Supporting Information

# Identification of β scission products from free radical polymerizations of butyl acrylate at high temperature

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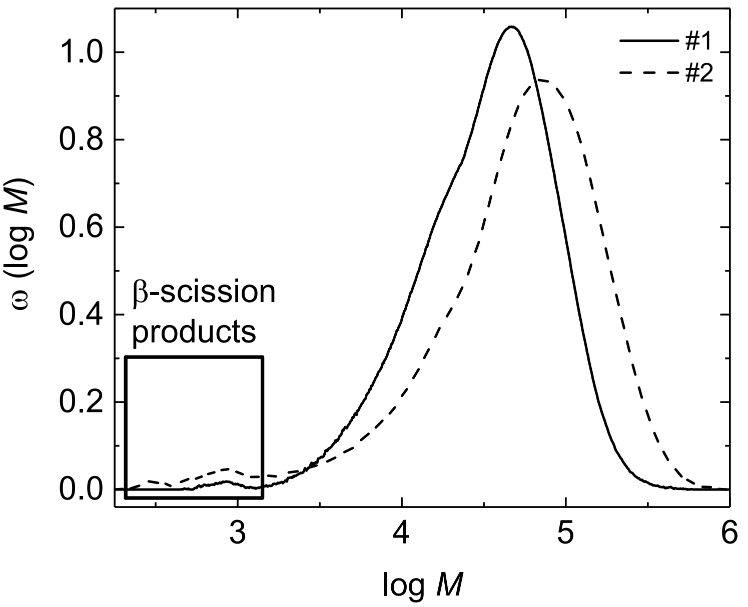


Figure S1: Molar mass distributions for polymer samples obtained from thermally initiated batch BA polymerizations at 120°C. #1 and #2 refer to the samples in Table 1.

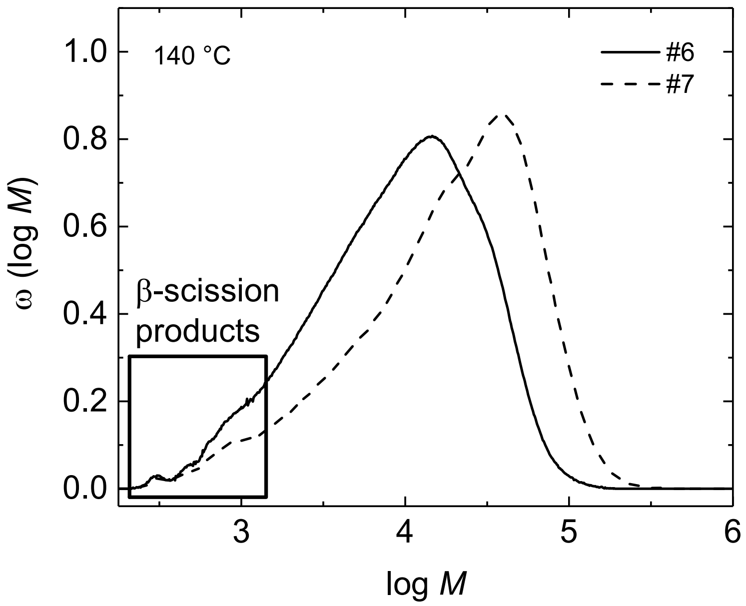


Figure S2: Molar mass distributions for polymer samples obtained from thermally initiated batch BA polymerizations at 140°C. #6 and #7 refer to the samples in Table 1.

Table S1: Analytical SEC results for the fractions obtained after preparative SEC of a polymer obtained via semi-batch polymerization at 130°C.

| fraction | content | $M_n$ / g·mol$^{-1}$ | $M_w$ / g·mol$^{-1}$ | D |
|---|---|---|---|---|
| 1 | 0.161 | 9056 | 10280 | 1.14 |
| 2 | 0.372 | 5733 | 6679 | 1.17 |
| 3 | 0.200 | 3541 | 4348 | 1.23 |
| 4 | 0.128 | 2178 | 2940 | 1.35 |
| 5 | 0.066 | 1352 | 2118 | 1.57 |
| 6 | 0.034 | 876 | 1600 | 1.83 |
| 7 | 0.039 | 588 | 1192 | 2.02 |
| 6+7 | 0.073 | 757 | 1443 | 1.91 |
| all | | 2148 | 4633 | 2.16 |

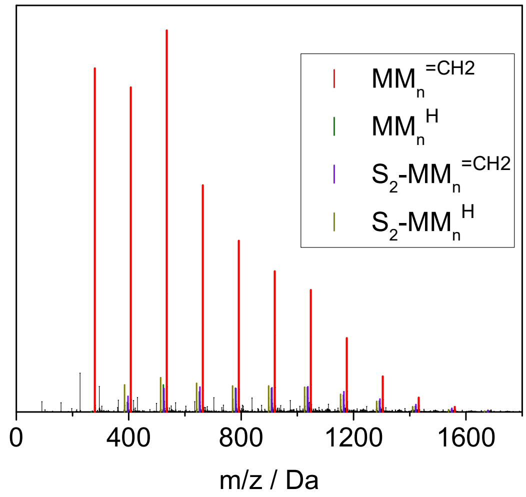


Figure S3: ESI-MS data of β scission products: semi-batch polymerization at 130°C after 1 h in xylene ($S_1$: xylene end group).

$MM_n^{=CH2}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 2 | 279.1567 | 279.1567 | 3.0E-05 | 591672 |
| 3 | 407.2404 | 407.2404 | 0.0E+00 | 558841 |
| 4 | 535.3240 | 535.3241 | -1.3E-04 | 657030 |
| 5 | 663.4076 | 663.4079 | -2.6E-04 | 390392 |
| 6 | 791.4911 | 791.4916 | -4.9E-04 | 294774 |
| 7 | 919.5746 | 919.5753 | -7.2E-04 | 242361 |
| 8 | 1047.6582 | 1047.6590 | -8.5E-04 | 210042 |
| 9 | 1175.7415 | 1175.7428 | -1.3E-03 | 127243 |
| 10 | 1303.8244 | 1303.8265 | -2.1E-03 | 61132 |
| 11 | 1431.9065 | 1431.9102 | -3.7E-03 | 24812 |
| 12 | 1559.9904 | 1559.9940 | -3.6E-03 | 8650 |

$MM_n^H$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 2 | 267.1568 | 267.1567 | 1.3E-04 | 709 |
| 3 | 395.2403 | 395.2404 | -1.0E-04 | 16453 |
| 4 | 523.3239 | 523.3241 | -2.3E-04 | 46569 |
| 5 | 651.4075 | 651.4079 | -3.6E-04 | 34533 |
| 6 | 779.491 | 779.4916 | -5.9E-04 | 40819 |
| 7 | 907.5744 | 907.5753 | -9.2E-04 | 40246 |
| 8 | 1035.6579 | 1035.6590 | -1.1E-03 | 42173 |
| 9 | 1163.7414 | 1163.7428 | -1.4E-03 | 28933 |
| 10 | 1291.8244 | 1291.8265 | -2.1E-03 | 18688 |
| 11 | 1419.9065 | 1419.9102 | -3.7E-03 | 9589 |
| 12 | 1547.9903 | 1547.9940 | -3.7E-03 | 4098 |
| 13 | 1676.0735 | 1676.0777 | -4.2E-03 | 1496 |

$S_1$-$MM_n^{=CH2}$ + $Na^+$

| n | *m*/*z* / Da experimental | *m*/*z* / Da theoretical | Δ *m*/*z* / Da | intensity |
|---|---|---|---|---|
| 2 | 397.2350 | 397.2349 | 1.0E-04 | 27019 |
| 3 | 525.3190 | 525.3186 | 3.7E-04 | 40510 |
| 4 | 653.4027 | 653.4024 | 3.4E-04 | 43093 |
| 5 | 781.4867 | 781.4861 | 6.1E-04 | 40455 |
| 6 | 909.5707 | 909.5698 | 8.8E-04 | 41588 |
| 7 | 1037.6552 | 1037.6535 | 1.7E-03 | 43402 |
| 8 | 1165.7388 | 1165.7373 | 1.5E-03 | 34815 |
| 9 | 1293.8227 | 1293.8210 | 1.7E-03 | 22421 |
| 10 | 1421.9053 | 1421.9047 | 5.6E-04 | 12791 |
| 11 | 1549.9901 | 1549.9885 | 1.6E-03 | 6255 |
| 12 | 1678.0731 | 1678.0722 | 9.0E-04 | 2903 |

