

Supporting Information

CO Homologation and Isocyanide Activation by a Trisilyl Alane Radical Anion

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1 General Methods and Instrumentation

All experiments were performed in an argon 4.6 ($\leq 99.996\%$; *Westfahlen AG*) atmosphere under the exclusion of H_2O and O_2 using standard Schlenk- or *LABstar* from *M. Braun Inertgas Systeme GmbH*. The glassware used for the reactions was heat-dried under vacuum before being sealed with Triboflon III grease. Solvent was purified via distillation in an inert gas atmosphere from sodium/ketyl radical, calcium hydride, or potassium mirror, and stored over molecular sieves (3 Å) under Schlenk conditions or in a Glovebox Workstation. Air- and moisture-sensitive compounds and reactions were measured in *J. Young* PTFE NMR tubes. Unless otherwise stated, all commercially available chemicals were purchased from *abcr GmbH* or *Sigma-Aldrich Chemie GmbH* and used without further purification. The starting materials $\text{HSi}^t\text{Bu}_2\text{Me}$, $\text{BrSi}^t\text{Bu}_2\text{Me}$, $\text{NaSi}^t\text{Bu}_2\text{Me}$, $\text{Al}(\text{Si}^t\text{Bu}_2\text{Me})_3$ (**1**) were prepared according to the literature procedures.¹⁻⁴

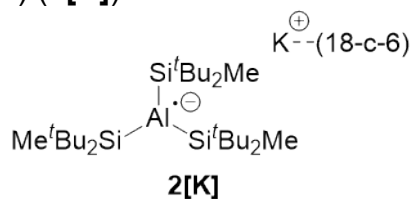
The NMR spectra were recorded at room temperature on a Bruker 500 MHz or a Bruker 400 MHz spectrometer. The δ -values are stated in parts per million [ppm]. Chemical shifts are referenced to (residual) solvent signal (C_6D_6 : $\delta(^1\text{H}) = 7.16$ ppm and $\delta(^{13}\text{C}) = 128.06$ ppm).⁵ The following abbreviations were used to assign the signals and those for the signal multiplicities: s-singlet, d-doublet, and sep-septet. Coupling constants are stated in Hertz [Hz].

Spectroscopy (LIFDI-MS) was measured directly from an inert atmosphere glovebox with a *Thermo Fisher Scientific Exactive Plus Orbitrap* equipped with an ion source from *Linden CMS*. HR-MS (ESI⁺) analysis was performed on a *Thermo Fisher Scientific Exactive Plus Orbitrap* mass spectrometer equipped with a *Thermo Fischer ESI* source.

Quantitative elemental analyses (EA) were carried out using a *EURO EA (HEKA tech)* instrument equipped with a CHNS combustion analyzer at the Laboratory for Microanalysis at the TUM Catalysis Research Center.

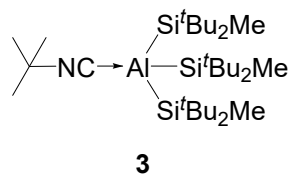
2 Synthesis and Characterization

2.1 $\text{Al}(\text{Si}^t\text{Bu}_2\text{Me})_3 \cdot \text{K}^+(18\text{-c-}6)$ (**2[K]**)



KC_8 (104 mg, 769 μmol , 1.20 eq.) was added to a solution of $\text{Al}(\text{Si}^t\text{Bu}_2\text{Me})_3$ (**1**, 320 mg, 641 μmol , 1.00 eq.) in THF (10 mL). The reaction mixture was stirred at room temperature for ten hours, during which time it turned deep red. To monitor the reaction progress, ^1H NMR spectra of the mixture were collected during the reaction. Once the peaks corresponding to the starting material **1** had completely disappeared, the reaction was complete. The mixture was then filtered and the volatiles were removed under reduced pressure. 18-crown-6 (169 mg, 641 μmol , 1.00 eq.) and toluene (10 mL) were subsequently added to the resulting deep red solid. After the mixture was stirred, the solvent was removed under reduced pressure to give compound **2[K]** as a deep red powder. (442 mg, 551 μmol , 86%).

2.2 ^tBuNC·Al(Si^tBu₂Me)₃ (**3**)



A solution of ^tBuNC (22.7 μ L, 16.7 mg, 200 μ mol, 1.00 eq.) in toluene (1 mL) was added to a solution of Al(Si^tBu₂Me)₃ (**1**, 100 mg, 200 μ mol, 1.00 eq.) in toluene (3 mL) at room temperature. The yellow solution decolorized immediately. After stirring for ten minutes, the solvent was removed under reduced pressure to give compound **3** as a white powder. (111 mg, 191 μ mol, 95%). Suitable crystals for SC-XRD analysis were obtained by storing a saturated solution of **3** in pentane at -30 °C for several days.

¹H NMR (400 MHz, C₆D₆): δ [ppm] = 1.29 (s, 54H, Si^tBu), 0.90 (s, 9H, NC^tBu), 0.49 (s, 9H, SiMe).

¹³C{¹H} NMR (126 MHz, C₆D₆): δ [ppm] = 58.37 (NCMe₃), 31.41 (SiCMe₃), 28.45 (NCMe₃), 22.69 (SiCMe₃), -0.39 (SiMe).

²⁹Si{¹H} NMR (99 MHz, C₆D₆): δ [ppm] = 13.68.

Melting point: 114 °C.

Elemental Analysis (%): Calcd: C 66.02, H 12.47, N 2.41; Found: C 65.14, H 12.05, N 2.54.

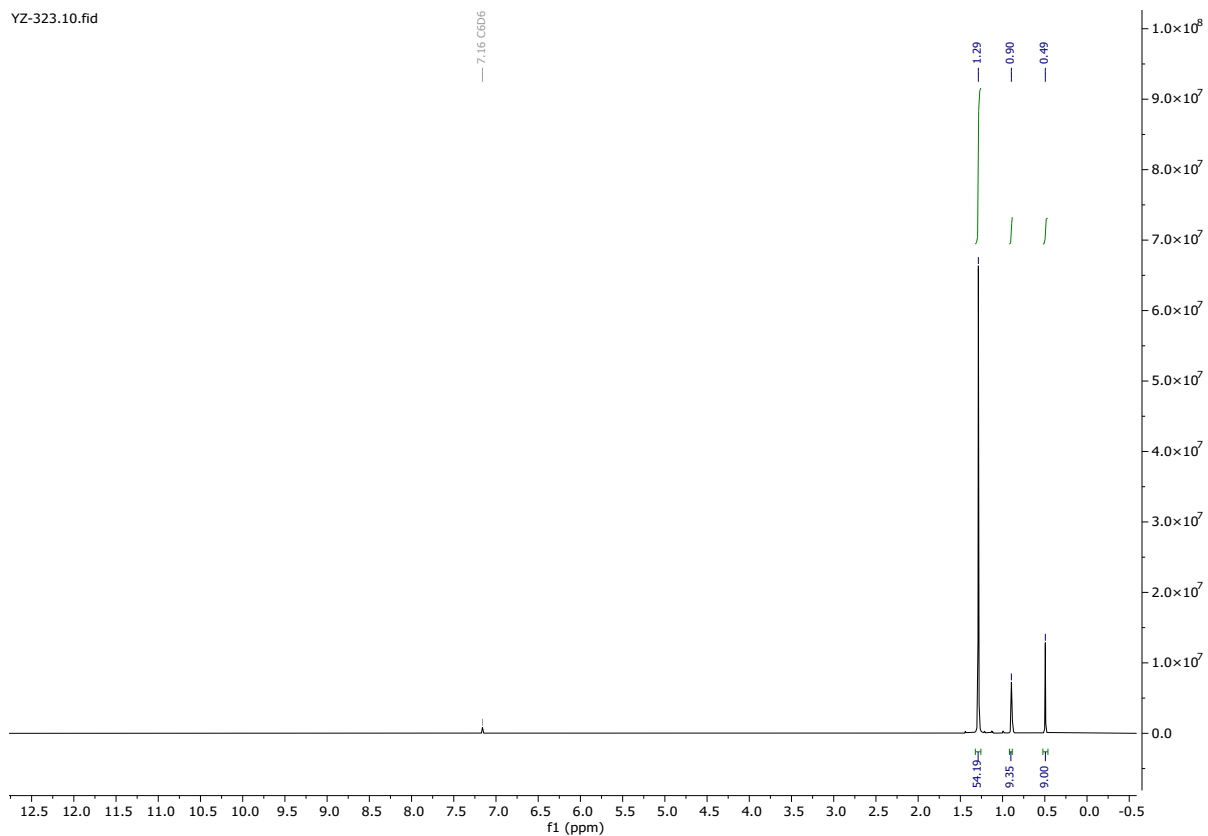


Figure S1: ^1H NMR spectrum of compound **3** in C_6D_6 at 298 K.

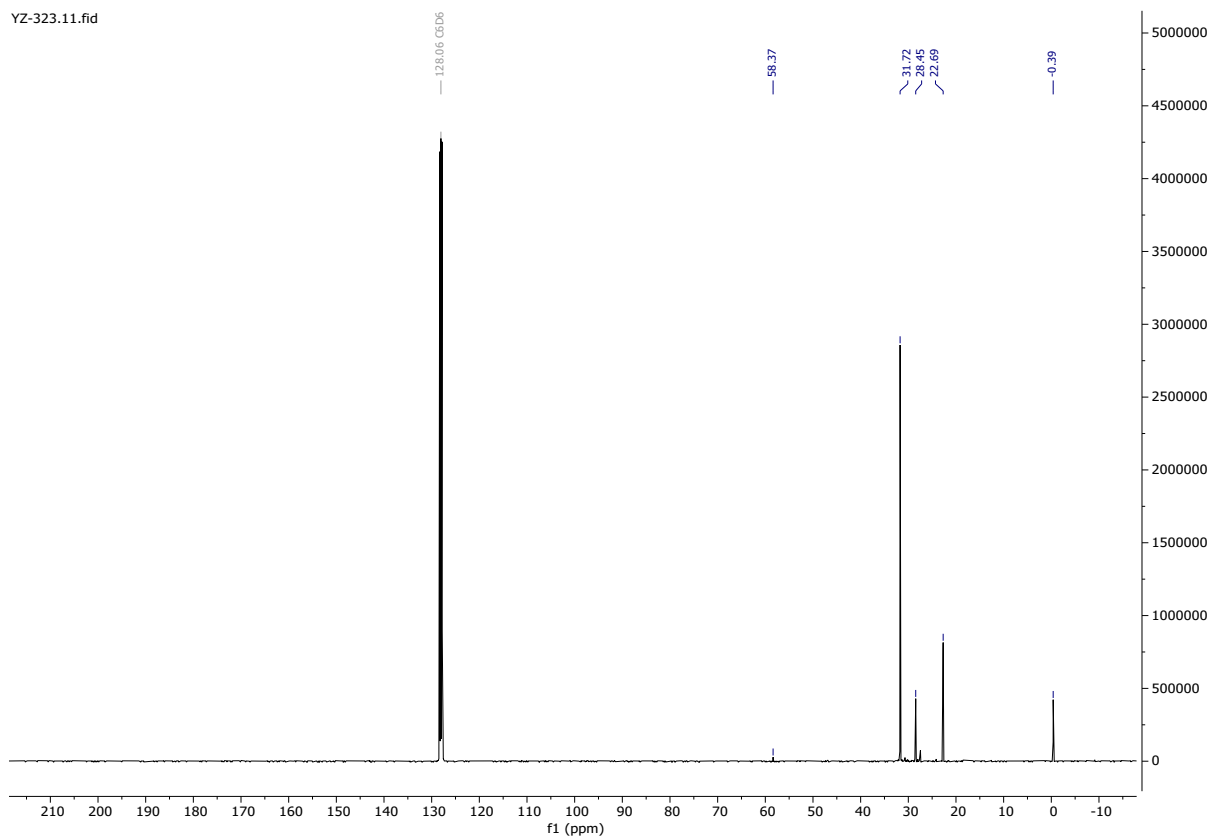


Figure S2: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3** in C_6D_6 at 298 K.

