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Supporting Information

for

Selective Mono- and Dimetallation of a Group 3 Sandwich Complex

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1 General procedures

All reactions were performed under a protective atmosphere of dry pure argon gas using standard Schlenk techniques. Products **3** and **4** were isolated inside an argon-filled dry box. *n*-hexane, methylcyclohexane and tetrahydrofuran (THF) were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. C_6D_6 was degassed and stored over 4 Å molecular sieves prior to use. [D_8]THF was degassed and stored over a potassium mirror prior to use. 2,2,6,6-Tetramethylpiperidine TMP(H) was purchased from Merck KGaA and used as received. *n*BuLi (1.6M in n-hexane solution, titrated prior to use), *i*Bu_2AlCl, I_2, 18-crown-6 and TMEDA were purchased from Aldrich and used as received. TMSCl was purchased from Aldrich and, after distillation, stored over 4 Å molecular sieves. LiTMP[1] and *i*Bu_2Al(TMP)[2] were prepared according to literature procedures. NMR spectra were recorded on a Bruker AVANCE 400 NMR spectrometer operating at 400.1, 155.5 and 100.6 MHz for ^{1}H, ^{7}Li, and ^{13}C, respectively. ^{1}H and ^{13}C{^{1}H} chemical shifts are expressed in parts per million (∂, ppm) and were referenced to the appropriate residual solvent signal, while ^{7}Li NMR spectra were referenced against an external sample of LiCl (0.00 ppm in D_2O). The NMR spectroscopic assignments were performed, in some cases, with the help of ^{13}C{^{1}H}-DEPT135, ^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HMQC and ^{1}H,^{13}C-HMBC experiments. All coupling constants (*J*) are absolute values (Hz) and descriptions of signals are: s (singlet), d (doublet), t (triplet), q (quartet), sept (septuplet) and m (multiplet). Satisfactory elemental analyses of the air-sensitive products **3** and **4** were obtained using a Perkin–Elmer 2400 elemental analyser.

2 Synthetic protocols

2.1 Control reaction of 1 with LiTMP to give Li{(η^5-C_5H_4)Sc(η^8-C_8H_8)}] (2)

[(η^5-C_5H_5)Sc(η^8-C_8H_8)] **1** (54 mg, 0.25 mmol) was reacted with LiTMP (37 mg, 0.25 mmol) in *n*-hexane (10 mL) at ambient temperature for 24 h. After that period of time, an aliquot from the *in situ* reaction mixture was analysed by NMR spectroscopy in [D_8]THF. Approximately 9% of **1** was lithiated to give [Li{(η^5-C_5H_4)Sc(η^8-C_8H_8)}] **2** as the unique metallated product. Lithiation at the Cot (C_8H_8) ring was not detected. ^{1}H NMR (400.1 MHz, 300 K, C_6D_6): δ **1** (91%): 5.13 (s, 5H, C_5H_5), 6.34 (s, 8H, C_8H_8); **2** (9%): 5.38 (m, 2H, C_5H_4), 5.58 (m, 2H, C_5H_4), 6.44 (s, 8H, C_8H_8).

2.2 Synthesis of [THF·Li(μ-TMP){μ-{(η^5-C_5H_4)Sc(η^8-C_8H_8)}}Al(*i*Bu)$_2$] (3)

LiTMP (147 mg, 1 mol) was added to a Schlenk tube containing a solution of *i*Bu$_2$Al(TMP) (282 mg, 1 mmol) in n-hexane (10 mL) at ambient temperature and the reaction mixture was stirred for 10 min. Then, THF (0.08 mL, 1 mmol) was added via syringe to give an off-white suspension which was stirred for 10 min. Next, [(C_5H_5)Sc(C_8H_8)] **1** (171 mg, 0.8 mmol) was added and the reaction mixture was heated to reflux for 12 hours to give a pale yellow suspension. The solid was collected by filtration, washed with n-hexane (3 x 3 mL) and dried under vacuum for 15 min to give **3** as a pale yellow solid (330 mg, 0.57 mmol, 72%).

Single crystals of **3** suitable for an X-ray diffraction we obtained by adding THF (2 mL) to the resulting overnight hot suspension and allowing the resulting solution to cool to room temperature when the Schlenk tube was placed in a Dewar containing hot water for 24 h. The crystalline material was filtered, washed with n-hexane (3 x 3 mL) and dried under vacuum for 15 min (302 mg, 0.53 mmol, 66%).

The NMR spectroscopic study of the isolated solid and the crystalline material are identical. In addition, an NMR spectroscopic analysis of an in situ aliquot of the corresponding reaction mixture under reflux conditions overnight showed near quantitative conversion of **1** into **3**.

Characterization data for [THF·Li(μ-TMP){μ-{(η^5-C_5H_4)Sc(η^8-C_8H_8)}}Al(*i*Bu)$_2$] (3)

^{1}H NMR (400.1 MHz, 300 K, [D_8]THF): δ –0.02 (m, 4H, 4 x CH_2 of *i*Bu), 0.99 (d, 6H, $^3J_{HH}$ = 6.4 Hz, 2 x Me of *i*Bu), 1.01 (d, 6H, $^3J_{HH}$ = 6.4 Hz, 2 x Me of *i*Bu), 1.03 (s, 12H, Me of TMP), 1.13 (m, 4H, 2 x β-CH_2 of TMP), 1.44 (m, 2H, γ-CH_2 of TMP), 1.76 (m, 4H, 2 x β-

CH_2 of THF), 1.99 (sept, 2H, $^3J_{HH}$ = 6.4 Hz, CH of *i*Pr), 3.61 (m, 4H, 2 x α-CH_2 of THF), 5.35 ("t", 2H, $^3J_{HH}$ = 2.2 Hz, C_5H_4), 5.46 ("t", 2H, $^3J_{HH}$ = 2.2 Hz, C_5H_4), 6.29 (s, 8H, C_8H_8). $^{13}C\{^1H\}$ NMR (100.6 MHz, 300 K, [D_8]THF): δ 20.0 (γ-CH_2, TMP), 26.4 (2 x β-CH_2, THF), 28.9 (2 x CH, *i*Bu), 29.4 (2 x Me, *i*Bu), 30.9 (2 x Me, *i*Bu), 34.6 (4 x Me, TMP), 45.4 (2 x β-CH_2, TMP), 52.3 (2 x α-C, TMP), 68.2 (2 x α-CH_2, THF), 92.2 (CH, C_8H_8), 93.3 (8 x CH, C_8H_8), 106.9 (2 x CH, C_5H_4), 118.3 (2 x CH, C_5H_4); note that the *C*Al resonances of the C_5H_4Al fragment could not be detected due to the quadrupolar nature of ^{27}Al nuclei. ^{7}Li NMR (155.5 MHz, 300 K, [D_8]THF): δ 1.05. Anal. Calcd (Found) for $C_{34}H_{56}AlLiNOSc$: C, 71.18 (70.92); H, 9.84 (9.91); N, 2.44% (2.57%).