$S_1$-$MM_n^{H}$ + $Na^+$

| n | *m*/*z* / Da experimental | *m*/*z* / Da theoretical | Δ *m*/*z* / Da | intensity |
|---|---|---|---|---|
| 2 | 385.2348 | 385.2349 | -1.0E-04 | 46644 |
| 3 | 513.3185 | 513.3186 | -1.3E-04 | 59076 |
| 4 | 641.4019 | 641.4024 | -4.6E-04 | 49278 |
| 5 | 769.4855 | 769.4861 | -5.9E-04 | 44869 |
| 6 | 897.5689 | 897.5698 | -9.2E-04 | 44715 |
| 7 | 1025.6524 | 1025.6535 | -1.1E-03 | 42558 |
| 8 | 1153.7357 | 1153.7373 | -1.6E-03 | 30332 |
| 9 | 1281.8184 | 1281.8210 | -2.6E-03 | 18299 |
| 10 | 1409.9005 | 1409.9047 | -4.2E-03 | 9131 |
| 11 | 1537.9843 | 1537.9885 | -4.2E-03 | 3997 |
| 12 | 1666.0663 | 1666.0722 | -5.9E-03 | 1433 |

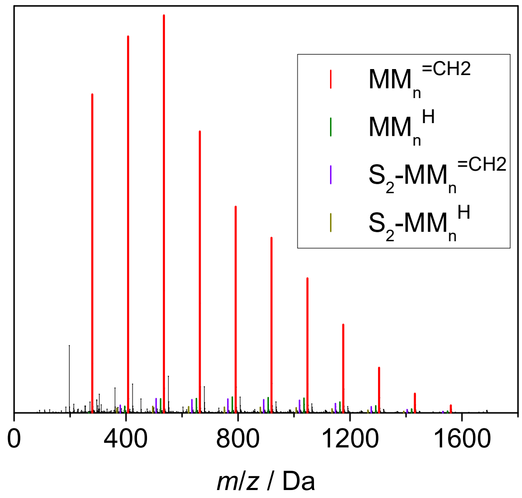


Figure S4: ESI-MS data of β scission products: batch polymerization at 130°C with $c_{BA,0}$ = 2.06 mol·L$^{-1}$ in dioxane ($S_2$: dioxane end group).

$MM_n^{=CH2}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 2 | 279.157 | 279.1567 | 3.3E-04 | 391271 |
| 3 | 407.2408 | 407.2404 | 4.0E-04 | 462495 |
| 4 | 535.3245 | 535.3241 | 3.7E-04 | 488422 |
| 5 | 663.4081 | 663.4079 | 2.4E-04 | 345787 |
| 6 | 791.4919 | 791.4916 | 3.1E-04 | 253310 |
| 7 | 919.5758 | 919.5753 | 4.8E-04 | 215149 |
| 8 | 1047.6595 | 1047.6590 | 4.5E-04 | 165288 |
| 9 | 1175.7431 | 1175.7428 | 3.2E-04 | 108448 |
| 10 | 1303.8263 | 1303.8265 | -2.1E-04 | 55494 |
| 11 | 1431.9104 | 1431.9102 | 1.6E-04 | 23667 |
| 12 | 1559.9948 | 1559.9940 | 8.3E-04 | 9138 |

$MM_n^{H}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 2 | 267.1565 | 267.1567 | -1.7E-04 | 558 |
| 3 | 395.2403 | 395.2404 | -1.0E-04 | 8036 |
| 4 | 523.3239 | 523.3241 | -2.3E-04 | 17225 |
| 5 | 651.4077 | 651.4079 | -1.6E-04 | 17600 |
| 6 | 779.4912 | 779.4916 | -3.9E-04 | 19433 |
| 7 | 907.5745 | 907.5753 | -8.2E-04 | 18614 |
| 8 | 1035.6580 | 1035.6590 | -1.0E-03 | 18023 |
| 9 | 1163.7412 | 1163.7428 | -1.6E-03 | 13366 |
| 10 | 1291.8245 | 1291.8265 | -2.0E-03 | 8657 |
| 11 | 1419.9076 | 1419.9102 | -2.6E-03 | 4851 |
| 12 | 1547.9926 | 1547.9940 | -1.4E-03 | 2111 |

$S_2$-$MM_n^{=CH2}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 2 | 379.2093 | 379.2091 | 2.0E-04 | 9398 |
| 3 | 507.2931 | 507.2928 | 2.7E-04 | 17464 |
| 4 | 635.3766 | 635.3766 | 4.1E-05 | 16127 |
| 5 | 763.4604 | 763.4603 | 1.1E-04 | 16967 |
| 6 | 891.5442 | 891.5440 | 1.8E-04 | 16107 |
| 7 | 1019.6283 | 1019.6277 | 5.5E-04 | 15392 |
| 8 | 1147.7116 | 1147.7115 | 1.2E-04 | 11410 |
| 9 | 1275.7945 | 1275.7952 | -7.1E-04 | 7458 |
| 10 | 1403.8780 | 1403.8789 | -9.4E-04 | 3915 |
| 11 | 1531.9630 | 1531.9627 | 3.3E-04 | 1749 |

$S_2$-$MM_n^{H}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 2 | 367.2094 | 367.2091 | 3.0E-04 | 5683 |
| 3 | 495.2931 | 495.2928 | 2.7E-04 | 7904 |
| 4 | 623.3766 | 623.3766 | 4.1E-05 | 7497 |
| 5 | 751.4604 | 751.4603 | 1.1E-04 | 6864 |
| 6 | 879.5440 | 879.5440 | -1.9E-05 | 6774 |
| 7 | 1007.6276 | 1007.6277 | -1.5E-04 | 6294 |
| 8 | 1135.7112 | 1135.7115 | -2.8E-04 | 4913 |
| 9 | 1263.7942 | 1263.7952 | -1.0E-03 | 3273 |
| 10 | 1391.8779 | 1391.8789 | -1.0E-03 | 1838 |

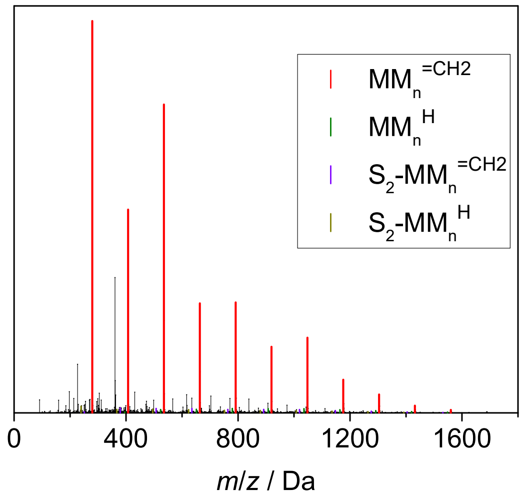


Figure S5: ESI-MS data of β scission products: batch polymerization at 120°C with $c_{BA,0}$ = 2.92 mol·L$^{-1}$ in dioxane ($S_2$: dioxane end group).

$MM_n^{=CH2} + Na^+$

| n | *m*/*z* / Da experimental | *m*/*z* / Da theoretical | Δ *m*/*z* / Da | intensity |
|---|---|---|---|---|
| 2 | 279.1562 | 279.1567 | -4.7E-04 | 192560 |
| 3 | 407.2398 | 407.2404 | -6.0E-04 | 99913 |
| 4 | 535.3233 | 535.3241 | -8.3E-04 | 151569 |
| 5 | 663.4066 | 663.4079 | -1.3E-03 | 53809 |
| 6 | 791.4902 | 791.4916 | -1.4E-03 | 54280 |
| 7 | 919.5739 | 919.5753 | -1.4E-03 | 32481 |
| 8 | 1047.6577 | 1047.6590 | -1.3E-03 | 36991 |
| 9 | 1175.7406 | 1175.7428 | -2.2E-03 | 16319 |
| 10 | 1303.8237 | 1303.8265 | -2.8E-03 | 9034 |
| 11 | 1431.9066 | 1431.9102 | -3.6E-03 | 3587 |
| 12 | 1559.9918 | 1559.9940 | -2.2E-03 | 1479 |

