## Supporting information

## Experimental Procedures

**General Methods.**
*n*-Hexane and deuterated solvents were dried with potassium and distilled. All synthetic work was carried out under an inert argon atmosphere using standard Schlenk and glove-box techniques.
$^{1}H$, $^{7}Li$, $^{13}C$, $^{1}H$-$^{13}C$ HSQC, and $^{133}C$ NMR spectra were recorded on a Bruker AV 400 spectrometer. All $^{1}H$ and $^{13}C$ spectra were referenced to the resonances of the deuterated [$D_{12}$]cyclohexane or the deuterated [$D_6$]benzene used. Melting points were measured on a Stuart Scientific SMP10 melting point apparatus.
Single crystals of **2**, **3**, **4**, and **5** were mounted in inert oil. Data for X-ray crystal structure determination were obtained with a Bruker SMART diffractometer using Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). All structures were refined to convergence against $F^2$ using programs from the SHELX family.[1]

**General synthesis of MO*t*Am (M = Li: 1, M = Na: 2, M = K: 3, M = Rb: 4, M = Cs: 5):** Pieces of the corresponding metal were placed in a Schlenk flask together with a glass coated magnetic stirring bar. Solvent was added (Li, K, Rb, Cs: *n*-hexane, Na : *n*-heptane). *t*-Amylalcohol was quickly added and the solution was allowed to stir for 1h. Then the solution was heated under reflux for 2-4 days. In the case of potassium, rubidium, and caesium the formation of a colourless, crystalline solid was observed, which often resulted in the partial solidification of the reaction mixture. As the reaction proceeded the precipitated intermediate redissolved. After cooling the excess metal was removed and all solvent was distilled off. The obtained crystalline solids (LiO*t*Am, **1**; NaO*t*Am, **2**; KO*t*Am, **3**; RbO*t*Am, **4**; CsO*t*Am, **5**) were purified in a vacuum sublimation with pressures of about $5 \cdot 10^{-2}$ mbar (rotary vane pump) using temperatures between 160-180°C (except **3**: 120°C because of melting point of 130°C) with good to excellent yields.

**Table S1: Experimental detail for the synthesis of 1, 2, 3, 4, and 5.**

| M | Metal | | *t*-Amylalcohol | | Solvent [ml] | MO*t*Am | | | Sublimation temperature | Melting point |
|---|---|---|---|---|---|---|---|---|---|---|
| | [g] | [mmol] | [ml] | [mmol] | | [g] | [mmol] | yield | | |
| Li | 1.2 | 173.0 | 10.0 | 92.0 | 50 | 6.74 | 71.6 | 77.8 % | 160°C | subl. 260°C |
| Na | 2.5 | 108.7 | 9.5 | 87.4 | 100 | 6.60 | 60.0 | 68.6 % | 180°C | subl. 190°C |
| K | 6.5 | 166.2 | 17.0 | 156.2 | 300 | 17.2 | 136.2 | 87.2 % | 120°C | 130°C |
| Rb | 1.4 | 16.4 | 1.3 | 12.0 | 40 | 2.0 | 11.6 | 96.7 % | 160°C | 248°C (subl.) |
| Cs | 0.85 | 6.4 | 0.73 | 6.7 | 40 | 1.24 | 5.6 | 87.5 % | 180°C | decomp. >295°C |

**Table S2:** Crystallographic data and refinement for compounds **2**, **3**, polymorph **3a**, **4**, and **5**.[2] Compound **2** was found to be severely disordered (positional disorder of six sodium atoms over eight positions and additional rotational disorder of *t*-amyloxy groups), so no structure and only cell constants are reported.

| Compound | **1** | **2** | **3** | **3a** | **4** | **5** |
|---|---|---|---|---|---|---|
| Formula | $C_5H_{11}OLi$ | $C_5H_{11}ONa$ | $C_5H_{11}OK$ | $C_5H_{11}OK$ | $C_5H_{11}ORb$ | $C_5H_{11}OCs$ |
| $M_r$ [g mol$^{-1}$] | 94.08 | 110.13 | 126.24 | 126.24 | 172.61 | 220.05 |
| Crystal size [mm$^3$] | 0.60x0.53x0.45 | 0.40x0.40x0.30 | 0.76x0.50x0.34 | 0.37x0.28x0.12 | 0.10x0.10x0.40 | 0.19x0.09x0.04 |
| Crystal system | trigonal | monoclinic | tetragonal | monoclinic | monoclinic | monoclinic |
| Space group | *P*3 | *C*2/m | $P4_2_1c$ | $P2_1/c$ | *I*a | *P*2/c |
| *a* [Å] | 18.1109(13) | 31.839(6) | 8.251(1) | 21.876(4) | 19.509(16) | 19.114(3) |
| *b* [Å] | 18.1109(13) | 18.868(4) | 8.251(1) | 8.181(2) | 8.686(6) | 8.875(2) |
| *c* [Å] | 10.3381(9) | 10.858(2) | 20.346(3) | 16.896(3) | 20.161(17) | 20.401(3) |
| *α* [°] | 90 | 90 | 90 | 90 | 90 | 90 |
| *β* [°] | 90 | 95.68(3) | 90 | 111.919(3) | 116.48(2) | 117.104(4) |
| *γ* [°] | 120 | 90 | 90 | 90 | 90 | 90 |
| *V* [Å$^3$] | 2936.6(4) | 6491(2) | 1385.1(2) | 2805.2(10) | 3058(4) | 3080.6(9) |
| Z | 18 | 36 | 8 | 16 | 16 | 16 |
| $\rho_{calcd}$ [g cm$^{-3}$] | 0.958 | 1.014 | 1.211 | 1.196 | 1.500 | 1.898 |
| $\mu(Mo_{K\alpha})$ [mm$^{-1}$] | 0.06 | 0.118 | 0.662 | 0.654 | 6.381 | 4.714 |
| *T* [K] | 193(2) | 243(2) | 173(2) | 173(2) | 223(2) | 173(2) |
| $2\theta_{max}$ [°] | 28.31 | 28.41 | 27.87 | 27.90 | 27.93 | 27.89 |
| measured refl. | 17141 | 43644 | 7105 | 29399 | 12649 | 37696 |
| independent refl. | 4846 | 8356 | 1664 | 6662 | 5571 | 7562 |
| R(int) | 0.0572 | 0.0907 | 0.0365 | 0.0903 | 0.0742 | 0.0828 |
| refined parameters | – | – | 71 | 291 | 292 | 280 |
| *R*1 (*R*1 all data) | – | – | 0.0222 (0.228) | 0.0719 (0.1172) | 0.0406 (0.1737) | 0.0695 (0.0965) |
| *wR*2 (*wR*2 all data) | – | – | 0.0568 (0.0571) | 0.1439 (0.1588) | 0.0818 (0.1045) | 0.2090 (0.2364) |
| max, min peaks [eÅ$^{-3}$] | – | – | 0.232, -0.151 | 0.565, -0.396 | 0.394, -0.223 | 3.191, -1.993 |
| CCDC Number | – | – | 1837111 | 1837112 | 1837113 | 1837114 |

**Figure S1-1:** Thermal ellipsoid plot of the structure of **3** with 30% probability. Selected hydrogen atoms and disordered units of minor occupancy are omitted for clarity.

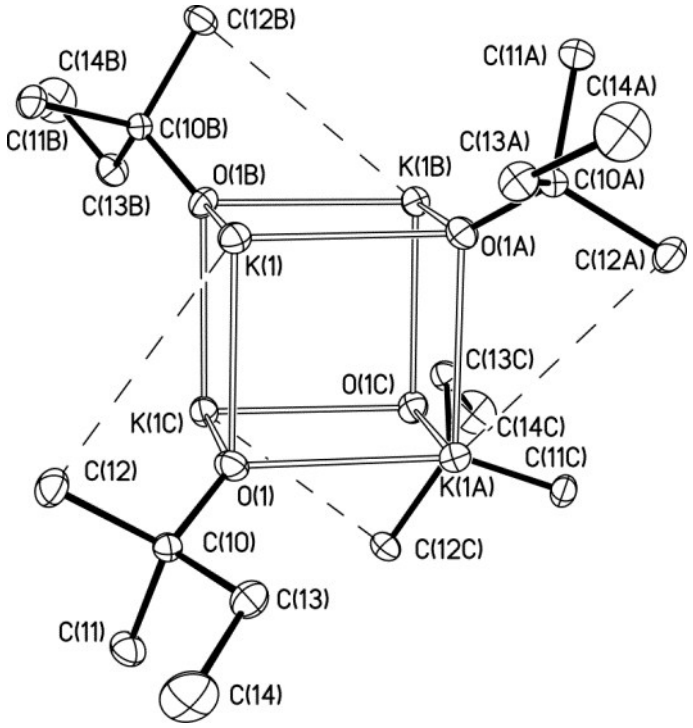



**Figure S1-2:** Thermal ellipsoid plot of the structure of **3a** with 30% probability. Selected hydrogen atoms and disordered units of minor occupancy are omitted for clarity.

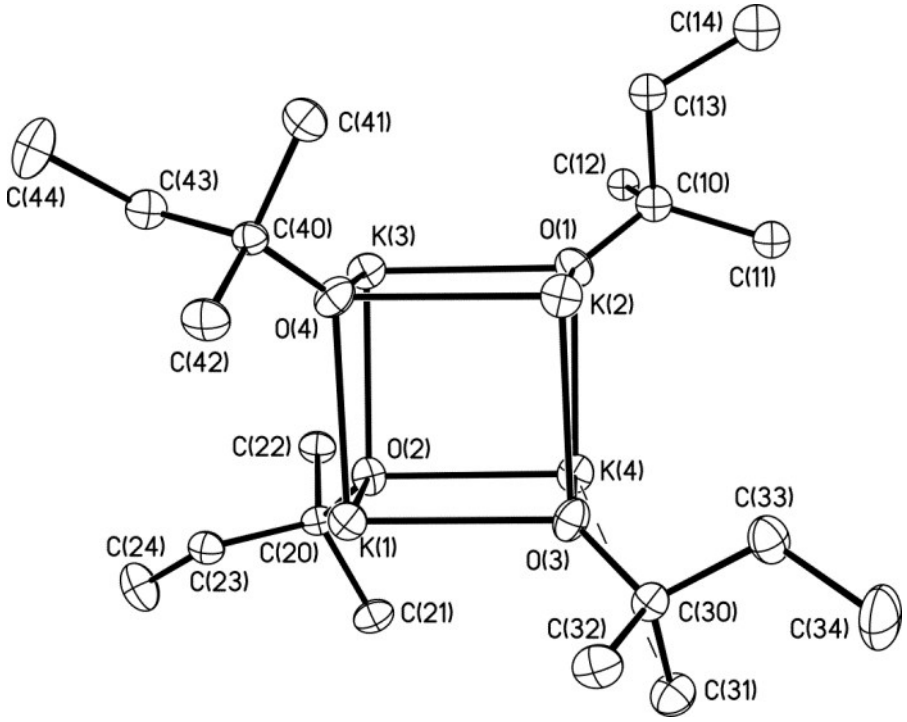


**Figure S1-3:** Thermal ellipsoid plot of the structure of **4** with 30% probability. Selected hydrogen atoms and disordered units of minor occupancy are omitted for clarity.

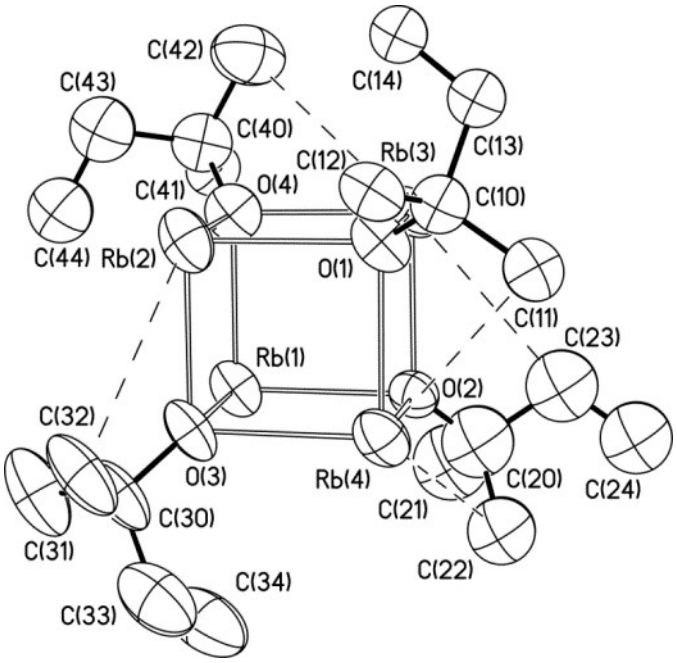



**Figure S1-4:** Thermal ellipsoid plot of the structure of **5** with 30% probability. Selected hydrogen atoms and disordered units of minor occupancy are omitted for clarity. Both crystallographically independent units are shown.