YZ-323.15.fid

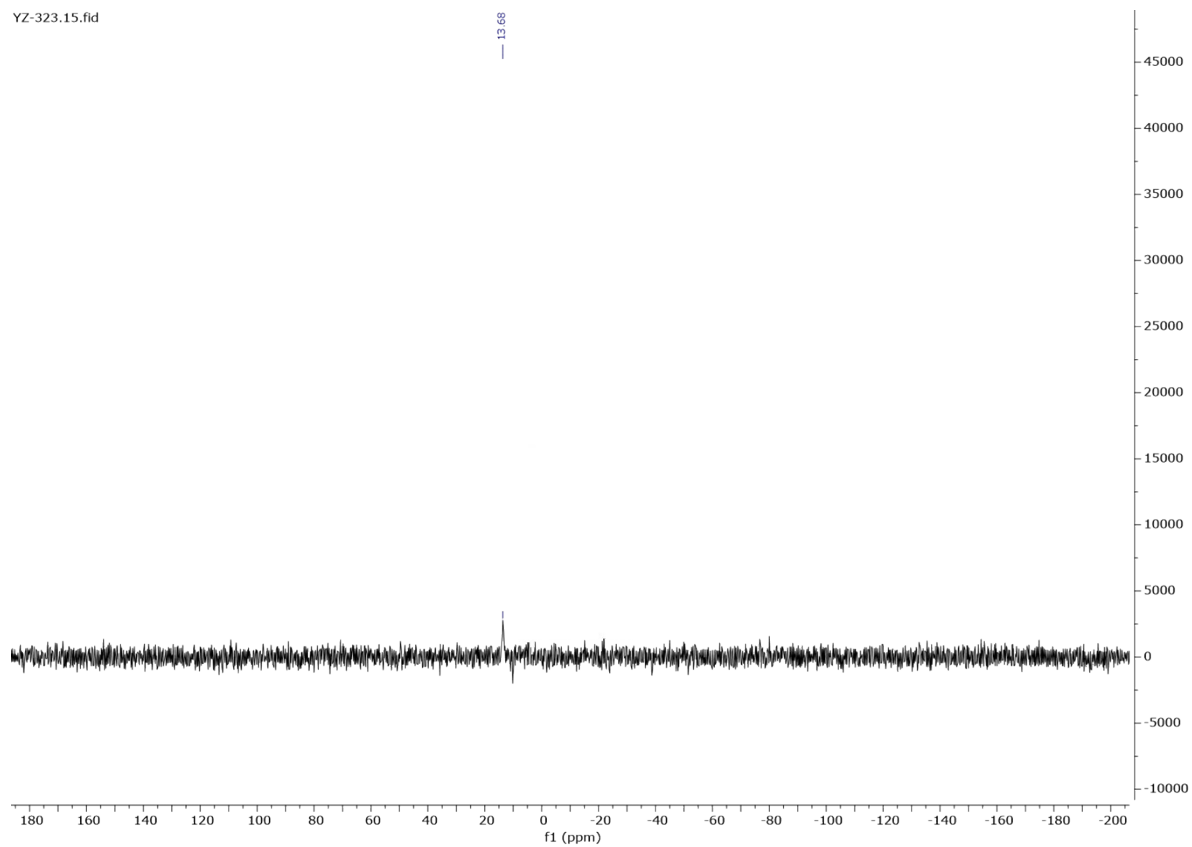
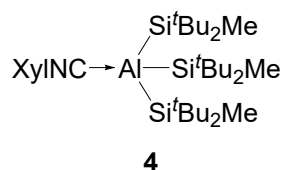


Figure S3: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound **3** in C_6D_6 at 298 K.

2.3 XyINC·Al(Si^tBu₂Me)₃ (**4**)



A solution of XyINC (26.3 mg, 200 μmol , 1.00 eq.) in toluene (1 mL) was added to a solution of Al(Si^tBu₂Me)₃ (**1**, 100 mg, 200 μmol , 1.00 eq.) in toluene (3 mL) at room temperature. The yellow solution decolorized immediately. After stirring for ten minutes, the solvent was removed under reduced pressure to give compound **4** as a white powder. (122 mg, 194 μmol , 97%). Suitable crystals for SC-XRD analysis were obtained by storing a saturated solution of **4** in pentane at $-30\text{ }^\circ\text{C}$ for several days.

¹H NMR (400 MHz, C₆D₆): δ [ppm] = 6.68-6.64 (m, 1H, *p*-H), 6.48 (d, *J* = 7.6 Hz, 2H, *m*-H), 2.25 (s, 6H, C_{aryl}Me), 1.33 (s, 54H, ^tBu), 0.09 (s, 6H, SiMe).

¹³C{¹H} NMR (126 MHz, C₆D₆): δ [ppm] = 136.20 (*o*-C), 130.59 (*p*-C), 128.92 (*m*-C), 32.15 (SiCMe₃), 23.25 (SiCMe₃), 19.53 (C_{aryl}Me), 0.09 (SiMe).

²⁹Si{¹H} NMR (99 MHz, C₆D₆): δ [ppm] = 14.42.

Melting point: 121 $^\circ\text{C}$.

Elemental Analysis (%): Calcd: C 68.61, H 11.52, N 2.22; Found: C 69.08, H 11.07, N 2.42.

YZ-369.10.fid

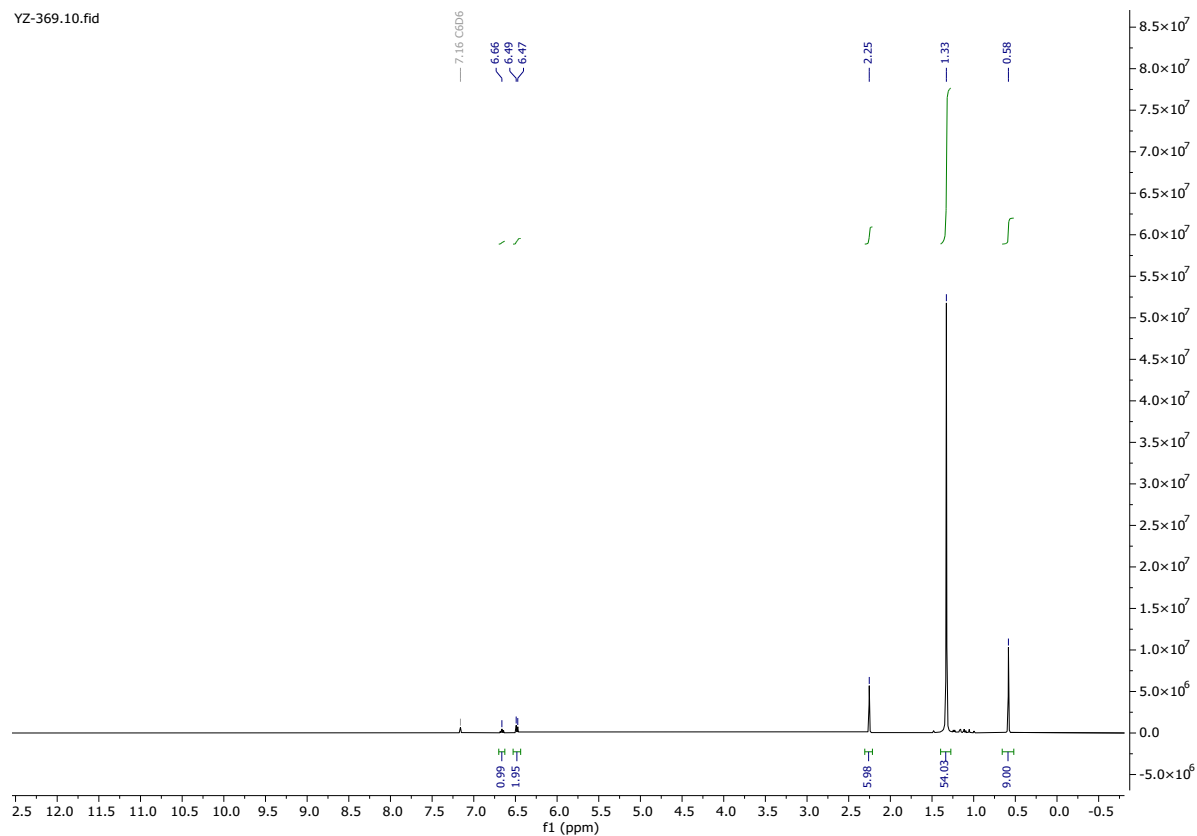


Figure S4: ¹H NMR spectrum of compound 4 in C₆D₆ at 298 K.

YZ-Al(SitBu2Me)3+XylINC.11.fid

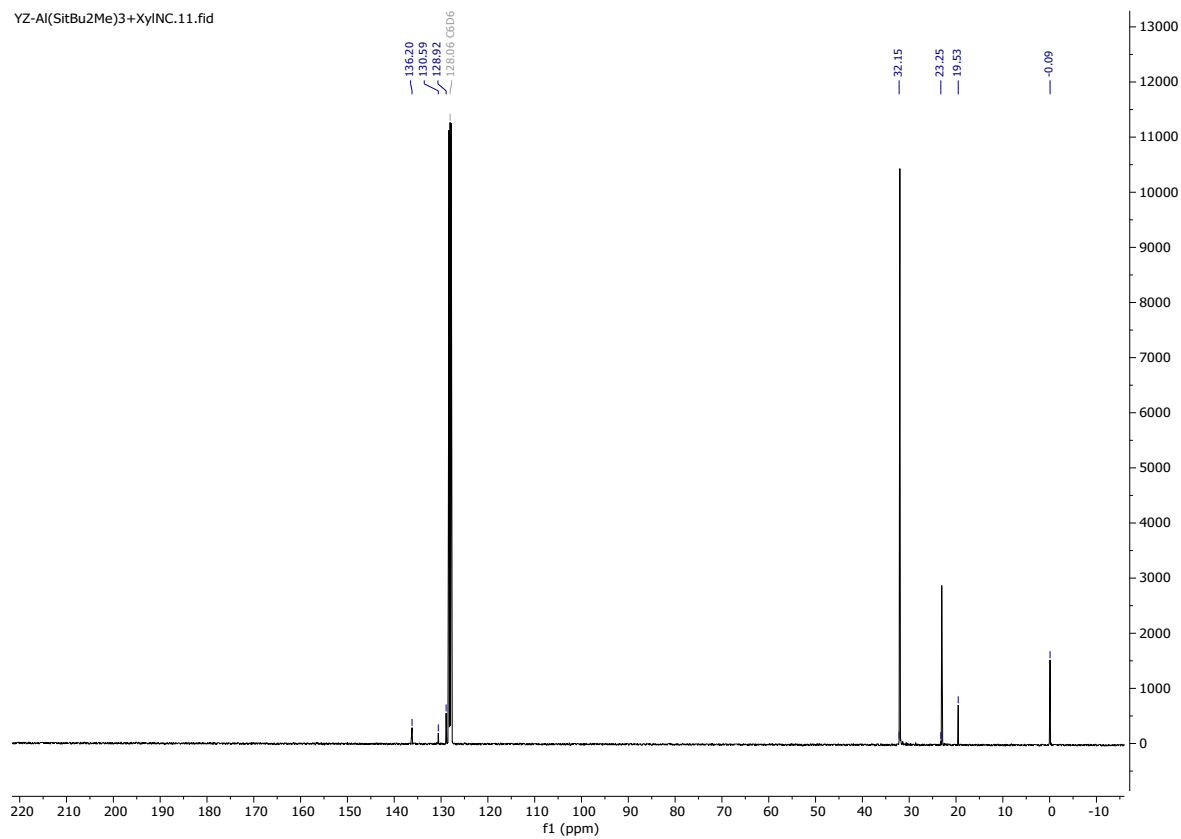


Figure S5: ¹³C{¹H} NMR spectrum of compound 4 in C₆D₆ at 298 K.