$MM_n^H + Na^+$

| n | *m*/*z* / Da experimental | *m*/*z* / Da theoretical | Δ *m*/*z* / Da | intensity |
|---|---|---|---|---|
| 3 | 395.2391 | 395.2404 | -1.3E-03 | 614 |
| 4 | 523.3226 | 523.3241 | -1.5E-03 | 1664 |
| 5 | 651.4059 | 651.4079 | -2.0E-03 | 1756 |
| 6 | 779.4896 | 779.4916 | -2.0E-03 | 2129 |
| 7 | 907.5729 | 907.5753 | -2.4E-03 | 2029 |
| 8 | 1035.6567 | 1035.6590 | -2.3E-03 | 2019 |
| 9 | 1163.7390 | 1163.7428 | -3.8E-03 | 1552 |
| 10 | 1291.8227 | 1291.8265 | -3.8E-03 | 1103 |
| 11 | 1419.9047 | 1419.9102 | -5.5E-03 | 621 |
| 12 | 1547.9893 | 1547.9940 | -4.7E-03 | 318 |

$S_2$-$MM_n^{=CH2}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 1 | 251.1247 | 251.1254 | -6.7E-04 | 502 |
| 2 | 379.2086 | 379.2091 | -5.0E-04 | 2443 |
| 3 | 507.2918 | 507.2928 | -1.0E-03 | 2165 |
| 4 | 635.3757 | 635.3766 | -8.6E-04 | 2150 |
| 5 | 763.4585 | 763.4603 | -1.8E-03 | 1686 |
| 6 | 891.5417 | 891.5440 | -2.3E-03 | 1701 |
| 7 | 1019.6251 | 1019.6277 | -2.6E-03 | 1643 |
| 8 | 1147.7085 | 1147.7115 | -3.0E-03 | 1159 |
| 9 | 1275.7909 | 1275.7952 | -4.3E-03 | 768 |
| 10 | 1403.8751 | 1403.8789 | -3.8E-03 | 464 |
| 11 | 1531.9609 | 1531.9627 | -1.8E-03 | 241 |

$S_2$-$MM_n^{H}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 1 | 239.1248 | 239.1254 | -5.7E-04 | 3234 |
| 2 | 367.2087 | 367.2091 | -4.0E-04 | 1724 |
| 3 | 495.2917 | 495.2928 | -1.1E-03 | 1848 |
| 4 | 623.3752 | 623.3766 | -1.4E-03 | 1561 |
| 5 | 751.4585 | 751.4603 | -1.8E-03 | 1264 |
| 6 | 879.5422 | 879.5440 | -1.8E-03 | 1215 |
| 7 | 1007.6264 | 1007.6277 | -1.3E-03 | 1120 |
| 8 | 1135.7094 | 1135.7115 | -2.1E-03 | 853 |
| 9 | 1263.7908 | 1263.7952 | -4.4E-03 | 549 |
| 10 | 1391.8752 | 1391.8789 | -3.7E-03 | 310 |

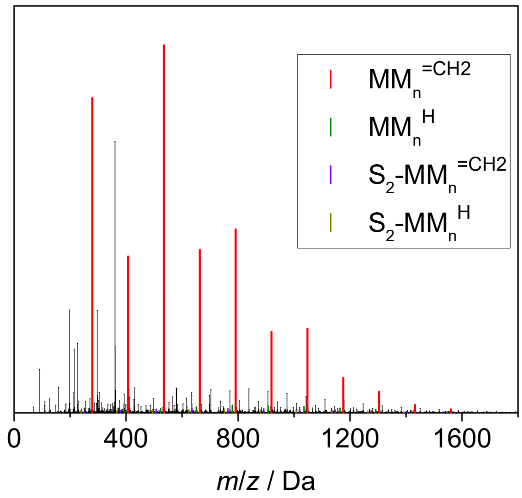


Figure S6: ESI-MS data of β scission products: batch polymerization at 120°C with $c_{BA,0}$ = 3.69 mol·L$^{-1}$ in dioxane ($S_2$: dioxane end group).

$MM_n^{=CH2}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 2 | 279.1567 | 279.1567 | 3.0E-05 | 154718 |
| 3 | 407.2402 | 407.2404 | -2.0E-04 | 76861 |
| 4 | 535.3238 | 535.3241 | -3.3E-04 | 180612 |
| 5 | 663.4073 | 663.4079 | -5.6E-04 | 80100 |
| 6 | 791.4908 | 791.4916 | -7.9E-04 | 90155 |
| 7 | 919.5742 | 919.5753 | -1.1E-03 | 39812 |
| 8 | 1047.658 | 1047.6590 | -1.0E-03 | 41404 |
| 9 | 1175.7415 | 1175.7428 | -1.3E-03 | 17176 |
| 10 | 1303.8253 | 1303.8265 | -1.2E-03 | 10424 |
| 11 | 1431.9083 | 1431.9102 | -1.9E-03 | 3881 |
| 12 | 1559.9919 | 1559.9940 | -2.1E-03 | 1694 |

$MM_n^H$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 3 | 395.2397 | 395.2404 | -7.0E-04 | 625 |
| 4 | 523.3236 | 523.3241 | -5.3E-04 | 2098 |
| 5 | 651.4073 | 651.4079 | -5.6E-04 | 2863 |
| 6 | 779.4906 | 779.4916 | -9.9E-04 | 3756 |
| 7 | 907.5732 | 907.5753 | -2.1E-03 | 3392 |
| 8 | 1035.6571 | 1035.6590 | -1.9E-03 | 3073 |
| 9 | 1163.7406 | 1163.7428 | -2.2E-03 | 2284 |
| 10 | 1291.8244 | 1291.8265 | -2.1E-03 | 1520 |
| 11 | 1419.9068 | 1419.9102 | -3.4E-03 | 817 |
| 12 | 1547.9911 | 1547.9940 | -2.9E-03 | 454 |

$S_2$-$MM_n^{=CH2}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 1 | 251.1255 | 251.1254 | 1.3E-04 | 251 |
| 2 | 379.2088 | 379.2091 | -3.0E-04 | 1099 |
| 3 | 507.2925 | 507.2928 | -3.3E-04 | 1735 |
| 4 | 635.3765 | 635.3766 | -5.9E-05 | 2402 |
| 5 | 763.4589 | 763.4603 | -1.4E-03 | 2039 |
| 6 | 891.5423 | 891.5440 | -1.7E-03 | 1939 |
| 7 | 1019.6247 | 1019.6277 | -3.0E-03 | 1738 |
| 8 | 1147.7096 | 1147.7115 | -1.9E-03 | 1289 |
| 9 | 1275.7926 | 1275.7952 | -2.6E-03 | 900 |
| 10 | 1403.8763 | 1403.8789 | -2.6E-03 | 544 |
| 11 | 1531.9603 | 1531.9627 | -2.4E-03 | 283 |

$S_2$-$MM_n^{H}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 1 | 239.1251 | 239.1254 | -2.7E-04 | 896 |
| 2 | 367.209 | 367.2091 | -1.0E-04 | 871 |
| 3 | 495.292 | 495.2928 | -8.3E-04 | 1357 |
| 4 | 623.3761 | 623.3766 | -4.6E-04 | 1437 |
| 5 | 751.4596 | 751.4603 | -6.9E-04 | 1348 |
| 6 | 879.5428 | 879.5440 | -1.2E-03 | 1320 |
| 7 | 1007.6271 | 1007.6277 | -6.5E-04 | 1136 |
| 8 | 1135.7099 | 1135.7115 | -1.6E-03 | 854 |
| 9 | 1263.7771 | 1263.7952 | -1.8E-02 | 767 |
| 10 | 1391.8779 | 1391.8789 | -1.0E-03 | 328 |

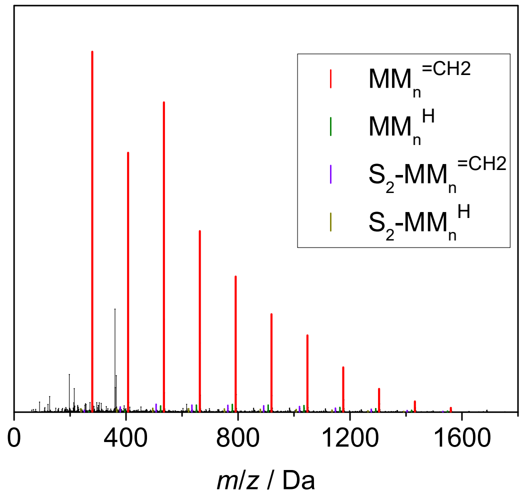


Figure S7: ESI-MS data of β scission products: batch polymerization at 130°C with $c_{BA,0}$ = 2.92 mol·L$^{-1}$ in dioxane ($S_2$: dioxane end group).