2.3 Synthesis of [{THF·Li(μ-TMP)Al(*i*Bu)$_2$}$_2${μ-{(η^5-C_5H_4)Sc(η^8-C_8H_7)}}] (4)

LiTMP (331 mg, 2.25 mol) was added to a Schlenk tube containing a solution of *i*Bu_2Al(TMP) (633 mg, 2.25 mmol) in methylcyclohexane (10 mL) at ambient temperature and the reaction mixture was stirred for 10 min. Then, THF (0.18 mL, 2.25 mmol) was added via syringe to give a solution which was stirred for 10 min. Next, [(η^5-C_5H_5)Sc(η^8-C_8H_8)] **1** (160 mg, 0.75 mmol) was added and the reaction mixture was heated to reflux for 3.5 h to give a pale yellow solution. The solution was filtered through Celite, concentrated under vacuum (5 mL). Single crystals of **4** suitable for an X-ray crystallographic study were obtained after 48 h at –27 °C. The crystalline material was filtered, rapidly washed with cold methylcyclohexane (2 mL) and dried under vacuum (298 mg, 0.32 mmol, 43 %).

An NMR spectroscopic analysis of an aliquot of the resulting *in situ* reaction mixture under reflux conditions in methylcyclohexane for 3.5 h showed near quantitative conversion of **1** into **4**.

Characterisation data for [{THF·Li(μ-TMP)Al(*i*Bu)$_2$}$_2${μ-{(η^5-C_5H_4)Sc(η^8-C_8H_7)}}] (4)

^{1}H NMR (400.1 MHz, 300 K, [D_8]THF): δ 0.16-0.20 (m, 4H, 4 x CH_2 of *i*Bu), 0.29 (d, 4H, $^3J_{HH}$ = 6.4 Hz, 4 x CH_2 of *i*Bu), 1.10 (d, 12H, $^3J_{HH}$ = 6.4 Hz, 4 x Me of *i*Bu), 1.06 (m, 16H, 4 x Me of *i*Bu and β-CH_2 of TMP), 1.12 (s, 12H, 2 x Me of TMP), 1.31 (m, 16H, 2 x β-CH_2 and 4 x Me of TMP), 1.45 (m, 2H, γ-CH_2 of TMP), 1.61 (m, 2H, γ-CH_2 of TMP), 1.78 (m, 8H, 4 x β-CH_2 of THF), 2.11 (m, 4H, CH of *i*Pr), 3.63 (m, 8H, 4 x α-CH_2 of THF), 5.30 ("t", 2H, $^3J_{HH}$ = 2.2 Hz, C_5H_4), 5.46 ("t", 2H, $^3J_{HH}$ = 2.2 Hz, C_5H_4), 6.11-6.23 (m, 3H, C_8H_7), 6.27-6.33 (m, 2H, C_8H_7), 7.06 ("s", 1H, C_8H_7), 7.09 ("s", 1H, C_8H_7); note that small signals of TMPH and **1** are also observed as a result of unavoidable hydrolysis of **4**. $^{13}C\{^1H\}$ NMR

(100.6 MHz, 300 K, [D_8]THF): δ 19.6 (γ-CH_2, TMP), 20.2 (γ-CH_2, TMP), 25.8 (4 x β-CH_2, THF), 28.7 (2 x CH, *i*Bu), 28.8 (2 x CH, *i*Bu), 29.8 (2 x Me, *i*Bu), 30.0 (2 x Me, *i*Bu), 30.6 (2 x Me, *i*Bu), 30.9 (2 x Me, *i*Bu), 32.3 (2 x CH_2, *i*Bu), 34.2 (4 x Me, TMP), 34.9 (4 x Me, TMP), 45.1 (2 x β-CH_2, TMP), 45.5 (2 x β-CH_2, TMP), 52.7 (2 x α-C, TMP), 52.8 (2 x α-C, TMP), 68.3 (2 x α-CH_2, THF), 92.2 (CH, C_8H_7), 93.1 (2 x CH, C_8H_7), 95.6 (2 x CH, C_8H_7), 104.3 (2 x CH, C_8H_7), 107.7 (2 x CH, C_5H_4), 115.3 (2 x CH, C_5H_4); note that the *C*Al resonances from "C_5H_4Al" and "C_8H_7Al" could not be detected due to the quadrupolar nature of ^{27}Al nuclei. ^{7}Li NMR (155.5 MHz, 300 K, [D_8]THF): δ –1.2. Anal. Calcd (Found) for $C_{55}H_{99}Al_2Li_2N_2O_2Sc$: C, 70.79 (70.98); H, 10.69 (10.40); N, 3.00% (2.73%).

Note that resonances in the ^{27}Al NMR spectra of **3** and **4** and starting aluminium reagent *i*Bu_2AlTMP are broadened such that they are essentially invisible due to the quadrupolar nature of ^{27}Al nuclei. Only the homoleptic aluminate gives a sharp signal as it is thought to be highly symmetrical.

2.4 Quenching Reaction of 3 with I_2

A sample of monometallated **3** (100 mg, 174 μmol) in Et_2O (3 mL) was cooled to −40 °C and treated with I_2 (39.7 mg, 157 μmol) in Et_2O (1 mL). The orange reaction mixture was stirred for another 30 minutes and after filtration all volatiles were removed under vacuum. The resulting oily residue was sublimed at 130 °C at 10^{-3} mbar yielding a small amount of slightly yellow solid that contained reprotonated **1** alongside a monosubstituted sandwich complex (Figure S21). Under HRMS conditions only the parent sandwich complex **1** was detected.

^{1}H NMR (400.1 MHz, 300 K, C_6D_6): δ 4.83 ("t", 2H, $^3J_{HH}$ = 2.8 Hz, C_5H_4), 5.22 ("t", 2H, $^3J_{HH}$ = 2.8 Hz, C_5H_4), 6.34 (s, 8H, COT).

