Supporting Information

Half-Sandwich Scandium Methylidenes

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Experimental Section

General Considerations

Caution! *$LiAlMe_4$, $AlMe_3$, $GaMe_3$ and their derivatives are highly pyrophoric and react violently when exposed to air and/or moisture.* All manipulations were performed under an inert argon atmosphere, either by using Schlenk techniques or a glovebox (MBraun 200B; <0.1 ppm O_2, <0.1 ppm H_2O). *n*-Hexane, tetrahydrofuran (THF), and toluene were dried over Grubbs-type columns (MBraun SPS, solvent purification system) and stored over 3 Å molecular sieves inside a glovebox. C_6D_6 and toluene-d_8 were purchased from Sigma Aldrich, degassed, stirred over NaK for at least 24 h, filtered and stored inside a glovebox. Sc_2O_3 and $AlMe_3$ were purchased from abcr and used as received. $GaMe_3$ was purchased from Dockweiler Chemicals and used as received. *n*-BuLi, $HC_5Me_4SiMe_3$ (HCp') and HC_5Me_5 (HCp*) were purchased from Sigma Aldrich. MeLi was purchased from Sigma Aldrich and the solvent was removed before storing inside a glovebox. $ScCl_3(thf)_3$,[1] $Cp^*Sc(CH_2C_6H_4NMe_2\text{-}o)_2$, $Cp'Sc(CH_2C_6H_4NMe_2\text{-}o)_2$,[2] $[Cp'ScMe_2]_2$,[3] $LiCp^R$ (R = Me_5, Me_4SiMe_3)[4] and $LiAlMe_4$[5] were synthesized according to literature procedures. ^1H, ^7Li, $^{13}C\{^1H\}$ and ^{45}Sc NMR spectra were recorded on a Bruker Avance AVII+400 (^1H: 400 MHz, ^{13}C: 101 MHz, ^7Li: 155 MHz, ^{45}Sc: 97 MHz), a Bruker Avance III HD 300 NanoBay (^1H: 300 MHz, ^{13}C: 75 MHz, ^7Li: 117 MHz) or a Bruker AVII+500 (^1H: 500 MHz, ^{13}C: 126 MHz , ^{45}Sc: 122 MHz). ^1H, $^{13}C\{^1H\}$, ^7Li, and ^{45}Sc NMR chemical shifts are referenced to internal solvent resonances and reported in parts per million (ppm) relative to tetramethylsilane (TMS), LiCl, and $Sc(NO_3)_3$. Analyses of NMR spectra were performed with Bruker Topspin (Version 3.6.1). Multiplicities of signals are given as s (singlet), d (duplet), m (multiplet) and br (broad). Coupling constants (*J*) are given in Hz. Crystallographic data collection was done on a Bruker APEX II Duo diffractometer using QUAZAR optics for Mo K_α (λ = 0.71073 Å) with ω and φ scans. Elemental analysis (C, H, N) was performed on an Elementar vario MICRO cube. DRIFTS spectra of the powdered methylidene complexes were measured on a Bruker Invenio R mixed with powdered KBr.

$Cp'ScCl_2(\mu\text{-}Cl)Li(thf)_3$ (1'). A cooled solution of LiCp' (625 mg, 3.12 mmol) in 5 mL of THF was added to a stirred suspension of $ScCl_3(thf)_3$ (1135 mg, 3.087 mmol) in 10 mL of THF at –40 °C. The resulting pale-yellow suspension was stirred for 3 days at ambient temperature. The solvent was removed *in vacuo*. The residue was extracted with *n*-hexane (3x10 mL), the combined extracts concentrated and kept at –40 °C. After one day, colorless crystals formed. After concentrating the slightly yellow mother liquor to half of the volume and storing it at –40 °C, a second batch of crystals formed to yield a combined amount of 1300 mg (2.289 mmol, 74%). ^1H NMR (400 MHz, C_6D_6, 26 °C): δ 3.54 (m, 12H, α-THF), 2.53 (s, 6H, 2,5-$C_5\underline{Me}_4SiMe_3$), 2.23 (s, 6H, 3,4-$C_5\underline{Me}_4SiMe_3$), 1.35 (m, 12H, β-THF), 0.62 (s, 9H, $C_5Me_4Si\underline{Me}_3$) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 26 °C): δ 133.4 (3,4-$\underline{C}_5Me_4SiMe_3$), 129.5 (2,5-$\underline{C}_5Me_4SiMe_3$), 123.2 (1-$\underline{C}_5Me_4SiMe_3$), 68.6 (α-THF), 25.5 (β-THF), 15.6 (2,5-$C_5\underline{Me}_4SiMe_3$), 12.3 (3,4-$C_5\underline{Me}_4SiMe_3$), 2.2 ($C_5Me_4Si\underline{Me}_3$) ppm. ^7Li NMR (117 MHz, C_6D_6, 26 °C): δ 0.0 ppm. $^{45}Sc\{^1H\}$ NMR (97 MHz, C_6D_6, 26 °C): δ 264.2 ppm. $C_{24}H_{45}Cl_3LiO_3ScSi$ (567.96 g/mol): calcd. (%) C 50.75, H 7.99; found C 50.21, H 8.49.

$Cp^*ScCl_2(\mu\text{-}Cl)Li(thf)_3$ (1*). A cooled solution of LiCp* (859 mg, 6.04 mmol) in 5 mL of THF was added to a stirred suspension of $ScCl_3(thf)_3$ (2201 mg, 5.987 mmol) in 10 mL of THF at –40 °C. The resulting pale-yellow suspension was stirred for 3 days at 40 °C. The solvent was removed *in vacuo*. The residue was extracted with 10 mL of *n*-hexane and 10 mL of toluene, the extracts concentrated and kept at –40 °C. After one day, colorless crystals formed from both slightly yellow extracts. The *n*-hexane extract yielded 103 mg, the toluene extract 1589 mg of product. (Combined 1.692 g, 3.319 mmol, 55%). ^1H NMR (400 MHz, C_6D_6, 26 °C): δ 3.55 (m, 12H, α-THF), 2.29 (s, 15H, C_5Me_5), 1.35 (m, 12H, β-THF) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 26 °C): δ 124.7 ($\underline{C}_5Me_5$), 68.6 (α-THF), 25.5 (β-THF), 12.2 ($C_5\underline{Me}_5$) ppm. ^7Li NMR (117 MHz, C_6D_6, 26 °C): δ 0.1 ppm. ^{45}Sc NMR (122 MHz, C_6D_6, 26 °C): δ 269.1 ppm. $C_{22}H_{39}Cl_3LiO_3Sc$ (509.81 g/mol): calcd. (%) C 51.83, H 7.71; found C 44.29, H 5.68. The analysis could indicate a loss of THF. The analysis matches $Cp^*ScCl_3Li(thf)_{0.6}$.

[Cp’ScCl$_2$*LiCl]$_n$ (2’). AlMe$_3$ (67.4 mg, 0.935 mmol) was added to a cooled, stirred solution of **1’** (102.0 mg, 0.180 mmol) in 3 mL of toluene. After one minute, a white precipitate had formed. All volatiles were removed, and the residue washed with *n*-hexane to yield **2’** (61.3 mg, 0.174 mmol, 97%). Single crystals suitable for X-ray diffraction were obtained by heating a C_6D_6 solution to 130 °C for one day and letting it cool to ambient temperature.

[Cp*ScCl$_2$*LiCl]$_n$ (2*). AlMe$_3$ (70.6 mg, 0.979 mmol) was added to a cooled, stirred solution of **1*** (90.7 mg, 0.178 mmol) in 3 mL of toluene. After one minute, a white precipitate had formed. All volatiles were removed, and the residue washed with *n*-hexane to yield **2’** (50.2 mg, 0.171 mmol, 96%). Single crystals suitable for X-ray diffraction were obtained by heating a C_6D_6 solution to 130 °C for one day and letting it cool to ambient temperature.

[Cp’Sc(AlMe$_4$)Cl]$_2$ (3’). A precooled toluene solution of **1’** (385.0 mg, 0.678 mmol) was added dropwise to a stirred, cooled suspension of LiAlMe$_4$ (112.8 mg, 1.199 mmol) and AlMe$_3$ (146.6 mg, 2.034 mmol) in toluene. The resulting yellowish suspension was stirred overnight at ambient temperature. The suspension was filtered, and the volatiles were removed *in vacuo* to yield a sticky yellow solid. The residue was redissolved in 3 mL *n*-hexane and cooled to –40 °C for two days to yield crystalline **3’** (87.2 mg, 0.121 mmol, 36%). ^{1}H NMR (300 MHz, C_6D_6, 26 °C): δ 2.12 (s, 6H, 2,5-$C_5\underline{Me}_4SiMe_3$), 1.77 (s, 6H, 3,4-$C_5\underline{Me}_4SiMe_3$), 0.31 (s, 9H, $C_5Me_4Si\underline{Me}_3$), –0.19 (s, br, 12H, AlMe$_4$) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 26 °C): δ 15.7 (2,5-$C_5\underline{Me}_4SiMe_3$), 11.9 (3,4-$C_5\underline{Me}_4SiMe_3$), 1.9 ($C_5Me_4Si\underline{Me}_3$) ppm. The ^{13}C{^{1}H} NMR signals of the quaternary carbon atoms of the Cp’ ligand and the methyl groups bound to scandium and aluminum could not be resolved. ^{45}Sc{^{1}H} NMR (97 MHz, C_6D_6, 26 °C): δ 404.1, 253.5, 213.0 ppm. $C_{32}H_{66}Al_2Cl_2Sc_2Si_2$ (721.82 g/mol): calcd. (%) C 53.25, H 9.22; found C 53.07, H 8.90.

[Cp*Sc(AlMe$_4$)Cl]$_2$ (3*). A precooled toluene solution of **1*** (99.8 mg, 0.196 mmol) was added dropwise to a stirred, cooled suspension of LiAlMe$_4$ (37.1 mg, 0.394 mmol) and AlMe$_3$ (78.0 mg, 1.08 mmol) in toluene. The resulting yellowish suspension was stirred overnight at ambient temperature. The suspension was filtered, and the volatiles were removed *in vacuo* to yield a sticky yellow solid. The residue was redissolved in 3 mL *n*-hexane and cooled to –40 °C for one day to yield crystalline **3*** (35.2 mg, 0.058 mmol, 59%). ^{1}H NMR (500 MHz, C_6D_6, 26 °C): 1.85 (s, 15H, C_5Me_5), −0.14 (br, 12H, AlMe$_4$) ppm. ^{13}C{^{1}H} NMR (126 MHz, Toluene-d_8, 26 °C): δ 124.4 ($\underline{C}_5Me_5$), 12.3 ($C_5\underline{Me}_5$) ppm. The ^{13}C{^{1}H} NMR signal of the methyl groups bound to scandium and aluminum could not be resolved. ^{45}Sc NMR (122 MHz, C_6D_6, 26 °C): δ 405.7, 244.0, 224.3 ppm. $C_{28}H_{54}Al_2Cl_2Sc_2$ (605.51 g/mol): calcd. (%) C 55.54, H 8.99; found C 53.70, H 8.52.

[Cp’Sc(AlMe$_4$)Me] (4’). Path A:[3] A precooled toluene solution of **1’** (42.2 mg, 0.074 mmol) was added dropwise to a stirred, cooled suspension of LiAlMe$_4$ (21.1 mg, 0.224 mmol) and AlMe$_3$ (21.1 mg, 0.293 mmol) in toluene. The resulting yellowish suspension was stirred for four days at ambient temperature. The suspension was filtered. Prolonged evacuation and repeated co-evaporation with toluene to completely remove AlMe$_3$(thf) yielded **4’** as an orange oil (25.0 mg, 0.073 mmol, 98%).

Path B: AlMe$_3$ (109 mg, 1.51 mmol) was added dropwise to a precooled, stirred solution of [Cp’ScMe$_2$]$_2$ (234 mg, 0.436 mmol). The resulting solution was stirred for 30 minutes at ambient temperature and the solvent was removed *in vacuo* to yield **4’** as a pale orange oil (141 mg, 0.414 mmol, 95%). The reaction of ate complex **7’** with at least 6 equiv. AlMe$_3$ proceeded the same way. In Path A and B, the oil contained about 5% of **8’**.

Path C: AlMe$_3$ (40.1 mg, 0.555 mmol) was added dropwise to a precooled, stirred solution of Cp’Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (93.6 mg, 0.184 mmol). The resulting solution was stirred for 30 minutes at ambient temperature. After removal of the solvent, a mixture of **4’** and the byproduct $Me_2Al(CH_2C_6H_4NMe_2$-*o*) was obtained as an orange oil. No yield was determined. ^{1}H NMR (300 MHz, C_6D_6, 26 °C): δ 2.10 (s, 6H, 2,5-$C_5\underline{Me}_4SiMe_3$), 1.75 (s, 6H, 3,4-$C_5\underline{Me}_4SiMe_3$), 0.28 (s, 9H, $C_5Me_4Si\underline{Me}_3$), −0.19 (s, br, 15H, AlMe$_4$/Me) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 26 °C): δ 131.7 (3,4-$\underline{C}_5Me_4SiMe_3$), 127.5 (2,5-$\underline{C}_5Me_4SiMe_3$), 121.4 (1-$\underline{C}_5Me_4SiMe_3$), 15.0 (2,5-$C_5\underline{Me}_4SiMe_3$), 11.5

(3,4-$C_5\underline{Me}_4SiMe_3$), 2.0 ($C_5Me_4Si\underline{Me}_3$) ppm. The $^{13}C\{^1H\}$ NMR signal of the methyl groups bound to scandium and aluminum could not be resolved. $^{45}Sc\{^1H\}$ NMR (97 MHz, C_6D_6, 26 °C): δ 404.2 ppm. $C_{17}H_{36}AlScSi$ (340.50 g/mol): calcd. (%) C 59.97, H 10.66; found C 58.19, H 9.83. All attempts to further purify 4' failed.

Cp'ScMe(Me/Cl)(dmap) (5'). Solid DMAP (105 mg, 0.859 mmol) was added in portions to a precooled, stirred solution of **4'** (150 mg, 0.428 mmol) in toluene. After 10 minutes into warming to ambient temperature, a dark orange solution formed. After stirring for one hour at ambient temperature, the solvent was removed *in vacuo*. The ^1H NMR spectrum of the crude product (240 mg) showed a 1:1 mixture of Cp'ScMe(Me/Cl)(dmap) and $AlMe_3$(dmap) which corresponds to 96% conversion. The solid was washed with 2 mL of *n*-hexane and extracted with 5 mL of toluene. The toluene extract was concentrated and stored at –40 °C for one week to yield 40.0 mg (0.103 mmol, 24%) of crystalline material. ^1H NMR (400 MHz, C_6D_6, 26 °C): δ 7.94 (d, 2H, $^3J_{HH}$ 7.1 Hz, $NC\underline{H}$), 5.63 (d, 2H, $^3J_{HH}$ 7.1 Hz, $NCHC\underline{H}$), 2.43 (s, 6H, 2,5-$C_5\underline{Me}_4SiMe_3$), 2.07 (s, 6H, 3,4-$C_5\underline{Me}_4SiMe_3$), 1.99 (s, 6H, NMe_2), 0.56 (s, 9H, $C_5Me_4Si\underline{Me}_3$), 0.12 (s, 6H, $Sc\underline{Me}_2$) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 26 °C): δ 155.0 ($N\underline{C}C$), 147.1 ($N\underline{C}H$), 127.0 (3,4-$\underline{C}_5Me_4SiMe_3$), 123.7 (2,5-$\underline{C}_5Me_4SiMe_3$), 115.7 (1-$\underline{C}_5Me_4SiMe_3$), 106.4 ($NCH\underline{C}H$), 38.1 ($N\underline{Me}_2$), 15.6 (2,5-$C_5\underline{Me}_4SiMe_3$), 12.3 (3,4-$C_5\underline{Me}_4SiMe_3$), 2.2 ($C_5Me_4Si\underline{Me}_3$) ppm. The $^{13}C\{^1H\}$ NMR signal of the methyl groups bound to scandium could not be resolved. $^{45}Sc\{^1H\}$ NMR (97 MHz, C_6D_6, 26 °C): δ 474.7, 365.6 ppm. $C_{21}H_{34}N_2ScSi$ (387.56 g/mol): calcd. (%) C 65.08, H 8.84, N 7.23; found C 63.44, H 9.19, N 6.99.

[Cp'ScMe$_2$]$_2$/(tmeda)(AlMe$_3$)$_2$. To an *n*-hexane solution of **4'** (28 mg, 0.082 mmol) was added an excess of 0.20 mL TMEDA (154 mg, 1.3 mmol) at ambient temperature, followed by precipitation of a colorless solid. The supernatant was removed and the solid dissolved in toluene. The toluene solution was concentrated and cooled to –40 °C for two weeks to yield single crystals of (tmeda)($AlMe_3$)$_2$, the identity of which was confirmed *via* a unit cell check.[6] A ^1H NMR spectrum of the crystalline material showed [Cp'$ScMe_2$]$_2$ (ref (22) besides (tmeda)($AlMe_3$)$_2$. (tmeda)($AlMe_3$)$_2$: ^1H NMR (400 MHz, C_6D_6, 26 °C): δ 2.45 (s, 4H, NCH_2CH_2N), 1.72 (s, 12H, NMe_2), −0.53 (s, 18H, $AlMe_3$). [Cp'$ScMe_2$]$_2$: ^1H NMR (400 MHz, C_6D_6, 26 °C): δ 2.25 (s, 12H, 2,5-$C_5\underline{Me}_4SiMe_3$), 1.89 (s, 12H, 3,4-$C_5\underline{Me}_4SiMe_3$), 0.36 (s, 18H, $C_5Me_4Si\underline{Me}_3$), 0.13 (s, 12H, $ScMe_2$). This is in line with previously published data.[3] $^{45}Sc\{^1H\}$ NMR (97 MHz, C_6D_6, 26 °C): δ 455.0 ppm.

[Cp'ScMe(OC_6H_9)]$_2$ (6'). To a toluene solution of **4'** (33 mg, 0.094 mmol) was added cyclohexanone (10.2 mg, 0.104 mmol) at ambient temperature. The solvent was removed *in vacuo*. The remaining orange oil was redissolved in *n*-pentane and cooled to –40 °C for 3 weeks to yield few colorless single crystals of **6'** (6 mg). No yield was determined due to insufficient purity. ^1H NMR (400 MHz, C_6D_6, 26 °C): δ 5.11 (s, 2H, OC=CH), 2.21 (s, 12H, 2,5-$C_5\underline{Me}_4SiMe_3$), 1.92 (s, 12H, 3,4-$C_5\underline{Me}_4SiMe_3$), 0.48 (s, 18H, $C_5Me_4Si\underline{Me}_3$), 0.01 (s, 6H, ScMe). Signals of the CH_2 groups were not resolved. $^{45}Sc\{^1H\}$ NMR (97 MHz, C_6D_6, 26 °C): δ 280.0 ppm.

[Li(thf)$_4$][Cp'ScMe$_3$] (7'). Solid MeLi (165 mg, 7.51 mmol) was added to a precooled, stirred suspension of $ScCl_3$(thf)$_3$ (551 mg, 1.50 mmol) and Cp'H (321 mg, 1.65 mmol) in THF. The resulting yellow suspension was stirred for 1 h at ambient temperature. Then, all volatiles were removed. The solid residue was extracted with toluene, and the solvent was removed from the extract. At this point, a ^1H NMR spectrum suggested the loss of 2 THF moieties to yield Cp'$ScMe_3$Li(thf)$_2$ (637 mg, 1.47 mmol, 98%) (*cf.* Supporting Information). Crystals of [Li(thf)$_4$][Cp'$ScMe_3$] suitable for SC-XRD were obtained by layering a concentrated THF solution with *n*-hexane and storing it at –40 °C for one week. Note that THF may be lost upon extended drying and co-evaporation with non-donating solvents. ^1H NMR (300 MHz, C_6D_6, 26 °C): δ 3.45 (m, 16H, α-THF), 2.49 (s, 6H, 2,5-$C_5\underline{Me}_4SiMe_3$), 2.22 (s, 6H, 3,4-$C_5\underline{Me}_4SiMe_3$), 1.31 (m, 16H, β-THF), 0.62 (s, 9H, $C_5Me_4Si\underline{Me}_3$), −0.31 (s, 9H, $ScMe_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 26 °C): δ 125.7 (3,4-$\underline{C}_5Me_4SiMe_3$), 122.6 (2,5-$\underline{C}_5Me_4SiMe_3$), 114.2 (1-$\underline{C}_5Me_4SiMe_3$), 68.2 (α-THF), 25.5 (β-THF), 19.5 (br, $ScMe_3$), 15.0 (2,5-$C_5\underline{Me}_4SiMe_3$), 11.9 (3,4-$C_5\underline{Me}_4SiMe_3$), 2.8 ($C_5Me_4Si\underline{Me}_3$) ppm. The $^{13}C\{^1H\}$ NMR signal of the methyl groups bound to scandium was detected *via* $^1H-^{13}C$

HSQC NMR. ^{7}Li NMR (155 MHz, C_6D_6, 26 °C): δ 0.2 ppm. ^{45}Sc{^{1}H} NMR (97 MHz, C_6D_6, 26 °C): δ 501.9 ppm. $C_{31}H_{62}LiO_4ScSi$ (578.81 g/mol): calcd. (%) C 64.33, H 10.80; found C 63.01, H 10.52. Elemental analysis may indicate loss of THF.

Cp'Sc(CH$_2$)(AlMe$_3$)$_2$ (8'). In a pressure tube, solid **1'** (350 mg, 0.616 mmol) was added to a stirred suspension of $LiAlMe_4$ (174 mg, 1.85 mmol) and $AlMe_3$ (178 mg, 2.47 mmol) in toluene. The pressure tube was taken outside the glovebox and heated in an oil bath to 70 °C for 9 days, turning into a red suspension. Then, the pressure tube was transferred back into the glovebox, the reaction mixture was filtered, and the volatiles were removed *in vacuo*. The remaining solid was washed at least three times with a maximum of 1 mL cold *n*-hexane to yield a colorless crystalline solid. Crystals suitable for SC-XRD were obtained from a saturated *n*-hexane solution at –40 °C (115 mg, 0.290 mmol, 47%). ^{1}H NMR (400 MHz, C_6D_6, 26 °C): δ 2.02 (s, 6H, 2,5-$C_5\underline{Me}_4SiMe_3$), 1.87 (s, 6H, 3,4-$C_5\underline{Me}_4SiMe_3$), 0.95 (br, 1H, $ScC\underline{H}H$), 0.20 (s, 9H, $C_5Me_4Si\underline{Me}_3$), −0.01 (br, 1H, $ScCH\underline{H}$), −0.33 (s, 18H, $AlMe_3$) ppm. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 26 °C): δ 133.5 (3,4-$\underline{C}_5Me_4SiMe_3$), 129.6 (2,5-$\underline{C}_5Me_4SiMe_3$), 122.2 (1-$\underline{C}_5Me_4SiMe_3$), 53.0 (br, $Sc\underline{C}H_2$), 15.2 (2,5-$C_5\underline{Me}_4SiMe_3$), 12.2 (3,4-$C_5\underline{Me}_4SiMe_3$), 1.9 ($C_5Me_4Si\underline{Me}_3$) ppm. The ^{13}C{^{1}H} NMR signal of the methyl groups bound to scandium and aluminum could not be resolved. ^{45}Sc{^{1}H} NMR (97 MHz, C_6D_6, 26 °C): δ 272.6 ppm. IR (KBr): $\tilde{\nu}$ = 2946 (vs), 2891 (s), 2819 (m), 2747 (vw), 1483 (w), 1460 (w), 1408 (w), 1320 (m), 1269 (w), 1252 (s), 1217 (w), 1186 (s), 1129 (w), 1020 (w), 846 (s), 760 (m), 740 (w), 708 (s), 665 (m), 632 (m), 600 (w), 580 (m), 540 (w), 483 (vw), 461 (w), 428 (m) cm^{-1}. $C_{19}H_{41}Al_2ScSi$ (396.54 g/mol): calcd. (%) C 57.77, H 10.41; found C 57.87, H 10.36.

Cp*Sc(CH$_2$)(AlMe$_3$)$_2$ (8*). In a pressure tube, solid **1*** (300 mg, 0.588 mmol) was added to a stirred suspension of $LiAlMe_4$ (166 mg, 1.76 mmol) and $AlMe_3$ (170 mg, 2.35 mmol) in toluene. The pressure tube was taken outside the glovebox and heated in an oil bath to 70 °C for 5 days, turning into a red suspension. Then, the pressure tube was transferred into the glovebox, the reaction mixture was filtered, and the volatiles were removed *in vacuo*. The remaining solid was washed at least three times with 1 mL cold *n*-hexane to yield a colorless crystalline solid. Crystals suitable for SC-XRD were obtained from a saturated *n*-hexane solution at –40 °C. After concentrating the slightly pale red mother liquor and storing it at –40 °C, a second batch of crystals formed for a combined yield of 131 mg (0.387 mmol, 66%). ^{1}H NMR (500 MHz, Toluene-*d*$_8$, 26 °C): δ 1.80 (s, 15H, $C_5\underline{Me}_5$), 0.84 (br, 1H, $ScC\underline{H}H$), −0.13 (br, 1H, $ScCH\underline{H}$), −0.43 (s, 18H, $AlMe_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, Toluene-*d*$_8$, 26 °C): δ 124.4 ($\underline{C}_5Me_5$), 53.2 (br, $Sc\underline{C}H_2$), 11.8 ($C_5\underline{Me}_5$), −1.4 (br, $AlMe_3$) ppm. ^{45}Sc NMR (122 MHz, Toluene-*d*$_8$, 26 °C): δ 279.6 ppm. IR (KBr): $\tilde{\nu}$ = 3015 (vw), 2974 (w), 2923 (s), 2886 (m), 2821 (w), 2767 (vw), 1487 (vw), 1434 (w), 1381 (w), 1210 (w), 1184 (s), 1024 (vw), 830 (m), 704 (vs), 664 (m), 620 (w), 578 (s), 542 (m), 480 (w), 415 (m) cm^{-1}. $C_{17}H_{35}Al_2Sc$ (338.39 g/mol): calcd. (%) C 60.34, H 10.43; found C 60.64, H 10.13.

[(Cp'ScCH$_2$)$_3$LiAlMeCl$_3$]$_n$ (9'). Colorless crystals (4 mg) of **9'** were obtained from the concentrated red supernatant of **8'** after two months at −40 °C. ^{1}H NMR (400 MHz, C_6D_6, 26 °C): δ 2.35 (s, 18H, 2,5-$C_5\underline{Me}_4SiMe_3$), 2.07 (s, 18H, 3,4-$C_5\underline{Me}_4SiMe_3$), 1.36 (br, 3H, $ScC\underline{H}H$), 0.97 (br, 3H, $ScCH\underline{H}$), 0.44 (s, 27H, $C_5Me_4Si\underline{Me}_3$), −0.50 (s, 3H, $Li\underline{Me}Al$) ppm. ^{45}Sc{^{1}H} NMR (97 MHz, C_6D_6, 26 °C): δ 429.2 ppm.

Cp'Sc(CH$_2$)(AlMe$_3$)(GaMe$_3$) (10'). In a J. Young-valved NMR tube, **4'** (145 mg, 0.43 mmol) was dissolved in 0.5 mL of C_6D_6. $GaMe_3$ (100 mg, 0.87 mmol) was added neat and another 0.2 mL of C_6D_6 was added. The NMR tube was taken outside the glovebox and heated in an oil bath to 80 °C for 6.5 h. The NMR tube was transferred into the glovebox and all volatiles were removed *in vacuo*. The remaining oily residue was dissolved in 1 mL of *n*-hexane and stored at −40 °C. After one week, colorless crystals of **10'** formed. The crystals were recrystallized two times from *n*-hexane. The mother liquor yielded a second crop of crystals for a combined yield of 31 mg (0.071 mmol, 17%). ^{1}H NMR (500 MHz, toluene-*d*$_8$, 26 °C): δ 2.03−2.02 (s, 6H, 2,5-$C_5\underline{Me}_4SiMe_3$), 1.90−1.86 (s, 6H, 3,4-$C_5\underline{Me}_4SiMe_3$), 0.94 (br, 1H, $ScC\underline{H}H$), 0.21−0.19 (s, 9H, $C_5Me_4Si\underline{Me}_3$), 0.10−0.07 (d, br, 1H, $^2J_{HH}$ 13.5 Hz, $ScCH\underline{H}$), −0.17 (s, 9H, $GaMe_3$), −0.41 (s, 9H, $AlMe_3$) ppm.

^{13}C{^{1}H} NMR (126 MHz, toluene-d_8, 26 °C): δ 132.9−132.4 (3,4-$\underline{\mathrm{C}}_5\mathrm{Me}_4\mathrm{SiMe}_3$), 129.6 (2,5-$\underline{\mathrm{C}}_5\mathrm{Me}_4\mathrm{SiMe}_3$), 122.1−121.5 (1-$\underline{\mathrm{C}}_5\mathrm{Me}_4\mathrm{SiMe}_3$), 53.1 (br, Sc$\underline{\mathrm{C}}\mathrm{H}_2$), 15.2 (2,5-$\mathrm{C}_5\underline{\mathrm{Me}}_4\mathrm{SiMe}_3$), 12.2 (3,4-$\mathrm{C}_5\underline{\mathrm{Me}}_4\mathrm{SiMe}_3$), 2.0−1.9 ($\mathrm{C}_5\mathrm{Me}_4\mathrm{Si}\underline{\mathrm{Me}}_3$) ppm. The ^{13}C{^{1}H} NMR signal of the methyl groups bound to scandium, aluminum and gallium could not be resolved. ^{45}Sc NMR (122 MHz, Toluene-d_8, 26 °C): δ 275.3 ppm. $\mathrm{C}_{19}\mathrm{H}_{41}\mathrm{AlGaScSi}$ (439.28 g/mol): calcd. (%) C 51.95, H 9.41; found C 52.77, H 8.66.

[Cp’Sc($\mathbf{CH_2}$)$_\mathbf{2}$AlMe]$_\mathbf{3}$ (11’). In a J. Young-valved NMR tube, GaMe_3 (25.0 mg, 0.218 mmol) was added dropwise to a solution of **4’** (37.5 mg, 0.110 mmol) in $\mathrm{C}_6\mathrm{D}_6$. The NMR tube was taken outside the glovebox and heated to 80 °C for 4 days. The NMR tube was transferred back into the glovebox and the volatiles were removed. The remaining solid was washed two times with 2 mL cold *n*-hexane to yield a colorless crystalline solid. Crystals suitable for SC-XRD were obtained from layering a saturated toluene solution with 3 mL *n*-hexane at ambient temperature (10.1 mg, 0.0109 mmol, 30%). ^{1}H NMR (400 MHz, $\mathrm{C}_6\mathrm{D}_6$, 26 °C): δ 2.30 (s, 18H, 2,5-$\mathrm{C}_5\underline{\mathrm{Me}}_4\mathrm{SiMe}_3$), 2.02 (s, 18H, 3,4-$\mathrm{C}_5\underline{\mathrm{Me}}_4\mathrm{SiMe}_3$), 0.73 (d, br, 3H, $^{2}J_{\mathrm{HH}}$ 14.0 Hz, AlC$\underline{\mathrm{H}}$H(Al)Sc), 0.45 (s, 27H, $\mathrm{C}_5\mathrm{Me}_4\mathrm{Si}\underline{\mathrm{Me}}_3$), −0.13 (s, 6H, ScCH_2(Sc)Al), −0.51 (s, 9H, AlMe), −1.37 (d, br, 3H, $^{2}J_{\mathrm{HH}}$ 14.0 Hz, AlCH$\underline{\mathrm{H}}$(Al)Sc) ppm. ^{13}C{^{1}H} NMR (126 MHz, $\mathrm{C}_6\mathrm{D}_6$, 26 °C): δ 130.5 (3,4-$\underline{\mathrm{C}}_5\mathrm{Me}_4\mathrm{SiMe}_3$), 126.5 (2,5-$\underline{\mathrm{C}}_5\mathrm{Me}_4\mathrm{SiMe}_3$), 119.2 (1-$\underline{\mathrm{C}}_5\mathrm{Me}_4\mathrm{SiMe}_3$), 81.2 (br, Sc$\underline{\mathrm{C}}\mathrm{H}_2$(Sc)Al), 35.0 (br, Al$\underline{\mathrm{C}}\mathrm{H}_2$(Al)Sc), 15.4 (2,5-$\mathrm{C}_5\underline{\mathrm{Me}}_4\mathrm{SiMe}_3$), 12.3 (3,4-$\mathrm{C}_5\underline{\mathrm{Me}}_4\mathrm{SiMe}_3$), 2.8 ($\mathrm{C}_5\mathrm{Me}_4\mathrm{Si}\underline{\mathrm{Me}}_3$), −5.8 (br, AlMe) ppm. ^{45}Sc{^{1}H} NMR (97 MHz, $\mathrm{C}_6\mathrm{D}_6$, 26 °C): δ 396.7 ppm. IR (KBr): $\tilde{\nu}$ = 2951 (s), 2918 (s), 2884 (m), 2810 (w), 2735 (vw), 1494 (vw), 1450 (w), 1405 (vw), 1379 (w), 1348 (w), 1326 (s), 1246 (s), 1183 (m), 1132 (vw), 1022 (w), 845 (vs), 755 (s), 728 (w), 657 (vs), 566 (s), 522 (s), 494 (m), 444 (m), 424 (s) cm^{-1}. $\mathrm{C}_{45}\mathrm{H}_{84}\mathrm{Al}_3\mathrm{Sc}_3\mathrm{Si}_3$ (925.23 g/mol): calcd. (%) C 58.42, H 9.15; found C 58.57, H 9.05.

[Cp*ScMeCl(thf)]$_\mathbf{2}$. To a precooled *n*-hexane suspension of [Cp*Sc(AlMe_4)Cl]$_2$ (**3***) was slowly added 1 mL precooled THF. The resulting solution was allowed to warm up to ambient temperature. After one hour, the solution was concentrated and kept at –40 °C. Few colorless crystals formed after 3 days. The compound was sensitive to temperatures higher than –20 °C and to vacuum, thus preventing a clean isolation and characterization. The product was not reproduced.

Methylenation of fluorenone using Cp$^\mathbf{R}$Sc($\mathbf{CH_2}$)($\mathbf{AlMe_3}$)$_\mathbf{2}$ (8$^\mathbf{R}$). **8*** (5.0 mg, 15 µmol) or **8’** (5.4 mg, 14 µmol) was dissolved in 0.3 mL $\mathrm{C}_6\mathrm{D}_6$ in a J. Young NMR tube and a solution of fluorenone (6.0 mg, 33 µmol) in 0.2 mL $\mathrm{C}_6\mathrm{D}_6$ was added. An immediate color change from yellow to brown was observed. The tube was shaken, and ^{1}H NMR spectra were measured (see Figures S61/S62). The yield of dibenzofulvene in the reaction of **8*** with fluorenone was 45%, in the reaction of **8’** with fluorenone, 46%.

Methylenation of fluorenone using [Cp’Sc($\mathbf{CH_2}$)$_\mathbf{2}$AlMe]$_\mathbf{3}$ (11’). **11’** (5.0 mg, 5.4 µmol) was dissolved in 0.3 mL $\mathrm{C}_6\mathrm{D}_6$ in a J. Young NMR tube and a solution of fluorenone (14.8 mg, 82 µmol, 2.5 equiv. per CH_2 group) in 0.2 mL $\mathrm{C}_6\mathrm{D}_6$ was added. The tube was shaken, and ^{1}H NMR spectra were measured. At ambient temperature, the reaction was very slow, only a fraction of the starting materials reacted over the course of one day. After heating for four hours to 80 °C, no signals of **11’** were seen (see Figure S63). The yield of dibenzofulvene in the reaction of **11’** with fluorenone was 19%.

References

1. P. G. Hayes, W. E. Piers, D. Adhikari and D. J. Mindiola, Scandium Trichloride Tris(Tetrahydrofuran) and β-Diketiminate-Supported Scandium Chloride Complexes, *Inorg. Synth.*, 2010, **35**, 20–24.

2. X. Li, M. Nishiura, K. Mori, T. Mashiko and Z. Hou, Cationic scandium aminobenzyl complexes. Synthesis, structure and unprecedented catalysis of copolymerization of 1-hexene and dicyclopentadiene, *Chem. Commun.*, 2007, 4137–4139.

