Supporting Info

# Using Functionalized Silyl Ligands to Suppress Solvent Coordination to Silyl Lanthanide(II) Complexes

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**Contents**

1. NMR Spectra of Compounds **2**, **3**, **7**, **8**, **9**, **10**, **14**, **16**, **19**, **21a**, and **22** ……..…..**S2**
2. Crystallographic Information of all Compounds …….....**S33**
3. ORTEP Plots of **3**, **7**, **10**, **20**, and **22** ……..……...…**S36**
4. Packing Plots of **22** and **23** ……....**S41**
5. Energy Levels of Complex **23** …….…….….**S18**
6. Cartesian Coordinates of **2**, **4**, and **23** ……..……...……..**S33**
7. References …….……..…..**S53**

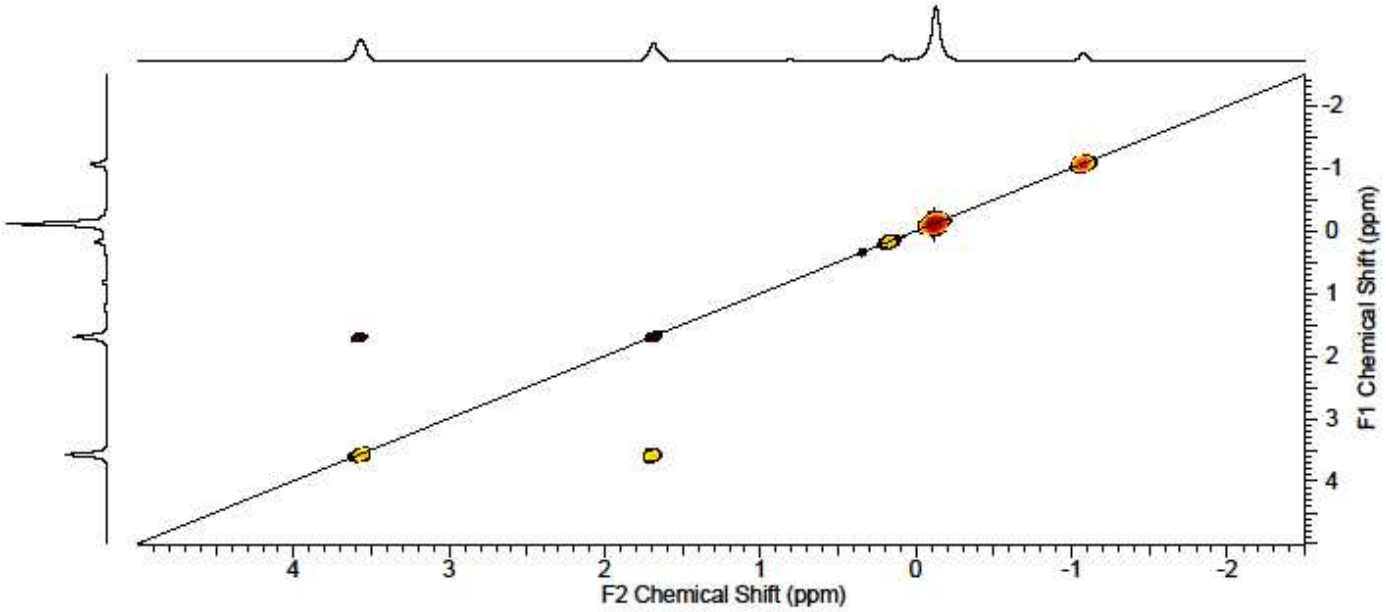


**Figure S1.** $^{1}H^{1}H$-gCOSY of compound **2** in THF-$d_8$.

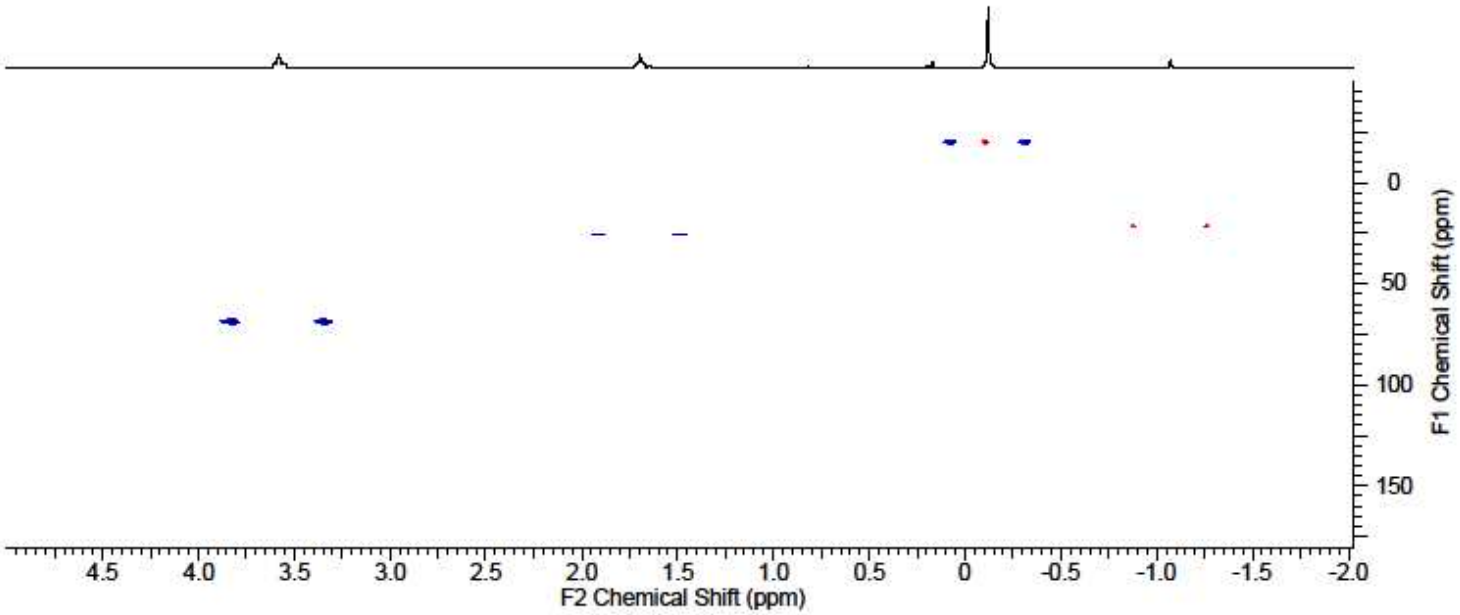


**Figure S2.** $^{1}H^{13}C$-gHSQC of compound **2** in THF-$d_8$.

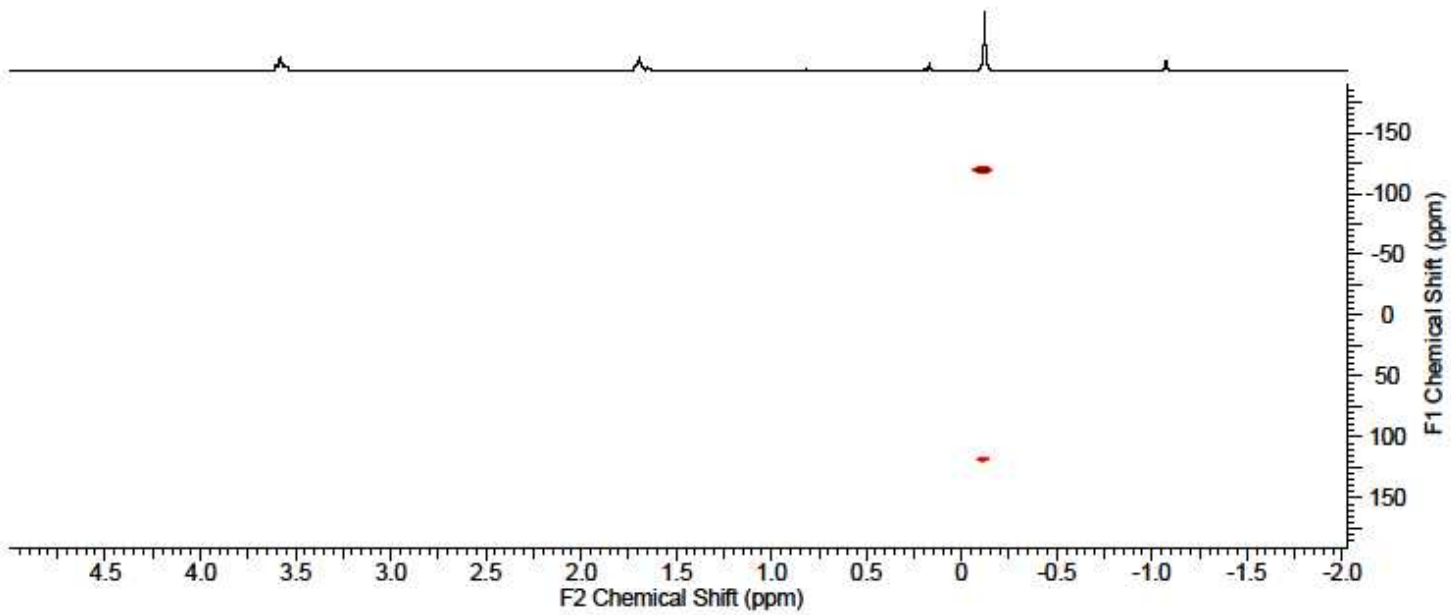


**Figure S3.** $^{1}H^{29}Si$-gHMBC of compound **2** in THF-$d_8$.

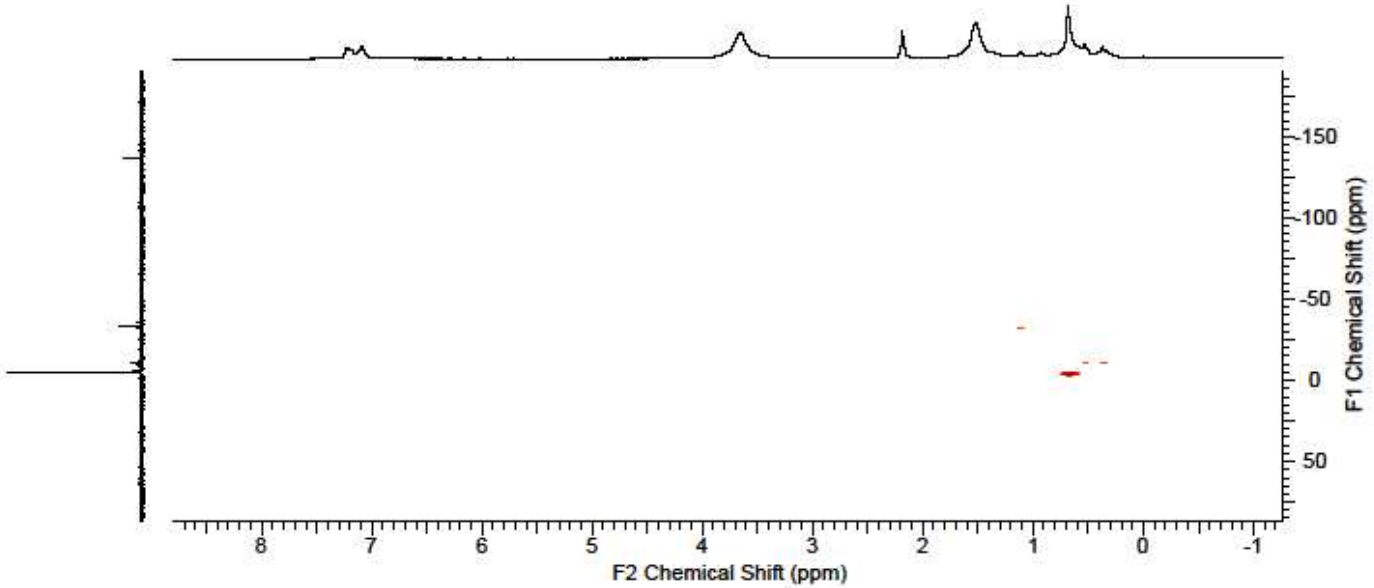


**Figure S4.** $^{1}H^{29}Si$-gHMBC of compound **3** in $C_6D_6$.

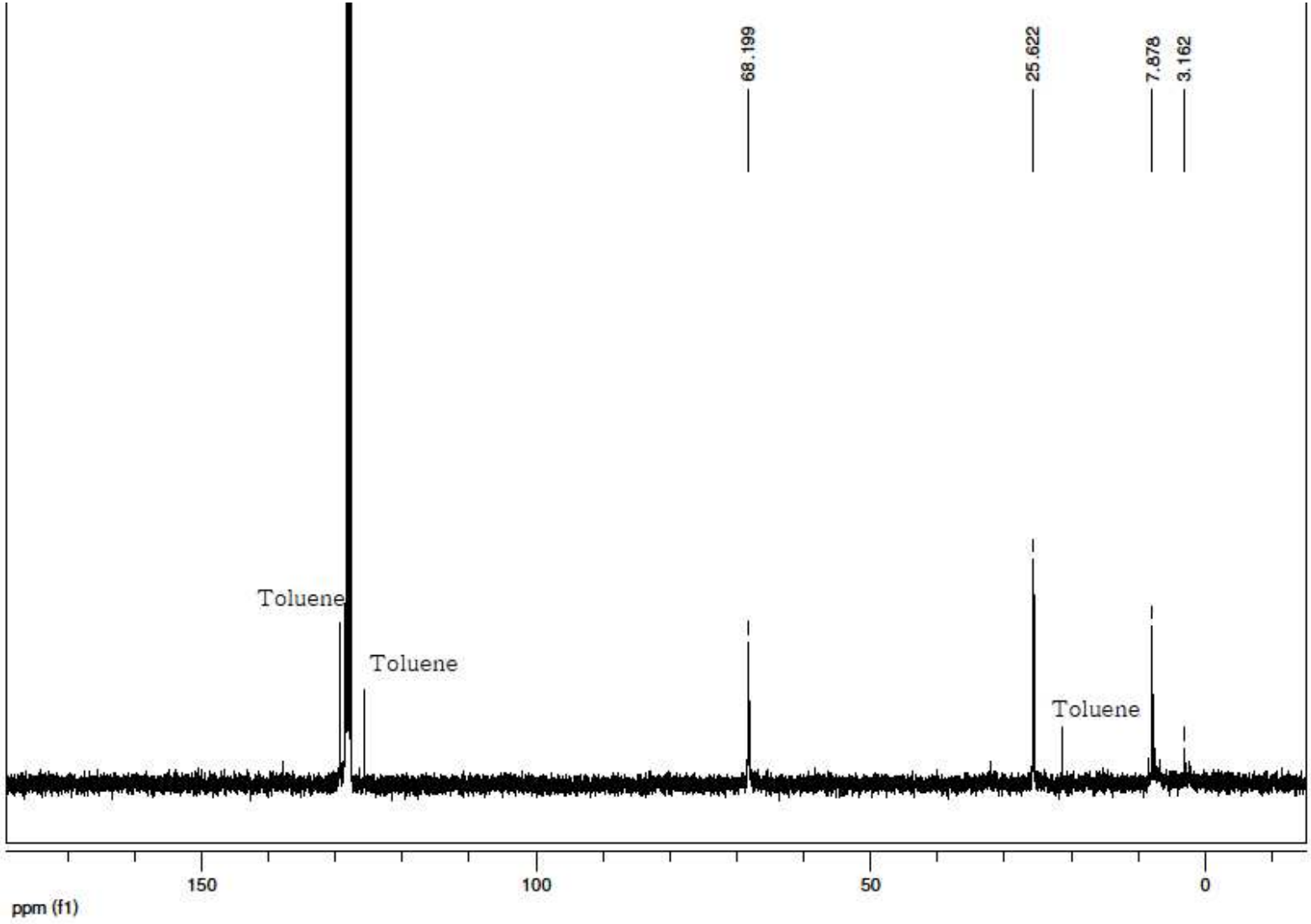


**Figure S5.** $^{13}C\{^{1}H\}$-NMR of compound **3**.

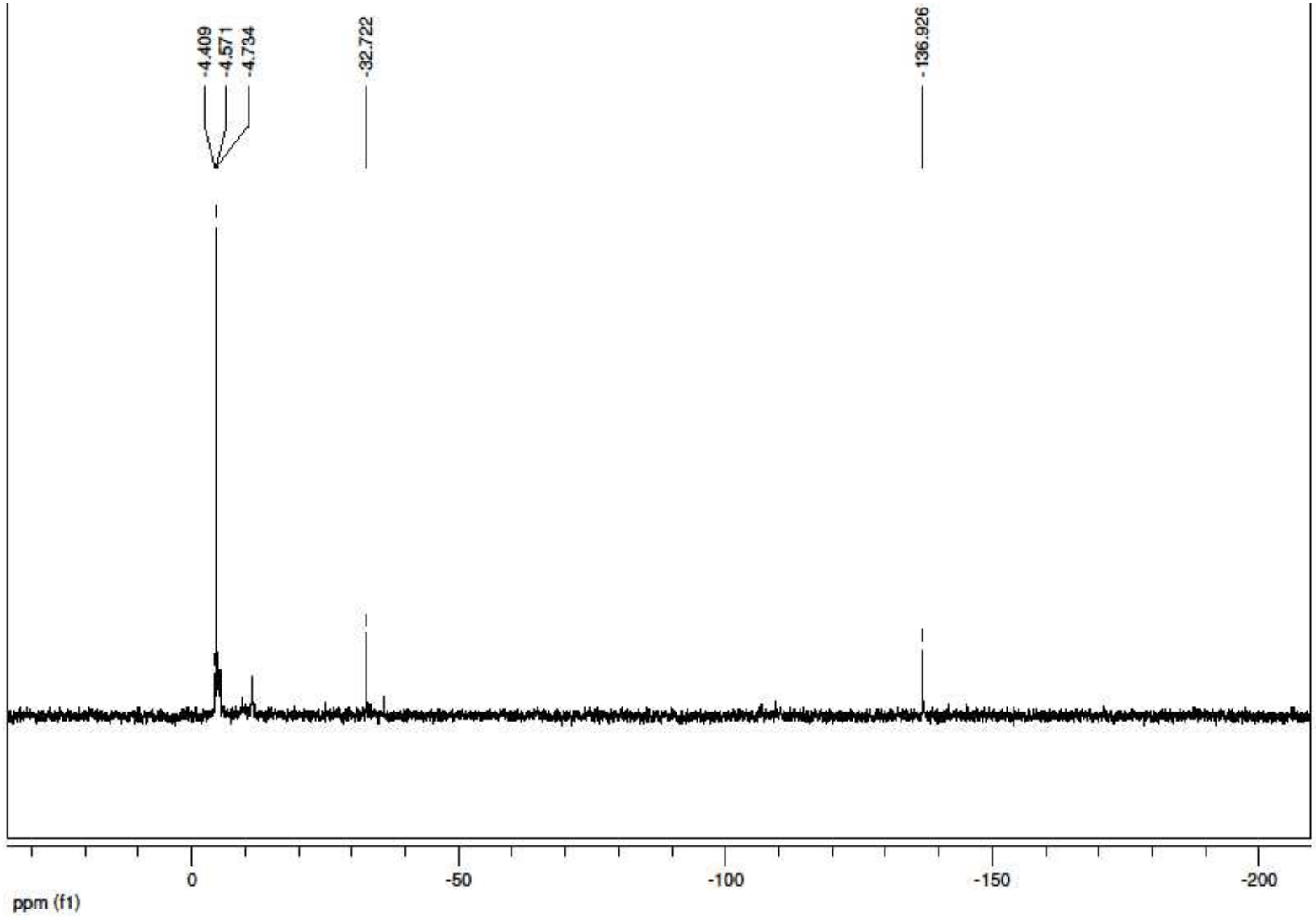


**Figure S6.** $^{29}Si\{^{1}H\}$-INEPT-NMR of compound **3**.

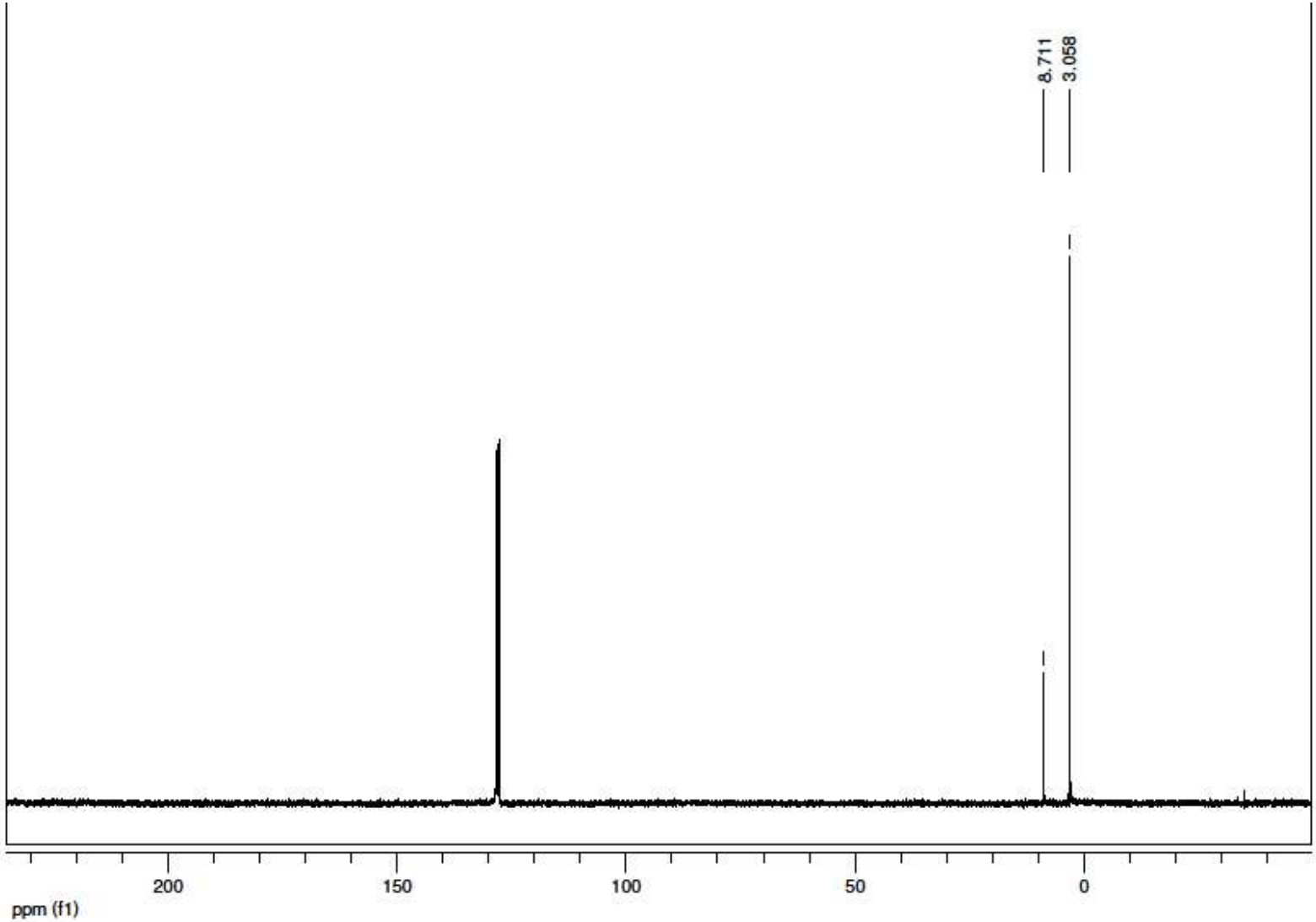


**Figure S7.** $^{13}C\{^{1}H\}$-NMR of compound **7**.

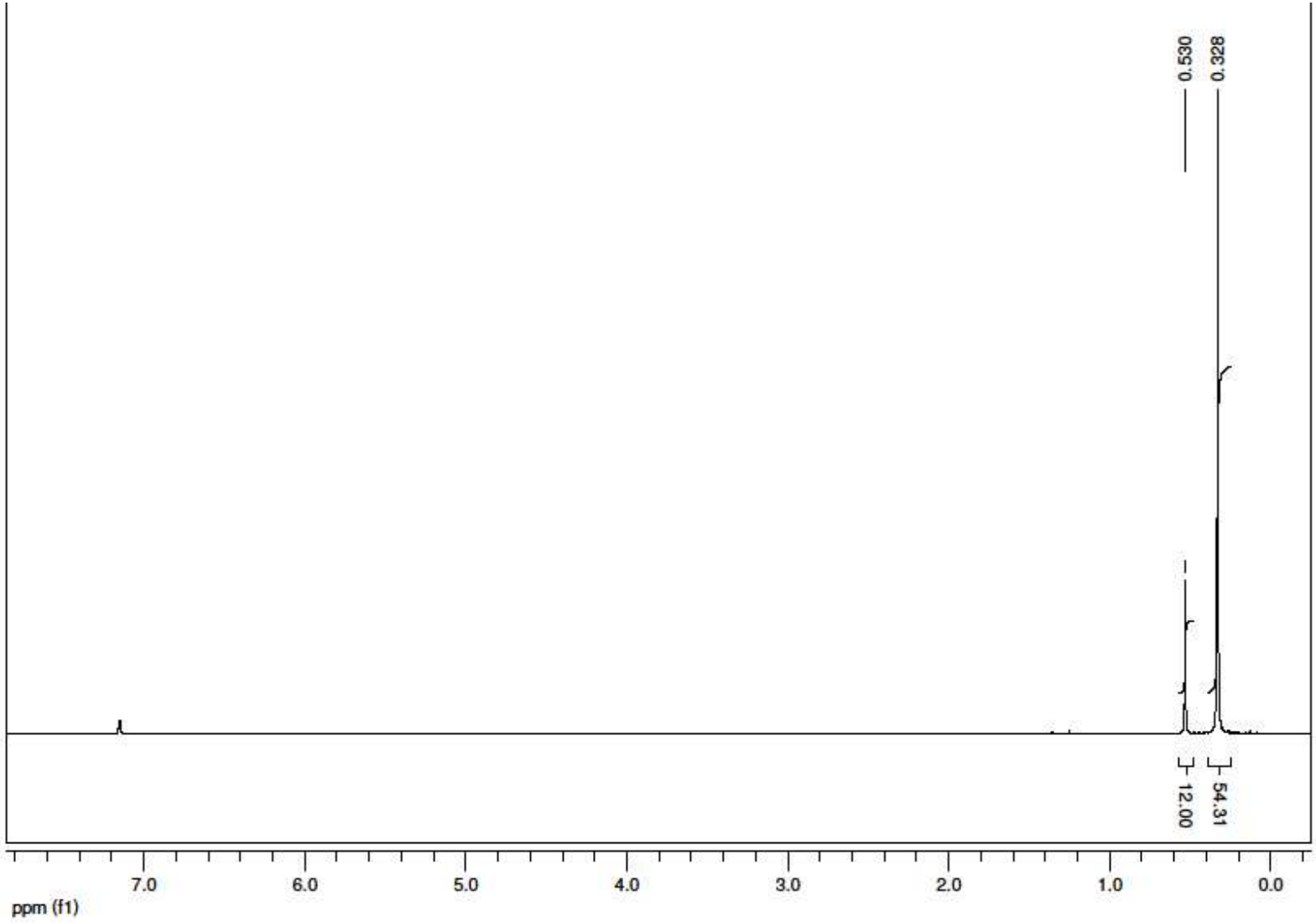


**Figure S8.** $^{1}$H-NMR of compound **7**.

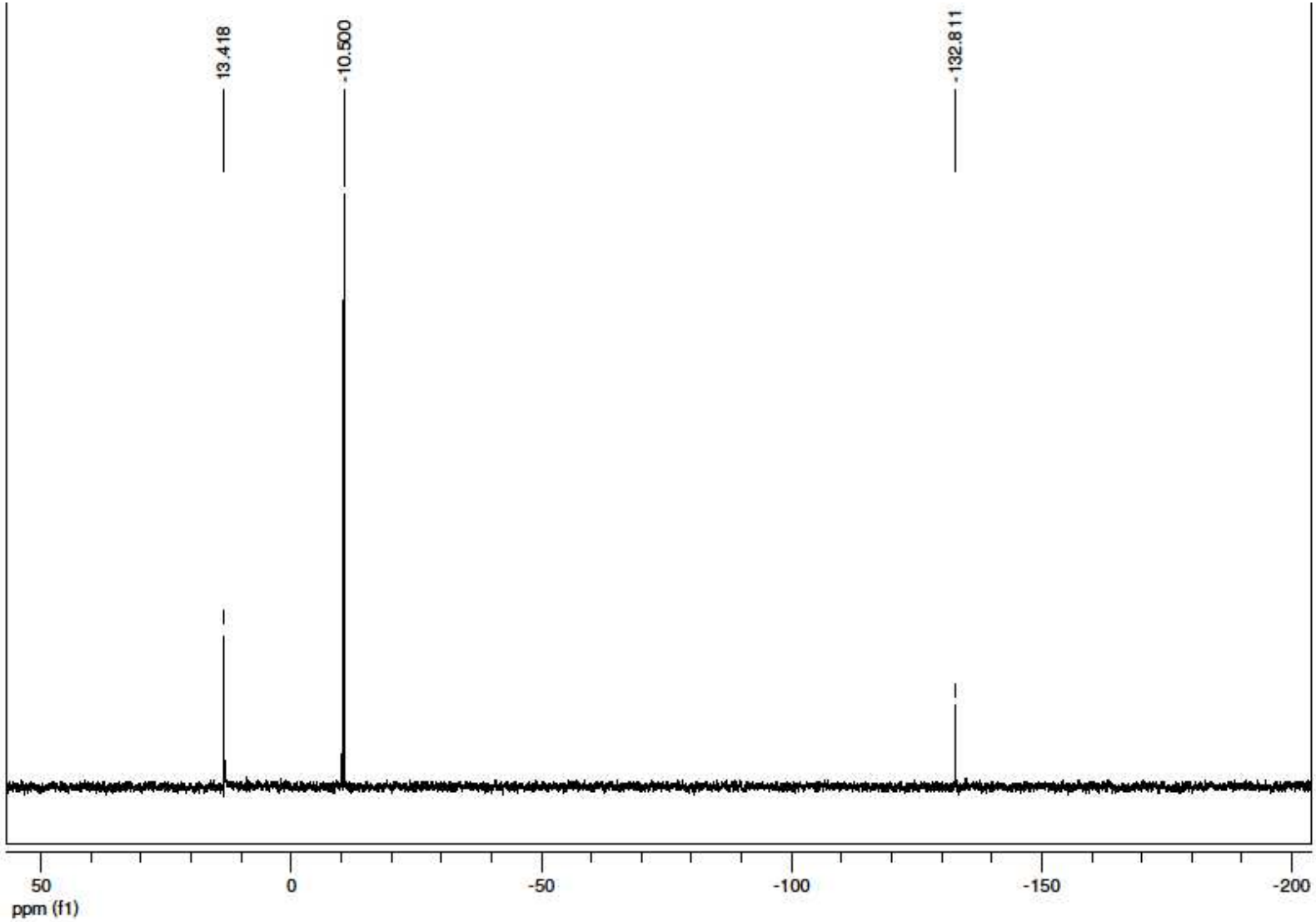