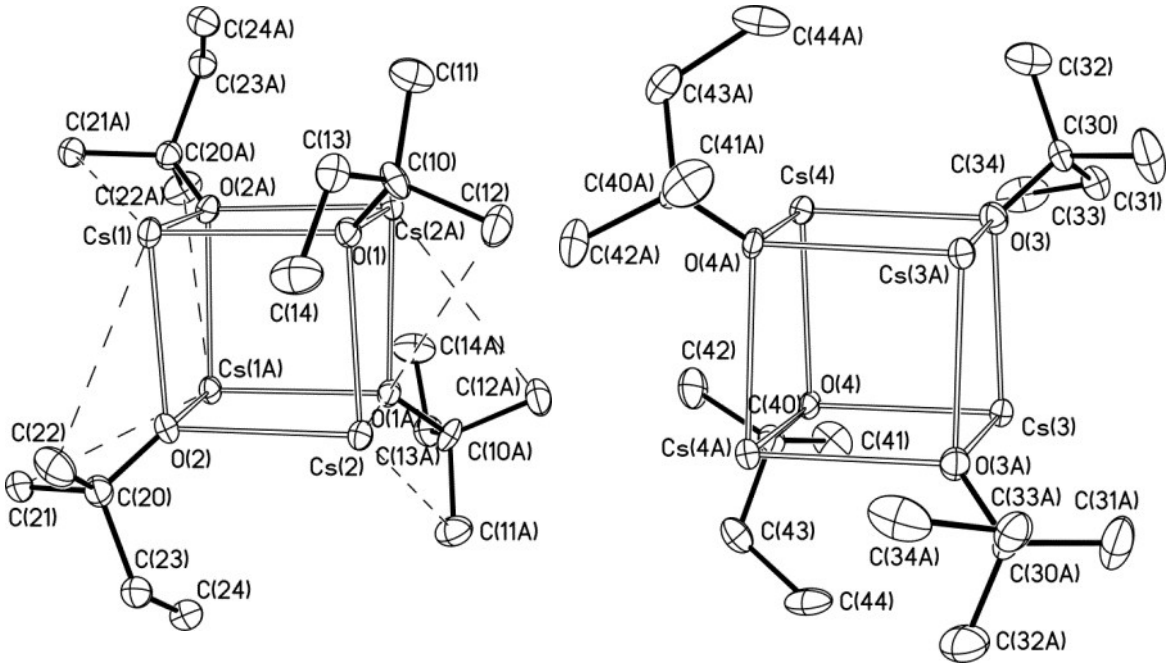



**Table S3: Selected bond lengths (Å) and angles (°) for compounds 3, polymorphic 3a, 4, and 5**:

| | **3** (M = K) | | **3a** (M = K) | | **4** (M = Rb) | | **5** (M = Cs) | |
|---|---|---|---|---|---|---|---|---|
| M-O | K(1)-O(1)#1 | 2.6023(12) | K(1)-O(3) | 2.605(3) | Rb(1)-O(3) | 2.751(9) | Cs(1)-O(1) | 2.895(10) |
| | K(1)-O(1)#2 | 2.6168(12) | K(1)-O(2) | 2.614(3) | Rb(1)-O(4) | 2.758(11) | Cs(1)-O(2) | 2.918(11) |
| | K(1)-O(1) | 2.6416(12) | K(1)-O(4) | 2.635(3) | Rb(1)-O(2) | 2.802(10) | Cs(1)-O(2)#1 | 2.925(11) |
| | | | K(2)-O(4) | 2.608(3) | Rb(2)-O(3) | 2.762(11) | Cs(2)-O(2) | 2.902(10) |
| | | | K(2)-O(3) | 2.613(3) | Rb(2)-O(1) | 2.763(10) | Cs(2)-O(1) | 2.932(10) |
| | | | K(2)-O(1) | 2.615(3) | Rb(2)-O(4) | 2.776(10) | Cs(2)-O(1)#1 | 2.938(10) |
| | | | K(3)-O(1) | 2.605(3) | Rb(3)-O(4) | 2.735(11) | Cs(3)-O(4) | 2.884(9) |
| | | | K(3)-O(4) | 2.622(3) | Rb(3)-O(1) | 2.772(9) | Cs(3)-O(3) | 2.915(11) |
| | | | K(3)-O(2) | 2.622(3) | Rb(3)-O(2) | 2.785(10) | Cs(3)-O(3)#4 | 2.917(11) |
| | | | K(4)-O(1) | 2.619(3) | Rb(4)-O(2) | 2.737(10) | Cs(4)-O(3) | 2.879(11) |
| | | | K(4)-O(2) | 2.621(3) | Rb(4)-O(1) | 2.780(10) | Cs(4)-O(4)#4 | 2.914(10) |
| | | | K(4)-O(3) | 2.625(3) | Rb(4)-O(3) | 2.788(10) | Cs(4)-O(4) | 2.932(10) |
| M-Me | K(1)-C(11)#3 | 3.498(2) | K(2)-C(13) | 3.40(5) | Rb(1)-C(21) | 3.65(2) | Cs(1)-C(21A)#1 | 3.75(11) |
| | K(1)-C(12) | 3.509(2) | K(2)-C(12B)#1 | 3.475(12) | Rb(2)-C(24A)#1 | 3.47(3) | Cs(1)-C(24A)#1 | 3.76(17) |
| | | | K(2)-C(12)#1 | 3.48(8) | Rb(2)-C(43A) | 3.67(3) | Cs(1)-C(12)#2 | 3.838(16) |
| | | | K(2)-C(12A)#1 | 3.504(12) | Rb(2)-C(32) | 3.707(16) | Cs(1)-C(23A)#1 | 3.84(11) |
| | | | K(4)-C(14)#2 | 2.91(5) | Rb(3)-C(23A) | 3.71(3) | Cs(1)-C(21)#1 | 3.89(2) |
| | | | K(4)-C(13A) | 3.421(10) | Rb(4)-C(22A) | 3.43(4) | Cs(2)-C(11)#1 | 3.821(19) |
| | | | K(4)-C(32)#3 | 3.463(4) | | | Cs(2)-C(21)#3 | 3.830(18) |
| | | | | | | | Cs(3)-C(31)#4 | 3.71(2) |
| | | | | | | | Cs(3)-C(33) | 3.863(19) |
| | | | | | | | Cs(4)-C(43)#4 | 3.810(19) |
| | | | | | | | Cs(4)-C(44)#4 | 3.903(18) |
| | | | | | | | Cs(4)-C(31)#2 | 3.91(2) |
| O-M-O | O(1)#1-K(1)-O(1)#2 | 90.84(4) | O(3)-K(1)-O(2) | 91.69(9) | O(3)-Rb(1)-O(4) | 88.9(3) | O(1)-Cs(1)-O(2) | 87.7(3) |
| | O(1)#1-K(1)-O(1) | 90.29(4) | O(3)-K(1)-O(4) | 91.35(9) | O(3)-Rb(1)-O(2) | 88.7(3) | O(1)-Cs(1)-O(2)#1 | 86.5(3) |
| | O(1)#2-K(1)-O(1) | 90.80(4) | O(2)-K(1)-O(4) | 90.33(9) | O(4)-Rb(1)-O(2) | 88.9(3) | O(2)-Cs(1)-O(2)#1 | 86.7(3) |
| | | | O(4)-K(2)-O(3) | 91.79(9) | O(3)-Rb(2)-O(1) | 91.1(3) | O(2)-Cs(2)-O(1)#1 | 86.1(3) |
| | | | O(4)-K(2)-O(1) | 90.21(9) | O(3)-Rb(2)-O(4) | 88.2(3) | O(1)-Cs(2)-O(1)#1 | 89.1(3) |
| | | | O(3)-K(2)-O(1) | 89.38(9) | O(1)-Rb(2)-O(4) | 88.5(3) | O(2)-Cs(2)-O(1) | 87.4(3) |
| | | | O(1)-K(3)-O(4) | 90.13(9) | O(4)-Rb(3)-O(1) | 89.1(3) | O(4)-Cs(3)-O(3) | 88.0(3) |
| | | | O(1)-K(3)-O(2) | 91.29(9) | O(4)-Rb(3)-O(2) | 89.8(3) | O(4)-Cs(3)-O(3)#4 | 85.8(3) |
| | | | O(4)-K(3)-O(2) | 90.46(9) | O(1)-Rb(3)-O(2) | 88.1(3) | O(3)-Cs(3)-O(3)#4 | 87.1(3) |
| | | | O(1)-K(4)-O(2) | 91.01(9) | O(2)-Rb(4)-O(1) | 88.9(3) | O(3)-Cs(4)-O(4)#4 | 86.0(3) |
| | | | O(1)-K(4)-O(3) | 89.05(9) | O(2)-Rb(4)-O(3) | 89.3(3) | O(3)-Cs(4)-O(4) | 87.8(3) |
| | | | O(2)-K(4)-O(3) | 91.07(9) | O(1)-Rb(4)-O(3) | 90.2(3) | O(4)#4-Cs(4)-O(4) | 88.9(3) |
| M-O-M | K(1)#4-O(1)-K(1)#2 | 89.70(4) | K(3)-O(1)-K(2) | 89.92(9) | Rb(2)-O(1)-Rb(3) | 90.9(3) | Cs(1)-O(1)-Cs(2) | 92.3(3) |
| | K(1)#4-O(1)-K(1) | 89.16(4) | K(3)-O(1)-K(4) | 89.06(9) | Rb(2)-O(1)-Rb(4) | 89.4(3) | Cs(1)-O(1)-Cs(2)#1 | 93.6(3) |
| | K(1)#2-O(1)-K(1) | 89.19(4) | K(2)-O(1)-K(4) | 90.80(9) | Rb(3)-O(1)-Rb(4) | 91.2(3) | Cs(2)-O(1)-Cs(2)#1 | 90.7(3) |
| | | | K(1)-O(2)-K(4) | 88.57(9) | Rb(4)-O(2)-Rb(3) | 91.9(3) | Cs(2)-O(2)-Cs(1) | 92.4(3) |
| | | | K(1)-O(2)-K(3) | 89.77(9) | Rb(4)-O(2)-Rb(1) | 91.0(3) | Cs(2)-O(2)-Cs(1)#1 | 93.8(3) |
| | | | K(4)-O(2)-K(3) | 88.63(9) | Rb(3)-O(2)-Rb(1) | 89.6(3) | Cs(1)-O(2)-Cs(1)#1 | 93.2(3) |
| | | | K(1)-O(3)-K(2) | 88.69(9) | Rb(1)-O(3)-Rb(2) | 91.7(3) | Cs(4)-O(3)-Cs(3) | 92.2(3) |
| | | | K(1)-O(3)-K(4) | 88.68(9) | Rb(1)-O(3)-Rb(4) | 91.0(3) | Cs(4)-O(3)-Cs(3)#4 | 94.1(3) |
| | | | K(2)-O(3)-K(4) | 90.69(9) | Rb(2)-O(3)-Rb(4) | 89.2(3) | Cs(3)-O(3)-Cs(3)#4 | 92.7(3) |
| | | | K(2)-O(4)-K(3) | 89.73(9) | Rb(3)-O(4)-Rb(1) | 91.6(3) | Cs(3)-O(4)-Cs(4)#4 | 94.1(3) |
| | | | K(2)-O(4)-K(1) | 88.16(8) | Rb(3)-O(4)-Rb(2) | 91.4(3) | Cs(3)-O(4)-Cs(4) | 91.7(3) |
| | | | K(3)-O(4)-K(1) | 89.32(9) | Rb(1)-O(4)-Rb(2) | 91.2(3) | Cs(4)#4-O(4)-Cs(4) | 90.9(3) |
| Symm | #1 y,-x+1,-z | | #1 x,y+1,z | | #1 x-1/2,y-1/2,z-1/2 | | #1 -x+1,y,-z+1/2 | |
| | #2 -x+1,-y+1,z | | #2 x,-y-1/2,z-1/2 | | | | #2 x,y+1,z | |
| | #3 x-1,y,z | | #3 x,y-1,z | | | | #3 x,y-1,z | |
| | #4 -y+1,x,-z | | #4 x,-y-1/2,z+1/2 | | | | #4 -x,y,-z+1/2 | |
| | #5 x+1,y,z | | | | | | | |

**NMR spectroscopy**

**Table S4:** NMR spectroscopic data for compounds **1**, **2**, **3**, **4,** and **5** at 21° in [$D_6$]benzene [ppm].

| | $^{1}$H | | | $^{13}$C | | | | $^{7}$Li/$^{133}$Cs |
|---|---|---|---|---|---|---|---|---|
| | Me | Et-Me | Et-$CH_2$ | Me | Et-Me | Et-$CH_2$ | *tert*-C | |
| **1**, LiO*t*Am | 1.24 | 0.99 | 1.51 | 32.5 | 10.9 | 41.5 | 69.3 | 0.94 |
| **2**, NaO*t*Am | 1.10 | 0.99 | 1.34 | 34.2 | 10.4 | 42.2 | 67.8 | — |
| **3**, KO*t*Am | 1.01 | 0.98 | 1.29 | 34.9 | 10.4 | 41.9 | 68.4 | — |
| **4**, RbO*t*Am | 1.05 | 0.99 | 1.34 | 34.9 | 10.4 | 41.8 | 68.9 | — |
| **5**, CsO*t*Am | 1.15 | 1.04 | 1.41 | 34.7 | 10.5 | 41.6 | 70.1 | 202.1 |

**Table S5:** NMR spectroscopic data for compounds **1**, **2**, **3**, **4,** and **5** at 21° in [$D_{12}$]cyclohexane [ppm].

| | $^{1}$H | | | $^{13}$C | | | | $^{7}$Li/$^{133}$Cs |
|---|---|---|---|---|---|---|---|---|
| | Me | Et-Me | Et-$CH_2$ | Me | Et-Me | Et- $CH_2$ | *tert*-C | |
| **1**, LiO*t*Am | 1.12 | 0.90 | 1.39 | 32.6 | 11.1 | 41.9 | 69.7 | 1.31 |
| **2**, NaO*t*Am | 1.00 | 0.89 | 1.25 | 34.3 | 10.5 | 42.6 | 68.2 | — |
| **3**, KO*t*Am | 0.91 | 0.83 | 1.20 | 34.7 | 10.3 | 42.3 | 68.9 | — |
| **4**, RbO*t*Am | 0.93 | 0.83 | 1.20 | 34.6 | 10.3 | 42.2 | 69.4 | — |
| **5**, CsO*t*Am | 0.98 | 0.84 | 1.24 | 33.8 | 10.2 | 41.5 | 70.1 | 211.2 |

