# "A Structural Study of Alkaline Earth Metal Complexes with Hybrid Disila-Crown Ethers"

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## Supplementary Information

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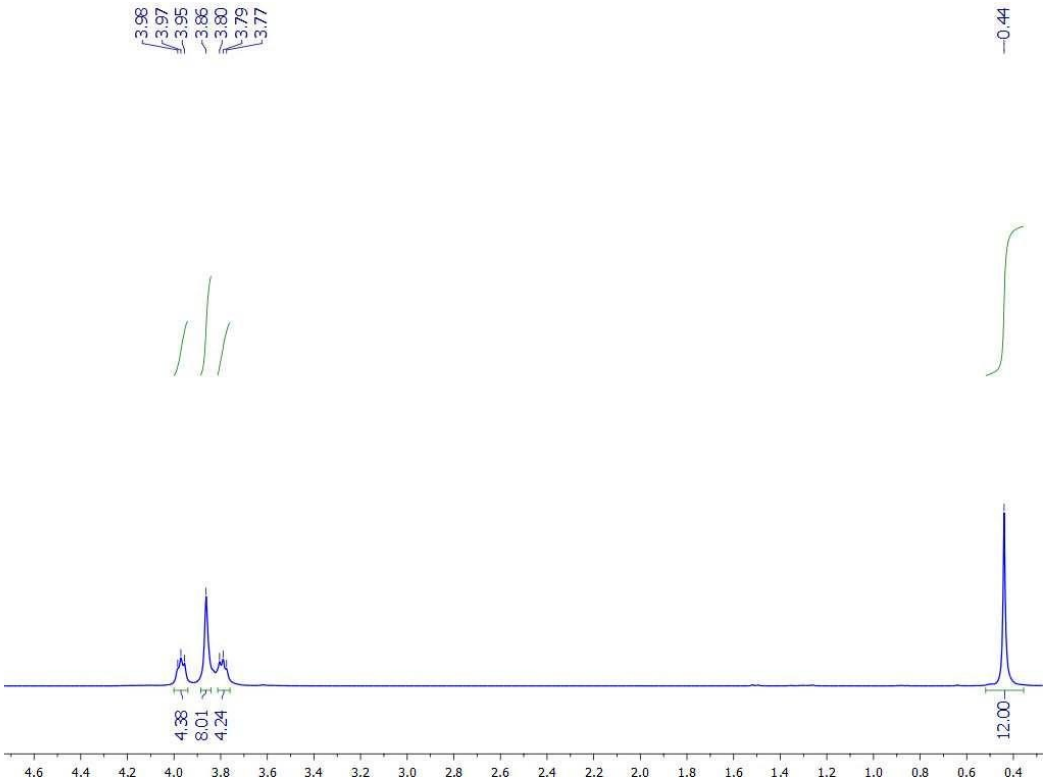
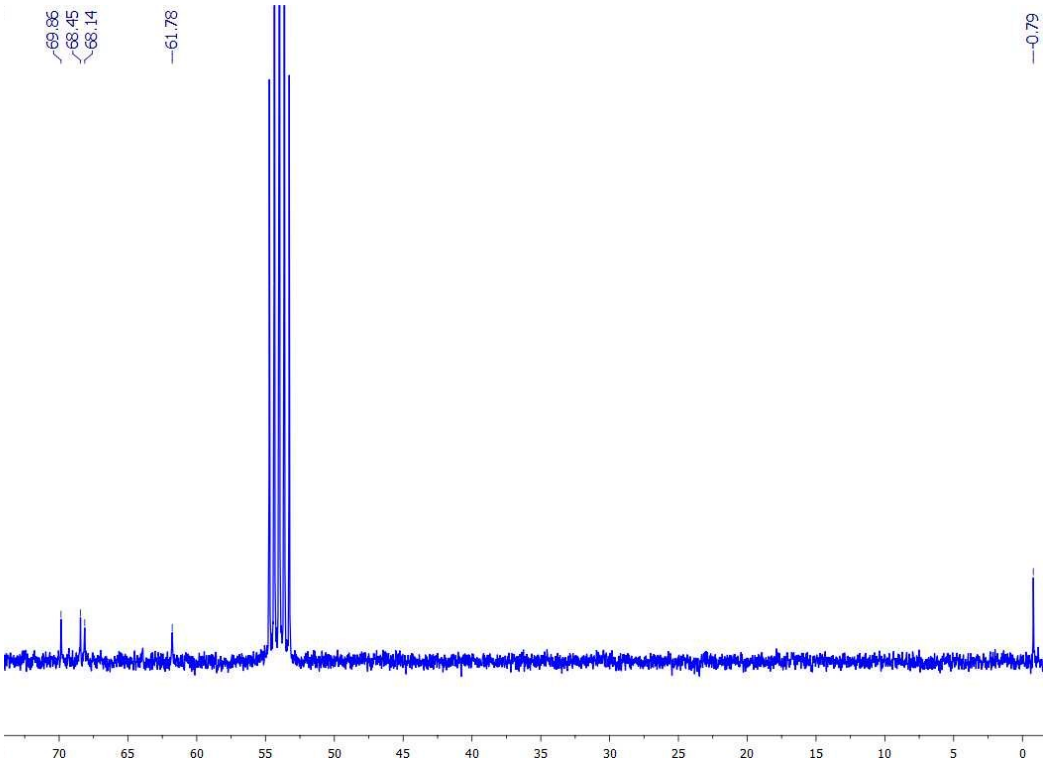
# 1. NMR spectra

**General**: NMR spectra were recorded on a Bruker AV III 500 MHz and a Bruker AV III HD 300 MHz. Coupling constants *J* are reported in Hertz (Hz) and the chemical shifts (δ) expressed in parts per million (ppm) relative to $CCl_3F$ ($^{19}F$) or $SiMe_4$ ($^{1}H$, $^{13}C$, $^{29}Si$). Given spectra represent compounds **3** to **8** after workup and were visualized with MestReNova.[1]

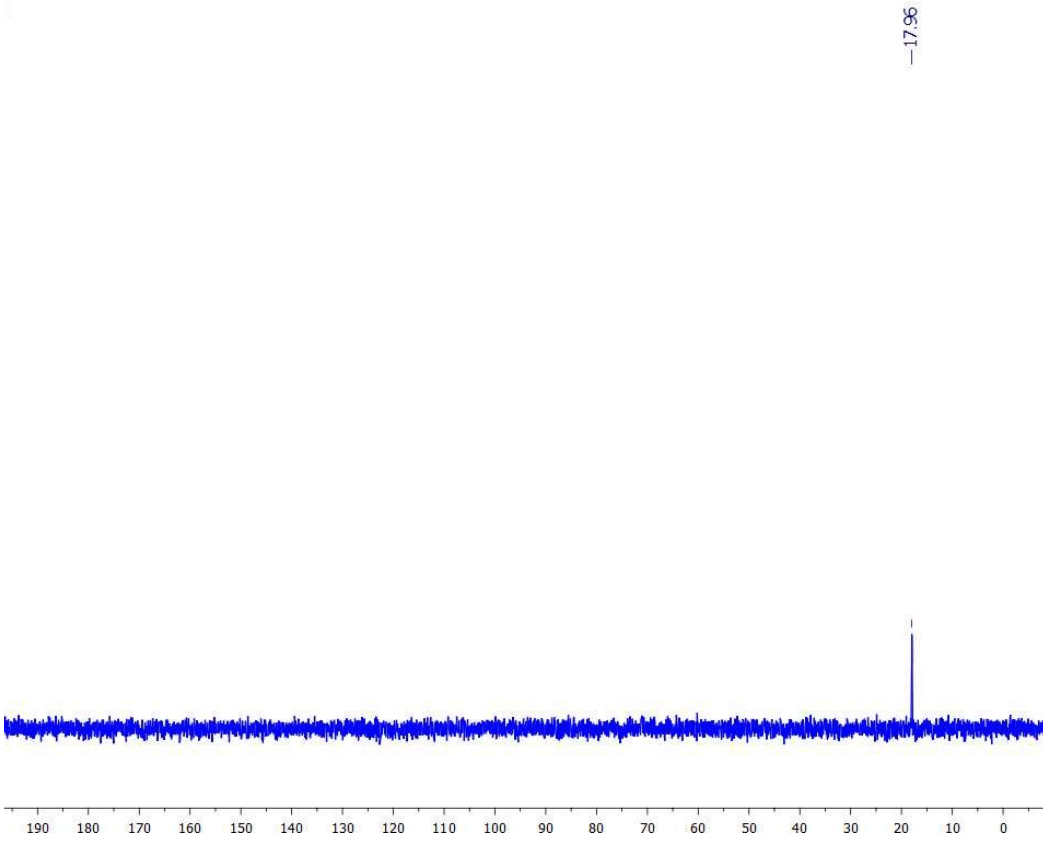
## 1.1 Compound 3




$^{1}H$ NMR of compound **3** in $CD_2Cl_2$.