YZ-369.11.fid

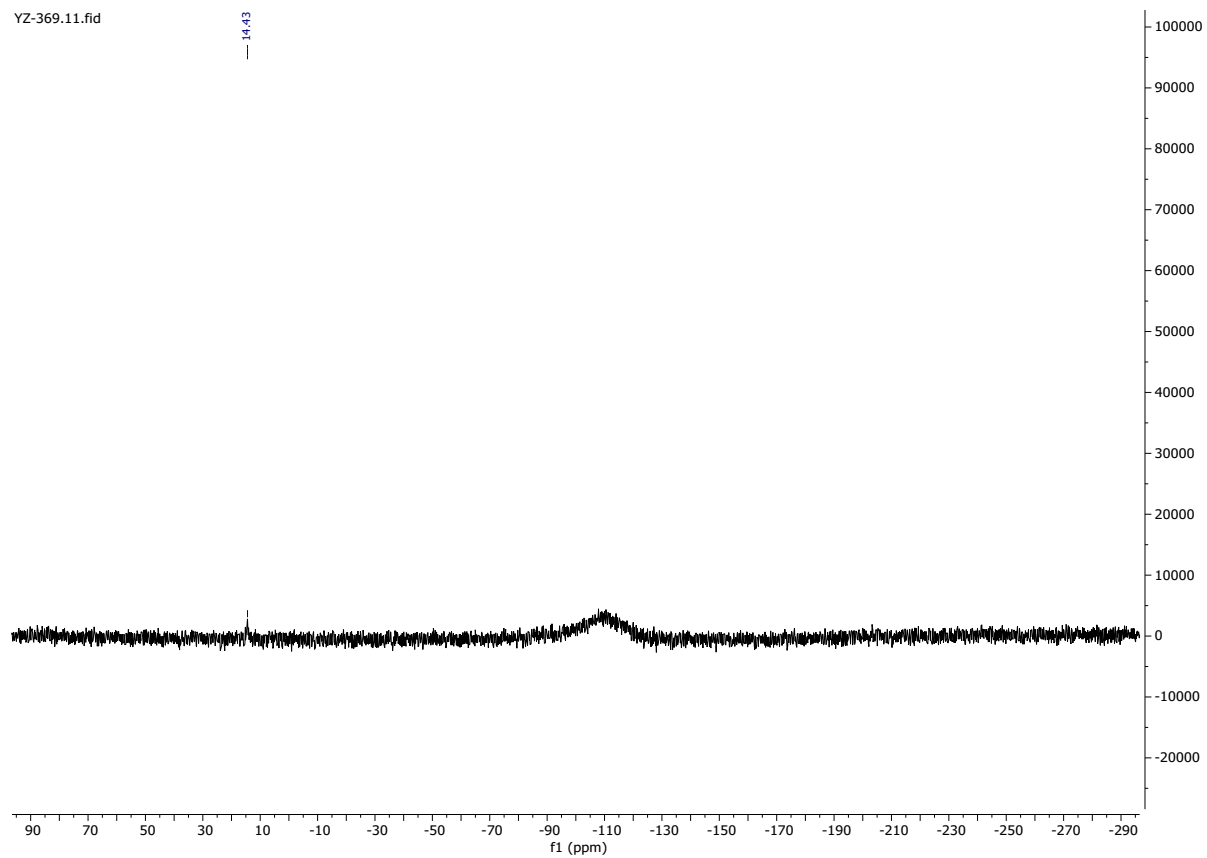
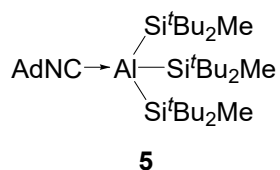


Figure S6: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound **4** in C_6D_6 at 298 K.

2.4 AdNC·Al(Si^tBu₂Me)₃ (**5**)



A solution of AdNC (32.3 mg, 200 μmol, 1.00 eq.) in toluene (1 mL) was added to a solution of Al(Si^tBu₂Me)₃ (**1**, 100 mg, 200 μmol, 1.00 eq.) in toluene (3 mL) at room temperature. The yellow solution decolorized immediately. After stirring for ten minutes, the solvent was removed under reduced pressure to give compound **5** as a white powder. (128 mg, 194 μmol, 97%). Suitable crystals for SC-XRD analysis were obtained by storing a saturated solution of **5** in pentane at -30 °C for several days.

¹H NMR (400 MHz, CDCl₃): δ [ppm] = 2.16 (s, 3H, C_c), 2.07 (s, 6H, C_b), 1.74-1.65 (m, 6H, C_d), 1.05 (s, 54H, Si^tBu), 0.19 (s, 6H, Me).

¹³C{¹H} NMR (126 MHz, CDCl₃): δ [ppm] = 58.56 (C_a), 41.69 (C_b), 35.31 (C_d), 31.46 (SiCMe₃), 28.58 (C_c), 22.49 (SiCMe₃), 0.88 (Me).

²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ [ppm] = 13.34.

Melting point: 142 °C.

Elemental Analysis (%): Calcd: C 69.12, H 11.91, N 2.12; Found: C 66.27, H 13.34, N 1.92.

YZ-363-CDCl3.10.fid

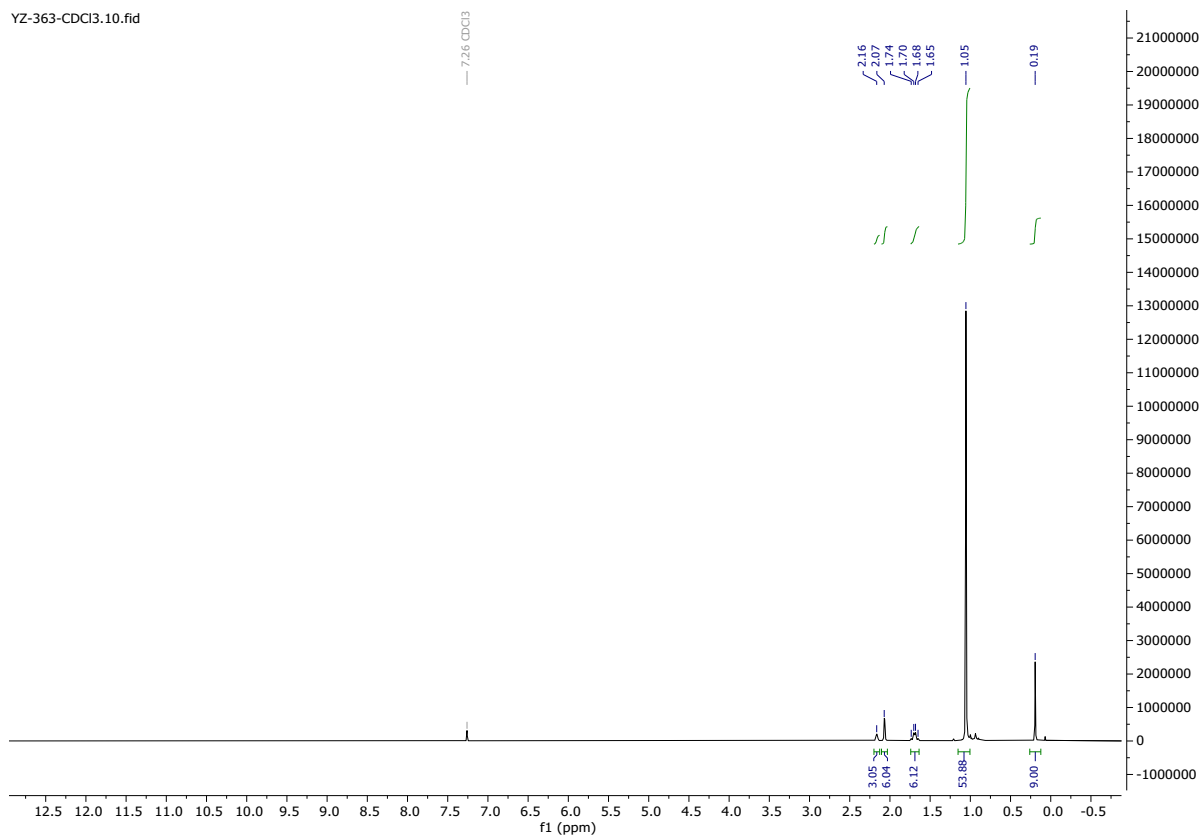


Figure S7: ¹H NMR spectrum of compound **5** in CDCl₃ at 298 K.