3. D. Robert, T. P. Spaniol and J. Okuda, Neutral and monocationic half-sandwich methyl rare-earth metal complexes: Synthesis, structure, and 1,3-butadiene polymerization catalysis, *Eur. J. Inorg. Chem.*, 2008, 2801–2809.

4. P. Courtot, R. Pichon, J. Y. Salaun and L. Toupet, , Electronic and Steric Influence of the Tetramethylcyclopentadienyl Ligand on Physical Properties and Reactivity of Titanium and Zirconium Complexes, *Can. J. Chem.*, 1991, **69**, 661–672.

5. D. T. Hurd, Complex Metal Alkyls, *J. Org. Chem.*, 1948, **13**, 711–713.

6. J. J. Byers, W. T. Pennington and G. H. Robinson, Bis-Adducts of Trimethylaluminum and Trimethylgallium with N,N,N',N'-Tetramethylethylenediamine, *Acta Cryst.*, 1992, **C48**, 2023−2025.

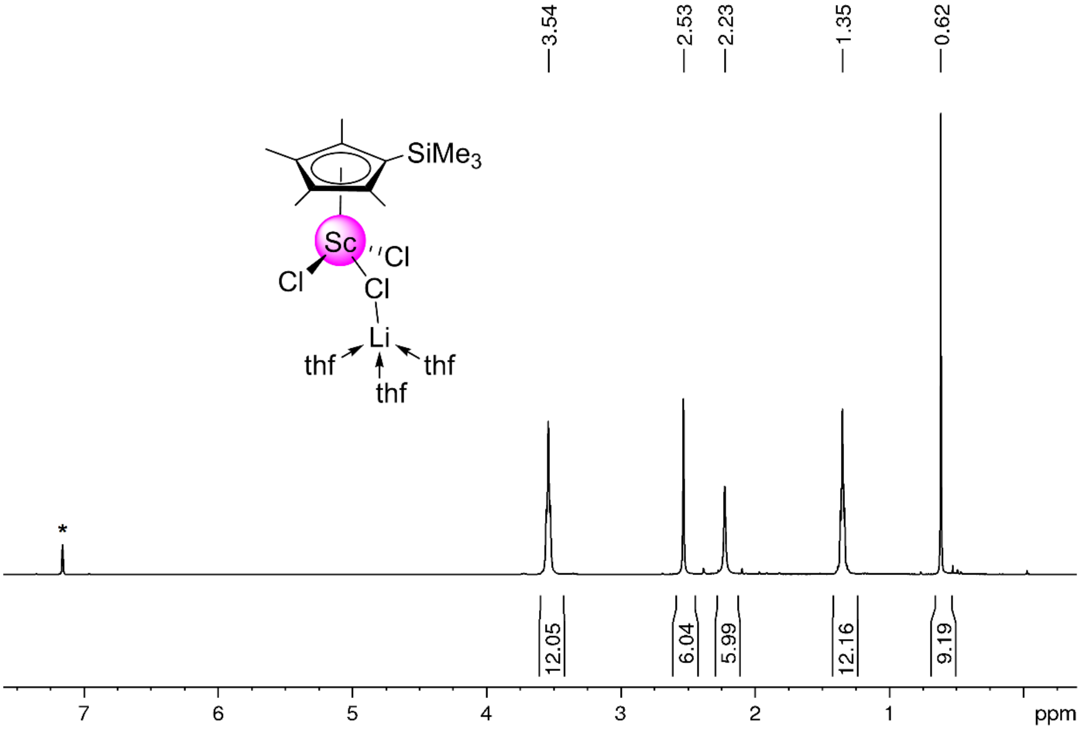

Figure S1. ^{1}H NMR spectrum (400 MHz) of compound Cp'ScCl$_2$(μ−Cl)Li(thf)$_3$ (**1'**) in C_6D_6 (marked with *) at 26 °C.

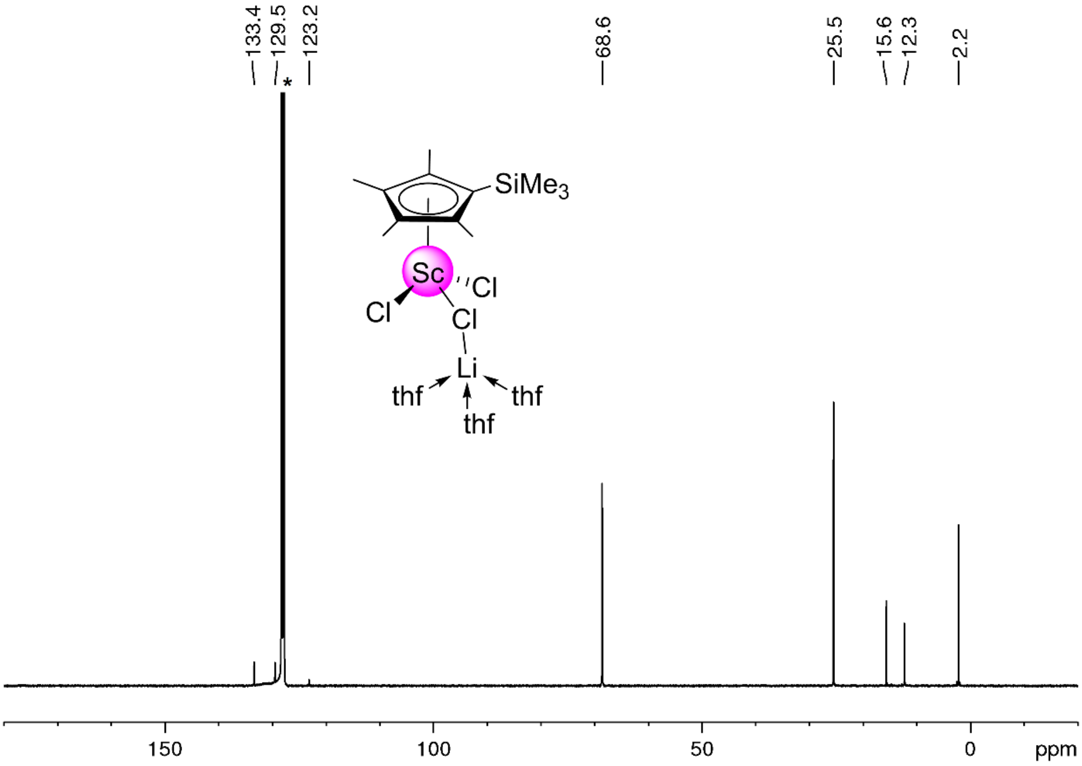

Figure S2. ^{13}C{^{1}H} NMR spectrum (101 MHz) of compound Cp'ScCl$_2$(μ−Cl)Li(thf)$_3$ (**1'**) in C_6D_6 (marked with *) at 26 °C.

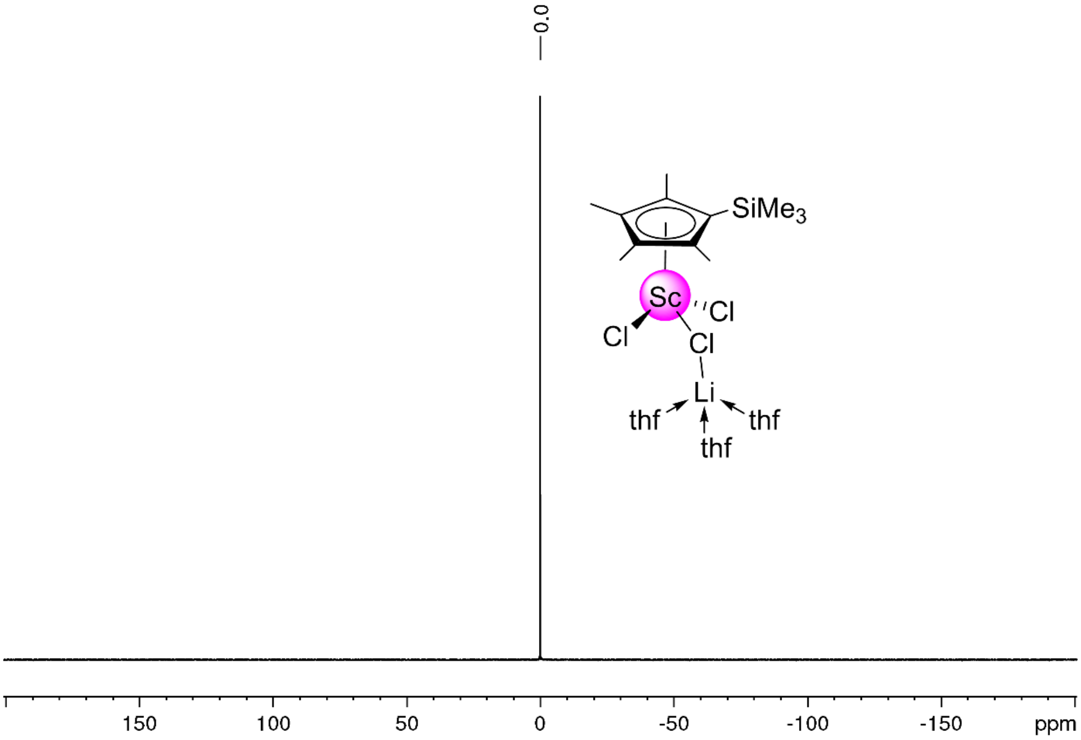

Figure S3. ^{7}Li NMR spectrum (117 MHz) of compound Cp'ScCl$_2$(μ−Cl)Li(thf)$_3$ (**1'**) in C$_6$D$_6$ at 26 °C.

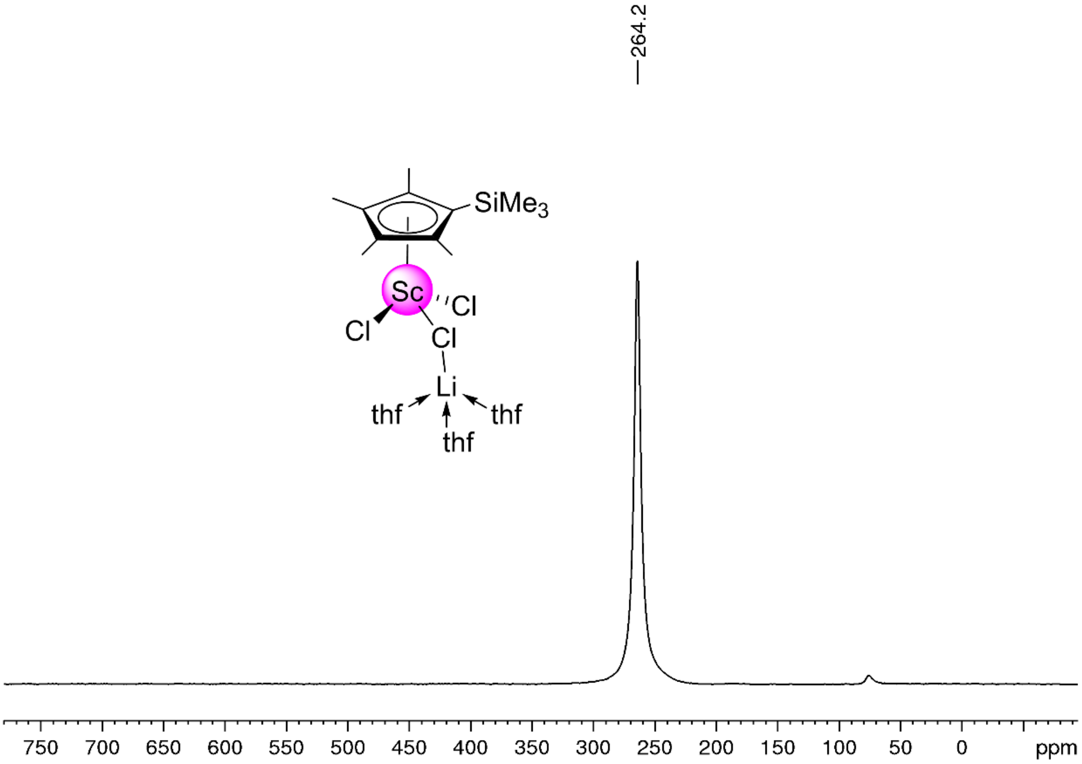

Figure S4. ^{45}Sc{^{1}H} NMR spectrum (97 MHz) of compound Cp'ScCl$_2$(μ−Cl)Li(thf)$_3$ (**1'**) in C$_6$D$_6$ at 26 °C.

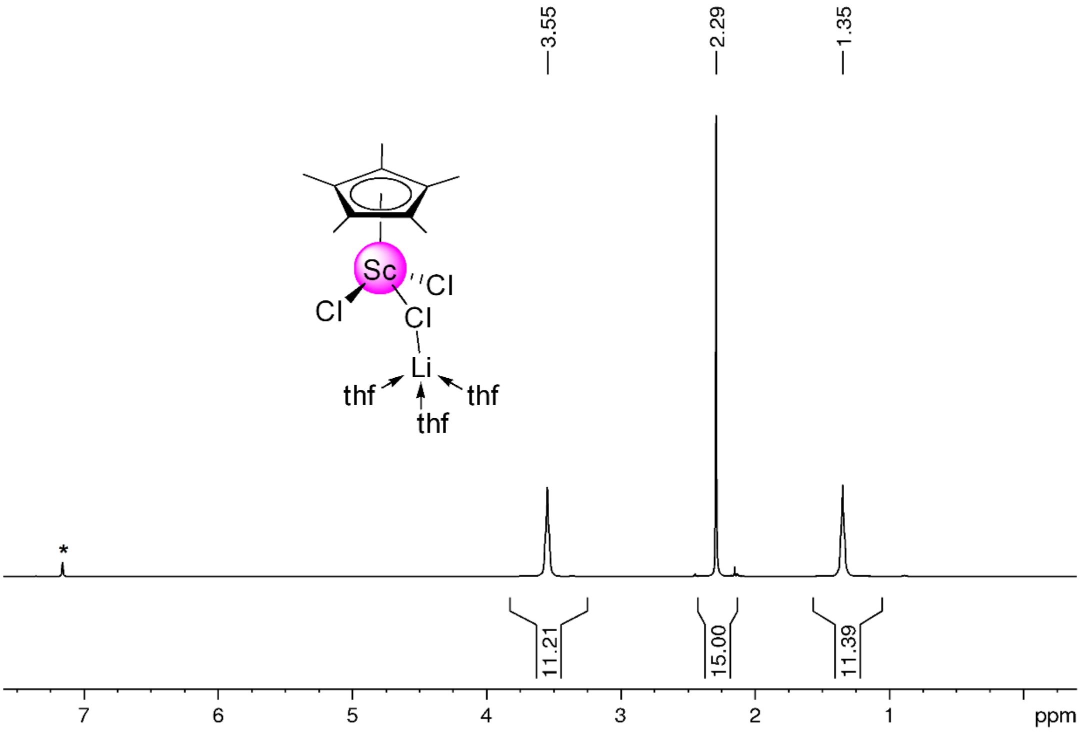

Figure S5. ^{1}H NMR spectrum (400 MHz) of compound Cp*ScCl$_2$(μ−Cl)Li(thf)$_3$ (**1***) in C_6D_6 (marked with *) at 26 °C.

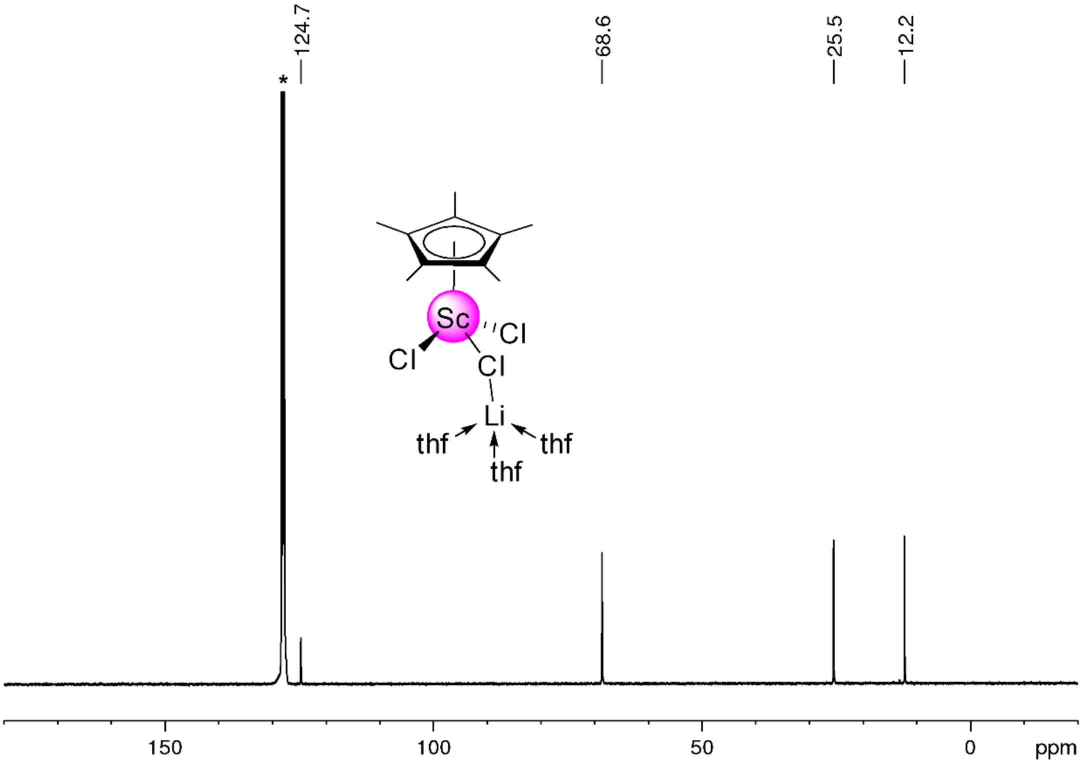

Figure S6. ^{13}C{^{1}H} NMR spectrum (101 MHz) of compound Cp*ScCl$_2$(μ−Cl)Li(thf)$_3$ (**1***) in C_6D_6 (marked with *) at 26 °C.

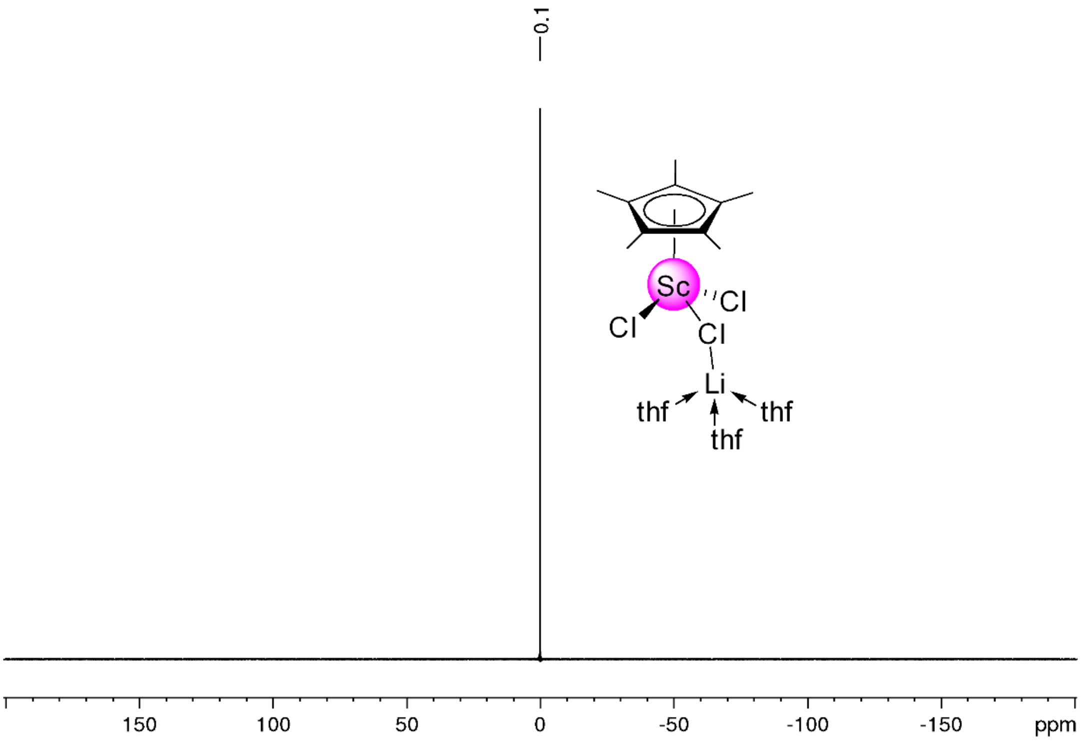

Figure S7. ^{7}Li NMR spectrum (117 MHz) of compound Cp*ScCl$_2$(μ−Cl)Li(thf)$_3$ (**1***) in C_6D_6 at 26 °C.

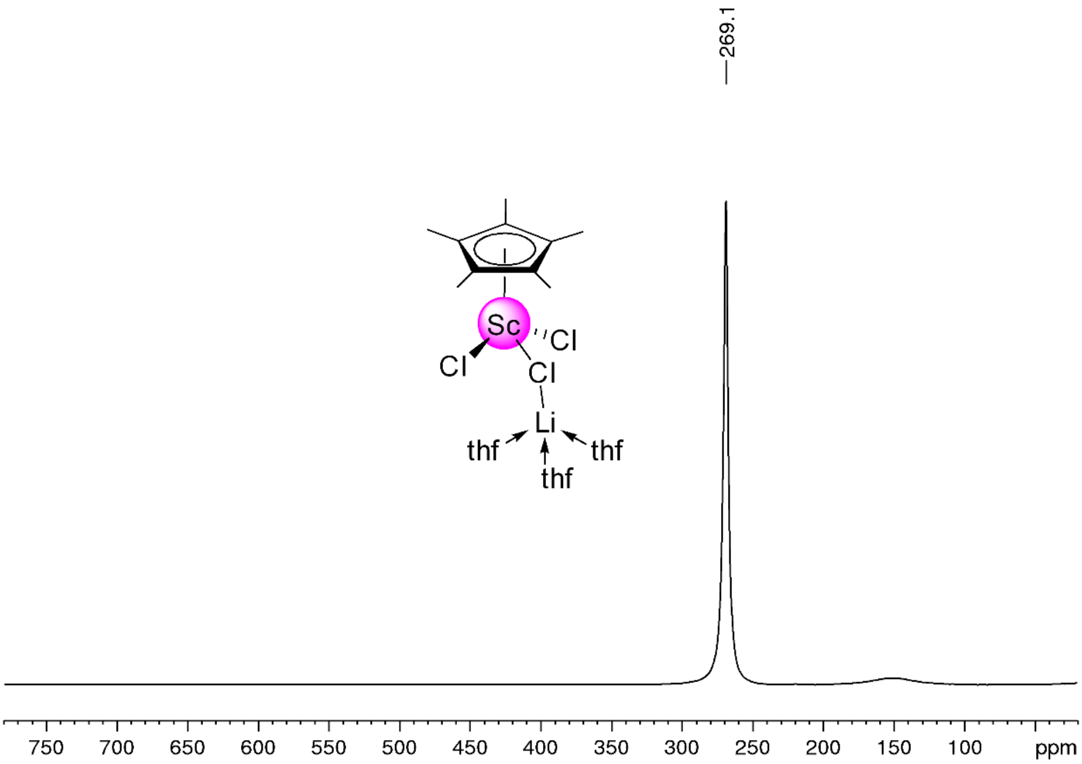

Figure S8. ^{45}Sc NMR spectrum (122 MHz) of compound Cp*ScCl$_2$(μ−Cl)Li(thf)$_3$ (**1***) in C_6D_6 at 26 °C.

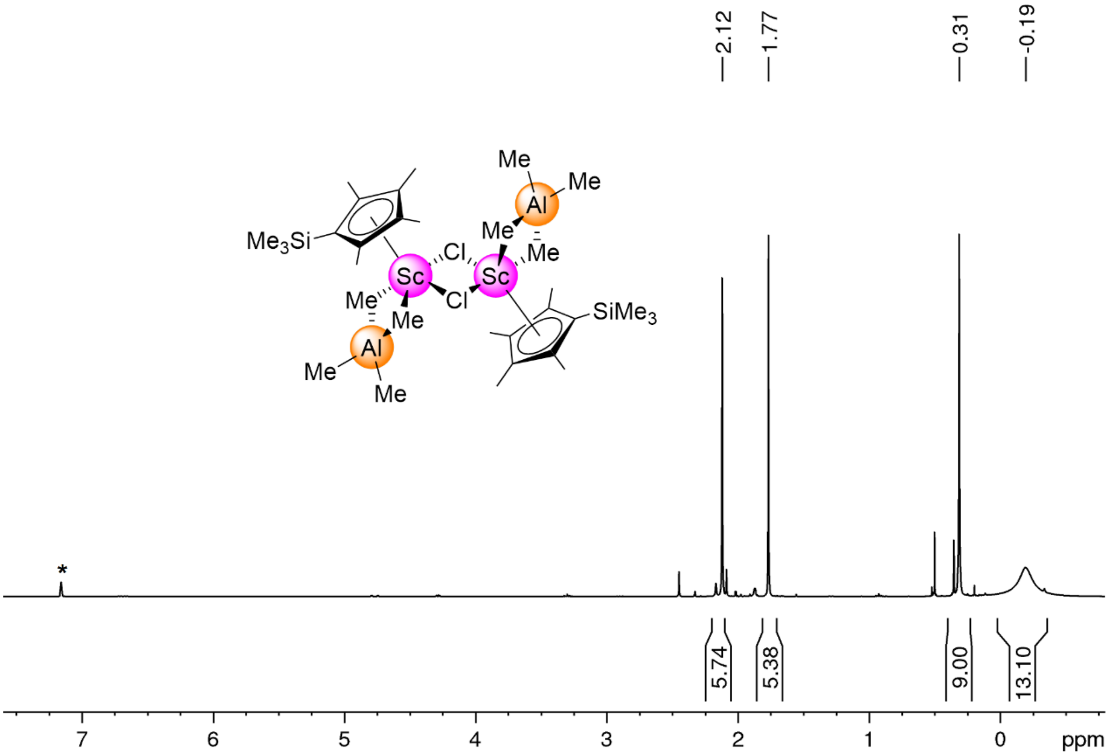

Figure S9. ^{1}H NMR spectrum (300 MHz) of compound [Cp'Sc(AlMe$_4$)Cl]$_2$ (**3'**) in C_6D_6 (marked with *) at 26 °C.

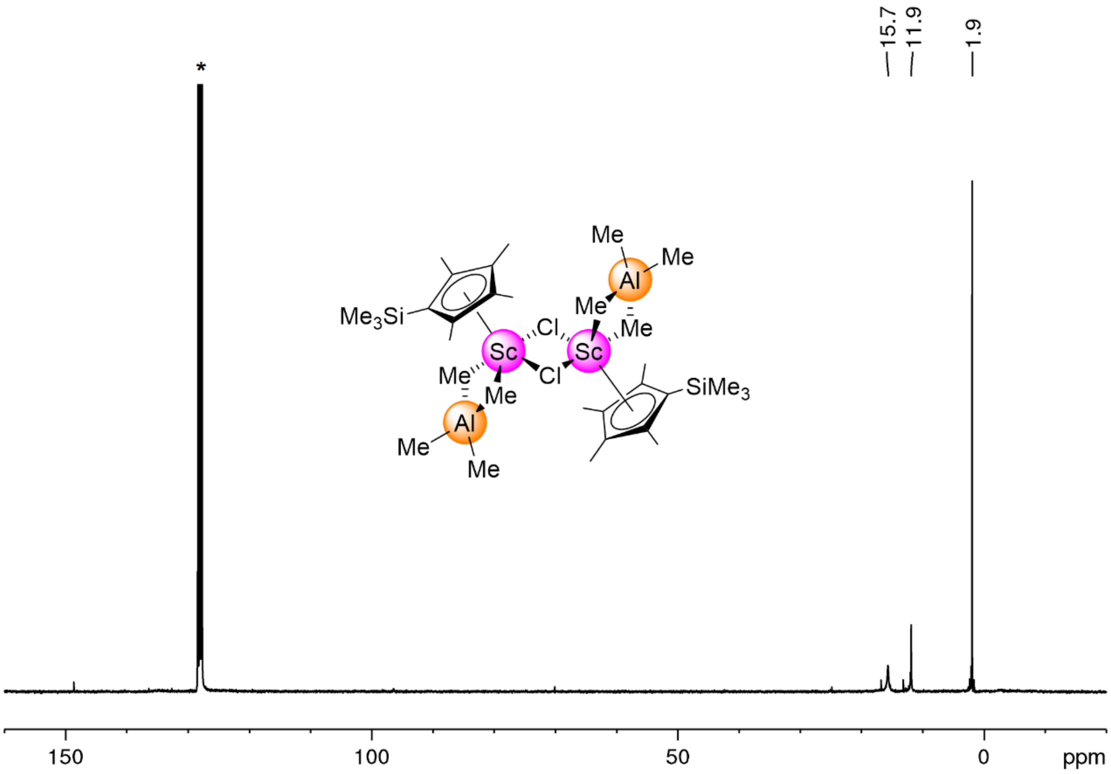

Figure S10. ^{13}C{^{1}H} NMR spectrum (75 MHz) of compound [Cp'Sc(AlMe$_4$)Cl]$_2$ (**3'**) in C_6D_6 (marked with *) at 26 °C.

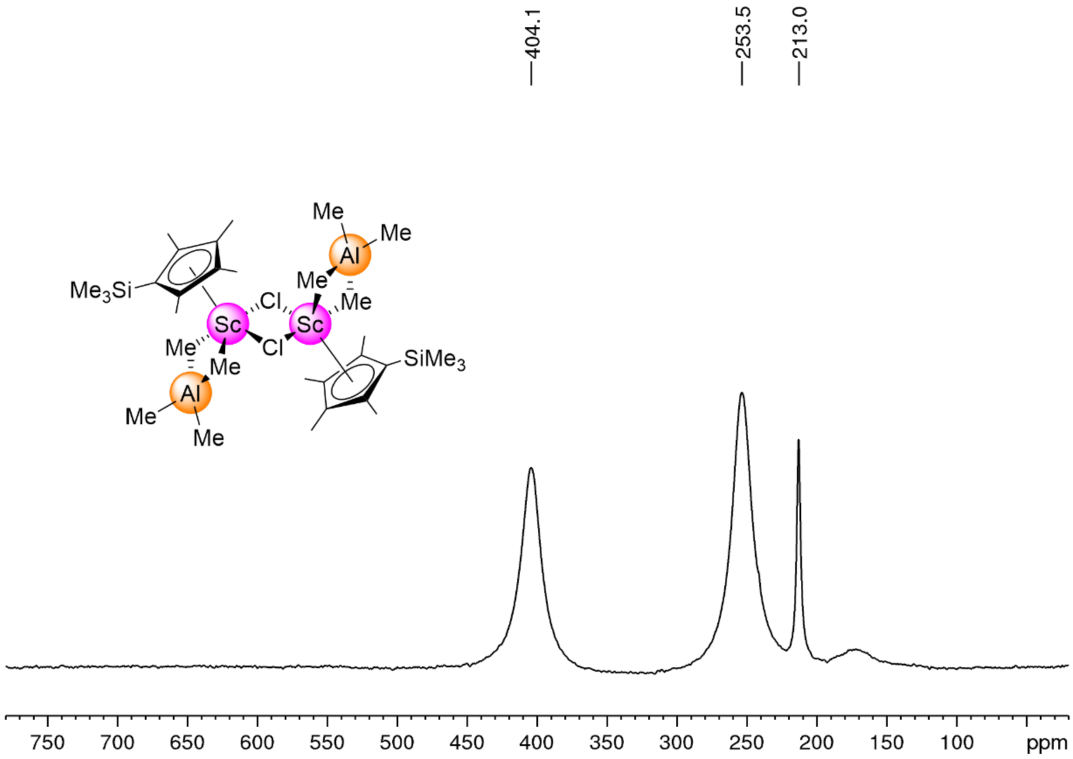

Figure S11. ^{45}Sc{^{1}H} NMR spectrum (97 MHz) of compound [Cp’Sc(AlMe$_4$)Cl]$_2$ (**3’**) in C$_6$D$_6$ at 26 °C.

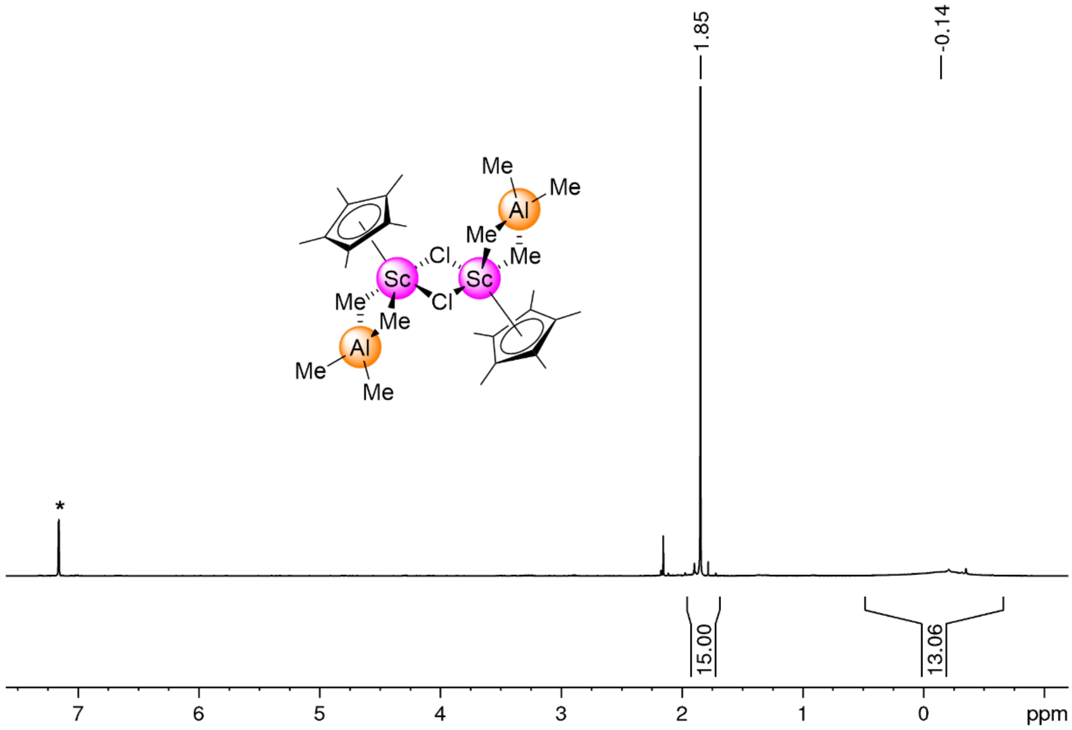

Figure S12. ^{1}H NMR spectrum (500 MHz) of compound [Cp*Sc(AlMe$_4$)Cl]$_2$ (**3***) in C$_6$D$_6$ (marked with *) at 26 °C.

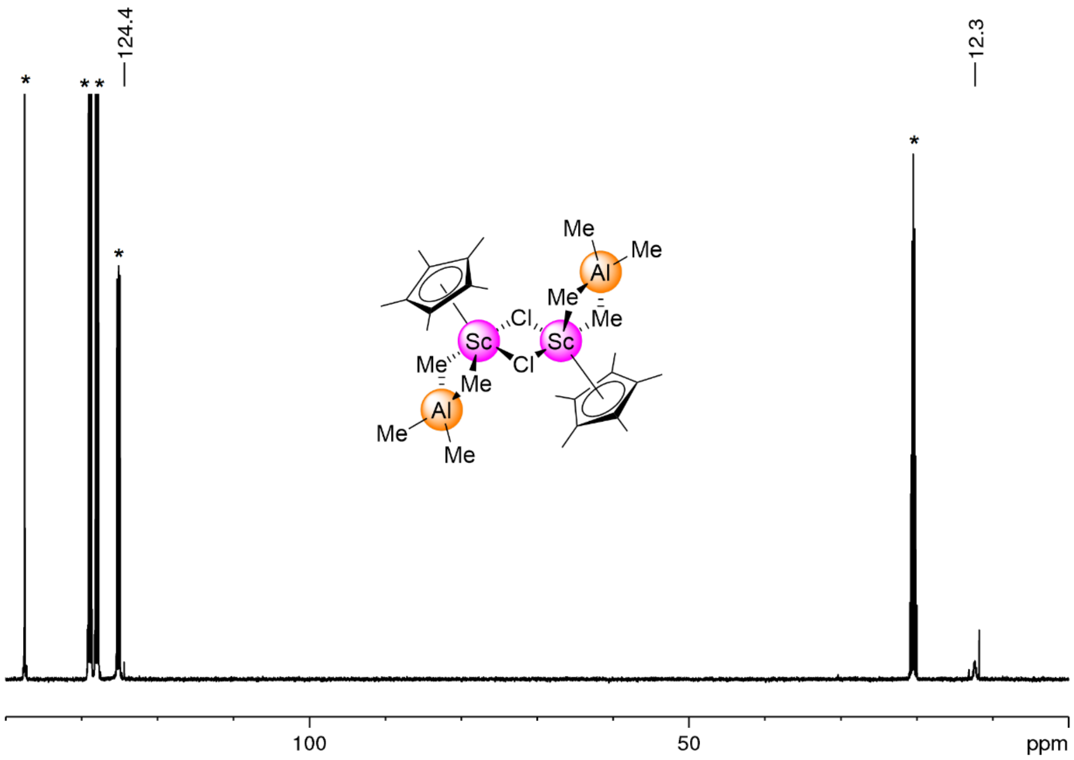

Figure S13. $^{13}C\{^1H\}$ NMR spectrum (126 MHz) of compound [Cp*Sc(AlMe$_4$)Cl]$_2$ (**3***) in toluene-d_8 (marked with *) at 26 °C.