3 NMR Spectra

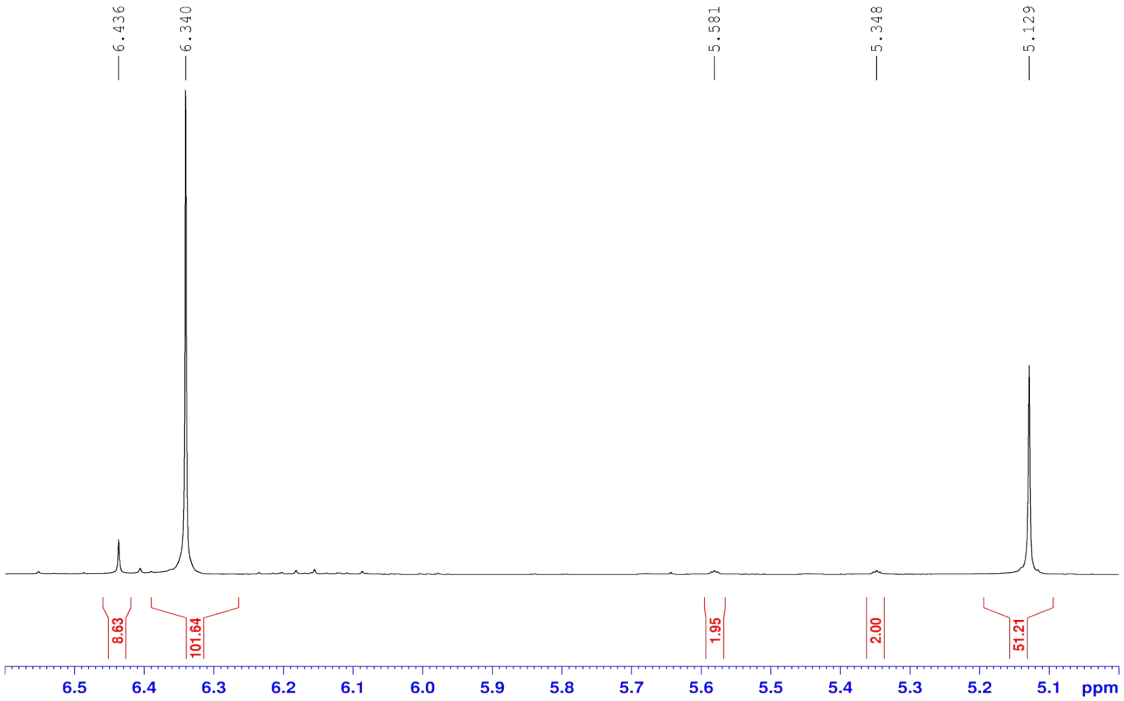

Figure S1. ^{1}H NMR (400.1 MHz, 300 K, C_6D_6) spectrum of an *in situ* aliquot from the reaction of **1** with LiTMP in 1:1 molar ratio at room temperature in *n*-hexane for 24 h.

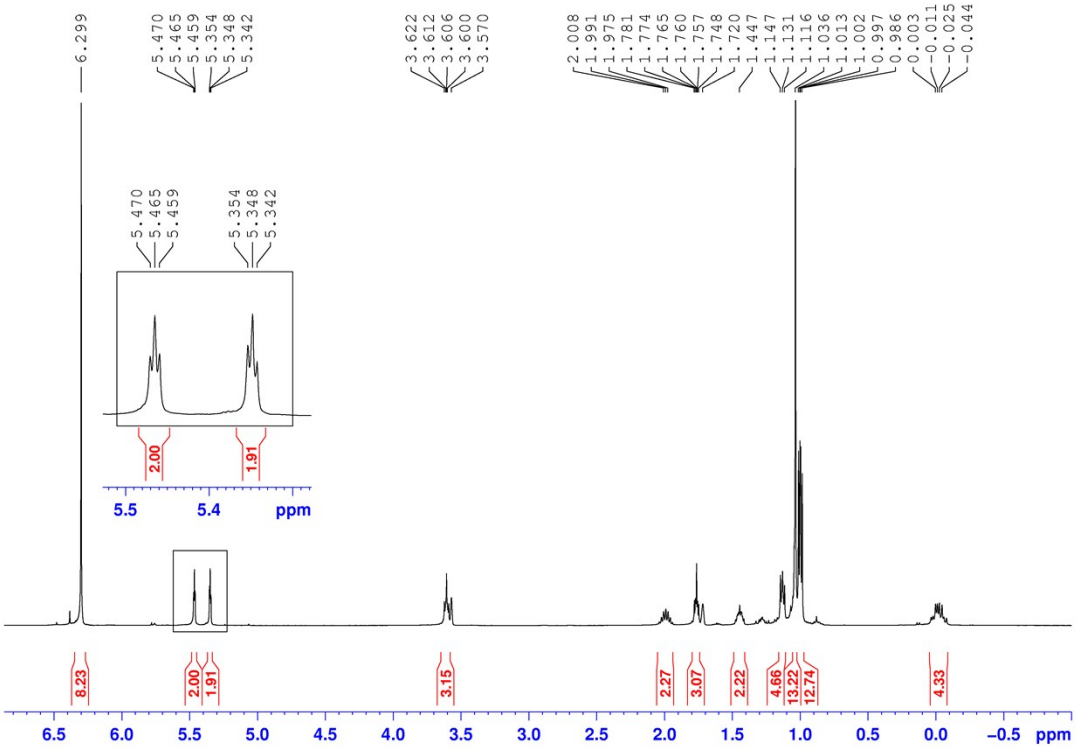

Figure S2. ^{1}H NMR (400.1 MHz, 300 K, [D_8]THF) spectrum of **3**.