**Figure S2-1:** $^{1}$H NMR of **1**, LiO*t*Am [LiOCMe$_2$Et] in [D$_6$]benzene:

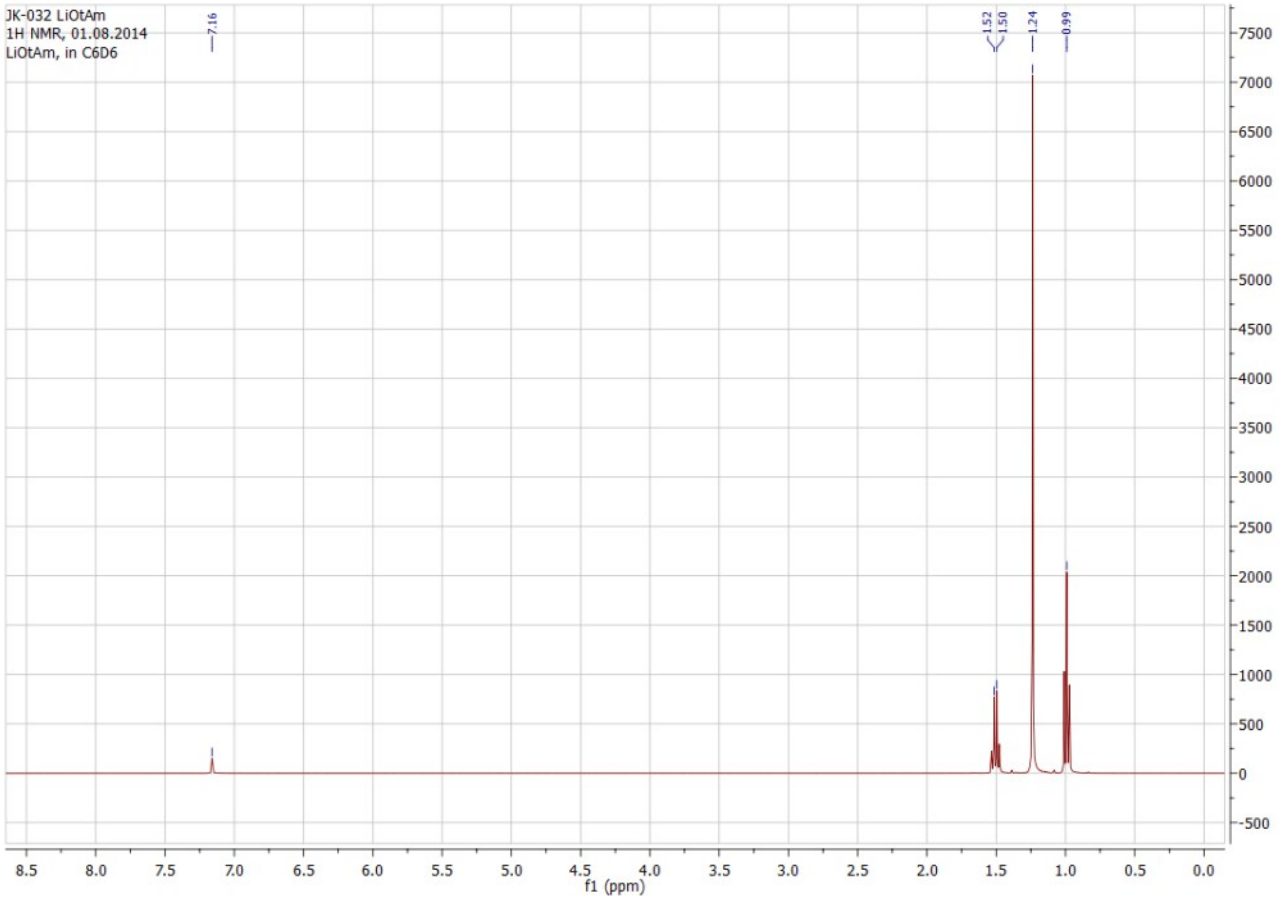



**Figure S2-2:** $^{13}$C NMR of **1**, LiO*t*Am [LiOCMe$_2$Et] in [D$_6$]benzene:

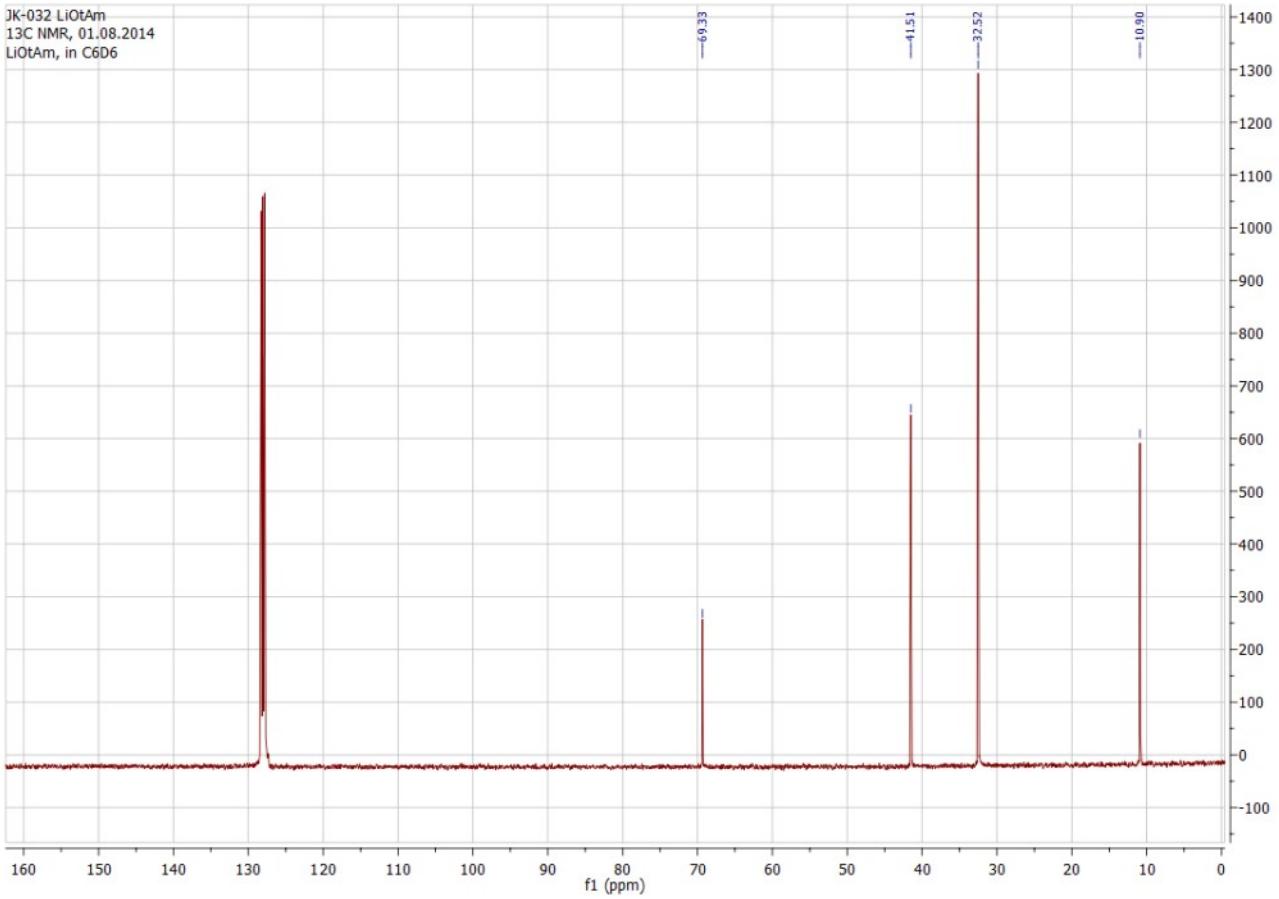


**Figure S2-3:** $^{1}H$-$^{13}C$ HSQC NMR of **1**, LiO*t*Am [$LiOCMe_2Et$] in [$D_6$]benzene:

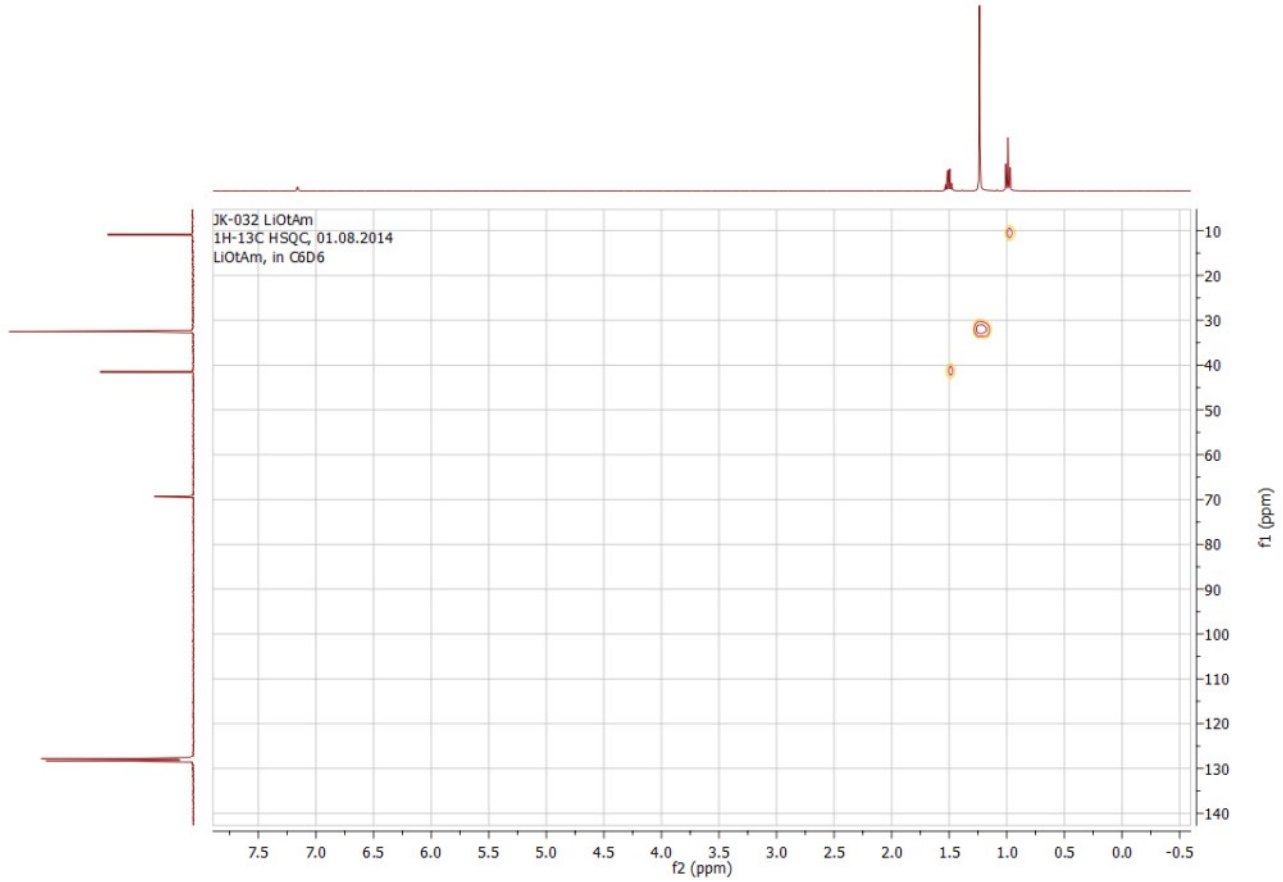



**Figure S2-4:** $^{1}H$ NMR of **1**, LiO*t*Am [$NaOCMe_2Et$] in [$D_6$]benzene:

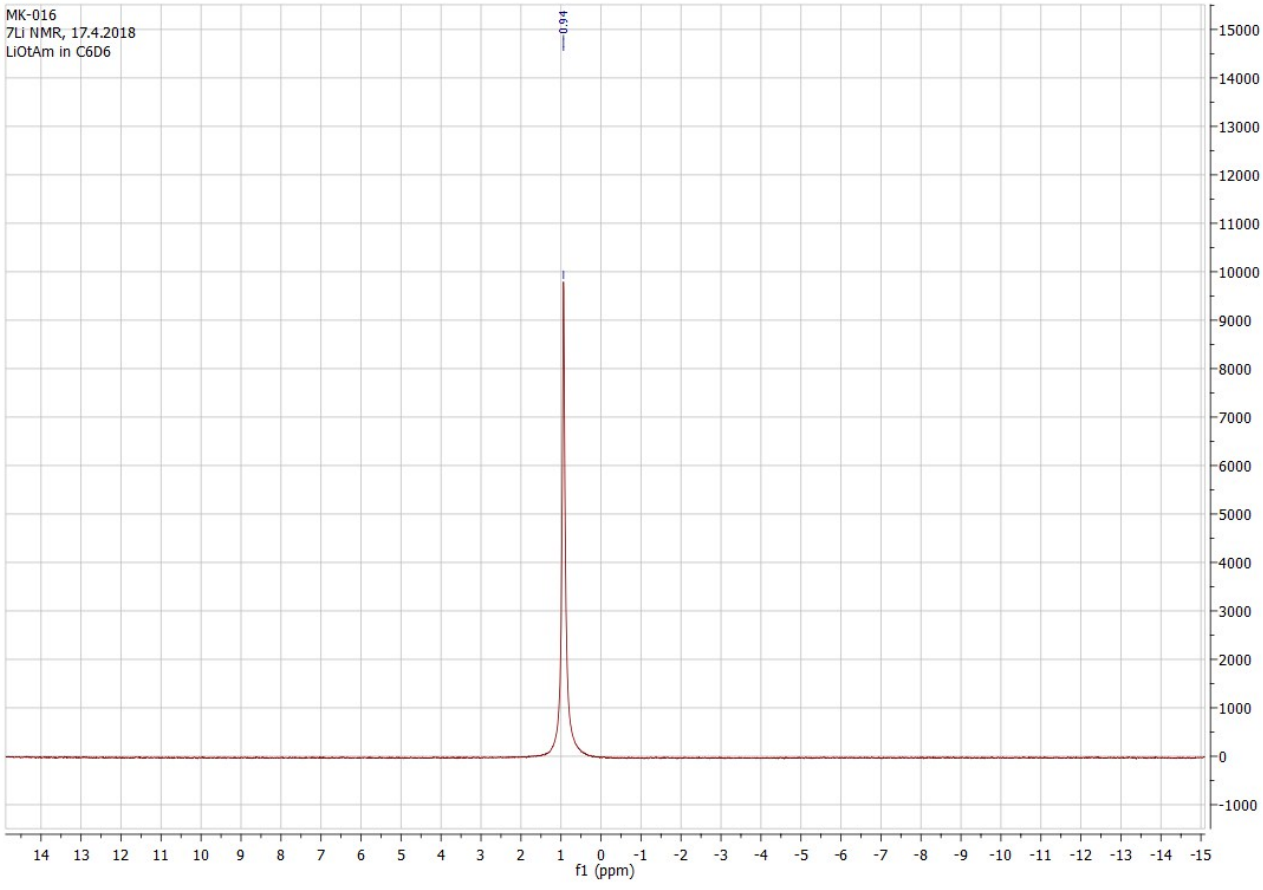


**Figure S2-5:** $^{1}$H NMR of **2**, NaO*t*Am [$NaOCMe_2Et$] in [$D_6$]benzene:

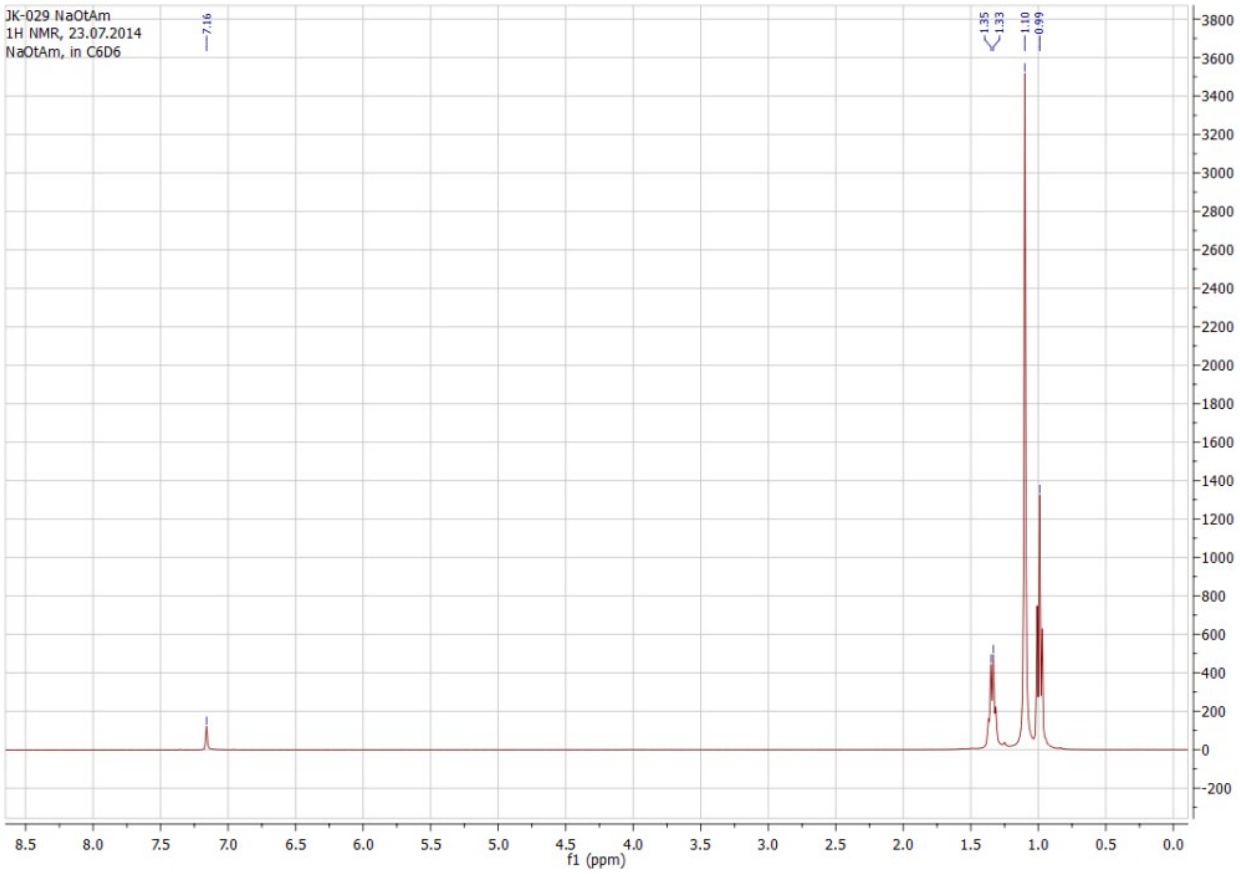



**Figure S2-6:** $^{13}$C NMR of **2**, NaO*t*Am [$NaOCMe_2Et$] in [$D_6$]benzene:

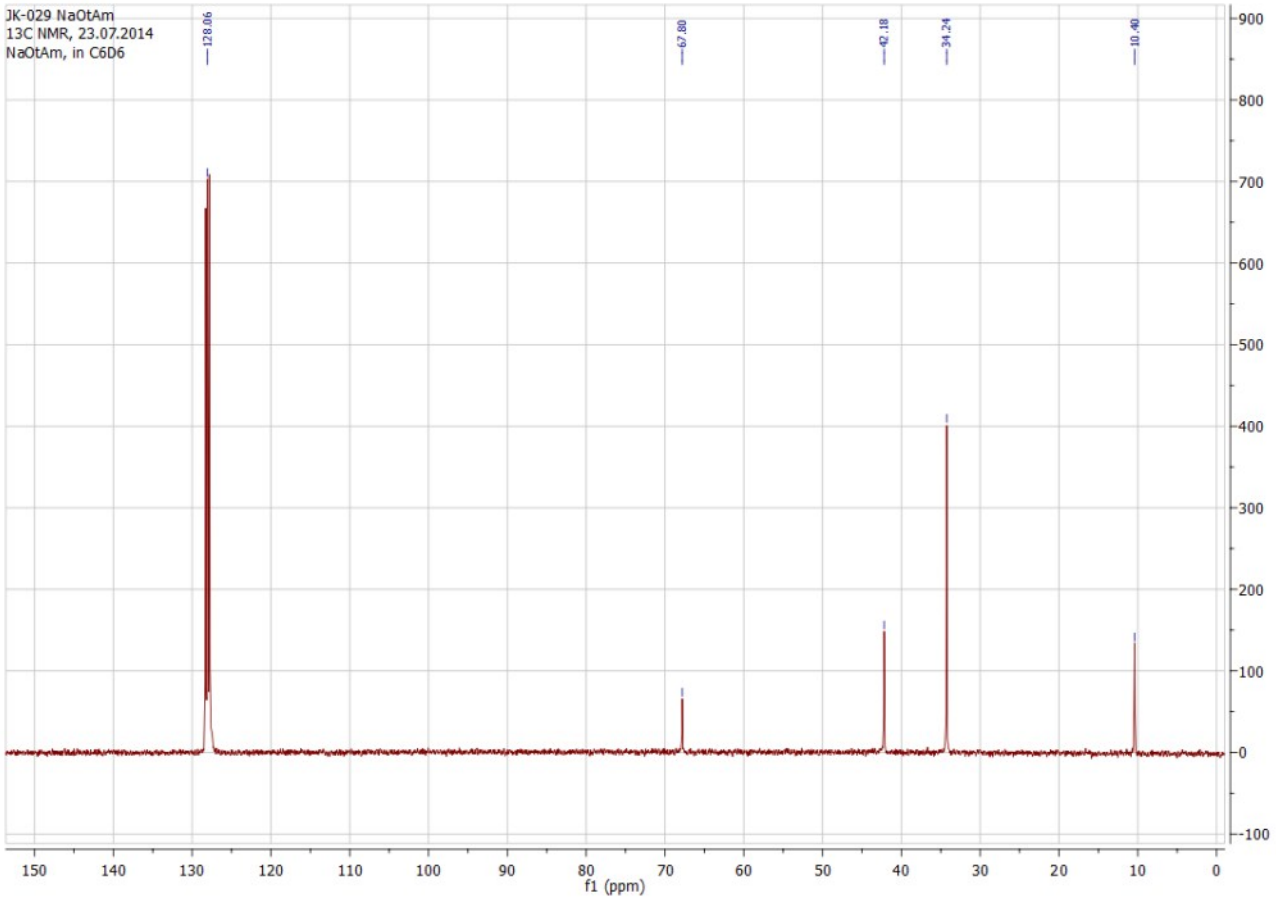


