion assignments[a]	*m/z* calculated[b]	*m/z* observed[b]
$[Bu\text{-}S_4\text{-}H+Na]^+$	1483.1	1482.0
$[(NaI)_{10}Na]^+$	1521.9	1521.9
$[(NaI)_{11}Na]^+$	1671.8	1671.8
$[(NaI)_{12}Na]^+$	1821.7	1821.7
$[Bu\text{-}S_5\text{-}H+Na]^+$	1833.3	1833.3
$[(NaI)_{13}Na]^+$	1971.6	1971.6
$[(NaI)_{14}Na]^+$	2121.5	2121.5
$[Bu\text{-}S_6\text{-}H+Na]^+$	2184.5	2184.5
$[(NaI)_{15}Na]^+$	2271.4	2271.4
$[(NaI)_{16}Na]^+$	2421.3	2421.2
$[Bu\text{-}S_7\text{-}H+Na]^+$	2533.8	2534.8
$[(NaI)_{17}Na]^+$	2571.2	2571.2
$[(NaI)_{18}Na]^+$	2721.1	2721.0
$[(NaI)_{19}Na]^+$	2871.0	2871.0
$[Bu\text{-}S_8\text{-}H+Na]^+$	2885.0	2886.1
$[(NaI)_{20}Na]^+$	3020.9	3020.8
$[(NaI)_{21}Na]^+$	3170.8	3170.8
$[Bu\text{-}S_9\text{-}H+Na]^+$	3235.3	3235.7

[a]S = $SiMes_2CHCH_2t$-Bu; [b]For the most intense signal within the isotopic cluster

Figure S3. Expansion of the ESI-TOF MS of PSBu-4K showing the (a) experimental isotopic pattern of m/z 2184.5 (b) calculated isotopic pattern

(a) (b)