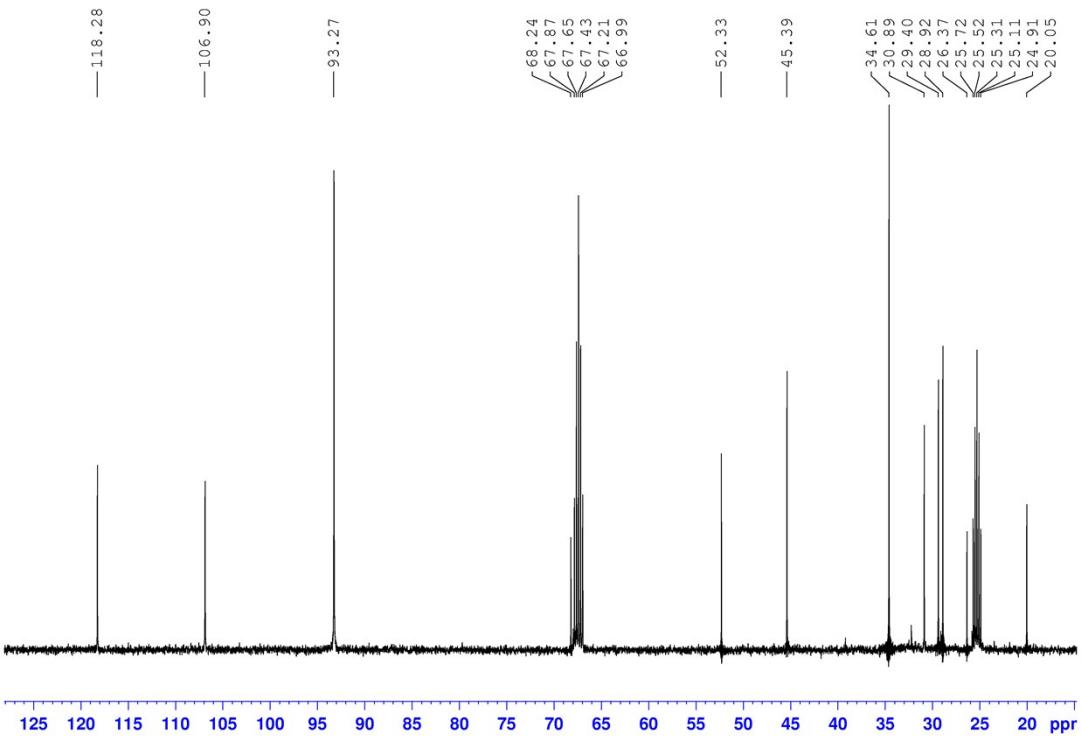

Figure S3. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, 300 K, [D_8]THF) spectrum of **3**.

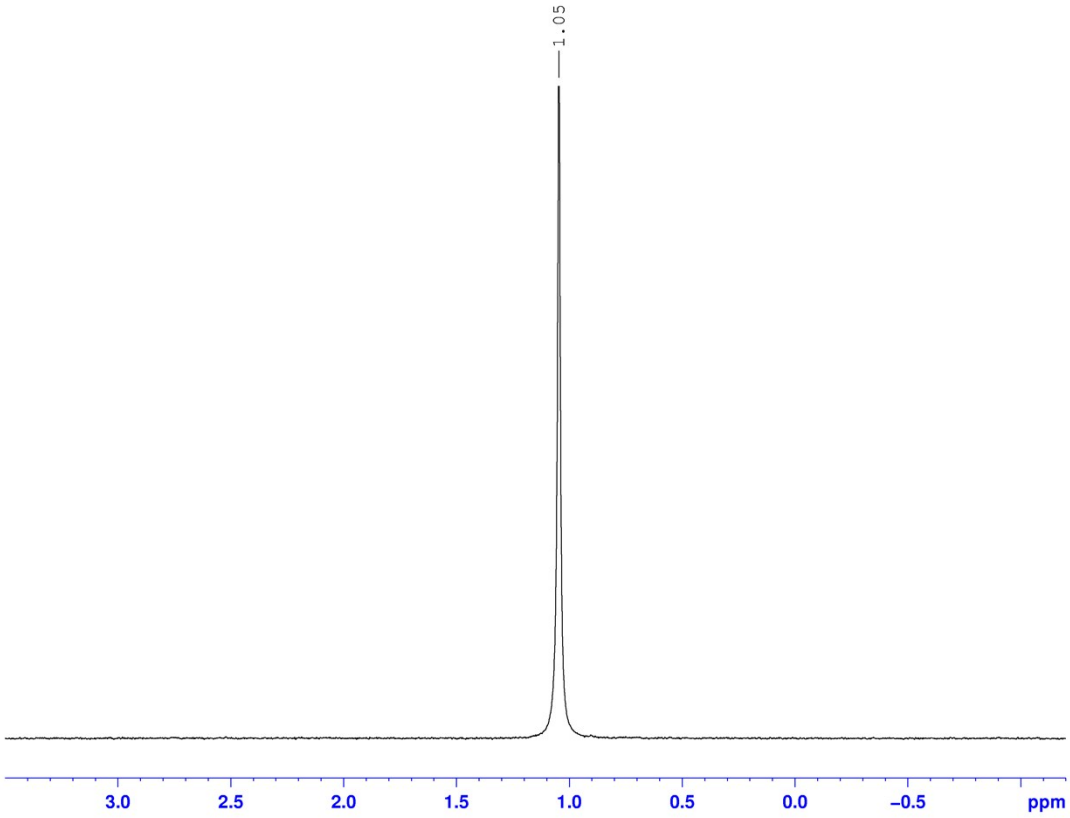

Figure S4. ^{7}Li NMR (155.6 MHz, 300 K, [D_8]THF) spectrum of **3**.

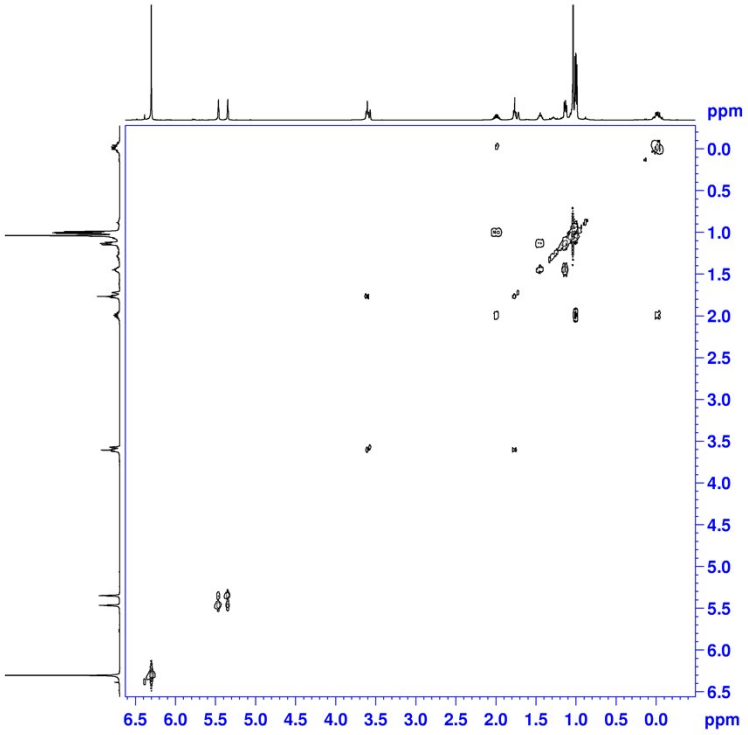

Figure S5. $^{1}H,^{1}H$-COSY NMR (400.1 MHz, 300 K, $[D_8]$THF) spectrum of **3**.