**Figure S2-7:** $^{1}H$-$^{13}C$ HSQC NMR of **2**, NaO*t*Am [$NaOCMe_2Et$] in [$D_6$]benzene:

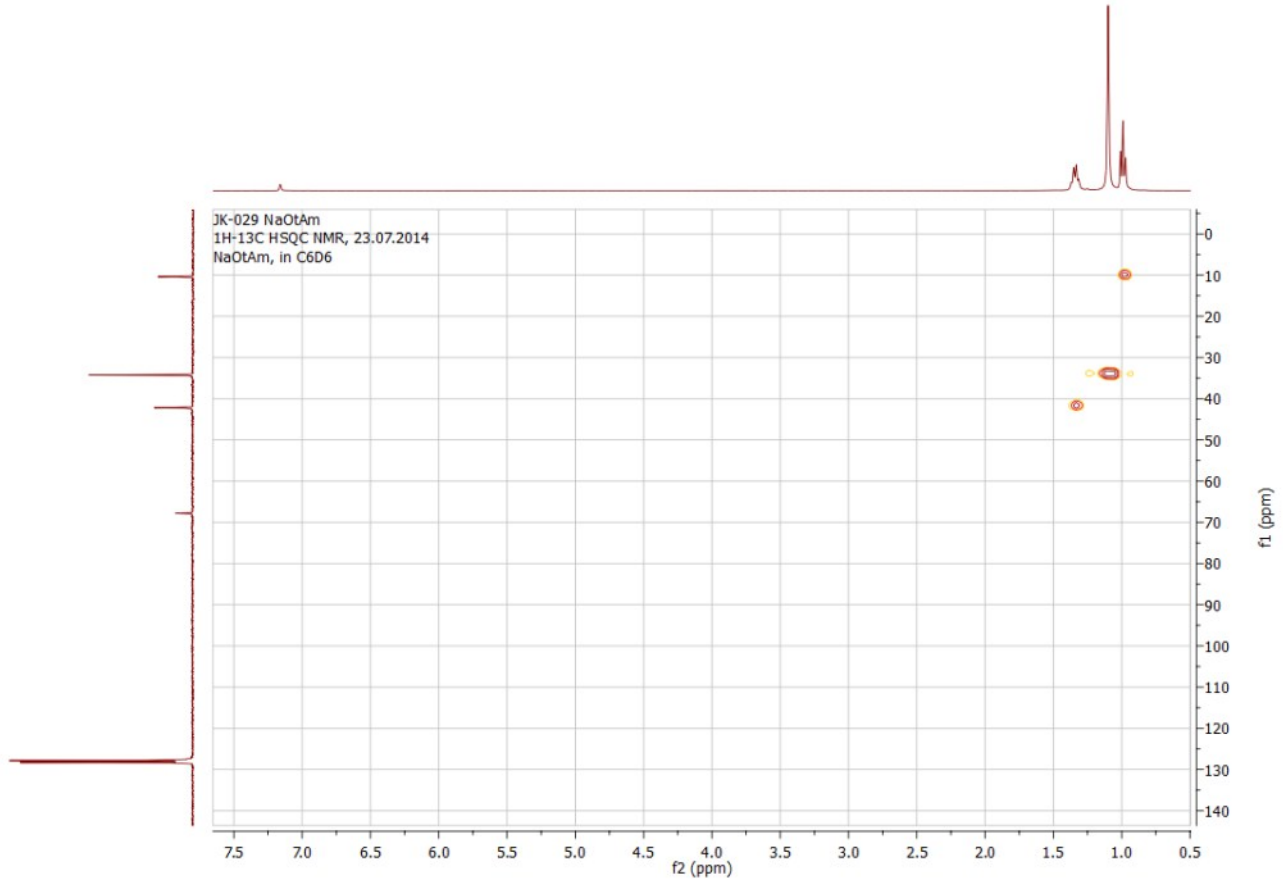



**Figure S2-8:** $^{1}H$ NMR of **3**, KO*t*Am [$KOCMe_2Et$] in [$D_6$]benzene:

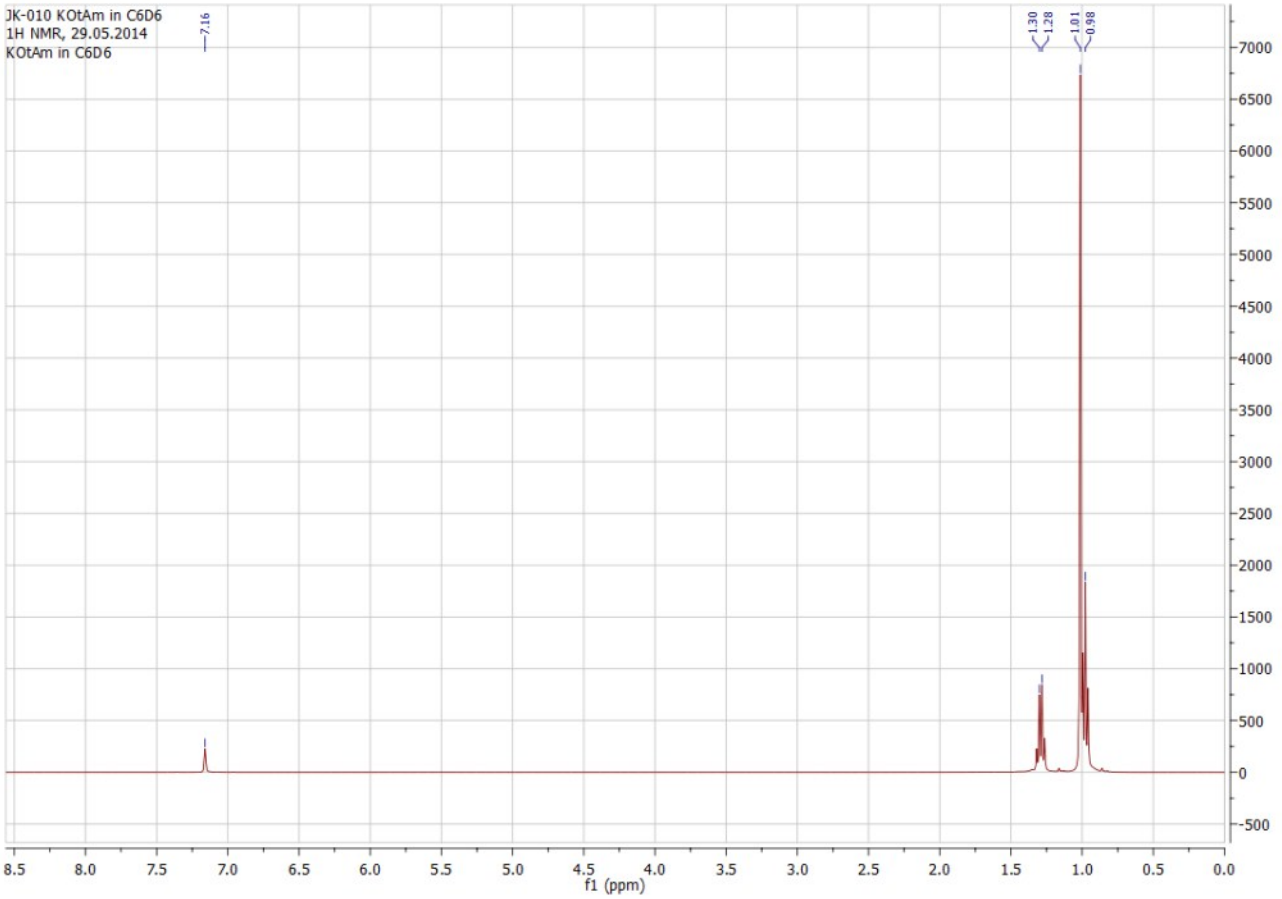


**Figure S2-9:** $^{13}C$ NMR of **3**, KO*t*Am [$KOCMe_2Et$] in [$D_6$]benzene:

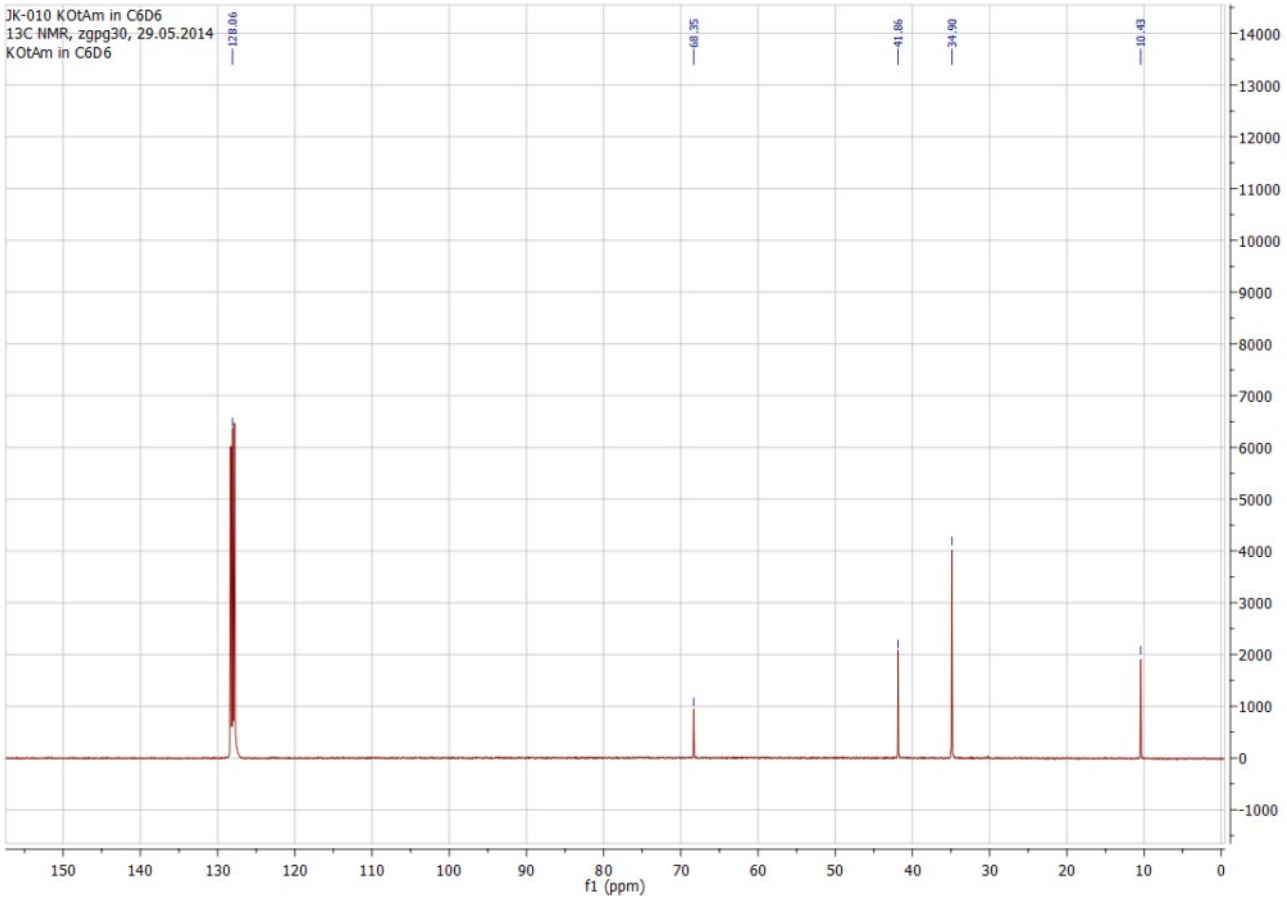



**Figure S2-10:** $^{1}H$-$^{13}C$ HSQC NMR of **3**, KO*t*Am [$KOCMe_2Et$] in [$D_6$]benzene:

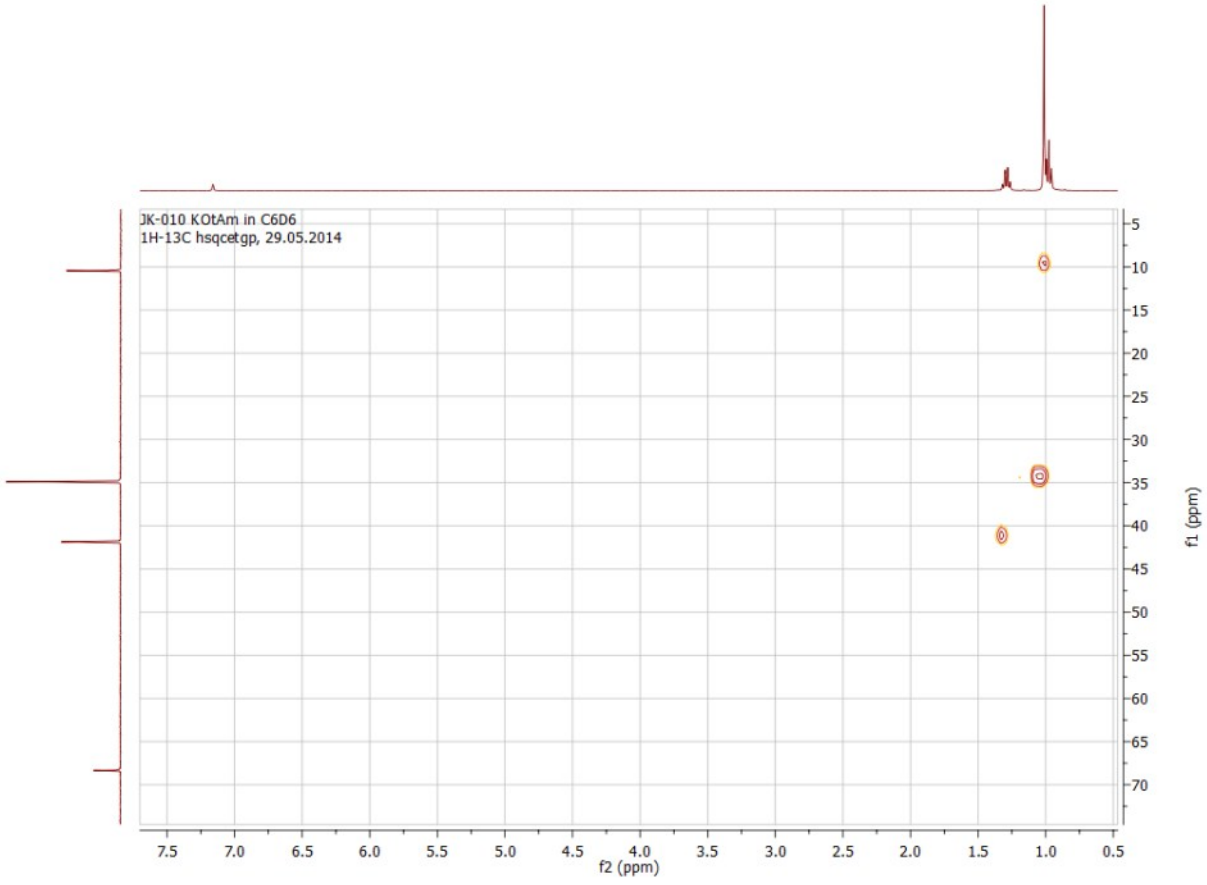


**Figure S2-11:** $^{1}$H NMR of **4**, RbO*t*Am [RbOCMe$_2$Et] in [D$_6$]benzene:

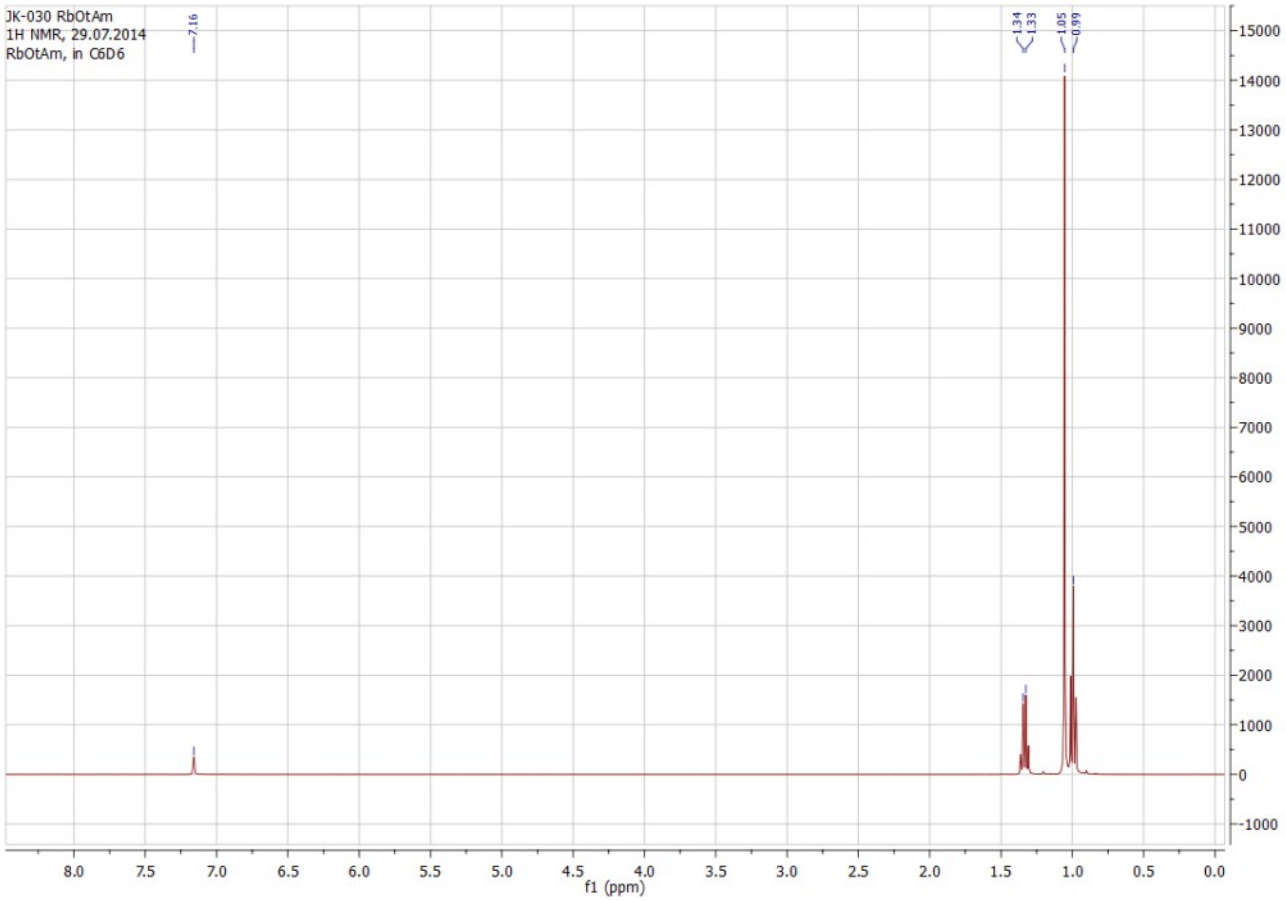



**Figure S2-12:** $^{13}$C NMR of **4**, RbO*t*Am [RbOCMe$_2$Et] in [D$_6$]benzene:

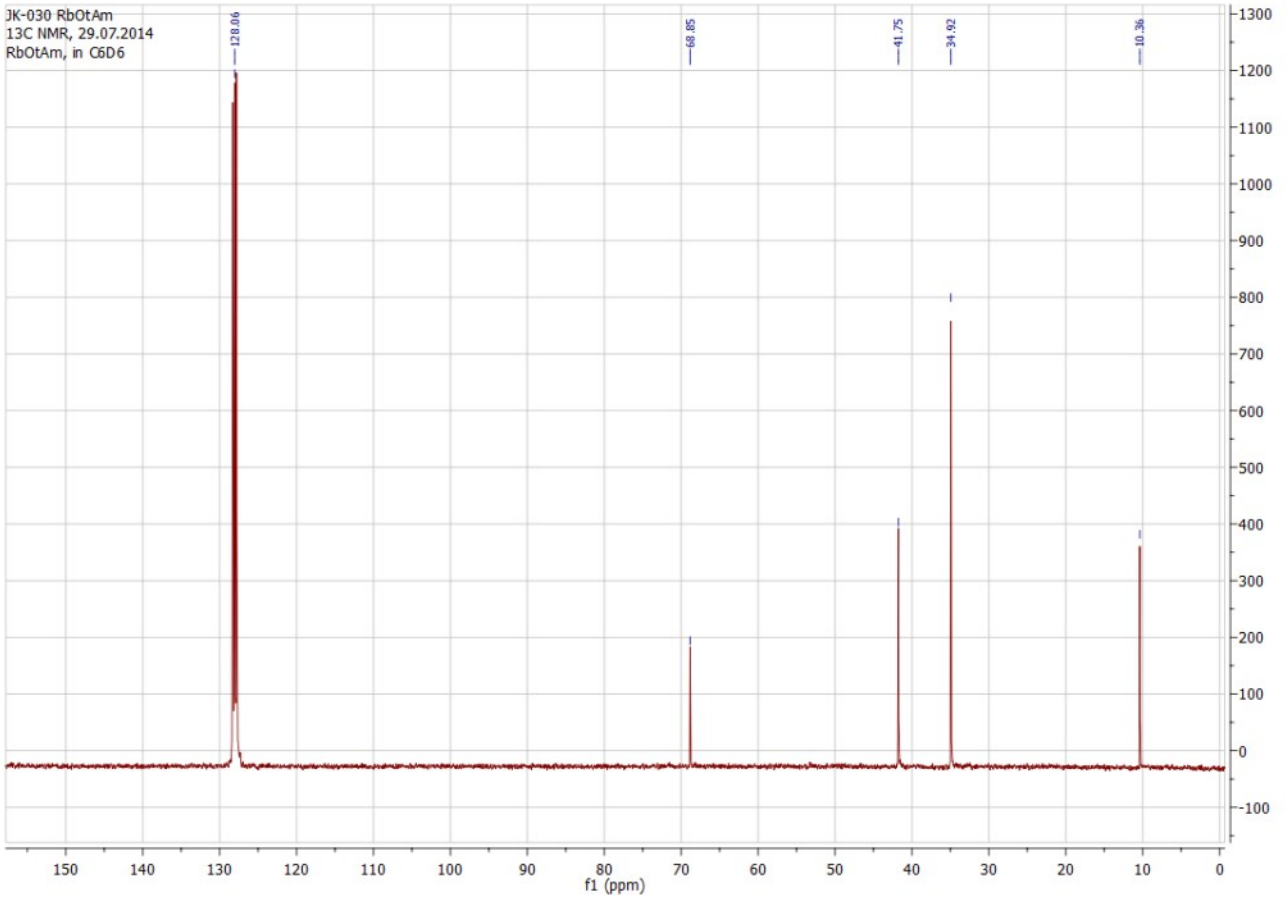