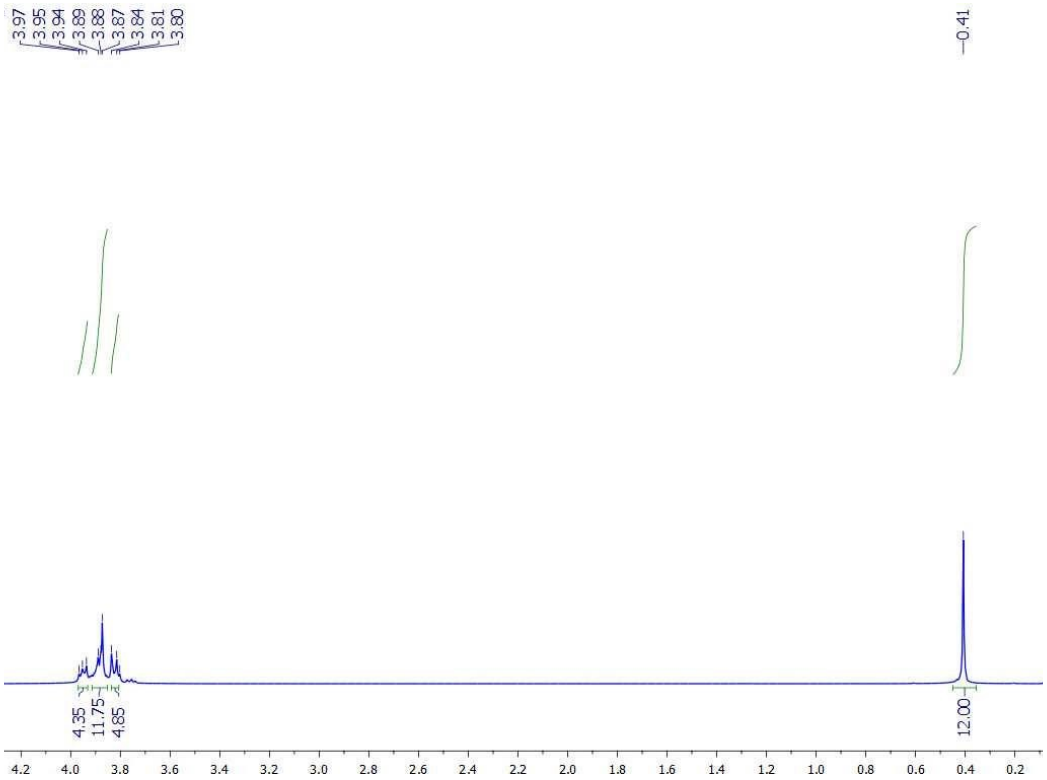



$^{13}C\{^{1}H\}$ NMR of compound **3** in $CD_2Cl_2$.

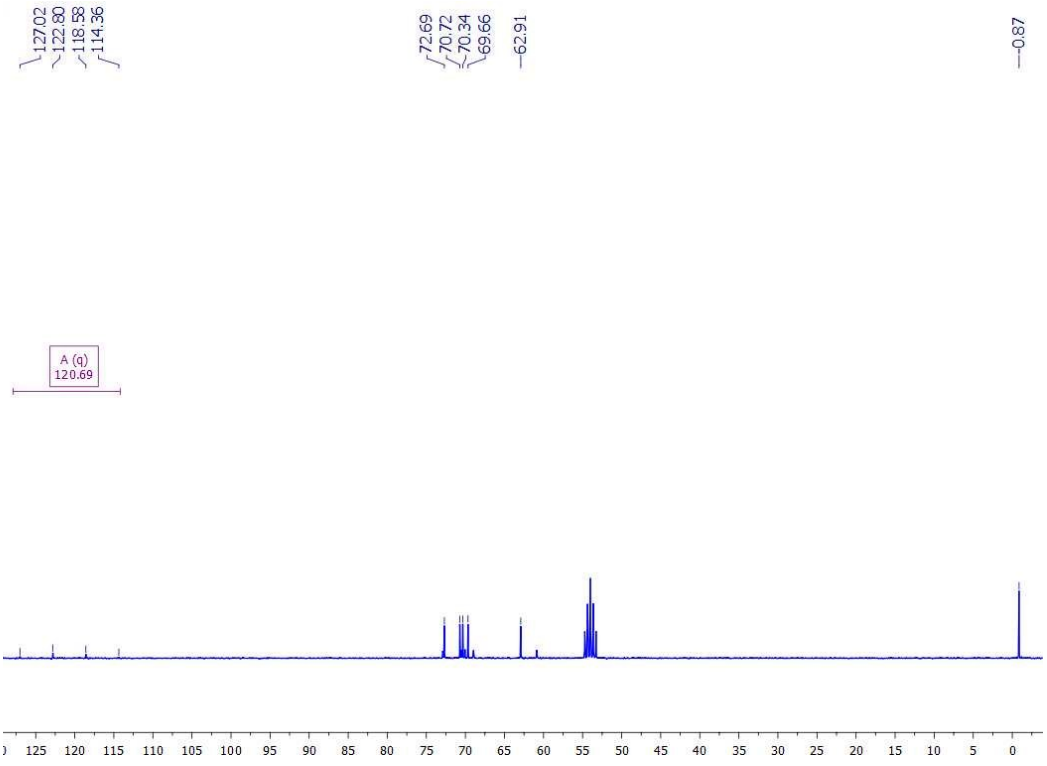



$^{29}Si\{^{1}H\}$ NMR of compound **3** $CD_2Cl_2$.

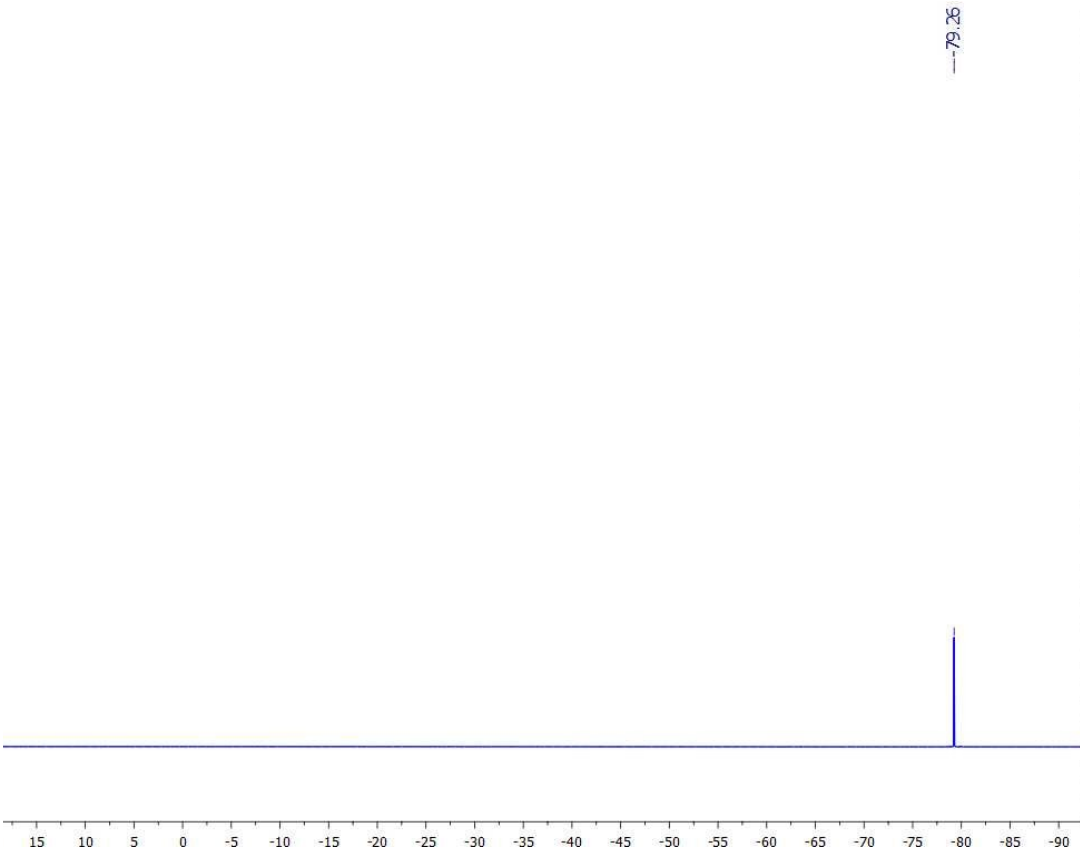
## 1.2 Compound 4



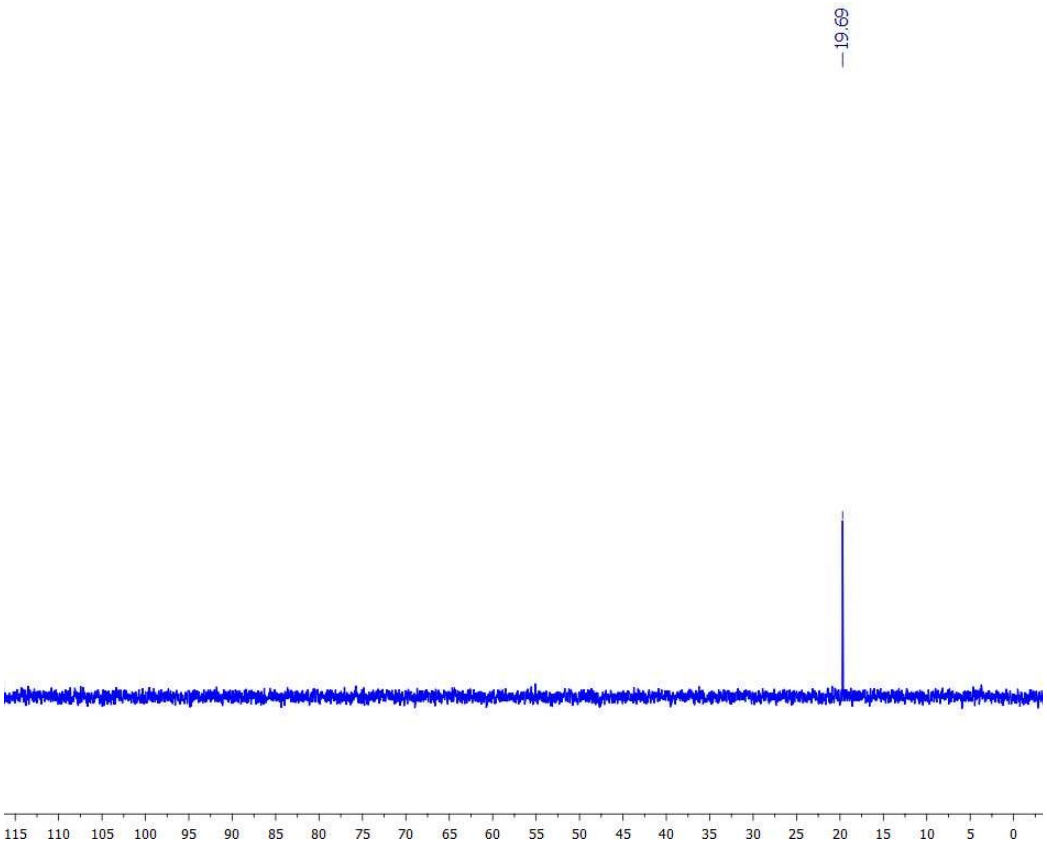

$^{1}$H NMR of compound **4** in $CD_2Cl_2$.