YZ-363-CDCl3.11.fid

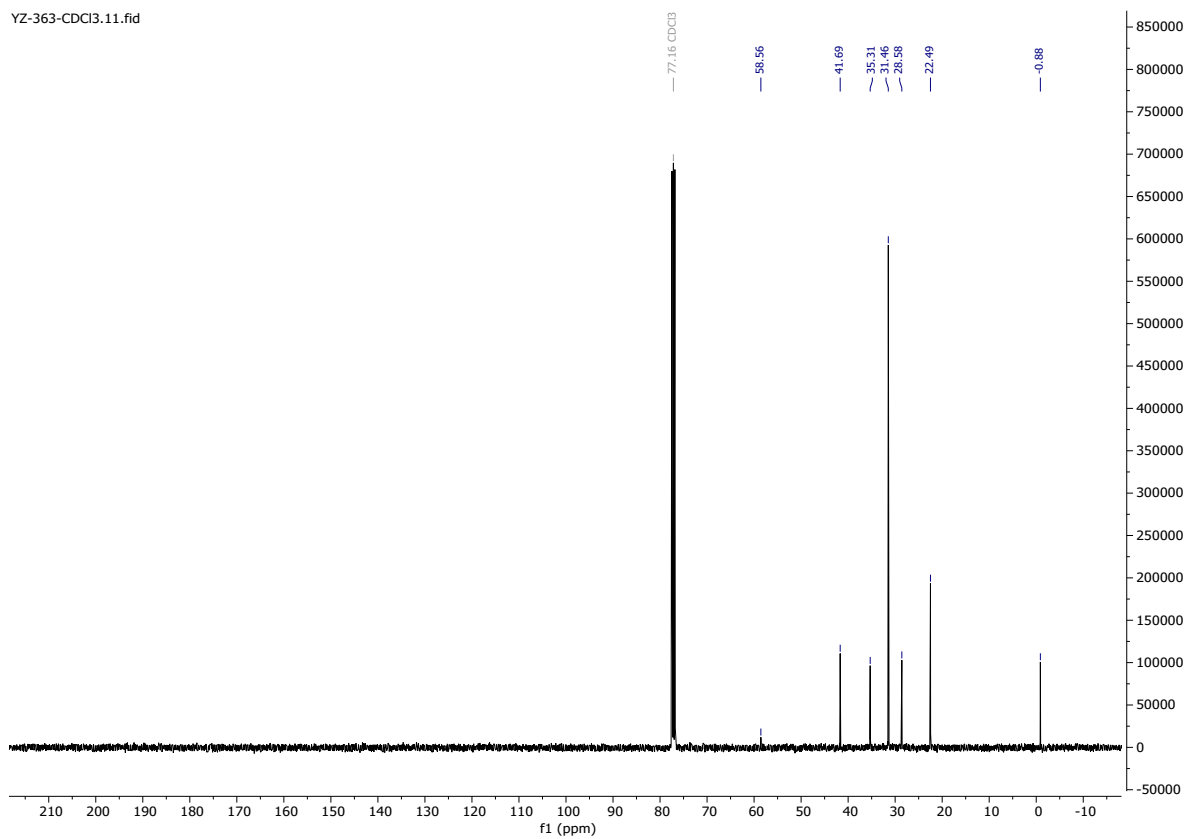


Figure S8: ¹³C{¹H} NMR spectrum of compound **5** in CDCl₃ at 298 K.

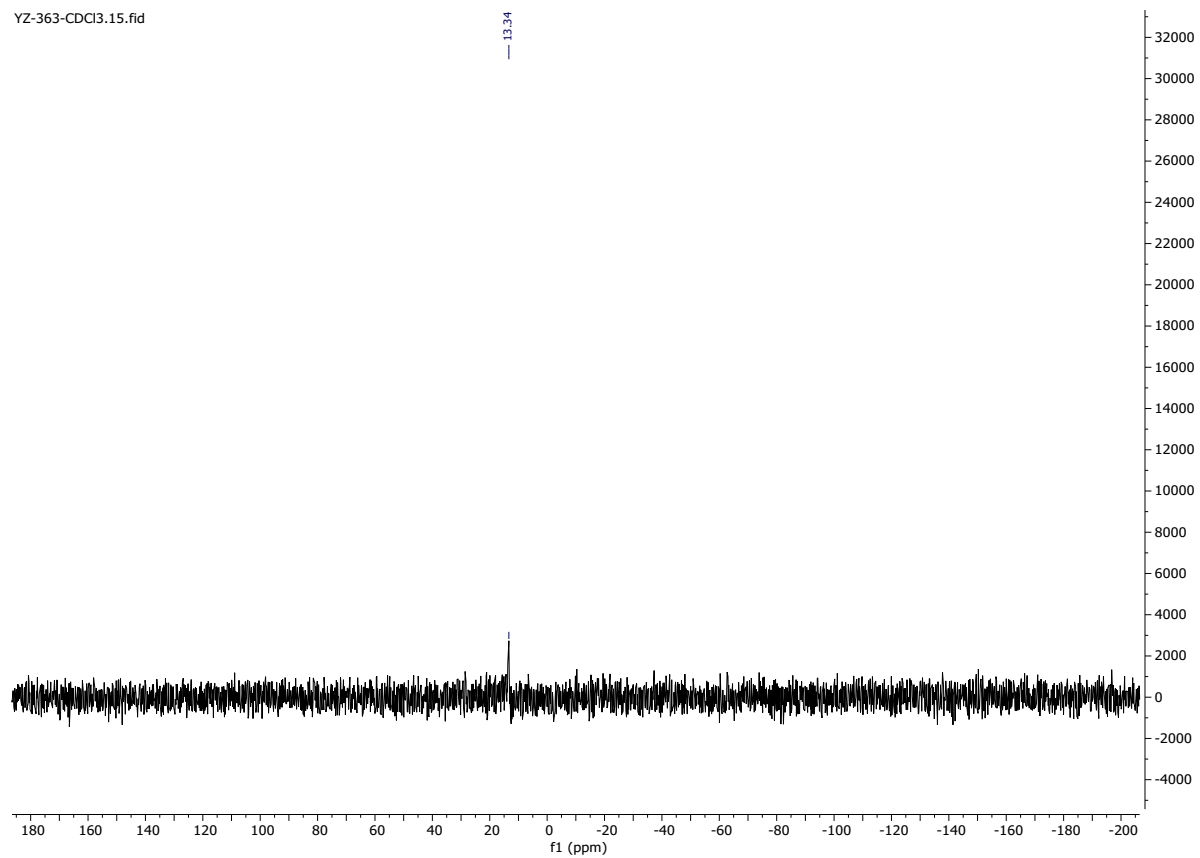
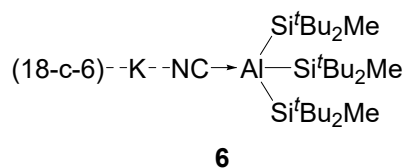


Figure S9: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound **5** in CDCl_3 at 298 K.

2.5 (18-c-6)K-NC·Al(Si^tBu₂Me)₃ (**6**)



A solution of RNC (R = ^tBu, 14.1 μL, 10.4 mg, 125 μmol, 1.00 eq.; R = Xyl, 16.4 mg, 125 μmol, 1.00 eq.; R = Ad, 20.1 mg, 125 μmol, 1.00 eq) in toluene (1 mL) was added to a solution of Al(Si^tBu₂Me)₃K⁺(18-c-6) (**2[K]**, 100 mg, 125 μmol, 1.00 eq.) in THF (3 mL) at room temperature. The deep red solution decolorized immediately. After stirring for ten minutes, the solvent was removed under reduced pressure to give compound **6** as a white powder. (R = ^tBu, 96.1 mg, 116 μmol, 93%; R = Xyl, 95.2 mg, 115 μmol, 92%; R = Ad, 96.9 mg, 117 μmol, 94%). Suitable crystals for SC-XRD analysis were obtained by storing a saturated solution of **6** in pentane at -30 °C for several days.

¹H NMR (400 MHz, C₆D₆): δ [ppm] = 3.04 (s, 24H, 18-c-6), 1.55 (s, 54H, Si^tBu), 0.74 (s, 6H, Me).

¹³C{¹H} NMR (126 MHz, C₆D₆): δ [ppm] = 69.95 (18-c-6), 32.20 (SiCMe₃), 22.89 (SiCMe₃), -0.20 (Me).

²⁹Si{¹H} NMR (99 MHz, C₆D₆): δ [ppm] = 10.20.

LIFDI-MS (positive ion mode): m/z found: 303.1176 [C₁₂H₂₄KO₆]⁺, Anion wasn't detected because of positive ion mode.

YZ-405.20.fid

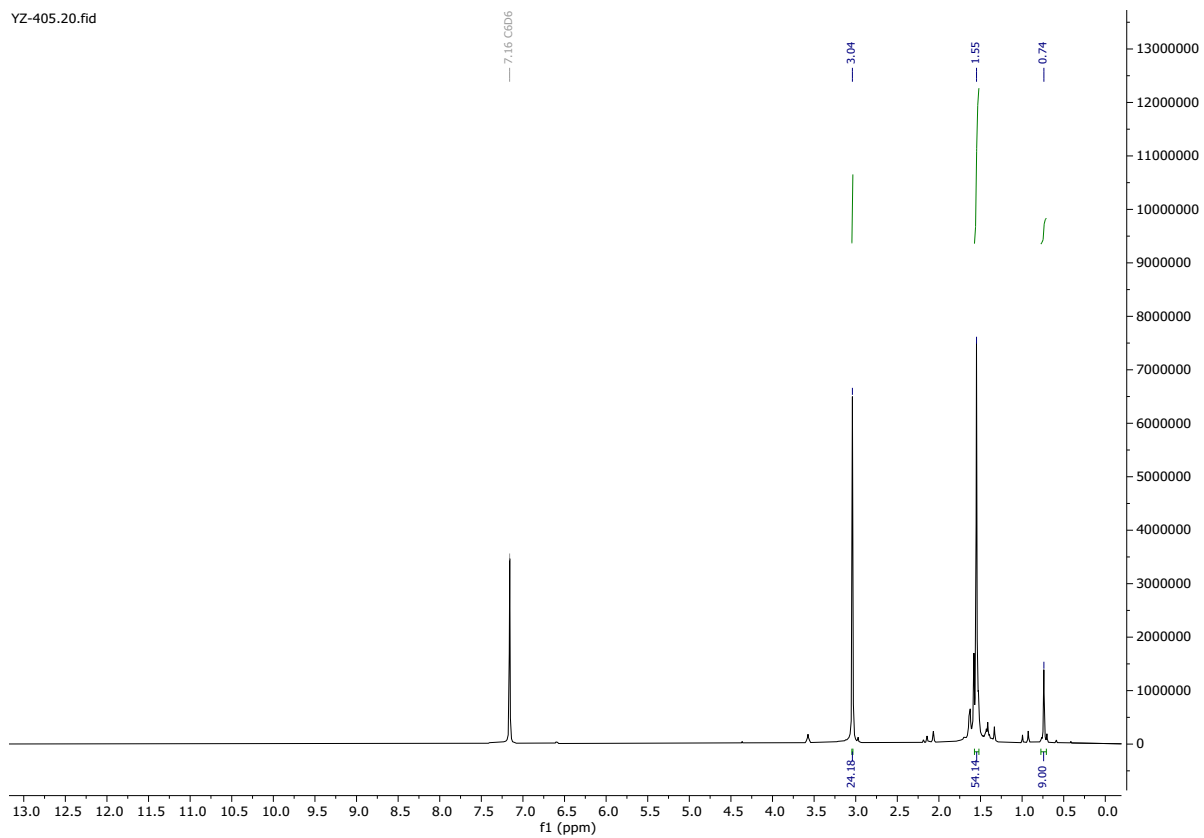


Figure S10: ¹H NMR spectrum of compound **6** in C₆D₆ at 298 K.