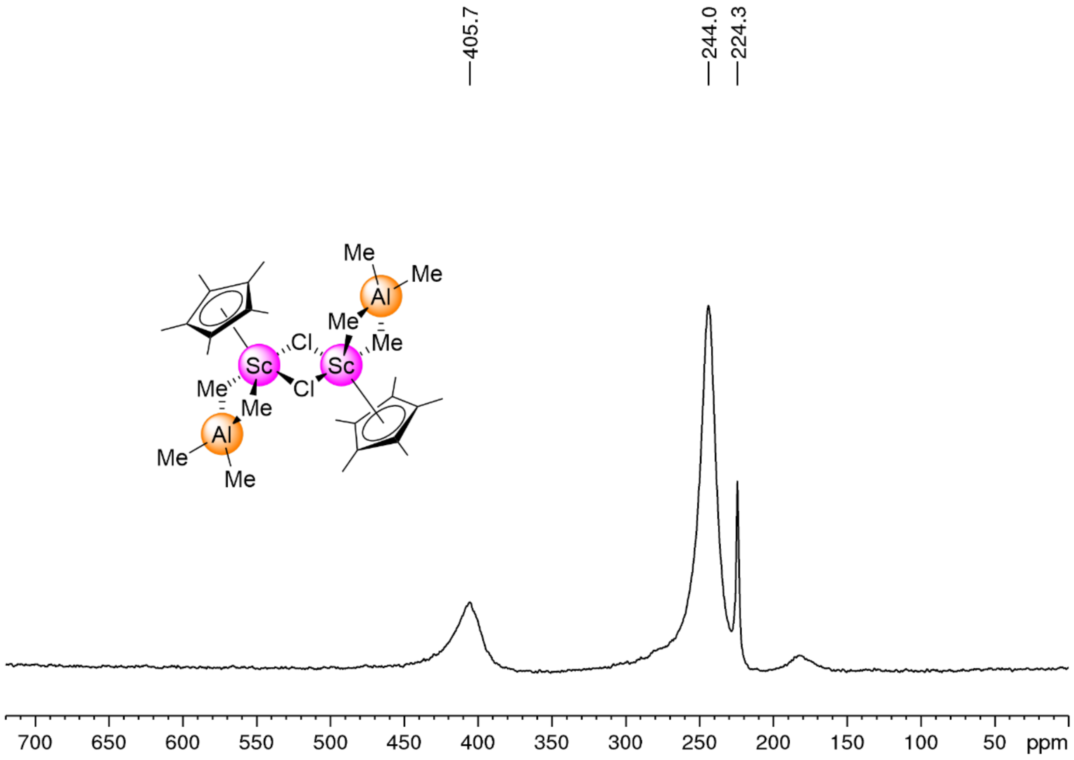

Figure S14. ^{45}Sc NMR spectrum (122 MHz) of compound [Cp*Sc(AlMe$_4$)Cl]$_2$ (**3***) in C_6D_6 at 26 °C.

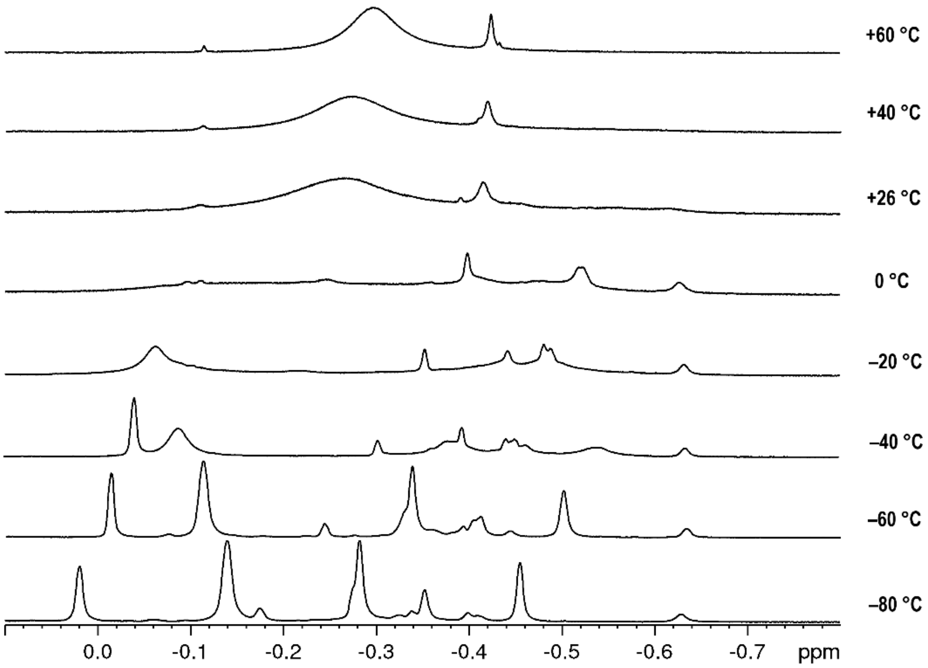

Figure S15. Detail of variable temperature ^{1}H NMR spectra (500 MHz) of compound [Cp’Sc($AlMe_4$)Cl]$_2$ (**3’**) in toluene-d_8 between −80 and 60 °C.

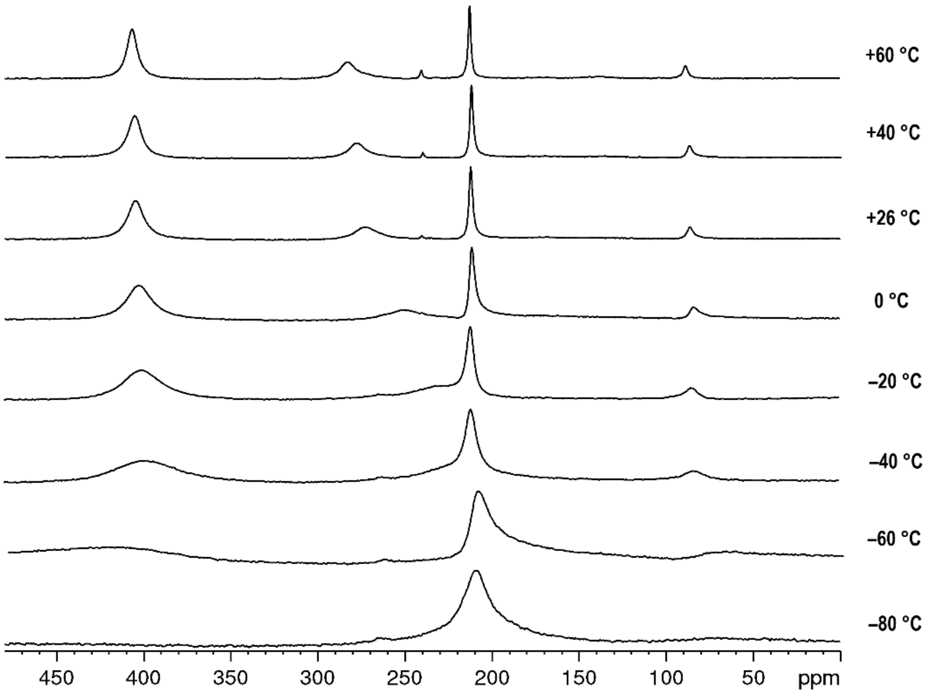

Figure S16. Variable temperature ^{45}Sc NMR spectra (122 MHz) of compound [Cp’Sc($AlMe_4$)Cl]$_2$ (**3’**) in toluene-d_8 between −80 and 60 °C.

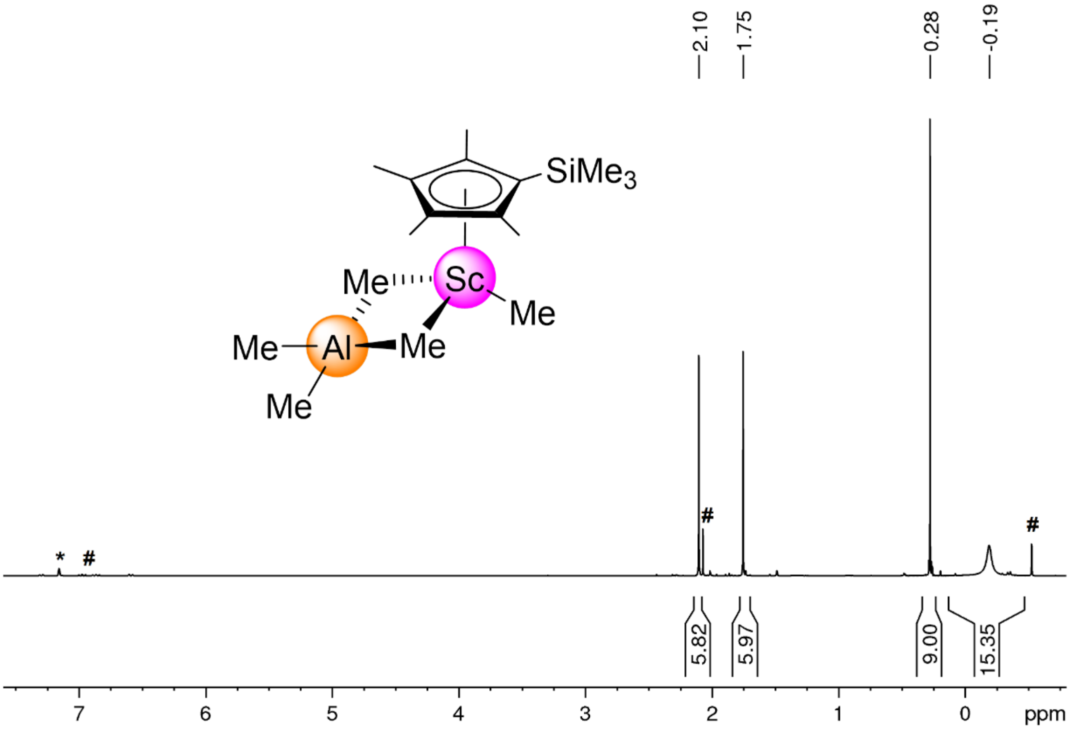

Figure S17. ^{1}H NMR spectrum (300 MHz) of compound Cp'Sc(AlMe$_4$)Me (**4'**) in C_6D_6 (marked with *) at 26 °C. Residual byproduct Me$_2$Al(CH$_2$C$_6$H$_4$NMe$_2$-*o*) is marked with #.

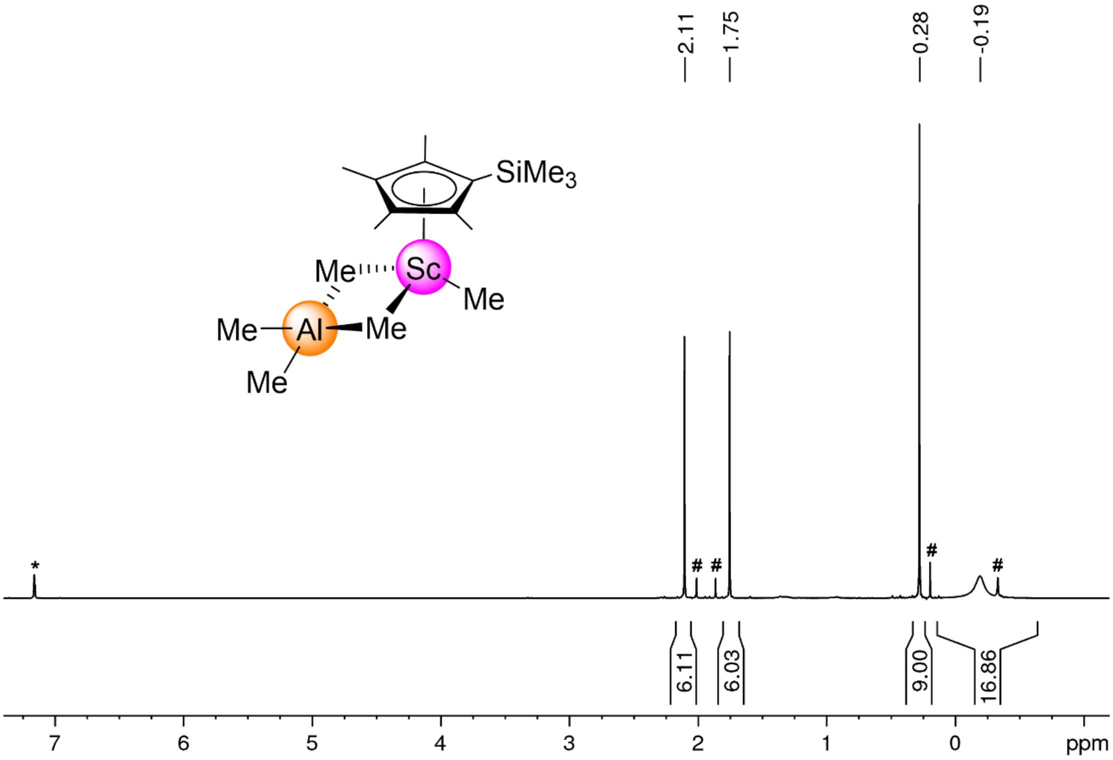

Figure S18. ^{1}H NMR spectrum (300 MHz) of compound Cp'Sc(AlMe$_4$)Me (**4'**) in C_6D_6 (marked with *) at 26 °C. Residual byproduct Cp'Sc(CH$_2$)(AlMe$_3$)$_2$ (**8'**) is marked with #.

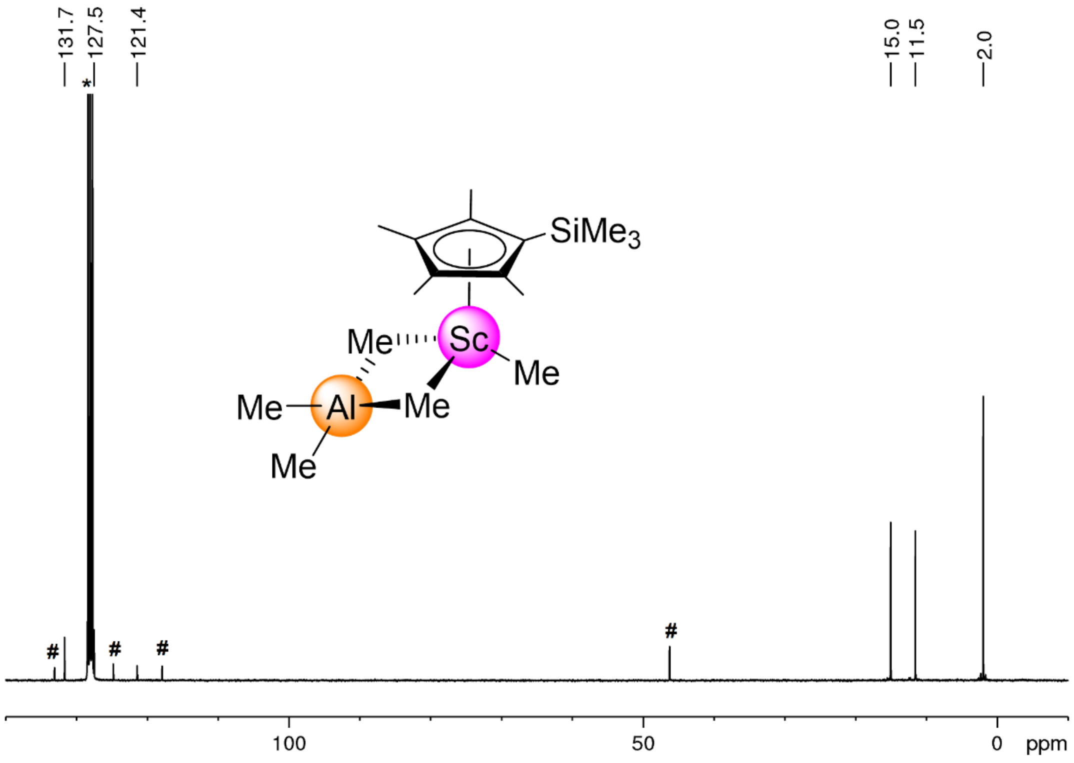

Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz) of compound Cp'Sc(AlMe$_4$)Me (**4'**) in C_6D_6 (marked with *) at 26 °C. Residual byproduct Me$_2$Al(CH$_2$C$_6$H$_4$NMe$_2$-*o*) is marked with #.

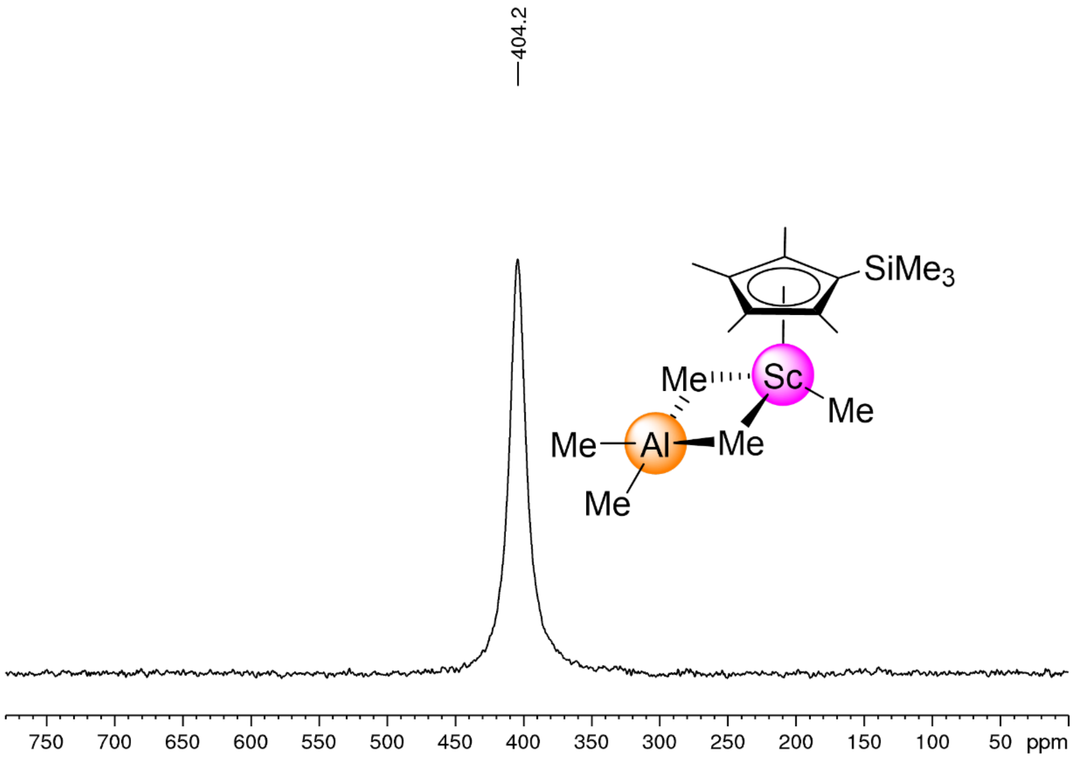

Figure S20. $^{45}Sc\{^{1}H\}$ NMR spectrum (97 MHz) of compound Cp'Sc(AlMe$_4$)Me (**4'**) in C_6D_6 at 26 °C.

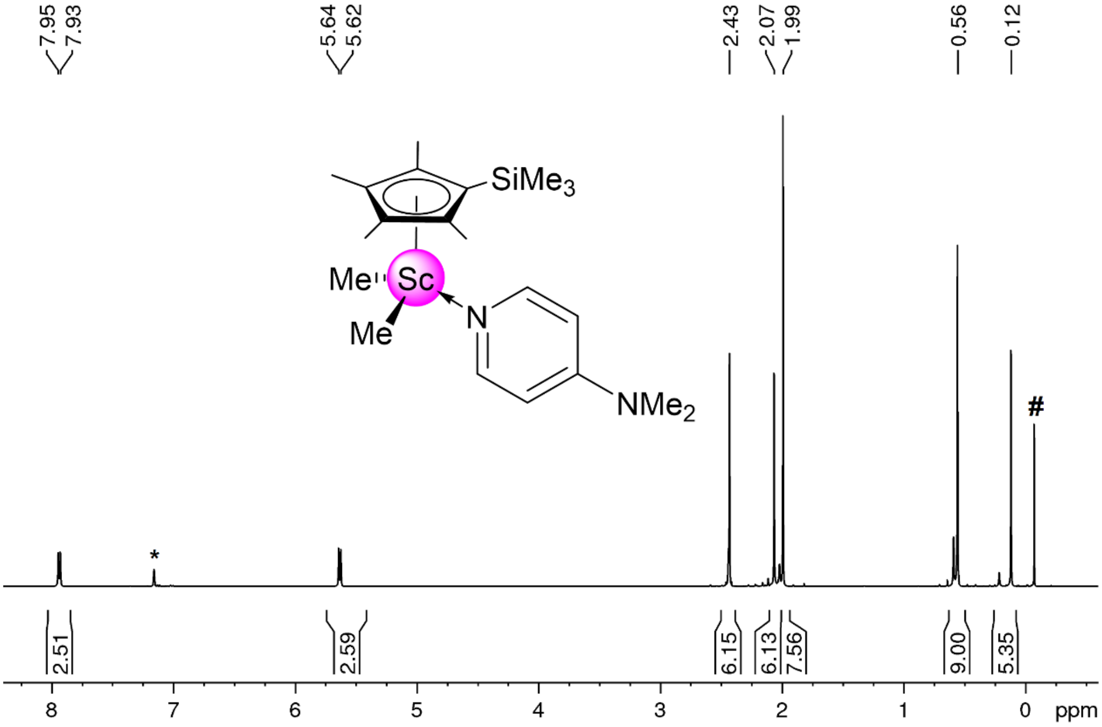

Figure S21. ^{1}H NMR spectrum (400 MHz) of compound Cp’ScMe(Me/Cl)(dmap) (**5’**) in C_6D_6 (marked with *) at 26 °C. Residual byproduct $AlMe_3$(dmap) is marked with #.

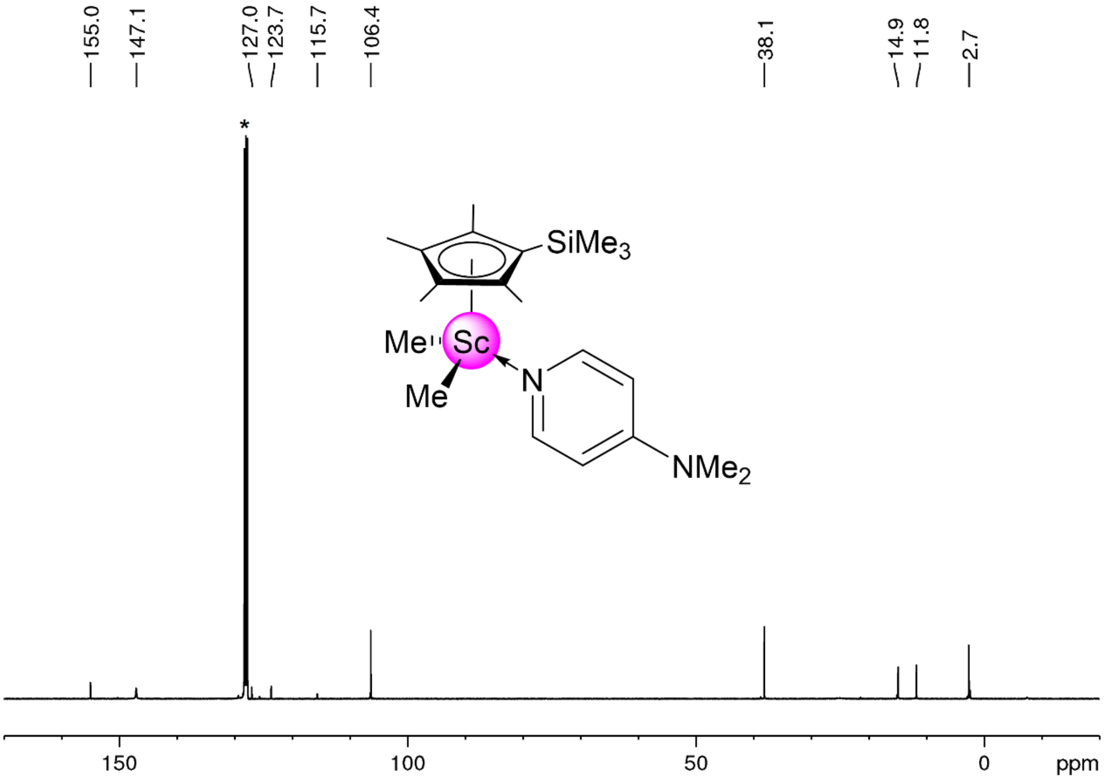

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of compound Cp’ScMe(Me/Cl)(dmap) (**5’**) in C_6D_6 (marked with *) at 26 °C.

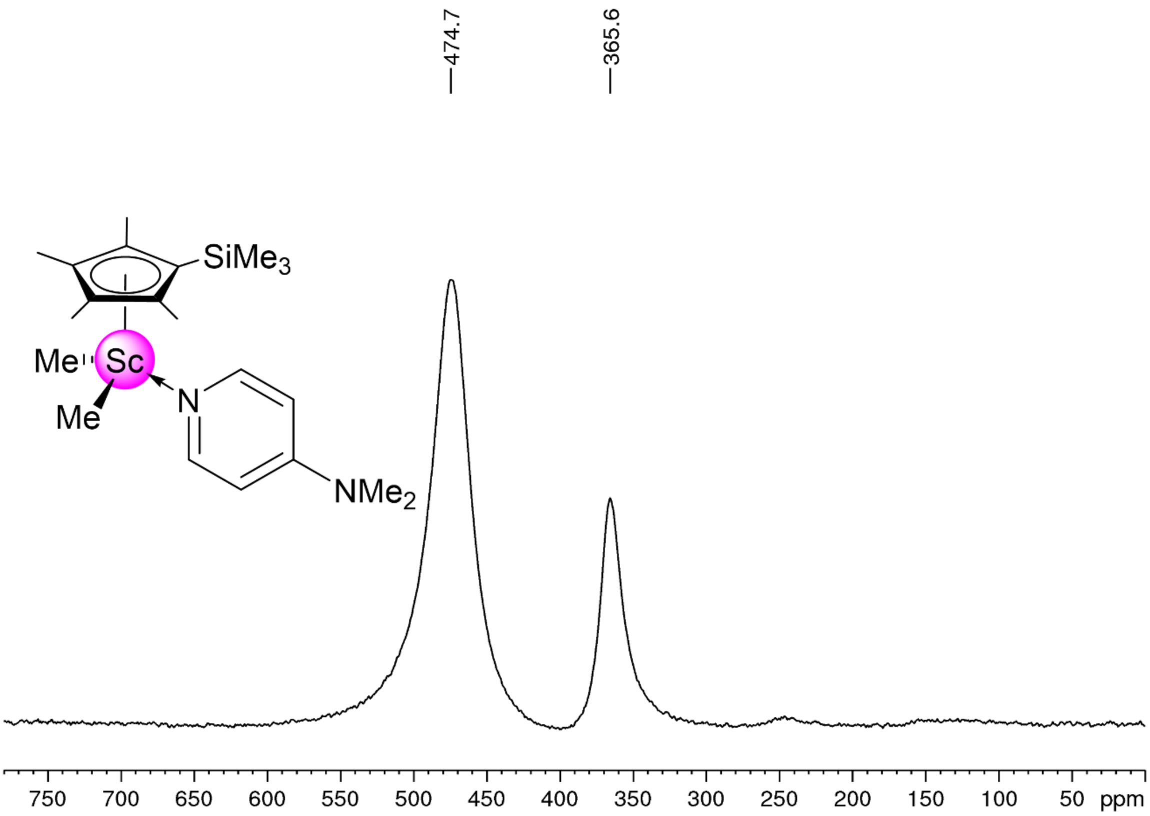

Figure S23. $^{45}Sc\{^{1}H\}$ NMR spectrum (97 MHz) of compound Cp'ScMe(Me/Cl)(dmap) (**5'**) in C_6D_6 at 26 °C.

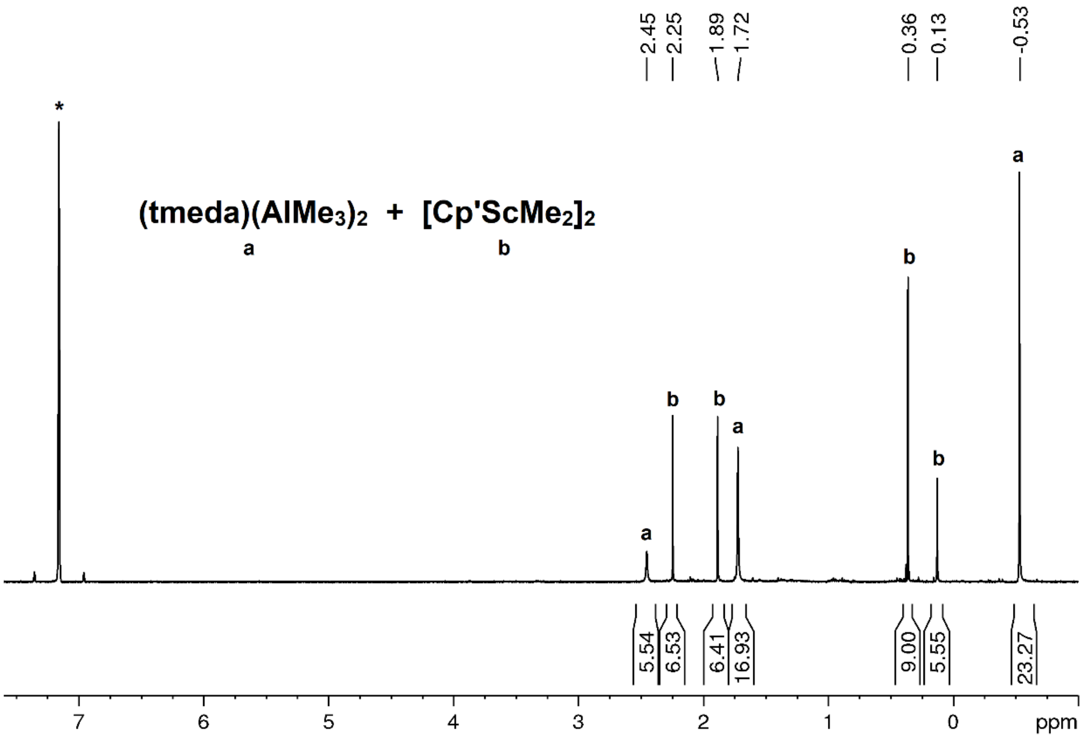

Figure S24. ^{1}H NMR spectrum (400 MHz) of compound $[Cp'ScMe_2]_2$ / $(tmeda)(AlMe_3)_2$ in C_6D_6 (marked with *) at 26 °C.

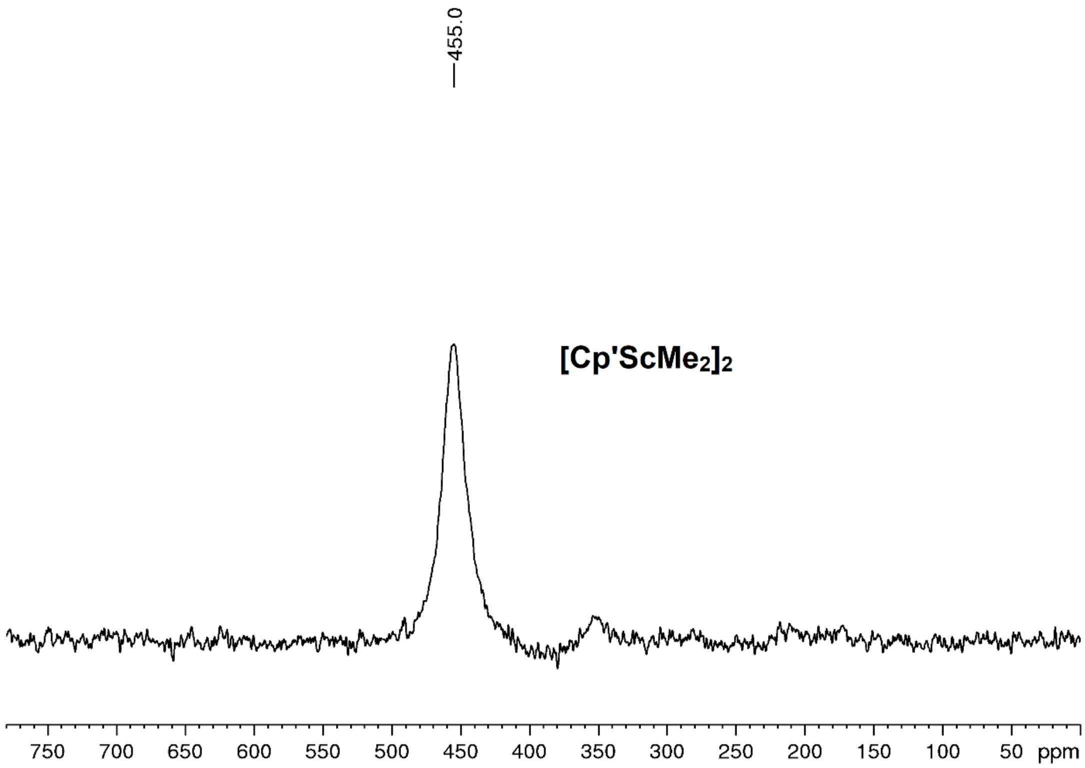

Figure S25. ^{45}Sc{^{1}H} NMR spectrum (97 MHz) of compound [Cp'ScMe$_2$]$_2$ / (tmeda)(AlMe$_3$)$_2$ in C_6D_6 at 26 °C.

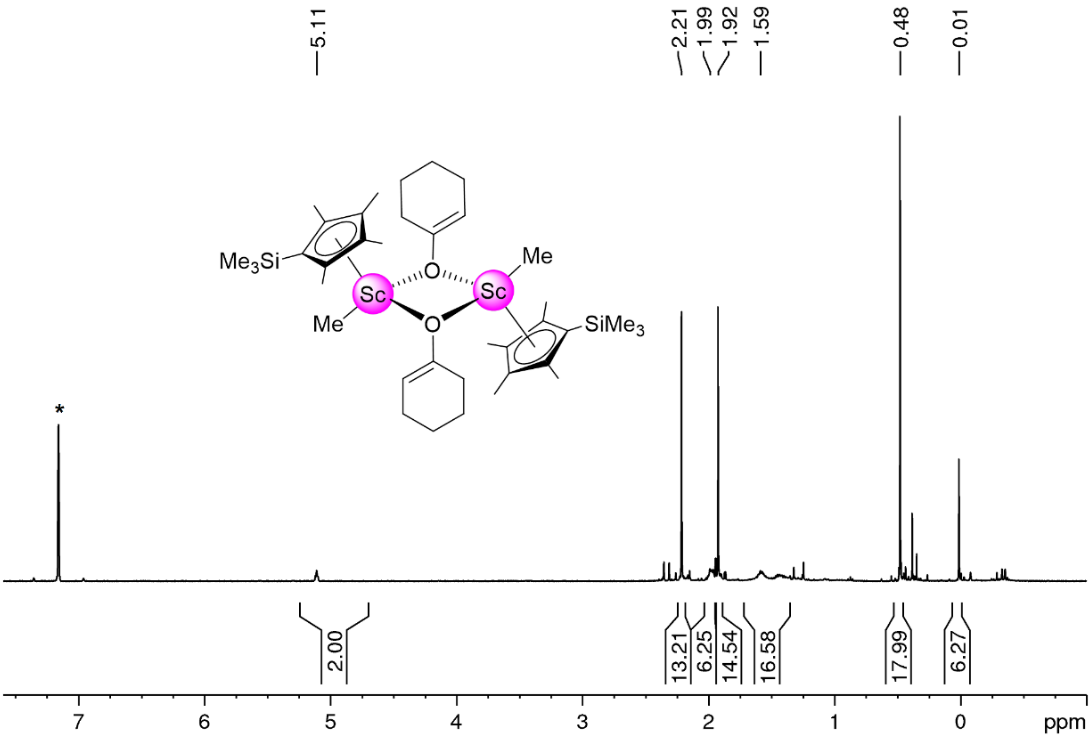

Figure S26. ^{1}H NMR spectrum (400 MHz) of compound [Cp'ScMe(OC$_6$H$_9$)]$_2$ (**6'**) in C_6D_6 (marked with *) at 26 °C.