$^{13}C\{^{1}H\}$ NMR of compound **4** in $CD_2Cl_2$.

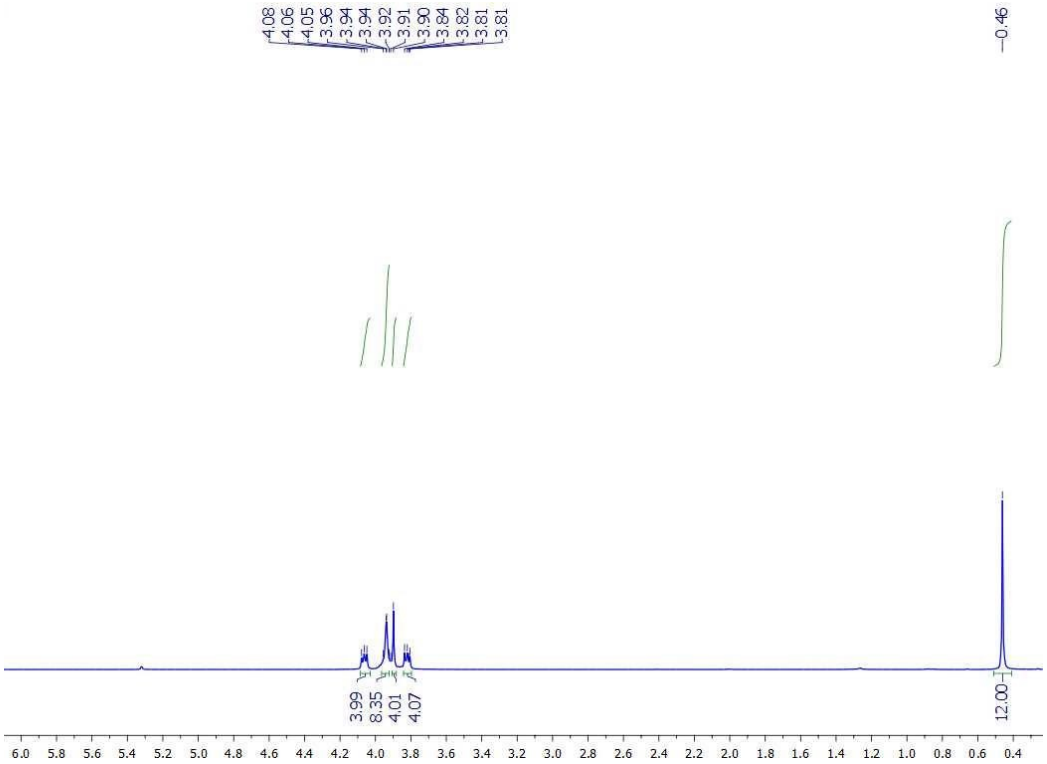



$^{19}F$ NMR of compound **4** in $CD_2Cl_2$.

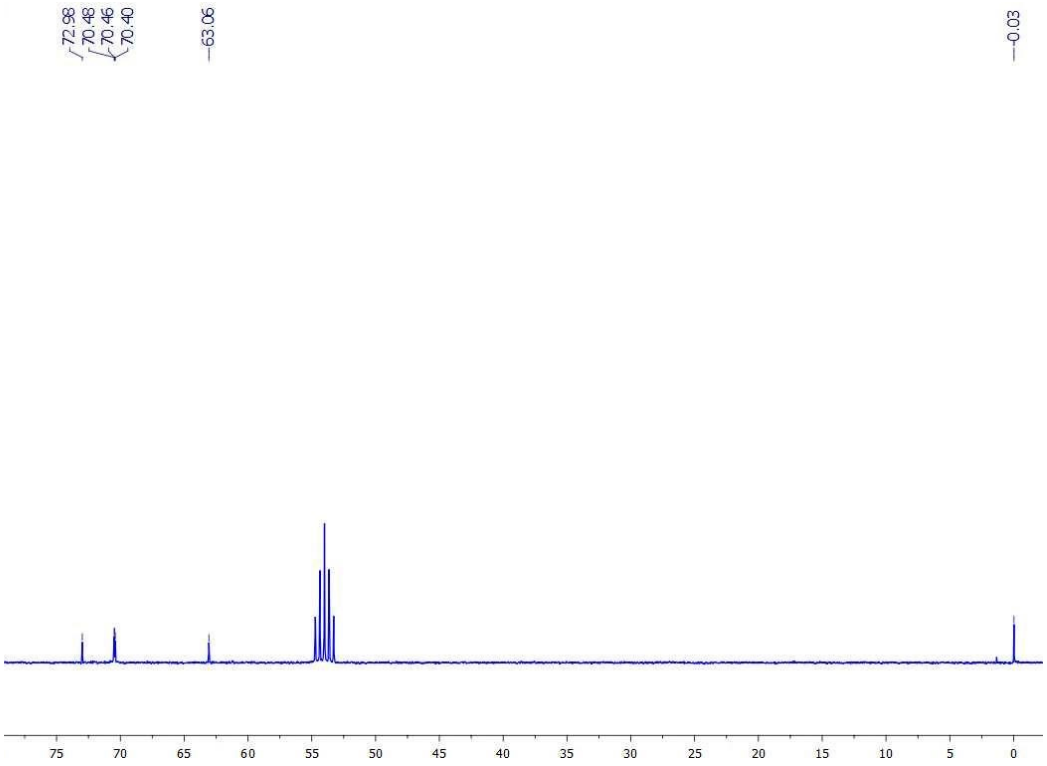



$^{29}Si\{^1H\}$ NMR of compound **4** $CD_2Cl_2$.

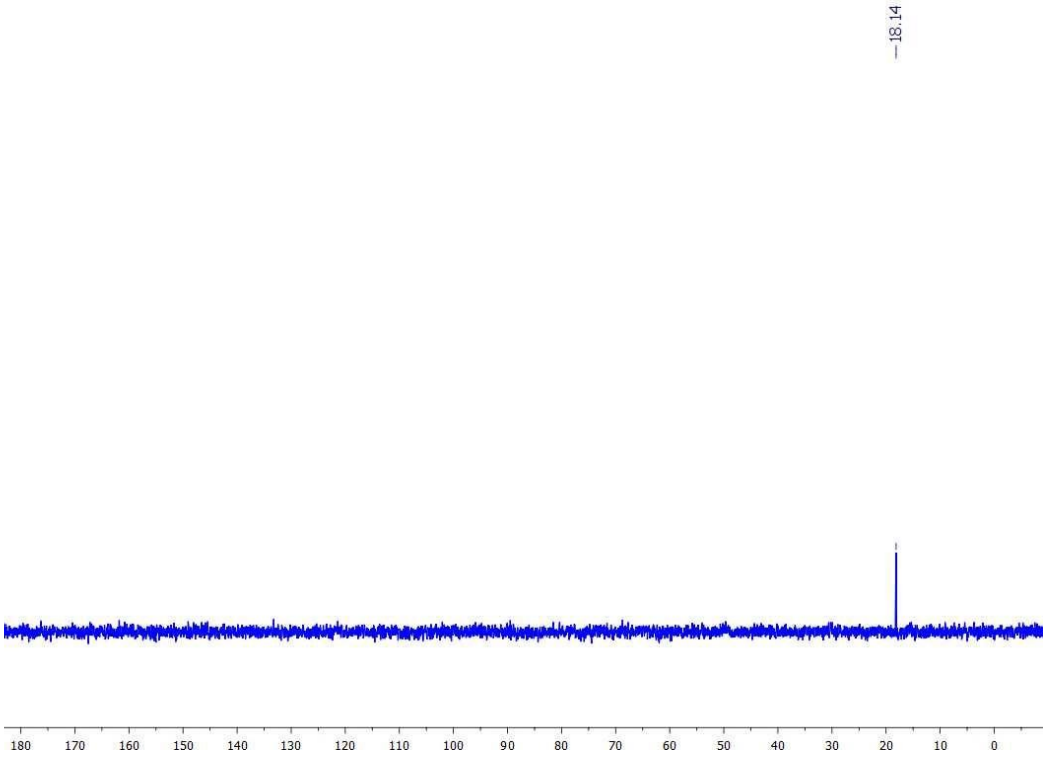
## 1.3 Compound 5




$^{1}H$ NMR of compound **5** in $CD_2Cl_2$.