**Figure S9.** $^{29}Si\{^{1}H\}$-INEPT-NMR of compound **7**.

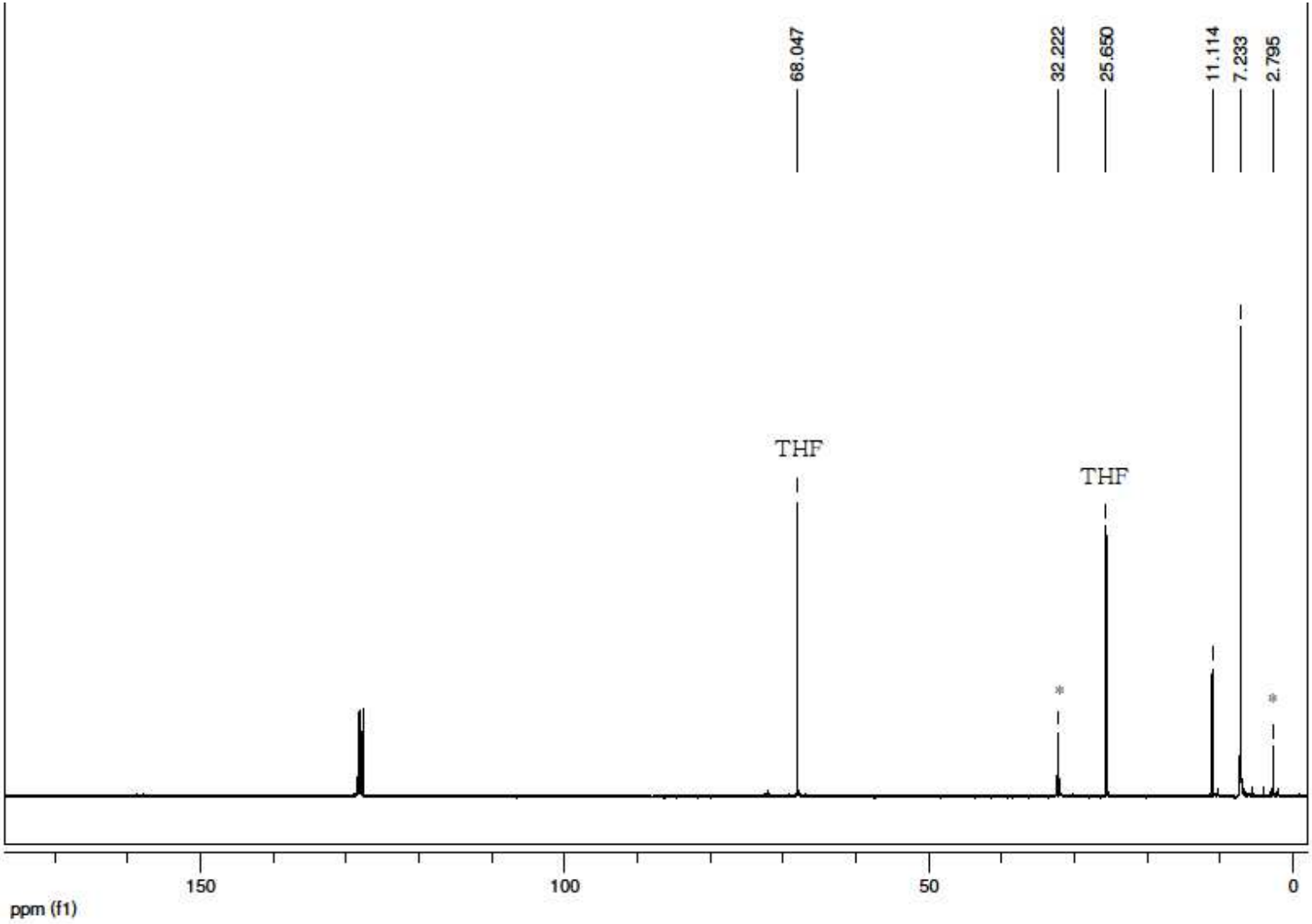


**Figure S10.** $^{13}C\{^{1}H\}$-NMR of compound **8** (* = $^{t}BuOSiMe_3$).

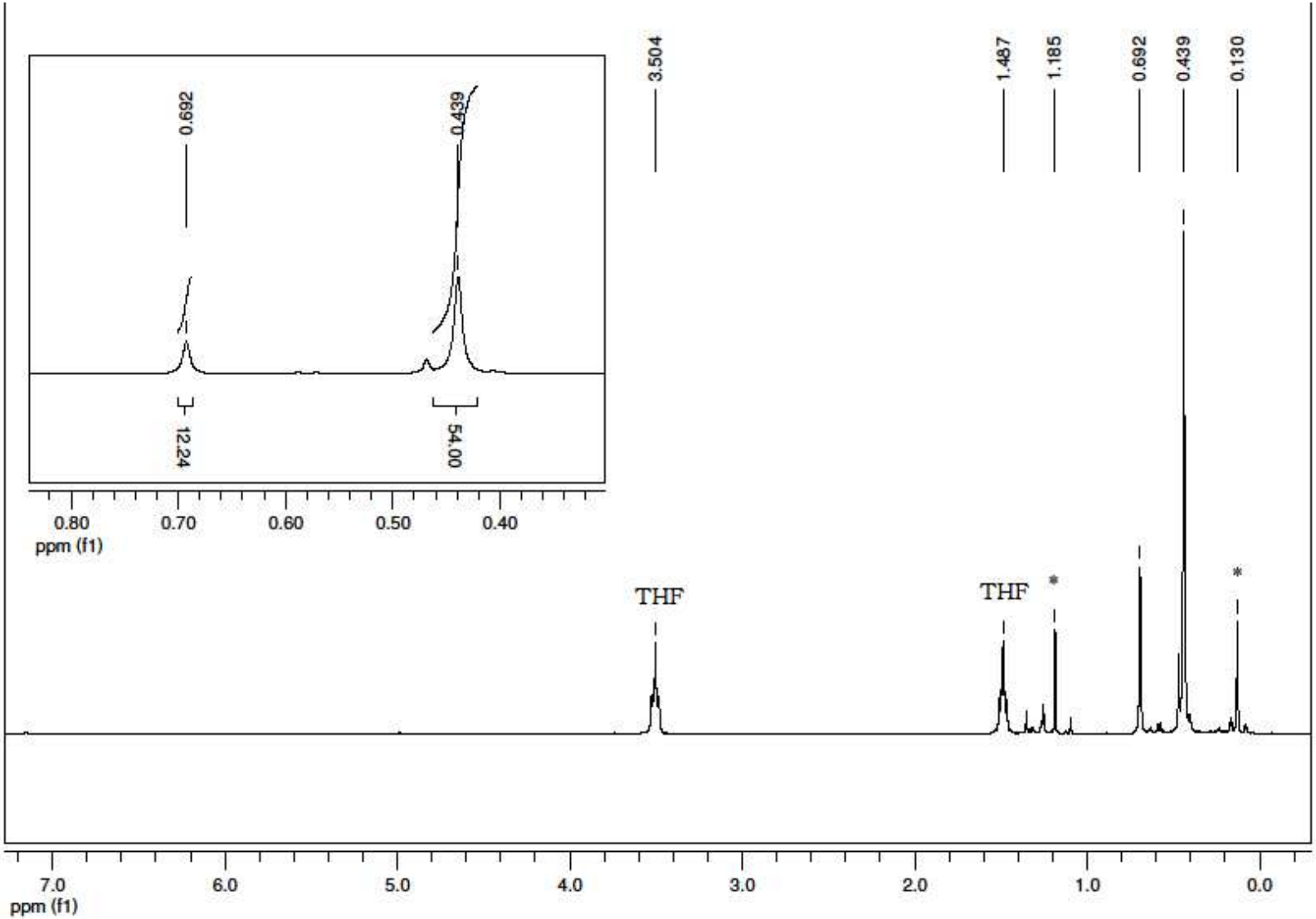


**Figure S11.** $^{1}$H-NMR of compound **8** (* = $^{t}$BuOSiMe$_3$).

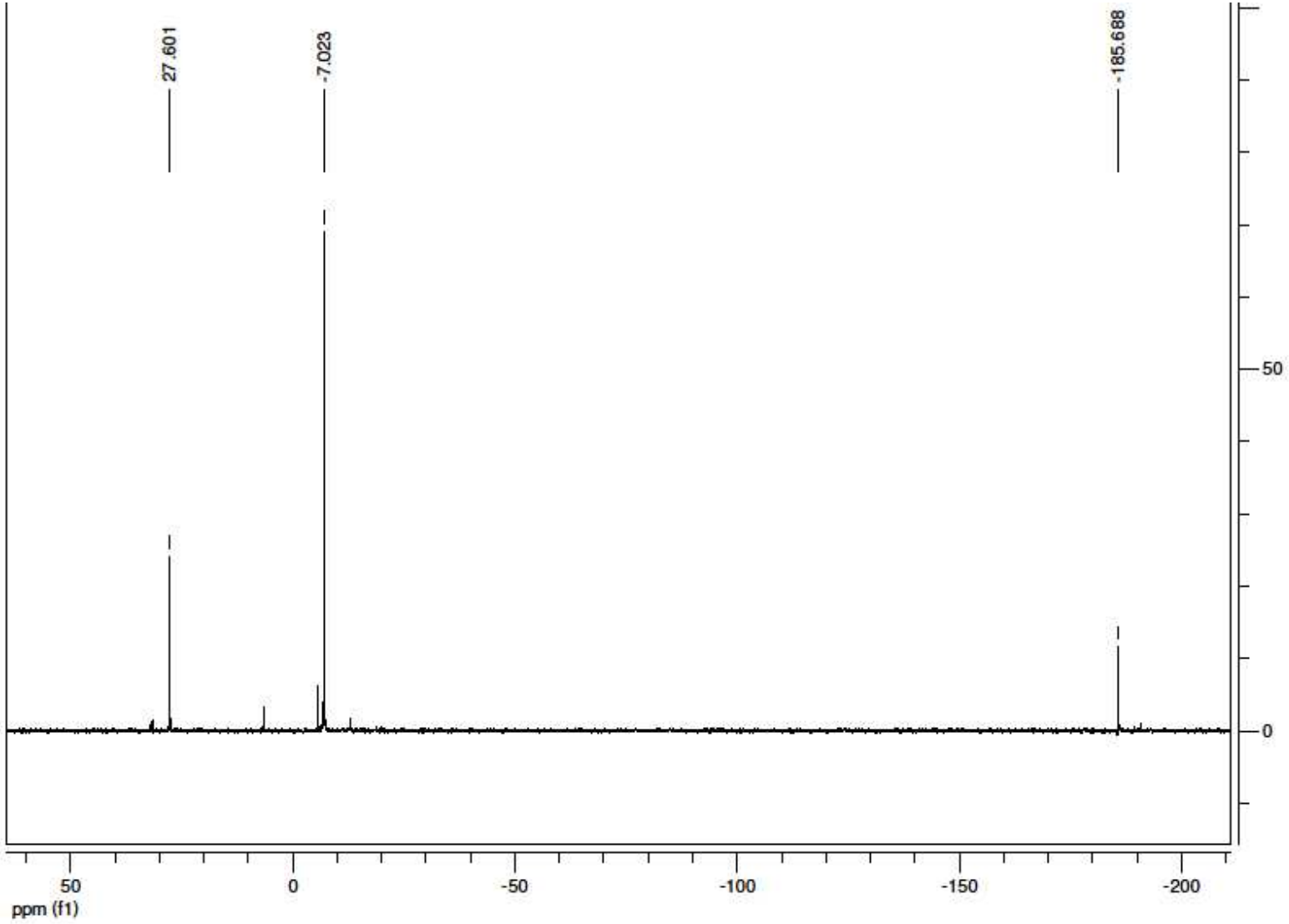


**Figure S12.** $^{29}Si\{^{1}H\}$-INEPT-NMR of compound **8**.

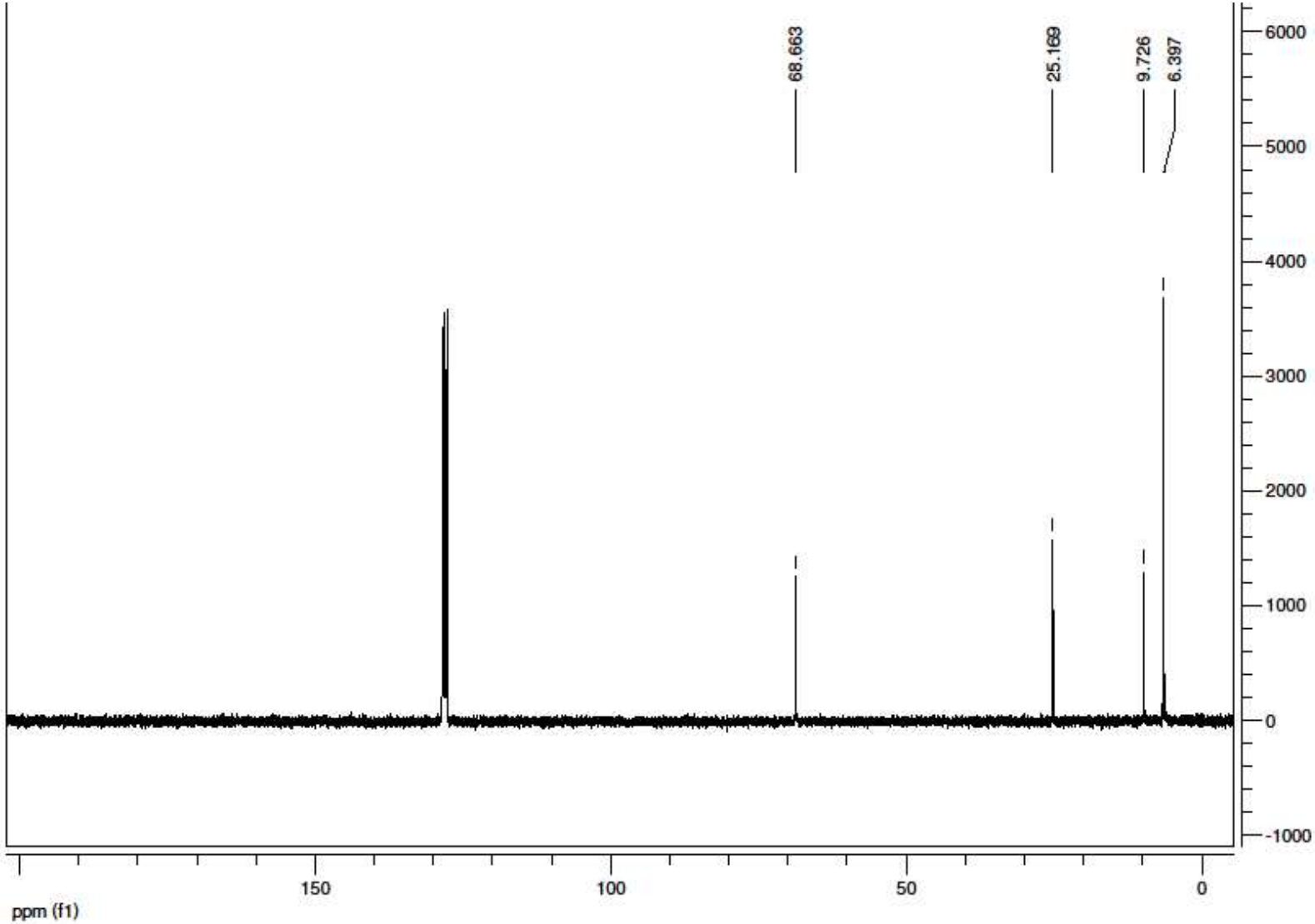


**Figure S13.** $^{13}C\{^{1}H\}$-NMR of compound **9**.

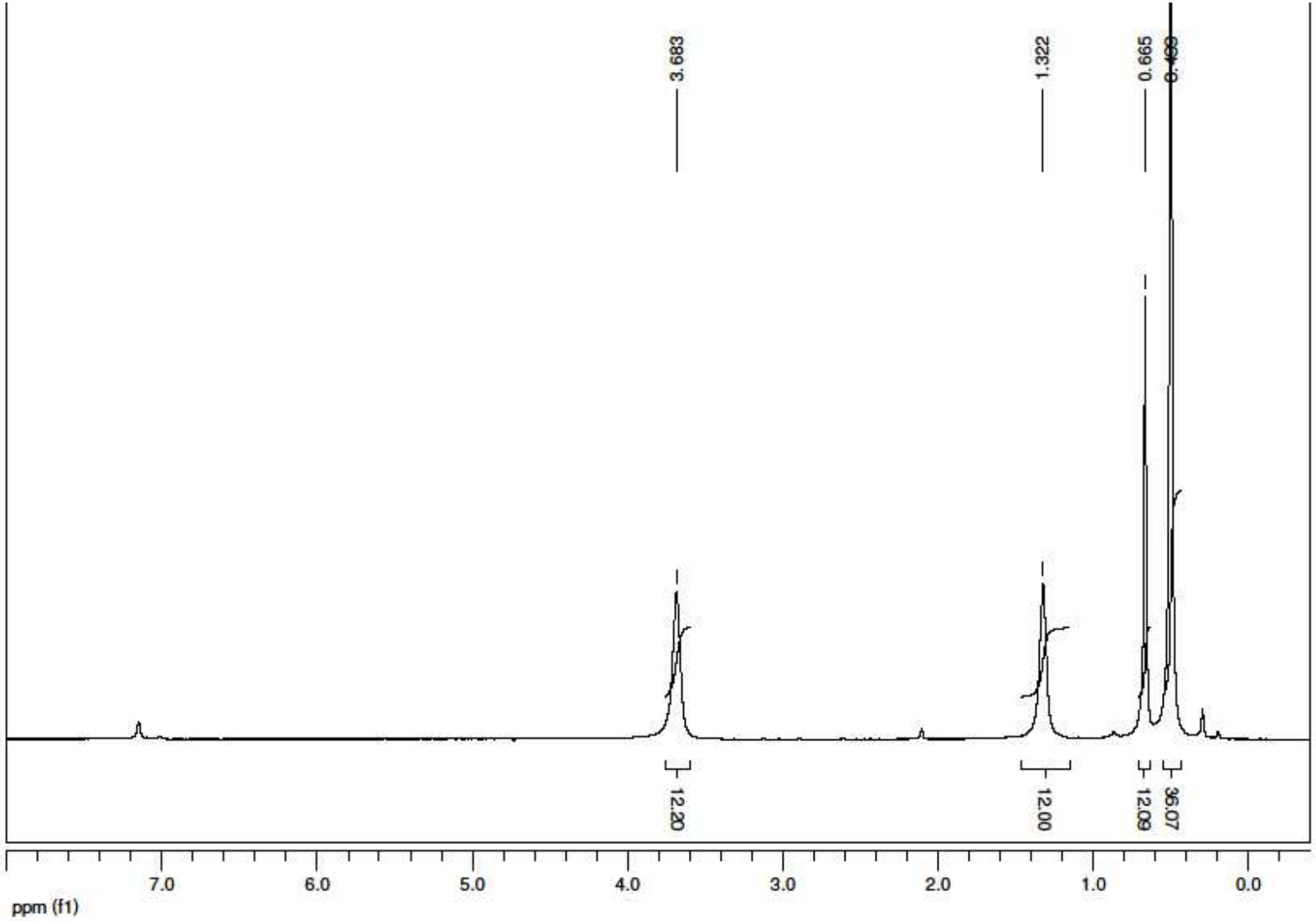


**Figure S14.** $^{1}$H-NMR of compound **9**.

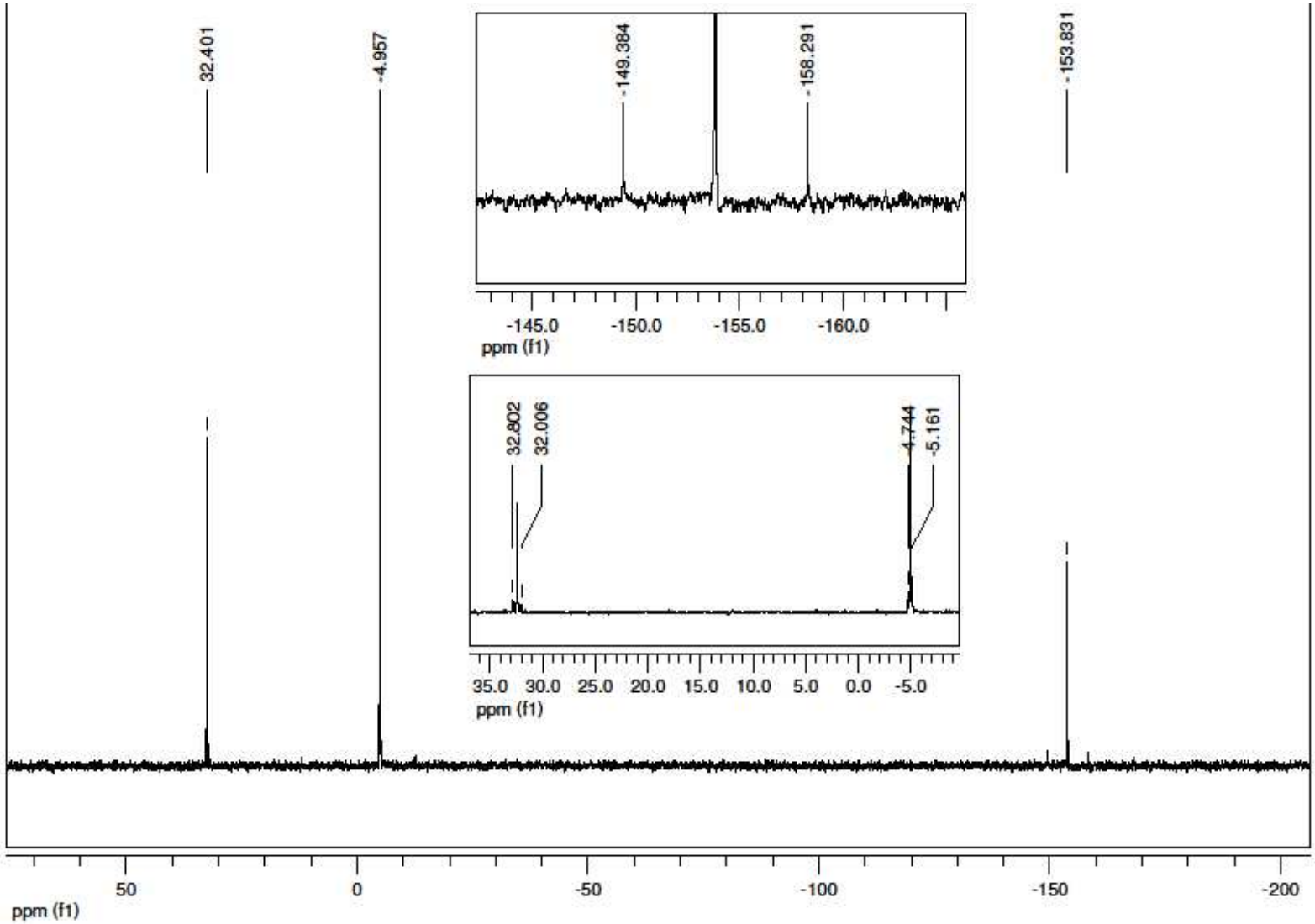


**Figure S15.** $^{29}Si\{^{1}H\}$-INEPT-NMR of compound **9**.

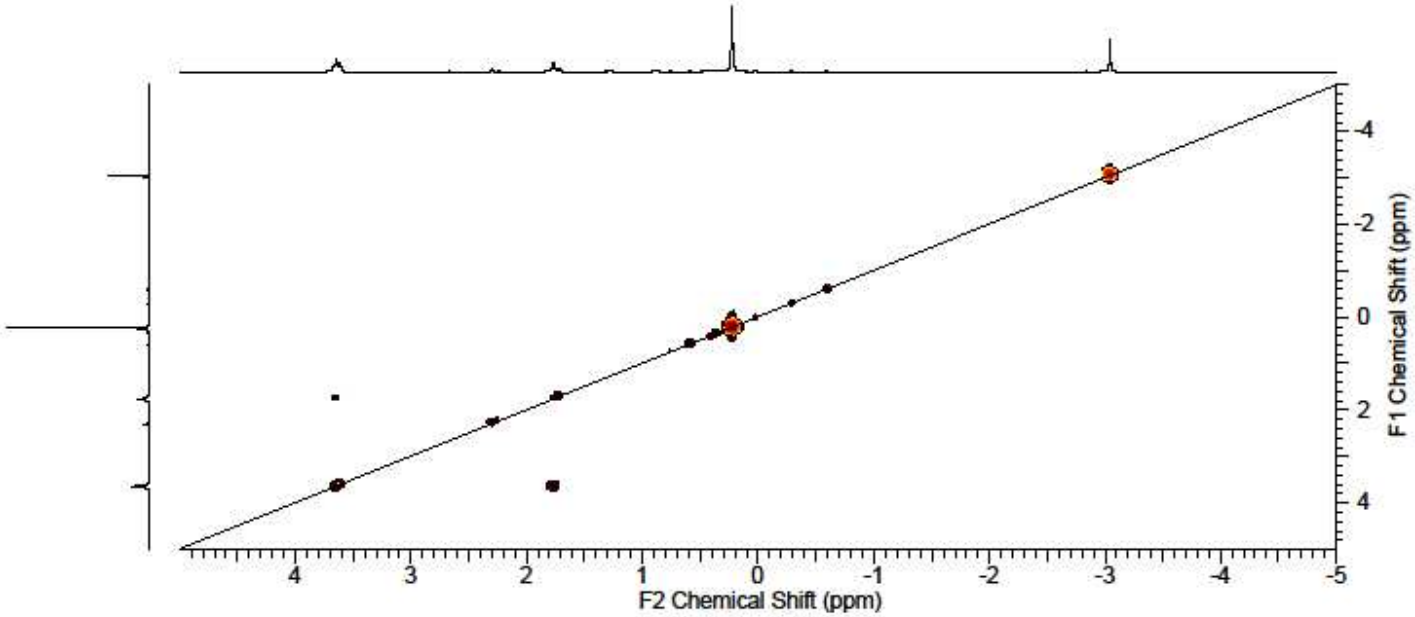


**Figure S16.** $^{1}H^{1}H$-gCOSY of compound **10** in d8-THF.

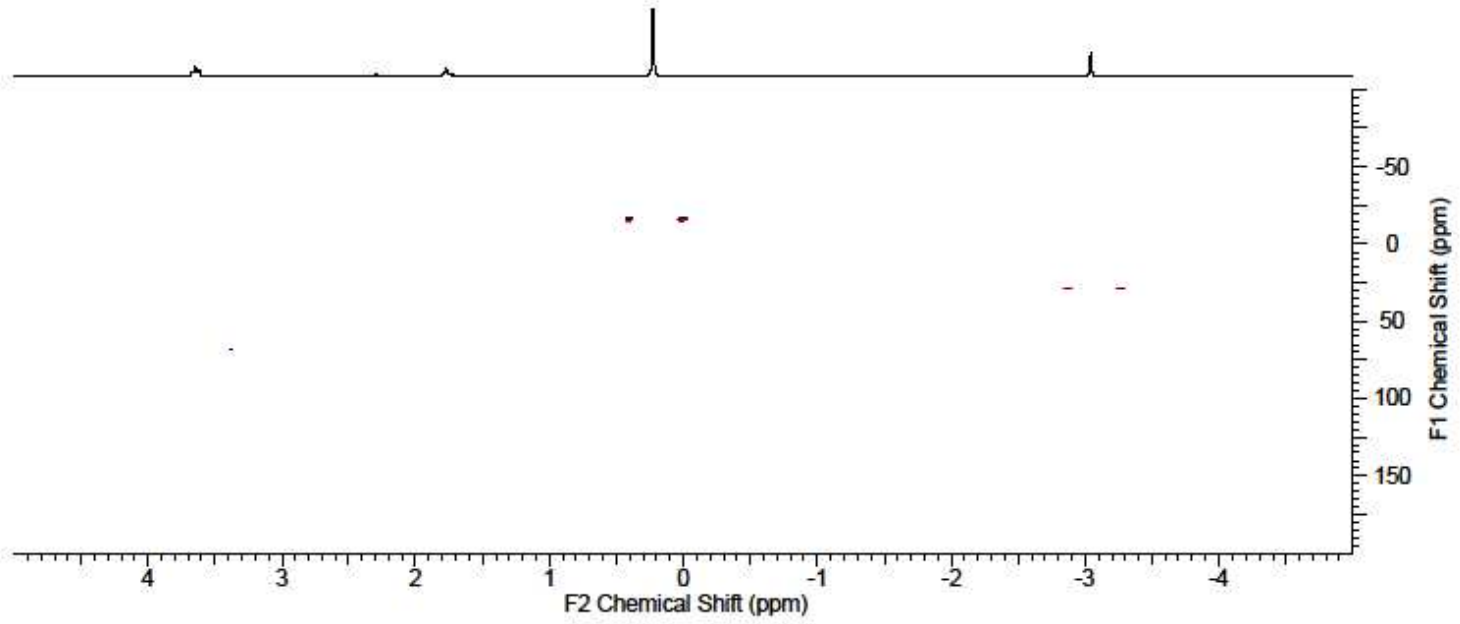


**Figure S17.** $^{1}H^{13}C$-gHSQC of compound **10** in d8-THF.

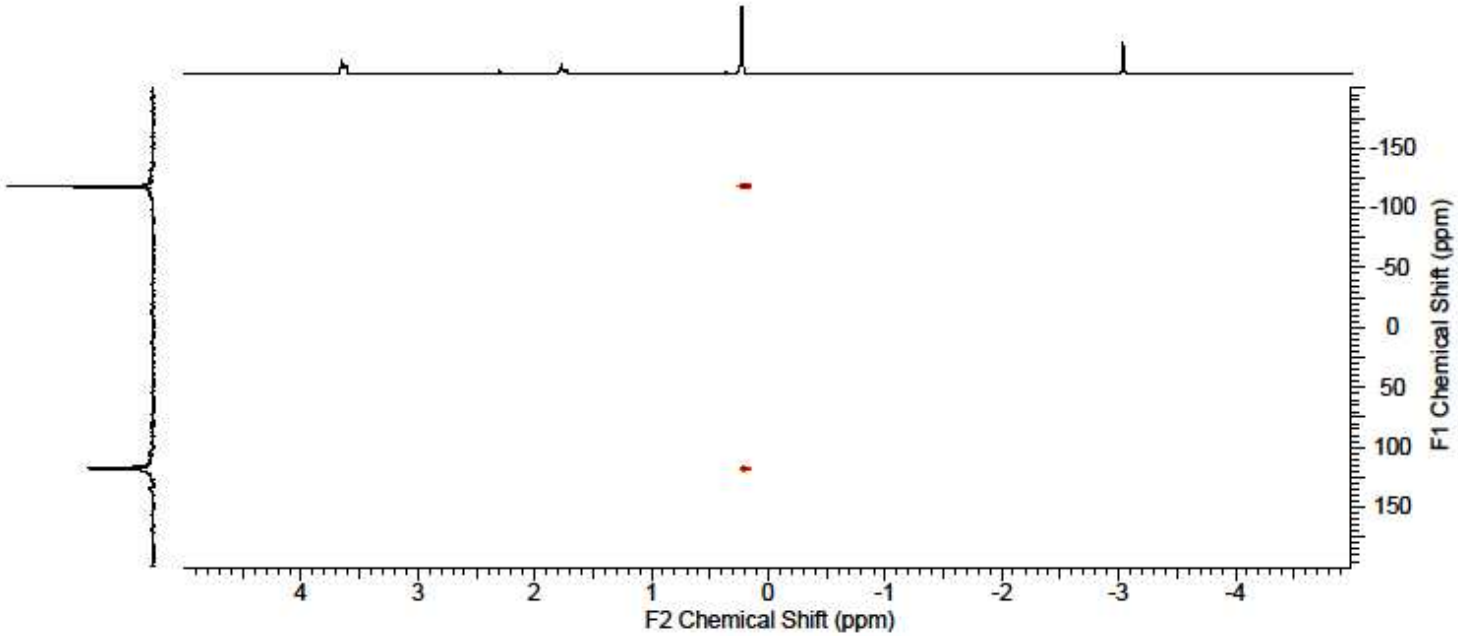


**Figure S18.** $^{1}H^{29}Si$-gHMBC of compound **10** in d8-THF.

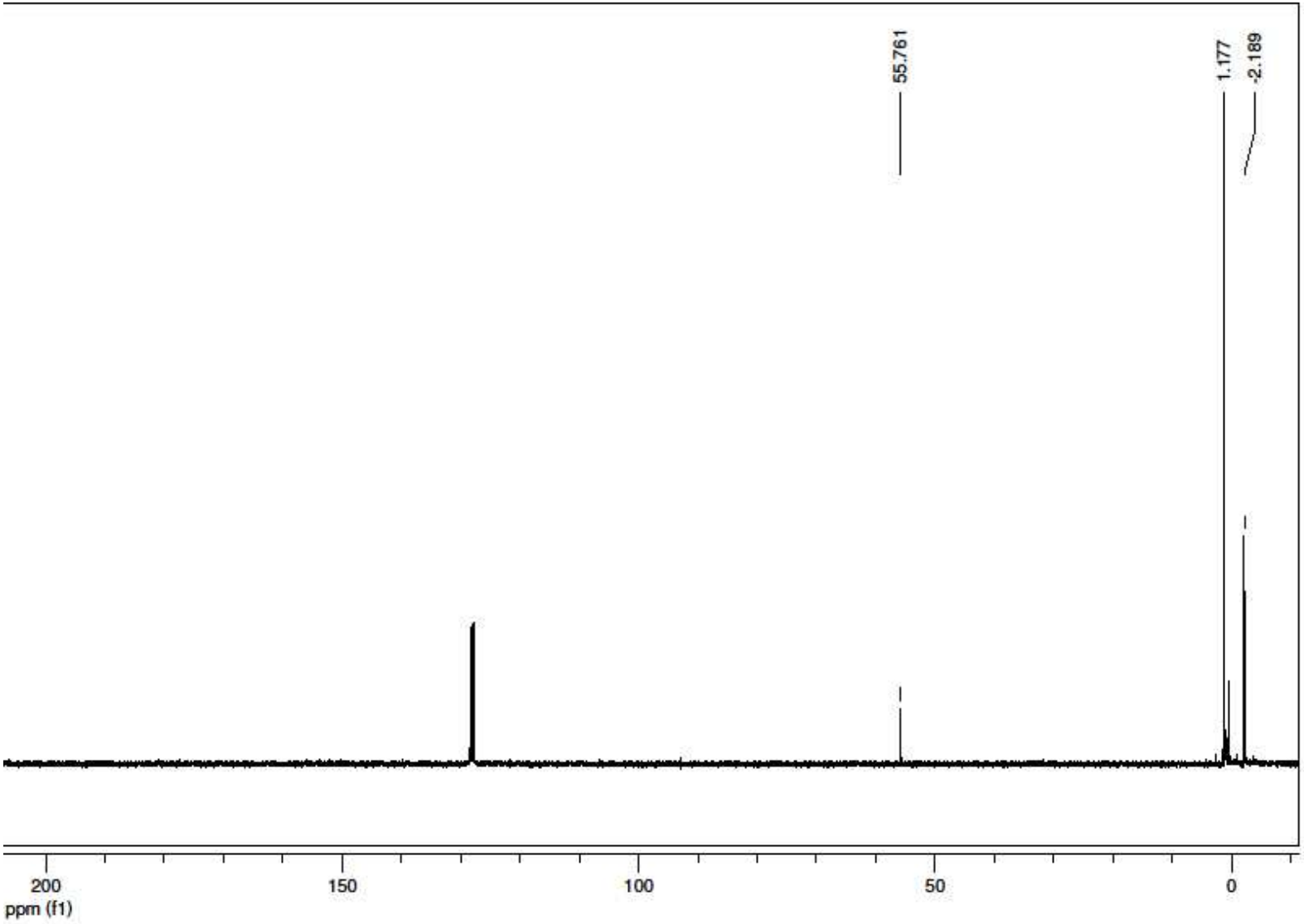


**Figure S19.** $^{13}C\{^{1}H\}$-NMR of compound **14**.

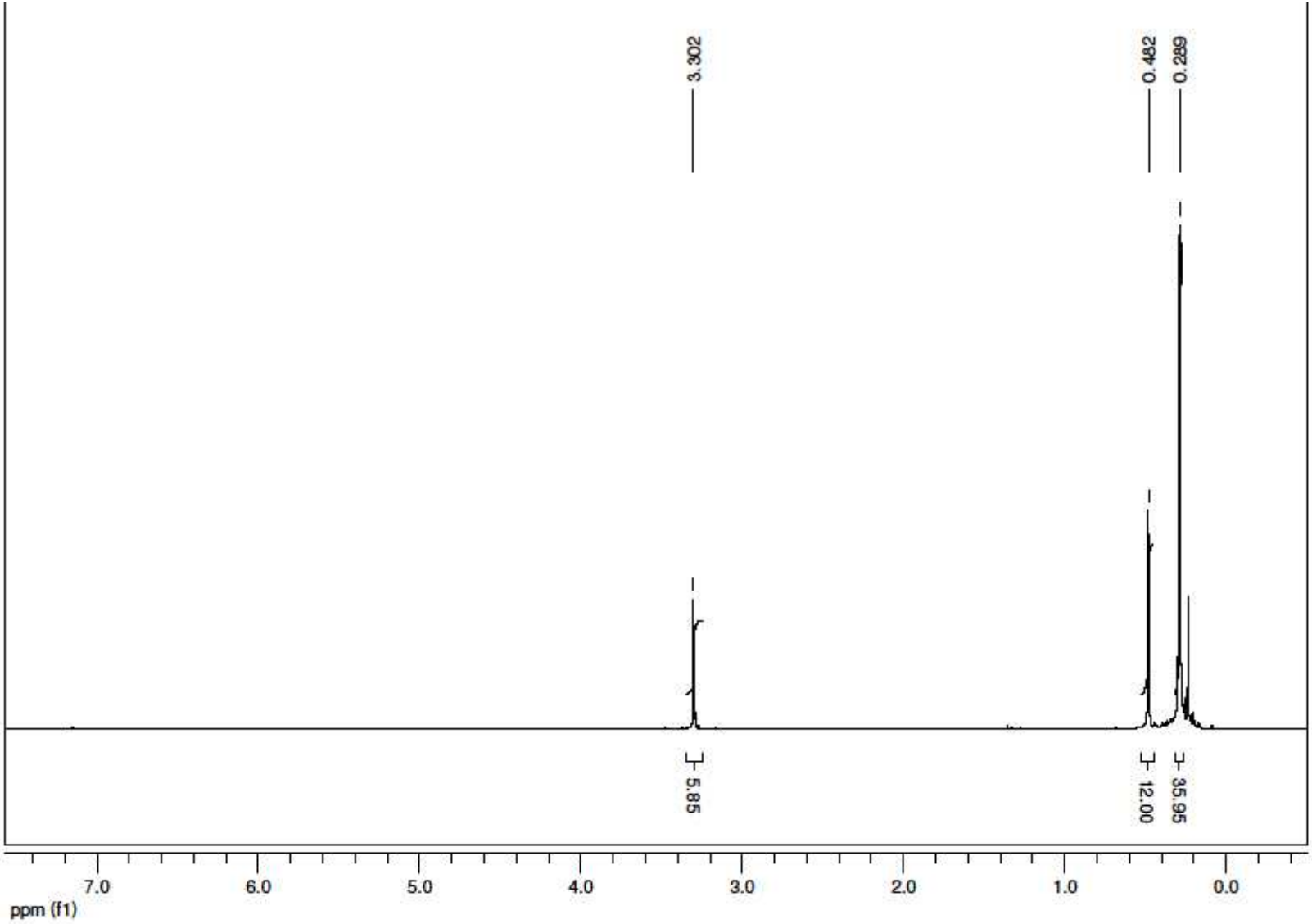


**Figure S20.** [1]H-NMR of compound **14**.

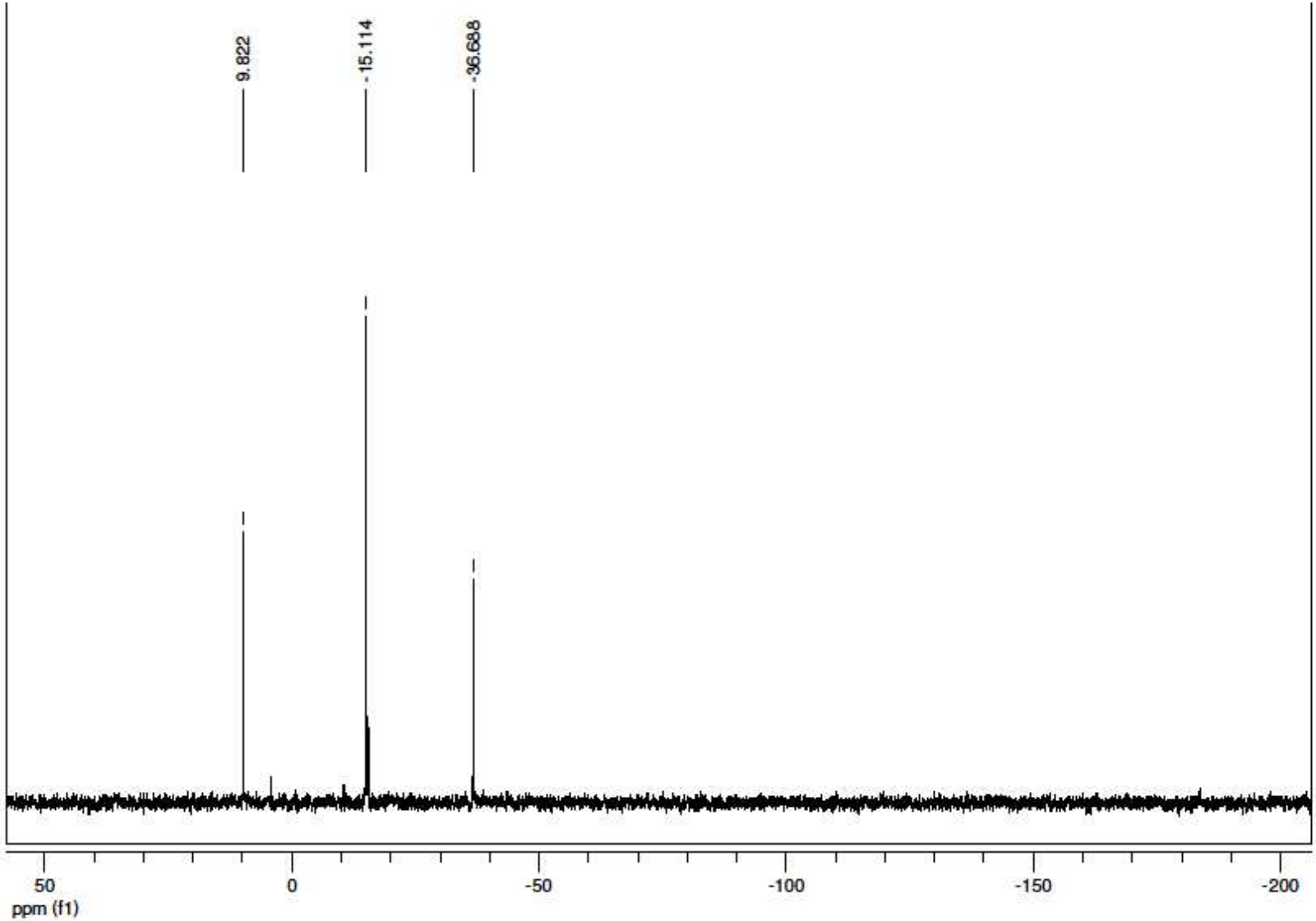


**Figure S21.** $^{29}Si\{^{1}H\}$-INEPT-NMR of compound **14**.

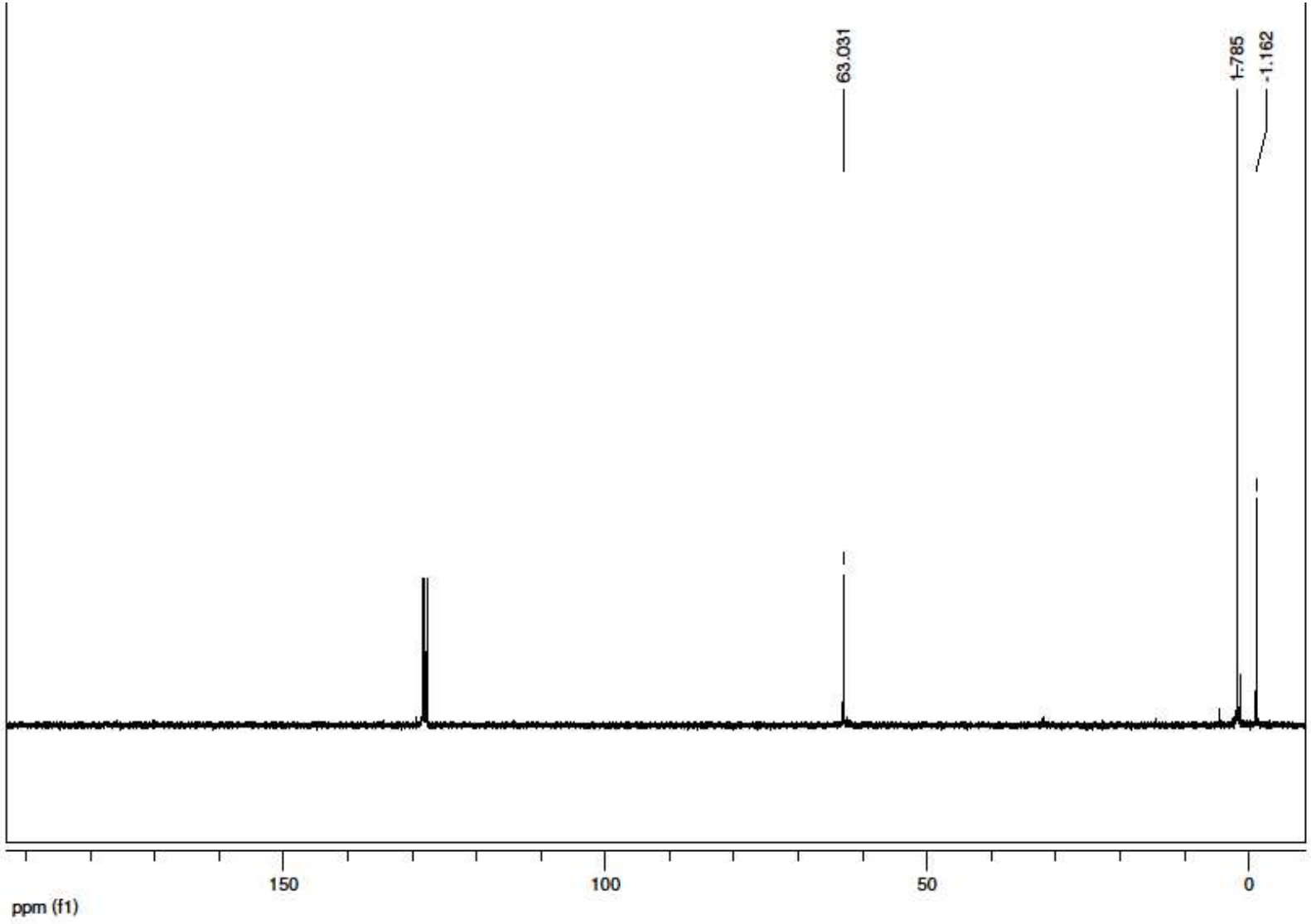


**Figure S22.** $^{13}C\{^{1}H\}$-NMR of compound **16**.

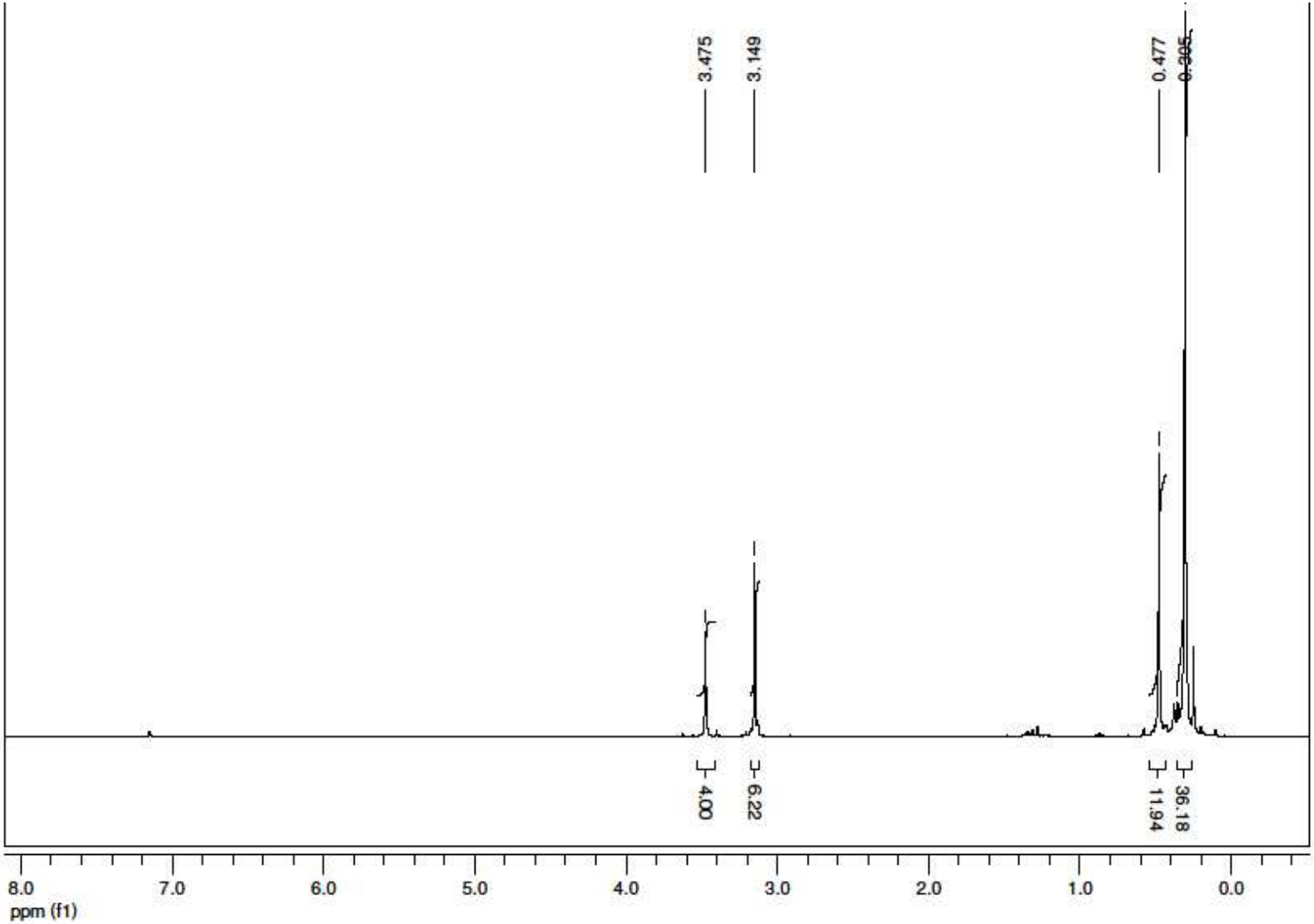


**Figure S23.** $^{1}$H-NMR of compound **16**.

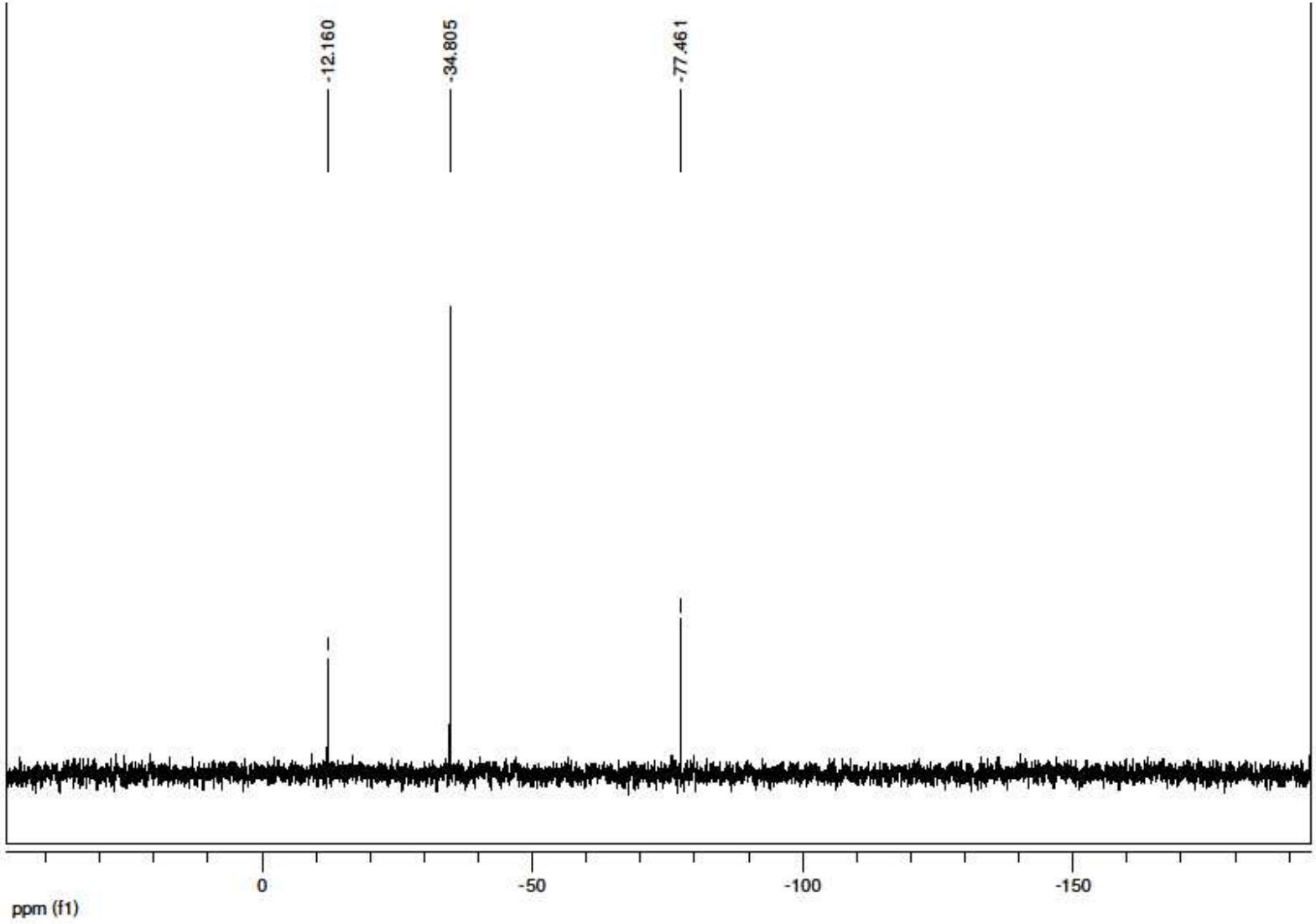