YZ-405-150425.11.fid

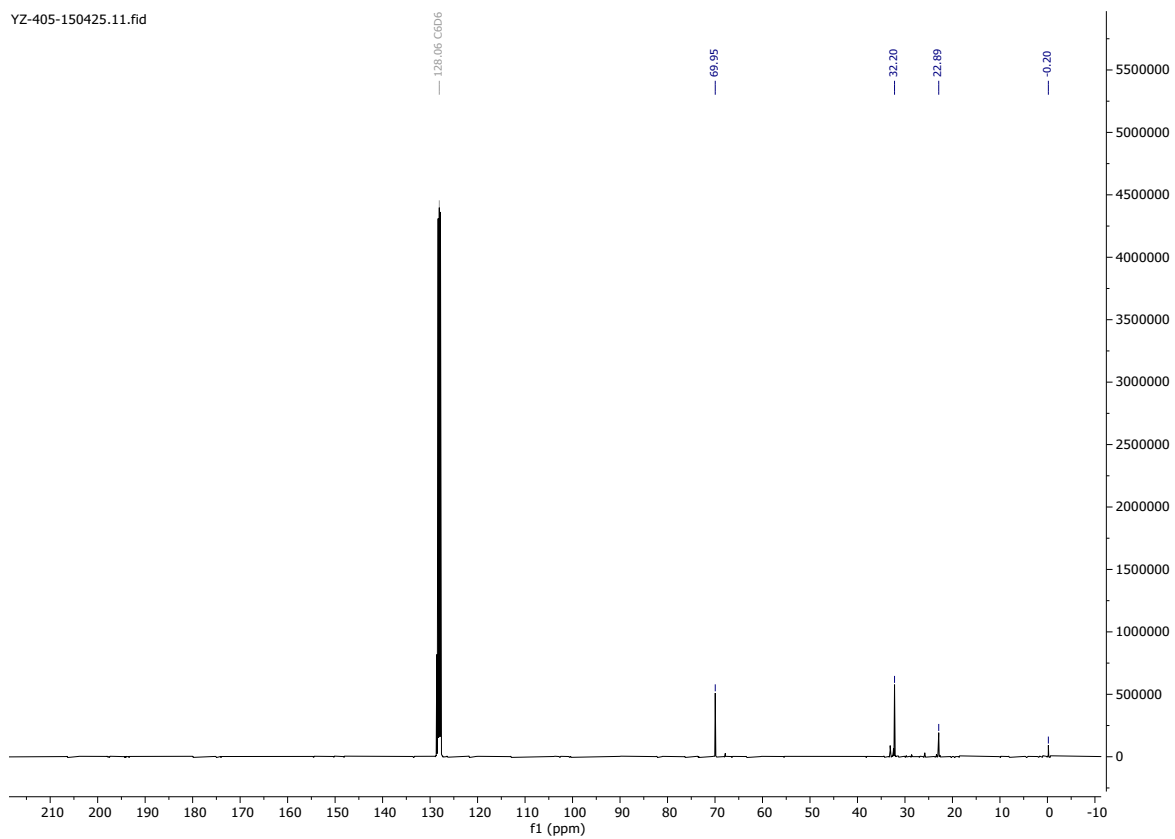


Figure S11: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **6** in C_6D_6 at 298 K.

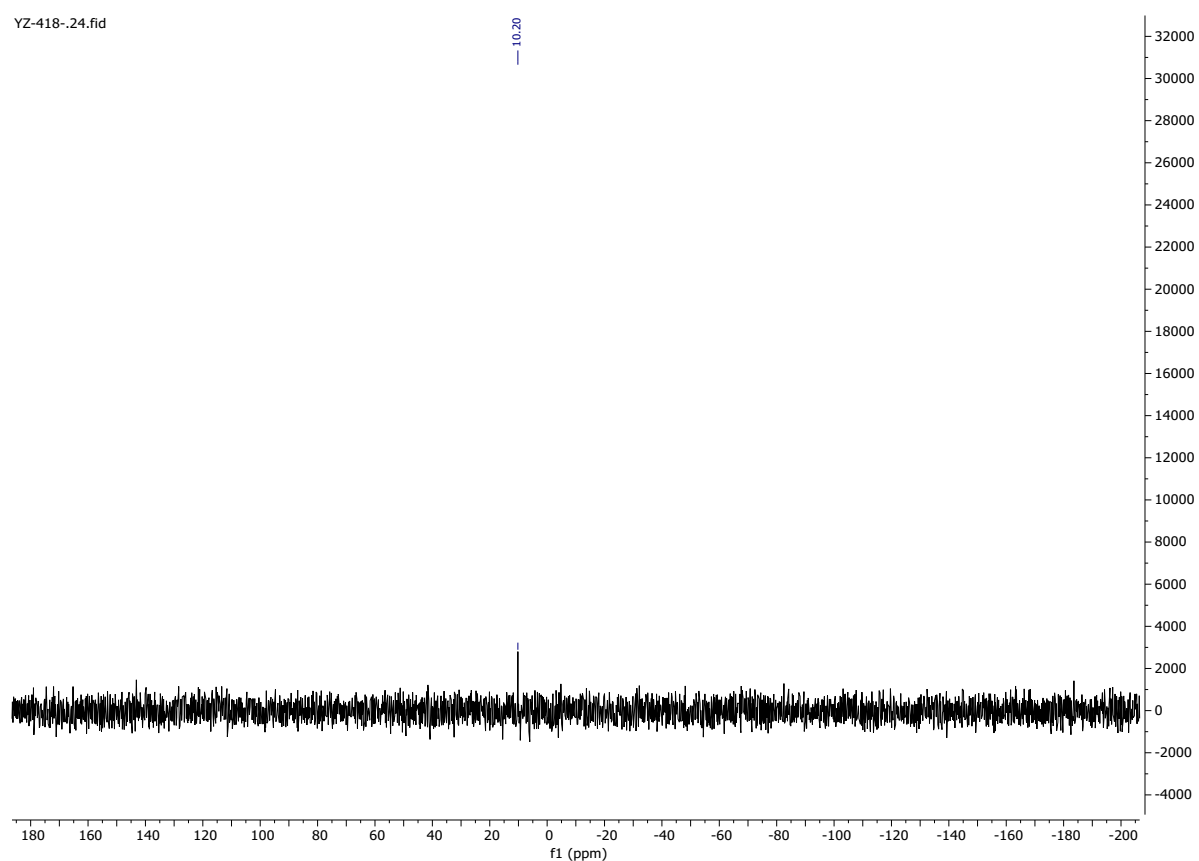


Figure S12: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound **6** in C_6D_6 at 298 K.

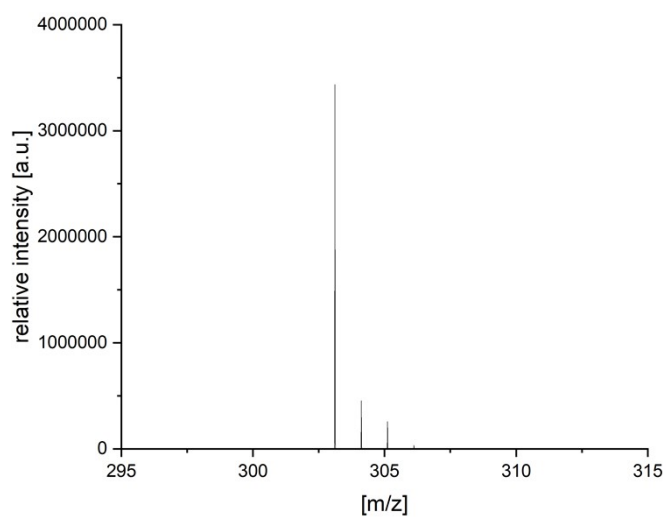


Figure S13: LIFDI-MS spectrometry (detail view with isotopic pattern) of **6**. Measured $m/z = 303.1176$
 $[\text{C}_{12}\text{H}_{24}\text{KO}_6]^+$.

^1H NMR spectra of the reaction mixture of **2[K]** and $t\text{BuNC}$

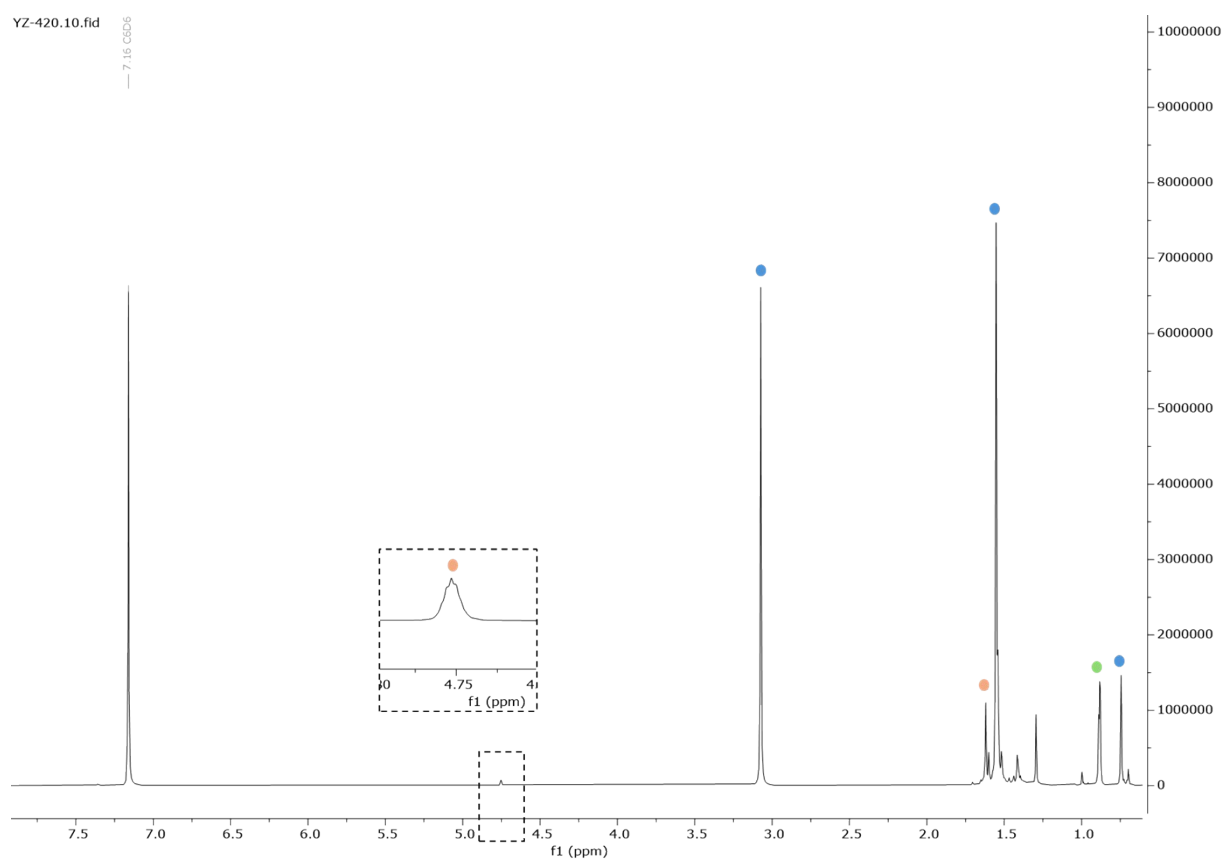


Figure S14: ^1H NMR spectrum of the reaction mixture of **2[K]** and $t\text{BuNC}$ (blue: **6**; orange: isobutylene; green: $t\text{BuNC}$).