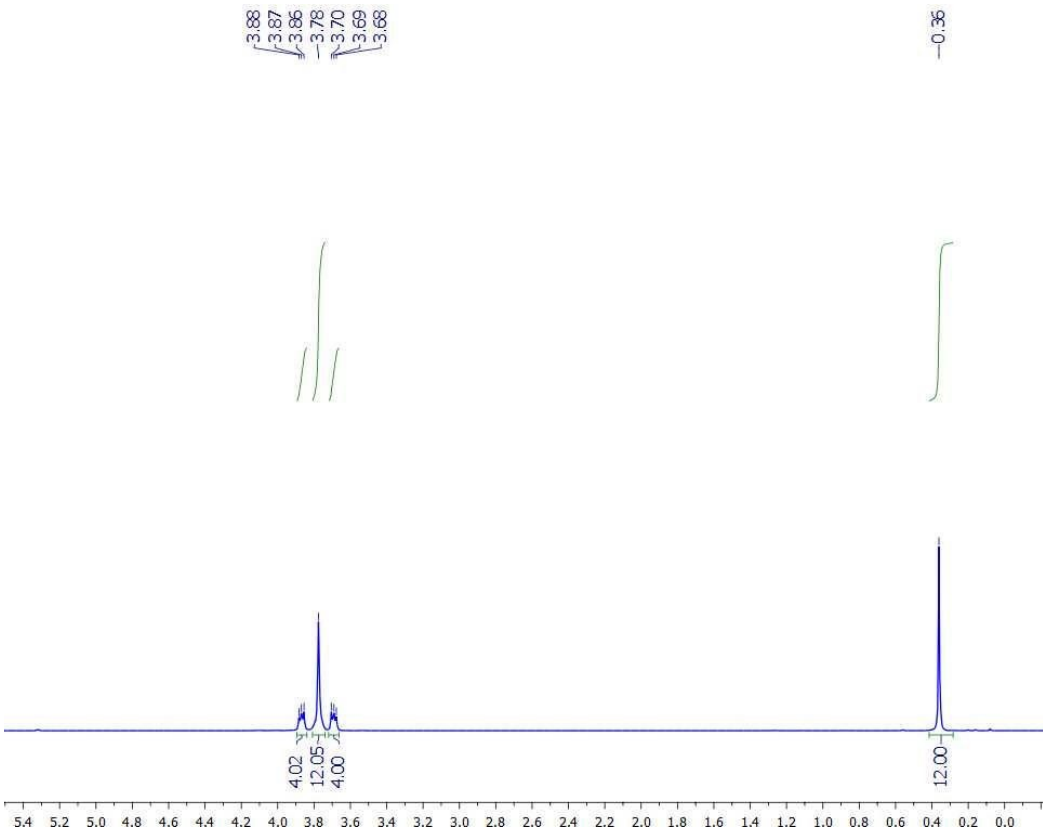



$^{13}C\{^{1}H\}$ NMR of compound **5** $CD_2Cl_2$.

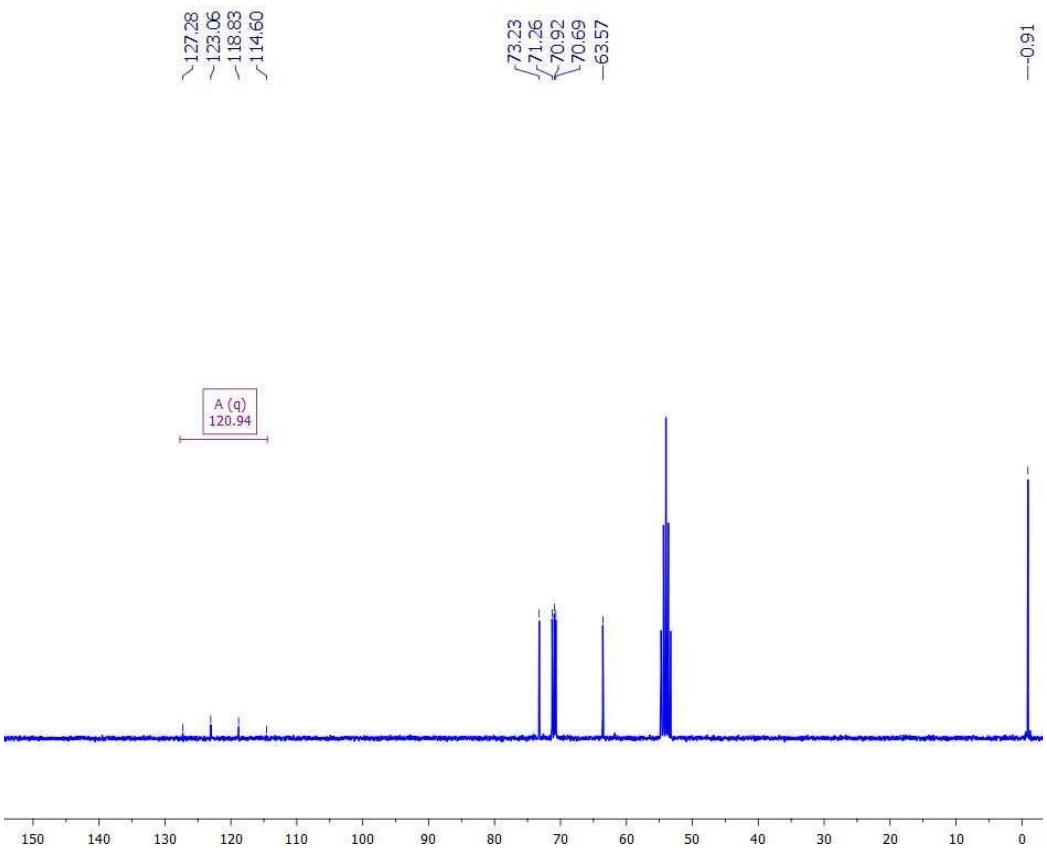



$^{29}Si\{^{1}H\}$ NMR of compound **5** $CD_2Cl_2$.

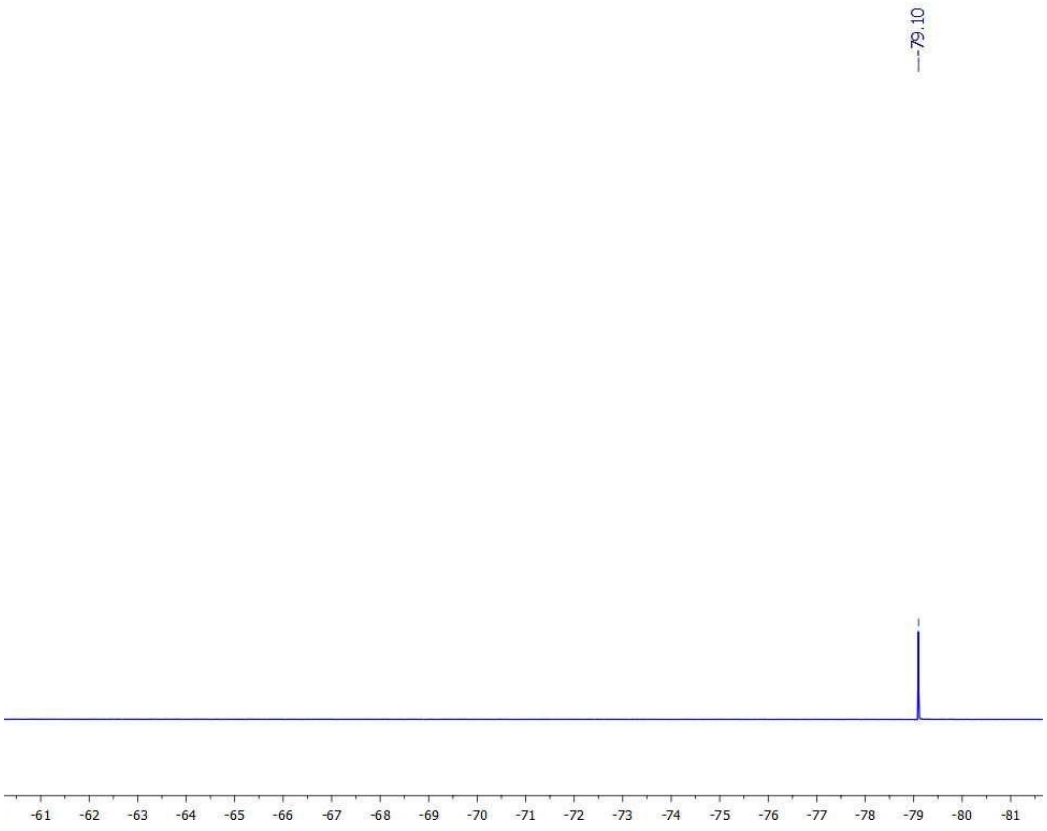
## 1.4 Compound 6



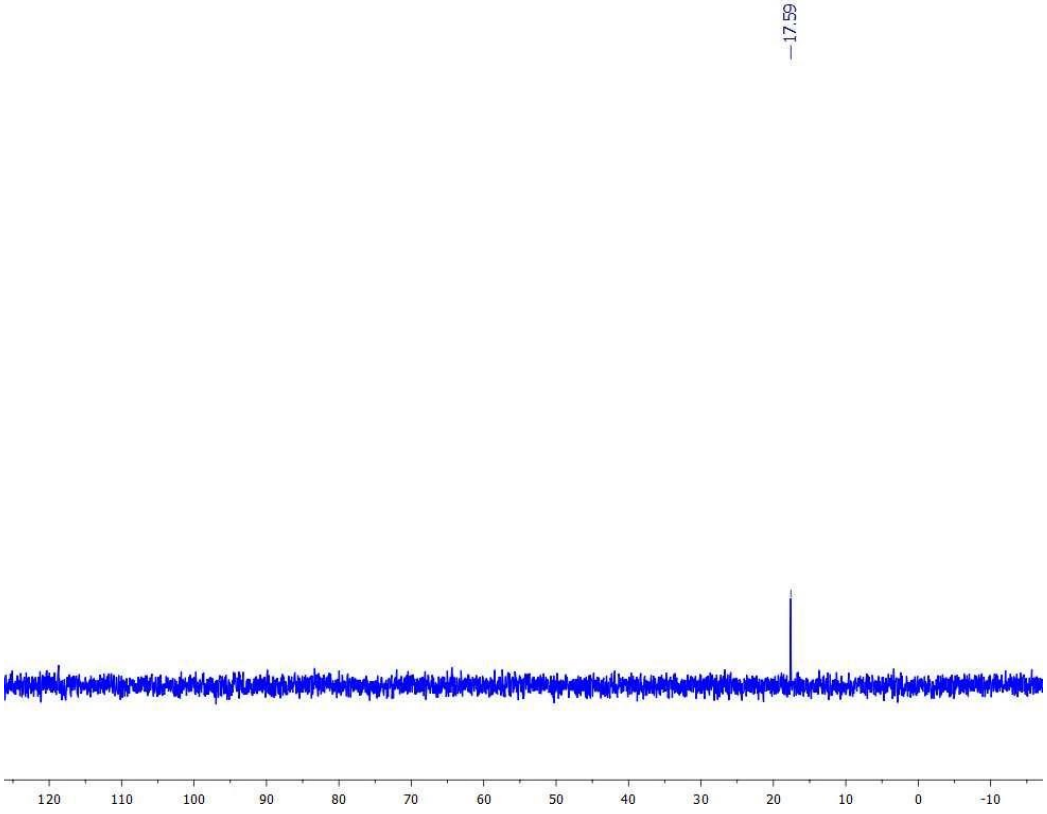

$^{1}H$ NMR of compound **6** in $CD_2Cl_2$.