$MM_n^{=CH2} + Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 2 | 279.1567 | 279.1567 | 3.0E-05 | 150724 |
| 3 | 407.2404 | 407.2404 | 0.0E+00 | 108442 |
| 4 | 535.3239 | 535.3241 | -2.3E-04 | 129539 |
| 5 | 663.4073 | 663.4079 | -5.6E-04 | 75672 |
| 6 | 791.4910 | 791.4916 | -5.9E-04 | 56691 |
| 7 | 919.5747 | 919.5753 | -6.2E-04 | 40972 |
| 8 | 1047.6583 | 1047.6590 | -7.5E-04 | 32089 |
| 9 | 1175.7414 | 1175.7428 | -1.4E-03 | 18723 |
| 10 | 1303.8246 | 1303.8265 | -1.9E-03 | 9742 |
| 11 | 1431.9078 | 1431.9102 | -2.4E-03 | 4454 |
| 12 | 1559.9929 | 1559.9940 | -1.1E-03 | 1761 |

$MM_n^{H} + Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 2 | 267.1573 | 267.1567 | 6.3E-04 | 262 |
| 3 | 395.2399 | 395.2404 | -5.0E-04 | 970 |
| 4 | 523.3237 | 523.3241 | -4.3E-04 | 2618 |
| 5 | 651.4071 | 651.4079 | -7.6E-04 | 2912 |
| 6 | 779.4904 | 779.4916 | -1.2E-03 | 3237 |
| 7 | 907.5735 | 907.5753 | -1.8E-03 | 2924 |
| 8 | 1035.6572 | 1035.6590 | -1.8E-03 | 2719 |
| 9 | 1163.7402 | 1163.7428 | -2.6E-03 | 1977 |
| 10 | 1291.8225 | 1291.8265 | -4.0E-03 | 1447 |
| 11 | 1419.9063 | 1419.9102 | -3.9E-03 | 748 |

| | | | | |
|---|---|---|---|---|
| 12 | 1547.9889 | 1547.9940 | -5.1E-03 | 411 |

$S_2$-$MM_n^{=CH2}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 1 | 251.1251 | 251.1254 | -2.7E-04 | 834 |
| 2 | 379.2092 | 379.2091 | 1.0E-04 | 2188 |
| 3 | 507.2926 | 507.2928 | -2.3E-04 | 3288 |
| 4 | 635.3759 | 635.3766 | -6.6E-04 | 2945 |
| 5 | 763.4596 | 763.4603 | -6.9E-04 | 2848 |
| 6 | 891.5431 | 891.5440 | -9.2E-04 | 2626 |
| 7 | 1019.6266 | 1019.6277 | -1.1E-03 | 2379 |
| 8 | 1147.7103 | 1147.7115 | -1.2E-03 | 1696 |
| 9 | 1275.7924 | 1275.7952 | -2.8E-03 | 1191 |
| 10 | 1403.8751 | 1403.8789 | -3.8E-03 | 668 |
| 11 | 1531.9591 | 1531.9627 | -3.6E-03 | 311 |

$S_2$-$MM_n^{H}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 1 | 239.1252 | 239.1254 | -1.7E-04 | 1353 |
| 2 | 367.2092 | 367.2091 | 1.0E-04 | 1337 |
| 3 | 495.2927 | 495.2928 | -1.3E-04 | 1610 |
| 4 | 623.3760 | 623.3766 | -5.6E-04 | 1430 |
| 5 | 751.4597 | 751.4603 | -5.9E-04 | 1354 |
| 6 | 879.5433 | 879.5440 | -7.2E-04 | 1168 |
| 7 | 1007.6273 | 1007.6277 | -4.5E-04 | 1086 |
| 8 | 1135.7104 | 1135.7115 | -1.1E-03 | 848 |
| 9 | 1263.7920 | 1263.7952 | -3.2E-03 | 524 |
| 10 | 1391.8730 | 1391.8789 | -5.9E-03 | 292 |

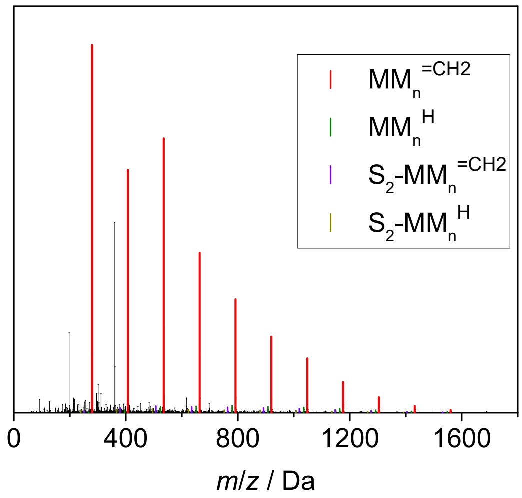


Figure S8: ESI-MS data of β scission products: batch polymerization at 130°C with $c_{BA,0}$ = 3.69 mol·L$^{-1}$ in dioxane ($S_2$: dioxane end group).

$MM_n^{=CH2}$ + $Na^+$

| n | *m*/*z* / Da experimental | *m*/*z* / Da theoretical | Δ *m*/*z* / Da | intensity |
|---|---|---|---|---|
| 2 | 279.1561 | 279.1567 | -5.7E-04 | 126665 |
| 3 | 407.2395 | 407.2404 | -9.0E-04 | 83707 |
| 4 | 535.3228 | 535.3241 | -1.3E-03 | 94514 |
| 5 | 663.4063 | 663.4079 | -1.6E-03 | 55015 |
| 6 | 791.4897 | 791.4916 | -1.9E-03 | 39079 |
| 7 | 919.5732 | 919.5753 | -2.1E-03 | 26225 |
| 8 | 1047.657 | 1047.6590 | -2.0E-03 | 18745 |
| 9 | 1175.7406 | 1175.7428 | -2.2E-03 | 10663 |
| 10 | 1303.824 | 1303.8265 | -2.5E-03 | 5336 |
| 11 | 1431.9076 | 1431.9102 | -2.6E-03 | 2387 |
| 12 | 1559.9906 | 1559.9940 | -3.4E-03 | 938 |

$MM_n^{H}$ + $Na^+$

| n | *m*/*z* / Da experimental | *m*/*z* / Da theoretical | Δ *m*/*z* / Da | intensity |
|---|---|---|---|---|
| 2 | 267.1559 | 267.1567 | -7.7E-04 | 203 |
| 3 | 395.2397 | 395.2404 | -7.0E-04 | 896 |
| 4 | 523.3225 | 523.3241 | -1.6E-03 | 2067 |
| 5 | 651.4063 | 651.4079 | -1.6E-03 | 2218 |
| 6 | 779.4891 | 779.4916 | -2.5E-03 | 2432 |
| 7 | 907.5723 | 907.5753 | -3.0E-03 | 2069 |
| 8 | 1035.6555 | 1035.6590 | -3.5E-03 | 1793 |
| 9 | 1163.7396 | 1163.7428 | -3.2E-03 | 1335 |
| 10 | 1291.8237 | 1291.8265 | -2.8E-03 | 873 |
| 11 | 1419.9054 | 1419.9102 | -4.8E-03 | 469 |
| 12 | 1547.9881 | 1547.9940 | -5.9E-03 | 242 |

$S_2$-$MM_n^{=CH2}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 1 | 251.1247 | 251.1254 | -6.7E-04 | 577 |
| 2 | 379.2083 | 379.2091 | -8.0E-04 | 1657 |
| 3 | 507.2916 | 507.2928 | -1.2E-03 | 2288 |
| 4 | 635.3747 | 635.3766 | -1.9E-03 | 2058 |
| 5 | 763.4584 | 763.4603 | -1.9E-03 | 1902 |
| 6 | 891.5415 | 891.5440 | -2.5E-03 | 1639 |
| 7 | 1019.6248 | 1019.6277 | -2.9E-03 | 1416 |
| 8 | 1147.7084 | 1147.7115 | -3.1E-03 | 990 |
| 9 | 1275.7929 | 1275.7952 | -2.3E-03 | 634 |
| 10 | 1403.8758 | 1403.8789 | -3.1E-03 | 370 |
| 11 | 1531.9598 | 1531.9627 | -2.9E-03 | 181 |

$S_2$-$MM_n^{H}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 1 | 239.1246 | 239.1254 | -7.7E-04 | 856 |
| 2 | 367.2082 | 367.2091 | -9.0E-04 | 1144 |
| 3 | 495.2917 | 495.2928 | -1.1E-03 | 1271 |
| 4 | 623.3745 | 623.3766 | -2.1E-03 | 1097 |
| 5 | 751.459 | 751.4603 | -1.3E-03 | 908 |
| 6 | 879.5419 | 879.5440 | -2.1E-03 | 831 |
| 7 | 1007.6259 | 1007.6277 | -1.8E-03 | 688 |
| 8 | 1135.709 | 1135.7115 | -2.5E-03 | 465 |
| 9 | 1263.7929 | 1263.7952 | -2.3E-03 | 296 |
| 10 | 1391.8754 | 1391.8789 | -3.5E-03 | 172 |