^1H NMR spectra of the reaction mixture of **2[K]** and XylINC

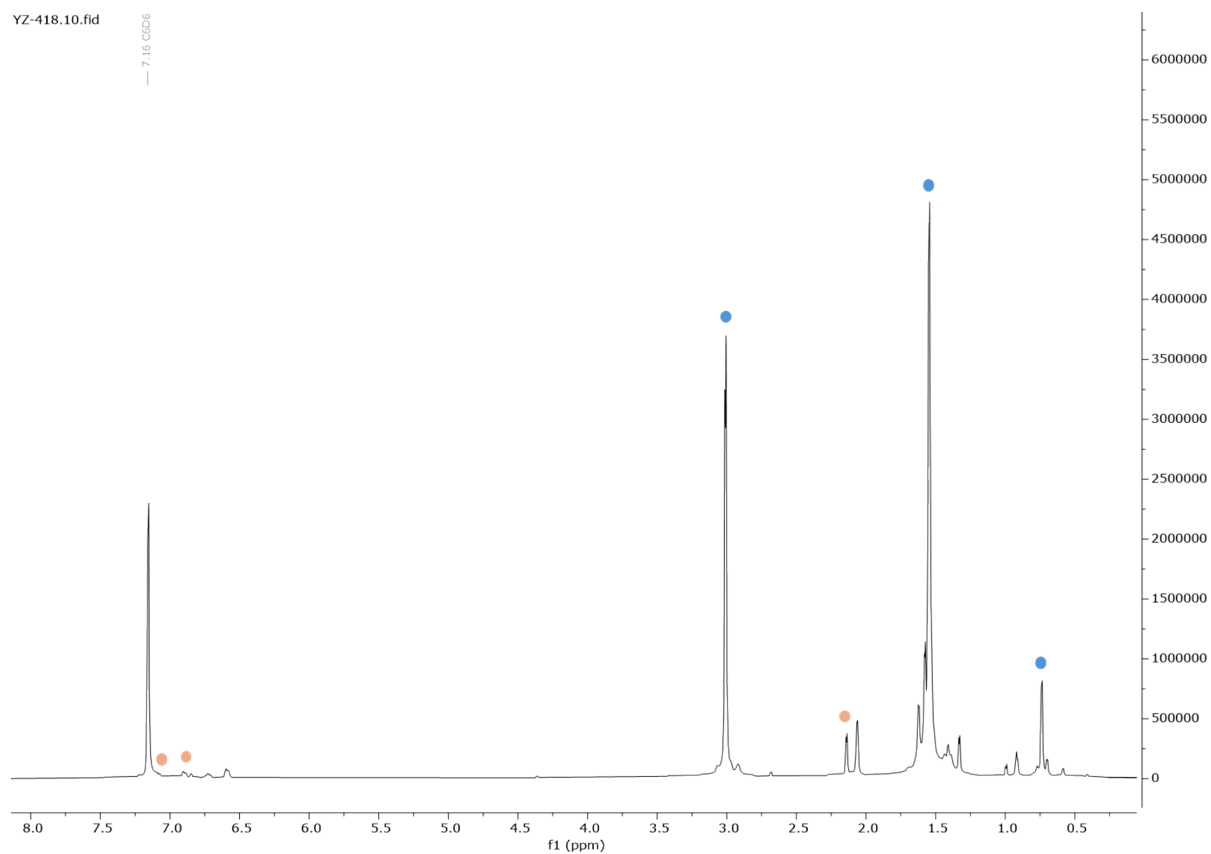


Figure S15: ^1H NMR spectrum of the reaction mixture of **2[K]** and XylINC (blue: **6**; orange: *m*-xylene).

^1H NMR spectra of the reaction mixture of **2[K]** and AdNC

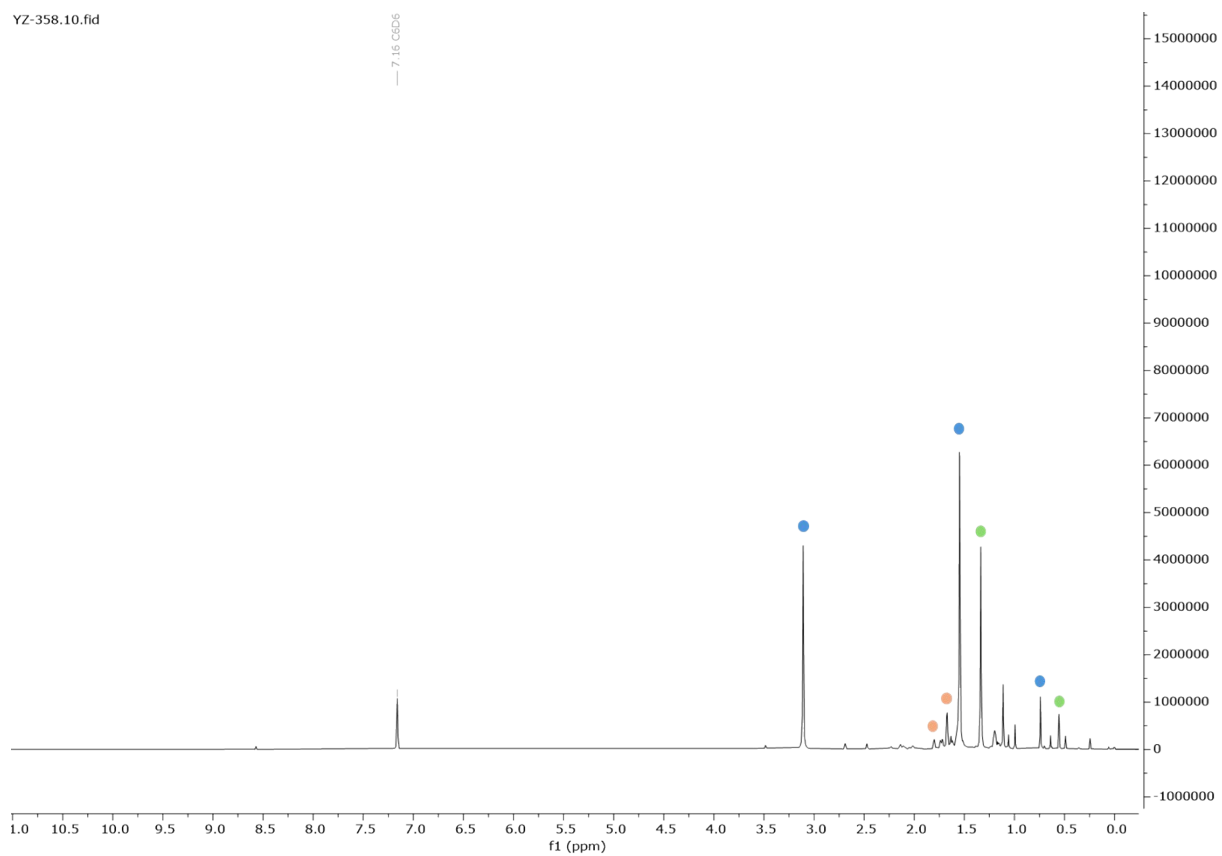
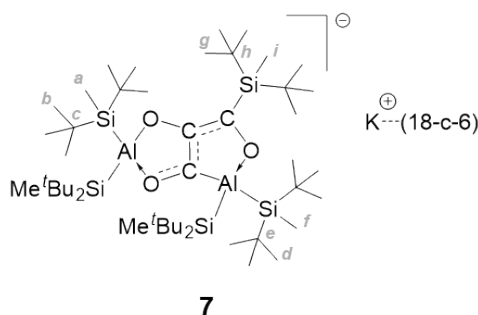


Figure S16: ^1H NMR spectrum of the reaction mixture of **2[K]** and AdNC (blue: **6**; orange: adamantane; green: $\text{Al}(\text{Si}^i\text{Bu}_2\text{Me})_3$).

2.6 CO homologation product **7**



A degassed solution of $\text{Al}(\text{Si}^t\text{Bu}_2\text{Me})_3\text{-K}^+(18\text{-c-6})$ (**2[K]**, 25.0 mg, 31.2 μmol , 1.00 eq.) in THF in a *J. Young* NMR tube was pressed with CO at room temperature. The deep red solution turned orange. The reaction mixture was concentrated and stored at $-30\text{ }^\circ\text{C}$ for several days to give compound **7** as an orange crystal (7.51 mg, 6.11 μmol , 39%). The crystals are suitable for SC-XRD analysis.

^1H NMR (400 MHz, $\text{THF-}d_8$): δ [ppm] = 3.62 (s, 24H, 18-c-6), 1.12 (s, 18H, H^g), 1.00-0.98 (m, 72H, H^b and H^d), 0.27 (s, 3H, H^i), -0.02 (s, 12H, H^b and H^f).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{THF-}d_8$): δ [ppm] = 192.48 (s, C^j), 175.56 (s, C^k), 71.39 (s, 18-c-6), 31.87 (d, $J = 11.3$ Hz, C^b), 31.58 (d, $J = 14.5$ Hz, C^d), 30.30 (s, C^g), 22.13 (d, $J = 11.3$ Hz, C^e), 21.69 (s, C^c), 20.79 (s, C^h), -3.51 (s, C^a), -4.03 (s, C^f), -6.87 (s, C^i).

$^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, $\text{THF-}d_8$): δ [ppm] = 5.06 (s, C^fSi), 4.47 (s, C^jSi), -4.42 (s, C^aSi). (Signals were assigned using the ^{29}Si -HMBC spectrum.)

LIFDI-MS (positive ion mode): m/z found: 303.1203 [$\text{C}_{12}\text{H}_{24}\text{KO}_6$] $^+$, Anion wasn't detected because of positive ion mode.

YZ-AIS13KCO-2recry.10.fid

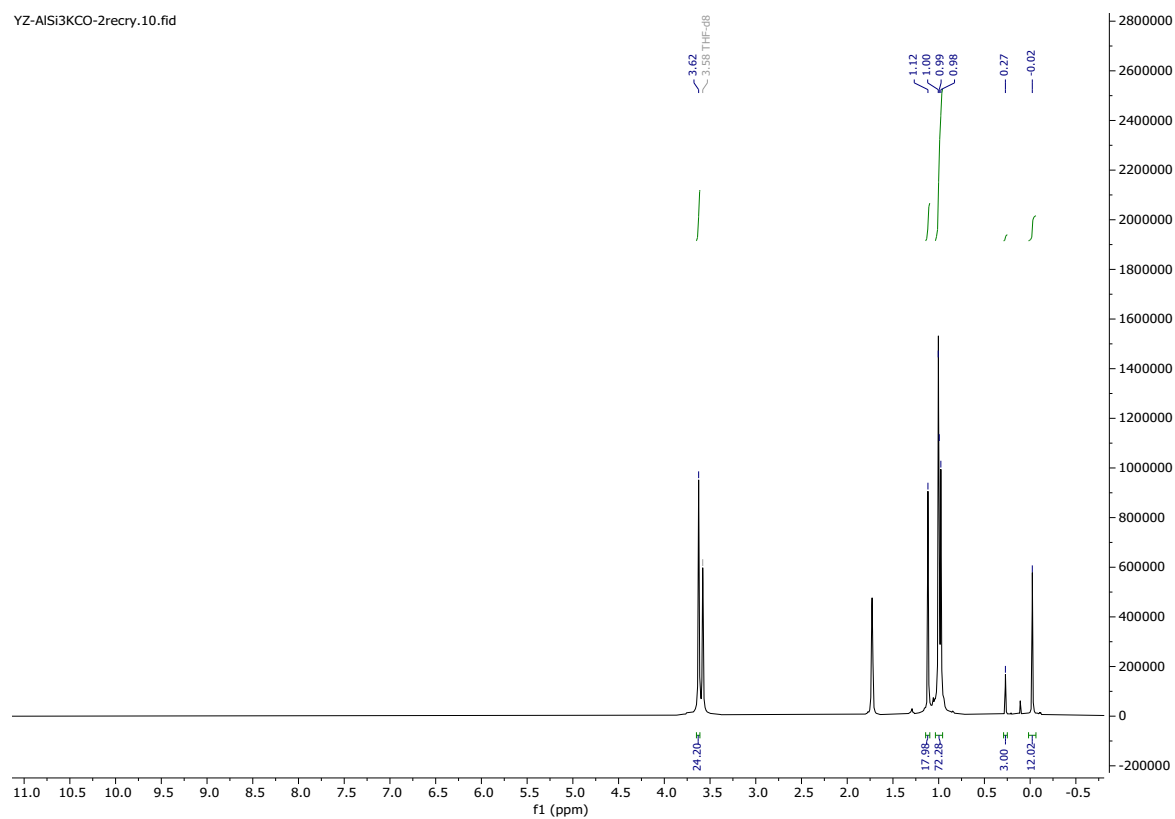


Figure S17: ^1H NMR spectrum of compound 7 in THF- d_8 at 298 K.