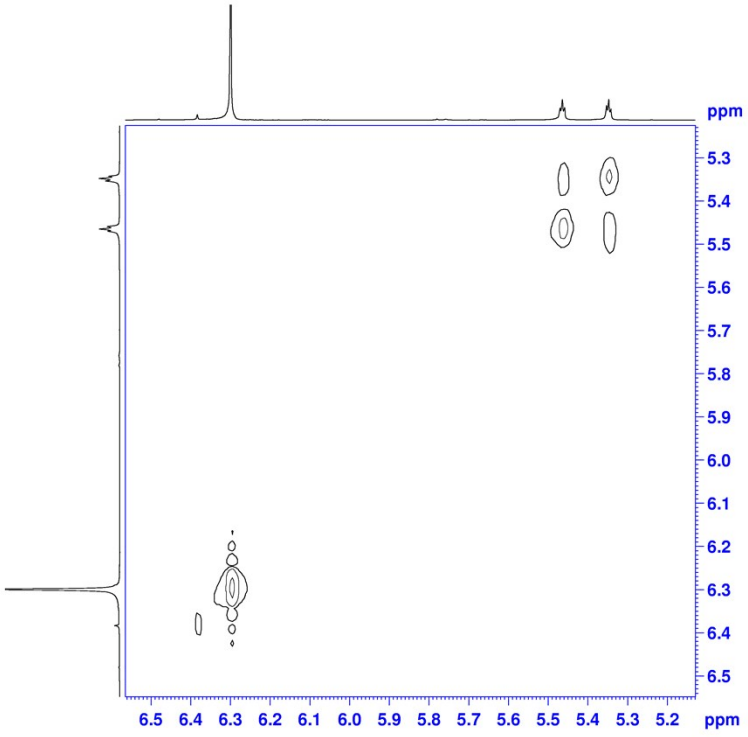

Figure S6. Section of the $^{1}H,^{1}H$-COSY NMR (400.1 MHz, 300 K, $[D_8]$THF) spectrum of **3**.

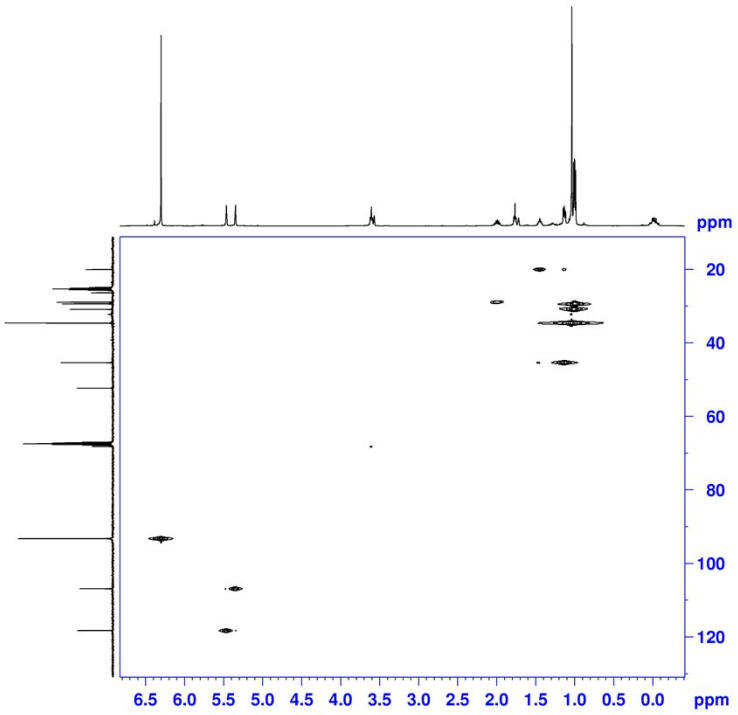

Figure S7. $^{1}H,^{13}C$-HSQC NMR (400.1 MHz, 300 K, $[D_8]$THF) spectrum of **3**.

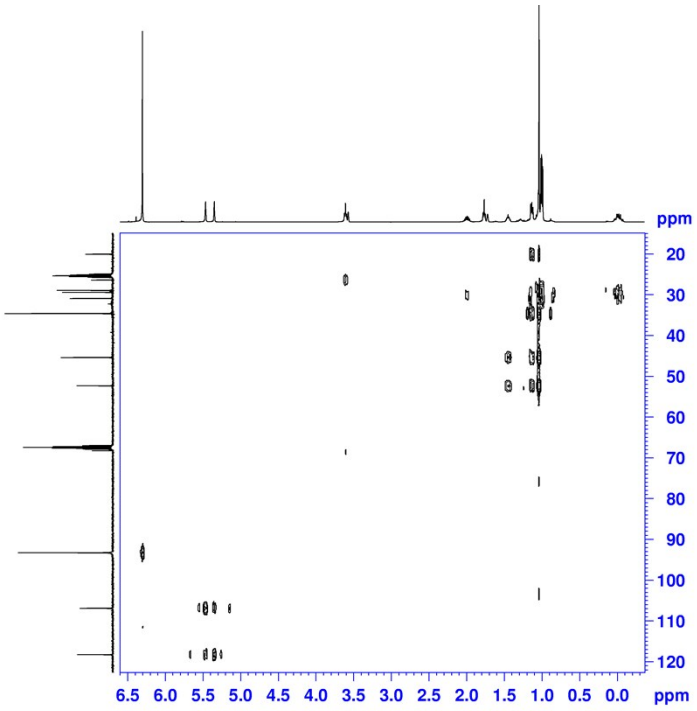

Figure S8. $^{1}H,^{13}C$-HMBC NMR (400.1 MHz, 300 K, $[D_8]$THF) spectrum of **3**.