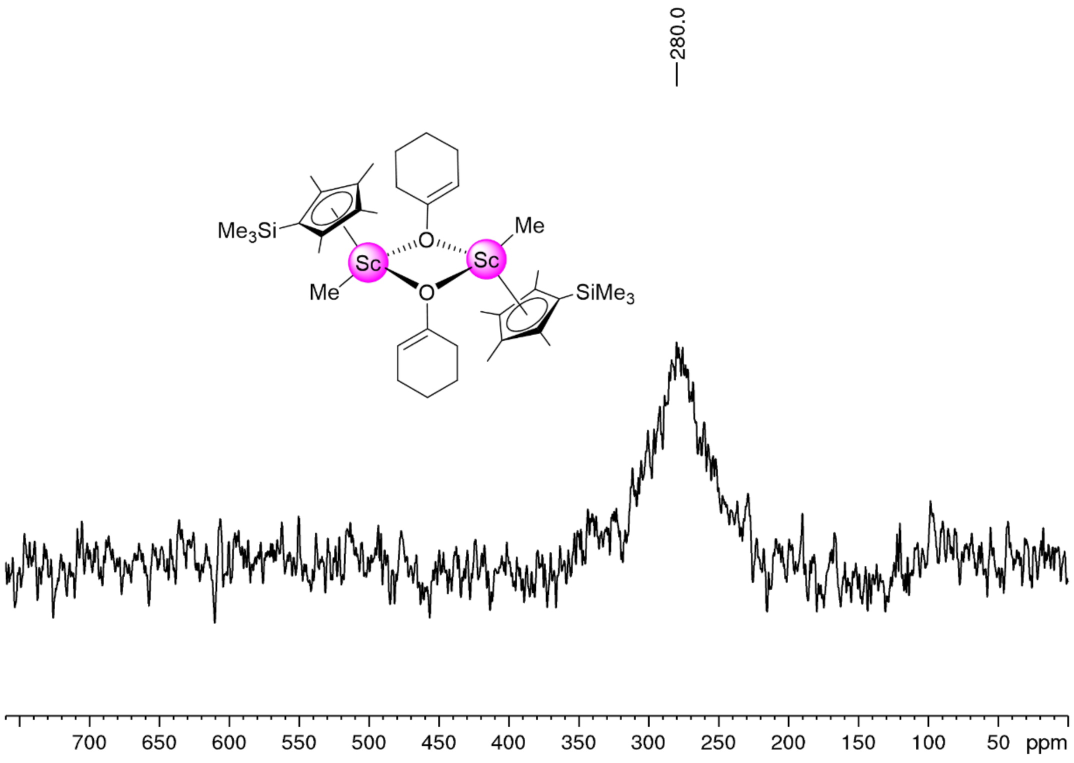

Figure S27. ^{45}Sc{^{1}H} NMR spectrum (97 MHz) of compound [Cp'ScMe(OC$_6$H$_9$)]$_2$ (**6'**) in C$_6$D$_6$ at 26 °C.

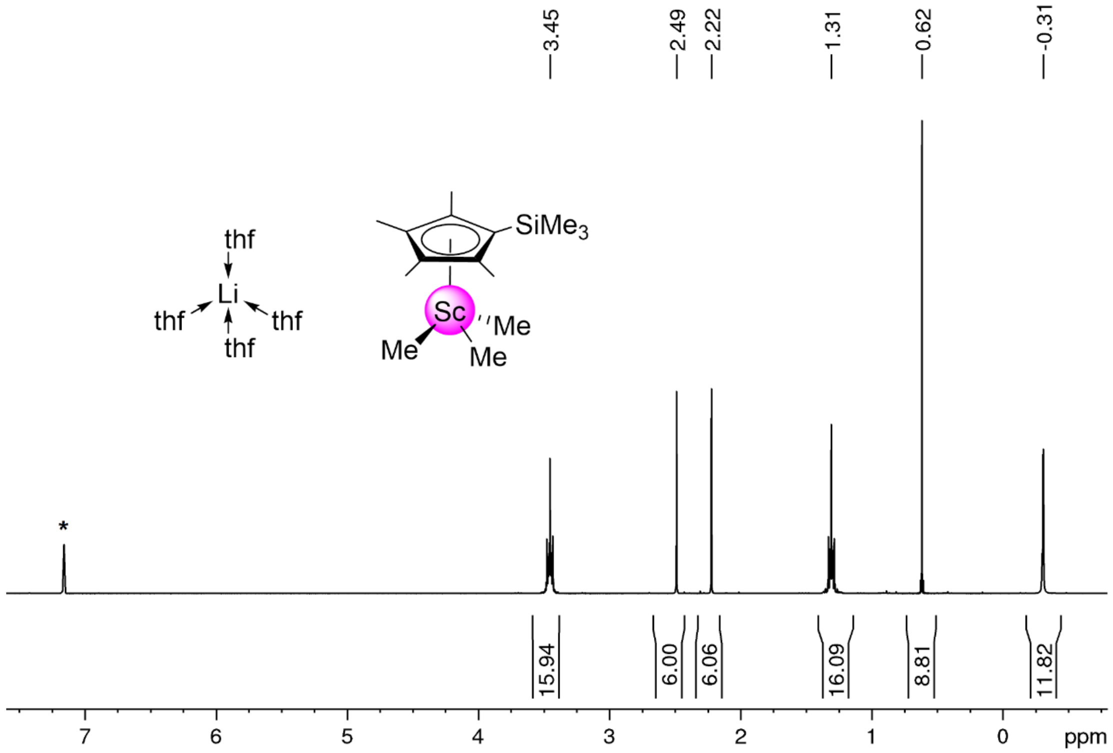

Figure S28. ^{1}H NMR spectrum (300 MHz) of compound [Li(thf)$_4$][Cp'ScMe$_3$] (**7'**) in C$_6$D$_6$ (marked with *) at 26 °C.

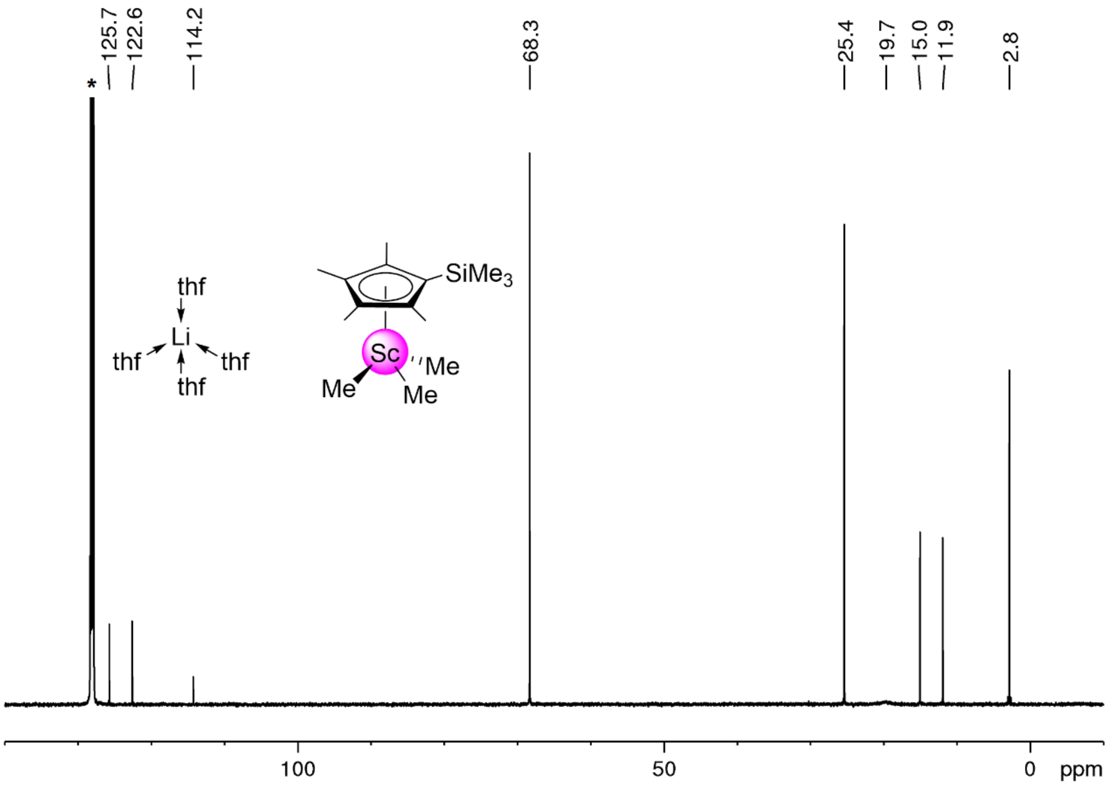

Figure S29. $^{13}C\{^1H\}$ NMR spectrum (75 MHz) of compound [Li(thf)$_4$][Cp'ScMe$_3$] (**7'**) in C_6D_6 (marked with *) at 26 °C.

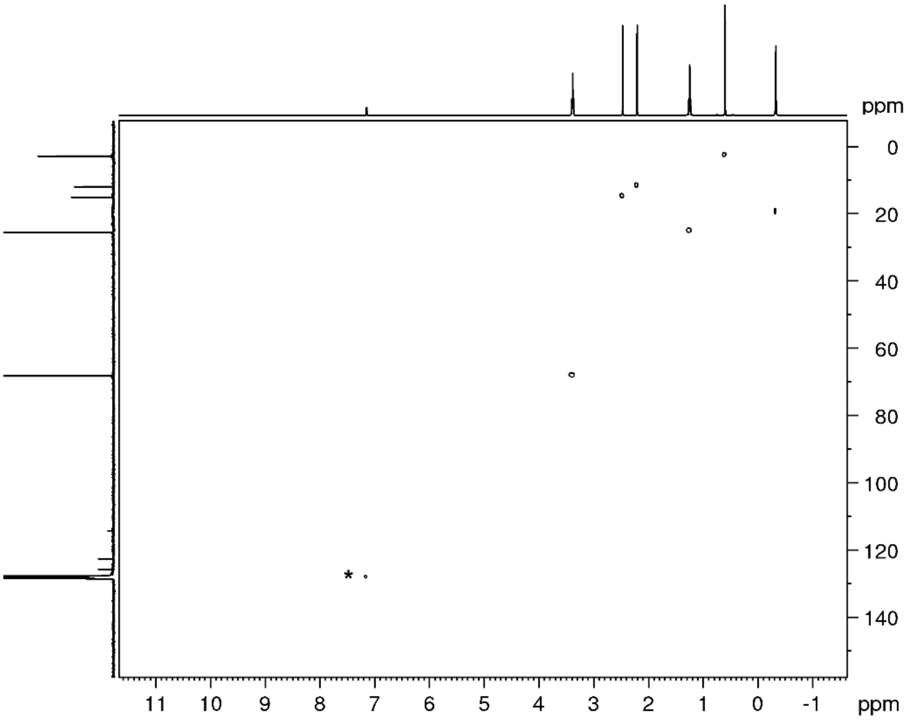

Figure S30. $^1H-^{13}C$ HSQC NMR spectrum (400 / 101 MHz) of compound [Li(thf)$_4$][Cp'ScMe$_3$] (**7'**) in C_6D_6 (marked with *) at 26 °C.

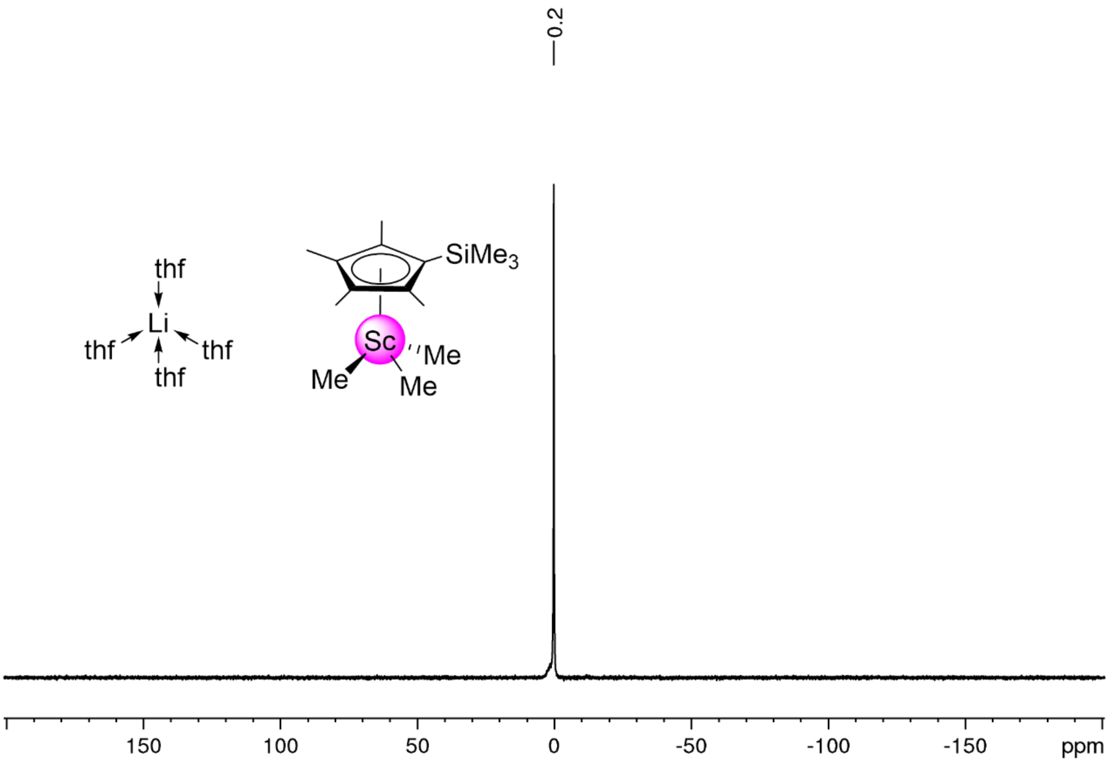

Figure S31. ^{7}Li NMR spectrum (155 MHz) of compound [Li(thf)$_4$][Cp'ScMe$_3$] (**7'**) in C_6D_6 at 26 °C.

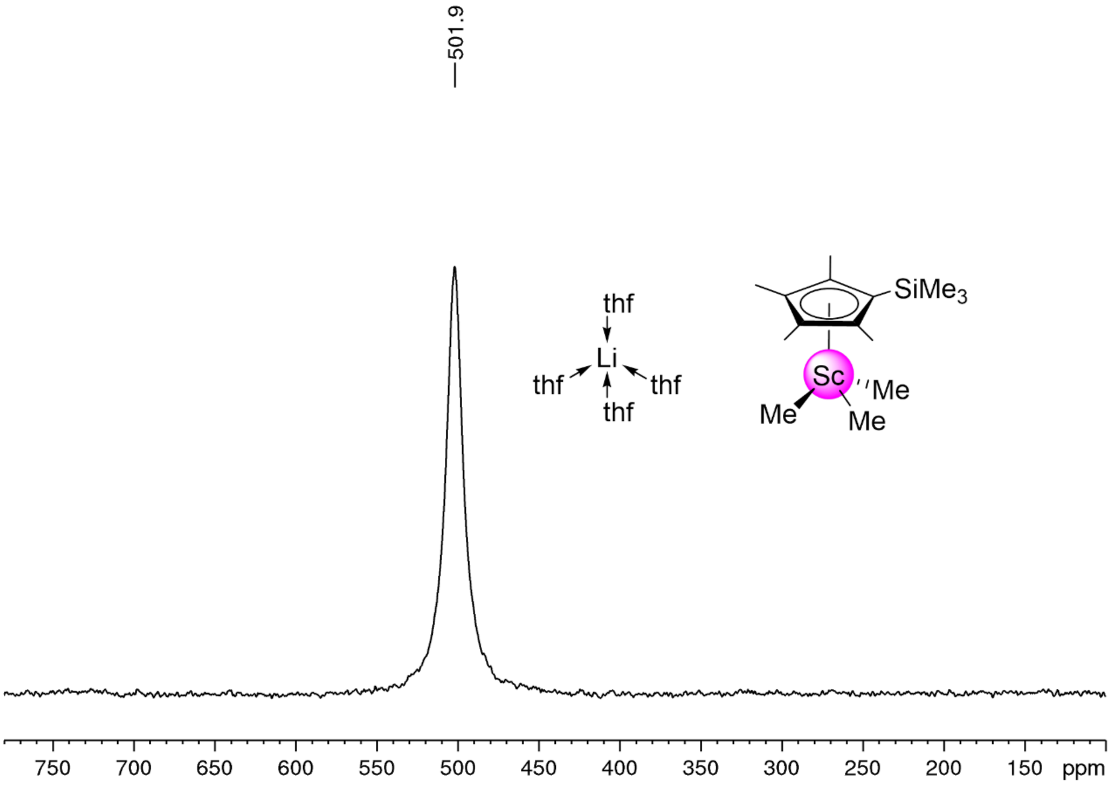

Figure S32. ^{45}Sc{^{1}H} NMR spectrum (97 MHz) of compound [Li(thf)$_4$][Cp'ScMe$_3$] (**7'**) in C_6D_6 at 26 °C.

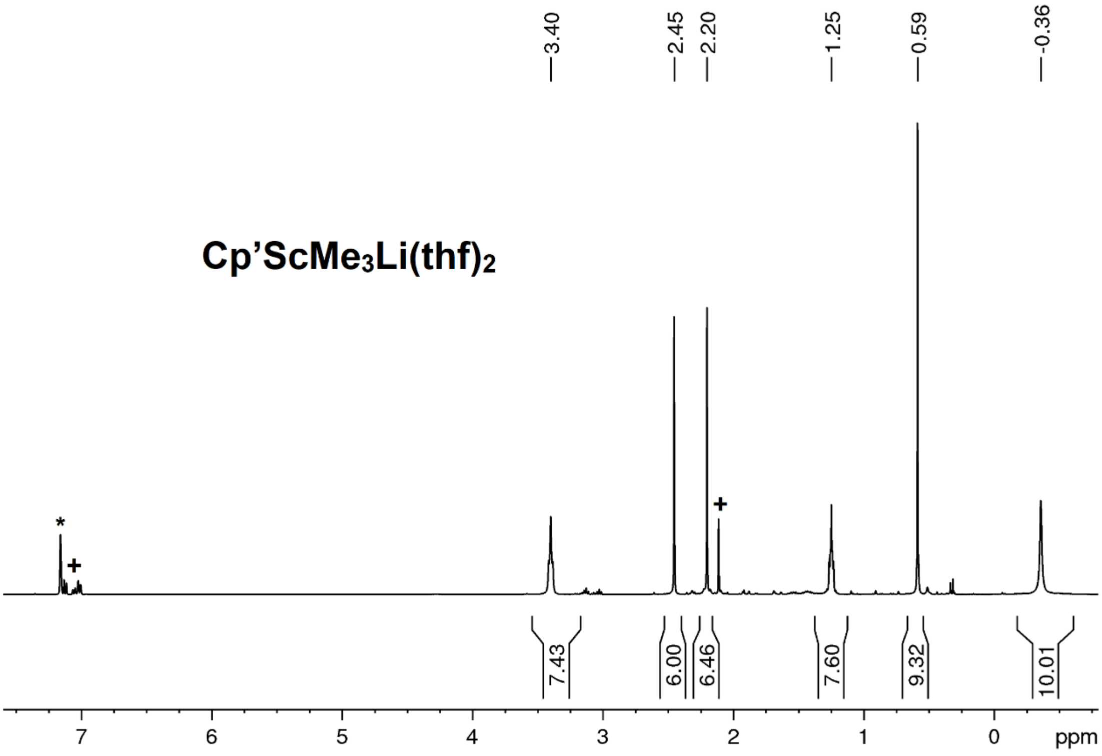

Figure S33. ^{1}H NMR spectrum (400 MHz) of raw compound Cp’ScMe$_3$Li(thf)$_2$ in C$_6$D$_6$ (marked with *) at 26 °C. Residual toluene is marked with +.

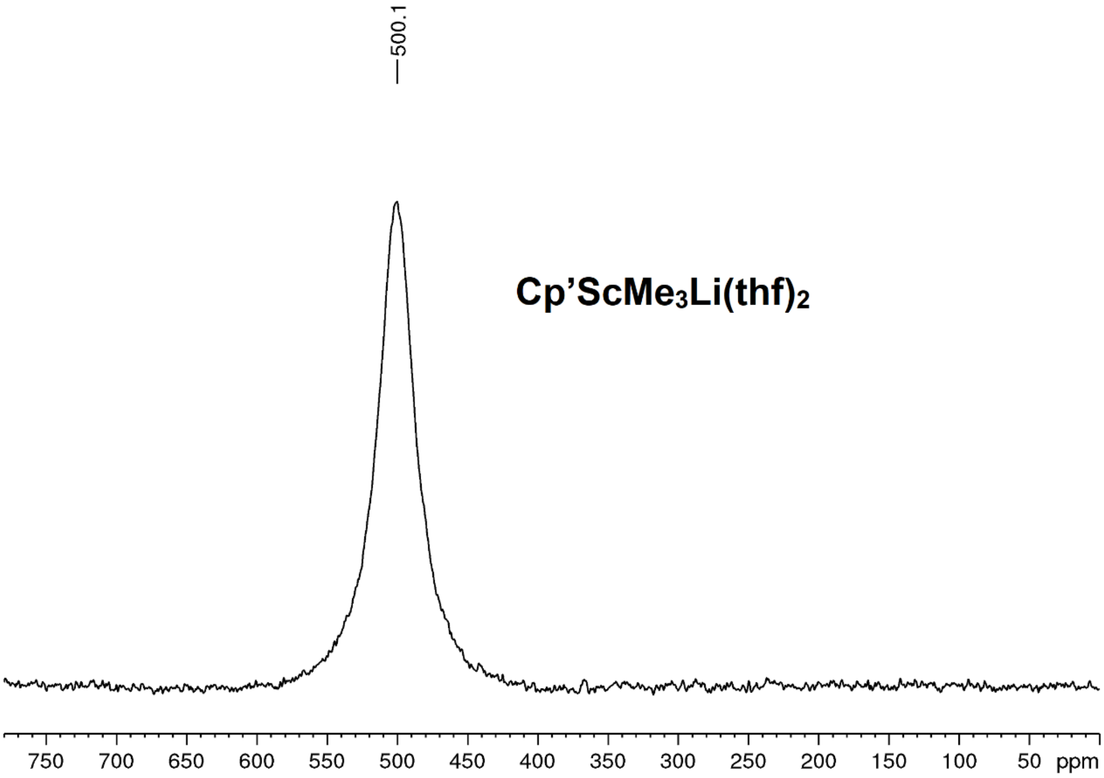

Figure S34. ^{45}Sc{^{1}H} NMR spectrum (97 MHz) of raw compound Cp’ScMe$_3$Li(thf)$_2$ in C$_6$D$_6$ at 26 °C.

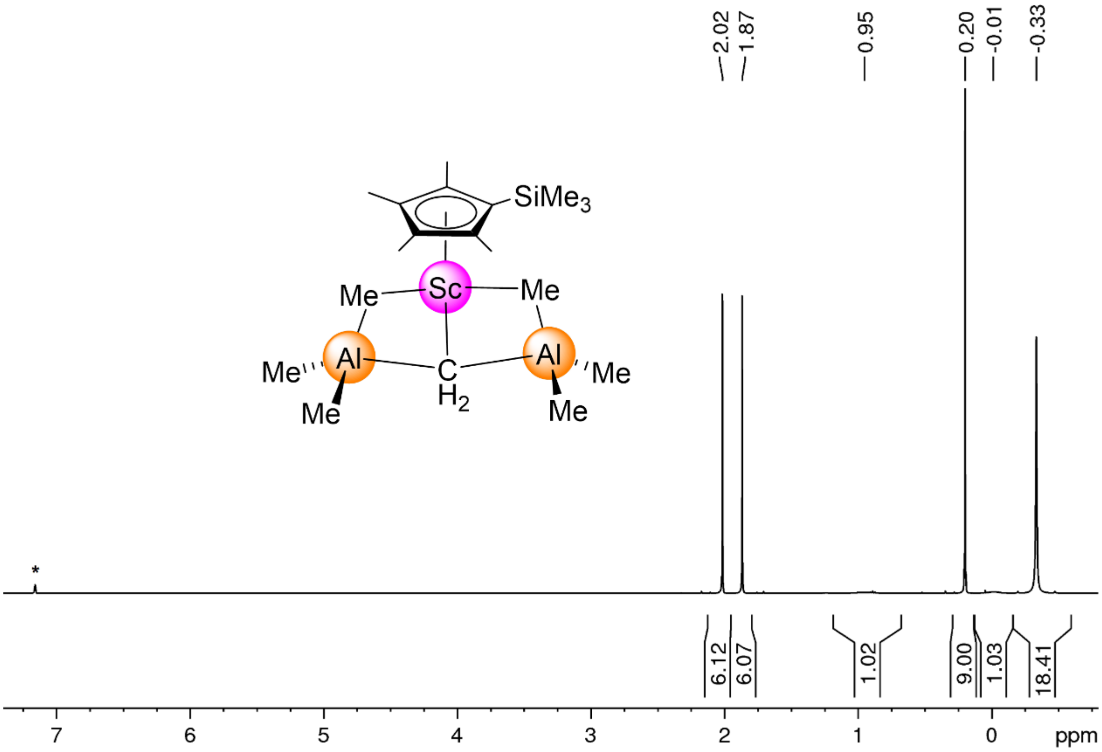

Figure S35. ^{1}H NMR spectrum (400 MHz) of compound Cp'Sc(CH$_2$)(AlMe$_3$)$_2$ (**8'**) in C$_6$D$_6$ (marked with *) at 26 °C.

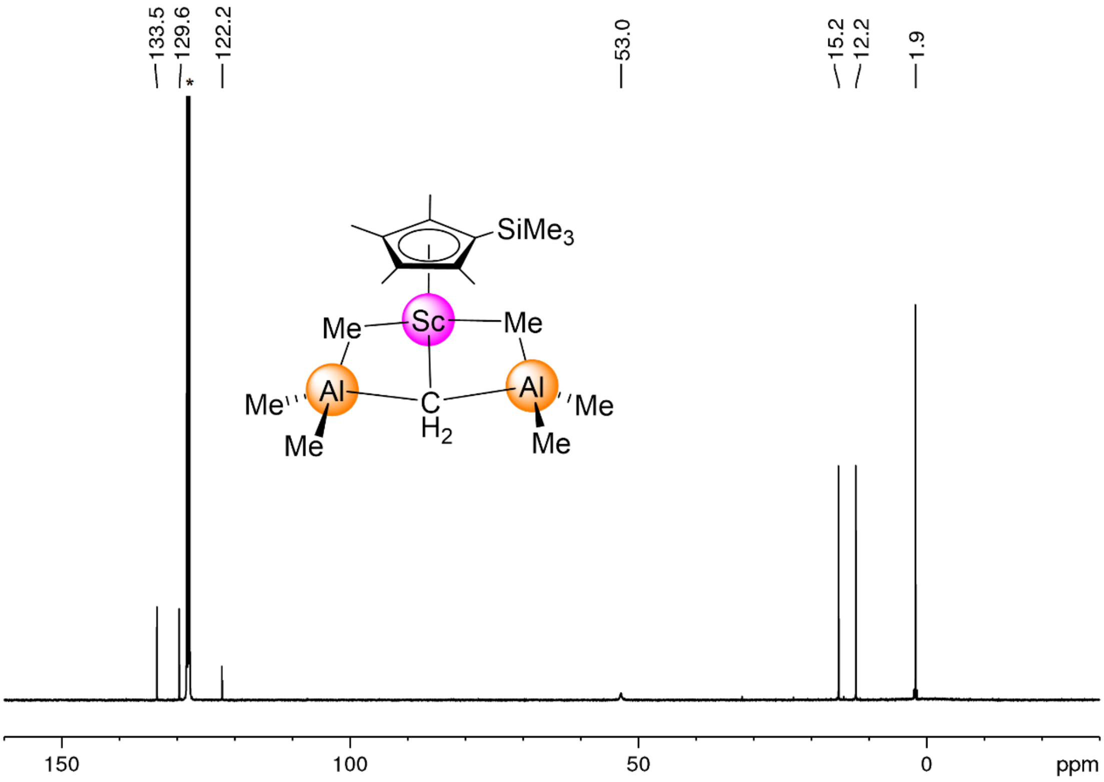

Figure S36. ^{13}C{^{1}H} NMR spectrum (101 MHz) of compound Cp'Sc(CH$_2$)(AlMe$_3$)$_2$ (**8'**) in C$_6$D$_6$ (marked with *) at 26 °C.

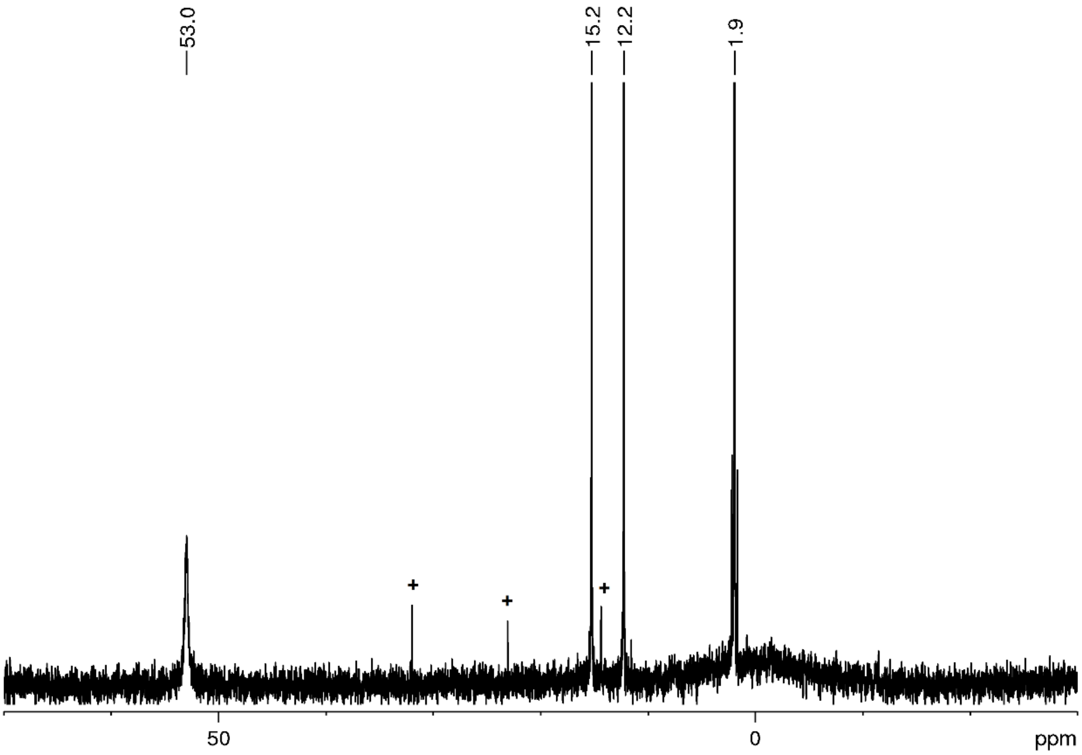

Figure S37. Detail of $^{13}C\{^1H\}$ NMR spectrum (101 MHz) of compound $Cp'Sc(CH_2)(AlMe_3)_2$ (**8'**) in C_6D_6 at 26 °C. Residual *n*-hexane is marked with +.

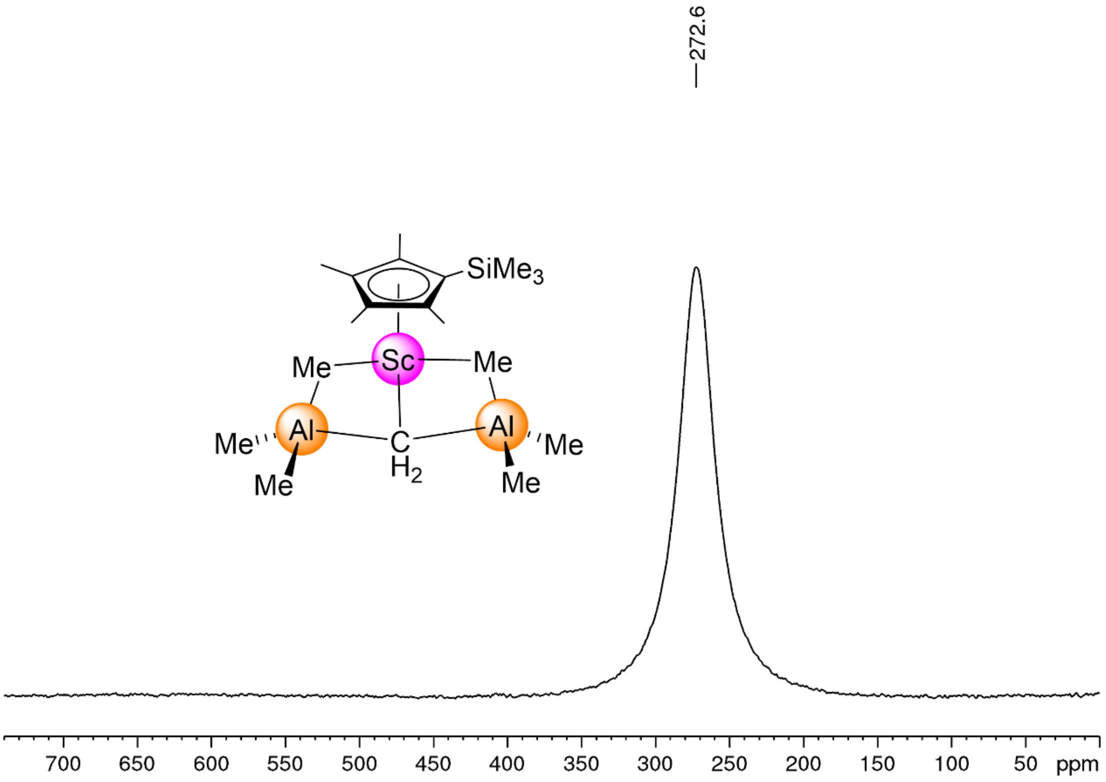

Figure S38. $^{45}Sc\{^1H\}$ NMR spectrum (97 MHz) of compound $Cp'Sc(CH_2)(AlMe_3)_2$ (**8'**) in C_6D_6 at 26 °C.