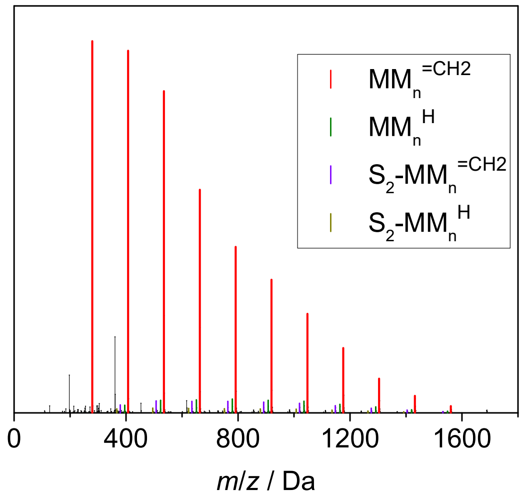


Figure S9: ESI-MS data of β scission products: batch polymerization at 140°C with $c_{BA,0}$ = 2.92 mol·L$^{-1}$ in dioxane ($S_2$: dioxane end group).

$MM_n^{=CH2}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 2 | 279.1558 | 279.1567 | -8.7E-04 | 45667 |
| 3 | 407.2393 | 407.2404 | -1.1E-03 | 44493 |
| 4 | 535.3226 | 535.3241 | -1.5E-03 | 39521 |
| 5 | 663.4058 | 663.4079 | -2.1E-03 | 27413 |
| 6 | 791.4894 | 791.4916 | -2.2E-03 | 20387 |
| 7 | 919.5730 | 919.5753 | -2.3E-03 | 16363 |
| 8 | 1047.6565 | 1047.6590 | -2.5E-03 | 12174 |
| 9 | 1175.7395 | 1175.7428 | -3.3E-03 | 7970 |
| 10 | 1303.8221 | 1303.8265 | -4.4E-03 | 4199 |
| 11 | 1431.9053 | 1431.9102 | -4.9E-03 | 2091 |
| 12 | 1559.9893 | 1559.9940 | -4.7E-03 | 836 |

$MM_n^H$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 3 | 395.2391 | 395.2404 | -1.3E-03 | 927 |
| 4 | 523.3226 | 523.3241 | -1.5E-03 | 1536 |
| 5 | 651.4057 | 651.4079 | -2.2E-03 | 1601 |
| 6 | 779.4889 | 779.4916 | -2.7E-03 | 1705 |
| 7 | 907.5723 | 907.5753 | -3.0E-03 | 1537 |
| 8 | 1035.6561 | 1035.6590 | -2.9E-03 | 1433 |
| 9 | 1163.7387 | 1163.7428 | -4.1E-03 | 1043 |
| 10 | 1291.8214 | 1291.8265 | -5.1E-03 | 736 |
| 11 | 1419.9040 | 1419.9102 | -6.2E-03 | 384 |
| 12 | 1547.9882 | 1547.9940 | -5.8E-03 | 200 |

$S_2$-$MM_n^{=CH2}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 2 | 379.2083 | 379.2091 | -8.0E-04 | 975 |
| 3 | 507.2914 | 507.2928 | -1.4E-03 | 1475 |
| 4 | 635.3747 | 635.3766 | -1.9E-03 | 1421 |
| 5 | 763.4580 | 763.4603 | -2.3E-03 | 1419 |
| 6 | 891.5419 | 891.5440 | -2.1E-03 | 1322 |
| 7 | 1019.6251 | 1019.6277 | -2.6E-03 | 1178 |
| 8 | 1147.7081 | 1147.7115 | -3.4E-03 | 872 |
| 9 | 1275.7915 | 1275.7952 | -3.7E-03 | 560 |
| 10 | 1403.8741 | 1403.8789 | -4.8E-03 | 341 |
| 11 | 1531.9586 | 1531.9627 | -4.1E-03 | 152 |

$S_2$-$MM_n^{H}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 2 | 367.2080 | 367.2091 | -1.1E-03 | 492 |
| 3 | 495.2912 | 495.2928 | -1.6E-03 | 575 |
| 4 | 623.3745 | 623.3766 | -2.1E-03 | 545 |
| 5 | 751.4577 | 751.4603 | -2.6E-03 | 510 |
| 6 | 879.5420 | 879.5440 | -2.0E-03 | 486 |
| 7 | 1007.6251 | 1007.6277 | -2.6E-03 | 454 |
| 8 | 1135.7090 | 1135.7115 | -2.5E-03 | 337 |
| 9 | 1263.7915 | 1263.7952 | -3.7E-03 | 229 |
| 10 | 1391.8735 | 1391.8789 | -5.4E-03 | 126 |

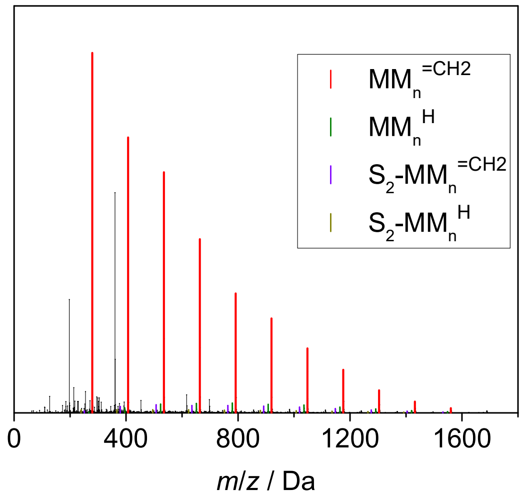


Figure S10: ESI-MS data of β scission products: batch polymerization at 140°C with $c_{BA,0}$ = 3.69 mol·L$^{-1}$ in dioxane ($S_2$: dioxane end group).

$MM_n^{=CH2}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 2 | 279.1558 | 279.1567 | -8.7E-04 | 150376 |
| 3 | 407.2391 | 407.2404 | -1.3E-03 | 115060 |
| 4 | 535.3224 | 535.3241 | -1.7E-03 | 100496 |
| 5 | 663.4058 | 663.4079 | -2.1E-03 | 72539 |
| 6 | 791.4891 | 791.4916 | -2.5E-03 | 49879 |
| 7 | 919.5724 | 919.5753 | -2.9E-03 | 39468 |
| 8 | 1047.656 | 1047.6590 | -3.0E-03 | 26957 |
| 9 | 1175.7396 | 1175.7428 | -3.2E-03 | 17989 |
| 10 | 1303.8232 | 1303.8265 | -3.3E-03 | 9417 |
| 11 | 1431.9059 | 1431.9102 | -4.3E-03 | 4720 |
| 12 | 1559.9895 | 1559.9940 | -4.5E-03 | 1976 |

$MM_n^{H}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 2 | 267.1561 | 267.1567 | -5.7E-04 | 319 |
| 3 | 395.2391 | 395.2404 | -1.3E-03 | 2090 |
| 4 | 523.3223 | 523.3241 | -1.8E-03 | 3657 |
| 5 | 651.4055 | 651.4079 | -2.4E-03 | 3925 |
| 6 | 779.4886 | 779.4916 | -3.0E-03 | 4094 |
| 7 | 907.5718 | 907.5753 | -3.5E-03 | 3574 |
| 8 | 1035.6547 | 1035.6590 | -4.3E-03 | 3276 |
| 9 | 1163.7384 | 1163.7428 | -4.4E-03 | 2421 |
| 10 | 1291.8221 | 1291.8265 | -4.4E-03 | 1659 |
| 11 | 1419.9046 | 1419.9102 | -5.6E-03 | 939 |
| 12 | 1547.9877 | 1547.9940 | -6.3E-03 | 492 |

$S_2$-$MM_n^{=CH2}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 1 | 251.1245 | 251.1254 | -8.7E-04 | 803 |
| 2 | 379.2079 | 379.2091 | -1.2E-03 | 2642 |
| 3 | 507.2911 | 507.2928 | -1.7E-03 | 3349 |
| 4 | 635.3744 | 635.3766 | -2.2E-03 | 3065 |
| 5 | 763.4577 | 763.4603 | -2.6E-03 | 3099 |
| 6 | 891.5407 | 891.5440 | -3.3E-03 | 2779 |
| 7 | 1019.6242 | 1019.6277 | -3.5E-03 | 2414 |
| 8 | 1147.7078 | 1147.7115 | -3.7E-03 | 1782 |
| 9 | 1275.7918 | 1275.7952 | -3.4E-03 | 1202 |
| 10 | 1403.8749 | 1403.8789 | -4.0E-03 | 718 |
| 11 | 1531.958 | 1531.9627 | -4.7E-03 | 357 |