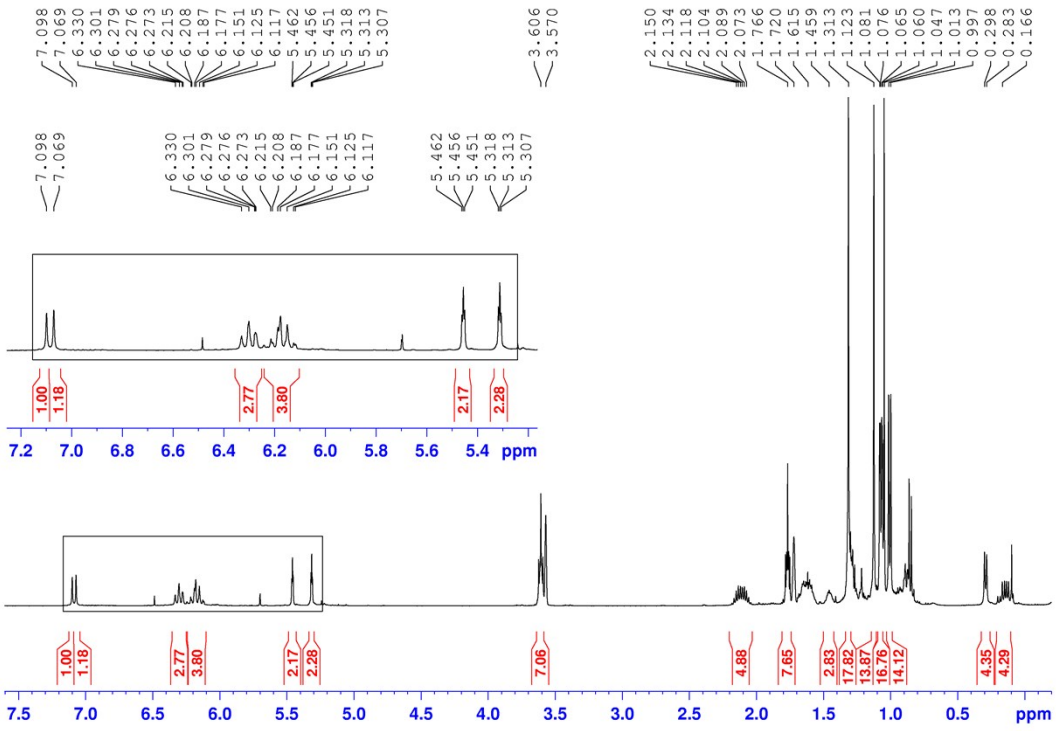

Figure S9. ^{1}H NMR (400.1 MHz, 300 K, [D_8]THF) spectrum of **4**.

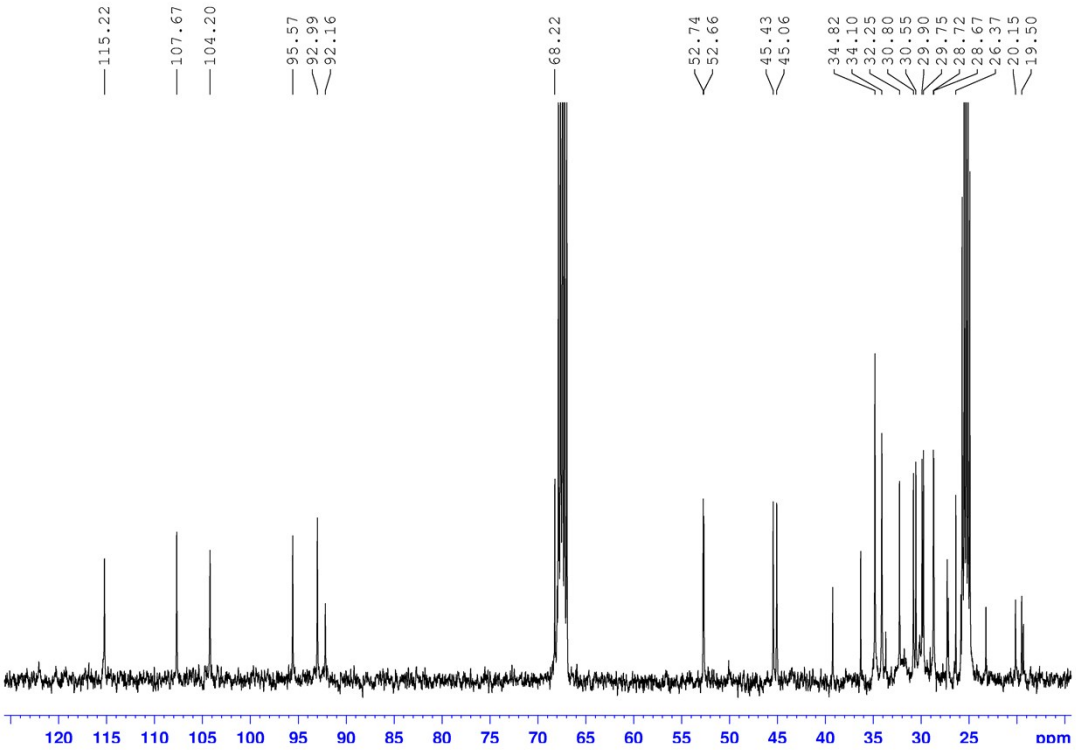

Figure S10. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, 300 K, [D_8]THF) spectrum of **4**.

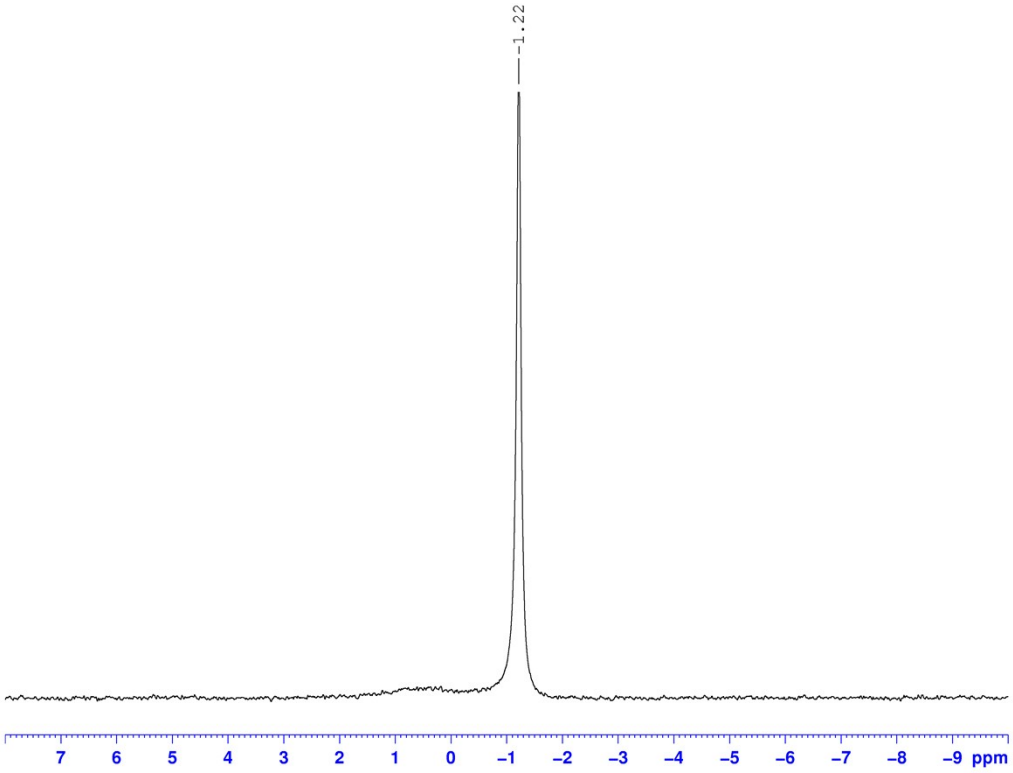

Figure S11. ^{7}Li NMR (155.6 MHz, 300 K, [D_8]THF) spectrum of **4**.