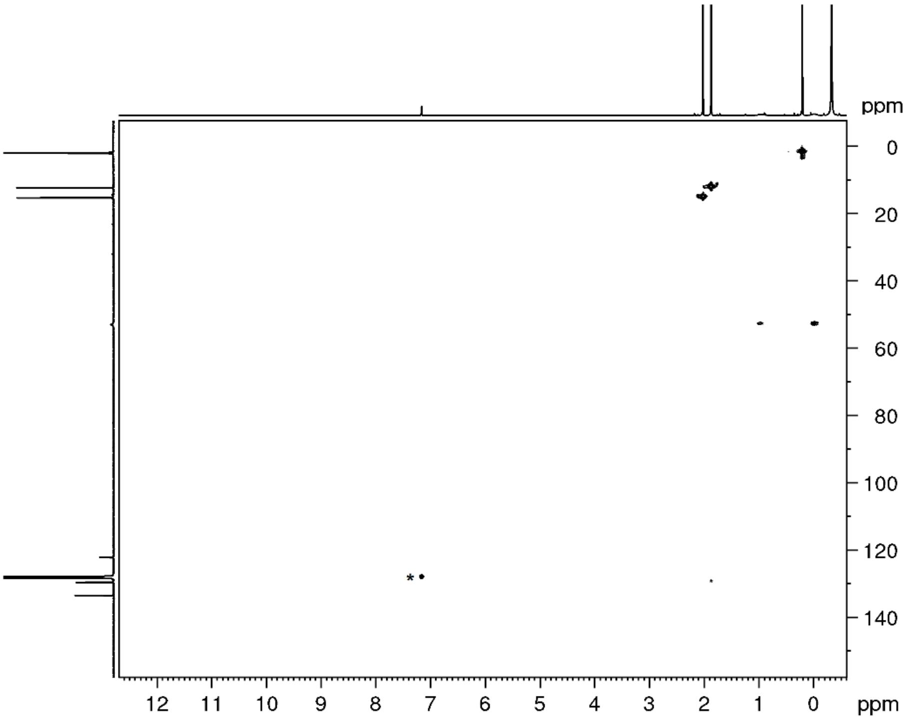

Figure S39. $^1H-^{13}C$ HSQC NMR spectrum (400 / 101 MHz) of compound Cp'Sc(CH$_2$)(AlMe$_3$)$_2$ (**8'**) in C$_6$D$_6$ (marked with *) at 26 °C.

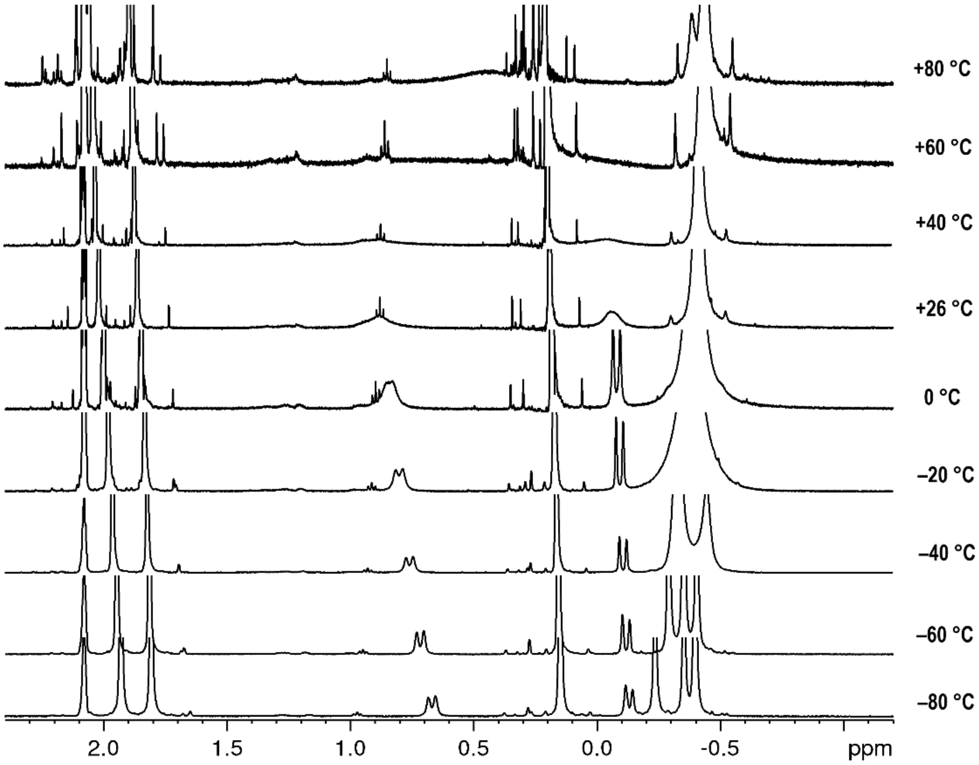

Figure S40. Variable temperature ^1H NMR spectra (500 MHz) of compound Cp'Sc(CH$_2$)(AlMe$_3$)$_2$ (**8'**) in toluene-d_8 between −80 and 80 °C.

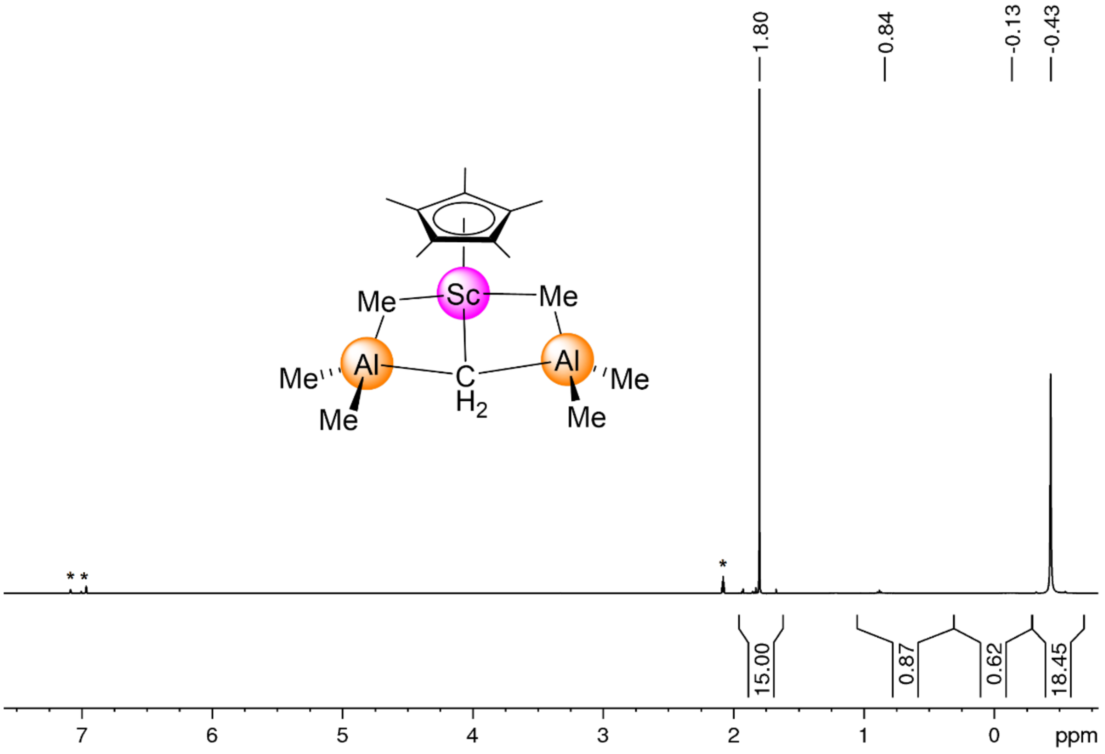

Figure S41. ^{1}H NMR spectrum (500 MHz) of compound Cp*Sc(CH$_2$)(AlMe$_3$)$_2$ (**8***) in toluene-*d*$_8$ (marked with *) at 26 °C.

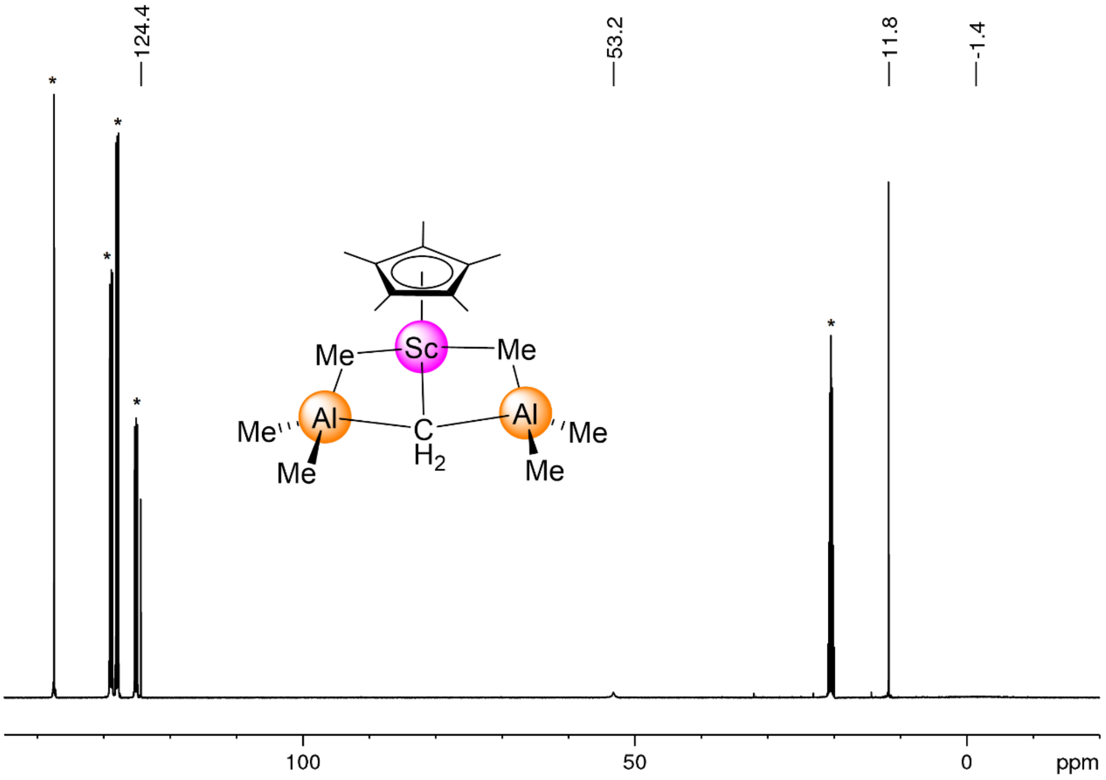

Figure S42. ^{13}C{^{1}H} NMR spectrum (126 MHz) of compound Cp*Sc(CH$_2$)(AlMe$_3$)$_2$ (**8***) in toluene-*d*$_8$ (marked with *) at 26 °C.

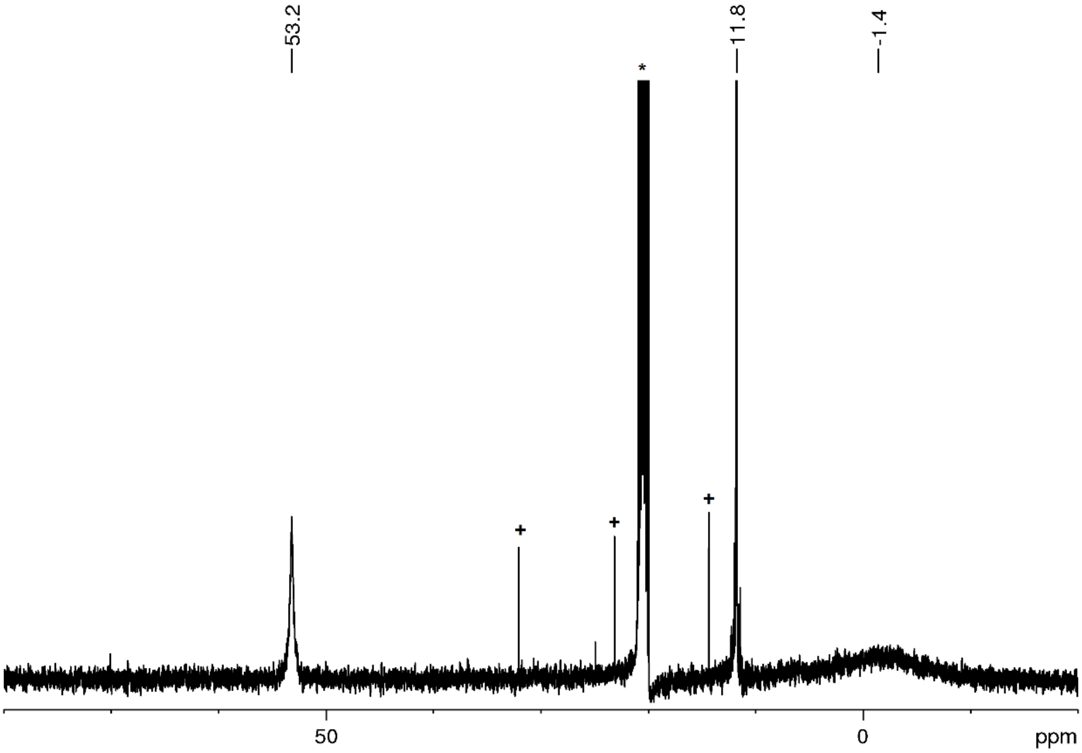

Figure S43. Detail of $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz) of compound Cp*Sc(CH$_2$)(AlMe$_3$)$_2$ (**8***) in toluene-*d*$_8$ at 26 °C. Residual *n*-hexane is marked with +.

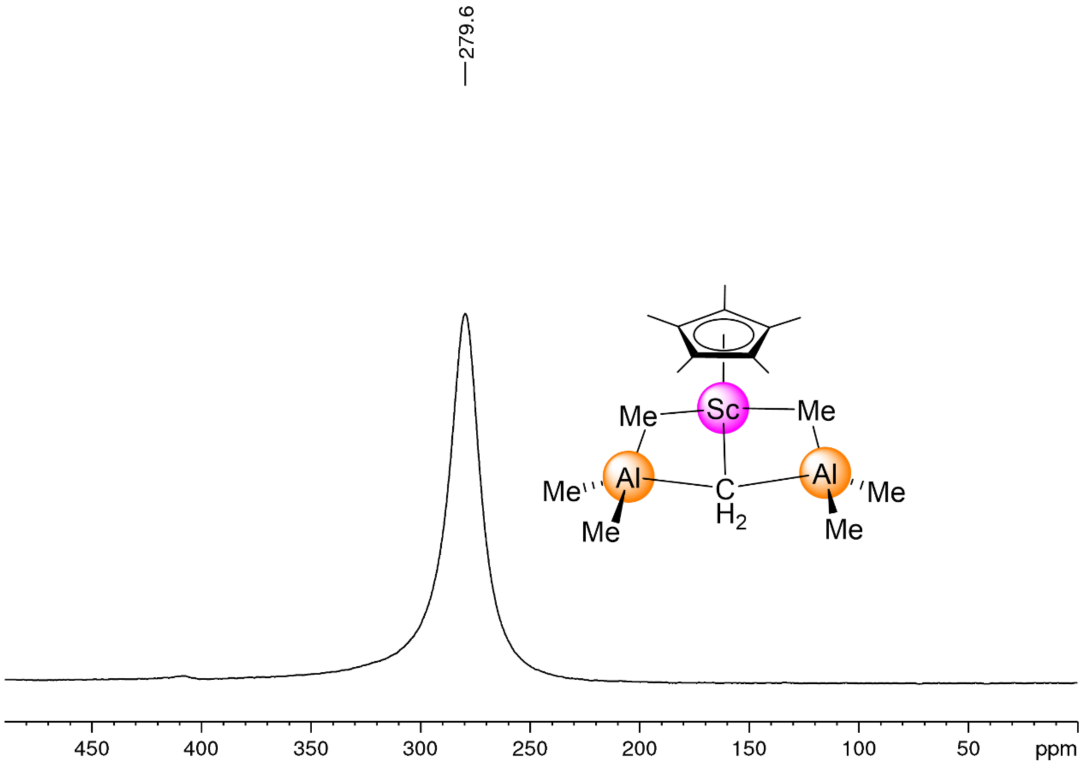

Figure S44. ^{45}Sc NMR spectrum (122 MHz) of compound Cp*Sc(CH$_2$)(AlMe$_3$)$_2$ (**8***) in toluene-*d*$_8$ at 26 °C.

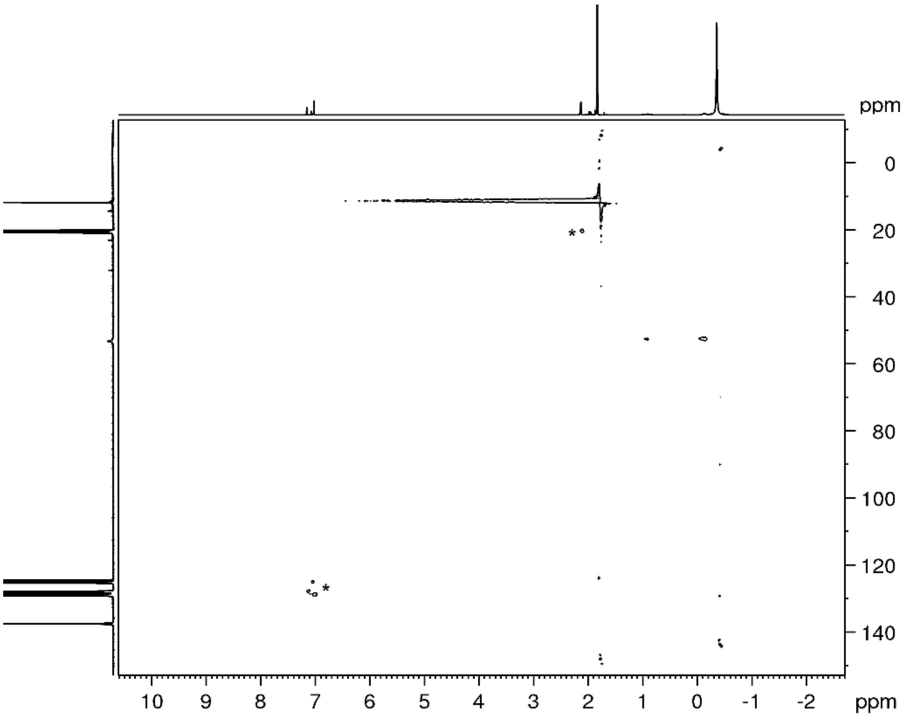

Figure S45. ^{1}H–^{13}C HSQC NMR spectrum (500 / 126 MHz) of compound $Cp^{*}Sc(CH_2)(AlMe_3)_2$ (**8***) in toluene-d_8 (marked with *) at 0 °C.

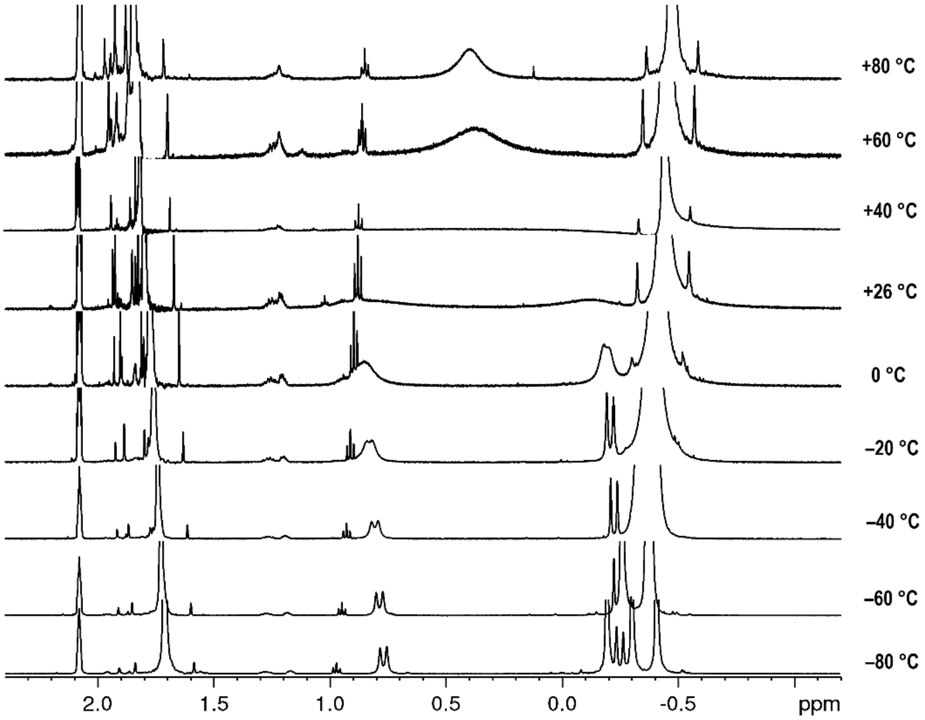

Figure S46. Variable temperature ^{1}H NMR spectra (500 MHz) of compound $Cp^{*}Sc(CH_2)(AlMe_3)_2$ (**8***) in toluene-d_8 between −80 and 80 °C.

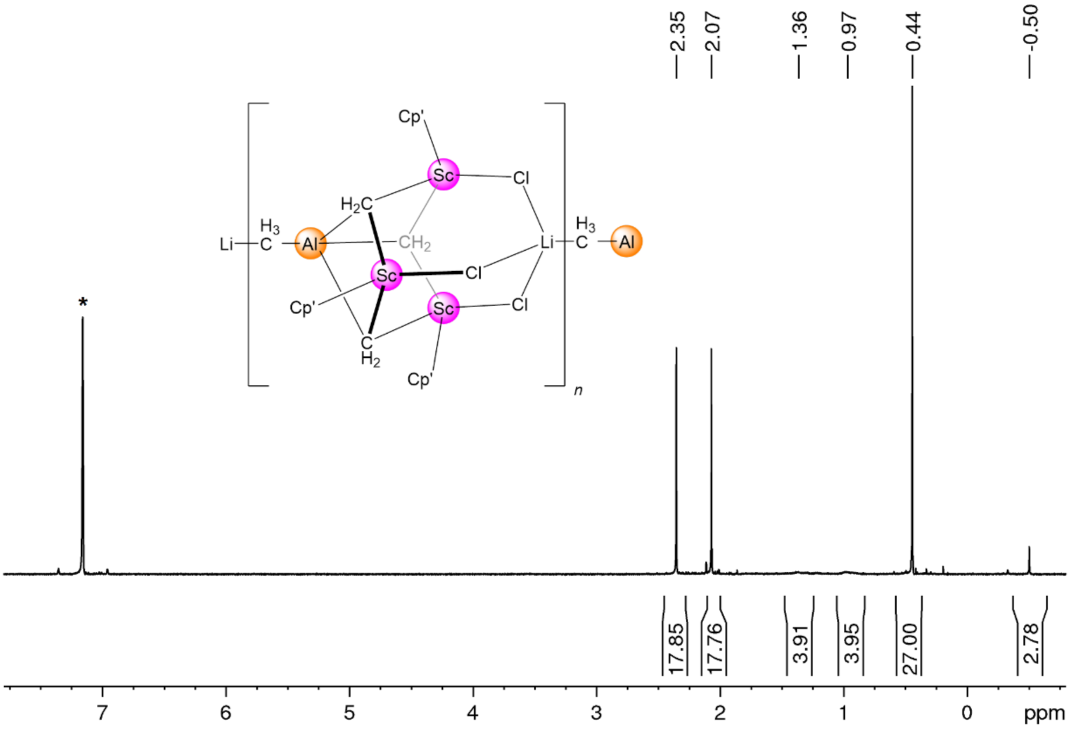

Figure S47. ^{1}H NMR spectrum (400 MHz) of compound [(Cp'ScCH$_2$)$_3$LiAlMeCl$_3$]$_n$ (**9'**) in C$_6$D$_6$ (marked with *) at 26 °C.

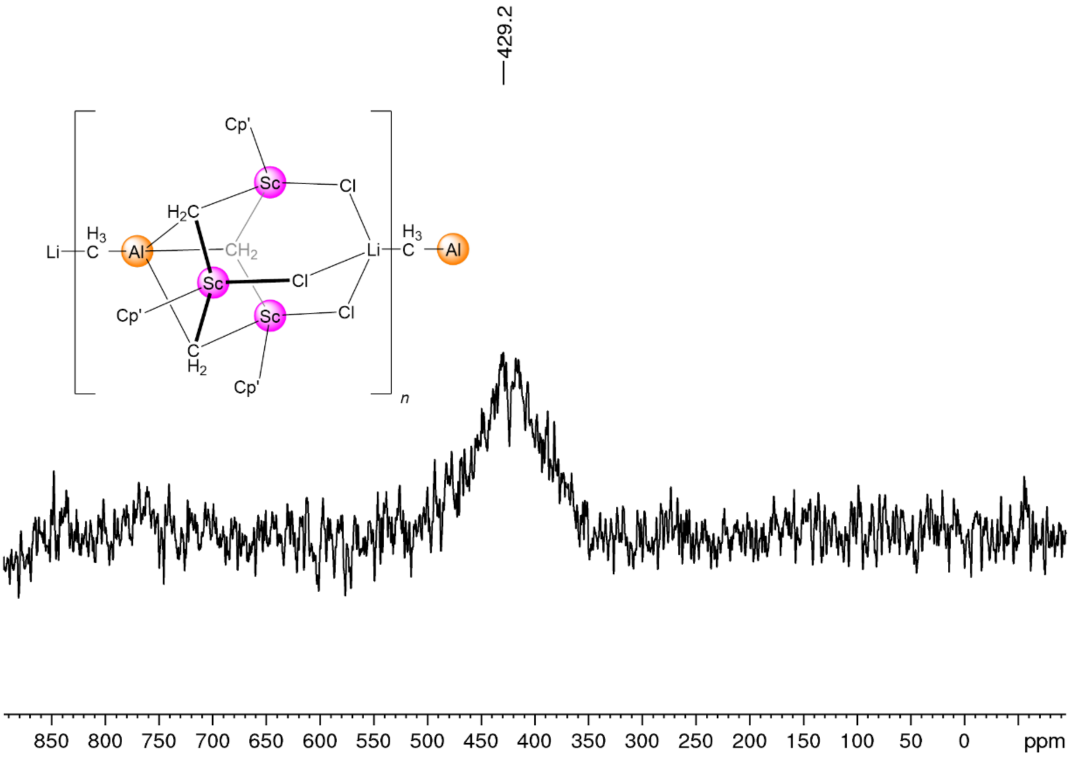

Figure S48. ^{45}Sc{^{1}H} NMR spectrum (97 MHz) of compound [(Cp'ScCH$_2$)$_3$LiAlMeCl$_3$]$_n$ (**9'**) in C$_6$D$_6$ at 26 °C.

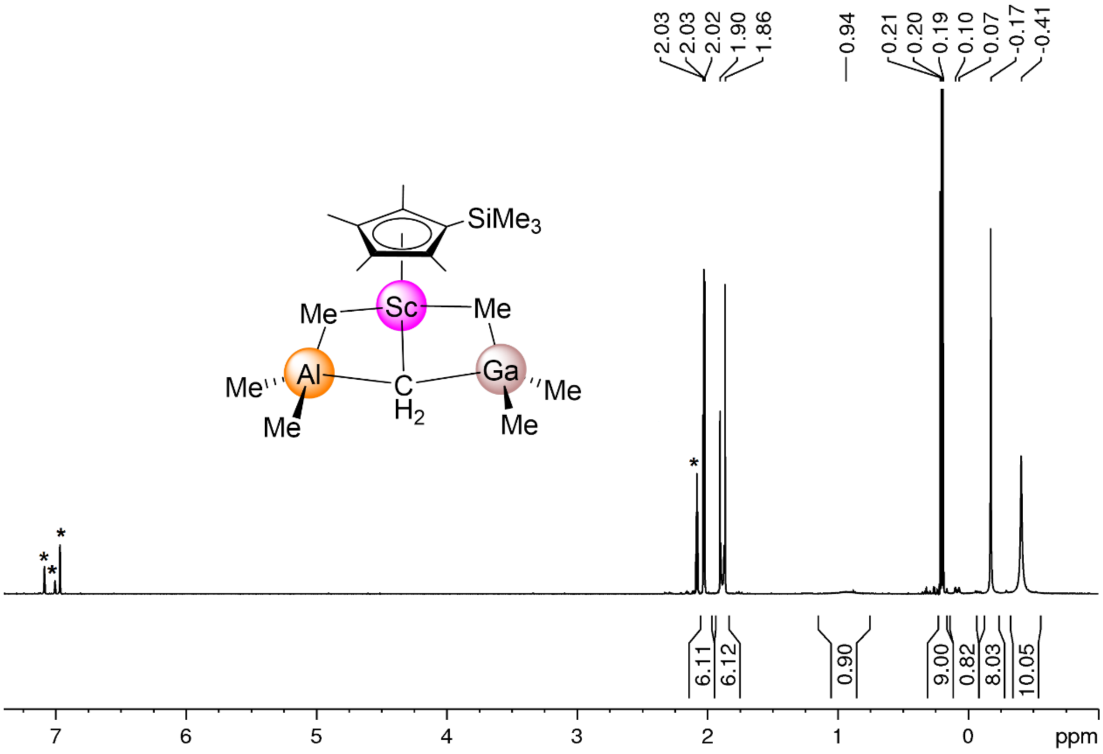

Figure S49. ^{1}H NMR spectrum (500 MHz) of compound Cp'Sc(CH$_2$)(AlMe$_3$)(GaMe$_3$) (**10'**) in toluene-*d*$_8$ (marked with *) at 26 °C.

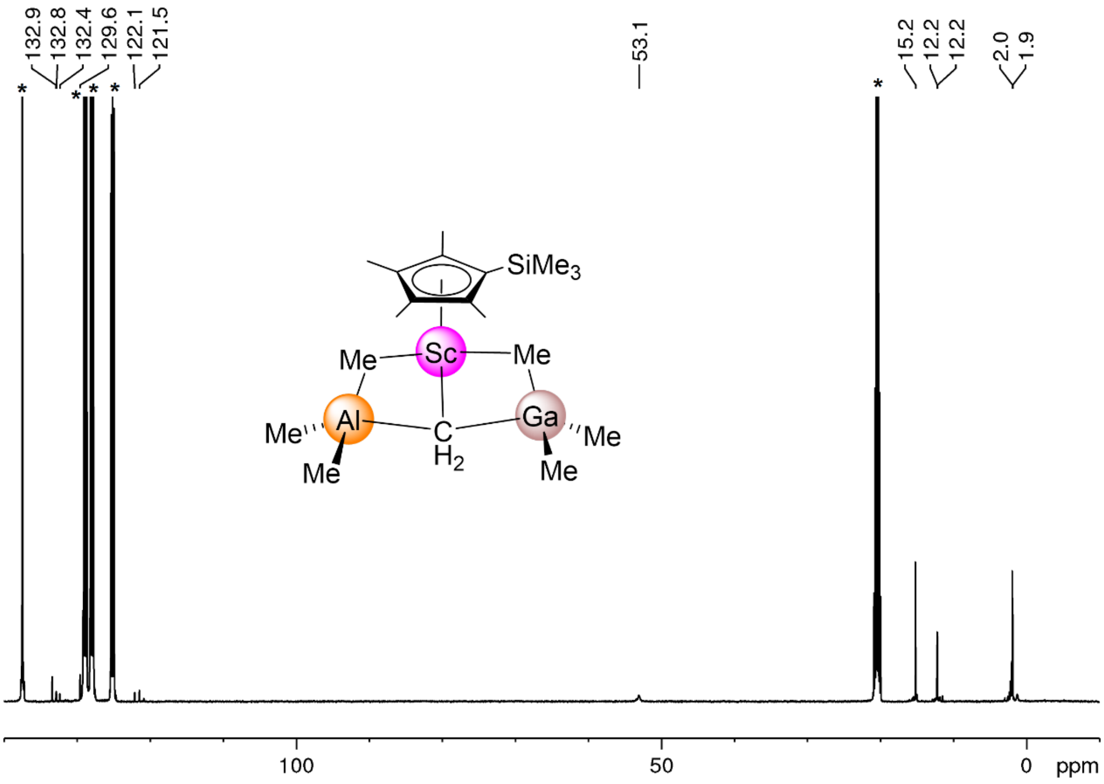

Figure S50. ^{13}C{^{1}H} NMR spectrum (126 MHz) of compound Cp'Sc(CH$_2$)(AlMe$_3$)(GaMe$_3$) (**10'**) in toluene-*d*$_8$ (marked with *) at 26 °C.

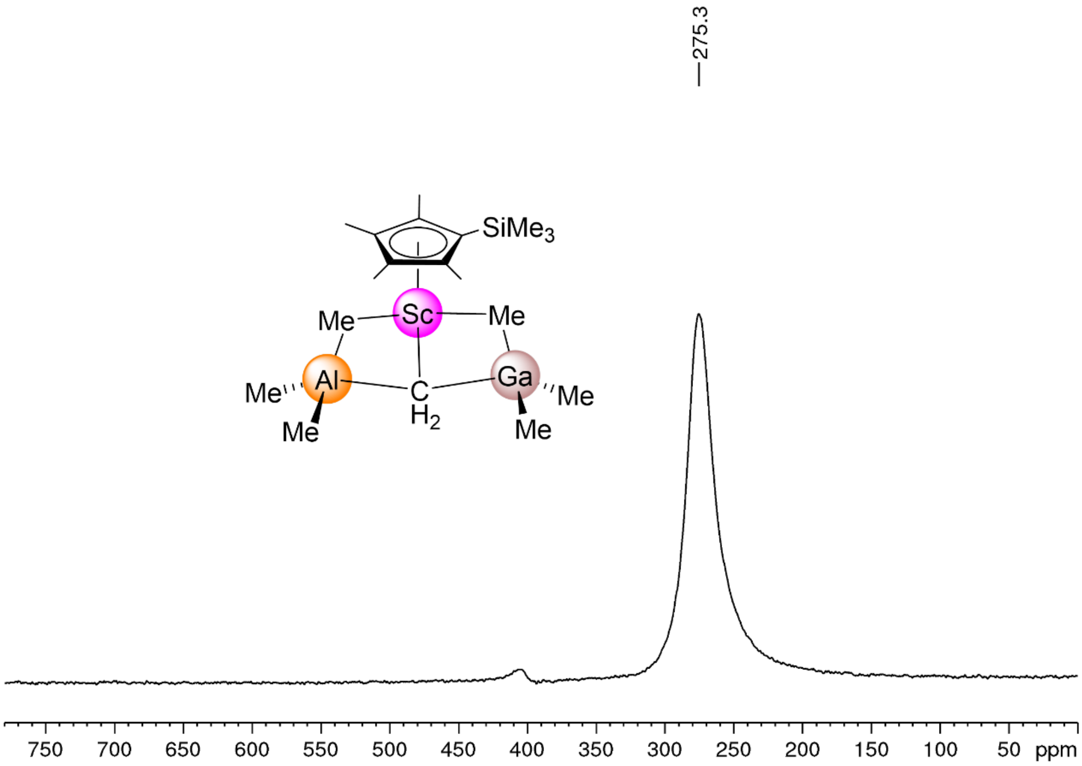

Figure S51. ^{45}Sc NMR spectrum (122 MHz) of compound Cp’Sc(CH$_2$)(AlMe$_3$)(GaMe$_3$) (**10’**) in toluene-d_8 at 26 °C.

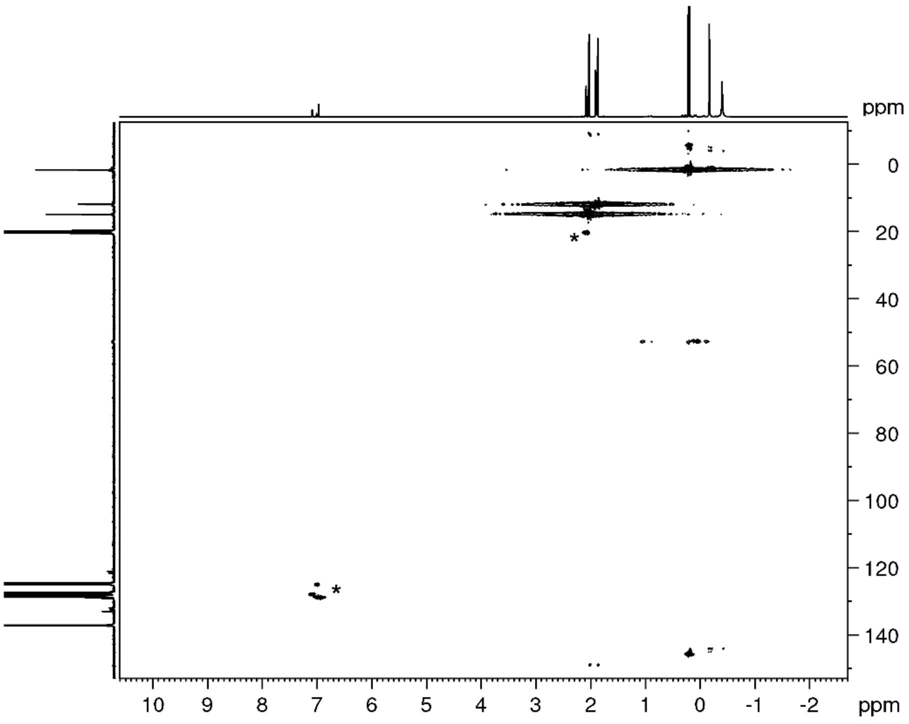

Figure S52. ^{1}H−^{13}C HSQC NMR spectrum (500 / 126 MHz) of compound Cp’Sc(CH$_2$)(AlMe$_3$)(GaMe$_3$) (**10’**) in toluene-d_8 (marked with *) at 26 °C.