YZ-AIS13KCO-2recry.11.fid

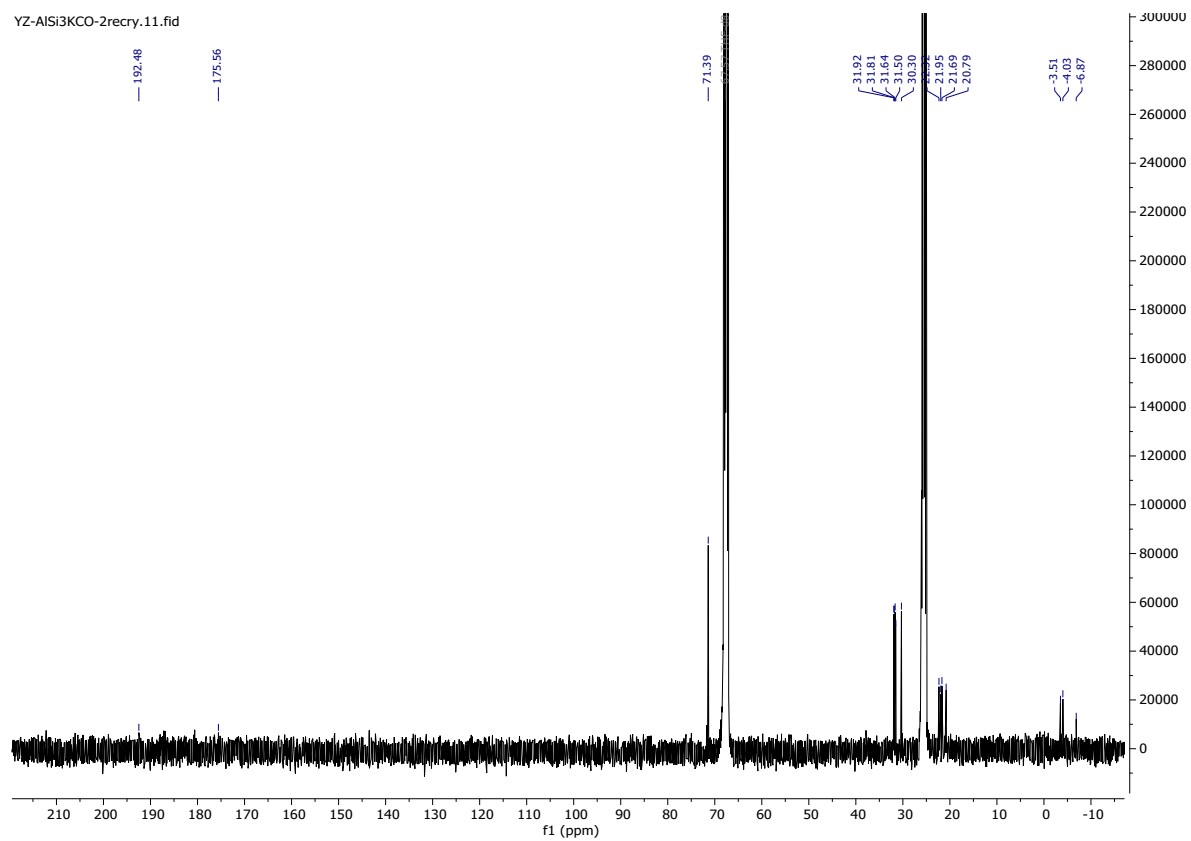


Figure S18: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 7 in THF- d_8 at 298 K.

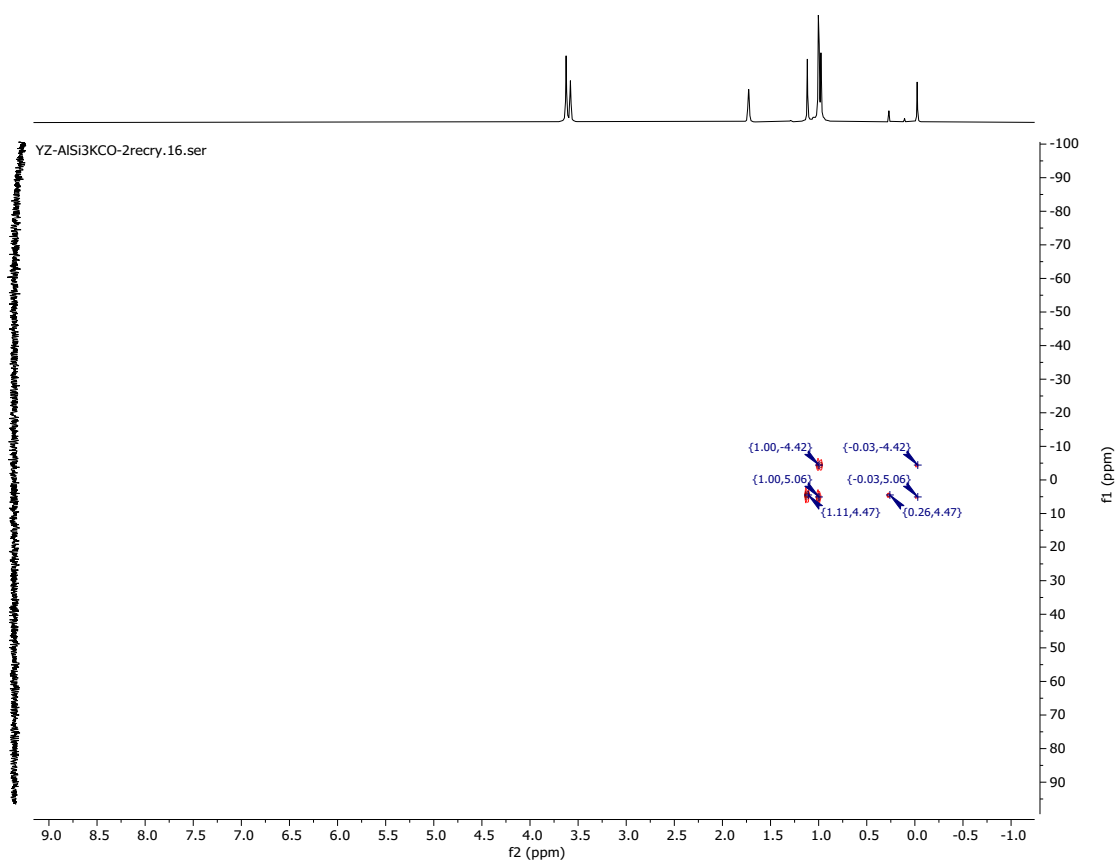


Figure S19: $^{29}\text{Si}\{^1\text{H}\}$ HMBC spectrum of compound **7** in $\text{THF-}d_8$ at 298 K.

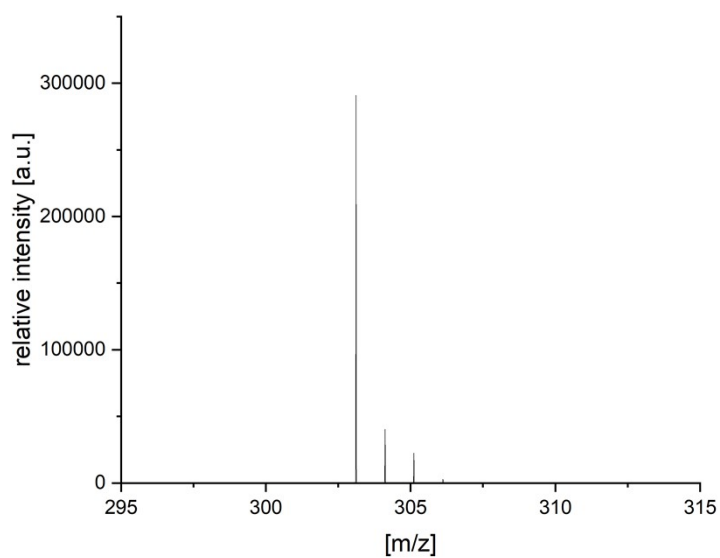


Figure S20: LIFDI-MS spectrometry (detail view with isotopic pattern) of **7**. Measured $m/z = 303.1203$
 $[\text{C}_{12}\text{H}_{24}\text{KO}_6]^+$.

^1H NMR spectra of the crude reaction mixture of **2[K]** and CO

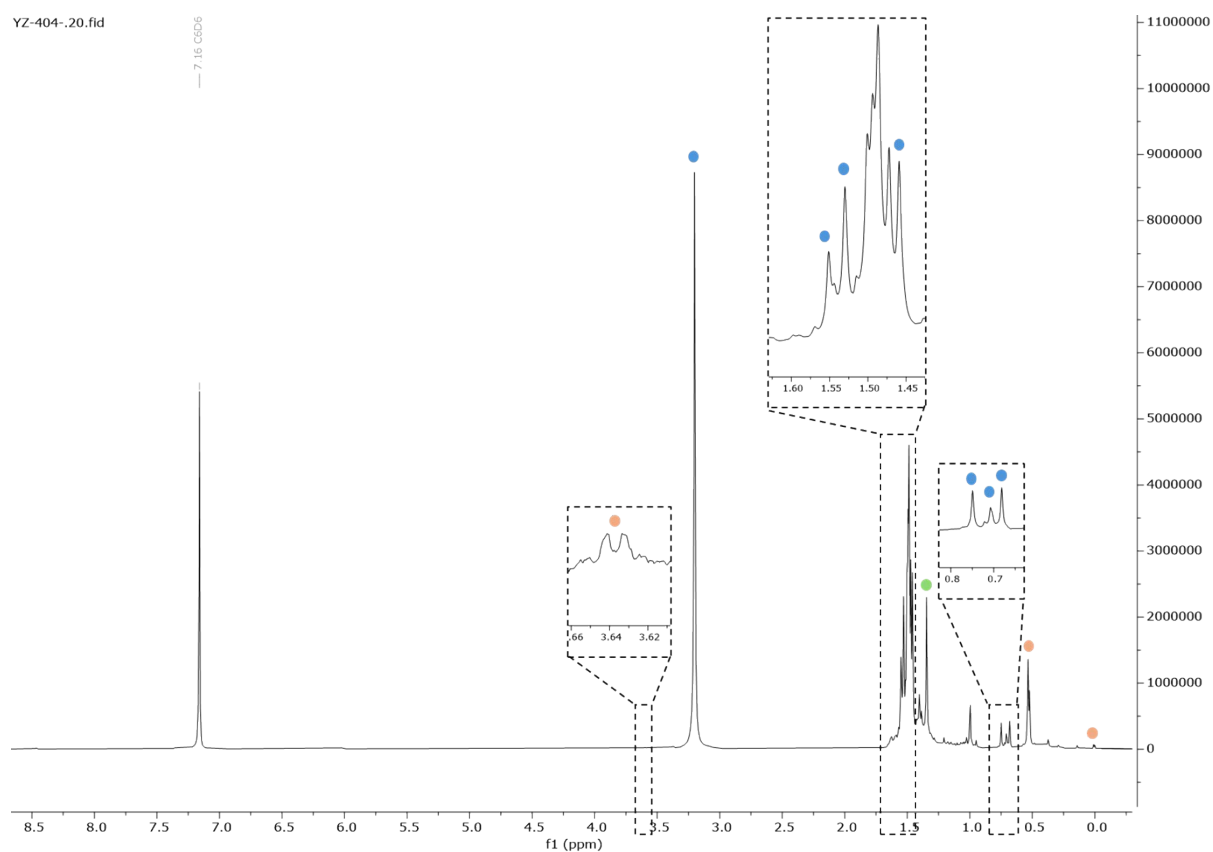


Figure S21: ^1H NMR spectrum of the crude reaction mixture of **2[K]** and CO (blue: compound **7**; orange: $\text{HSi}^i\text{Bu}_2\text{Me}$, green: $\text{Al}(\text{Si}^i\text{Bu}_2\text{Me})_3$ (**1**)).