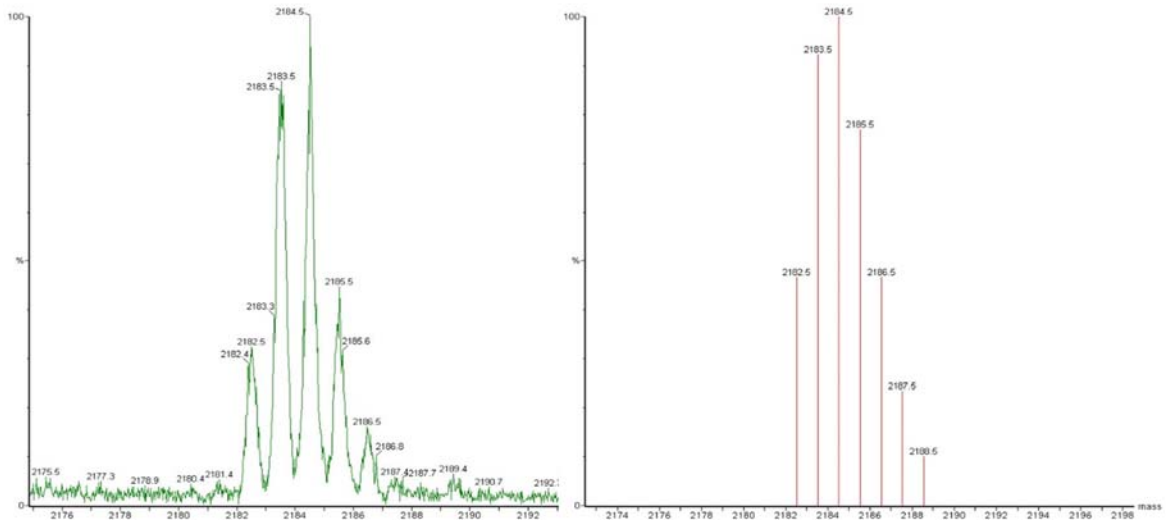
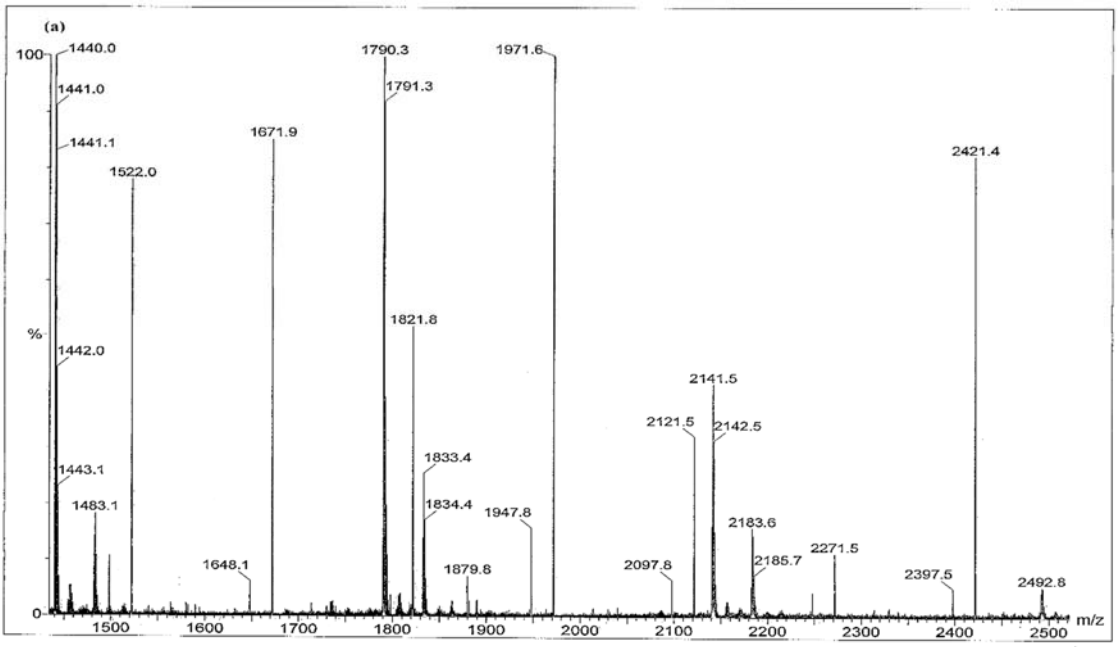


Figure S4. ESI-TOF MS of oligosilene PSMe-4K (a) from m/z 1450 to 2500, (b) from m/z 2400 to 3400