**Figure S2-13:** $^{1}H$-$^{13}C$ HSQC NMR of **4**, RbO*t*Am [$RbOCMe_2Et$] in [$D_6$]benzene:

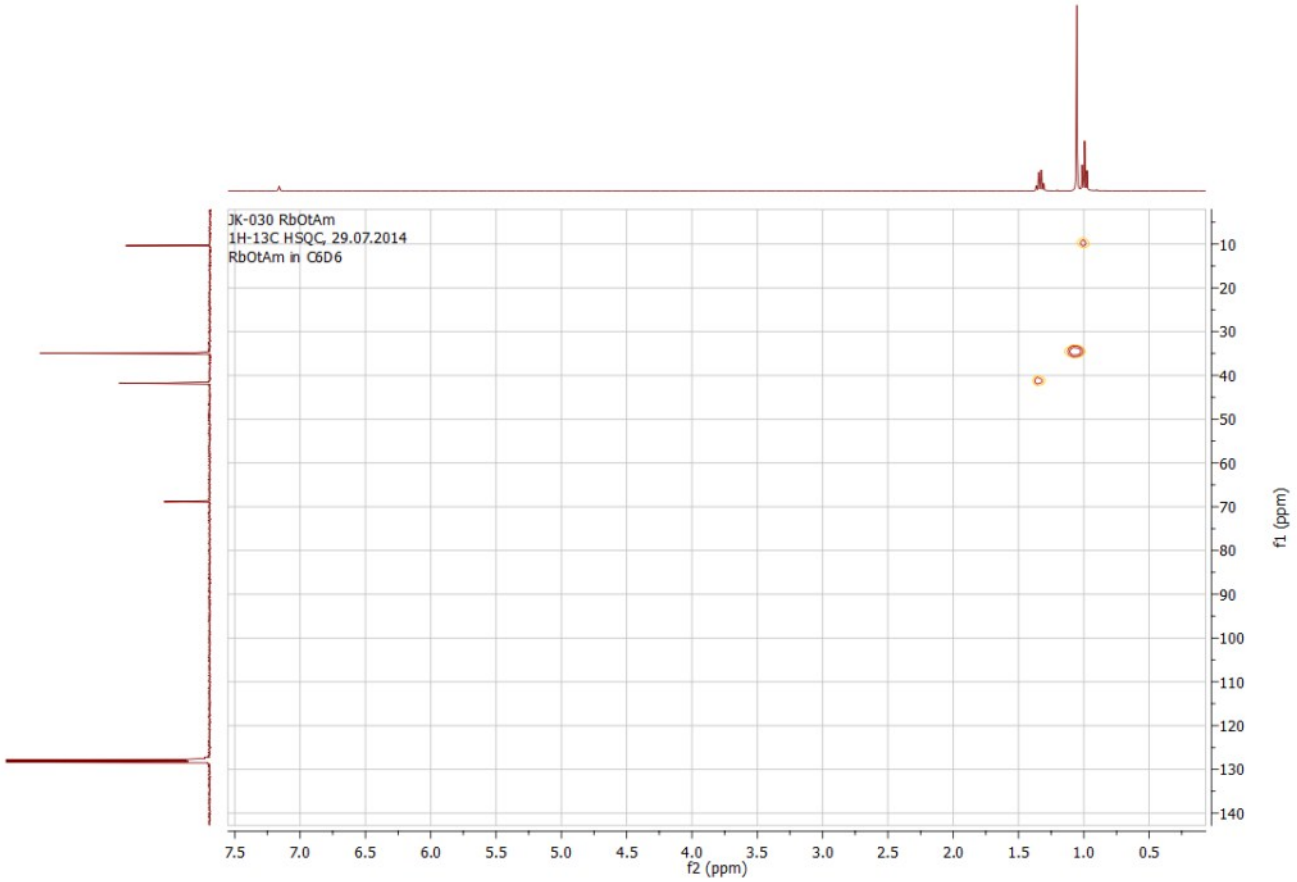



**Figure S2-14:** $^{1}H$ NMR of **5**, CsO*t*Am [$CsOCMe_2Et$] in [$D_6$]benzene:

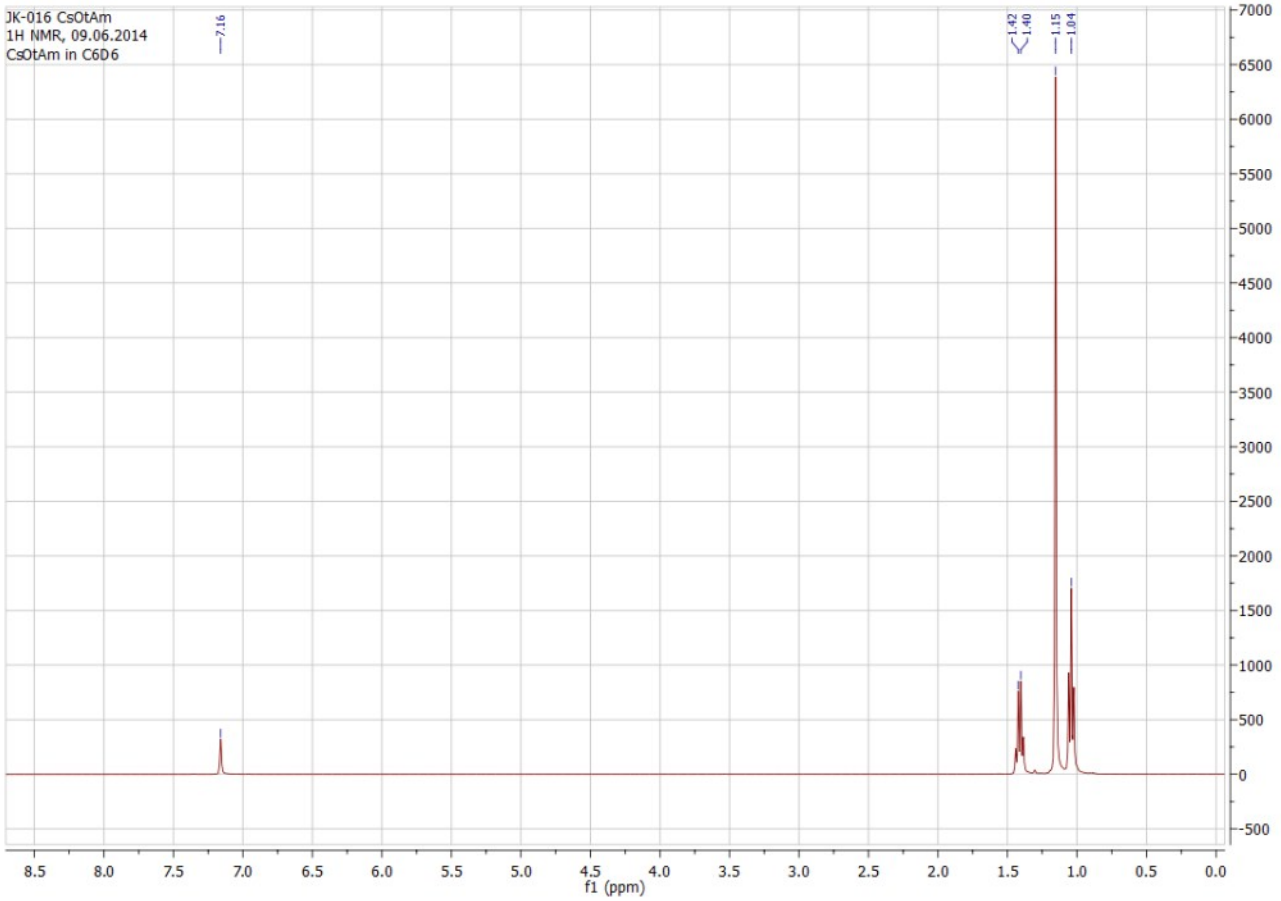


**Figure S2-15:** $^{13}C$ NMR of **5**, CsO*t*Am [$CsOCMe_2Et$] in [$D_6$]benzene:

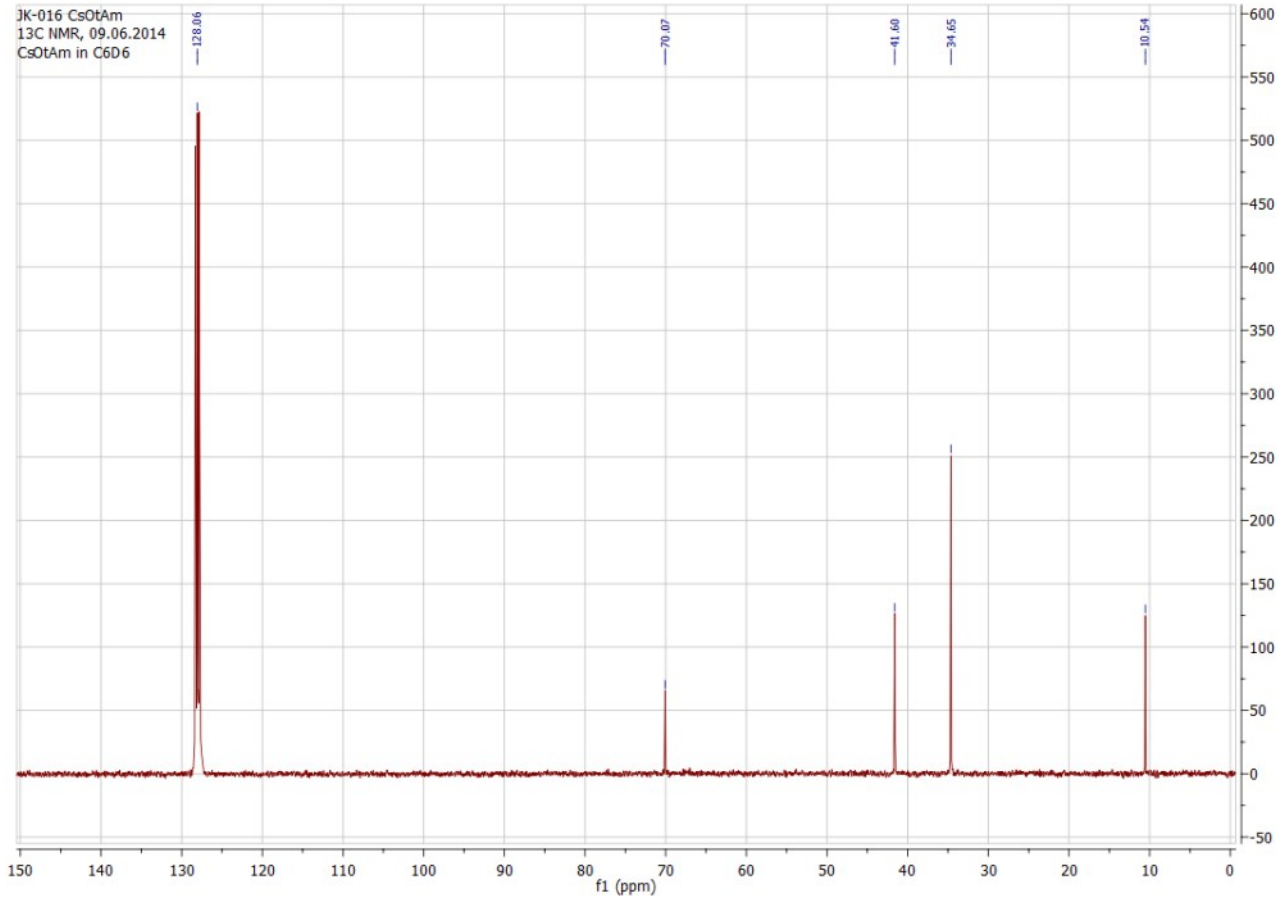



**Figure S2-16:** $^{1}H$-$^{13}C$ HSQC NMR of **5**, CsO*t*Am [$CsOCMe_2Et$] in [$D_6$]benzene:

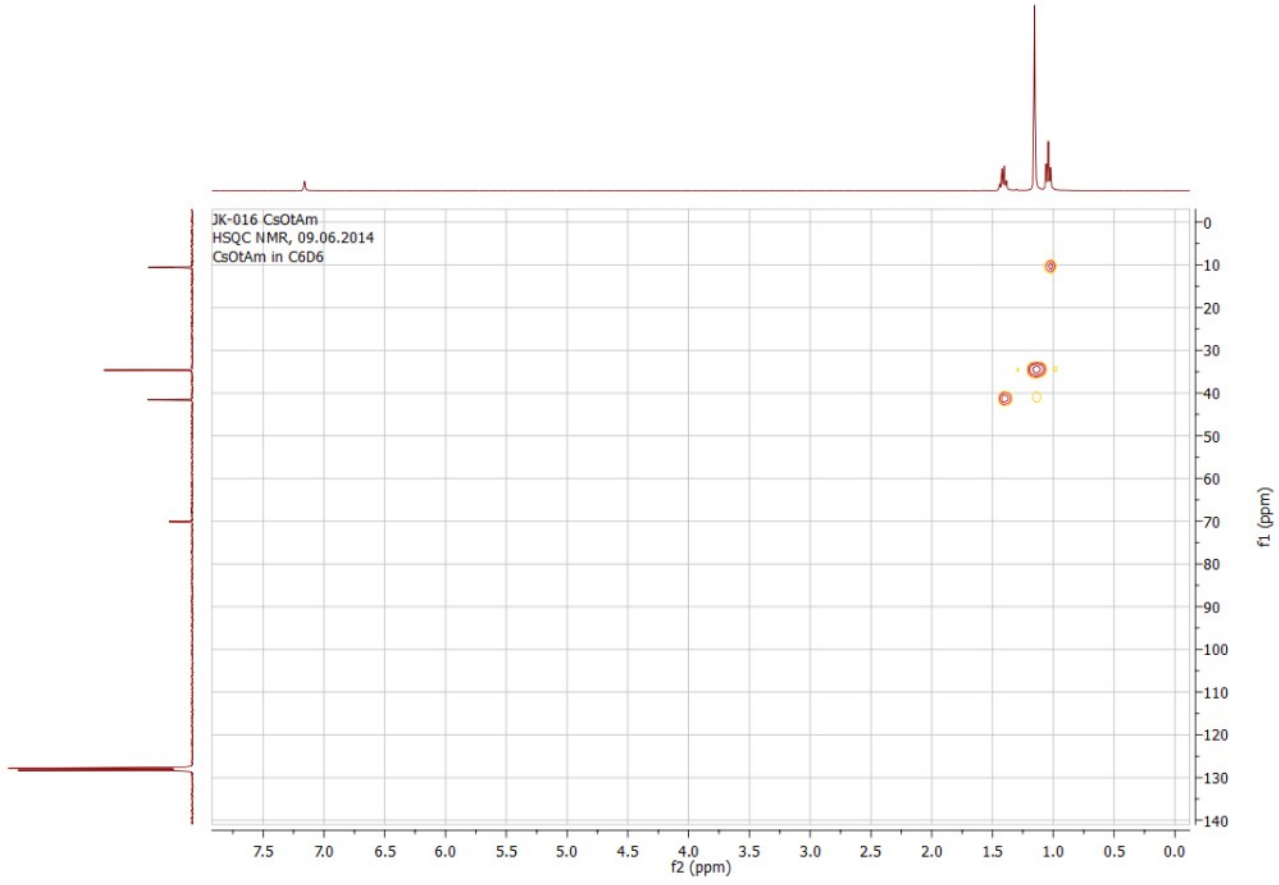


**Figure S2-17:** $^{133}$Cs NMR of **5**, CsO*t*Am [$CsOCMe_2Et$] in [$D_6$]benzene:

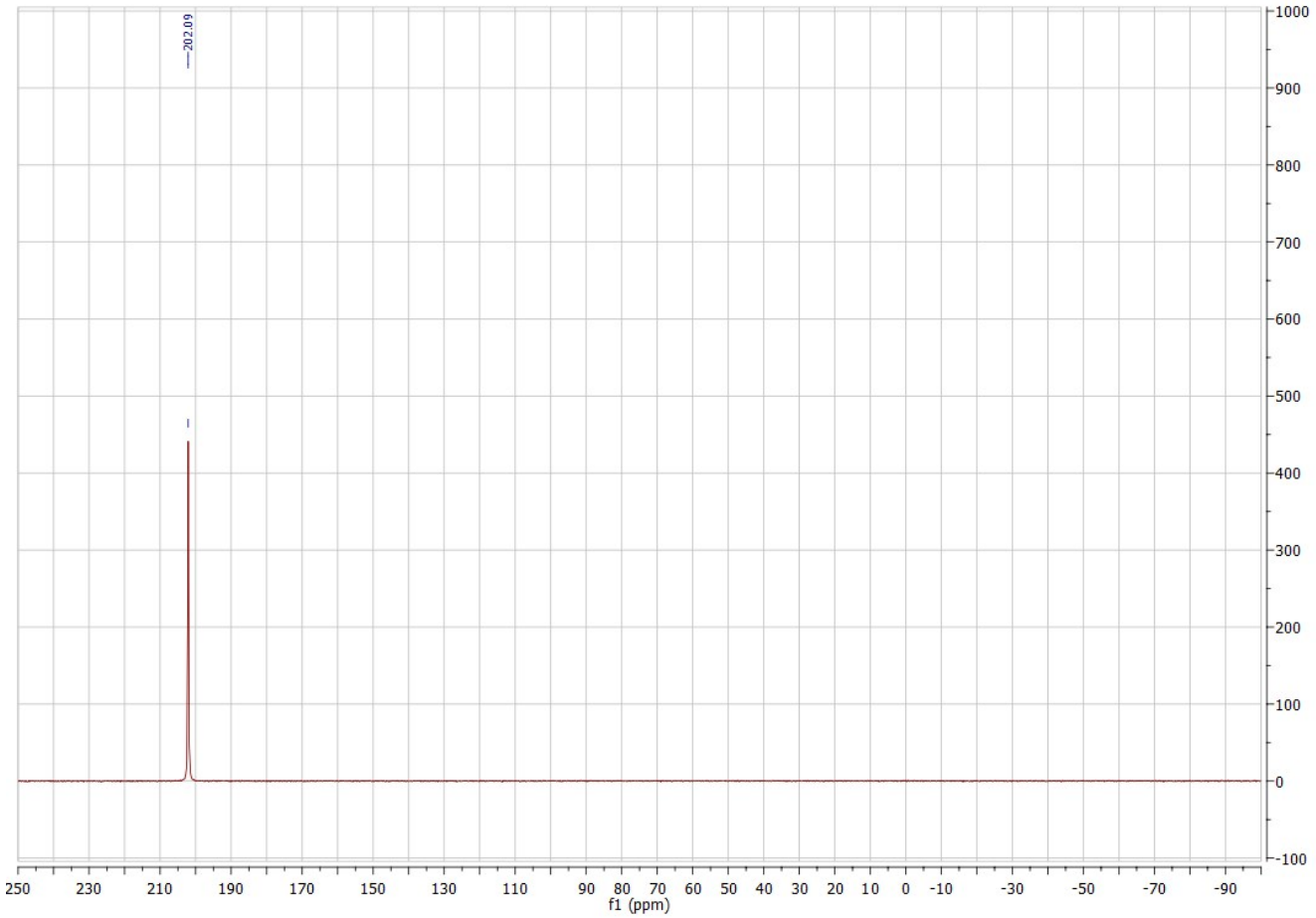



**Figure S2-18:** $^{1}$H NMR of **2**, LiO*t*Am [$LiOCMe_2Et$] in [$D_{12}$]cyclohexane:

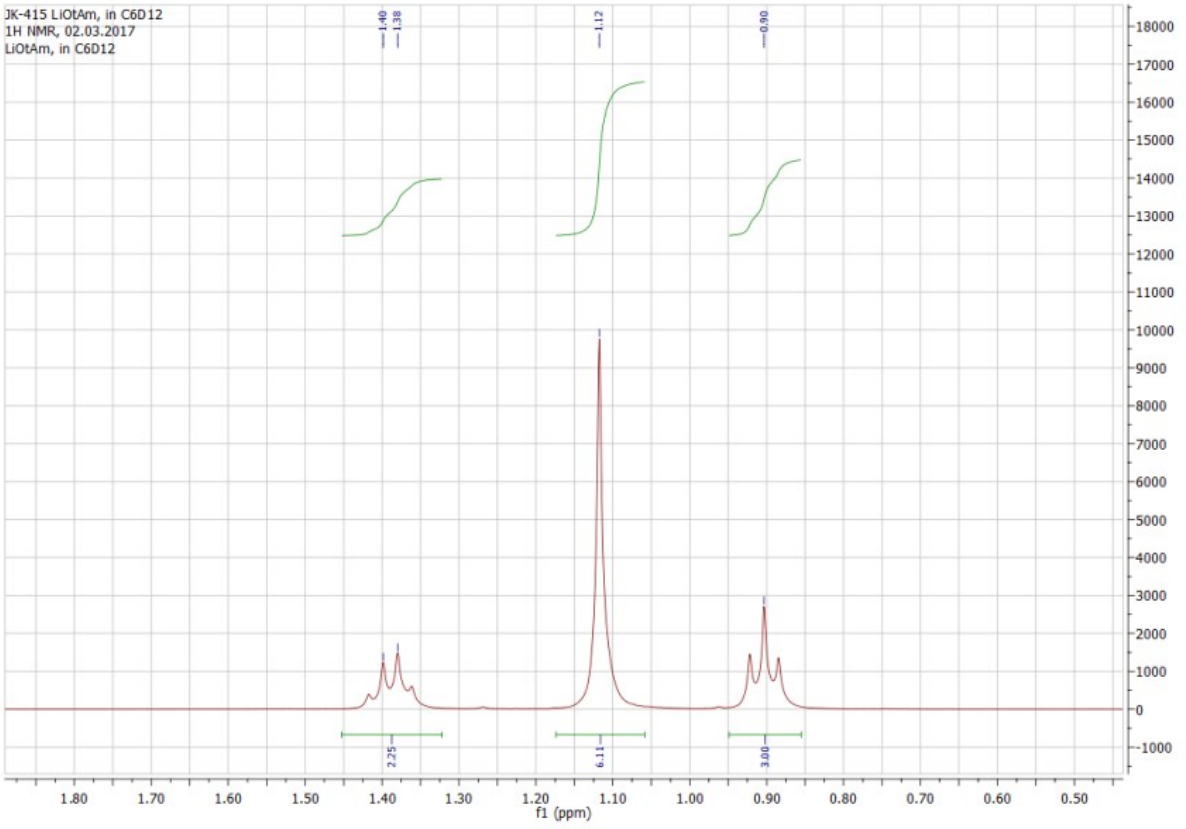