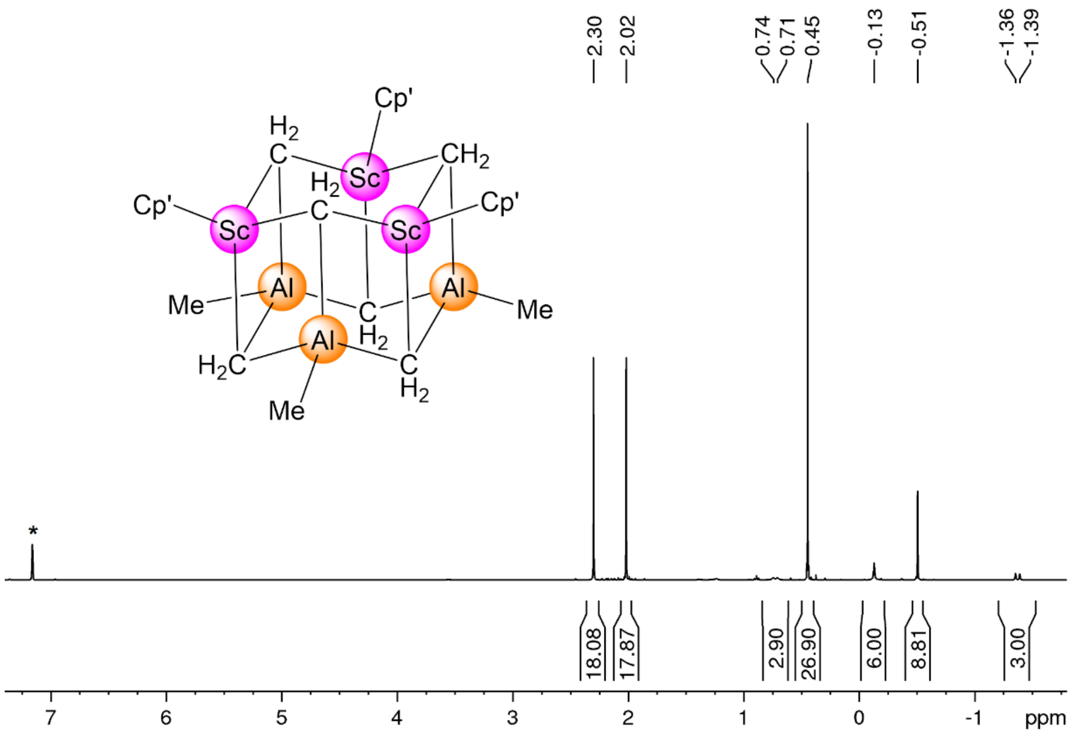

Figure S53. ^{1}H NMR spectrum (400 MHz) of compound [Cp’Sc(CH_2)$_2$AlMe]$_3$ (**11’**) in C_6D_6 (marked with *) at 26 °C.

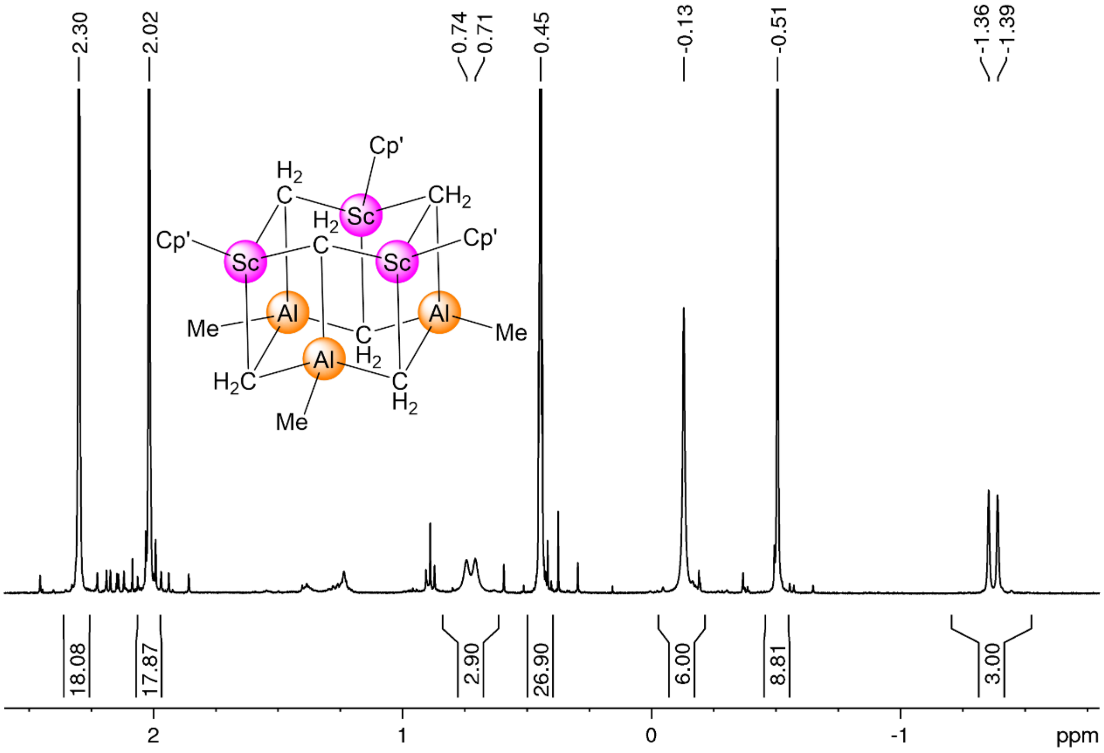

Figure S54. Detail of ^{1}H NMR spectrum (400 MHz) of compound [Cp’Sc(CH_2)$_2$AlMe]$_3$ (**11’**) in C_6D_6 at 26 °C.

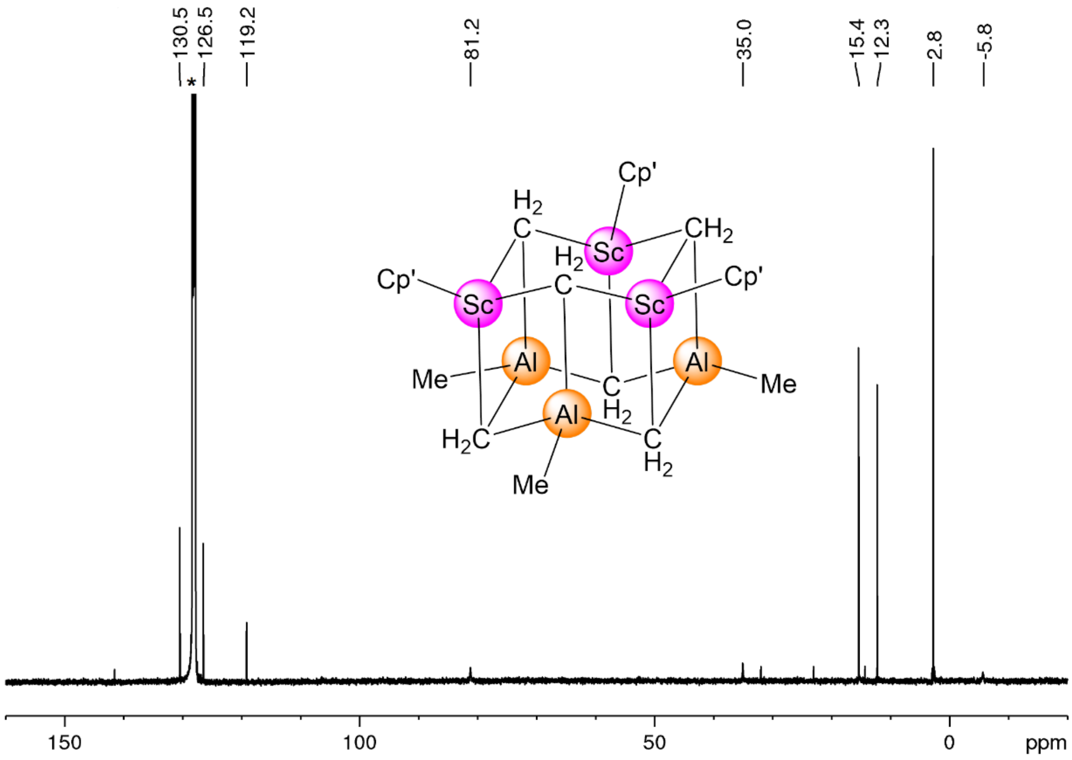

Figure S55. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz) of compound [Cp'Sc(CH$_2$)$_2$AlMe]$_3$ (**11'**) in C_6D_6 (marked with *) at 26 °C.

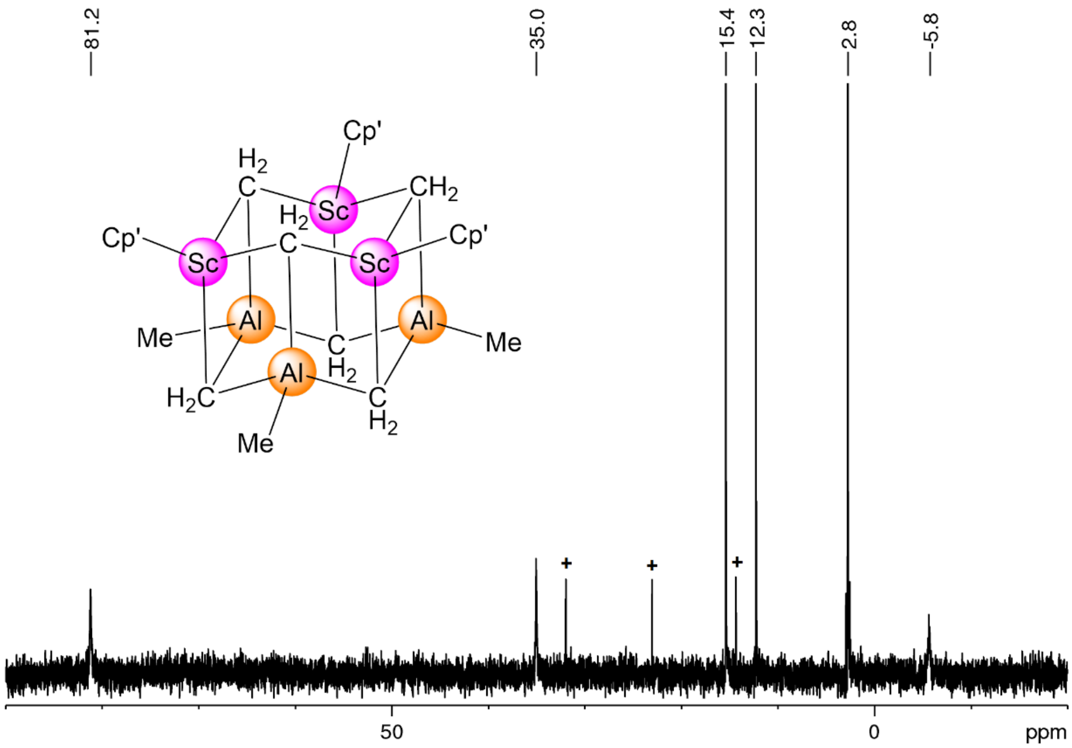

Figure S56. Detail of $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz) of compound [Cp'Sc(CH$_2$)$_2$AlMe]$_3$ (**11'**) in C_6D_6 at 26 °C. Residual *n*-hexane is marked with +.

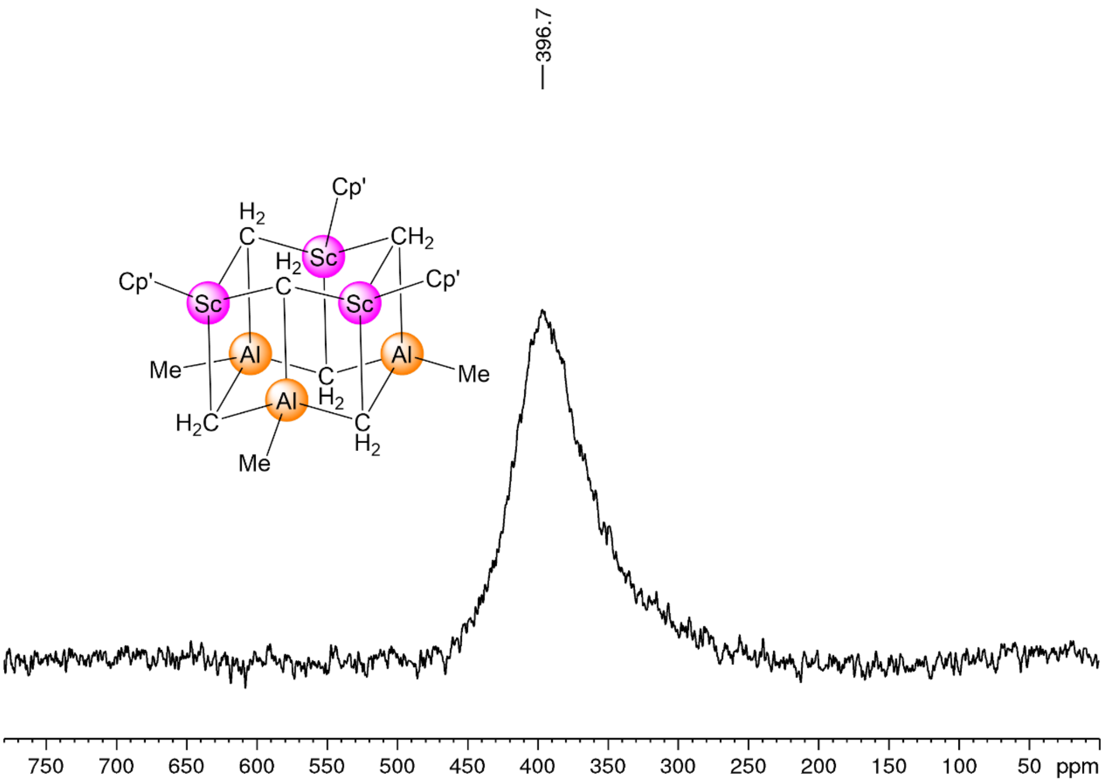

Figure S57. ^{45}Sc{^{1}H} NMR spectrum (97 MHz) of compound [Cp'Sc(CH$_2$)$_2$AlMe]$_3$ (**11'**) in C$_6$D$_6$ at 26 °C.

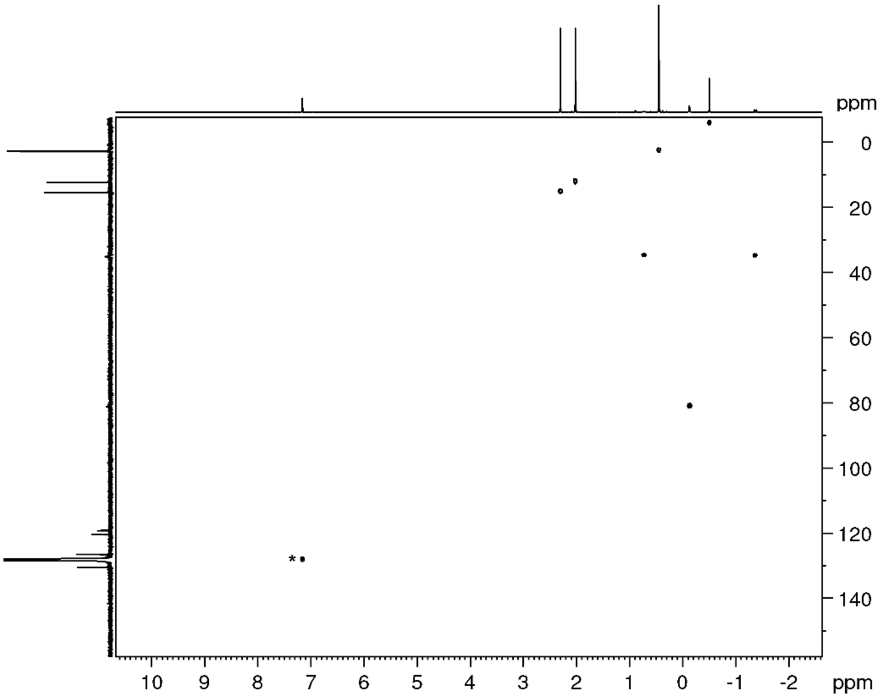

Figure S58. ^{1}H−^{13}C HSQC NMR spectrum (400 / 101 MHz) of compound [Cp'Sc(CH$_2$)$_2$AlMe]$_3$ (**11'**) in C$_6$D$_6$ (marked with *) at 26 °C.

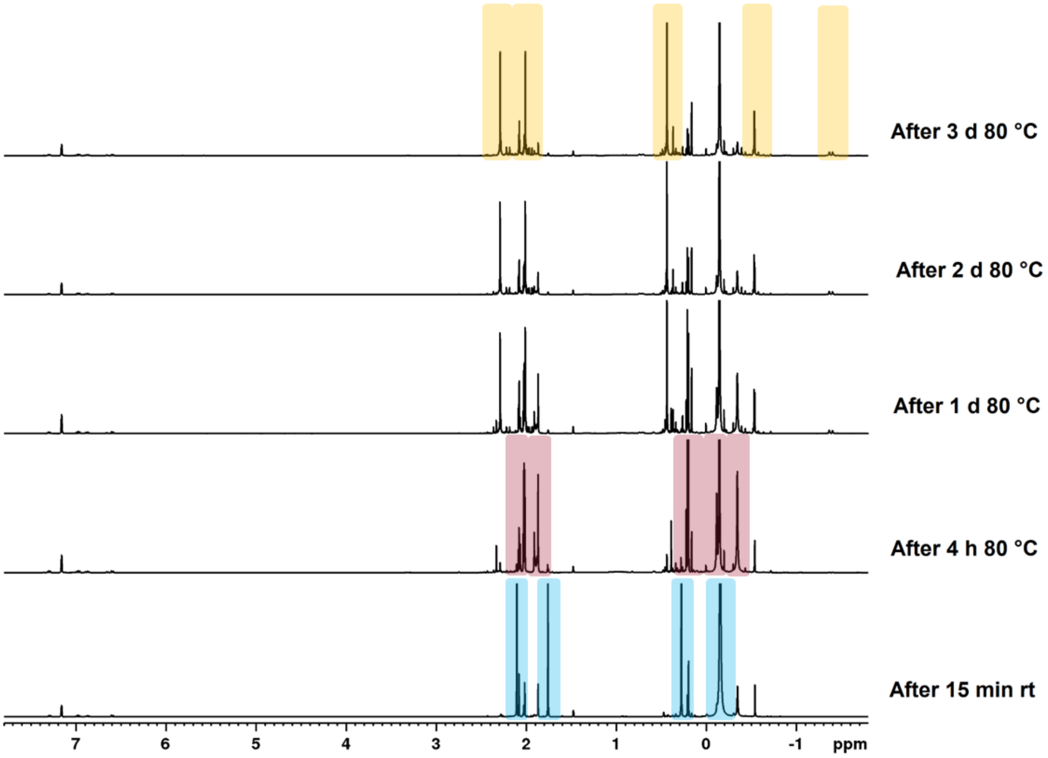

Figure S59. Monitoring of the reaction of **4'** (blue) with 1 equiv. $GaMe_3$ in a J. Young-valved NMR tube without agitation *via* ^1H NMR spectroscopy (400 MHz) in C_6D_6 at 26 °C with intermediate **10'** (red) and final product **11'** (yellow).

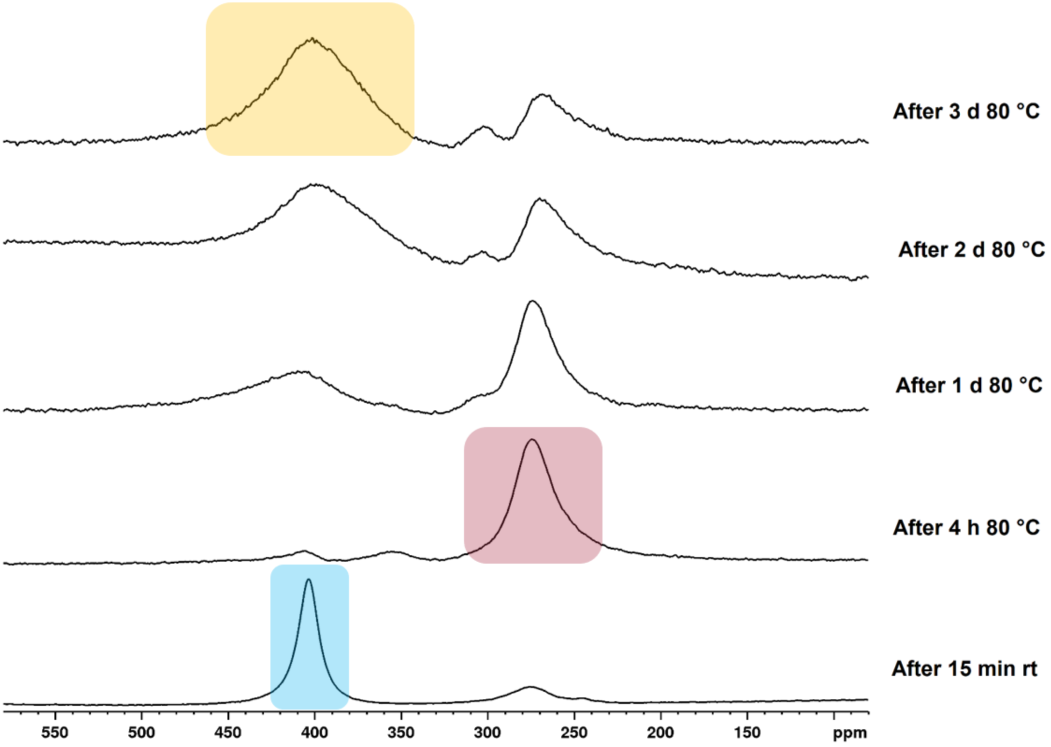

Figure S60. Monitoring of the reaction of **4'** (blue) with 1 equiv. $GaMe_3$ in a J. Young-valved NMR tube without agitation *via* $^{45}Sc\{^1H\}$ NMR spectroscopy (97 MHz) in C_6D_6 at 26 °C with intermediate **10'** (red) and final product **11'** (yellow).

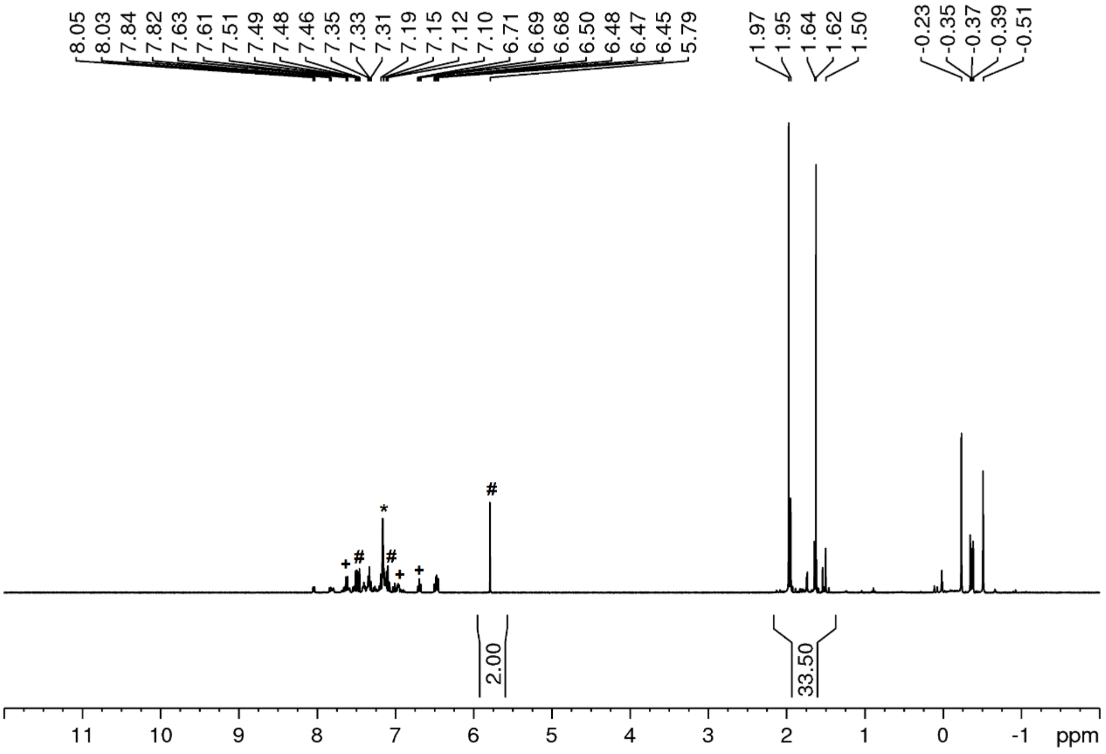

Figure S61. ^{1}H NMR spectrum (400 MHz) of the reaction mixture of **8*** with fluorenone after 15 min at ambient temperature in C_6D_6 (marked with *) at 26 °C. Dibenzofulvene is marked with #. Fluorenone is marked with +. All other peaks cannot be assigned to a known compound.

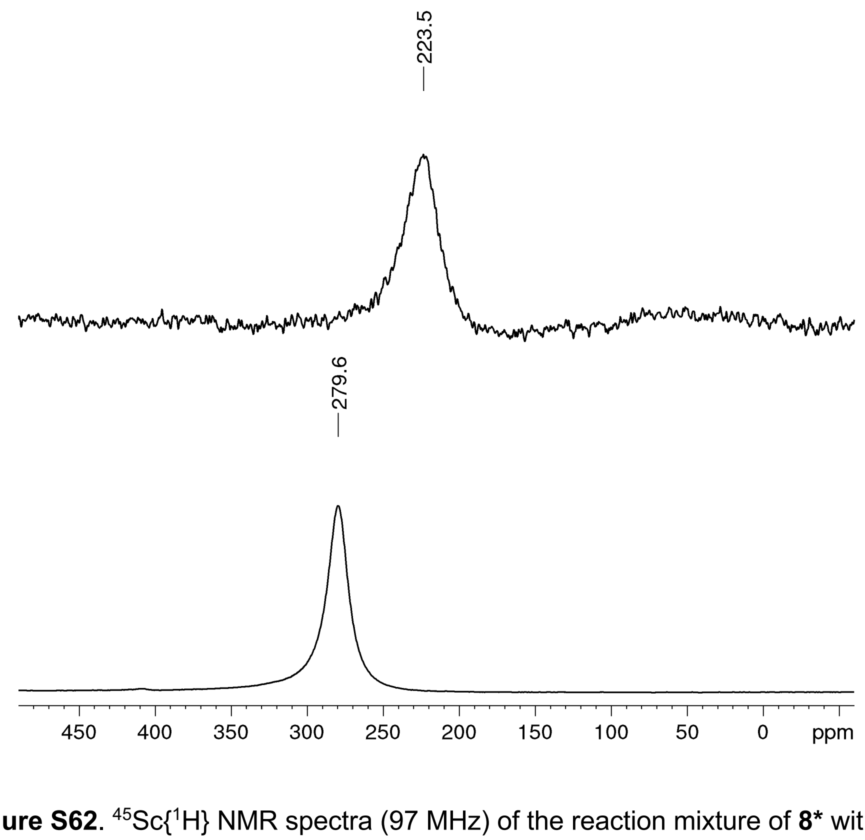

Figure S62. ^{45}Sc{^{1}H} NMR spectra (97 MHz) of the reaction mixture of **8*** with fluorenone after 20 min (top) and **8*** (bottom) at ambient temperature in C_6D_6 at 26 °C.

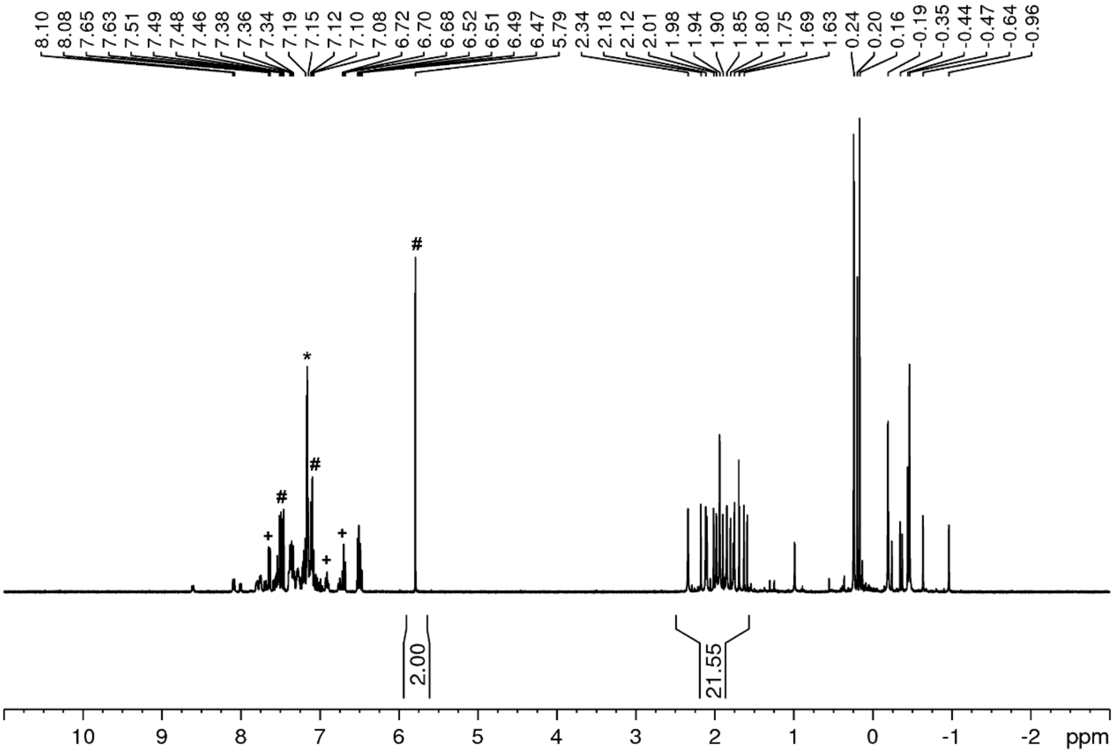

Figure S63. ^{1}H NMR spectrum (400 MHz) of the reaction mixture of **8'** with fluorenone after 15 min at ambient temperature in C_6D_6 (marked with *) at 26 °C. Dibenzofulvene is marked with #. Fluorenone is marked with +. All other peaks cannot be assigned to a known compound.

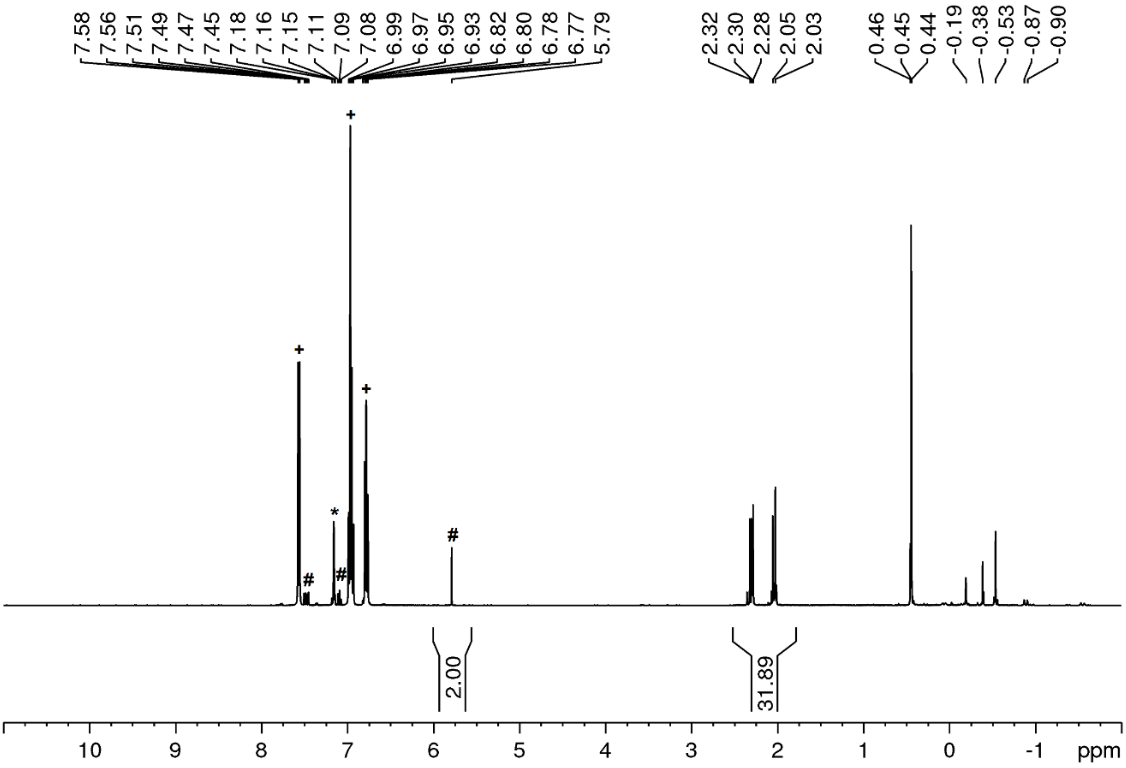

Figure S64. ^{1}H NMR spectrum (400 MHz) of the reaction mixture of **11'** with fluorenone after 4 h at 80 °C in C_6D_6 (marked with *) measured at 26 °C. Dibenzofulvene is marked with #. Fluorenone is marked with +. All other peaks cannot be assigned to a known compound.

Crystallography

X-Ray crystallography and crystal structure determination

All crystals, if not noted otherwise, were grown at -40 °C. Crystals of **1’, 1*, 3’, 3*, 8’** and **10’** were grown from a solution of *n*-hexane. For **7’**, crystals could be obtained by layering a concentrated THF solution with *n*-hexane and for **11’** a toluene solution was layered with *n*-hexane. **2’** and **2*** were crystallized from C_6D_6 at ambient temperature, **6’** from *n*-pentane. Colorless crystals of **9’** (4 mg) were obtained from the concentrated red supernatant of **8’** after two months.

Single crystals suitable for X-ray diffraction were selected inside a glovebox and coated with Parabar (10312 Hampton Research) on a glass fiber. X-ray data for all compounds except **8’** were recorded on a Bruker APEX II DUO diffractometer equipped with an IµS microfocus sealed tube and QUAZAR optics for MoKα (λ = 0.71073 Å). For **8‘**, the measurement has been carried out on a Bruker SMART APEX II instrument equipped with a fine focus sealed tube and TRIUMPH monochromator using MoK_{α} radiation (λ = 0.71073 Å). The Data collection strategy was determined using COSMO[1] employing ω-scans. Raw data were processed by APEX[2] and SAINT,[3] corrections for absorption effects were applied using SADABS[4] and TWINABS.[5] The structures were solved by direct methods and refined against all data by full-matrix least-squared methods on F^2 using SHELXTL[6] and Shelxle,[7] and plots were generated by using MERCURY[8] and POV-Ray.[9]

[1] *COSMO V. 1.61*, Bruker AXS Inc., Madison, WI, 2012.

[2] APEX3 V. 2019.11-0, Bruker AXS Inc., Madison, WI, 2019.
APEX *2 V. 2012.10_0*, Bruker AXS Inc., Madison, WI, 2012.

[3] *SAINT V. 8.38A*, Bruker AXS Inc., Madison, WI, 2017.
SAINT V. 8.40B, Bruker Nano, Inc., Madison, WI, 2019.

[4] *SADABS* Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48,** 3-10.

[5] Sheldrick, G. M. (2009). *TWINABS*. University of Göttingen, Germany.

[6] Sheldrick G.M., SHELXT- Integrated space-group and crystal-structure determination, *Acta Cryst.,* **2015**, A71, 3-8.
Sheldrick, G. M., Crystal structure refinement with SHELXL, *Acta Cryst.* **2015***,* C71, 3-8

[7] ShelXle, C. B. Huebschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281-1284.