**Figure S24.** $^{29}Si\{^{1}H\}$-INEPT-NMR of compound **16**.

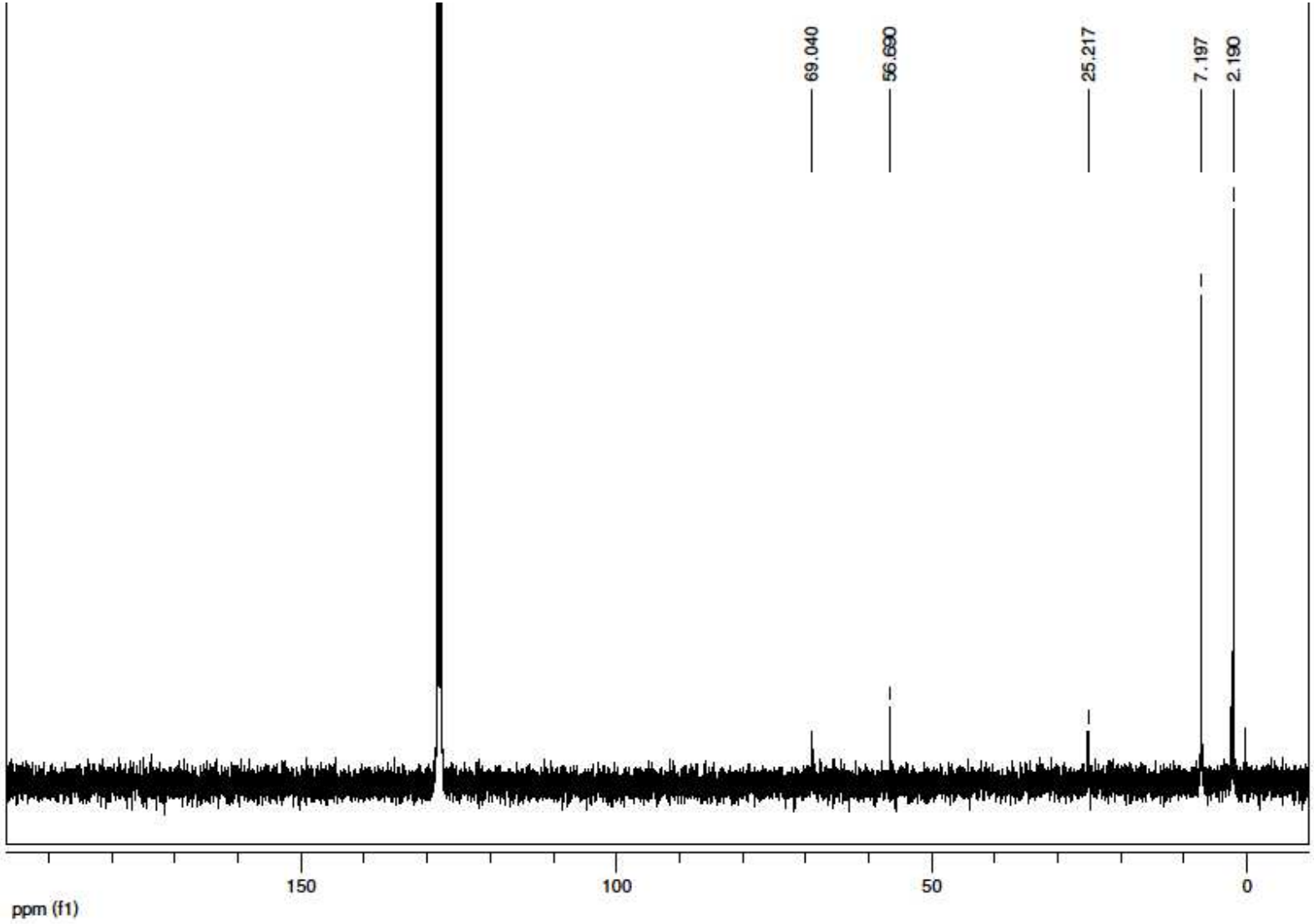


**Figure S25.** $^{13}C\{^{1}H\}$-NMR of compound **19**.

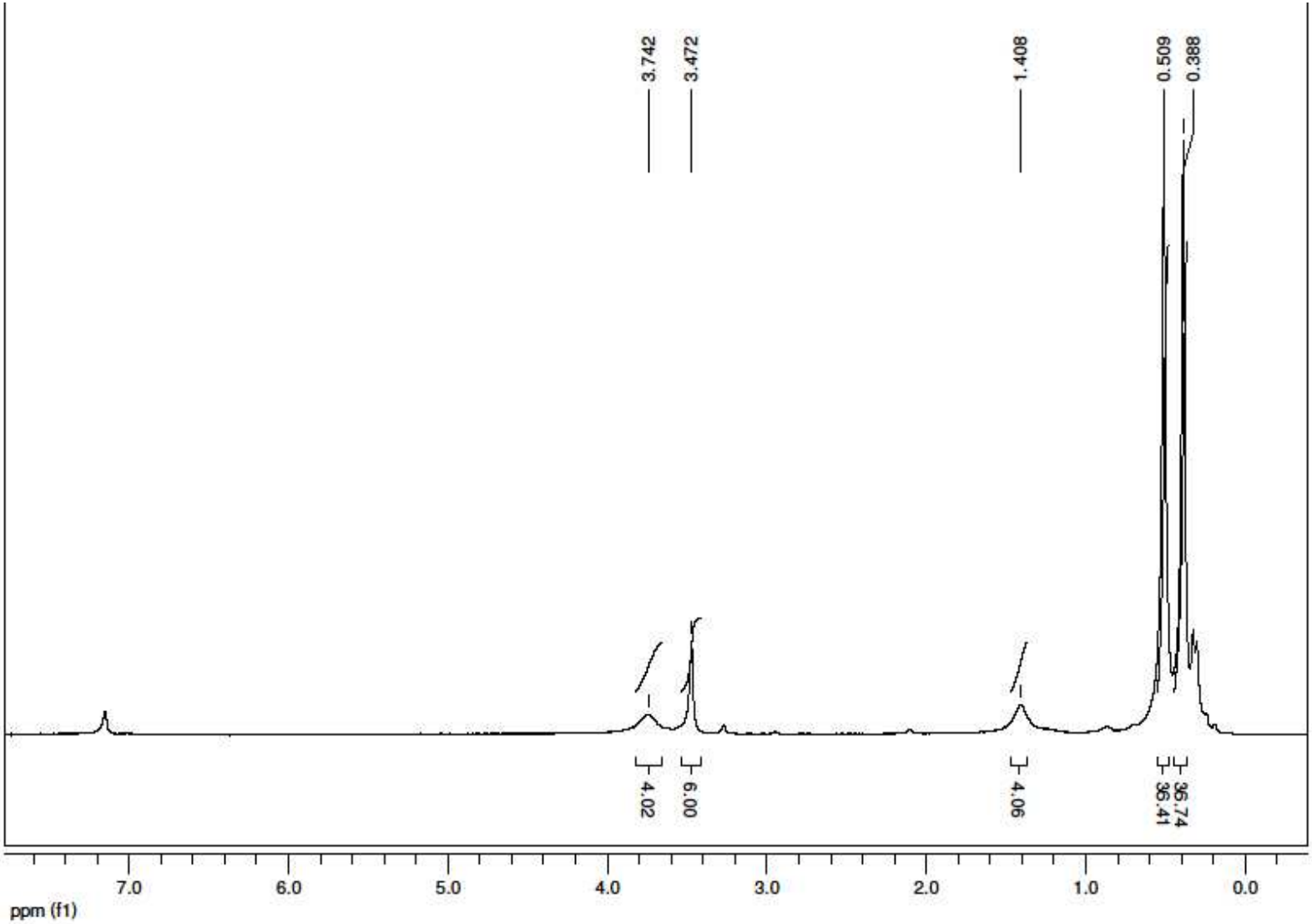


**Figure S26.** $^{1}$H-NMR of compound **19**.

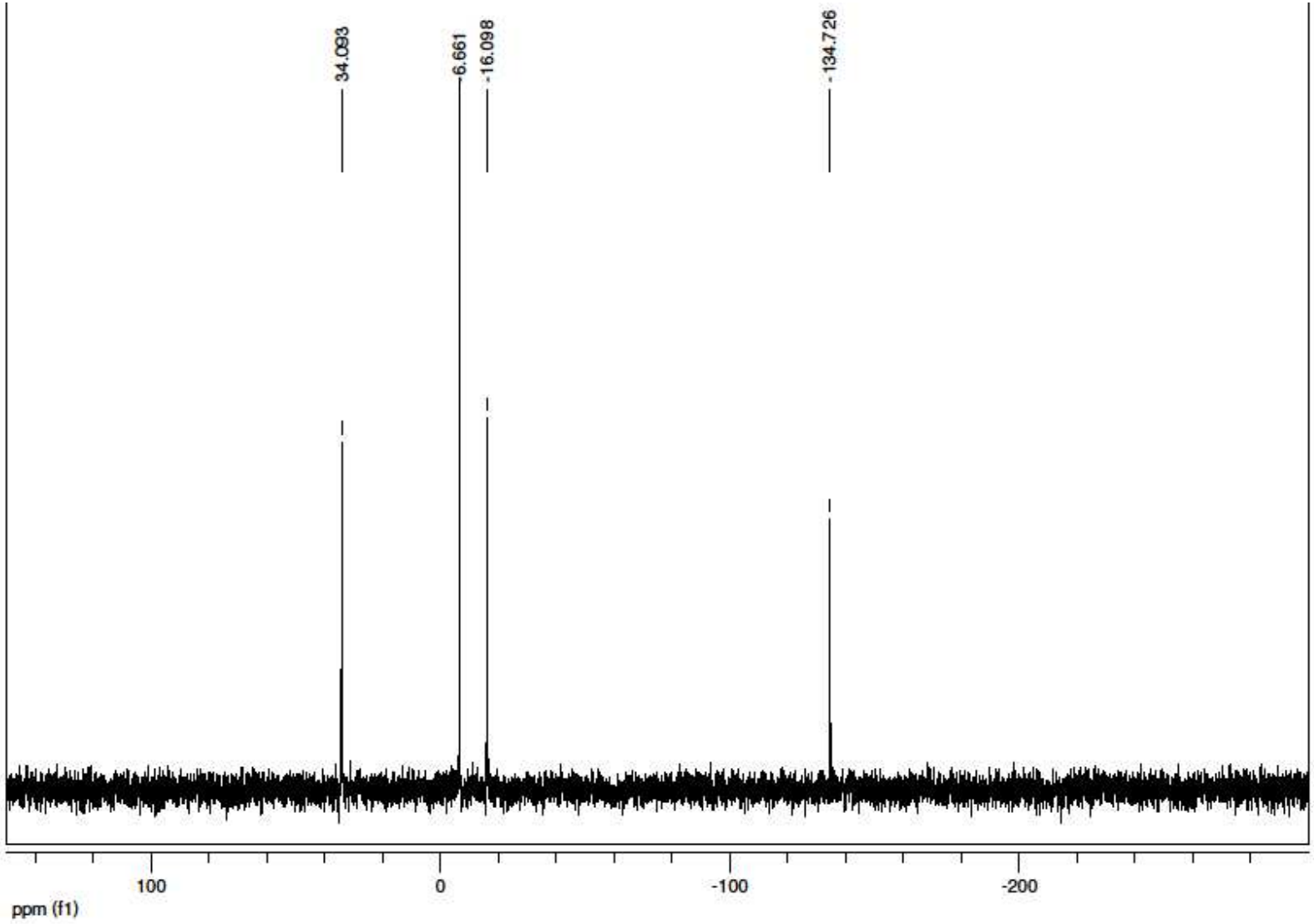


**Figure S27.** $^{29}Si\{^{1}H\}$-INEPT-NMR of compound **19**.

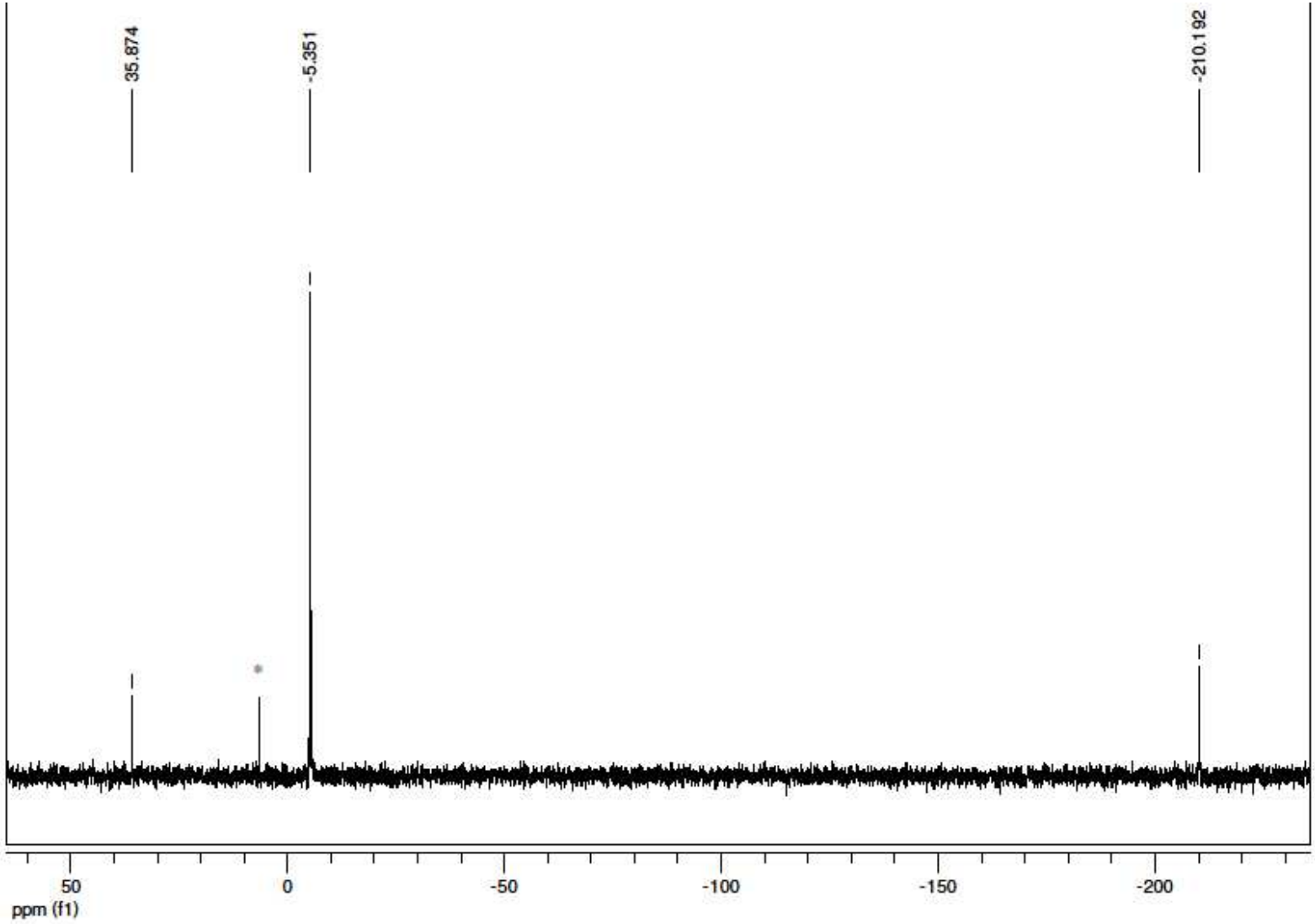


**Figure S28.** $^{29}Si\{^{1}H\}$-INEPT-NMR of compound **21a** (* = $^{t}BuOSiMe_3$)..

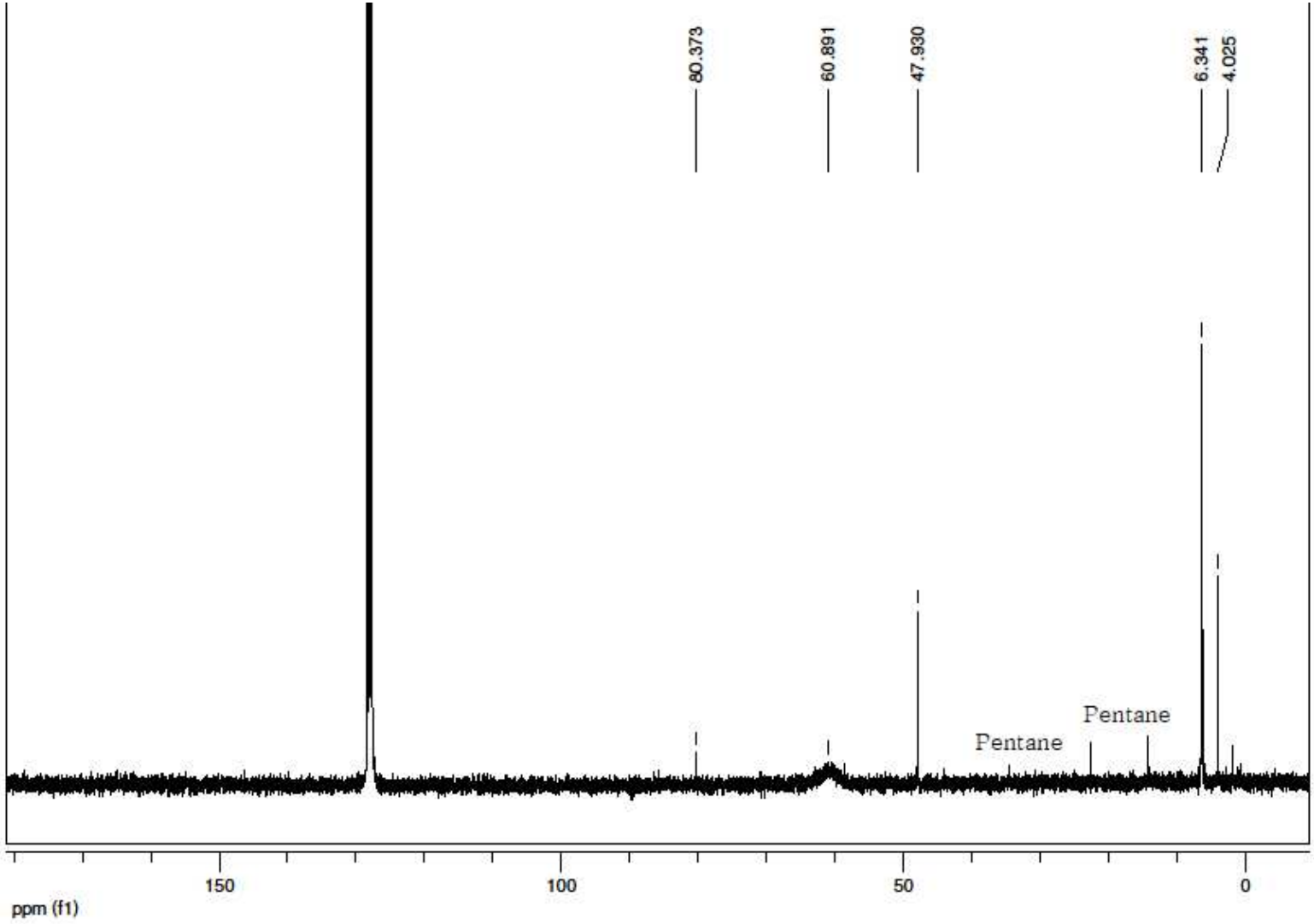


**Figure S29.** $^{13}C\{^{1}H\}$-NMR of compound **22**.

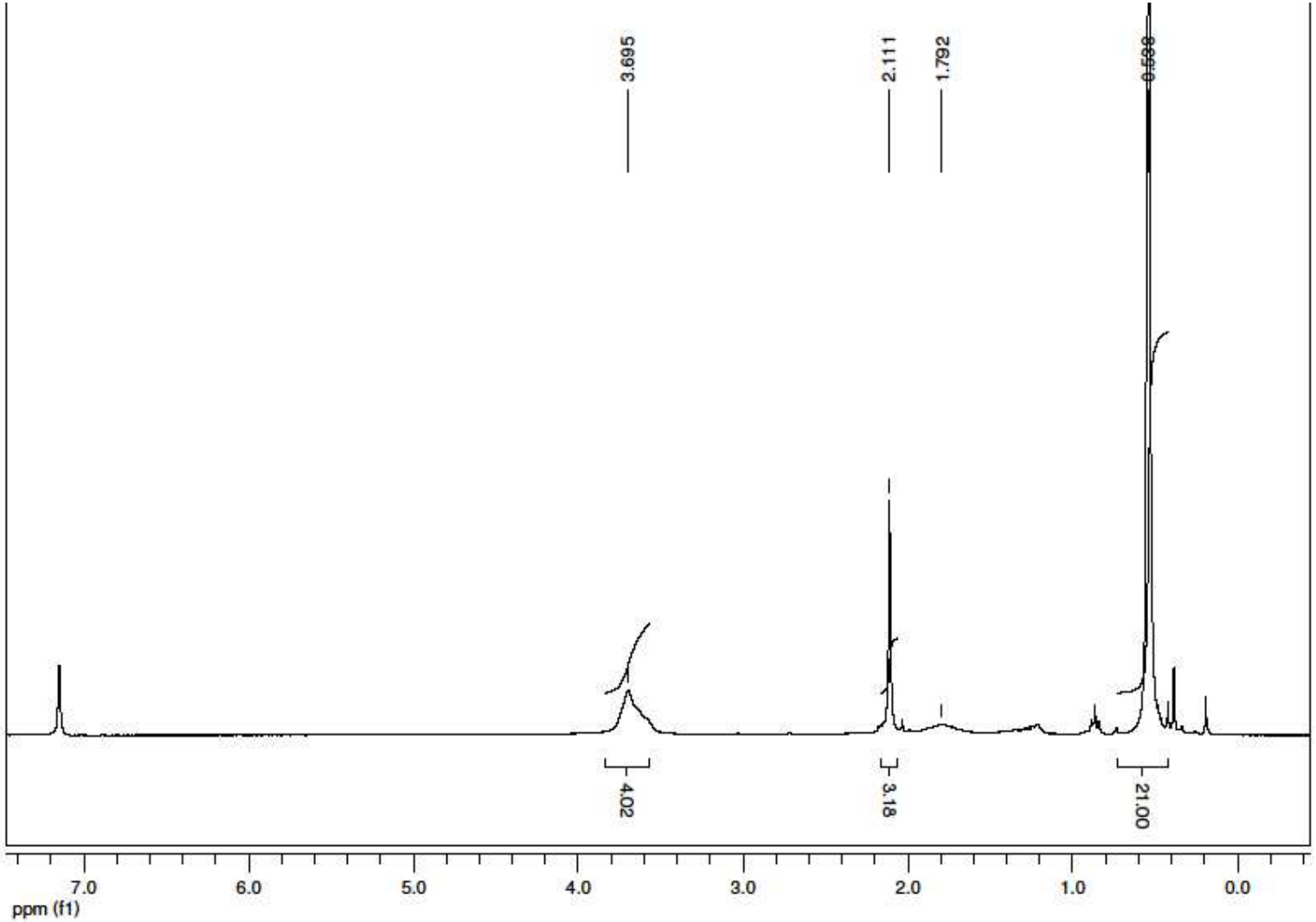


**Figure S30.** [1]H-NMR of compound **22**.

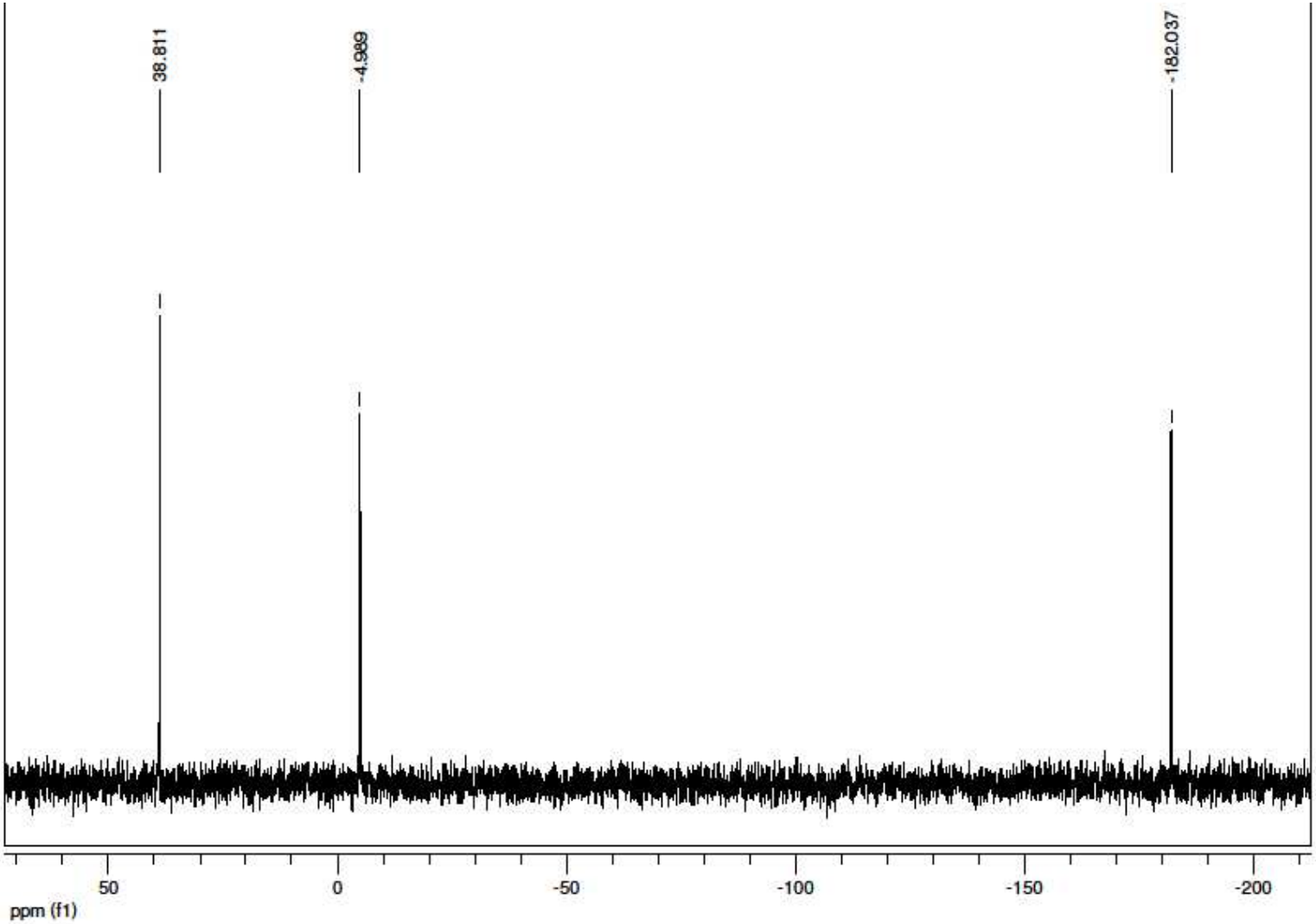


**Figure S31.** $^{29}Si\{^{1}H\}$-INEPT-NMR of compound **22**.

**Table S1.** Crystallographic data for compounds **2**, **3**, **4**, and **6**.

| | **2** | **3** | **4** | **6** |
|---|---|---|---|---|
| Empirical formula | $C_{30}H_{74}O_4Si_7Sm$ | $C_{30}H_{74}O_4Si_7Yb$ | $C_{36}H_{100}O_2Si_{14}Sm_2$ | $C_{38}H_{106}O_2Si_{14}Yb$ |
| $M_w$ | 845.87 | 868.56 | 1259.12 | 1161.53 |
| Temperature [K] | 100(2) | 200(2) | 100(2) | 100(2) |
| Size [mm] | 0.34×0.34×0.14 | 0.34×0.17×0.13 | 0.44×0.29×0.23 | 0.30×0.22×0.16 |
| Crystal system | monoclinic | orthorhombic | monoclinic | orthorhombic |
| Space group | P2(1)/c | Pna2(1) | C2/c | Pbca |
| a [Å] | 10.182(2) | 22.675(5) | 23.027(5) | 19.344(4) |
| b [Å] | 20.869(4) | 11.418(2) | 14.538(3) | 20.358(4) |
| c [Å] | 22.152(4) | 17.749(4) | 19.296(4) | 36.442(7) |
| α [°] | 90 | 90 | 90 | 90 |