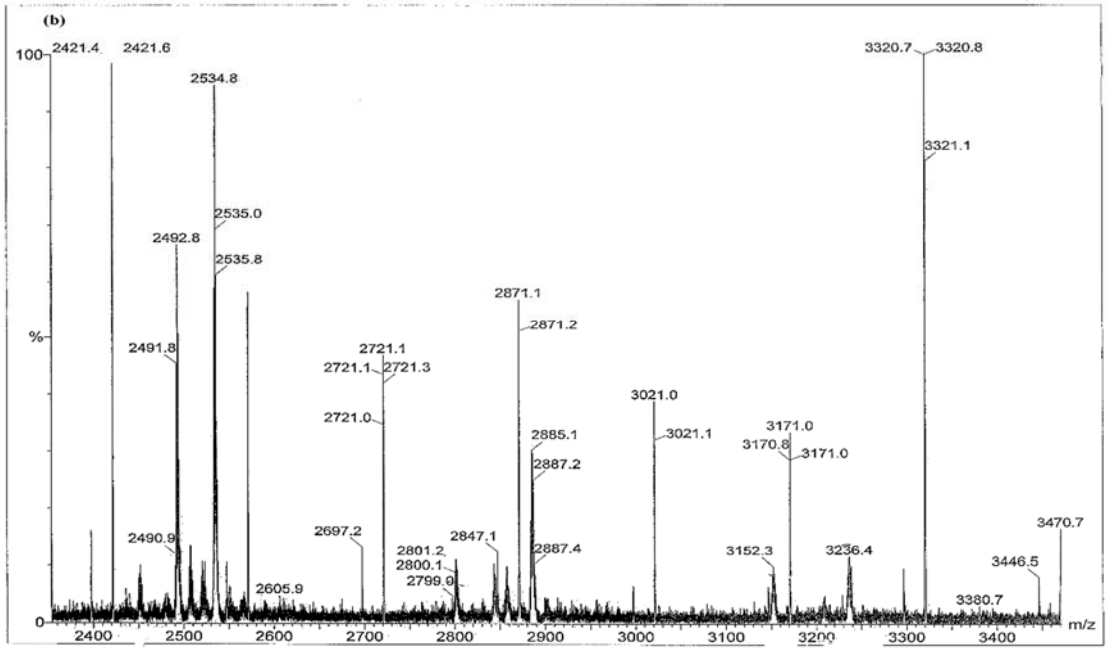


Figure S5. Expansion of the MS of PSMe-4K showing (a) the experimental isotopic pattern of *m/z* 1790.3, (b) calculated isotopic pattern

(b)