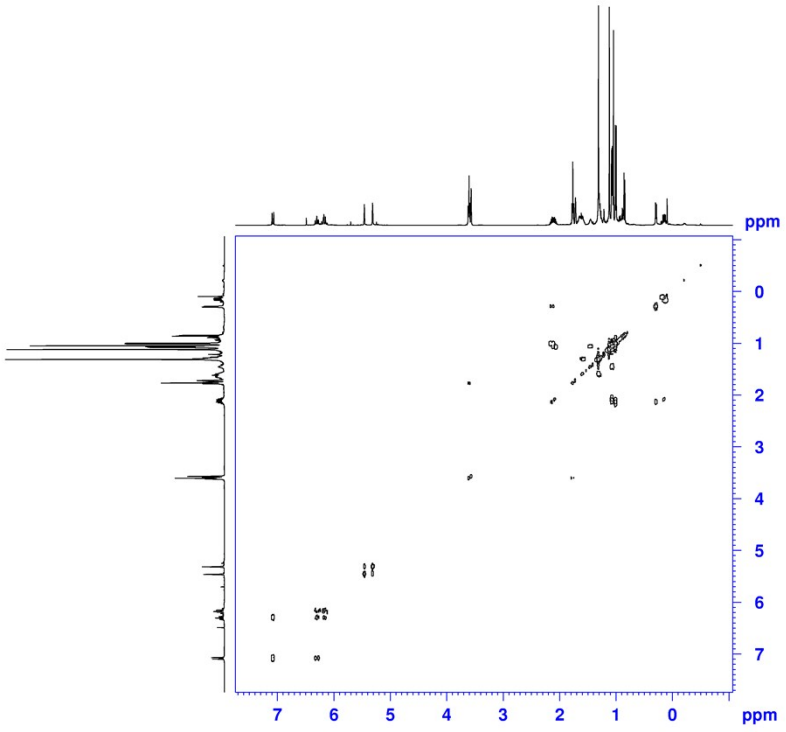

Figure S12. ^{1}H,^{1}H-COSY NMR (400.1 MHz, 300 K, [D_8]THF) spectrum of **4**.

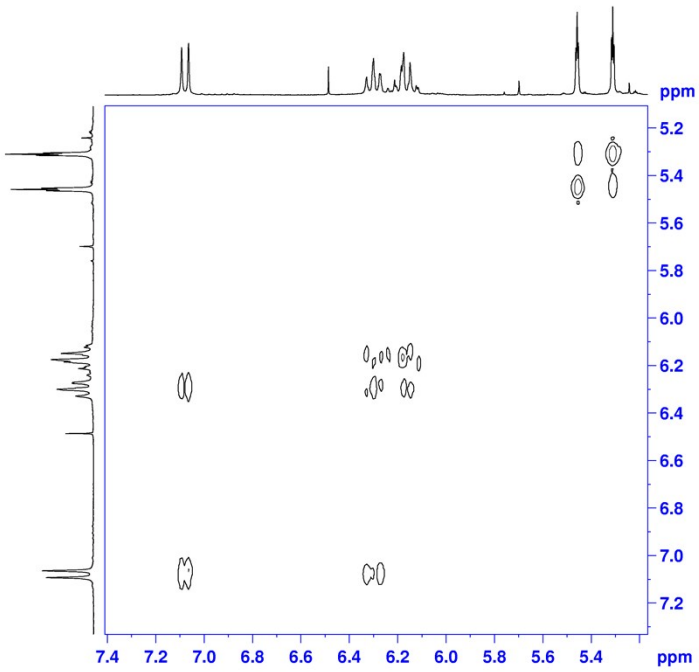

Figure S13. Section of the ^{1}H,^{1}H-COSY NMR (400.1 MHz, 300 K, [D_8]THF) spectrum of **4**.

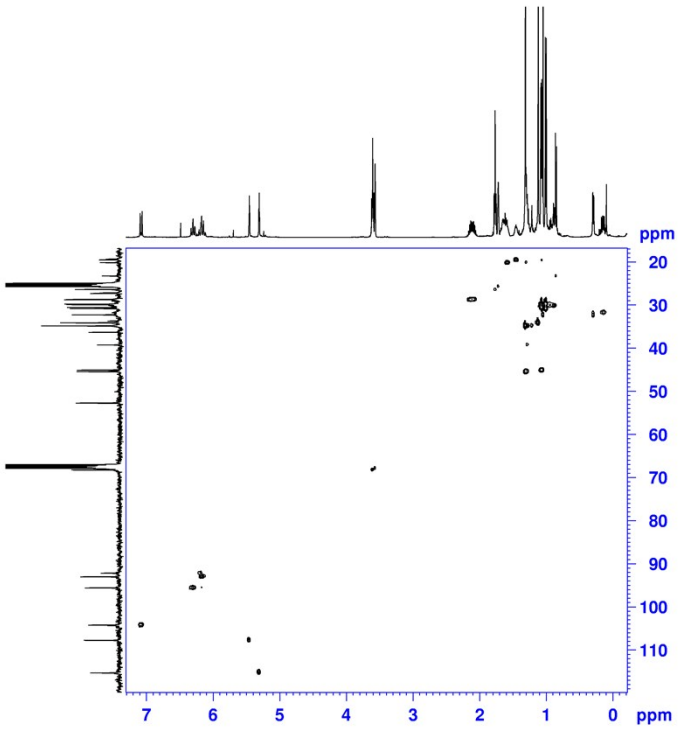

Figure S14. ^{1}H,^{13}C-HSQC NMR (400.1 MHz, 300 K, [D_8]THF) spectrum of **4**.