| β [°] | 102.83(3) | 90 | 102.44(3) | 90 |
| γ [°] | 90 | 90 | 90 | 90 |
| V [$Å^3$] | 4589(2) | 4595(2) | 6308(2) | 14351(5) |
| Z | 4 | 4 | 4 | 8 |
| $\rho_{calc}$ [$gcm^{-3}$] | 1.224 | 1.255 | 1.326 | 1.075 |
| Absorption coefficient [$mm^{-1}$] | 1.490 | 2.245 | 2.136 | 1.561 |
| F(000) | 1784 | 1816 | 2608 | 4928 |
| θ range | 1.34<θ<26.37 | 1.80<θ<26.37 | 1.67<θ<26.36 | 1.54<θ<26.39 |
| Reflections collected/unique | 36096/9410 | 35364/9359 | 24683/6401 | 110630/14683 |
| Completeness to θ [%] | 99.7 | 100 | 99.5 | 99.8 |
| Data/restraints/parameters | 9410/0/393 | 9359/1/394 | 6401/0/258 | 14683/76/555 |
| Goodness of fit on $F^2$ | 1.10 | 1.03 | 1.04 | 1.03 |
| Final R indices [I>2σ(I)] | R1=0.045 | R1=0.037 | R1=0.020 | R1=0.084 |
| | *w*R2=0.103 | *w*R2=0.076 | *w*R2=0.050 | *w*R2=0.218 |
| R indices (all data) | R1=0.054 | R1=0.042 | R1=0.021 | R1=0.117 |
| | *w*R2=0.106 | *w*R2=0.078 | *w*R2=0.050 | *w*R2=0.237 |
| Largest diff. Peak/hole [$e^-$/ $Å^3$] | 2.53/−0.87 | 1.27/−0.91 | 0.80/−0.38 | 2.66/−0.91 |

**Table S2.** Crystallographic data for compounds **7**, **9**, **10**, and **19.**

| | **7** | **9** | **10** | **19** |
|---|---|---|---|---|
| Empirical formula | $C_{22}H_{66}OSi_{10}$ | $C_{28}H_{72}O_4Si_8Yb$ | $C_{28}H_{72}O_4Si_8Sm$ | $C_{30}H_{86}O_3Si_{12}Yb$ |
| $M_w$ | 627.65 | 870.62 | 847.93 | 1005.11 |
| Temperature [K] | 100(2) | 100(2) | 100(2) | 100(2) |
| Size [mm] | 0.40×0.23×0.20 | 0.40×0.20×0.18 | 0.22×0.17×0.11 | 0.40×0.23×0.20 |
| Crystal system | monoclinic | monoclinic | monoclinic | triclinic |