3 Single-Crystal X-ray Diffraction Analysis

3.1 General information

The X-ray intensity data were collected on an X-ray single crystal diffractometer equipped with a CMOS detector (Bruker Photon-100), a rotating anode (Bruker TXS) with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and a Helios mirror optic by using the APEX4 software package or an X-ray single crystal diffractometer equipped with a CMOS detector (Bruker Photon-100), an IMS microsource with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and a Helios mirror optic by using the APEX4 software package.⁶ The measurement was performed on single crystals coated with perfluorinated ether. The crystal was fixed on the top of a microsampler, transferred to the diffractometer and measured under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorentz and polarization effects, scan speed, and background using SAINT. Absorption corrections, including odd and even ordered spherical harmonics, were performed using SADABS.⁷ Space group assignments were based on systematic absences, E statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined against all data using the APEX4⁸ in conjunction with SHELXL-2018/3.^{9, 10} and SHELXLE.¹¹ Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 \AA and $U_{iso}(\text{H}) = 1.5 \cdot U_{eq}(\text{C})$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 and 0.95 \AA , respectively, and $U_{iso}(\text{H}) = 1.2 \cdot U_{eq}(\text{C})$. If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Delta w(\text{Fo}^2 - \text{Fc}^2)^2$ with SHELXL-97¹² weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.¹³ Refinement afforded using the function SQUEEZE/Platon¹⁴, a volume of 241 \AA^3 in 1 void per unit cell for one benzene molecule per asymmetric unit was found. Images of the crystal structures were generated by PLATON and MERCURY.^{15, 16} The CCDC numbers CCDC 2543012, 2543016 and 2543019 contain the supplementary

crystallographic data for structure **4**, **5** and **7**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>. The CIF files were generated using FinalCif.¹⁷

3.2 Molecular structure of **3**

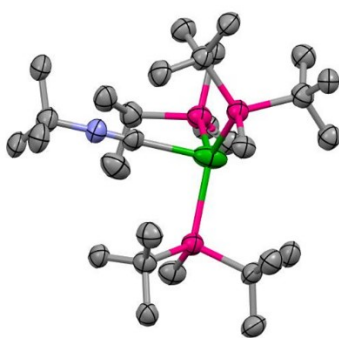


Figure S22: Connectivity of **3**.

3.3 Molecular structure of **4**

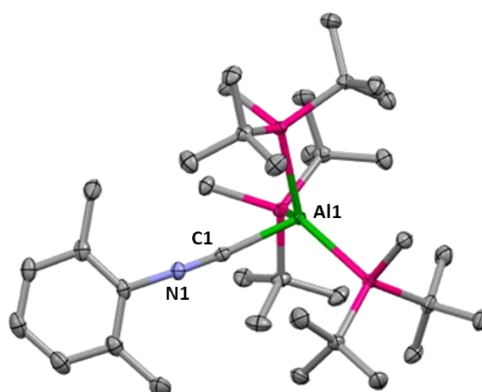


Figure S23: Molecular structure of **4**. Thermal ellipsoids are shown at a 50% probability level. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-Al1 2.093(1), N1-C1-Al1 169.93(9).

Table S1: Crystallographic details of **4**.

CCDC number	2543012
Empirical formula	C ₃₆ H ₇₂ AlNSi ₃
Formula weight	630.19
Temperature [K]	100
Crystal system	monoclinic
Space group (number)	<i>P</i> 2 ₁ / <i>n</i> (14)
<i>a</i> [Å]	13.0203(13)
<i>b</i> [Å]	17.9076(16)
<i>c</i> [Å]	17.2429(18)
α [°]	90
β [°]	95.970(4)
γ [°]	90
Volume [Å³]	3998.6(7)
<i>Z</i>	4
ρ_{calc} [gcm⁻³]	1.047
μ [mm⁻¹]	0.164
<i>F</i>(000)	1400
Radiation	MoK _α (λ = 0.71073 Å)
2θ range [°]	3.74 to 51.38
Index ranges	-15 ≤ <i>h</i> ≤ 15 -21 ≤ <i>k</i> ≤ 21 -21 ≤ <i>l</i> ≤ 21

Independent reflections	7565
Completeness to $\theta = 25.242^\circ$	0.995
Data / Restraints / Parameters	7565 / 104 / 471
Absorption correction T_{\min}/T_{\max} (method)	0.720 / 0.745 (multi-scan)
Goodness-of-fit on F^2	1.053
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0283$ $wR_2 = 0.0769$

3.4 Molecular structure of **5**

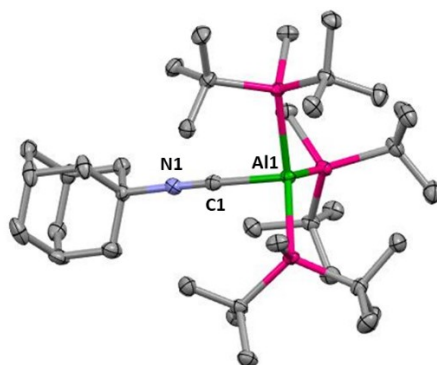


Figure S24: Molecular structure of **5**. Thermal ellipsoids are shown at a 50% probability level. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-Al1 2.086(2), N1-C1-Al1 177.3(2).

Table S2: Crystallographic details of **5**.

CCDC number	2543016
Empirical formula	C ₃₈ H ₇₈ AlNSi ₃
Formula weight	660.26
Temperature [K]	100
Crystal system	monoclinic
Space group (number)	<i>P</i> 2 ₁ / <i>c</i> (14)
<i>a</i> [Å]	13.7786(17)
<i>b</i> [Å]	13.5158(17)
<i>c</i> [Å]	22.678(3)
α [°]	90
β [°]	96.784(5)
γ [°]	90
Volume [Å³]	4193.7(9)
<i>Z</i>	4
ρ_{calc} [gcm⁻³]	1.046
μ [mm⁻¹]	0.159
<i>F</i>(000)	1472
Radiation	MoK _α (λ=0.71073 Å)
2θ range [°]	4.47 to 52.91
Index ranges	-17 ≤ <i>h</i> ≤ 17 -16 ≤ <i>k</i> ≤ 16 -28 ≤ <i>l</i> ≤ 28

Independent reflections	8591
Completeness to $\theta = 25.242^\circ$	99.4 %
Data / Restraints / Parameters	8591 / 0 / 409
Absorption correction T_{\min}/T_{\max} (method)	0.680 / 0.745 (multi-scan)
Goodness-of-fit on F^2	1.203
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0465$ $wR_2 = 0.1487$

3.5 Molecular structure of **6**

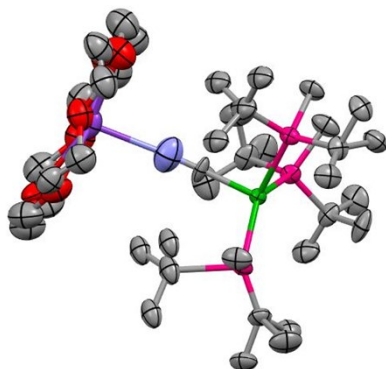


Figure S25: Connectivity of **6**.

3.6 Molecular structure of 7

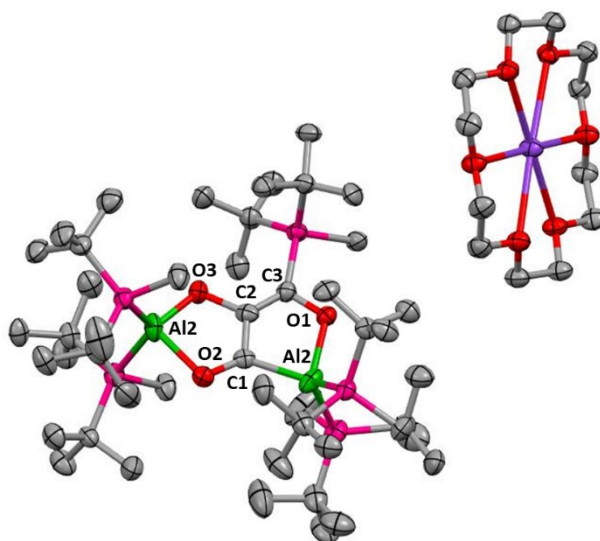


Figure S26: Molecular structure of **7**. Thermal ellipsoids are shown at a 50% probability level. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al1-O3 1.718(4), Al1-O2 1.998(4), C2-O3 1.501(5), C1-O2 1.291(7), C2-C3 1.322(5), C1-C2 1.380(7), C3-O1 1.341(6), Al2-O1 2.006(4), Al2-C1 1.954(6).

Table S3: Crystallographic details of **7**.

CCDC number	2543019
Empirical formula	C ₆₈ H ₁₄₄ Al ₂ KN ₀ O ₁₁ Si ₅
Formula weight	1371.34
Temperature [K]	100
Crystal system	monoclinic
Space group (number)	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	19.6166(11)
<i>b</i> [Å]	21.0516(12)
<i>c</i> [Å]	21.7848(12)
α [°]	90
β [°]	91.664(2)
γ [°]	90
Volume [Å³]	8992.5(9)
Z	4
ρ_{calc} [gcm⁻³]	1.013

μ [mm⁻¹]	0.191
$F(000)$	3020
Radiation	MoK α ($\lambda=0.71073$ Å)
2θ range [°]	3.87 to 55.14
Index ranges	-25 \leq h \leq 25 -27 \leq k \leq 27 -28 \leq l \leq 28
Independent reflections	20708
Completeness to $\theta = 25.242^\circ$	99.4 %
Data / Restraints / Parameters	20708 / 2565 / 1212
Absorption correction T_{min}/T_{max} (method)	0.711 / 0.746 (multi-scan)
Goodness-of-fit on F^2	1.189
Final R indexes [$\geq 2\sigma(I)$]	$R_1 = 0.0655$ $wR_2 = 0.2244$

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