$^{13}C\{^{1}H\}$ NMR of compound **6** $CD_2Cl_2$.

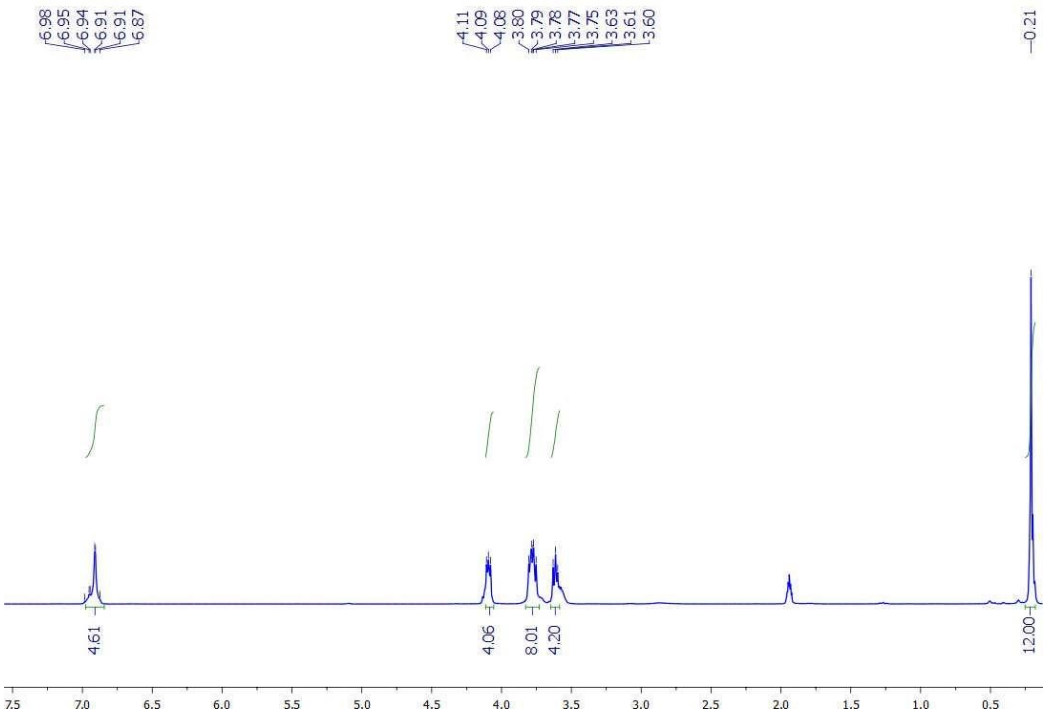



$^{19}F$ NMR of compound **6** in $CD_2Cl_2$.

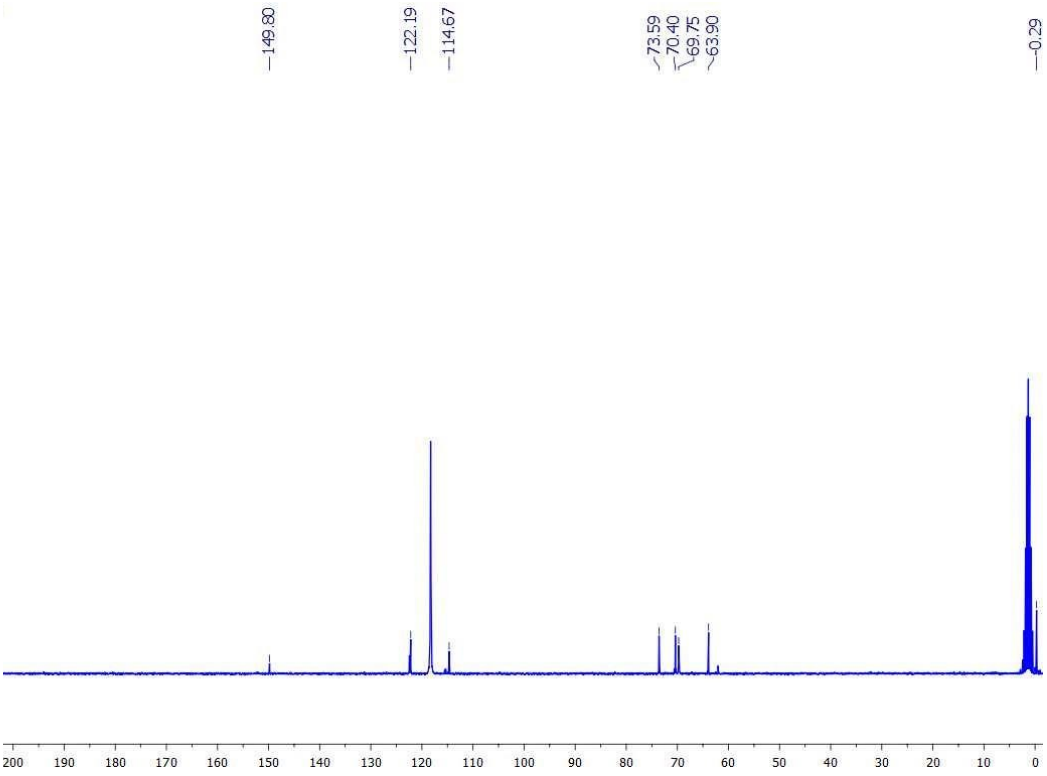



$^{29}Si\{^{1}H\}$ NMR of compound **6** $CD_2Cl_2$.

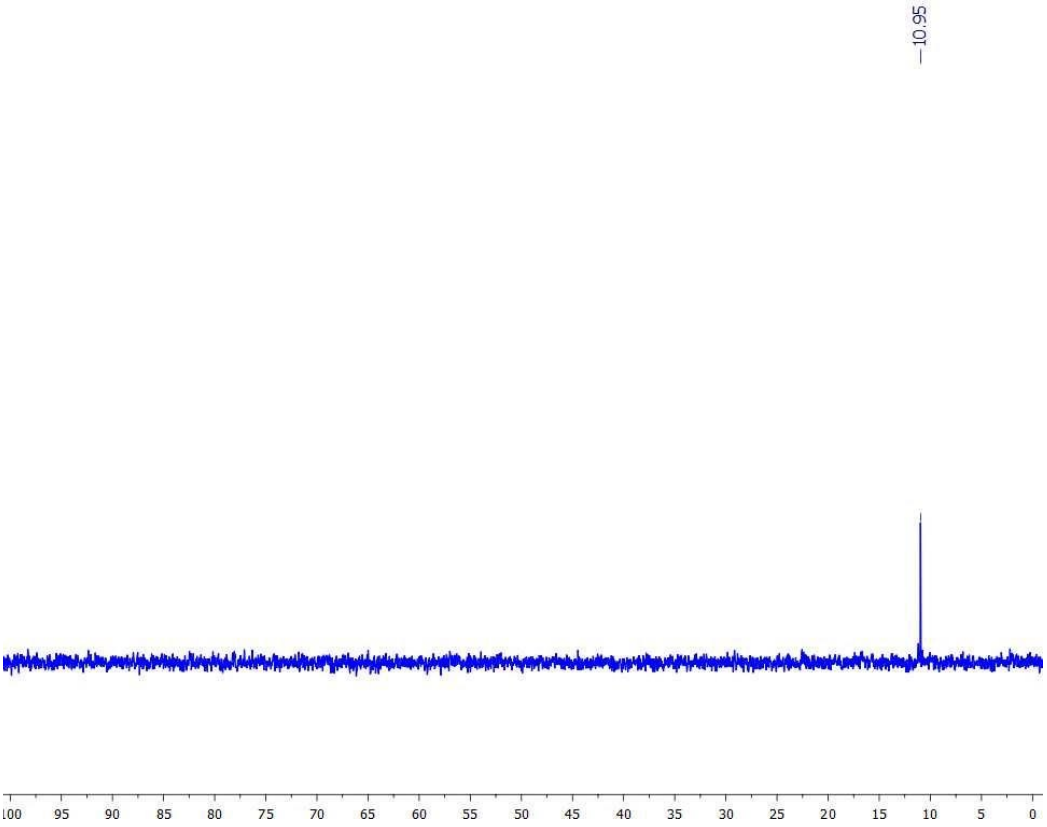
## 1.5 Compound 7




$^{1}H$ NMR of compound **7** in $CD_3CN$.