$S_2$-$MM_n^{H}$ + $Na^+$

| n | *m/z* / Da experimental | *m/z* / Da theoretical | Δ *m/z* / Da | intensity |
|---|---|---|---|---|
| 1 | 239.1246 | 239.1254 | -7.7E-04 | 1194 |
| 2 | 367.2079 | 367.2091 | -1.2E-03 | 1305 |
| 3 | 495.2909 | 495.2928 | -1.9E-03 | 1320 |
| 4 | 623.3744 | 623.3766 | -2.2E-03 | 1286 |
| 5 | 751.4578 | 751.4603 | -2.5E-03 | 1100 |
| 6 | 879.5412 | 879.5440 | -2.8E-03 | 1013 |
| 7 | 1007.6244 | 1007.6277 | -3.3E-03 | 886 |
| 8 | 1135.7082 | 1135.7115 | -3.3E-03 | 695 |
| 9 | 1263.7919 | 1263.7952 | -3.3E-03 | 466 |
| 10 | 1391.8741 | 1391.8789 | -4.8E-03 | 282 |

**Figures S11 – S16 give the following NMR spectra of $MM_3^{=CH2}$**

$^{1}H$ spectrum (600 MHz)

$^{13}C\{^{1}H\}$ spectrum (150 MHz)

$^{13}C$-DEPT135 spectrum (150 MHz)

$^{1}H,^{1}H$-COSY (DQF-COSY, 600 MHz)

$^{1}H,^{13}C$-HSQC (600 MHz)

$^{1}H,^{13}C$-HMBC (600 MHz)

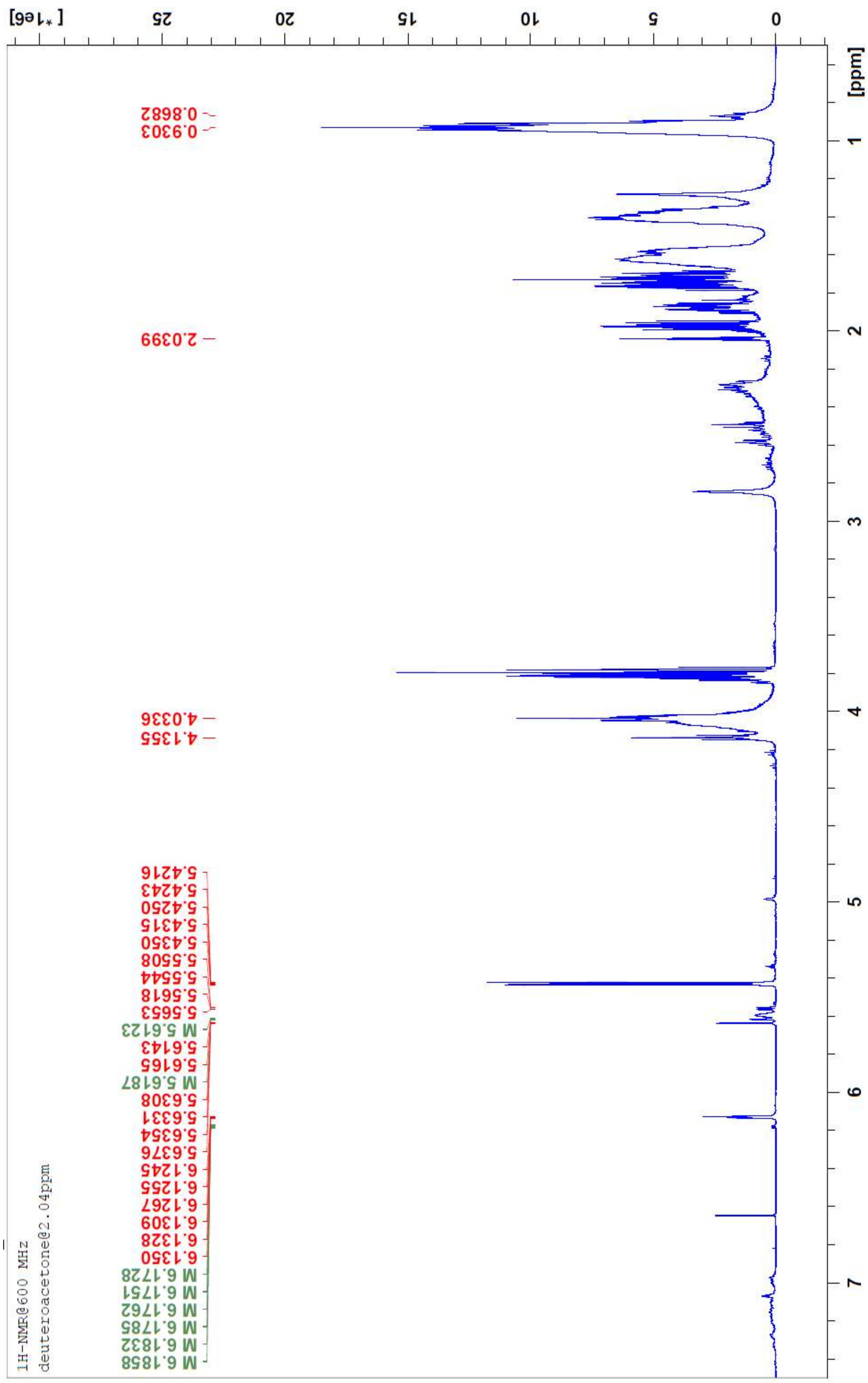


Figure S11: $^1$H spectrum of the unsaturated trimer ($MM_3^{=CH2}$) (600 MHz).