| Space group | P2(1) | P2(1)/c | P2(1)/c | P-1 |
| a [Å] | 9.391(2) | 15.441(3) | 15.491(4) | 10.444(3) |
| b [Å] | 13.142(3) | 18.603(4) | 18.840(5) | 15.475(5) |
| c [Å] | 16.586(3) | 16.113(3) | 16.136(4) | 19.428(6) |
| α [°] | 90 | 90 | 90 | 67.632(5) |
| β [°] | 93.003(3) | 102.583(3) | 103.266(4) | 86.605(5) |
| γ [°] | 90 | 90 | 90 | 71.706(5) |
| V [$Å^3$] | 2044(2) | 4517(2) | 4584(2) | 2751(2) |
| Z | 2 | 4 | 4 | 2 |
| $\rho_{calc}$ [$gcm^{-3}$] | 1.020 | 1.280 | 1.229 | 1.214 |
| Absorption coefficient [$mm^{-1}$] | 0.335 | 2.309 | 1.516 | 1.986 |
| F(000) | 692 | 1816 | 1784 | 1056 |
| θ range | 1.23<θ<26.34 | 1.35<θ<26.37 | 1.69<θ<26.35 | 1.50<θ<26.34 |
| Reflections collected/unique | 16479/8261 | 35249/9216 | 35696/9288 | 21715/10990 |
| Completeness to θ [%] | 99.6 | 99.6 | 99.4 | 98.1 |
| Data/restraints/parameters | 8261/113/545 | 9216/0/386 | 9288/0/386 | 10990/0/441 |
| Goodness of fit on $F^2$ | 1.08 | 1.08 | 1.08 | 1.09 |
| Final R indices [I>2σ(I)] | R1=0.079 | R1=0.025 | R1=0.041 | R1=0.059 |
| | *w*R2=0.162 | *w*R2=0.065 | *w*R2=0.094 | *w*R2=0.130 |
| R indices (all data) | R1=0.095 | R1=0.029 | R1=0.049 | R1=0.068 |
| | *w*R2=0.173 | *w*R2=0.067 | *w*R2=0.098 | *w*R2=0.134 |
| Largest diff. Peak/hole [$e^-$/ $Å^3$] | 0.74/−0.61 | 1.67/−1.09 | 2.63/−0.89 | 3.77/−2.47 |

**Table S3.** Crystallographic data for compounds **20**, **22**, and **23**.

| | **20** | **22** | **23** |
|---|---|---|---|
| Empirical formula | $C_6H_{14}ClNO_2Si$ | $C_{24}H_{64}N_2O_4Si_8Yb$ | $C_{24}H_{64}EuN_2O_4Si_8$ |
| $M_w$ | 195.72 | 842.53 | 821.45 |