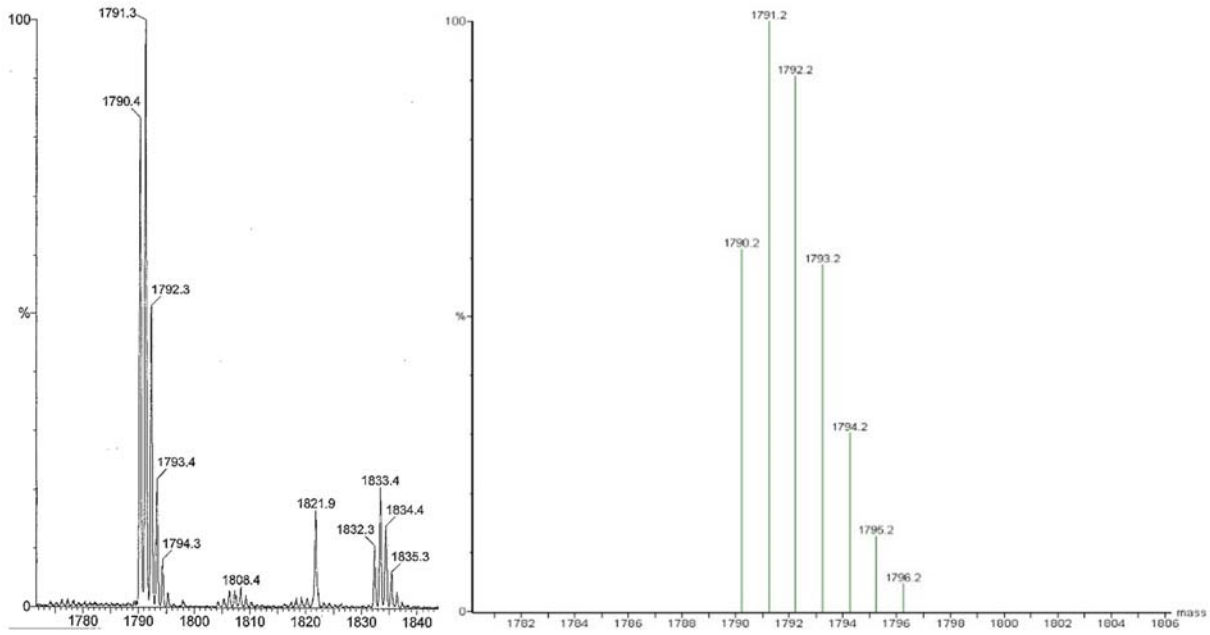


Table S3. Signal assignment for the mass spectrum of PSMe-4K

Ion assignment[a]	*m/z* calculated[b]	*m/z* observed[b]
$[Me\text{-}S_4\text{-}H+Na]^+$	1440.0	1440.0
$[Me\text{-}S_5\text{-}H+Na]^+$	1790.2	1790.3
$[Me\text{-}S_6\text{-}H+Na]^+$	2140.4	2141.5
$[Me\text{-}S_7\text{-}H+Na]^+$	2490.6	2492.8
$[Me\text{-}S_8\text{-}H+Na]^+$	2840.8	2842.9
$[MeO\text{-}S_4\text{-}H+Na]^+$	1456.0	1458.5
$[MeO\text{-}S_5\text{-}H+Na]^+$	1806.2	1808.3
$[MeO\text{-}S_6\text{-}H+Na]^+$	2156.4	2158.7
$[MeO\text{-}S_7\text{-}H+Na]^+$	2506.6	2508.4
$[MeO\text{-}S_8\text{-}H+Na]^+$	2856.8	2858.5
$[t\text{-}Bu\text{-}S_4\text{-}H+Na]^+$	1483.1	1483.1
$[t\text{-}Bu\text{-}S_5\text{-}H+Na]^+$	1833.3	1833.4
$[t\text{-}Bu\text{-}S_6\text{-}H+Na]^+$	2184.5	2183.6
$[t\text{-}Bu\text{-}S_7\text{-}H+Na]^+$	2533.8	2534.8
$[t\text{-}Bu\text{-}S_8\text{-}H+Na]^+$	2885.0	2883.6
$[t\text{-}Bu\text{-}S_9\text{-}H+Na]^+$	3235.3	3233.7

[a]S = $SiMes_2CHCH_2t$-Bu; [b]For the most intense signal within the isotopic cluster