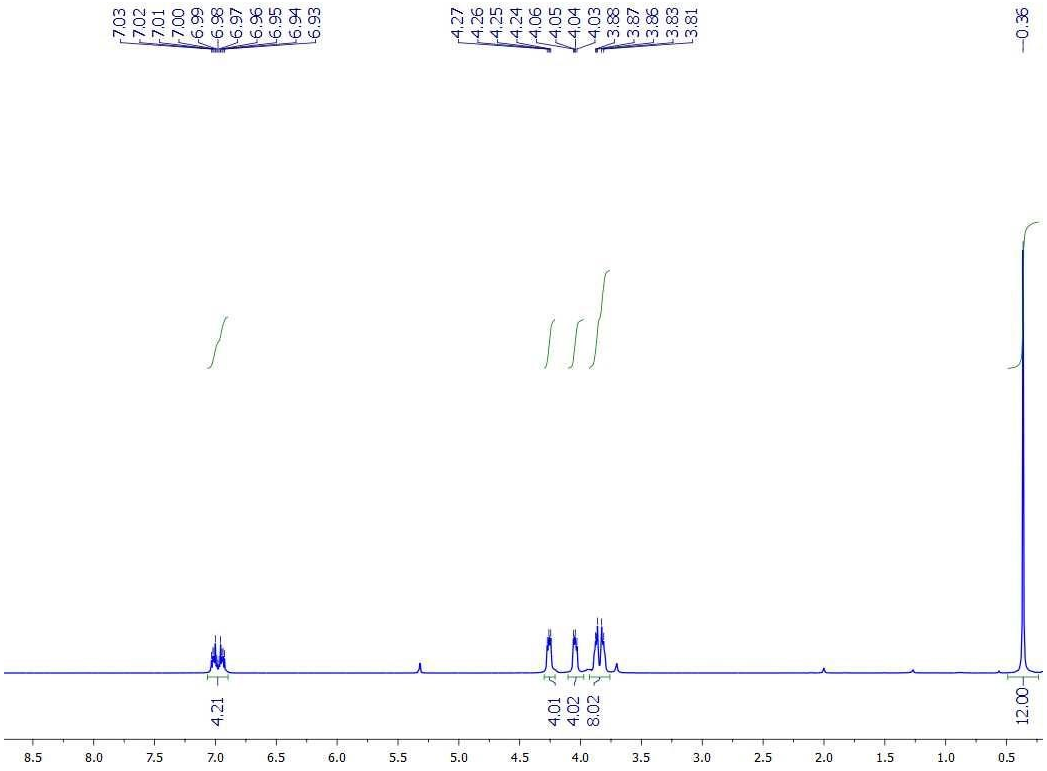



$^{13}C\{^{1}H\}$ NMR of compound **7** $CD_3CN$.

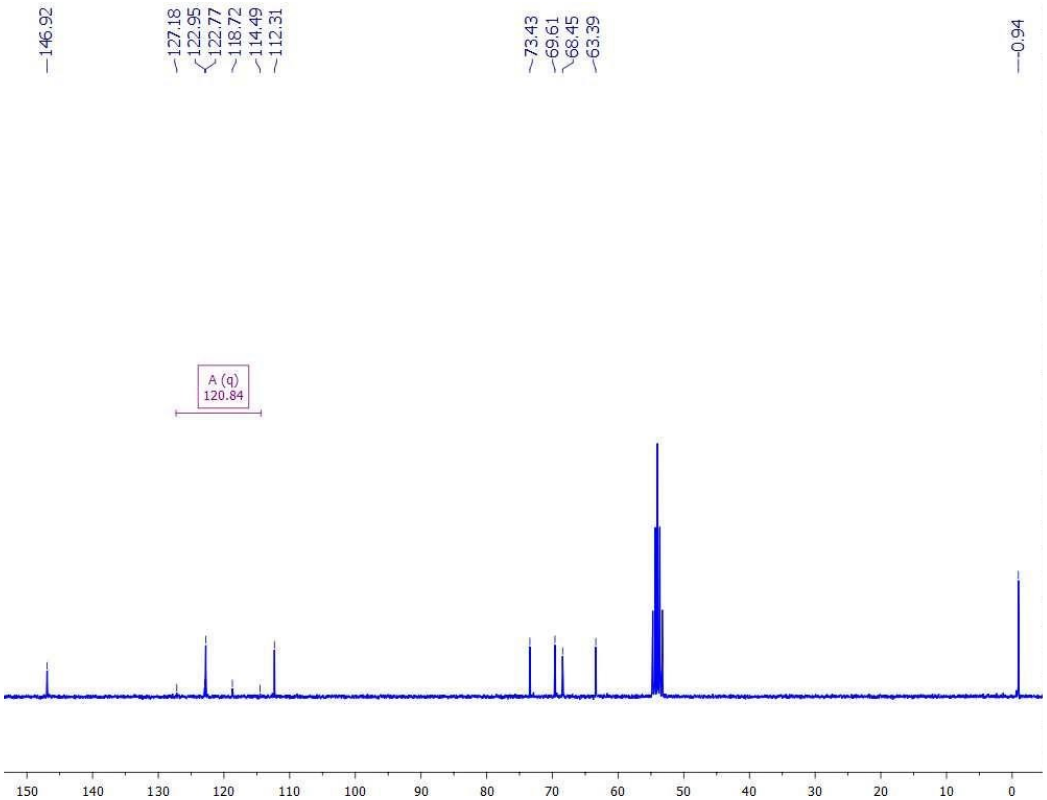



$^{29}Si\{^{1}H\}$ NMR of compound **7** $CD_3CN$.

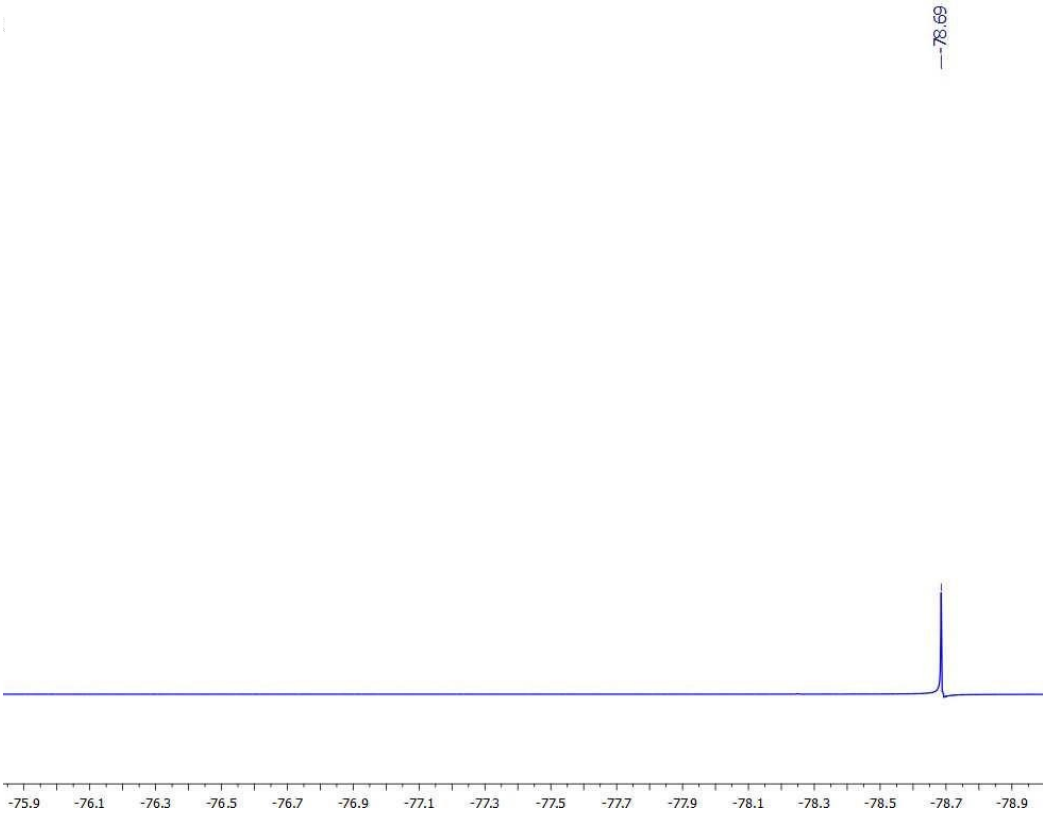
## 1.6 Compound 8



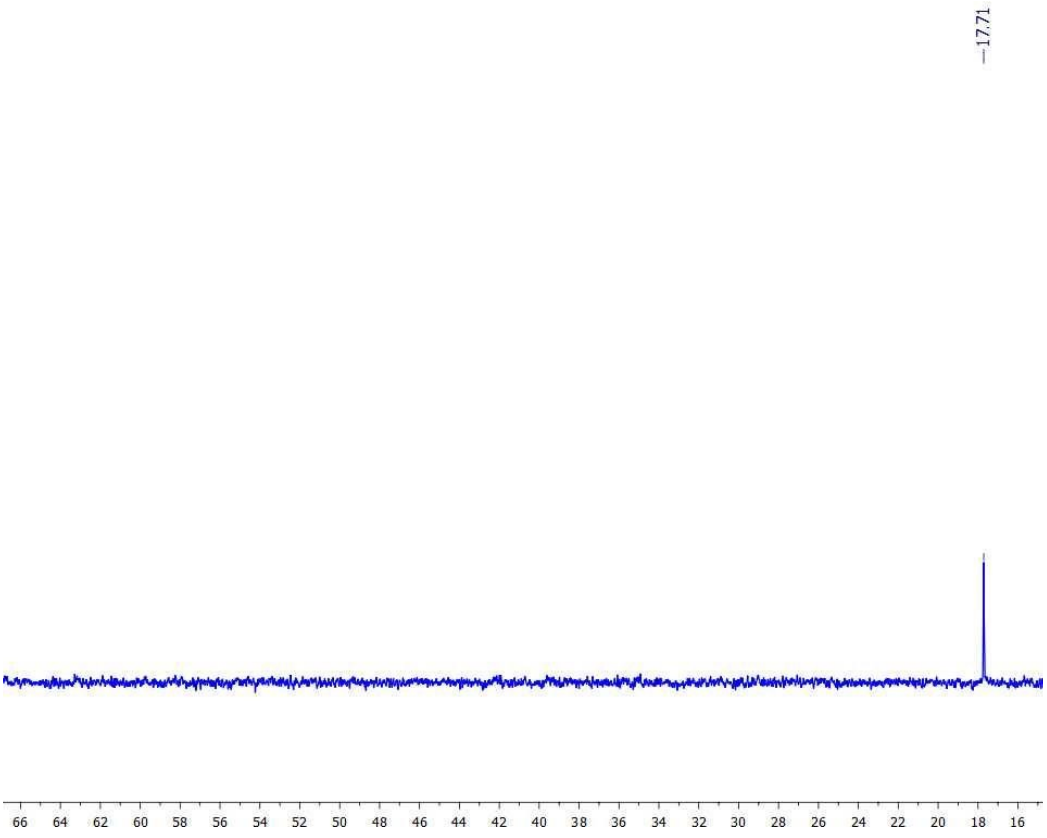

$^{1}H$ NMR of compound **8** in $CD_2Cl_2$.