| Temperature [K] | 100(2) | 100(2) | 100(2) |
| Size [mm] | 0.52×0.33×0.11 | 0.18×0.16×0.08 | 0.34×0.12×0.08 |
| Crystal system | monoclinic | monoclinic | monoclinic |
| Space group | P2(1)/n | C2 | C2/c |
| a [Å] | 6.884(2) | 17.833(3) | 23.45(2) |
| b [Å] | 11.800(2) | 10.295(3) | 10.198(5) |
| c [Å] | 11.154(2) | 13.216(3) | 17.953(9) |
| α [°] | 90 | 90 | 90 |
| β [°] | 92.907(3) | 121.406(5) | 100.48(2) |
| γ [°] | 90 | 90 | 90 |
| V [$Å^3$] | 904.9(3) | 2071(2) | 4221(4) |
| Z | 4 | 2 | 4 |
| $\rho_{calc}$ [$gcm^{-3}$] | 1.437 | 1.351 | 1.292 |
| Absorption coefficient [$mm^{-1}$] | 0.509 | 2.517 | 1.740 |
| F(000) | 416 | 872 | 1716 |
| θ range | 2.51<θ<26.28 | 1.81<θ<26.35 | 1.77<θ<26.38 |
| Reflections collected/unique | 7036/1833 | 8284/4085 | 15593/4301 |
| Completeness to θ [%] | 99.8 | 99.3 | 99.8 |
| Data/restraints/parameters | 1833/0/102 | 4085/0/186 | 4301/0/185 |
| Goodness of fit on $F^2$ | 1.12 | 1.12 | 1.13 |
| Final R indices [I>2σ(I)] | R1=0.026 | R1=0.066 | R1=0.069 |
| | *w*R2=0.069 | *w*R2=0.177 | *w*R2=0.163 |
| R indices (all data) | R1=0.027 | R1=0.066 | R1=0.081 |
| | *w*R2=0.070 | *w*R2=0.177 | *w*R2=0.170 |
| Largest diff. Peak/hole [$e^-$/ $Å^3$] | 0.39/−0.20 | 2.86/−1.80 | 2.28/−1.06 |

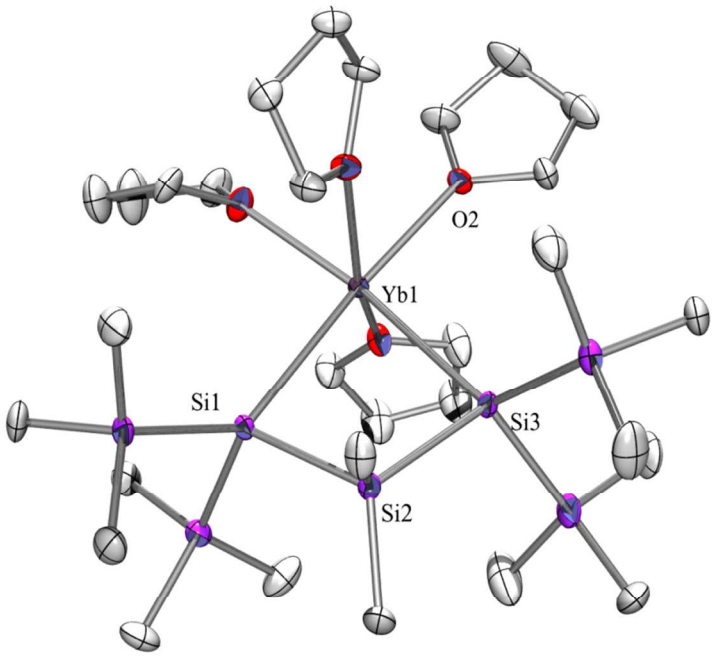


**Figure S32**. Molecular structure of **3** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Yb(1)-O(3) 2.437(3), Yb(1)-O(2) 2.464(4), Yb(1)-O(1) 2.482(3), Yb(1)-O(4) 2.492(4), Yb(1)-Si(3) 3.0571(13), Yb(1)-Si(1) 3.0658(13), Si(1)-Si(4) 2.335(2), Si(4)-C(5) 1.882(6), Si(3)-Yb(1)-Si(1) 76.29(4).