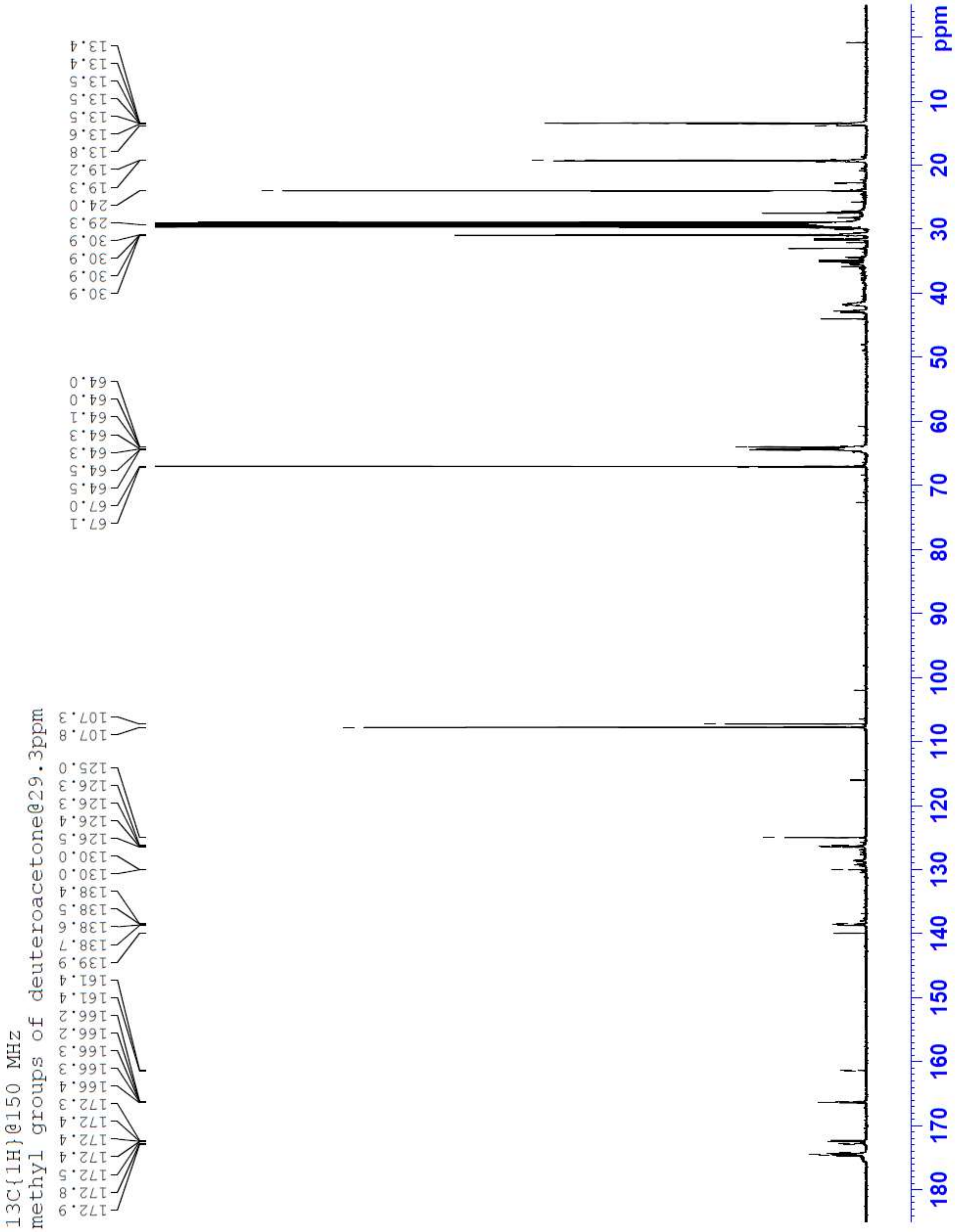


Figure S12: $^{13}C\{^{1}H\}$ spectrum of $MM_3^{=CH2}$ (150 MHz).

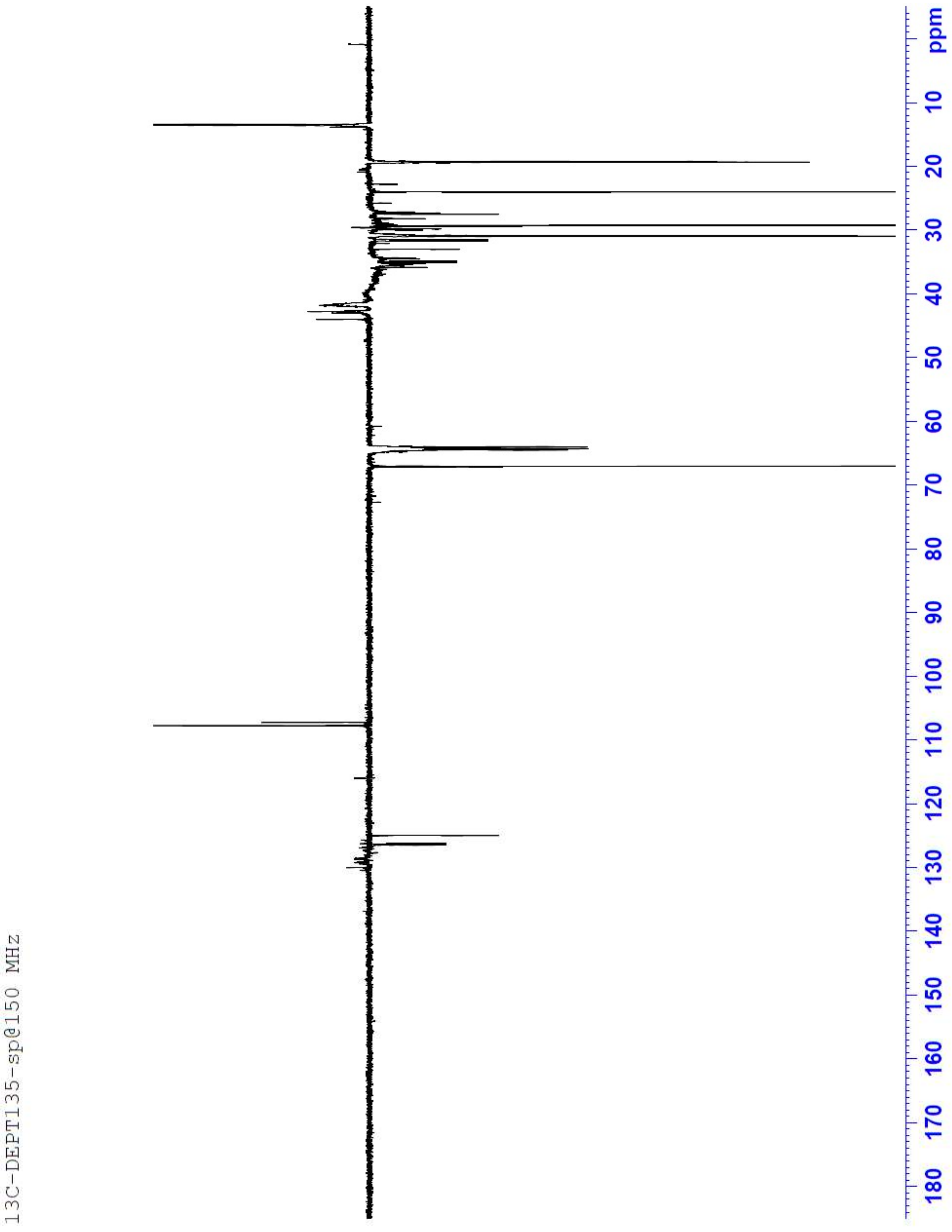


Figure S13: $^{13}$C-DEPT135 spectrum of $MM_3^{=CH2}$ (150 MHz).

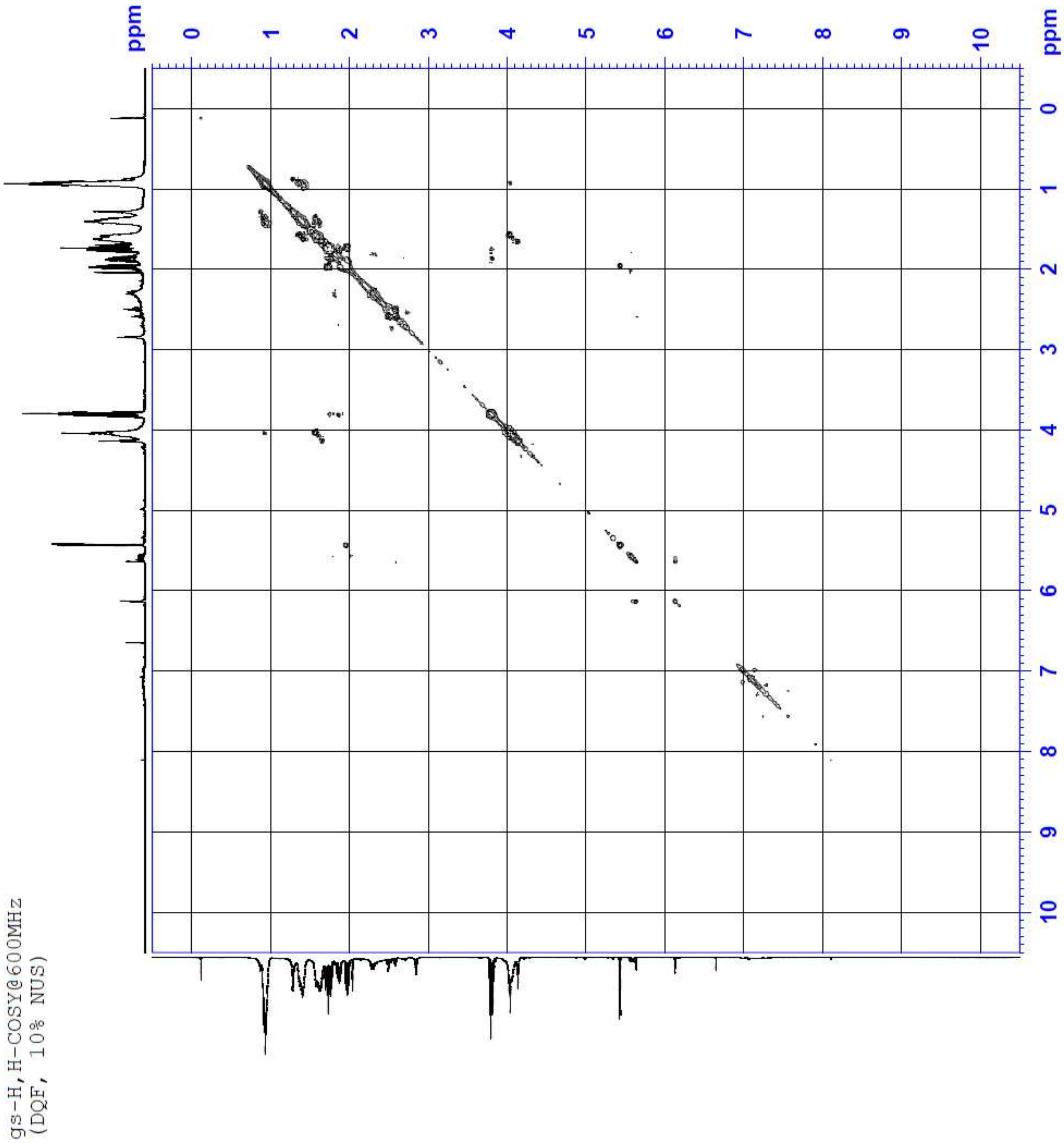


Figure S14: $^{1}H,^{1}H$-COSY (DQF-COSY) of $MM_3^{=CH2}$ (600 MHz).