$^{13}C\{^{1}H\}$ NMR of compound **8** $CD_2Cl_2$.




$^{19}F$ NMR of compound **8** in $CD_2Cl_2$.



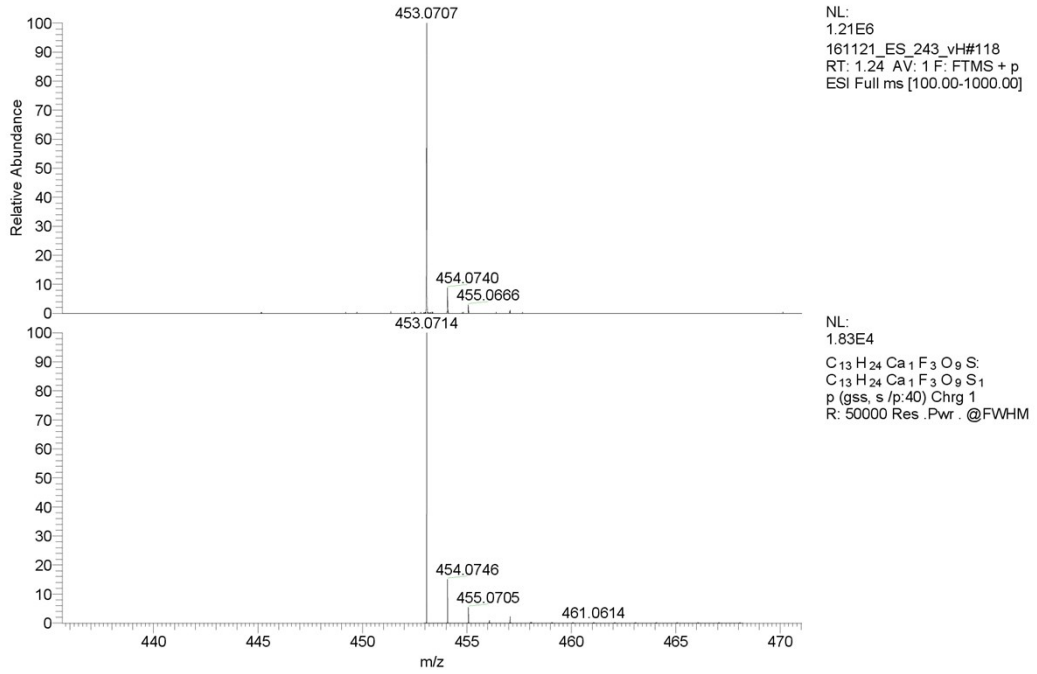

$^{29}Si\{^1H\}$ NMR of compound **8** $CD_2Cl_2$.

# 2. Mass Spectra

**General**: MS spectrometry was carried out on JEOL AccuTOF-GC as for Liquid Injection field desorption (LIFDI) or LTQ-FT as for Electrospray Ionization (ESI).

## 2.1 ESI-MS spectrum of [Ca([18]crown-6)$OTf_2$]

The given MS spectrum proofs the presence of [Ca([18]crown-6)$OTf_2$] in solution as was assumed in dynamic $^1$H NMR spectroscopy (see full text).

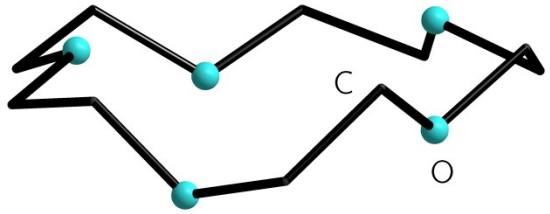



ESI-MS spectrum of [Ca([18]crown-6)$OTf_2$] - Found [Ca([18]crown-6)OTf]$^+$.

# 3. XYZ data of quantum chemical calculations

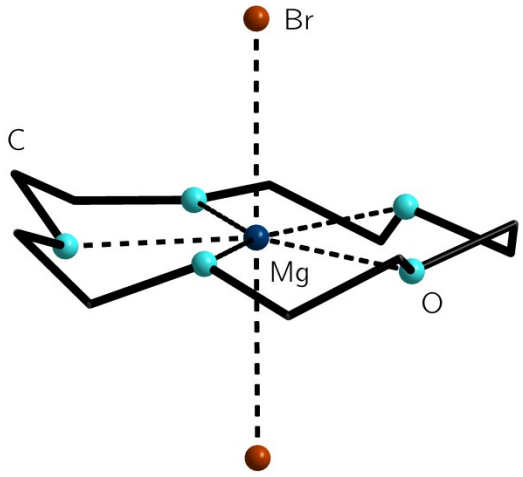
**General**: Calculations were performed with the program system TURBOMOLE V7.0.1.[2] The resolution of identity (RI) approximation, dispersion corrections, and the conductor-like screening model (COSMO) were applied throughout, the latter with default settings. For all calculations, the BP86 functional was chosen, utilizing a def2-TZVP basis set.[3] Optimized structures were visualized with help of Diamond.[4]

## 3.1 XYZ data and optimized structure of [15]crown-5



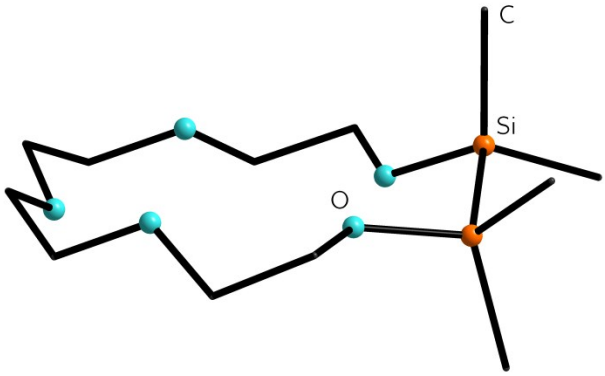

| | | | |
|---|---|---|---|
| H | 0.3073713 | 1.1047252 | -4.7607728 |
| C | -0.2377617 | 1.0382155 | -5.7215397 |
| O | -1.6122295 | 1.3582188 | -5.5321783 |
| C | -0.1562788 | -0.3694516 | -6.2690797 |
| H | 0.2405863 | 1.7389734 | -6.4335821 |
| O | -3.0806126 | -2.2841254 | -4.3571284 |
| C | -3.9087638 | -2.7822630 | -3.3108712 |
| C | -1.9585963 | -3.1176554 | -4.6256062 |
| H | -3.2977484 | -3.0495304 | -2.4273808 |
| H | -4.4465183 | -3.6933515 | -3.6390805 |
| C | -4.9084322 | -1.7139920 | -2.9323251 |
| H | -2.2826622 | -4.1273192 | -4.9457475 |
| H | -1.3413534 | -3.2334279 | -3.7137952 |
| C | -1.1433823 | -2.4895333 | -5.7327333 |
| O | -4.2492192 | -0.7167853 | -2.1472153 |
| H | -5.3334294 | -1.2771158 | -3.8527797 |
| H | -5.7366231 | -2.1643993 | -2.3530954 |
| O | -0.5623820 | -1.2814771 | -5.2495460 |
| H | -0.3657003 | -3.2036501 | -6.0658517 |
| H | -1.7999772 | -2.2741101 | -6.5957547 |
| C | -4.9922754 | 0.4982547 | -2.0208101 |
| C | -4.8698486 | 1.4154630 | -3.2247855 |
| H | -4.5862944 | 1.0081117 | -1.1345016 |
| H | -6.0619050 | 0.2880698 | -1.8358766 |
| H | -0.8233692 | -0.4579227 | -7.1453820 |
| H | 0.8767545 | -0.5816007 | -6.6039683 |
| O | -3.5099017 | 1.8119382 | -3.3649144 |
| H | -5.2108751 | 0.9106408 | -4.1485313 |
| H | -5.5269778 | 2.2933741 | -3.0640395 |
| C | -3.2885301 | 2.6763961 | -4.4791547 |
| C | -1.8311750 | 2.6034458 | -4.8762582 |
| H | -3.5589063 | 3.7183095 | -4.2226377 |
| H | -3.9140278 | 2.3637403 | -5.3356165 |
| H | -1.1926403 | 2.6826901 | -3.9760317 |
| H | -1.5835547 | 3.4505537 | -5.5448581 |