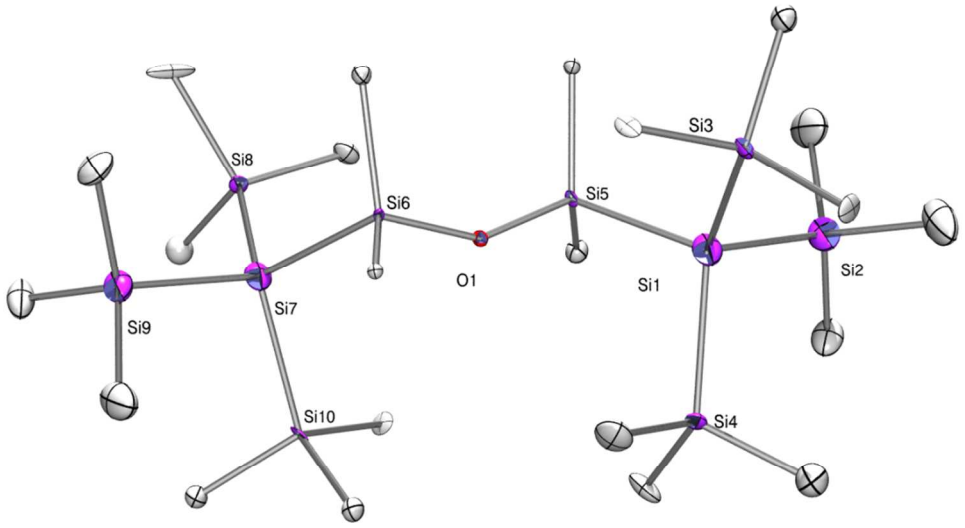


**Figure S33**. Molecular structure of **7** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). O(1)-Si(5) 1.628(6), O(1)-Si(6) 1.645(7), Si(1)-Si(2) 2.358(2), Si(2)-C(1) 1.896(9), Si(5)-O(1)-Si(6) 149.5(5).

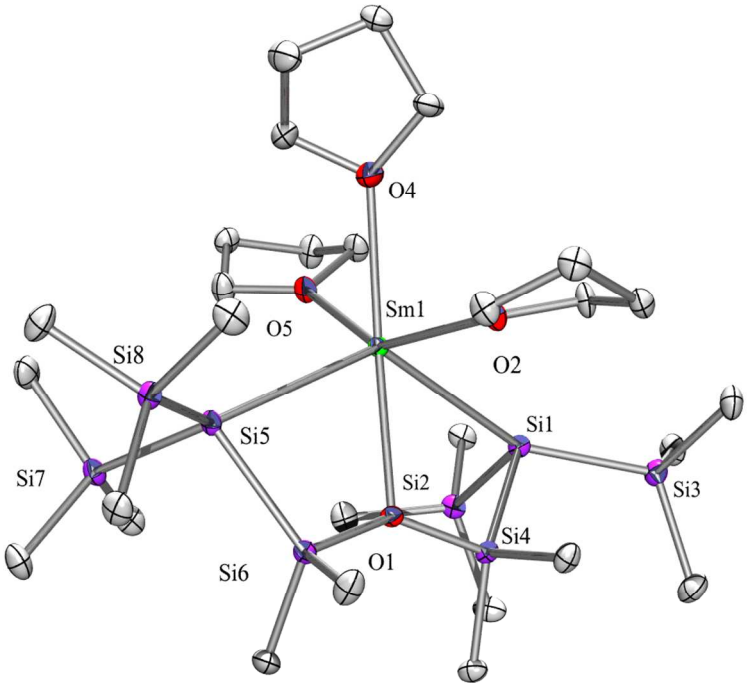


**Figure S34**. Molecular structure of **10** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). C(1)-Si(2) 1.888(4), O(1)-Si(6) 1.693(2), O(1)-Si(4) 1.696(2), O(1)-Sm(1) 2.588(2), O(2)-Sm(1) 2.562(2), O(4)-Sm(1) 2.568(3), O(5)-Sm(1) 2.558(2), Si(1)-Si(2) 2.3347(14), Si(1)-Sm(1) 3.1827(10), Si(5)-Sm(1) 3.1472(11), O(5)-Sm(1)-O(1) 125.67(7), O(2)-Sm(1)-O(1) 85.67(8), O(4)-Sm(1)-O(1) 156.14(8), O(1)-Sm(1)-Si(5) 66.95(5), O(1)-Sm(1)-Si(1) 66.66(5), Si(5)-Sm(1)-Si(1) 130.52(3).

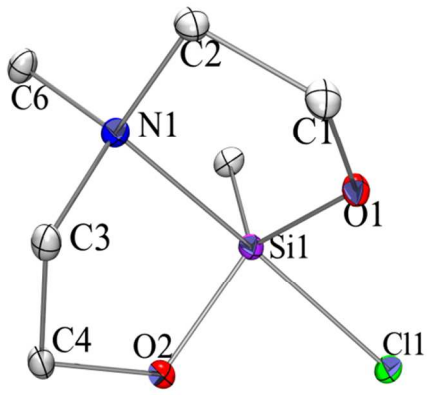


**Figure S35**. Molecular structure of **20** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Cl(1)-Si(1) 2.2297(5), Si(1)-O(1) 1.6553(9), Si(1)-N(1) 2.1168(11), O(1)-Si(1)-O(2) 121.69(5), C(5)-Si(1)-N(1) 94.41(5), N(1)-Si(1)-Cl(1) 169.95(3).

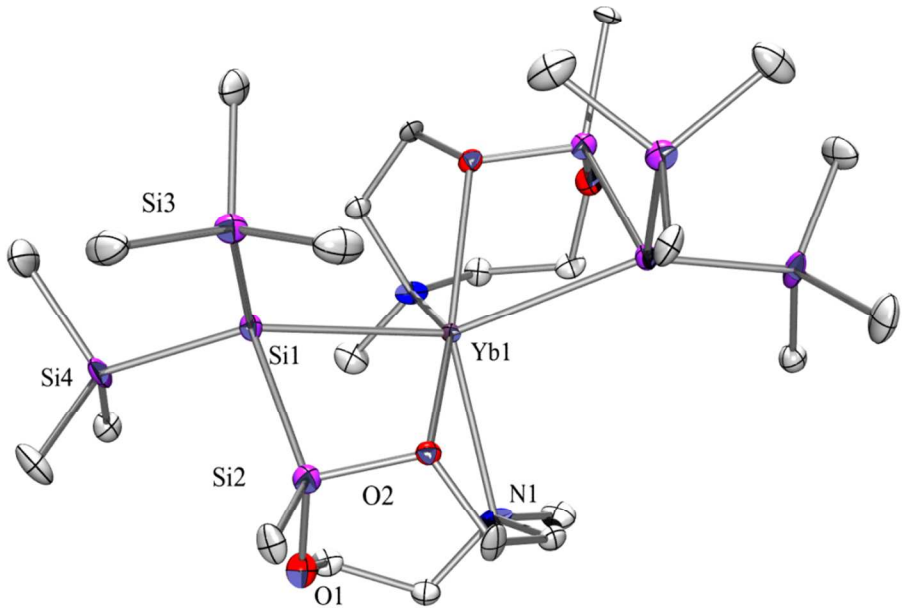


**Figure S36**. Molecular structure of **22** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Yb(1)-O(2) 2.491(8), Yb(1)-N(1) 2.705(9), Yb(1)-Si(1) 3.050(3), Si(1)-Si(2) 2.311(5), Si(2)-O(1) 1.6497(11), Si(2)-O(2) 1.717(9), Si(2)-C(1) 1.862(12), C(3)-N(1) 1.513(15), N(1)-C(6) 1.439(18), O(2)-Yb(1)-O(2A) 143.8(4), O(2A)-Yb(1)-N(1) 147.0(3), N(1)-Yb(1)-N(1A) 94.3(4), O(2)-Yb(1)-Si(1) 67.49(19), N(1)-Yb(1)-Si(1) 108.8(3), Si(1)-Yb(1)-Si(1A) 140.56(11).

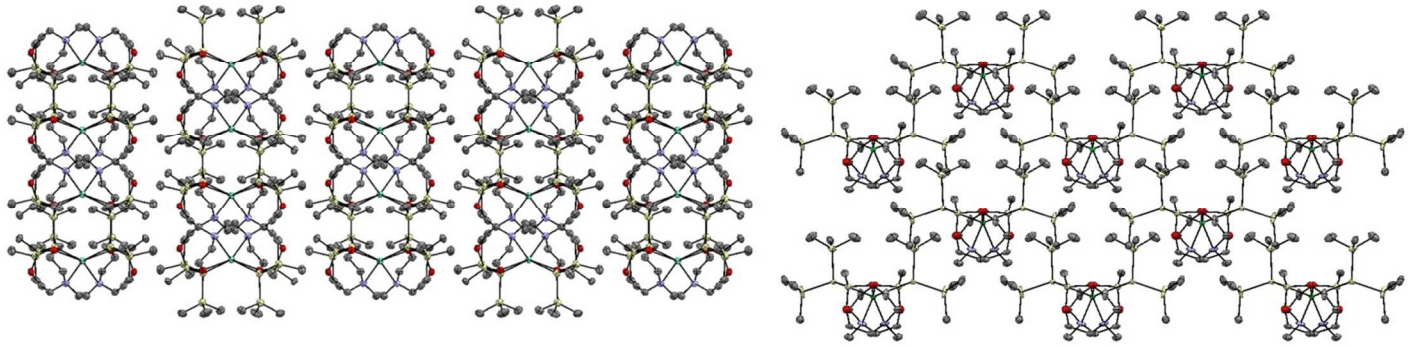

**Figure S37**. left: packing of Sm compound **23** along c-axis. right: packing of Yb compound **22** along the c-axis.

## Density Functional Calculations

DFT calculations were carried out by using the GAUSSIAN 09 program.[1] Geometry optimization was performed with the B3PW91 functional,[2-4] because we have shown that this methodology can afford good agreement with experimental results in case of f-block-silyl complexes.[5] We employed the Stuttgart RSC 1997 ECP[6] basis set from Basis Set Exchange[7,8] for f-elements, 6-31G(d)[9] for Si atoms and 6-31G(d)[10,11] basis for the other atoms, denoted as Basis1 in the manuscript. Natural Population Analysis was performed with NBO program 5.0[12-14] implemented in Gaussian 09.

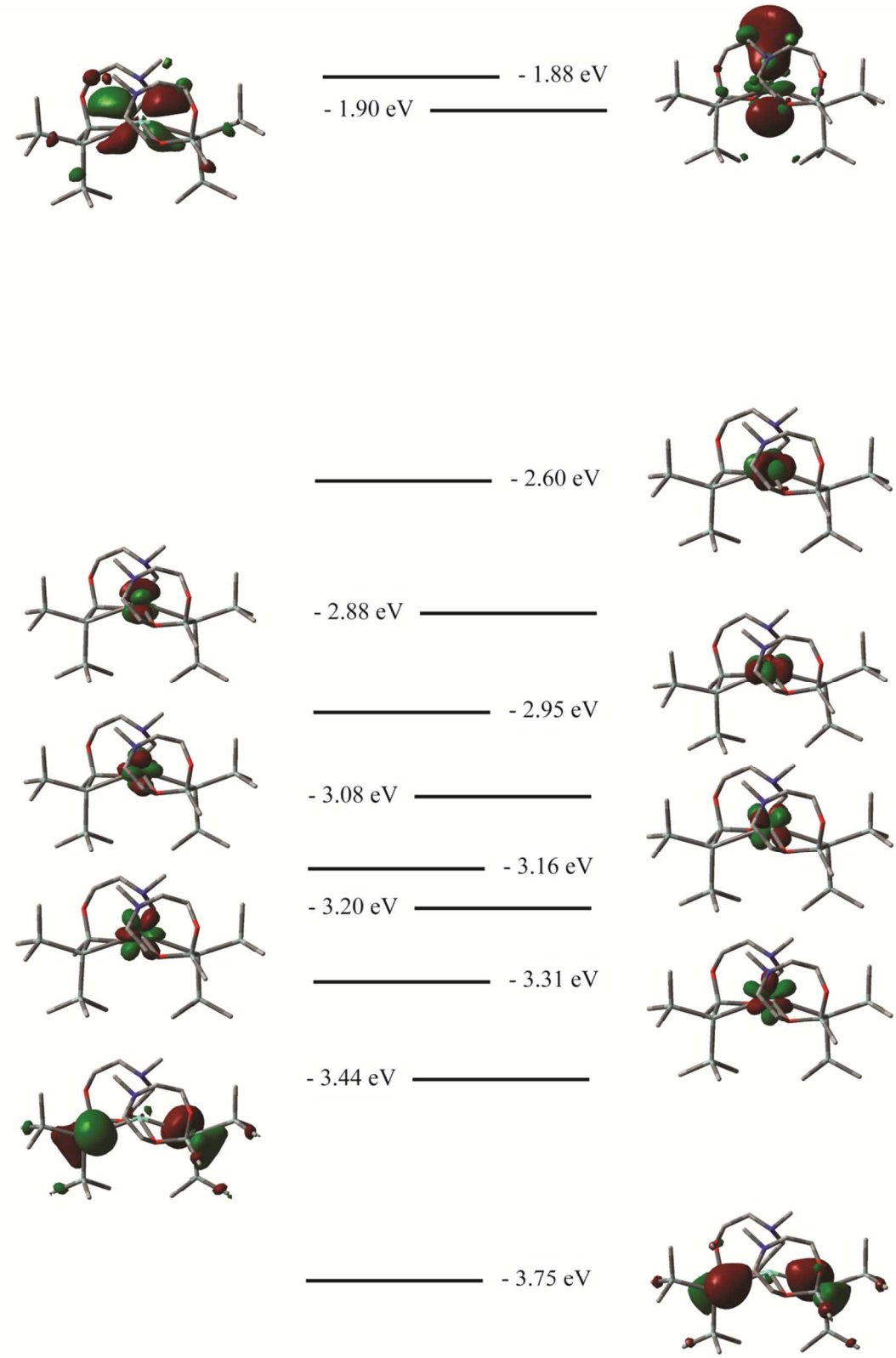


**Figure S38**. Energy levels of **23**.

**Table S4**. Cartesian coordinates of **2** in Angstrom. (Energy = -4389.872036 Hartree)

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | 2.085163 | 4.262991 | -0.134407 |
| O | 2.030036 | 2.818009 | -0.012621 |
| C | 3.41078 | 2.376666 | -0.130918 |
| C | 3.991949 | 3.233075 | -1.268056 |
| C | 3.248762 | 4.586327 | -1.107921 |
| Sm | 0.052239 | 1.084081 | 0.226773 |
| O | -1.639374 | 2.900781 | 0.9987 |
| C | -2.742376 | 2.460709 | 1.842686 |
| C | -3.996863 | 3.004032 | 1.152654 |
| C | -3.516421 | 4.387524 | 0.664292 |
| C | -2.015899 | 4.160072 | 0.366487 |
| O | -0.602633 | 2.183333 | -2.010894 |
| C | -1.874436 | 1.831986 | -2.648911 |
| C | -1.983198 | 2.720387 | -3.894468 |
| C | -0.509374 | 2.923985 | -4.28332 |
| C | 0.166847 | 3.034229 | -2.910146 |
| Si | -1.950277 | -1.37615 | -0.000567 |
| Si | -3.35942 | -2.123194 | -1.732108 |
| C | -2.553157 | -2.149751 | -3.463504 |
| O | 0.514541 | 1.406739 | 2.733522 |
| C | 1.13278 | 0.343413 | 3.524812 |
| C | 2.270846 | 1.023037 | 4.291013 |
| C | 1.655707 | 2.401538 | 4.600865 |
| C | 0.856404 | 2.699611 | 3.318786 |
| Si | 1.919588 | -1.463064 | -0.107971 |
| Si | -0.039386 | -2.81437 | 0.098399 |
| C | 0.077208 | -3.72532 | 1.780748 |
| Si | -3.241566 | -1.883676 | 1.90544 |
| C | -4.954344 | -1.031908 | 1.841329 |
| C | -3.618567 | -3.711035 | 2.325063 |
| C | -2.395503 | -1.20177 | 3.480383 |
| Si | 3.63632 | -2.659753 | 0.956995 |
| C | 3.76068 | -4.509658 | 0.497561 |
| Si | 2.520941 | -1.574557 | -2.379251 |
| C | 2.864968 | -3.274503 | -3.163347 |
| C | 5.347795 | -1.906057 | 0.569774 |
| C | 3.51287 | -2.569483 | 2.866508 |
| C | 4.111831 | -0.593455 | -2.785229 |
| C | 1.165096 | -0.773528 | -3.449999 |
| C | -0.138762 | -4.261179 | -1.162808 |