**Figure S2-19:** $^{13}C$ NMR of **2**, LiO*t*Am [$LiOCMe_2Et$] in [$D_{12}$]cyclohexane:

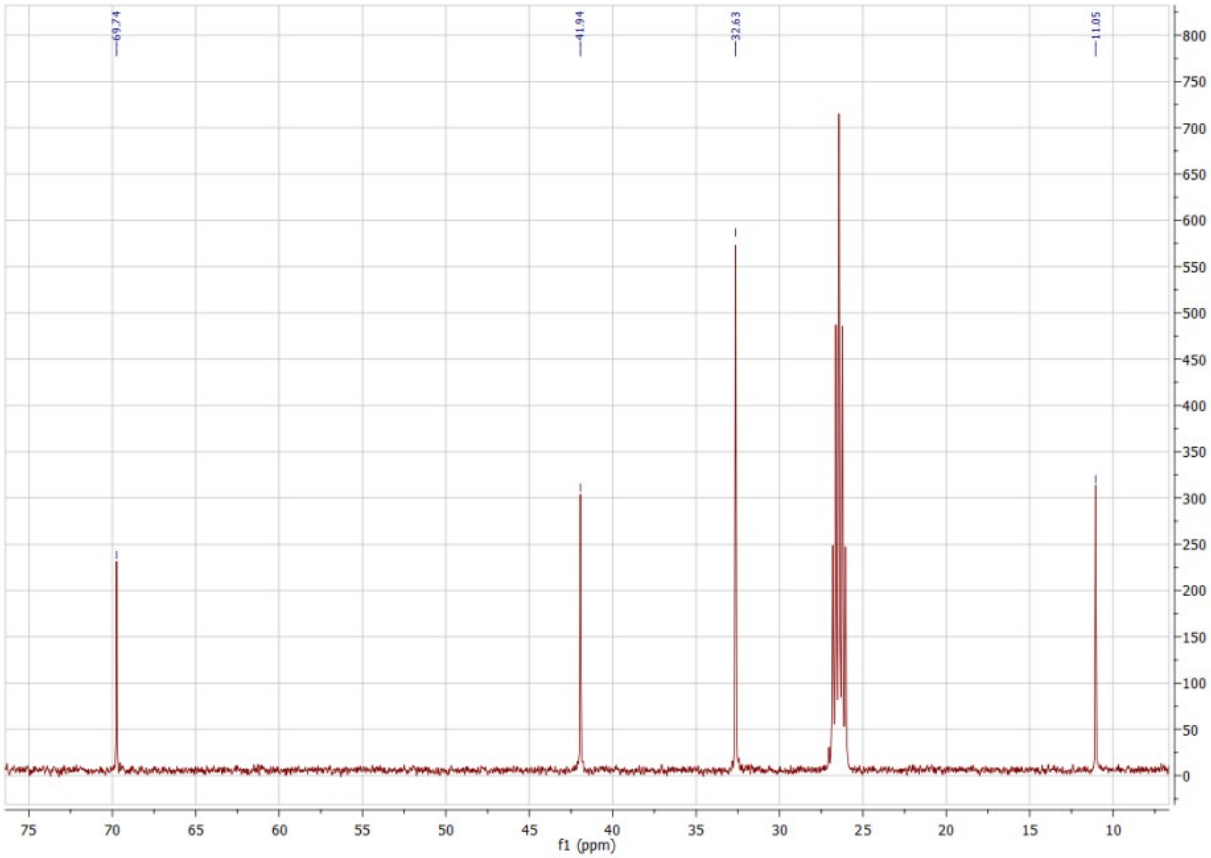



**Figure S2-20:** $^{7}Li$ NMR of **2**, LiO*t*Am [$LiOCMe_2Et$] in [$D_{12}$]cyclohexane:

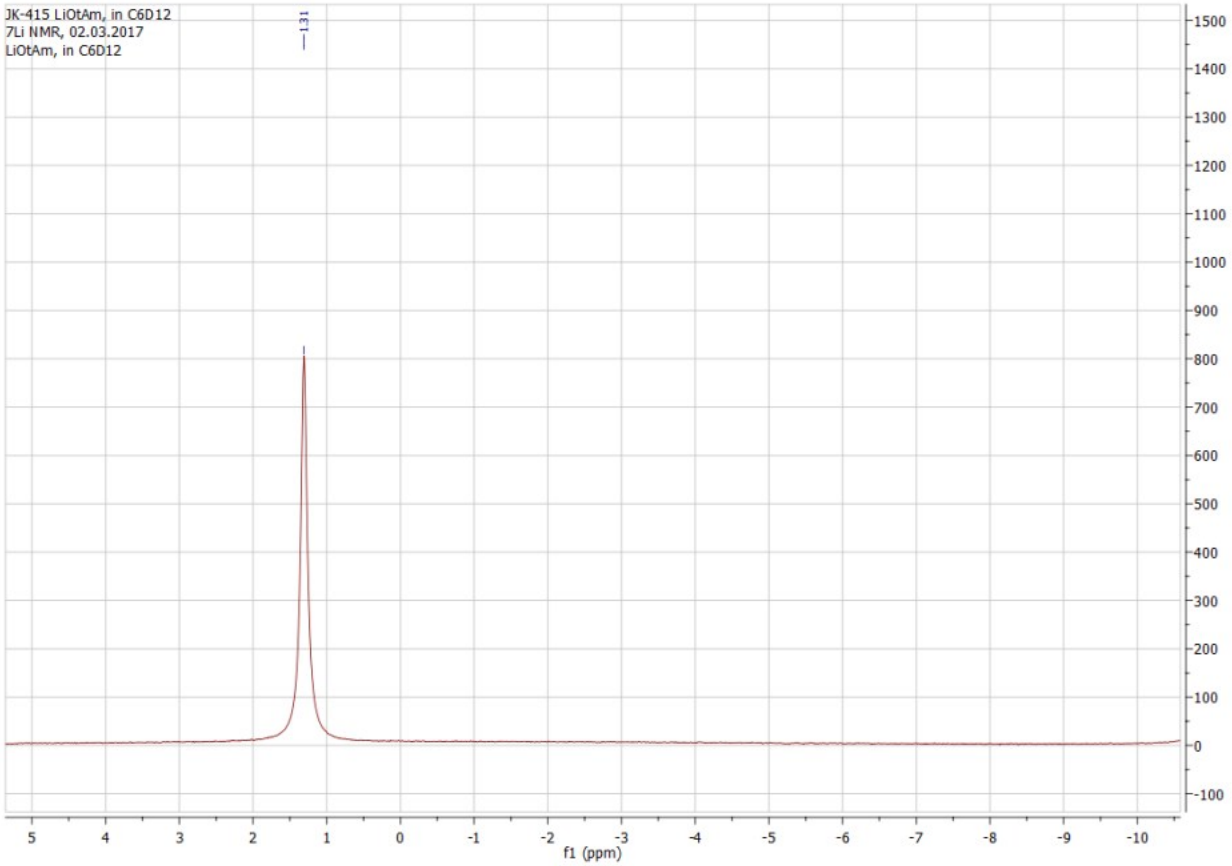


**Figure S2-21:** $^{1}$H NMR of **2**, NaO*t*Am [$NaOCMe_2Et$] in [$D_{12}$]cyclohexane:

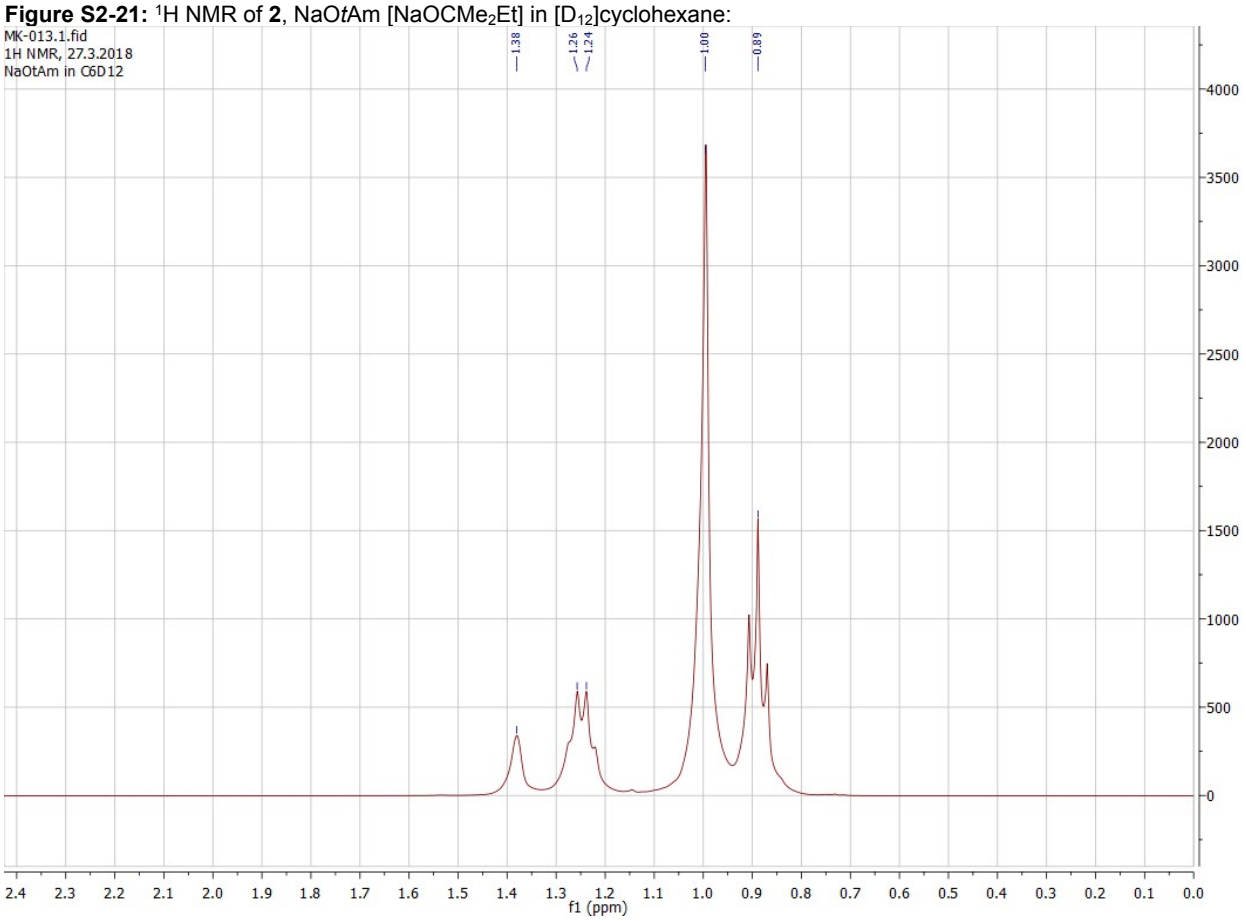



**Figure S2-22:** $^{13}$C NMR of **2**, NaO*t*Am [$NaOCMe_2Et$] in [$D_{12}$]cyclohexane:

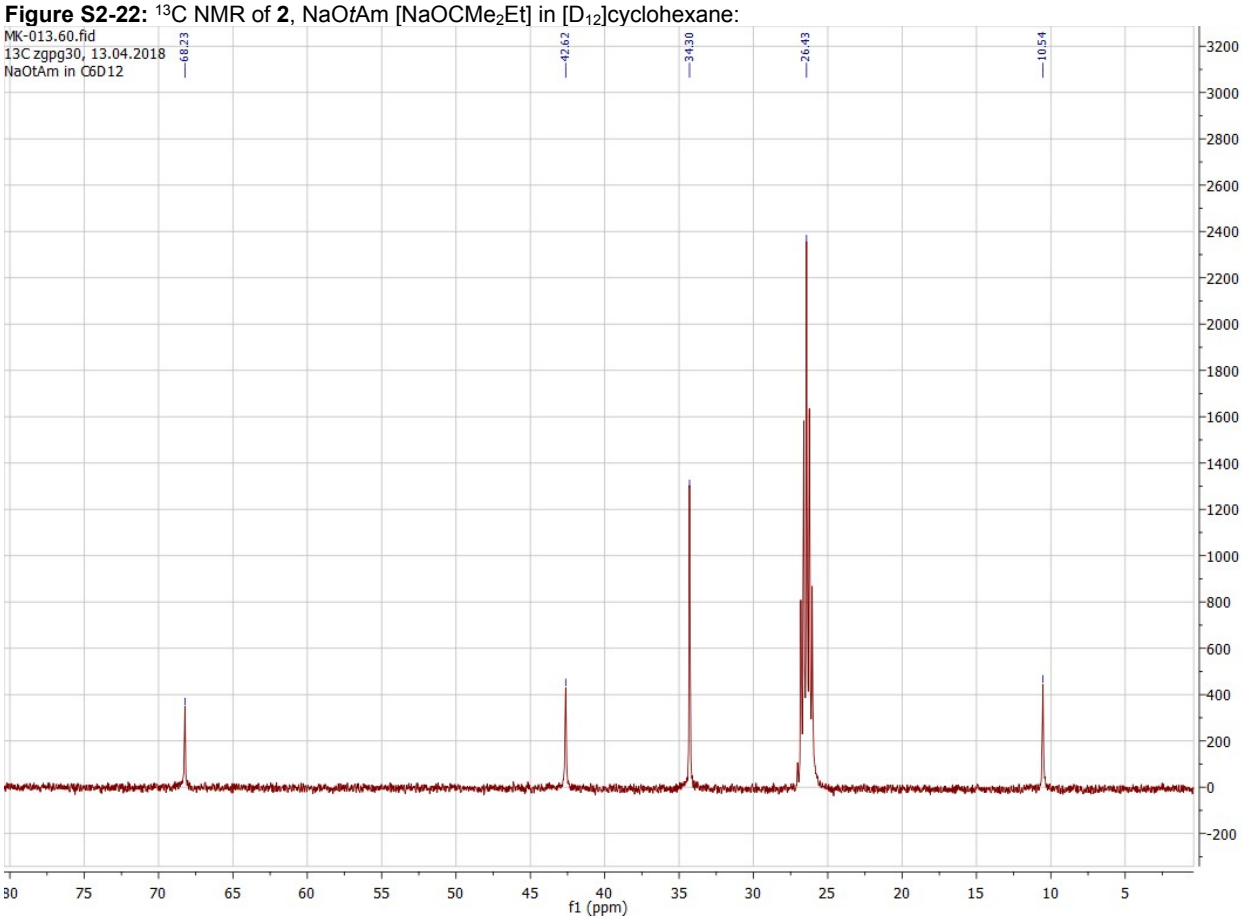


**Figure S2-23:** $^{1}$H NMR of **3**, KO*t*Am [KOCMe$_2$Et] in [D$_{12}$]cyclohexane:

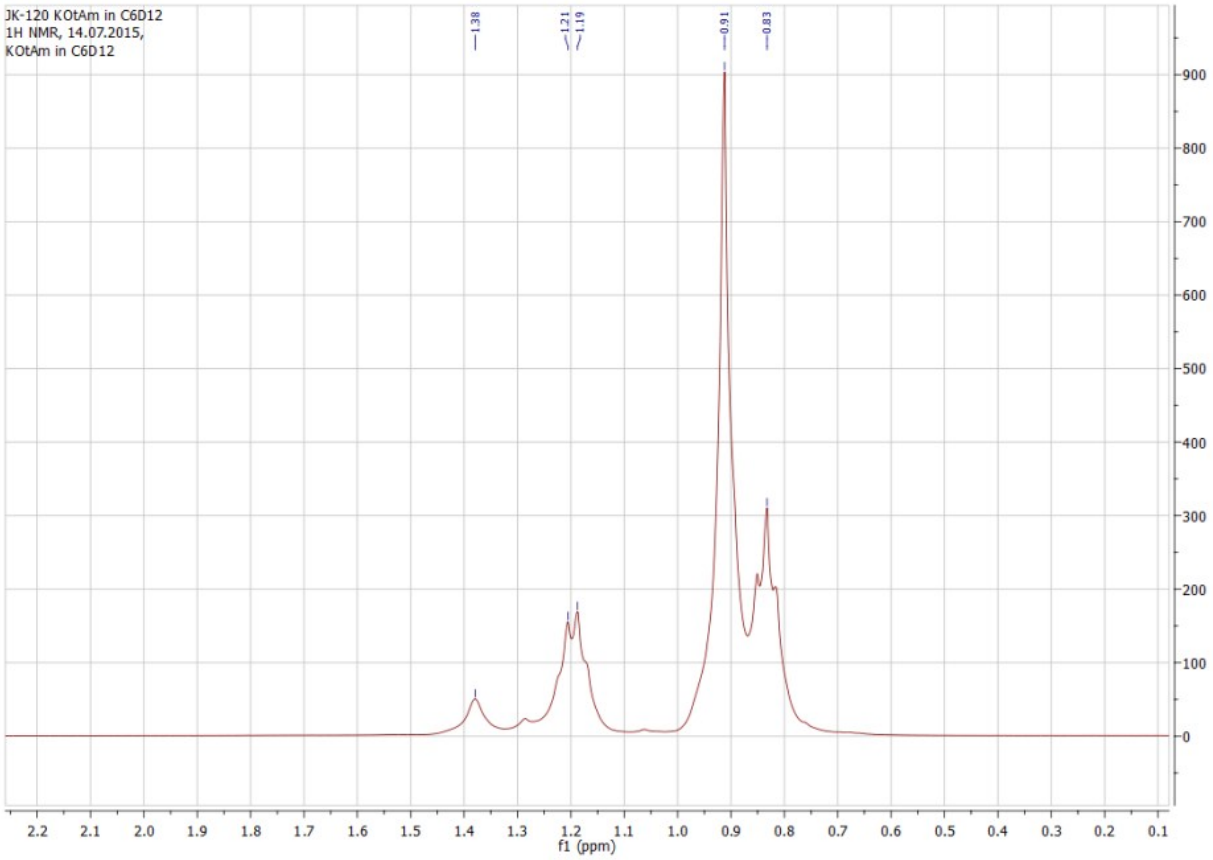



**Figure S2-24:** $^{13}$C NMR of **3**, KO*t*Am [KOCMe$_2$Et] in [D$_{12}$]cyclohexane:

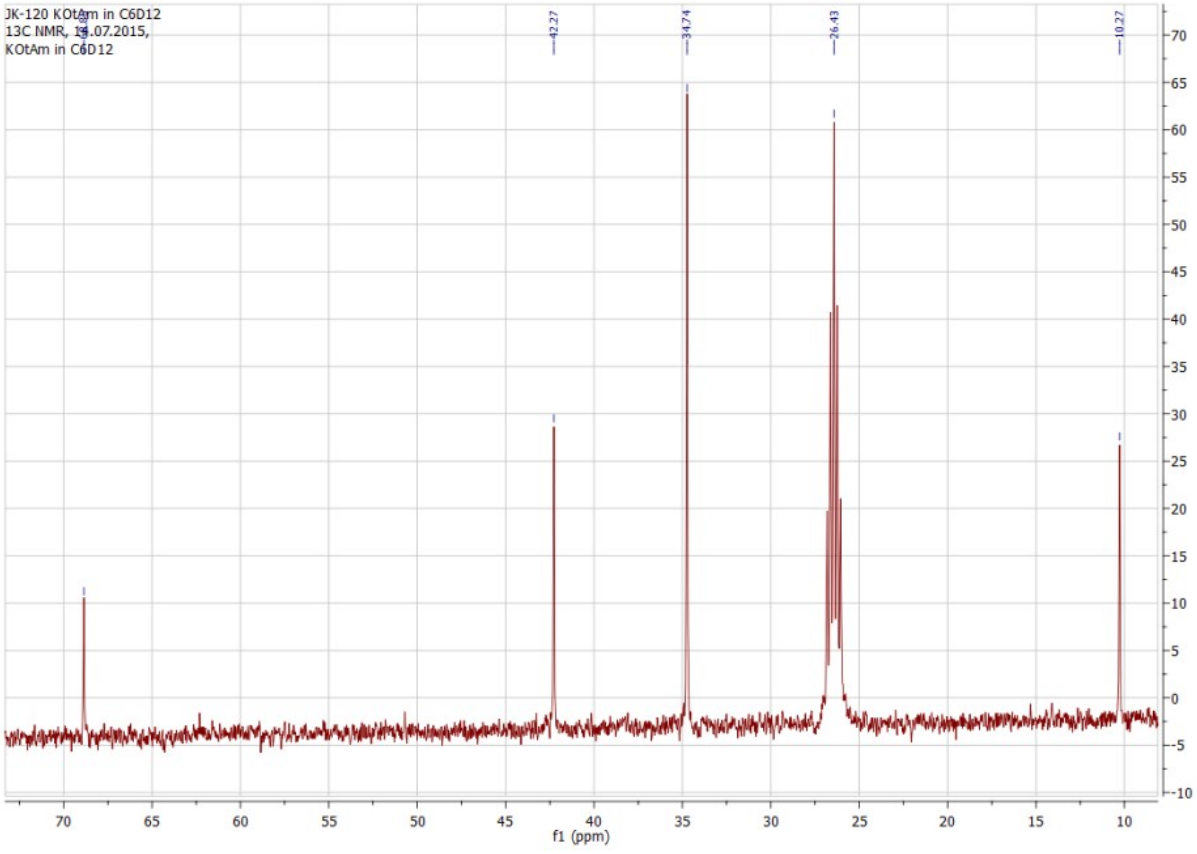