Figure S6. ESI-TOF MS of oligogermene 4-7K

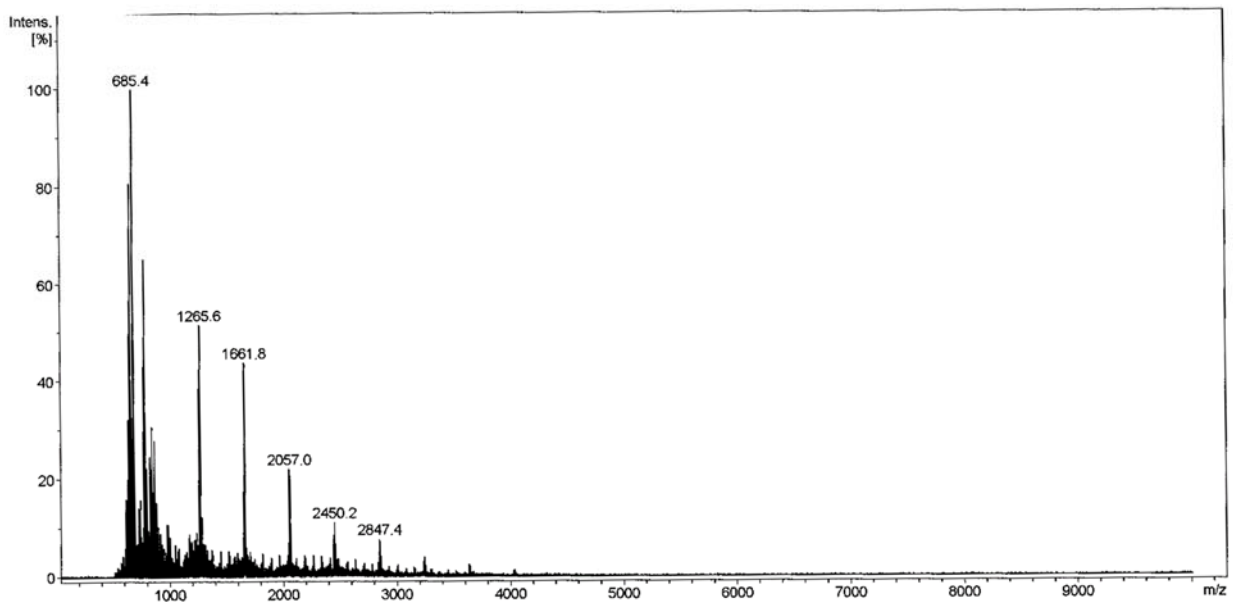


Table S4. Signal assignment for the mass spectrum of 4-7K

Ion assignment[a]	*m/z* calculated[b]	*m/z* observed[b]
[*t*-Bu-G$_3$-H+Na]$^+$	1265.6	1265.6
[*t*-Bu-G$_4$-H+Na]$^+$	1661.8	1661.8
[*t*-Bu-G$_5$-H+Na]$^+$	2057.0	2057.0
[*t*-Bu-G$_6$-H+Na]$^+$	2452.2	2450.2
[*t*-Bu-G$_7$-H+Na]$^+$	2847.4	2847.4
[*t*-Bu-G$_8$-H+Na]$^+$	3242.5	3242.6
[*t*-Bu-G$_9$-H+Na]$^+$	3637.7	3639.8

[a]G = GeMes$_2$CHCH$_2$*t*-Bu; [b]For the most intense signal within the isotopic cluster

Figure S7. Expansion of the ESI-TOF MS of oligogermene 4-7K in CH_2Cl_2/MeOH with an expansion from *m/z* 800 to 2000. The sensitivity of the instrument was optimized for lower *m/z* values. Also visible are a series of signals with a spacing of *m/z* 74 which are assigned to silicone grease.

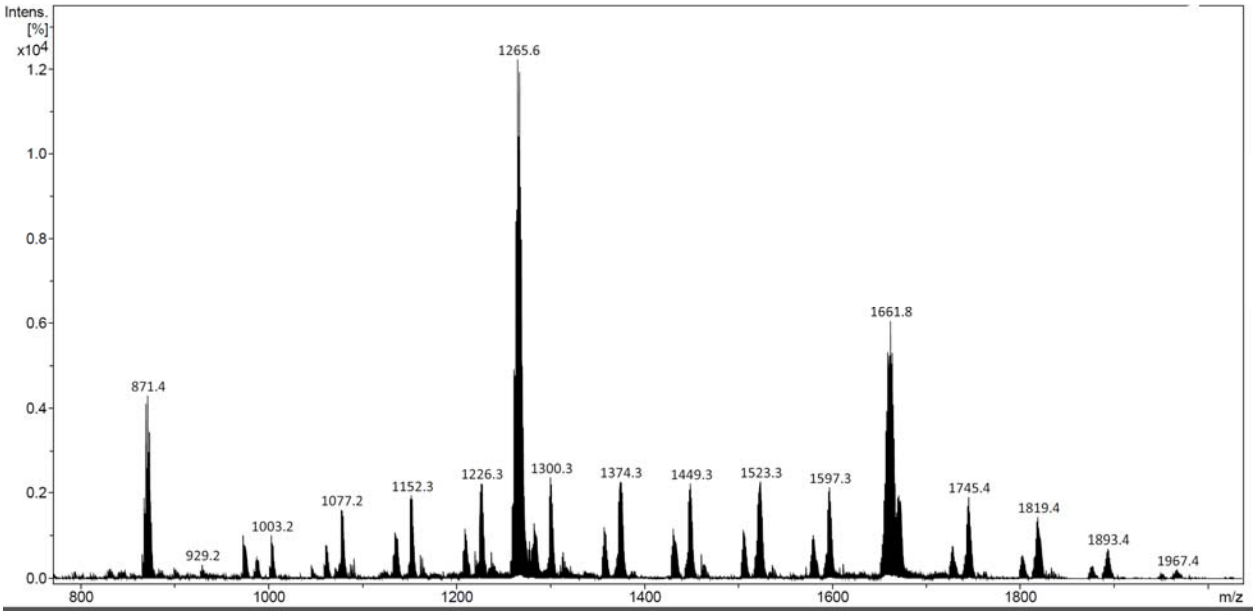


Table S5. High resolution mass data for oligogermene 4-7K

$[t\text{-Bu}[GeMes_2CHCH_2t\text{-Bu}]_nH+Na]^+$	Exact mass (calc.)	Exact mass (exp.)	Error (ppm)
n = 2	871.4434	871.4444	1
n = 3	1265.6345	1265.6343	0.02
n = 4	1661.8194	1661.8242	0.48