| | | | |
|---|---|---|---|
| C | -4.818626 | -0.904505 | -1.911739 |
| C | -4.136972 | -3.852207 | -1.512192 |
| H | -2.752333 | 1.36402 | 1.895468 |
| H | -2.63815 | 2.876178 | 2.857967 |
| H | -4.293386 | 2.361128 | 0.312567 |
| H | -4.839313 | 3.094309 | 1.853528 |
| H | -3.652521 | 5.150648 | 1.443352 |
| H | -4.060272 | 4.701843 | -0.237819 |
| H | -1.409368 | 4.979923 | 0.781533 |
| H | -1.831493 | 4.091671 | -0.714292 |
| H | 3.953394 | 2.554516 | 0.811779 |
| H | 3.437592 | 1.304884 | -0.366854 |
| H | 5.078954 | 3.355848 | -1.158951 |
| H | 3.77984 | 2.779064 | -2.244929 |
| H | 2.868638 | 4.941356 | -2.075475 |
| H | 3.909898 | 5.355895 | -0.685536 |
| H | 1.126046 | 4.633593 | -0.520313 |
| H | 2.27078 | 4.71691 | 0.852513 |
| H | 0.152897 | 4.074835 | -2.549252 |
| H | 1.207745 | 2.683981 | -2.950327 |
| H | -0.124152 | 2.062754 | -4.846498 |
| H | -0.369048 | 3.838285 | -4.878405 |
| H | -2.549393 | 2.223085 | -4.695089 |
| H | -2.468086 | 3.679059 | -3.658167 |
| H | -2.701935 | 2.017126 | -1.95027 |
| H | 2.523685 | 0.475689 | 5.210474 |
| H | 3.169977 | 1.115044 | 3.665211 |
| H | 2.431945 | 3.160412 | 4.776956 |
| H | 0.994986 | 2.354586 | 5.478101 |
| H | 1.459694 | 3.279749 | 2.605663 |
| H | -0.063179 | 3.257758 | 3.547535 |
| H | -1.871038 | 0.767712 | -2.920033 |
| H | -0.99906 | -4.901525 | -0.911299 |
| H | -0.26541 | -3.863761 | -2.180424 |
| H | 0.78992 | -4.850562 | -1.113769 |
| H | -0.766559 | -4.425215 | 1.872912 |
| H | -4.842306 | 0.013398 | 1.514754 |
| H | -5.606789 | -1.563686 | 1.132074 |
| H | -4.021632 | -4.222996 | 1.438733 |
| H | -2.242496 | -1.132431 | -3.746132 |
| H | -1.670708 | -2.807208 | -3.458088 |
| H | -3.284849 | -2.525299 | -4.197108 |
| H | -5.302972 | -0.754444 | -0.936189 |

| | | | |
|---|---|---|---|
| H | -4.448219 | 0.06326 | -2.284475 |
| H | -5.555288 | -1.313752 | -2.623101 |
| H | -4.690138 | -4.122487 | -2.426859 |
| H | -3.346326 | -4.596246 | -1.32992 |
| H | -4.829498 | -3.843199 | -0.656524 |
| H | 4.518461 | -4.995956 | 1.134178 |
| H | 2.787827 | -5.000095 | 0.65234 |
| H | 4.050545 | -4.60778 | -0.559379 |
| H | 5.620793 | -2.116747 | -0.475489 |
| H | 5.316993 | -0.815962 | 0.723906 |
| H | 3.678197 | -3.777711 | -2.619362 |
| H | 1.961443 | -3.901104 | -3.119115 |
| H | 3.161025 | -3.134844 | -4.216191 |
| H | 4.274905 | -0.603945 | -3.87548 |
| H | 4.012252 | 0.446801 | -2.440003 |
| H | 4.9734 | -1.058184 | -2.28289 |
| H | 0.198822 | -1.262155 | -3.256643 |
| H | 1.084528 | 0.296413 | -3.204073 |
| H | 1.423725 | -0.884338 | -4.5164 |
| H | 0.394319 | -0.090457 | 4.215393 |
| H | 1.508535 | -0.444385 | 2.85749 |
| H | 1.023508 | -4.284862 | 1.828641 |
| H | 0.040844 | -3.000035 | 2.607582 |
| H | -5.4093 | -1.054617 | 2.845288 |
| H | -2.69558 | -4.216052 | 2.645705 |
| H | -4.360889 | -3.751267 | 3.139669 |
| H | -3.076093 | -1.314752 | 4.340778 |
| H | -1.468413 | -1.762807 | 3.671482 |
| H | -2.153473 | -0.136656 | 3.34505 |
| H | 4.270891 | -3.232926 | 3.314219 |
| H | 3.692556 | -1.533973 | 3.194816 |
| H | 2.51088 | -2.886294 | 3.194118 |
| H | 6.101929 | -2.349598 | 1.240686 |

**Table S5**. Cartesian coordinates of **4** in Angstrom. (Energy = -6951.758503 Hartree)

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | 2.117263 | 3.696651 | -3.087466 |
| O | 2.540796 | 2.797171 | -2.012119 |
| C | 3.921859 | 3.128157 | -1.676521 |
| C | 4.028400 | 4.632944 | -1.912191 |
| C | 3.156496 | 4.835355 | -3.155417 |
| Sm | 1.451703 | 1.240150 | -0.366924 |

| | | | |
|---|---|---|---|
| Si | 1.231210 | -1.756277 | -1.480078 |
| Si | 3.591166 | -1.585357 | -1.047338 |
| C | 4.382435 | -3.321683 | -0.999297 |
| Sm | -1.451914 | -1.240576 | 0.367256 |
| Si | -1.230953 | 1.755900 | 1.480356 |
| Si | -3.590897 | 1.585254 | 1.047403 |
| C | -4.381720 | 3.321799 | 0.999014 |
| O | -2.543966 | -2.796062 | 2.011765 |
| C | -2.121694 | -3.695466 | 3.087556 |
| C | -3.161845 | -4.833337 | 3.155343 |
| C | -4.033007 | -4.630698 | 1.911661 |
| C | -3.925195 | -3.126077 | 1.675581 |
| Si | -3.965768 | 0.134331 | -0.788273 |
| Si | -3.299644 | 1.376358 | -2.659944 |
| C | -4.035621 | 3.113097 | -2.911103 |
| Si | -6.301157 | -0.083467 | -0.975300 |
| C | -7.281203 | 1.541374 | -0.856147 |
| C | -6.749275 | -0.822881 | -2.667395 |
| C | -7.042216 | -1.237860 | 0.340973 |
| Si | 3.966245 | -0.134481 | 0.788463 |
| Si | 3.301704 | -1.376822 | 2.660399 |
| C | 4.038475 | -3.113273 | 2.911417 |
| Si | 6.301598 | 0.083956 | 0.975090 |
| C | 7.282092 | -1.540594 | 0.855665 |
| C | 7.042106 | 1.238628 | -0.341262 |
| C | 6.749792 | 0.823409 | 2.667139 |
| Si | -0.592427 | 4.012282 | 1.129255 |
| C | -1.247663 | 5.257950 | 2.399023 |
| Si | -0.991980 | 1.615496 | 3.832235 |
| C | -2.098481 | 2.754495 | 4.884930 |
| C | -1.032881 | 4.749147 | -0.567392 |
| C | 1.323454 | 4.128825 | 1.223320 |
| Si | 0.991726 | -1.615484 | -3.831892 |
| C | 2.098261 | -2.754091 | -4.884964 |
| Si | 0.593671 | -4.013221 | -1.129882 |
| C | -1.322108 | -4.131389 | -1.224093 |
| C | 1.386573 | 0.138739 | -4.459963 |
| C | -0.796080 | -2.022696 | -4.315303 |
| C | -1.387305 | -0.138560 | 4.460573 |
| C | 0.795810 | 2.022450 | 4.315885 |
| C | -4.438476 | 0.737395 | 2.547946 |

| | | | |
|---|---|---|---|
| C | 1.249606 | -5.257928 | -2.400225 |
| C | 1.034576 | -4.750374 | 0.566537 |
| C | 4.438141 | -0.737003 | -2.548016 |
| C | -3.655407 | 0.454655 | -4.289770 |
| C | -1.411701 | 1.621460 | -2.520680 |
| C | 3.657895 | -0.454904 | 4.289993 |
| C | 1.413965 | -1.622606 | 2.521869 |
| H | -4.070844 | -0.273248 | 2.655619 |
| H | 1.195545 | -2.146067 | 1.601016 |
| H | 0.925307 | -0.657145 | 2.518654 |
| H | 1.059963 | -2.202816 | 3.364981 |
| H | 3.595671 | -3.567659 | 3.789141 |
| H | 5.108802 | -3.037826 | 3.046960 |
| H | 3.831660 | -3.729094 | 2.047809 |
| H | 2.996861 | -0.820676 | 5.065401 |
| H | 3.497995 | 0.605388 | 4.155064 |
| H | 4.684752 | -0.626280 | 4.581857 |
| H | 6.585739 | 0.086690 | 3.441169 |
| H | 6.133064 | 1.690253 | 2.864300 |
| H | 7.791728 | 1.117991 | 2.665392 |
| H | 1.481051 | 1.491378 | 3.670956 |
| H | 0.963228 | 3.086196 | 4.217599 |
| H | 0.969855 | 1.724825 | 5.341961 |
| H | -1.832219 | 3.787353 | 4.713036 |
| H | -3.135575 | 2.608104 | 4.617927 |
| H | -1.959191 | 2.516923 | 5.932021 |
| H | -1.194162 | -0.187989 | 5.524699 |
| H | -2.427865 | -0.364117 | 4.272897 |
| H | -0.766921 | -0.860876 | 3.950239 |
| H | 1.608622 | 5.113536 | 1.568674 |
| H | 1.707005 | 3.387115 | 1.911969 |
| H | -1.749098 | -3.965179 | -0.243358 |
| H | -0.865917 | 5.016523 | 3.380734 |
| H | 0.698785 | -5.778835 | 0.603764 |
| H | 0.553224 | -4.185625 | 1.352189 |
| H | 2.104357 | -4.716921 | 0.715095 |
| H | -1.136519 | -4.082710 | 2.869641 |
| H | -2.086267 | -3.155064 | 4.023882 |
| H | -3.752810 | -4.759270 | 4.057793 |
| H | -2.679830 | -5.801294 | 3.137612 |
| H | -3.646884 | -5.185827 | 1.067795 |

| | | | |
|---|---|---|---|
| H | -5.057286 | -4.928009 | 2.092006 |
| H | -4.608939 | -2.581422 | 2.313956 |
| H | -4.128386 | -2.870188 | 0.644461 |
| H | -5.507496 | 0.714956 | 2.385220 |
| H | -4.224297 | 1.292597 | 3.450388 |
| H | -4.142049 | 3.850774 | 1.911696 |
| H | -4.001027 | 3.875768 | 0.153766 |
| H | -5.455038 | 3.224907 | 0.908287 |
| H | -7.150366 | 1.978300 | 0.124054 |
| H | -6.926090 | 2.236315 | -1.604587 |
| H | -8.331910 | 1.338431 | -1.021830 |
| H | -8.109112 | -1.325971 | 0.180224 |
| H | -6.585202 | -2.215625 | 0.266441 |
| H | -6.860059 | -0.833400 | 1.327279 |
| H | -2.327945 | 5.224625 | 2.419781 |
| H | -0.923569 | 6.253237 | 2.122153 |
| H | 5.507186 | -0.714319 | -2.385541 |
| H | 4.070326 | 0.273604 | -2.655589 |
| H | 4.223870 | -1.292122 | -3.450480 |
| H | 4.142706 | -3.850605 | -1.911997 |
| H | 4.002045 | -3.875825 | -0.154031 |
| H | 5.455748 | -3.224546 | -0.908773 |
| H | -1.193438 | 2.144783 | -1.599650 |
| H | -0.923458 | 0.655811 | -2.517311 |
| H | -1.057277 | 2.201589 | -3.363709 |
| H | -2.993858 | 0.820201 | -5.064849 |
| H | -3.495986 | -0.605702 | -4.154813 |
| H | 7.151215 | -1.977513 | -0.124534 |
| H | 6.927300 | -2.235668 | 1.604132 |
| H | 8.332770 | -1.337361 | 1.021174 |
| H | 8.109005 | 1.327032 | -0.180695 |
| H | 6.584832 | 2.216262 | -0.266596 |
| H | 6.859900 | 0.834173 | -1.327563 |
| H | -1.481322 | -1.491869 | -3.670172 |
| H | -0.963267 | -3.086495 | -4.217182 |
| H | -0.970386 | -1.724919 | -5.341287 |
| H | 1.832238 | -3.787034 | -4.713208 |
| H | 3.135379 | -2.607551 | -4.618132 |
| H | 1.958731 | -2.516356 | -5.931983 |
| H | 1.193221 | 0.188319 | -5.524046 |
| H | 2.427121 | 0.364489 | -4.272443 |

| | | | |
|---|---|---|---|
| H | 0.766126 | 0.860792 | -3.949341 |
| H | -1.606117 | -5.116309 | -1.569852 |
| H | -1.706370 | -3.389892 | -1.912485 |
| H | 1.749747 | 3.961797 | 0.242356 |
| H | 2.329872 | -5.223966 | -2.421044 |
| H | 0.867655 | -5.016291 | -3.381802 |
| H | 0.926121 | -6.253527 | -2.123764 |
| H | -0.551879 | 4.183770 | -1.352793 |
| H | 1.131910 | 4.083082 | -2.868905 |
| H | 2.081754 | 3.156499 | -4.023928 |
| H | 3.747073 | 4.762047 | -4.058186 |
| H | 2.673776 | 5.802952 | -3.137121 |
| H | 3.642263 | 5.187498 | -1.067955 |
| H | 5.052368 | 4.931087 | -2.092932 |
| H | 4.605719 | 2.584260 | -2.315398 |
| H | 4.125781 | 2.872087 | -0.645535 |
| H | -3.592231 | 3.567336 | -3.788598 |
| H | -5.105917 | 3.038087 | -3.047118 |
| H | -3.828941 | 3.728772 | -2.047360 |
| H | -4.682055 | 0.626439 | -4.582133 |
| H | -6.584882 | -0.086254 | -3.441442 |
| H | -6.132762 | -1.689913 | -2.864402 |
| H | -7.791296 | -1.117165 | -2.665813 |
| H | -0.696411 | 5.777374 | -0.604971 |
| H | -2.102685 | 4.716353 | -0.715942 |

**Table S6**. Cartesian coordinates of **23** in Angstrom. (Energy = -4389.74682 Hartree)

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | 3.792593 | -1.120891 | 3.121330 |
| Si | 2.890075 | -0.093953 | 1.837154 |
| Si | 2.942562 | -0.456594 | -0.451679 |
| Si | 5.107838 | 0.251556 | -0.982647 |
| C | 5.635768 | -0.479436 | -2.642897 |
| O | 3.252358 | 1.453084 | 2.316622 |
| C | 2.657704 | 2.612597 | 1.750158 |
| C | 1.401779 | 3.085784 | 2.453245 |
| N | 0.147427 | 2.389260 | 2.097273 |
| C | -0.954577 | 3.351952 | 1.894645 |
| Eu | 0.000000 | 0.593189 | 0.000000 |
| N | -0.147428 | 2.389261 | -2.097272 |
| C | -1.401780 | 3.085784 | -2.453245 |
| C | -2.657705 | 2.612597 | -1.750157 |
| O | -3.252358 | 1.453084 | -2.316623 |
| Si | -2.890076 | -0.093952 | -1.837154 |
| C | -3.792592 | -1.120891 | -3.121331 |
| O | 1.203572 | -0.215309 | 2.160380 |
| C | 0.719336 | 0.326206 | 3.403320 |
| C | -0.292321 | 1.405154 | 3.120747 |
| Si | -2.942562 | -0.456593 | 0.451679 |
| Si | -5.107838 | 0.251556 | 0.982646 |
| C | -5.635768 | -0.479438 | 2.642896 |
| O | -1.203572 | -0.215309 | -2.160379 |
| C | -0.719336 | 0.326206 | -3.403319 |
| C | 0.292321 | 1.405155 | -3.120746 |
| Si | -3.038079 | -2.796422 | 0.482926 |
| C | -4.715522 | -3.610223 | 0.182168 |
| C | -1.846119 | -3.569431 | -0.765103 |
| C | -2.462046 | -3.383827 | 2.175561 |
| Si | 3.038079 | -2.796423 | -0.482927 |
| C | 4.715521 | -3.610222 | -0.182168 |
| C | 1.846119 | -3.569431 | 0.765103 |
| C | 2.462046 | -3.383827 | -2.175562 |
| C | 0.954577 | 3.351952 | -1.894644 |
| C | 5.149032 | 2.113915 | -1.171761 |
| C | 6.421759 | -0.179615 | 0.300166 |
| C | -5.149033 | 2.113914 | 1.171760 |

| | | | |
|---|---|---|---|
| C | -6.421759 | -0.179615 | -0.300166 |
| H | 0.301998 | -0.391734 | 3.941404 |
| H | 1.473582 | 0.702512 | 3.922054 |
| H | -0.488679 | 1.887519 | 3.961656 |
| H | -1.133467 | 0.980917 | 2.812560 |
| H | 1.540163 | 2.992982 | 3.429011 |
| H | 2.438834 | 2.424953 | 0.802772 |
| H | 3.600137 | -0.769060 | 4.014045 |
| H | 3.491229 | -2.051969 | 3.064659 |
| H | 4.755909 | -1.079079 | 2.953080 |
| H | 1.772351 | 2.867548 | -1.650631 |
| H | 6.030421 | 2.388241 | -1.506870 |
| H | 4.456395 | 2.394360 | -1.806131 |
| H | 4.986446 | 2.535093 | -0.302591 |
| H | 1.727866 | -4.520904 | 0.557306 |
| H | 2.211599 | -3.474589 | 1.668713 |
| H | 0.978900 | -3.114600 | 0.713339 |
| H | -1.513386 | -3.172729 | 2.287995 |
| H | 2.981802 | -2.931036 | -2.873091 |
| H | 2.593949 | -4.351617 | -2.246964 |
| H | 6.210767 | 0.267057 | 1.146236 |
| H | 6.437088 | -1.149444 | 0.437894 |
| H | 7.297377 | 0.120206 | -0.018199 |
| H | 5.384999 | -3.204342 | -0.771819 |
| H | 4.979436 | -3.477649 | 0.752163 |
| H | 4.652856 | -4.568835 | -0.373357 |
| H | -0.301997 | -0.391733 | -3.941404 |
| H | -1.473582 | 0.702513 | -3.922053 |
| H | 0.488679 | 1.887520 | -3.961655 |
| H | 1.133467 | 0.980918 | -2.812559 |
| H | -1.540163 | 2.992983 | -3.429009 |
| H | -2.438834 | 2.424953 | -0.802773 |
| H | -3.600136 | -0.769060 | -4.014045 |
| H | -3.491227 | -2.051968 | -3.064660 |
| H | -4.755908 | -1.079079 | -2.953081 |
| H | -1.772352 | 2.867547 | 1.650632 |
| H | -6.030421 | 2.388240 | 1.506870 |
| H | -4.456396 | 2.394359 | 1.806132 |
| H | -4.986446 | 2.535092 | 0.302592 |
| H | -1.727866 | -4.520904 | -0.557308 |
| H | -2.211598 | -3.474589 | -1.668714 |

| | | | |
|---|---|---|---|
| H | -0.978900 | -3.114600 | -0.713340 |
| H | 1.513386 | -3.172728 | -2.287996 |
| H | -2.981803 | -2.931037 | 2.873089 |
| H | -2.593949 | -4.351617 | 2.246964 |
| H | -6.210767 | 0.267057 | -1.146237 |
| H | -6.437088 | -1.149445 | -0.437895 |
| H | -7.297377 | 0.120206 | 0.018198 |
| H | -6.419815 | 0.004967 | 2.978193 |
| H | -5.863029 | -1.425812 | 2.526151 |
| H | -4.901576 | -0.395814 | 3.285811 |
| H | -5.384999 | -3.204343 | 0.771818 |
| H | -4.979435 | -3.477649 | -0.752164 |
| H | -4.652856 | -4.568835 | 0.373357 |
| H | 1.286214 | 4.049495 | 2.262039 |
| H | 3.322581 | 3.345833 | 1.763515 |
| H | -0.718054 | 3.975049 | 1.175350 |
| H | -1.109047 | 3.852673 | 2.723047 |
| H | -1.286215 | 4.049495 | -2.262039 |
| H | -3.322582 | 3.345833 | -1.763514 |
| H | 0.718053 | 3.975050 | -1.175349 |
| H | 1.109047 | 3.852674 | -2.723047 |
| H | 6.419814 | 0.004969 | -2.978194 |
| H | 5.863029 | -1.425811 | -2.526152 |
| H | 4.901575 | -0.395813 | -3.285811 |

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