[8] Mercury CSD 2.0 - New Features for the Visualization and Investigation of Cryst. Structure C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, J. Appl. Cryst., 41, 466-470, 2008.

[9] v. 3.6, P. o. V. P. L., POV-Ray Williamstown, Victoria, Australia, **2004,** http://www.povray.org.

Table S1. Crystallographic Data for

Compound	**1’**	**1***	**2’**	**2***
Formula	$C_{24}H_{45}Cl_3LiO_3ScSi$	$C_{22}H_{39}Cl_3LiO_3Sc$	$C_{54}H_{84}Cl_8D_6Sc_4Si_4$	$C_{40}H_{60}Cl_8Sc_4$
CCDC	2410885	2410878	2410884	2410880
M [g mol^{-1}]	567.94	509.78	1321.09	1004.32
color/shape	colorless/plate	colorless/block	colorless/block	colorless/block
Crystal dimensions [mm]	0.225 x 0.207 x 0.077	0.199 x 0.174 x 0.163	0.288 x 0.274 x 0.227	0.229 x 0.164 x 0.104
cryst. system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/c$	$P2_1/n$	$C2/c$	$C2/$c
a [Å]	15.7267(3)	8.8126(18)	25.8300(15)	24.5153(12)
b [Å]	26.1915(6)	21.449(5)	13.7225(8)	11.9624(6)
c [Å]	15.6481(4)	14.063(3)	19.4273(11)	15.9770(8)
α [°]	90	90	90	90
β [°]	108.3260(10)	90.144(4)	107.0500(10)	101.6870(10)
γ [°]	90	90	90	90
V [Å^3]	6118.6(2)	2658.2(10)	6583.4(7)	4588.3(4)
Z	8	4	4	4
T [K]	100(2)	100(2)	100(2)	100(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm^{-3}]	1.233	1.274	1.333	1.454
μ [mm^{-1}]	0.563	0.598	0.825	1.060
F(000)	2416	1080	2760	2080
Θ range [°]	1.364/28.328	1.899/29.934	1.698/30.506	1.902/28.706
unique reflns	15222	14233	10031	5933
observed reflns	210224	57744	74920	45707
R1[b]/wR2(I>2σ)[c]	0.0509/0.1199	0.0510/0.1175	0.0322/0.0757	0.0281/0.0661
R1[b]/wR2(all data)[c]	0.0873/0.1423	0.0749/0.1297	0.0410/0.0812	0.0349/0.0716
GOF[a]	1.019	1.058	1.061	1.052

[a]GOF = $[\Sigma w(F_0^2 - F_c^2)^2/(n_0 - n_p)]^{1/2}$. [b]$R_1 = \Sigma(| |F_0| - |F_c| |) / \Sigma |F_0|$, $F_0 > 4\sigma(F_0)$. [c]$wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2 / \Sigma[w(F_0^2)^2]\}^{1/2}$.

Table S2. Crystallographic Data for

Compound	**3’**	**3***	**5’**	**6’**
Formula	$C_{39}H_{74}Al_2Cl_2Sc_2Si_2$	$C_{28}H_{54}Al_2Cl_2Sc_2$	$C_{20.85}H_{36.55}Cl_{0.15}N_2ScSi$	$C_{38}H_{66}O_2Sc_2Si_2$
CCDC	2410879	2410888	2410875	2410876
M [g mol^{-1}]	813.94	605.49	393.69	701.00
color/shape	colorless/column	light-yellow /plate	colorless/block	colorless/plate
Crystal dimensions [mm]	0.233 x 0.106 x 0.089	0.179 x 0.069 x 0.066	0.375 x 0.279 x 0.185	0.205 x 0.139 x 0.050
cryst. system	Monoclinic	Monoclinic	Monoclinic	Triclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a [Å]	10.4378(7)	12.2609(9)	10.0479(14)	9.0744(7)
b [Å]	18.9550(13)	8.2407(6)	26.729(4)	10.3670(7)
c [Å]	12.6350(8)	16.6707(12)	9.0223(13)	10.5664(8)
α [°]	90	90	90	79.788(2)
β [°]	113.1830(10)	92.5960(10)	110.160(2)	81.495(3)
γ [°]	90	90	90	85.520(3)
V [Å^3]	2298.0(3)	1682.7(2)	2274.6(6)	966.15(12)
Z	2	2	4	1
T [K]	100(2)	100(2)	100(2)	100(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm^{-3}]	1.176	1.195	1.150	1.205
μ [mm^{-1}]	0.526	0.629	0.400	0.443
F(000)	876	648	853	380
Θ range [°]	2.056/30.859	2.019/28.721	2.159/30.489	1.977/28.351
unique reflns	6837	4358	6833	4788
observed reflns	39655	33118	13687	7983
R1[b]/*w*R2(I>2σ)[c]	0.0421/0.0941	0.03680/0.0917	0.0421/0.1056	0.0474/0.1018
R1[b]/*w*R2(all data)[c]	0.0648/0.1061	0.0469/0.0983	0.0576/0.1159	0.0638/0.1099
GOF[a]	1.028	1.058	1.018	1.043

[a] GOF = $[\Sigma w(F_0^2 - F_c^2)^2/(n_0 - n_p)]^{1/2}$. [b] $R_1 = \Sigma(\mathrm{I}\,|F_0| - |F_c|\,\mathrm{I}) / \Sigma\,|F_0|$, $F_0 > 4\sigma(F_0)$. [c] $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2/ \Sigma[w(F_0^2)^2]\}^{1/2}$.

Table S3. Crystallographic Data for

Compound	**7’**	**8’**	**8***	**9’**
Formula	$C_{31}H_{62}LiO_4ScSi$	$C_{19}H_{41}Al_2ScSi$	$C_{17}H_{35}Al_2Sc$	$C_{40}H_{72}AlCl_3Sc_3Si_3$
CCDC	2410883	2410886	2410874	2410882
M [g mol^{-1}]	578.79	396.53	338.37	912.39
color/shape	colorless/plate	colorless/prism	colorless/block	colorless/needle
Crystal dimensions [mm]	0.252 x 0.148 x 0.091	0.380 x 0.350 x 0.330	0.317 x 0.243 x 0.235	0.187 x 0.091 x 0.084
cryst. system	Monoclinic	Monoclinic	Triclinic	Trigonal
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$R3$
a [Å]	15.6250(11)	15.2876(4)	10.172(3)	21.5428(5)
b [Å]	9.8614(7)	15.4052(4)	10.270(3)	21.5428(5)
c [Å]	23.2842(16)	10.2560(3)	10.276(3)	8.8508(3)
α [°]	90	90	103.596(4)	90
β [°]	91.129(2)	93.8500(10)	97.957(4)	90
γ [°]	90	90	98.653(4)	120
V [Å^3]	3587.0(4)	2409.92(11)	1014.5(5)	3557.3(2)
Z	4	4	2	3
T [K]	100(2)	100(2)	100(2)	100(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm^{-3}]	1.072	1.093	1.108	1.278
μ [mm^{-1}]	0.267	0.427	0.441	0.707
F(000)	1272	864	368	1452
Θ range [°]	1.303/28.754	2.963/27.520	2.078/30.767	1.891/28.288
unique reflns	9280	5508	6221	3917
observed reflns	76319	61482	31305	36040
R1[b]/*w*R2(I>2σ)[c]	0.0499/0.1229	0.0354/0.0937	0.0446/0.1139	0.0393/0.0891
R1[b]/*w*R2(all data)[c]	0.0794/0.1400	0.0373/0.0946	0.0611/0.1213	0.0482/0.0941
GOF[a]	1.035	1.170	1.083	1.080

[a] GOF = $[\Sigma w(F_0^2 - F_c^2)^2/(n_0 - n_p)]^{1/2}$. [b] $R_1 = \Sigma(\mid \mid F_0\mid - \mid F_c\mid \mid) / \Sigma \mid F_0\mid$, $F_0 > 4\sigma(F_0)$. [c] $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2/ \Sigma[w(F_0^2)^2]\}^{1/2}$.

Table S4. Crystallographic Data for

Compound	**10’**	**11’**	**[Cp*ScMeCl(thf)]$_2$**	**AlMe$_3$(pyr)**
Formula	$C_{19}H_{41}Al_{1.08}Ga_{0.92}ScSi$	$C_{45}H_{84}Al_3Sc_3Si_3$	$C_{30}H_{52}Cl_2O_2Sc_2$	$C_8H_{14}AlN$
CCDC	2410881	2410889	2410887	2410877
M [g mol^{-1}]	435.85	925.21	605.53	151.18
color/shape	colorless/plate	colorless/plate	colorless/block	colorless/plate
Crystal dimensions [mm]	0.171 x 0.116 x 0.064	0.176 x 0.118 x 0.051	0.202 x 0.188 x 0.130	0.187 x 0.149 x 0.074
cryst. system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/c$	$P2_1/m$	$P2_1/n$	$P2_1/c$
a [Å]	15.2773(12)	10.1305(17)	11.029(5)	8.483(4)
b [Å]	15.3617(12)	21.570(4)	12.453(6)	17.537(8)
c [Å]	10.2549(8)	12.702(2)	11.537(6)	7.321(3)
α [°]	90	90	90	90
β [°]	93.6970(10)	112.085(2)	90.168(9)	115.351(7)
γ [°]	90	90	90	90
V [Å^3]	2401.7(3)	2571.9(7)	1584.6(13)	984.2(8)
Z	4	2	2	4
T [K]	100(2)	100(2)	100(2)	100(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm^{-3}]	1.205	1.195	1.269	1.020
μ [mm^{-1}]	1.405	0.534	0.621	0.142
F(000)	930	996	648	328
Θ range [°]	1.336/28.798	1.888/28.744	2.406/28.728	2.323/30.855
unique reflns	6255	6827	4074	3095
observed reflns	38855	41345	24865	22619
R1[b]/wR2(I>2σ)[c]	0.0286/0.0671	0.0496/0.0977	0.0430/0.1087	0.0578/0.1455
R1[b]/wR2(all data)[c]	0.0387/0.0719	0.0856/0.1129	0.0558/0.1172	0.0905/0.1646
GOF[a]	1.035	1.018	1.034	1.047

[a]GOF = $[\Sigma w(F_0^2 - F_c^2)^2/(n_0 - n_p)]^{1/2}$. [b]$R_1 = \Sigma(| |F_0| - |F_c| |) / \Sigma |F_0|$, $F_0 > 4\sigma(F_0)$. [c]$wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2 / \Sigma[w(F_0^2)^2]\}^{1/2}$.

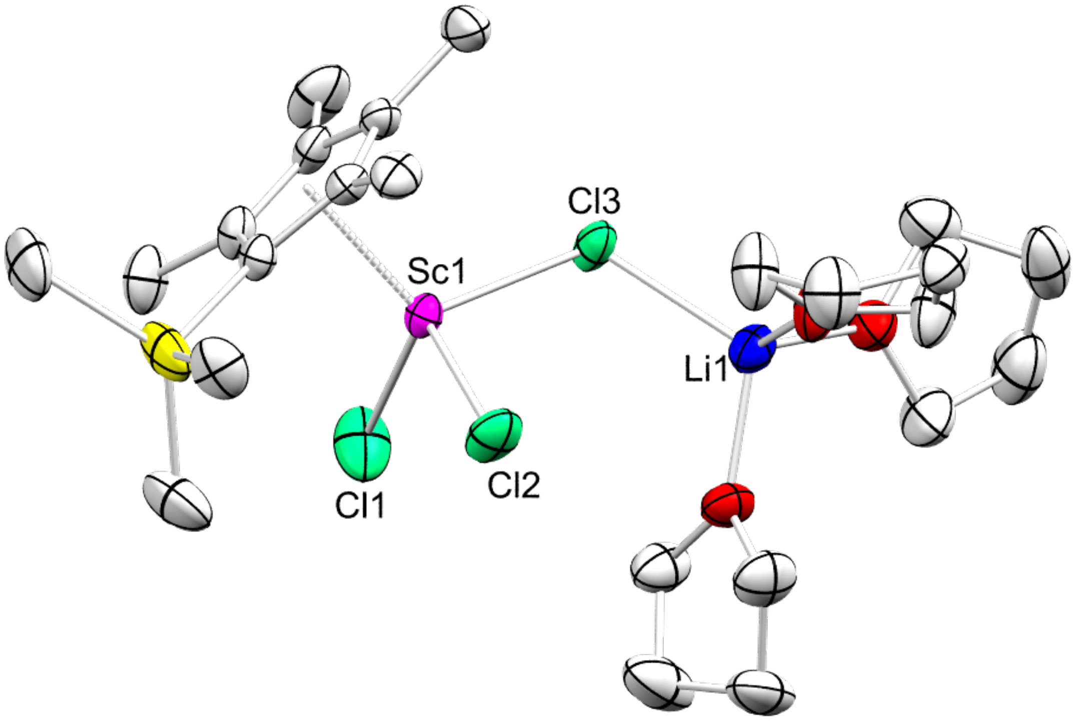

Figure S65. Crystal structure of **1’**. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms and a second molecule in the unit cell omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sc1−Cl1 2.3781(8), Sc1−Cl2 2.3686(8), Sc1−Cl3 2.4323(7), Sc1−Cnt1 2.132, Li1−Cl3 2.355(4); Cl1−Sc1−Cl2 102.09(4), Cl1−Sc1−Cl3 101.14(3), Cl2−Sc1−Cl3 101.93(3), Sc1−Cl3−Li1 112.28(12).

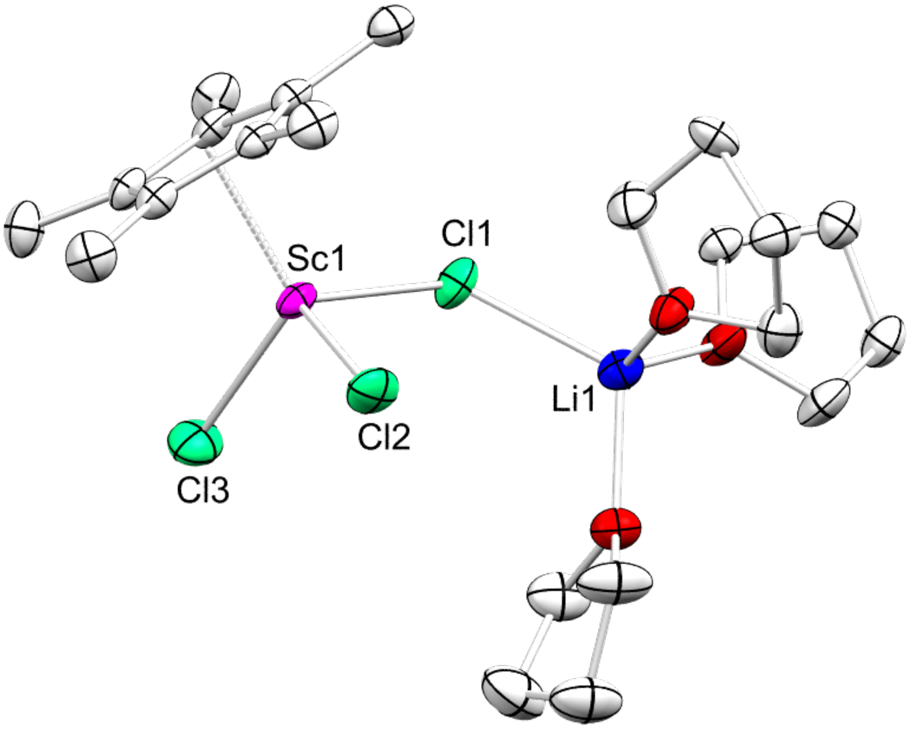

Figure S66. Crystal structure of **1***. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sc1−Cl1 2.4306(10), Sc1−Cl2 2.3705(10), Sc1−Cl3 2.3593(11), Sc1−Cnt1 2.130, Li1−Cl1 2.394(5); Cl1−Sc1−Cl2 102.16(4), Cl1−Sc1−Cl3 102.17(4), Cl2−Sc1−Cl3 102.58(4), Sc1−Cl1−Li1 114.88(13).

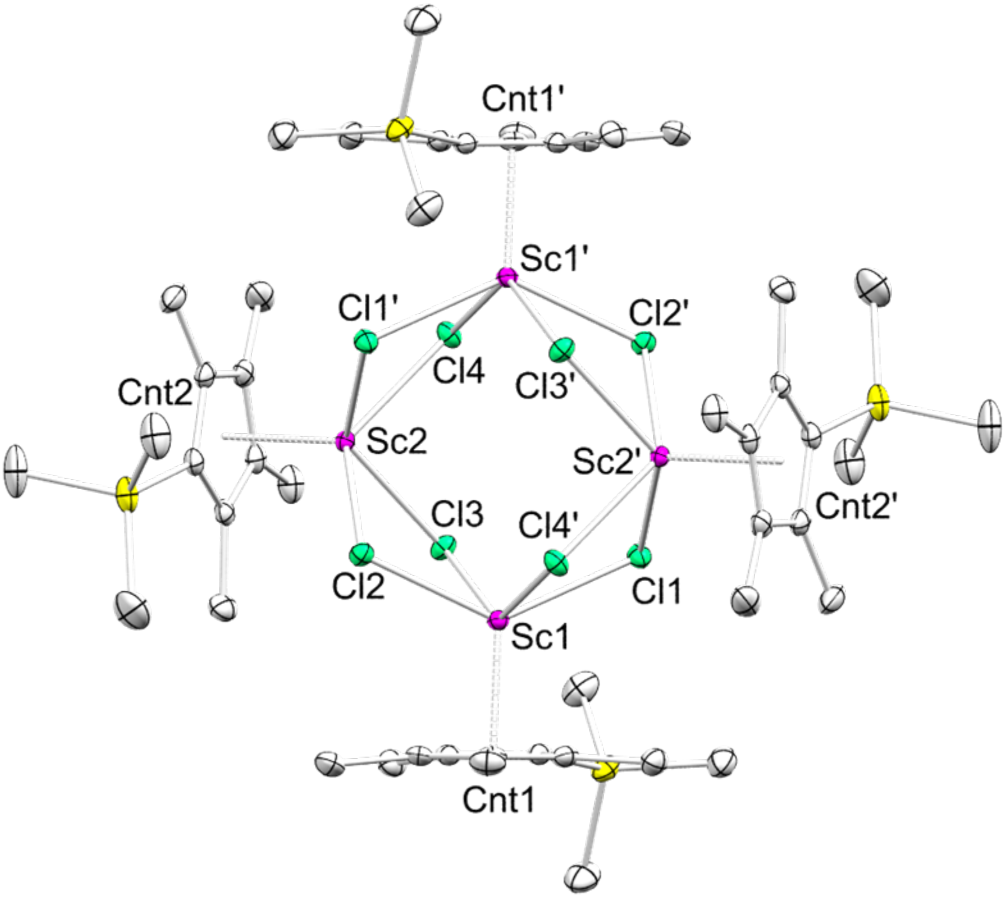

Figure S67. Crystal structure of **2'**. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms and one molecule of C_6D_6 omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sc1−Cl1 2.5504(4), Sc1−Cl2 2.5357(4), Sc1−Cl3 2.5317(4), Sc1−Cl4' 2.5550(4), Sc2'−Cl1 2.5498(4), Sc2−Cl2 2.5338(4), Sc2−Cl3 2.5578(4), Sc2−Cl4 2.5304(4), Sc1−Cnt1 2.142, Sc2−Cnt2 2.134; Cl1−Sc1−Cl2 132.211(15), Cl1−Sc1−Cl3 83.597(14), Cl2−Sc2−Cl3 77.611(13), Sc1−Cl2−Sc2 98.486(14), Sc1−Cl1−Sc2' 98.139(14).

'= -x+1/2, -y+3/2, -z+1

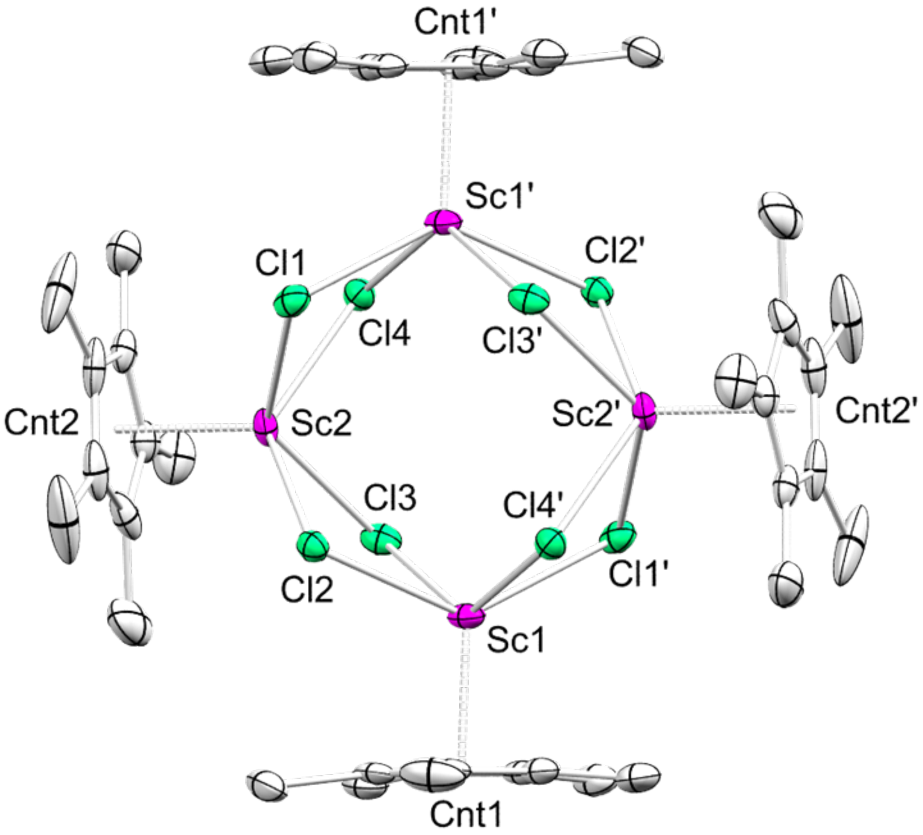

Figure S68. Crystal structure of **2***. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms and disorders in Cp* rings omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sc1−Cl1 2.5598(1), Sc1’−Cl4 2.5453(5), Sc1−Cl3 2.5457(5), Sc1−Cl2 2.5522(1), Sc2−Cl1’ 2.5485(1), Sc2−Cl2 2.5475(1), Sc2−Cl3 2.5 253 (5), Sc2−Cl4 2.5444(5), Sc1−Cnt1 2.140, Sc2−Cnt2 2.118; Cl1−Sc1−Cl2 132.83(1), Cl3−Sc1−Cl4’ 132.435(16), Cl4’−Sc1−Cl2 83.94(1), Cl1−Sc2−Cl4’ 77.68(1), Cl3−Sc2−Cl4 83.425(15), Sc1−Cl1−Sc2’ 96.592(15), Sc1−Cl2−Sc2 98.641(15).

‘-x+3/2, -y+1/2, -z+1

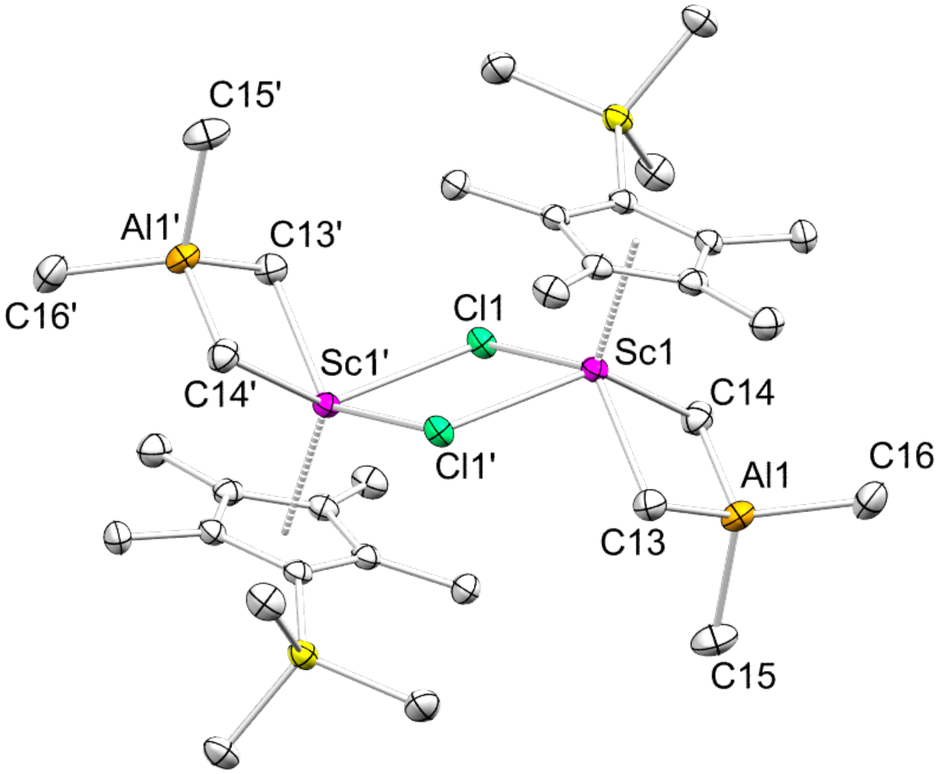

Figure S69. Crystal structure of **3'**. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms and one molecule of toluene omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sc1'−Cl 2.5658(5), Sc1−Cl1 2.5597(5), Sc1−C13 2.456(2), Sc1−C14 2.415(2), Sc1···Al1 2.9611(7), Al1−C15 1.968(2), Al1−C16 1.977(2), Sc1−Cnt1 2.147; Cl1'−Sc1−Cl1 76.802(17), Cl1'−Sc1−C13 135.79(5), Cl1−Sc1−C13 79.87(5), Sc1−Cl1−Sc1' 103.198(17), Sc1−C13−Al1 80.96(8), Sc1−C14−Al1 82.26(7), C13−Sc1−C14 87.59(7).

'-x+1, -y+1, -z+1

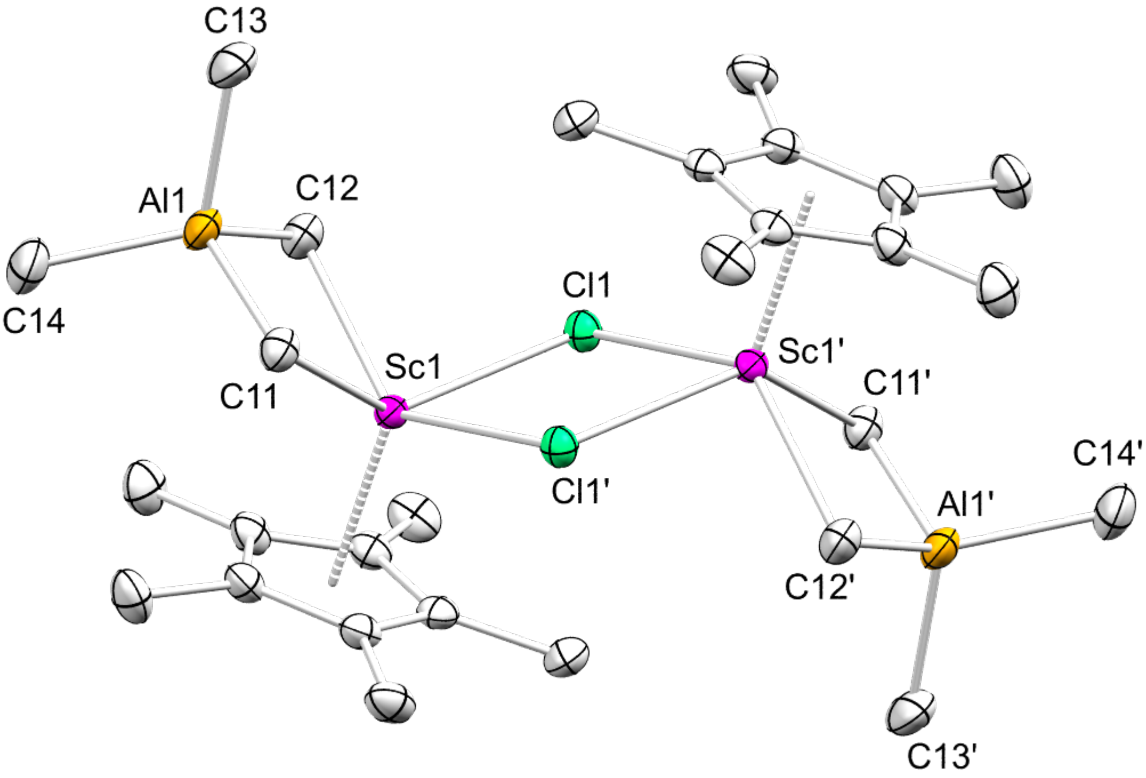

Figure S70. Crystal structure of **3***. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms and one molecule of toluene omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sc1−Cl1’ 2.5845(5), Sc1−Cl1 2.5628(5), Sc1−C11 2.4163(19), Sc1−C12 2.441(2), Sc1···Al1 2.9575(6), Al1−C13 1.972(2), Al1−C14 1.978(2), Sc1−Cnt1 2.145; Cl1’−Sc1−Cl1 76.674(17), Cl1−Sc1−C11 133.37(5), Cl1’−Sc1···Al1 117.273(19), Sc1−Cl1−Sc1’ 103.326(17), Sc1−C11−Al1 82.22(7), Sc1−C12−Al1 81.45(7), C11−Sc1−C12 86.96(7).

‘-x+1, -y+1, -z+1

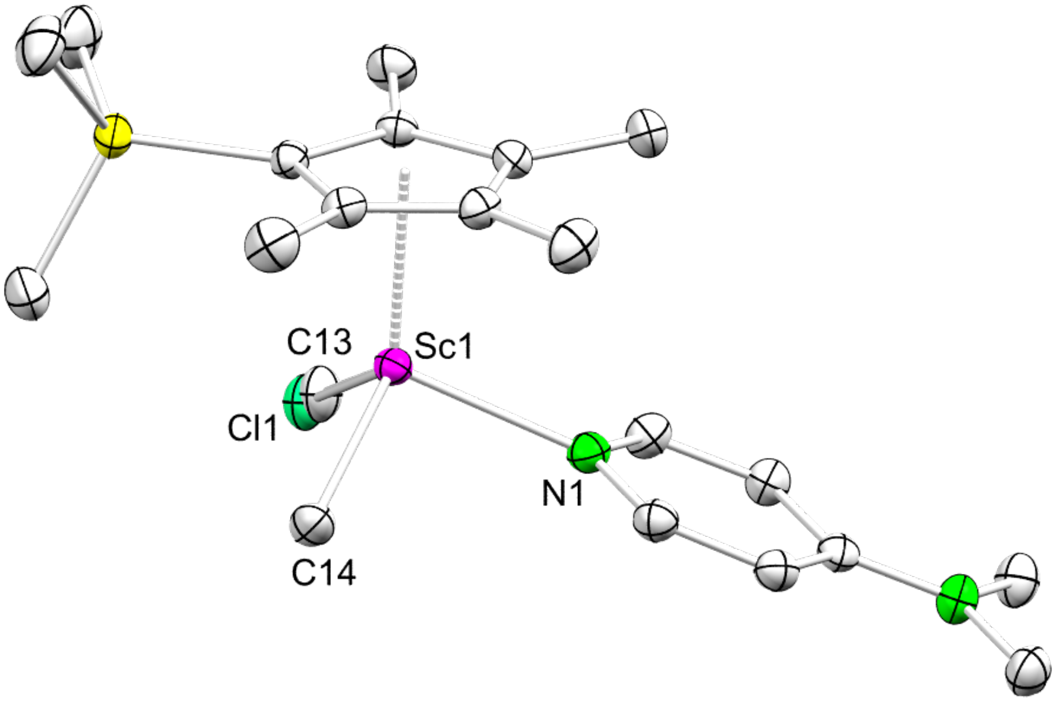

Figure S71. Crystal structure of **5'**. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms omitted for clarity. The structure shows a disorder in one of the methyl groups with 15% chloride and 85% carbon. Selected interatomic distances [Å] and angles [deg]: Sc1−Cl1 2.405(16), Sc1−C13 2.258(11), Sc1−C14 2.2588(15), Sc1−N1 2.2416(13), Sc1−Cnt1 2.168; N1−Sc1−C13 96.4(3), N1−Sc1−C14 97.83(5), C13−Sc1−C14 108.7(3), Cl1−Sc1−N1 98.1(4), Cl1−Sc1−C14 105.9(4).

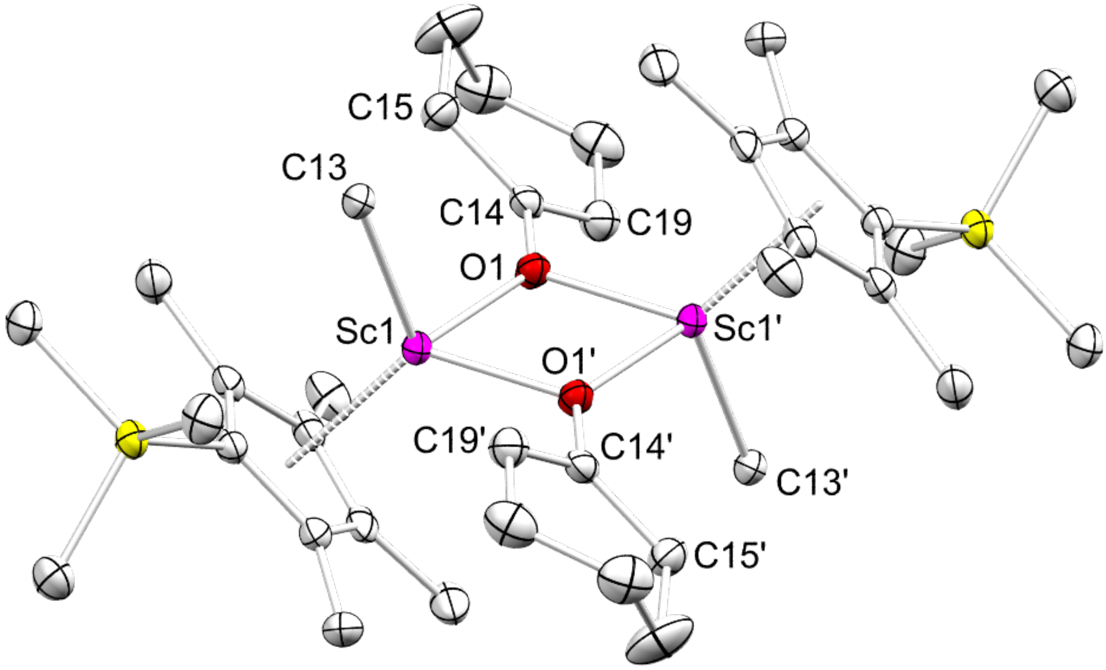

Figure S72. Crystal structure of **6’**. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sc1−O1’ 2.0952(17), Sc1−O1 2.0780(17), Sc1−C13 2.236(2), O1−C14 1.384(4), C14−C15 1.462(3), C14−C19 1.359(4), Sc1−Cnt1 2.164; O1’−Sc1−O1 76.14(7), O1−Sc1−C13 102.16(8), O1’−Sc1−C13 106.65(9), Sc1−O1−Sc1’ 103.86(7), O1−C14−C19 119.1(2), C15−C14−C19 125.1(2), C14−O1−Sc1 136.05(15), C14−O1−Sc1’ 120.09(15).