Figure S8. Expansion of the ^{1}H-^{13}C HSQC NMR spectrum of 3-17K (aromatic region) (600 MHz for ^{1}H, C_6D_6, 25 °C; δ ^{1}H 6.5-6.8, δ ^{13}C 123-136 ppm; correlations in red correspond to CH_2 groups and those in blue correspond to CH/CH_3 groups)

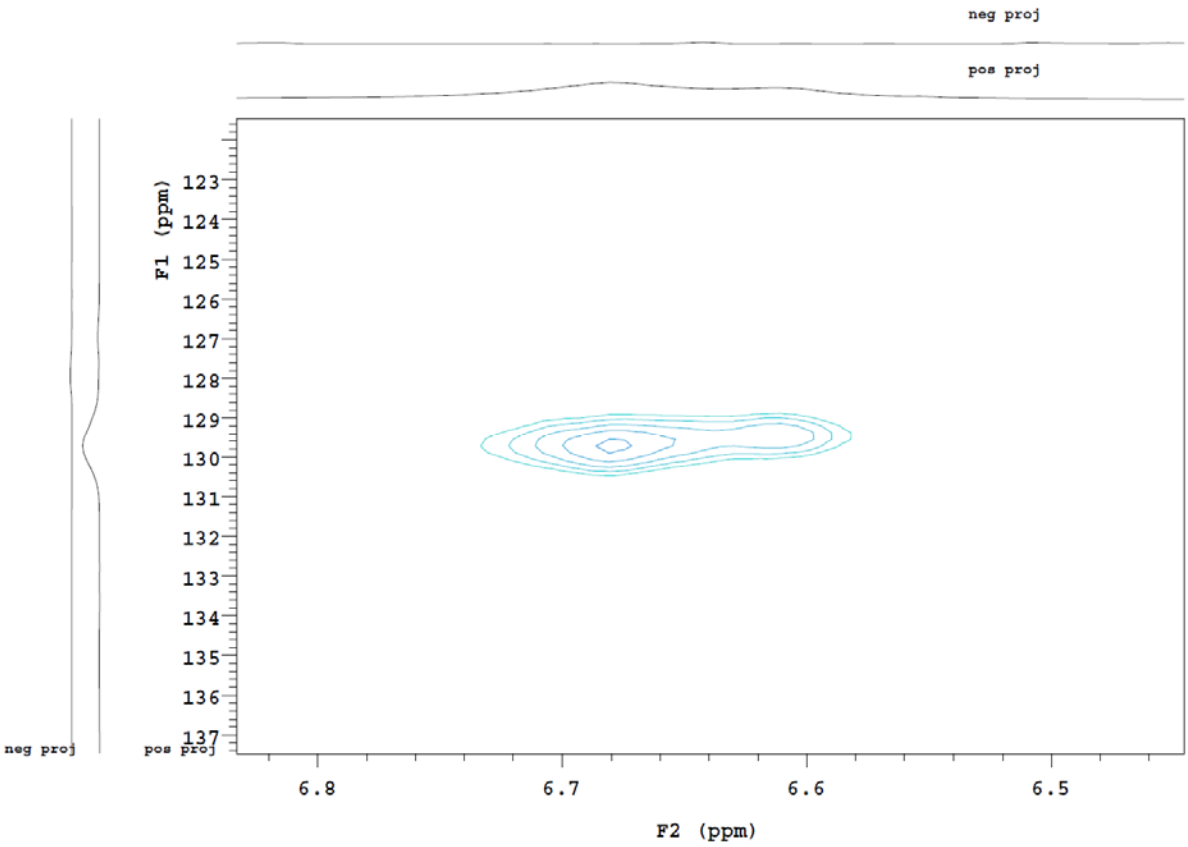


Figure S9. Expansion of the ^{1}H-^{13}C HSQC NMR spectrum of 4-7K (aliphatic region) (600 MHz for ^{1}H, C_6D_6, 25 °C; δ ^{1}H 0.4-3.2, δ ^{13}C 0-50 ppm; correlations in red correspond to CH_2 groups and those in blue correspond to CH/CH_3 groups)