**Figure S2-25:** $^{1}$H NMR of **4**, RbO*t*Am [$RbOCMe_2Et$] in [$D_{12}$]cyclohexane:

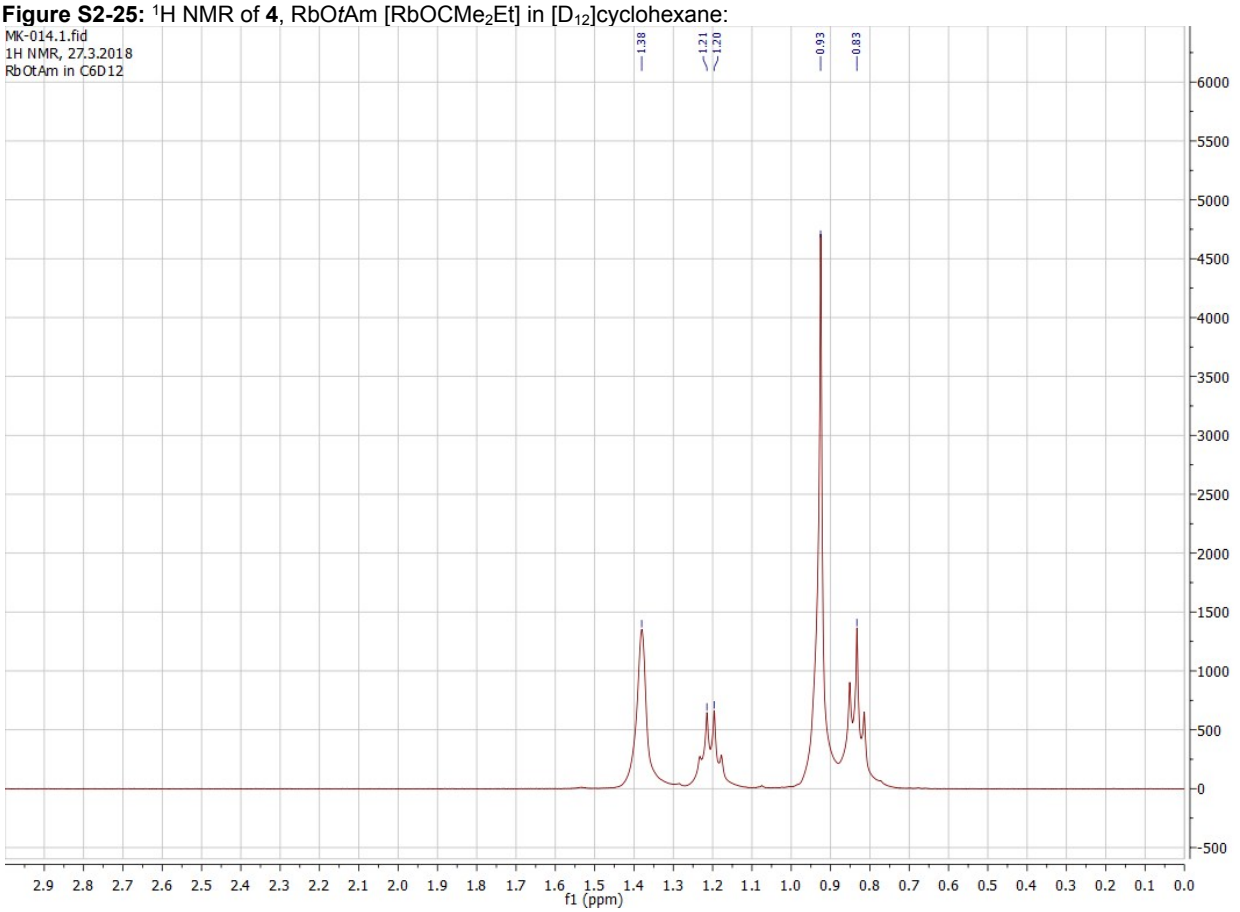



**Figure S2-26:** $^{13}$C NMR of **4**, RbO*t*Am [$RbOCMe_2Et$] in [$D_{12}$]cyclohexane:

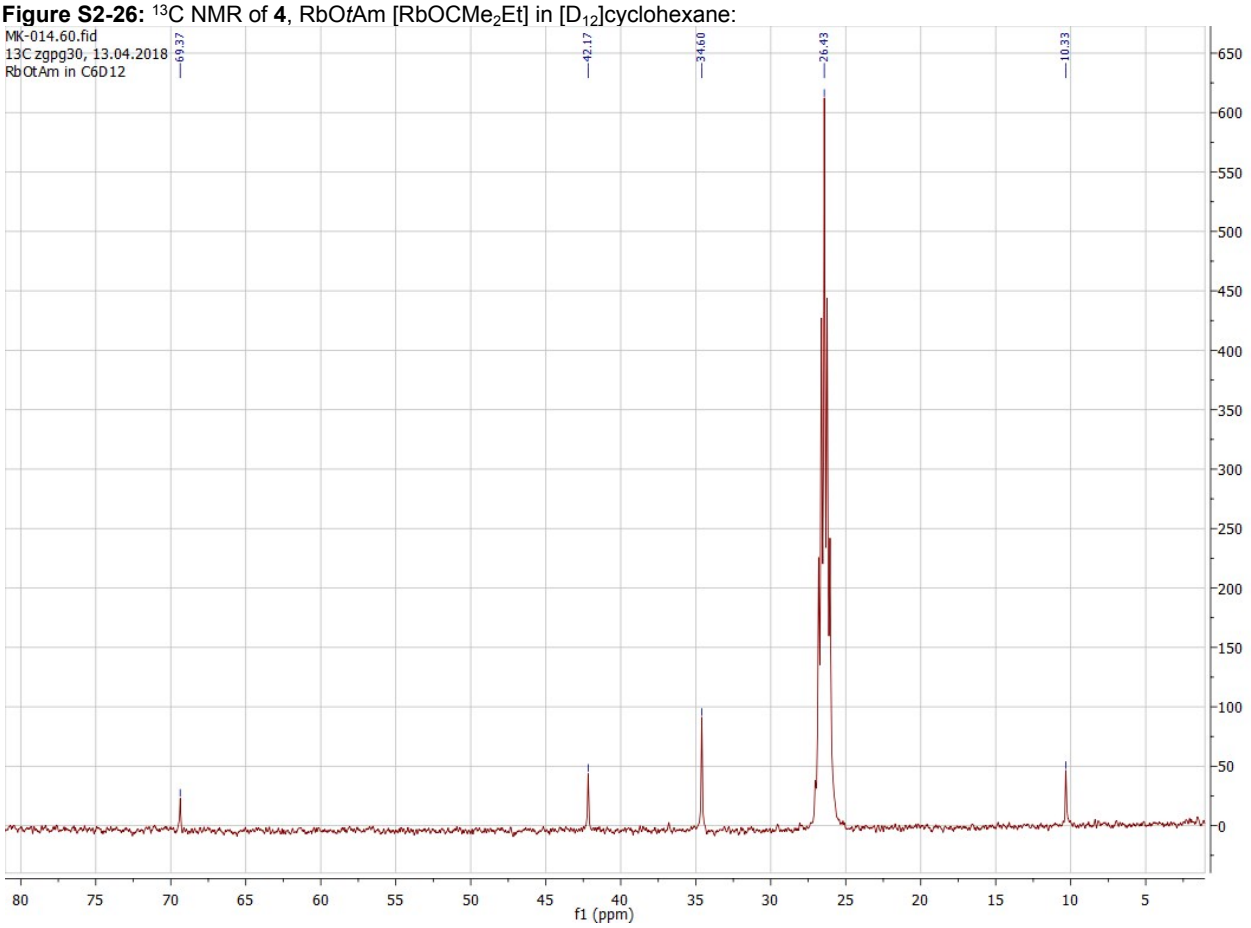


**Figure S2-27:** $^{1}$H NMR of **5**, CsO*t*Am [CsOCMe$_2$Et] in [D$_{12}$]cyclohexane:

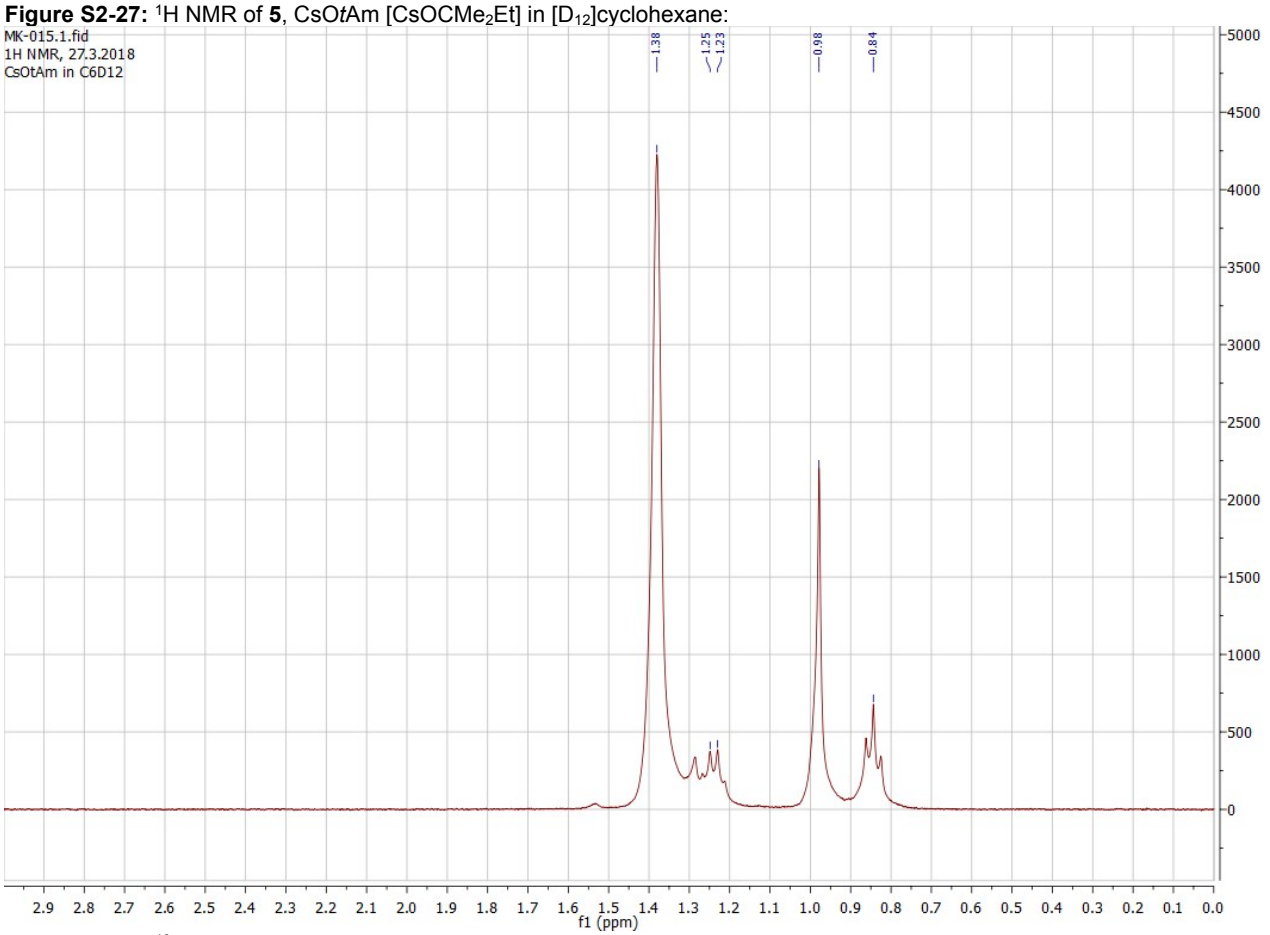



**Figure S2-28:** $^{13}$C NMR of **5**, CsO*t*Am [CsOCMe$_2$Et] in [D$_{12}$]cyclohexane:

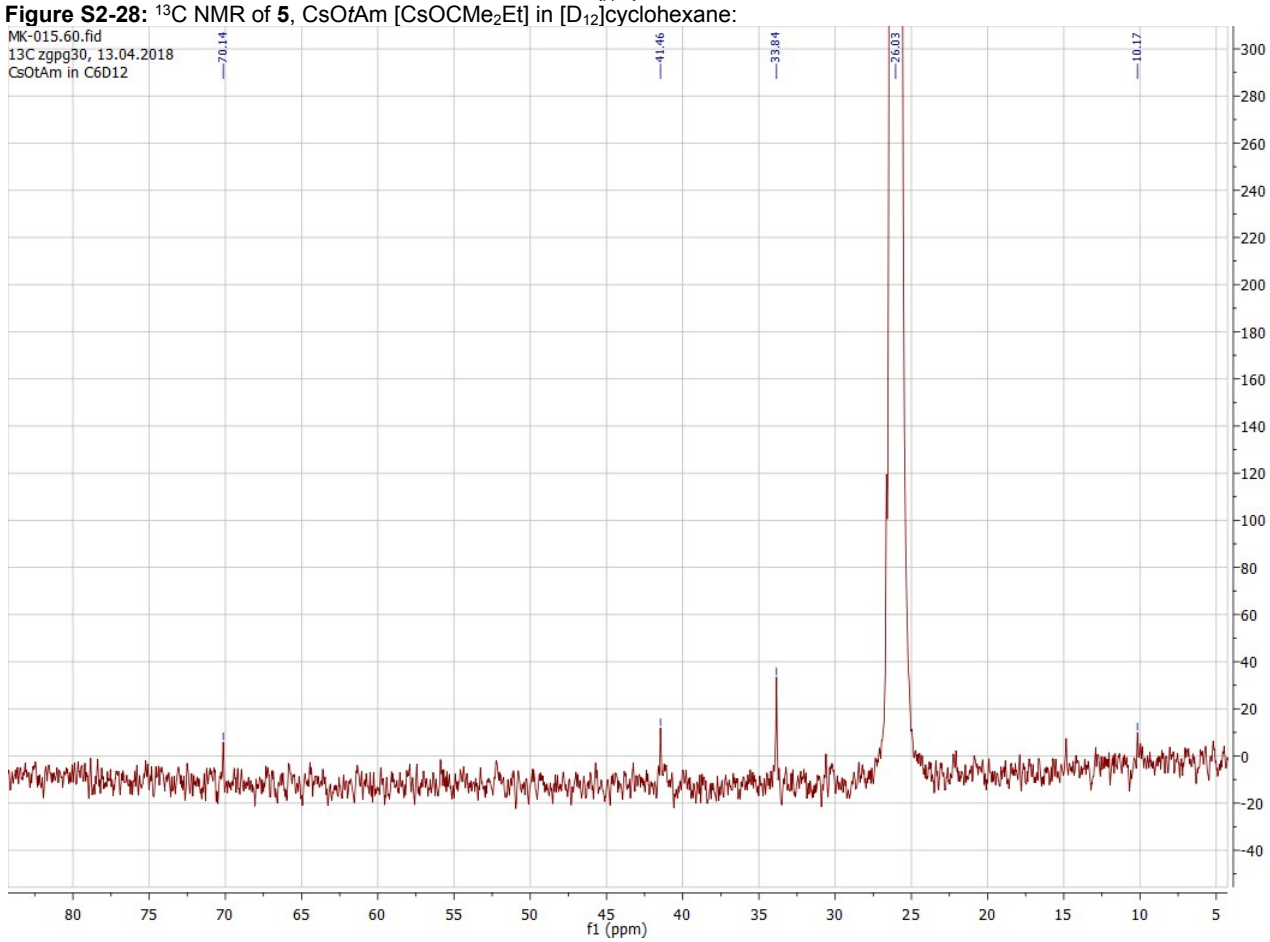
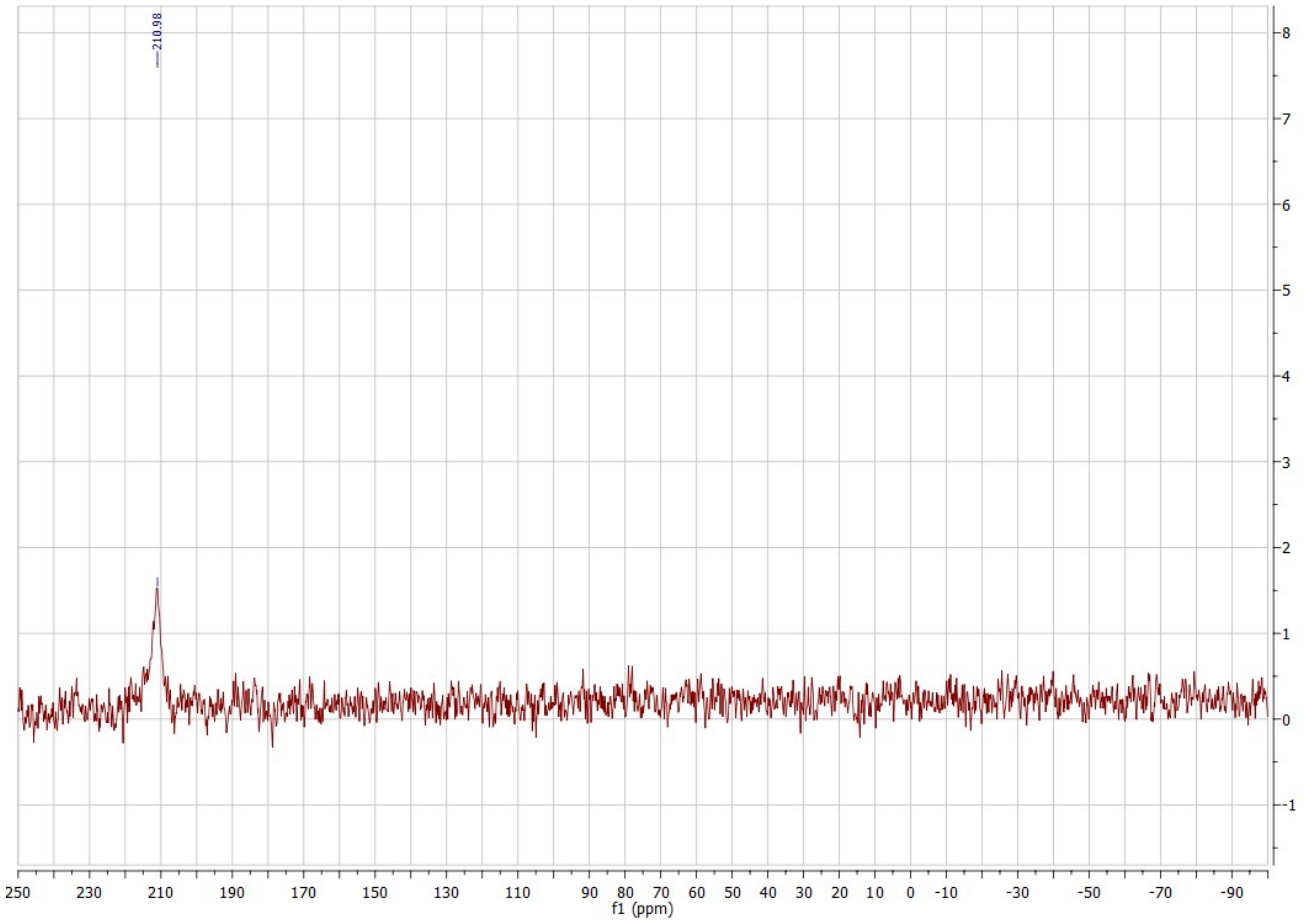


**Figure S2-29:** $^{133}$Cs NMR of **5**, CsO*t*Am [$CsOCMe_2Et$] in [$D_{12}$]cyclohexane:



## Formula Index

**1** Li*O*t*A*m
**2** Na*O*t*A*m
**3** K*O*t*A*m, tetragonal form
**3a** K*O*t*A*m, monoclinic form, polymorph
**4** Rb*O*t*A*m
**5** Cs*O*t*A*m

## Author Contributions

J.K. conceived the project, wrote the manuscript, performed the experiments, carried out spectroscopic studies and the crystallographic work. M. K. performed experiments and carried out spectroscopic studies.

## References

[1] a) P. Müller, *Crystal structure refinement. A crystallographer's guide to SHELXL*, Oxford Univ. Press, Oxford, **2010**; b) G. M. Sheldrick, *Acta crystallographica. Section A, Foundations of crystallography* **2008**, *64*, 112–122.
[2] *CCDC 1837111, CCDC 1837111, CCDC 18371119, and CCDC 1837111 contain the supplementary crystallographic data for this publication. These data are provided free of charge by The Cambridge Crystallographic Data Centre.*