## 3.2 XYZ data and optimized structure of [Mg([15]crown-5)$Br_2$]




| | | | |
|---|---|---|---|
| C | 0.4105972 | -0.4281371 | -0.0556492 |
| C | -0.0411259 | -0.1894040 | 1.3685209 |
| O | 0.9405438 | 0.6703683 | 1.9648666 |
| C | 1.0021971 | 0.6859257 | 3.3988560 |
| C | 1.5549039 | 2.0378787 | 3.7989171 |
| O | 2.6744906 | 2.2944772 | 2.9308957 |
| C | 3.3261160 | 3.5513937 | 3.1896854 |
| C | 4.3171381 | 3.7554384 | 2.0693400 |
| O | 3.5492091 | 3.6876398 | 0.8574488 |
| C | 4.2880135 | 3.9205022 | -0.3527775 |
| C | 3.2763479 | 3.8282894 | -1.4714351 |
| O | 2.6401454 | 2.5506840 | -1.3127733 |
| C | 1.6430921 | 2.2296704 | -2.2949052 |
| C | 1.1848334 | 0.8294425 | -1.9636476 |
| O | 0.7443371 | 0.8640721 | -0.5941892 |
| Mg | 2.1132480 | 2.0144562 | 0.7650904 |
| H | 5.0864587 | 2.9647714 | 2.0642906 |
| H | 5.0694305 | 3.1500553 | -0.4610425 |
| H | 1.3073668 | -1.0687361 | -0.0821762 |
| H | -0.3967693 | -0.8904376 | -0.6439786 |
| H | -1.0233019 | 0.3088720 | 1.4047609 |
| H | -0.0944301 | -1.1468672 | 1.9074772 |
| H | 1.6532780 | -0.1368882 | 3.7341924 |
| H | -0.0015726 | 0.5552496 | 3.8300602 |
| H | 0.8027946 | 2.8299136 | 3.6495121 |
| H | 1.8813497 | 2.0246733 | 4.8501099 |
| H | 3.8374068 | 3.5205630 | 4.1640005 |
| H | 2.5729580 | 4.3574877 | 3.1920735 |
| H | 4.8000243 | 4.7405396 | 2.1590249 |
| H | 4.7500632 | 4.9192530 | -0.3292474 |
| H | 2.5221745 | 4.6291095 | -1.3906731 |
| H | 3.7754983 | 3.8853600 | -2.4508448 |
| H | 2.0795191 | 2.2611948 | -3.3049310 |
| H | 0.8108909 | 2.9505302 | -2.2273692 |
| H | 0.3564602 | 0.5233190 | -2.6210364 |
| H | 2.0187495 | 0.1142667 | -2.0601766 |
| Br | 4.0278221 | 0.2021124 | 0.5491360 |
| Br | 0.2278524 | 3.8670423 | 0.9425425 |

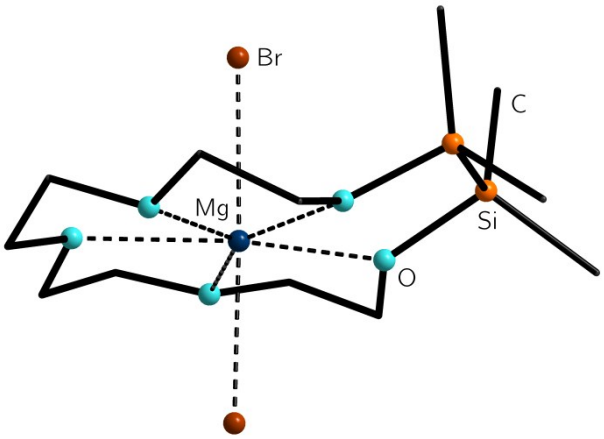
## 3.3 XYZ data and optimized structure of 1,2-disila[15]crown-5 (1)




| | | | |
|---|---|---|---|
| O | -2.1603410 | 14.0798010 | 11.4924428 |
| O | -0.1736153 | 16.1931537 | 11.5075118 |
| O | 0.9306801 | 12.3810551 | 8.2767718 |
| O | 2.0819638 | 14.7700263 | 9.3384278 |
| C | 2.6965389 | 14.0095680 | 8.2937402 |
| O | -1.8461394 | 12.4140474 | 9.1426357 |
| C | -2.7161600 | 12.1201188 | 10.2327918 |
| C | -2.4489975 | 15.4373473 | 11.8142863 |
| C | -1.1701808 | 11.2732906 | 8.6191892 |
| C | -1.2324491 | 16.0674420 | 12.4607580 |
| C | -3.2261746 | 13.4240456 | 10.8080918 |
| C | -0.1554586 | 11.7452508 | 7.6000409 |
| C | 1.6474298 | 13.3022090 | 7.4584710 |
| Si | 1.4043560 | 16.6235405 | 11.9006449 |
| Si | 2.6654297 | 16.2350289 | 9.9230037 |
| H | 3.3802264 | 13.2641436 | 8.7374434 |
| H | 3.2907612 | 14.6468171 | 7.6143404 |
| H | -2.1771321 | 11.5487193 | 11.0128939 |
| H | -3.5754191 | 11.5072082 | 9.8968133 |
| H | -3.3016445 | 15.5024106 | 12.5196442 |
| H | -2.7226567 | 15.9962962 | 10.8981585 |
| H | -1.8846402 | 10.5806392 | 8.1321236 |
| H | -0.6616913 | 10.7197202 | 9.4318447 |
| H | -1.5264152 | 17.0581704 | 12.8524268 |
| H | -0.9139403 | 15.4448411 | 13.3156749 |
| H | -3.6076998 | 14.0642420 | 9.9896861 |
| H | -4.0678749 | 13.2187367 | 11.4978452 |
| H | 0.2049871 | 10.8838939 | 7.0061405 |
| H | -0.6408198 | 12.4560301 | 6.9056187 |
| H | 0.9483293 | 14.0423574 | 7.0241144 |
| H | 2.1541305 | 12.7801828 | 6.6222872 |
| C | 2.0383270 | 15.5605858 | 13.3296112 |
| C | 1.4812322 | 18.4385891 | 12.4235048 |
| C | 2.4235839 | 17.5849210 | 8.6226634 |
| C | 4.5102150 | 16.1119076 | 10.3198497 |
| H | 2.0022574 | 14.4892858 | 13.0841833 |
| H | 1.4508513 | 15.7241979 | 14.2462372 |
| H | 3.0835274 | 15.8220274 | 13.5555028 |
| H | 2.5235859 | 18.7433554 | 12.6065613 |
| H | 0.9171462 | 18.6081247 | 13.3539586 |
| H | 1.0683943 | 19.0982101 | 11.6463884 |

| | | | |
|---|---|---|---|
| H | 1.3622463 | 17.7041066 | 8.3610404 |
| H | 2.9797799 | 17.3517764 | 7.7010320 |
| H | 2.7935457 | 18.5513915 | 8.9983538 |
| H | 4.8676285 | 17.0512834 | 10.7692682 |
| H | 5.1023852 | 15.9347529 | 9.4084478 |
| H | 4.7190515 | 15.2970909 | 11.0282738 |

## 3.4 XYZ data and optimized structure of [Mg(1,2-disila[15]crown-5)$Br_2$] (3)




| | | | |
|---|---|---|---|
| Br | 0.7143947 | 11.8166413 | 11.4594283 |
| Mg | -0.0561147 | 13.9055094 | 10.1078039 |
| Br | -0.8904089 | 15.9663674 | 8.7155641 |
| O | -1.9073626 | 13.9257505 | 11.4465588 |
| O | 0.3497477 | 15.2777907 | 11.8471139 |
| O | 0.6214018 | 12.8204674 | 8.2209806 |
| O | 2.0733457 | 14.5279924 | 9.6577492 |
| C | 2.7403513 | 13.6868233 | 8.6918390 |
| O | -1.8347124 | 12.7581843 | 9.1159972 |
| C | -2.8927653 | 12.3688358 | 9.9994191 |
| C | -1.9718646 | 15.0271443 | 12.3590770 |
| C | -1.4650758 | 11.7519678 | 8.1666681 |
| C | -0.5856693 | 15.1398693 | 12.9388952 |
| C | -3.1660453 | 13.5779991 | 10.8556698 |
| C | -0.3954002 | 12.3789687 | 7.3115169 |
| C | 1.7690537 | 13.3894546 | 7.5787829 |
| Si | 1.3429311 | 16.6660088 | 11.7936751 |
| Si | 2.7339397 | 16.0637209 | 10.0092114 |
| H | 3.0375019 | 12.7594190 | 9.2027137 |
| H | 3.6394885 | 14.1742155 | 8.2875385 |
| H | -2.5669108 | 11.5129381 | 10.6151179 |
| H | -3.7894894 | 12.0884494 | 9.4240298 |
| H | -2.7113279 | 14.8217436 | 13.1500003 |
| H | -2.2556874 | 15.9450070 | 11.8157410 |
| H | -2.3342935 | 11.4649553 | 7.5537209 |
| H | -1.0786527 | 10.8643535 | 8.6964783 |
| H | -0.5319663 | 15.9986123 | 13.6245051 |
| H | -0.3238120 | 14.2257714 | 13.4910559 |

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H    -3.5339689   14.4201257   10.2448877
H    -3.9017903   13.3426109   11.6404078
H     0.0212476   11.6426441    6.6060860
H    -0.7913567   13.2436092    6.7528014
H     1.4762704   14.3102622    7.0456741
H     2.1995372   12.6691220    6.8641547
C     2.3115139   16.7592417   13.4004020
C     0.3013596   18.2067968   11.5741248
C     2.6943204   17.1667561    8.4963114
C     4.5072584   15.8294743   10.5839411
H     2.8586093   15.8247511   13.5888147
H     1.6583921   16.9620946   14.2617752
H     3.0450779   17.5775374   13.3373365
H     0.9530833   19.0898016   11.4919219
H    -0.3703271   18.3619585   12.4317037
H    -0.2994360   18.1205418   10.6588024
H     1.6614882   17.2702204    8.1381360
H     3.3164869   16.7578138    7.6860583
H     3.0864509   18.1630843    8.7517030
H     4.9095280   16.7953149   10.9252762
H     5.1565587   15.4661285    9.7735403
H     4.5644592   15.1209288   11.4220290
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