‘-x+1, -y+1, -z+1

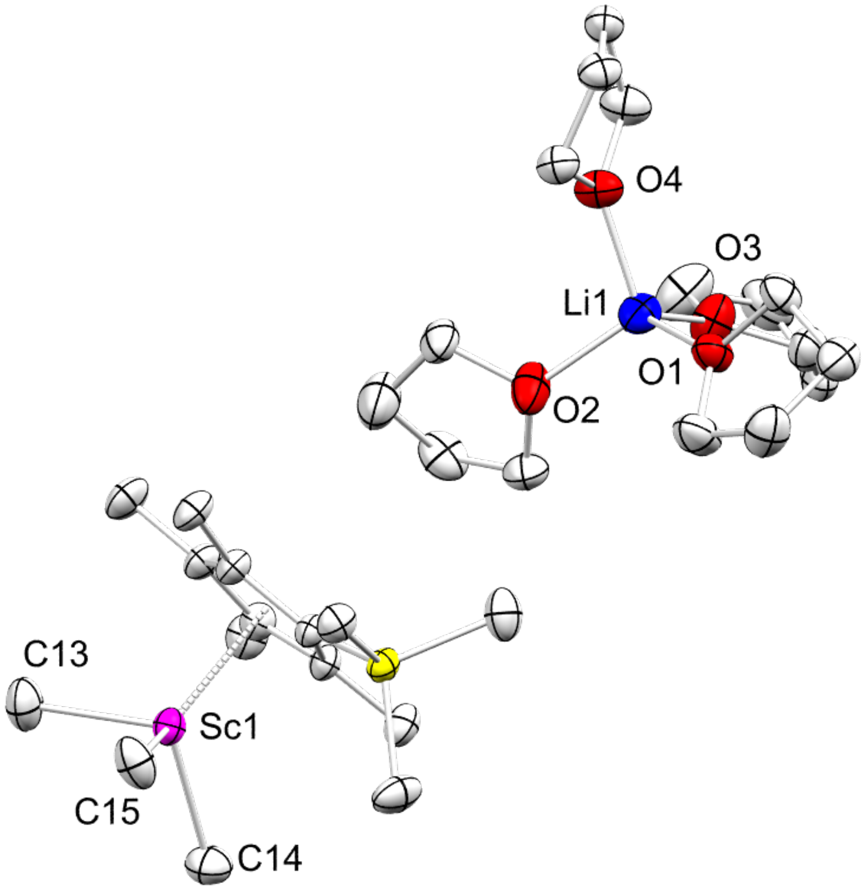

Figure S73. Crystal structure of **7’**. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms omitted for clarity. Disorders in two THF molecules were omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sc1−C13 2.254(2), Sc1−C14 2.258(2), Sc1−C15 2.262(2), Li1−O1 1.928(4), Li1−O2 1.907(4), Sc1−Cnt1 2.238; C13−Sc1−C14 102.32(9), C13−Sc1−C15 100.10(9), C14−Sc1−C15 103.32(9).

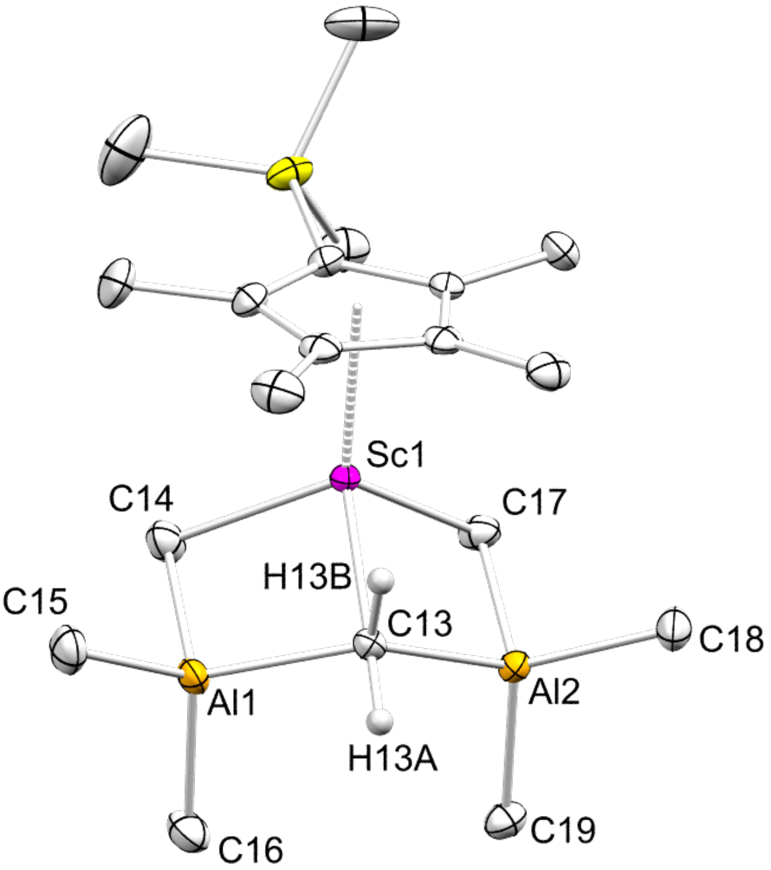

Figure S74. Crystal structure of **8'**. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms except methylidene hydrogen atoms omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sc1−C13 2.1735(18), Sc1−C14 2.340(2), Sc1−C17 2.3327(19), Sc1···Al1 2.8399(6), Sc1···Al2 2.8456(6), Al1−C13 2.0879(18), Al1−C14 2.128(2), Al1−C15 1.971(2), Al1−C16 1.969(2), Al2−C13 2.0898(18), Al2−C17 2.124(2), Al2−C18 1.9743(19), Al2−C19 1.9683(19), Sc1−Cnt1 2.137, Sc1−H13B 2.14(3); Sc1−C13−H13A 177.3(15), Sc1−C13−H13B 75.1(16), Sc1−C13−Al1 83.56(6), Sc1−C13−Al2 83.72(6), Al1−C13−Al2 122.75(9), Sc1−C14−Al1 78.79(7), Sc1−C17−Al2 79.20(6), C14−Sc1−C17 100.00(8), C13−Sc1−C14 93.03(7), C13−Sc1−C17 92.76(7).

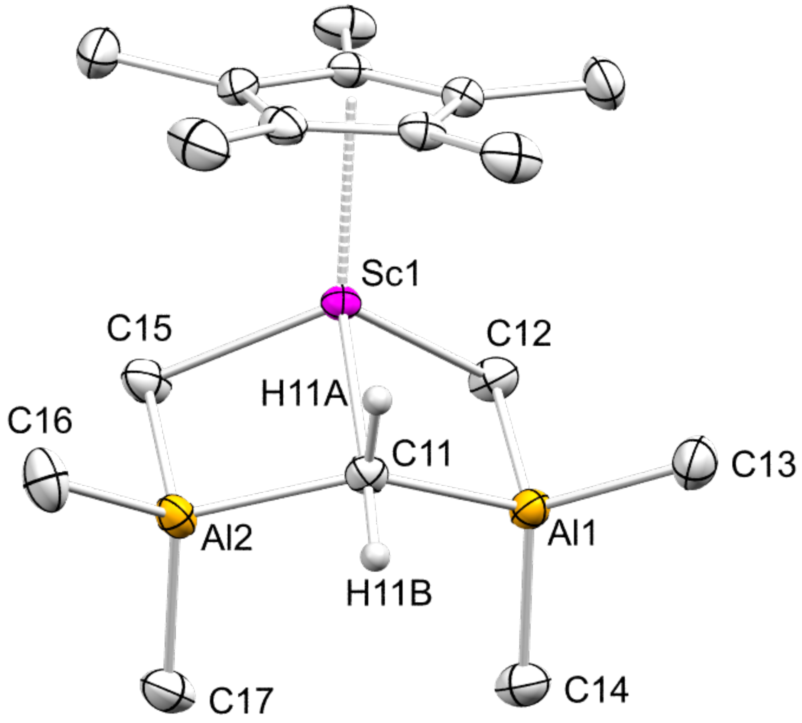

Figure S75. Crystal structure of **8***. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms except methylidene hydrogen atoms omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sc1−C11 2.1624(17), Sc1−C12 2.3600(19), Sc1−C15 2.3211(19), Sc1···Al1 2.8453(9), Sc1···Al2 2.8314(9), Al1−C11 2.0914(18), Al1−C12 2.1271(19), Al1−C13 1.953(2), Al1−C14 1.968(2), Al2−C11 2.0647(17), Al2−C15 2.129(2), Al2−C16 1.986(2), Al2−C17 1.970(2), Sc1−Cnt1 2.136, Sc1−H11A 2.17(2); Sc1−C11−H11B 177.8(13), Sc1−C11−H11A 77.2(13), Sc1−C11−Al1 83.95(6), Sc1−C11−Al2 84.07(6), Al1−C11−Al2 123.68(8), Sc1−C12−Al1 78.52(6), Sc1−C15−Al2 78.90(6), C12−Sc1−C15 100.66(7), C11−Sc1−C12 92.64(7), C11−Sc1−C15 92.95(7).

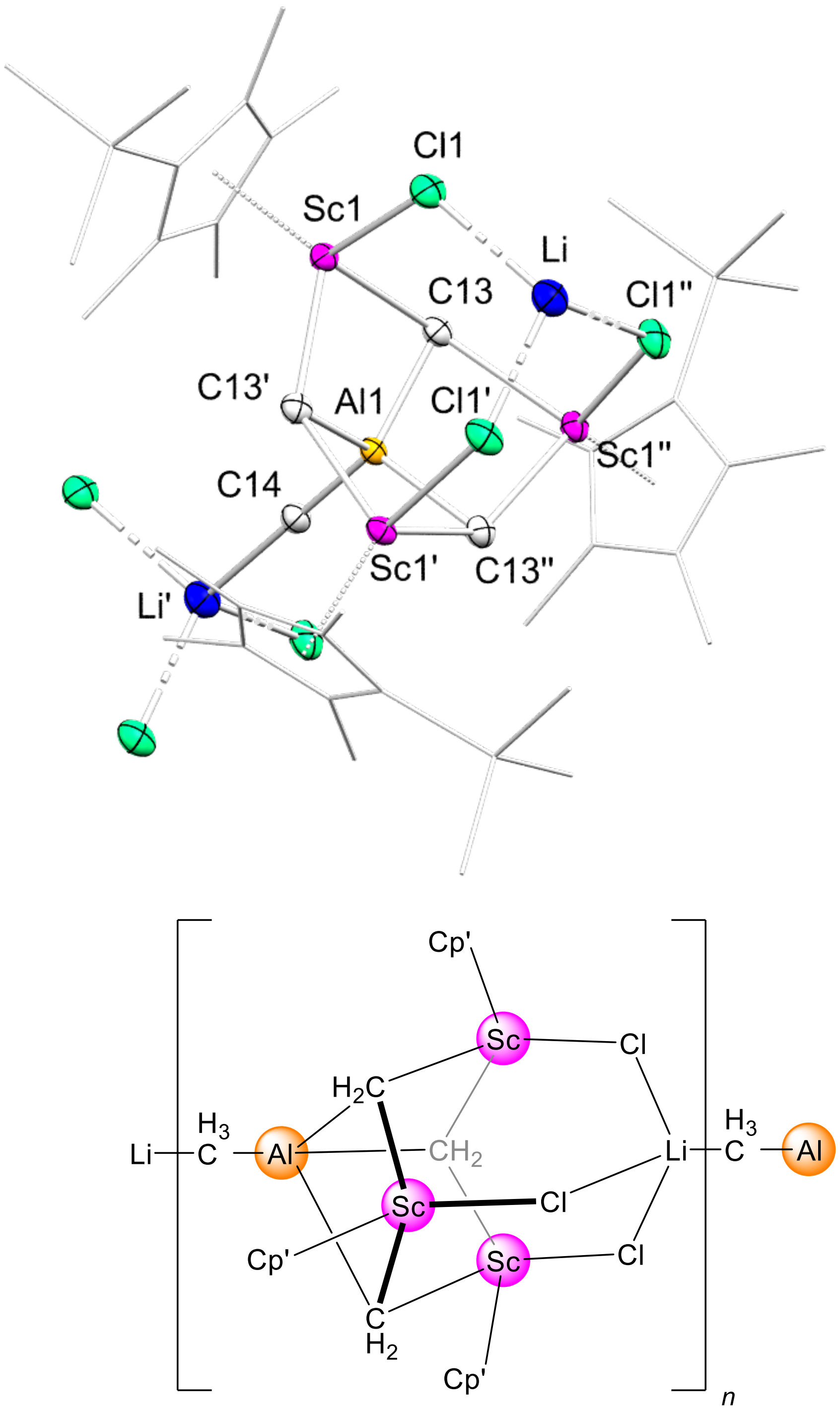

Figure S76. Crystal structure of **9’**. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms omitted for clarity. Cp’ rings are shown as wireframe for clarity. Selected interatomic distances [Å] and angles [deg]: Sc1−Cl1 2.4388(11), Li1−Cl1 2.365(4), Sc1−C13 2.316(4), Sc1−C13’ 2.334(4), Sc1···Al1 2.8592(11), Al1−C13 2.007(4), Al1−C14 1.973(7), Li1−C14 2.383(14), Sc1−Cnt1 2.152; Sc1−C13−Al1 82.49(15), Sc1−C13−Sc1” 139.2(2), C13−Sc1−C13’ 86.7(2). For a better description of the molecular structure and the methyl and methylidene moieties, **9’** is shown by a ChemDraw representation.

’ -y+1, x-y, z
” -x+y+1, -x+1, z

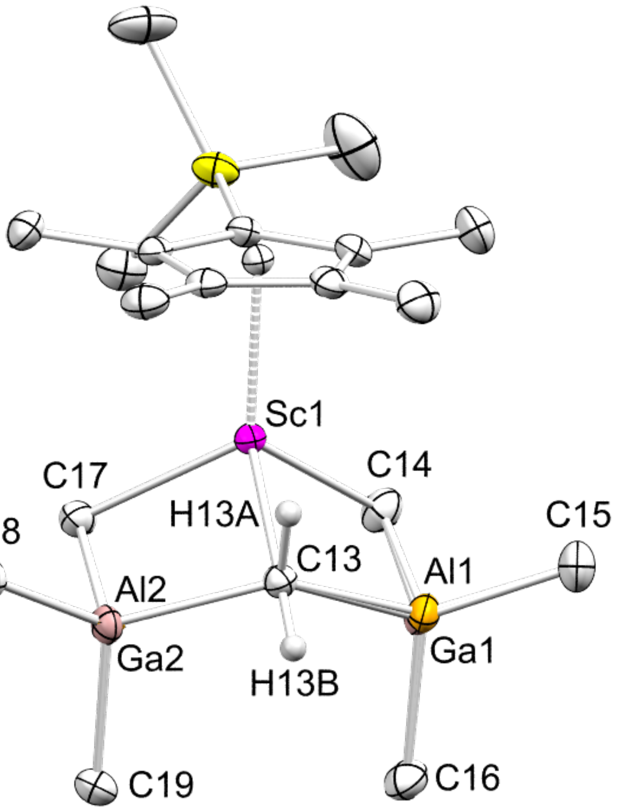

Figure S77. Crystal structure of **10’**. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms except methylidene hydrogen atoms omitted for clarity. There is a disorder between aluminum and gallium of approximately 50% on each position. Selected interatomic distances [Å] and angles [deg]: Sc1−C13 2.1724(15), Sc1−C14 2.3411(17), Sc1−C17 2.3331(16), Sc1···Al1 2.823(13), Sc1···Al2 2.818(6), Sc1···Ga1 2.830(5), Sc1···Ga2 2.842(3), Al1−C13 2.111(12), Al1−C14 2.135(11), Al1−C15 1.932(15), Al1−C16 2.014(15), Ga2−C13 2.102(4), Ga2−C17 2.149(4), Ga2−C18 1.966(4), Ga2−C19 1.971(3), Sc1−Cnt1 2.145, Sc1−H13A 2.195(18); Sc1−C13−H13B 176.1(11), Sc1−C13−H13A 78.5(11), Sc1−C13−Al1 82.4(3), Sc1−C13−Ga2 83.32(10), Al1−C13−Ga2 123.8(4), Sc1−C14−Al1 78.0(3), Sc1−C17−Ga2 78.57(10), C14−Sc1−C17 99.44(6), C13−Sc1−C14 94.07(6), C13−Sc1−C17 93.74(6).

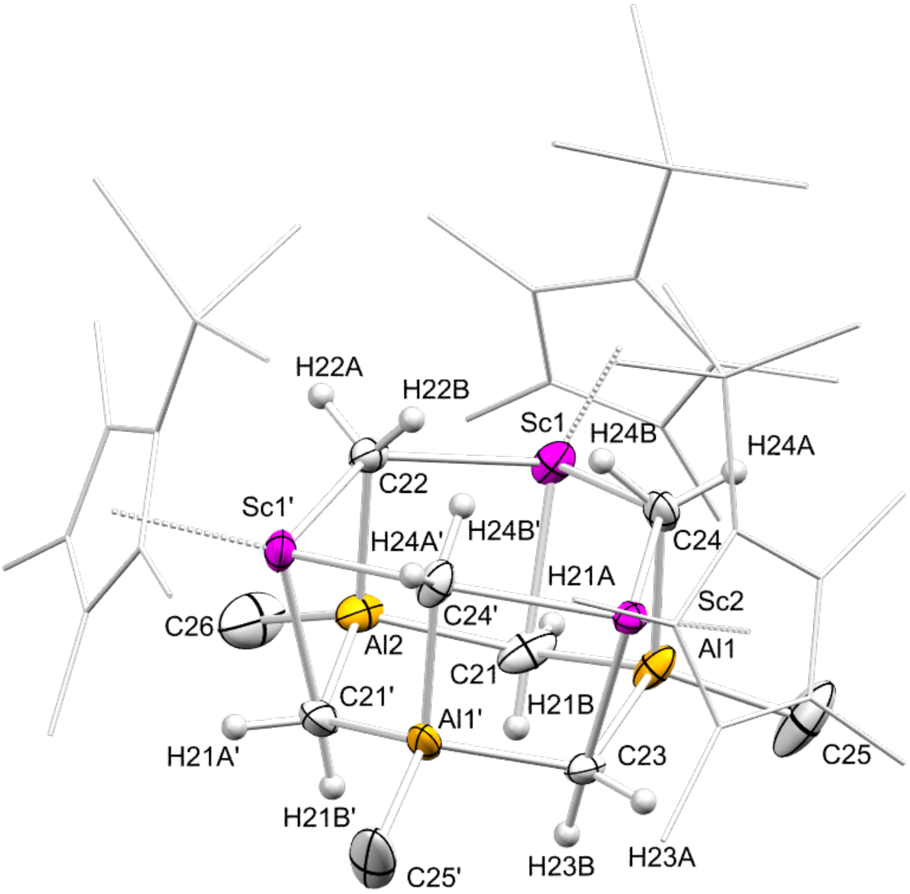

Figure S78. Crystal structure of **11'**. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms except methylidene hydrogen atoms omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sc1−C21 2.246(3), Sc1−C22 2.3338(15), Sc1−C24 2.322(3), Sc2−C23 2.245(3), Sc2−C24 2.316(2), Sc1···Al1 2.8470(9), Sc1···Al2 2.8595(9), Sc2···Al1 2.8444(9), Al1−C21 2.054(3), Al1−C23 2.0486(17), Al1−C24 2.015(3), Al1−C25 1.963(3), Al2−C21 2.052(3), Al2−C22 2.020(3), Al2−C26 1.972(4), Sc1−Cnt1 2.153, Sc1−H21A 2.29(3), Sc1−H24B 2.41(3), Sc2−H23A 2.24(4); Sc1−C21−H21A 79.6(17), Sc2−C23−H23A 76(2), Sc1−C21−Al1 82.80(10), Sc1−C24−Al1 81.74(9), Sc1−C21−Al2 83.29(9), Sc1−C22−Al2 81.78(8), C21−Sc1−C24 88.74(9), C21−Al1−C23 105.15(13).

‘=x, -y+3/2, z

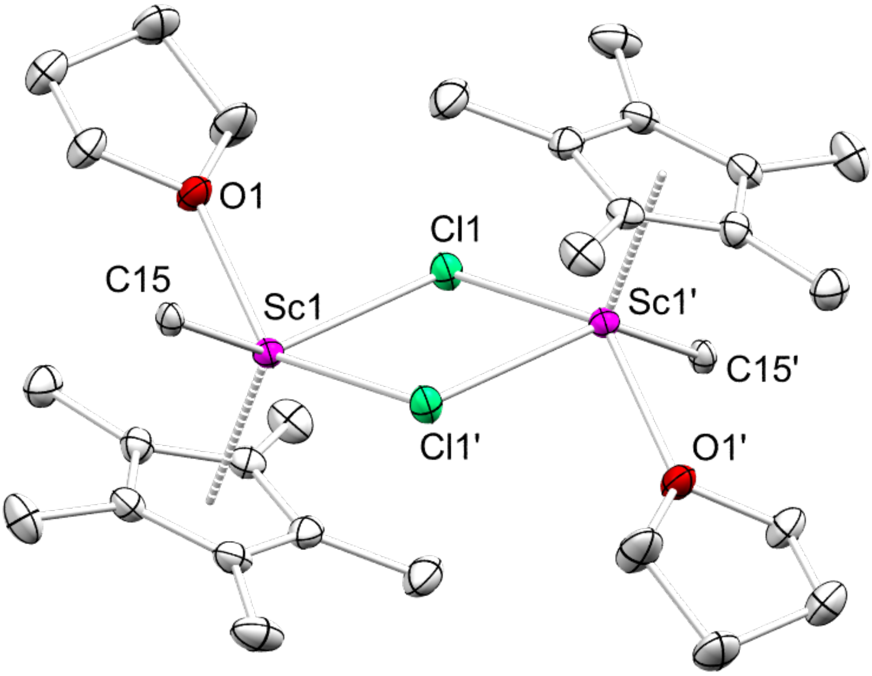

Figure S79. Crystal structure of [Cp*ScMeCl(thf)]$_2$. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sc1−Cl1' 2.5829(10), Sc1−Cl1 2.5815(13), Sc1−C15 2.285(2), Sc1−O1 2.2540(17), Sc1−Cnt1 2.175; Cl1'−Sc1−Cl1 76.01(3), Cl1−Sc1−C15 135.26(5), Cl1'−Sc1−C15 83.05(6), Sc1−Cl1−Sc1' 103.99(3), O1−Sc1−Cl1 81.46(4), O1−Sc1−C15 87.27(6).

'=-x+1, -y+1, -z+1

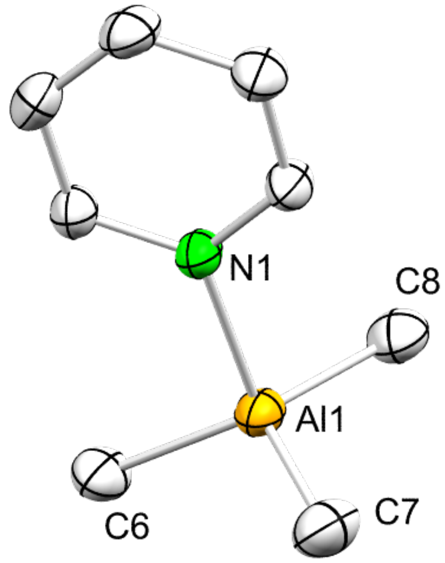

Figure S80. Crystal structure of $AlMe_3$(pyr) from the reaction of **4'** with pyridine. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Al1−C6 1.970(3), Al1−C7 1.960(3), Al1−C8 1.979(4), Al1−N1 2.017(2); C6−Al1−C7 115.73(14), C6−Al1−C8 114.85(14), N1−Al1−C6 104.52(10), N1−Al1−C7 101.98(12).

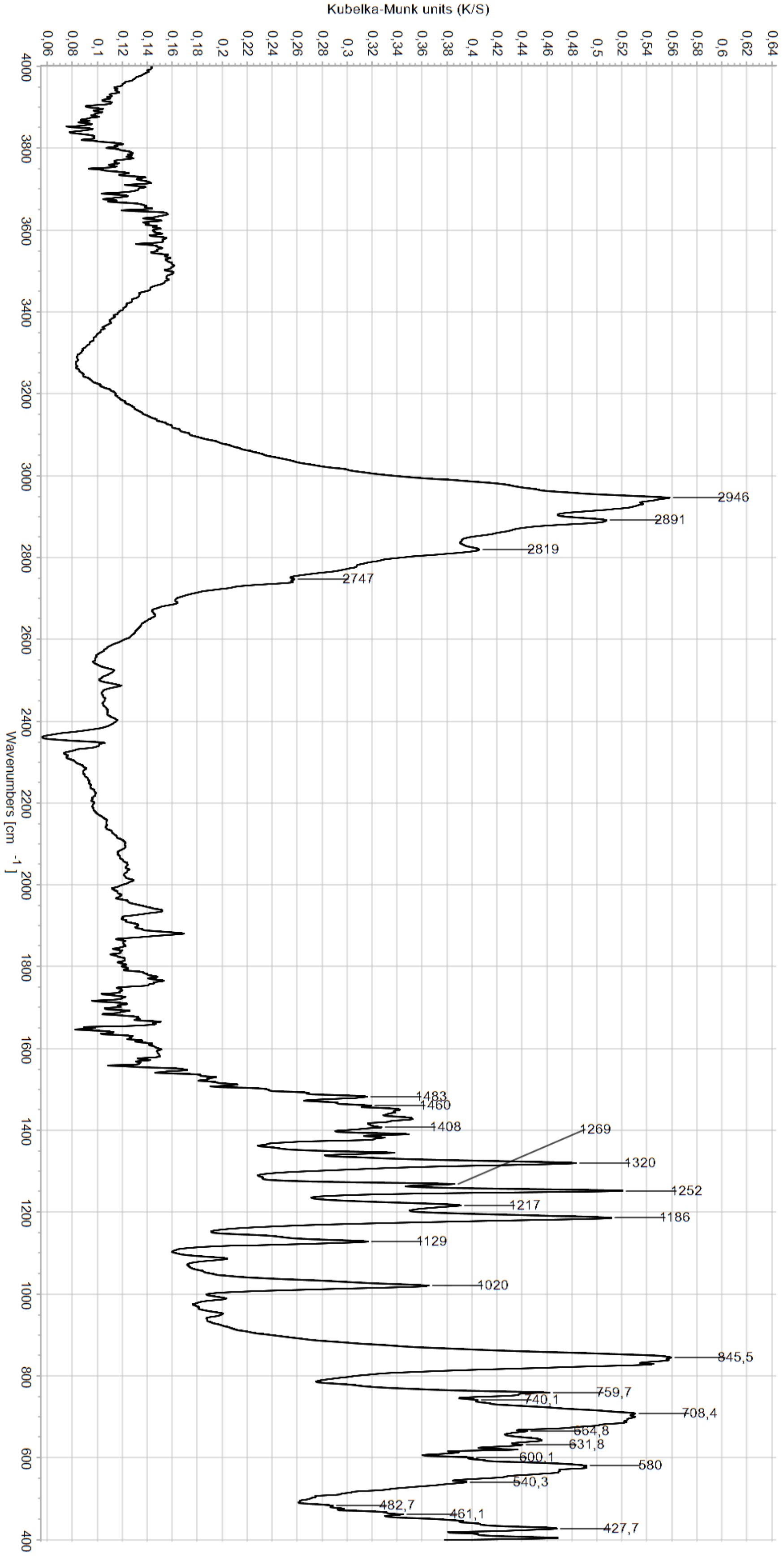

Figure S81. DRIFTS spectrum of Cp’Sc(CH$_2$)(AlMe$_3$)$_2$ (**8’**) as a powder on KBr at 25 °C.

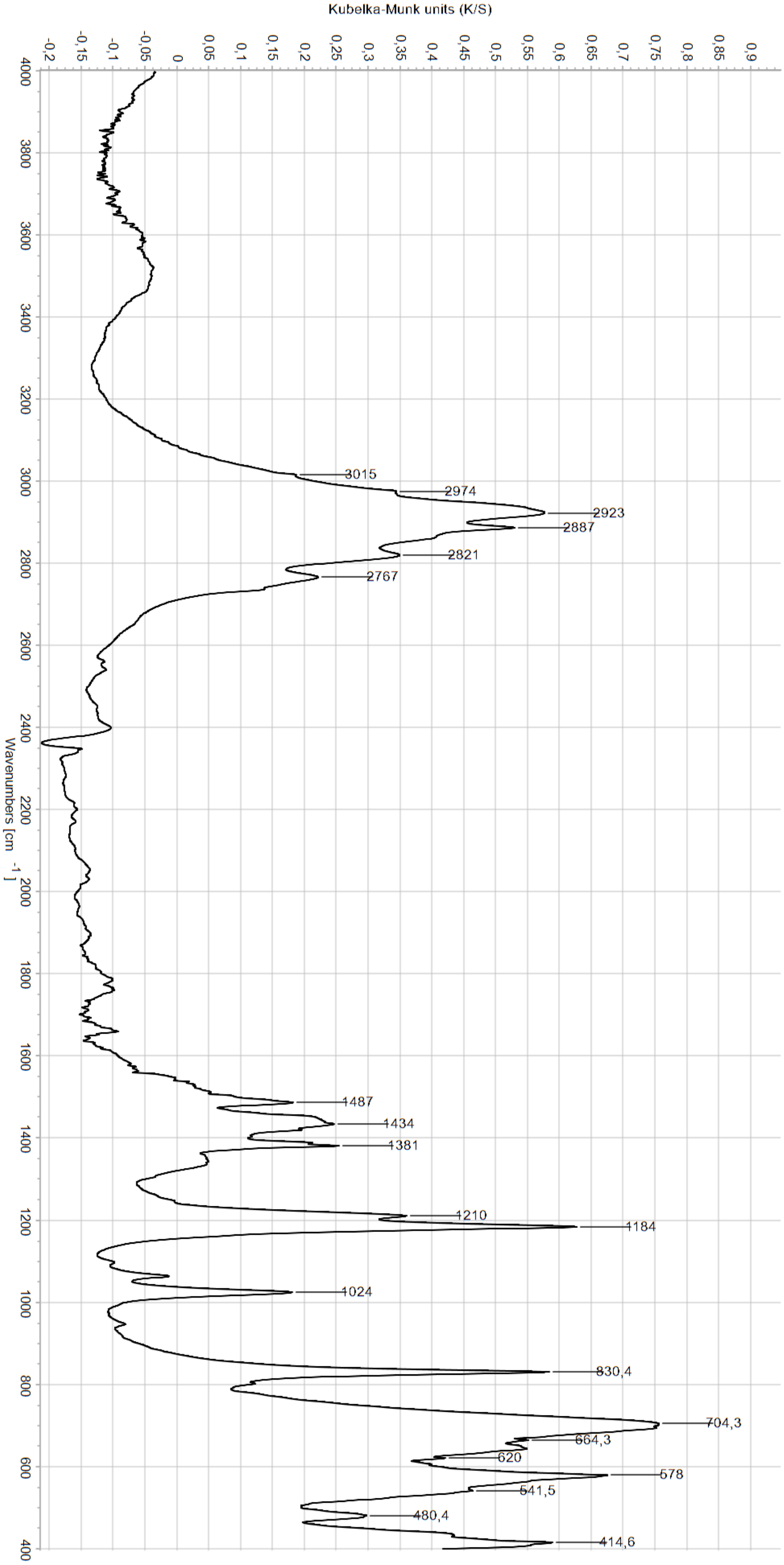

Figure S82. DRIFTS spectrum of Cp*Sc(CH_2)($AlMe_3$)$_2$ (**8***) as a powder on KBr at 25 °C.

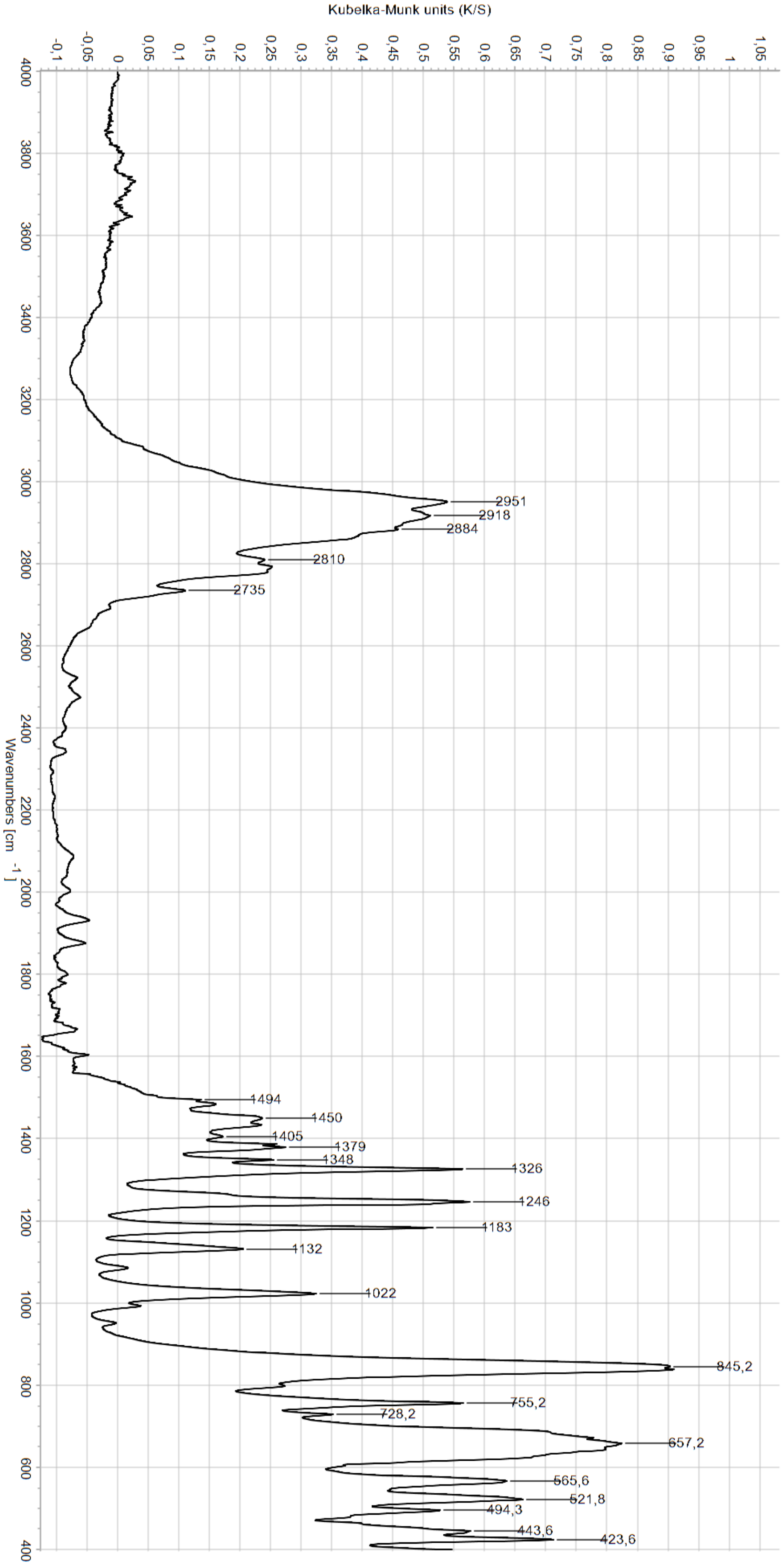

Figure S83. DRIFTS spectrum of [Cp’Sc$(CH_2)_2$AlMe]$_3$ (**11’**) as a powder on KBr at 25 °C.

Table S5. Oligomerization and polymerization of δ-valerolactone

entry[a]	catalyst	yield (%)	M_n (10^3 g·mol^{-1})[b]	PDI[b]
1	**8***	81	0.43	2.8
2	**8'**	88	0.21	4.7
3	**11'**	18	0.17	12.7
4	$[\mathrm{Cp'ScMe_2}]_2$	90	15.22	3.3
5	$\mathrm{Cp^*_2YMe(thf)}$[c]	32	8.90	2.7
6	Y(O*i*Pr)$_3$[d]	19	0.44	2.9

[a] δ-Valerolactone was purchased from Sigma-Aldrich and distilled prior to use. Every oligomerization or polymerization was done with 0.1 mol% catalyst with 500 mg δ-valerolactone in 4 mL toluene for 1 h at ambient temperature. The oligomerization or polymerization was stopped using 2 mL of a 5% HCl. Then, 10 mL *n*-hexane were added and stirred for 30 min. After this time, the precipitated oligomer or polymer was separated from the supernatant, washed three times with 2 mL *n*-hexane and dried for 7 days under reduced pressure at 25 °C.

[b] Determined by SEC of the crude polymer on an Agilent 1260 Infinity III device with a 1260 Infinity III RID in THF solutions (40 °C) with a flow rate of 1 mL/min against polystyrene standards.

[c] $\mathrm{Cp^*_2YMe(thf)}$ was synthesized according to literature procedures: M. Bonath, V. M. Birkelbach, C. Stuhl, C. Maichle-Mössmer, R. Anwander, Rare-earth-metallocene alkylaluminates trigger distinct tetrahydrofuran activation, *Chem. Commun.*, 2021, **57**, 7918–7921. DOI: 10.1039/D1CC03024H.

[d] Yttrium(III) isopropoxide was purchased from Fisher Scientific and used as received.