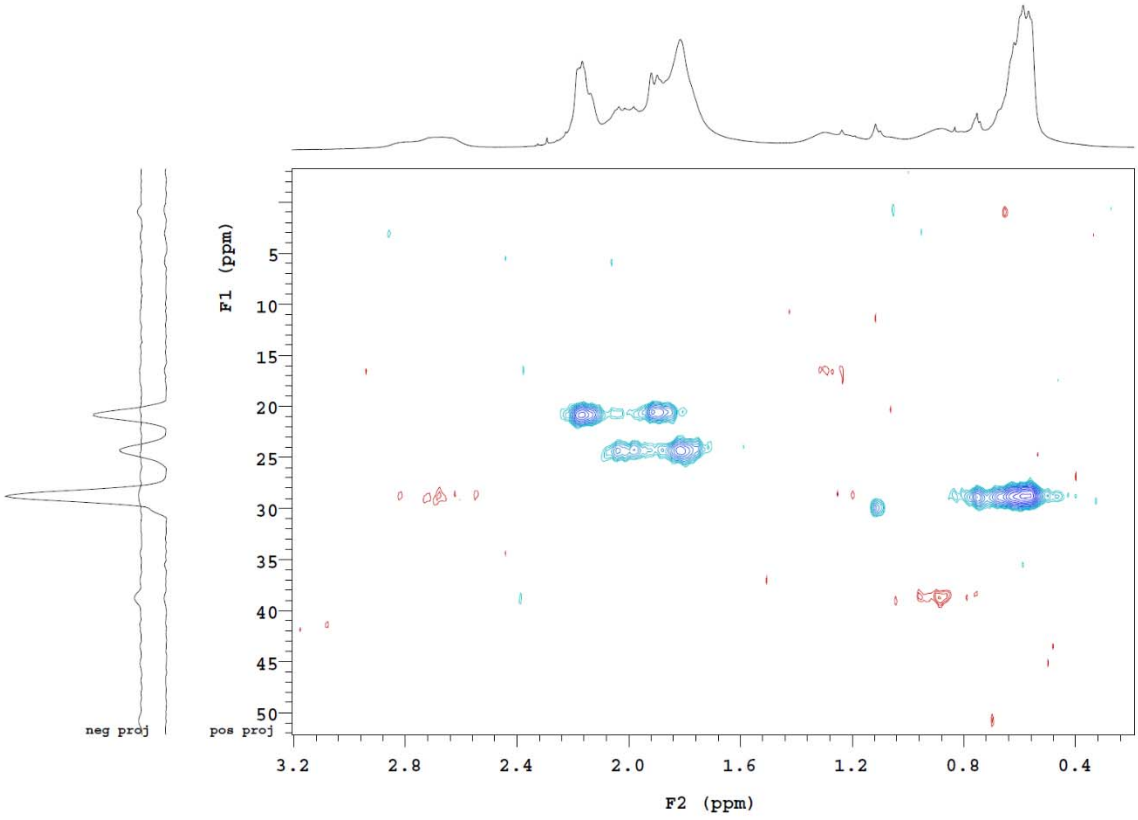


Figure S10. Expansion of the ^{1}H-^{13}C HSQC NMR spectrum of 4-7K (aromatic region) (600 MHz for ^{1}H, C_6D_6, 25 °C; δ ^{1}H 6.4-6.7, δ ^{13}C 124-134 ppm; correlations in red correspond to CH_2 groups and those in blue correspond to CH/CH_3 groups)