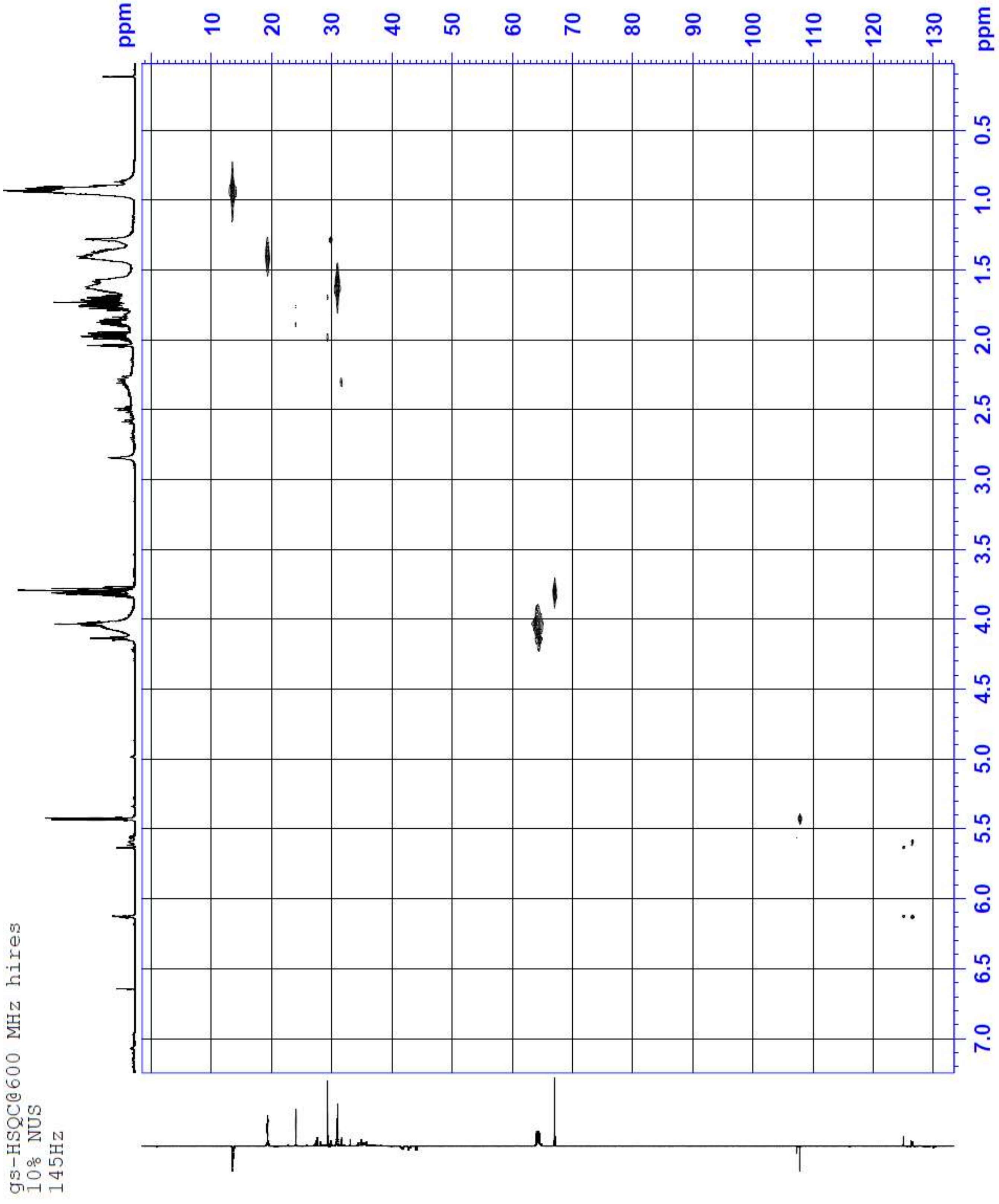


Figure S15: ${}^{1}H,{}^{13}C$-HSQC of $MM_3{}^{=CH2}$ (600 MHz).

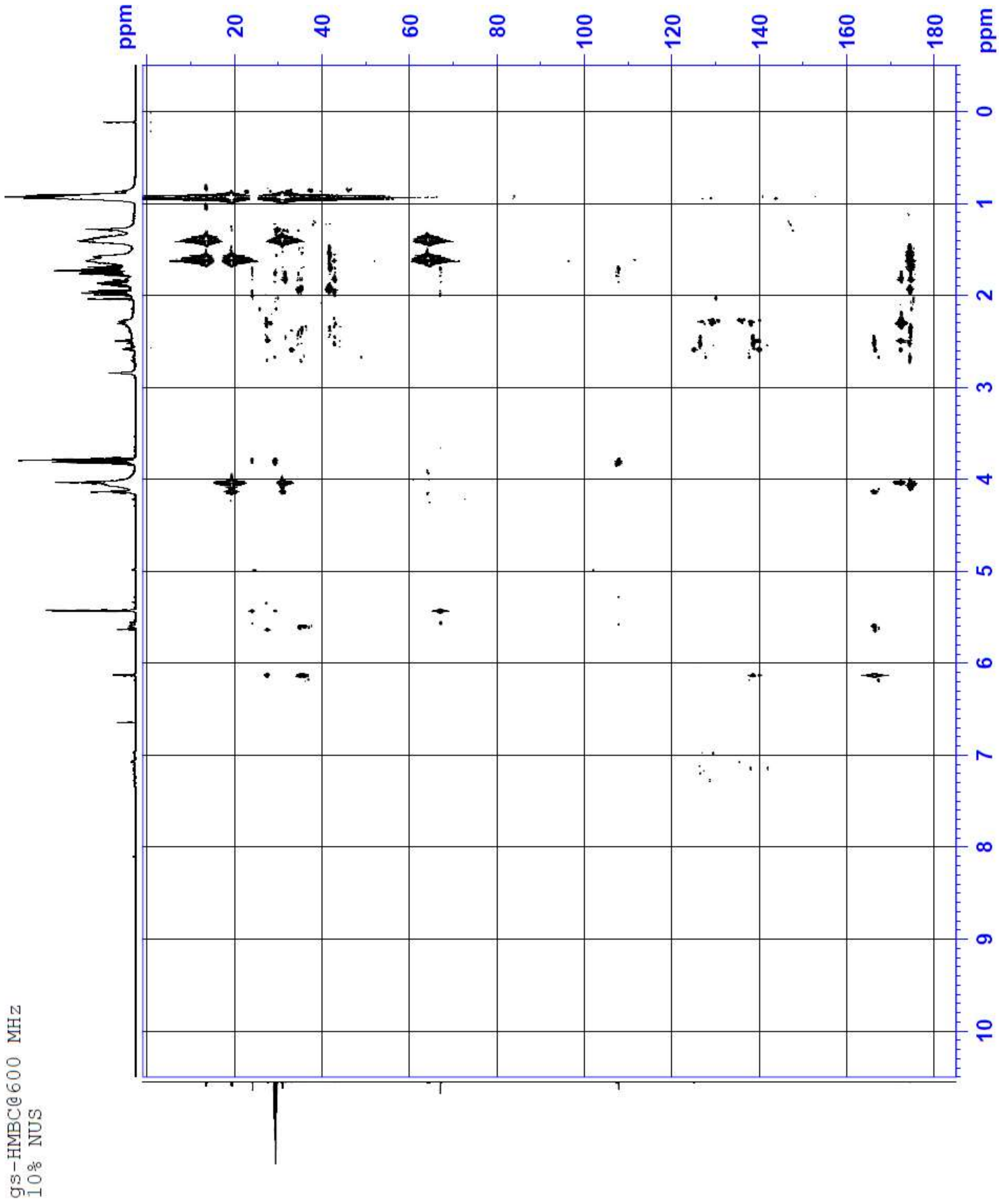


Figure S16: $^{1}H,^{13}C$-HMBC of $MM_3^{=CH2}$ (600 MHz).