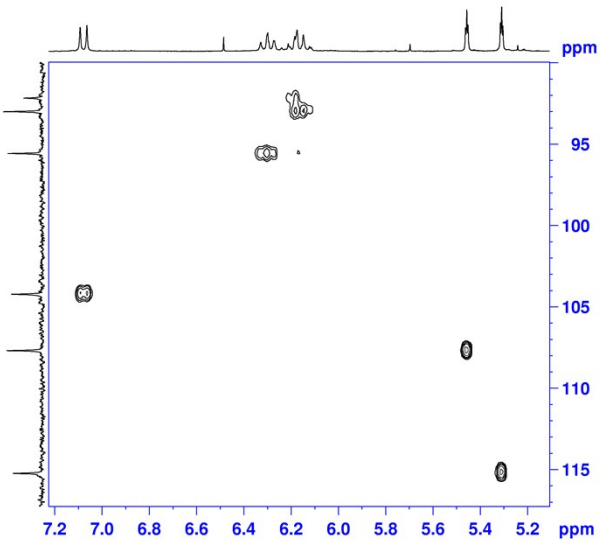

Figure S15. Section of the $^{1}H,^{13}C$-HSQC NMR (400.1 MHz, 300 K, [D_8]THF) spectrum of **4**.

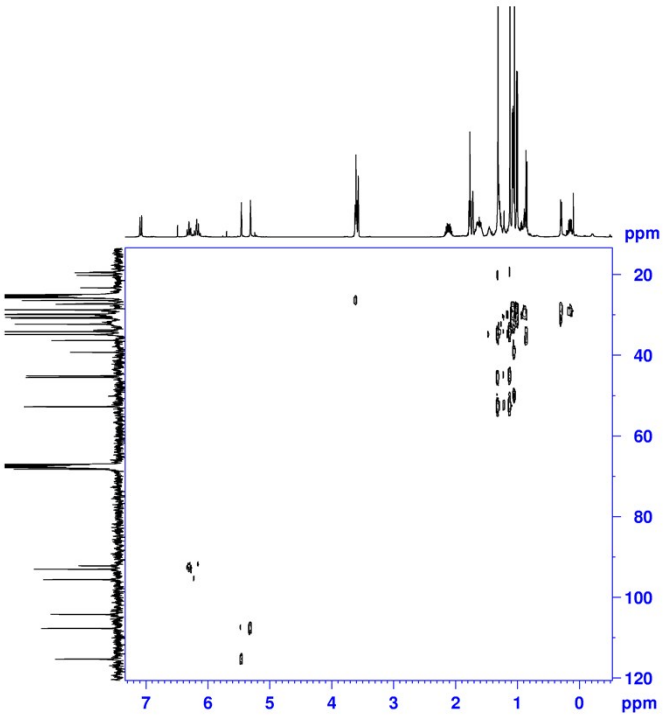

Figure S16. $^{1}H,^{13}C$-HMBC NMR (400.1 MHz, 300 K, [D_8]THF) spectrum of **4**.

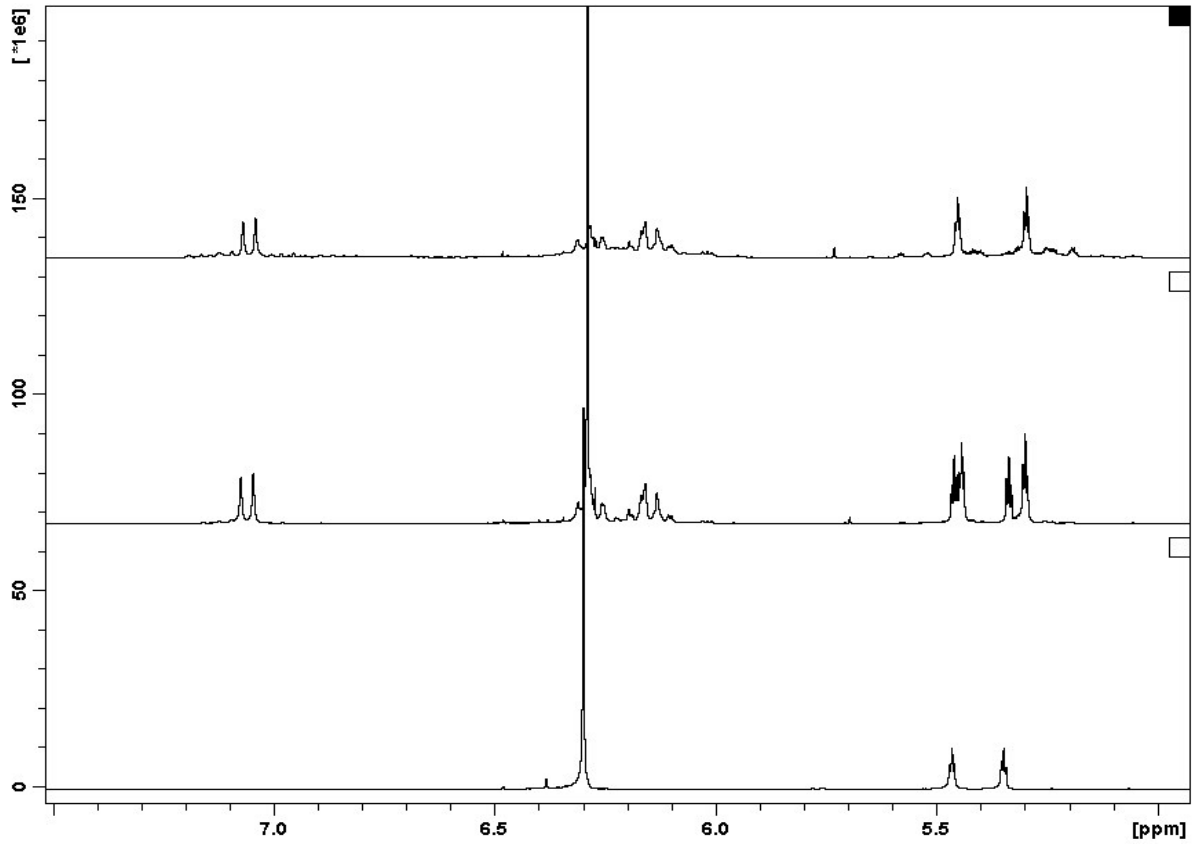

Figure S17. ^{1}H NMR (400.1 MHz, 300 K, [D_8]THF) spectra of an *in situ* reaction mixture of **1** and "LiTMP/*i*Bu_2AlTMP/THF" in 1:3 molar ratio under reflux conditions in methylcyclohexane for 3.5 h (top, full conversion to **4**), 1:2 molar ratio in methylcyclohexane under reflux conditions for 3.5 h (middle, mixture **3**:**4** in 0.4:0.6 ratio) and 1:1.2 molar ratio in *n*-hexane under reflux conditions overnight (bottom, full conversion to **3**).

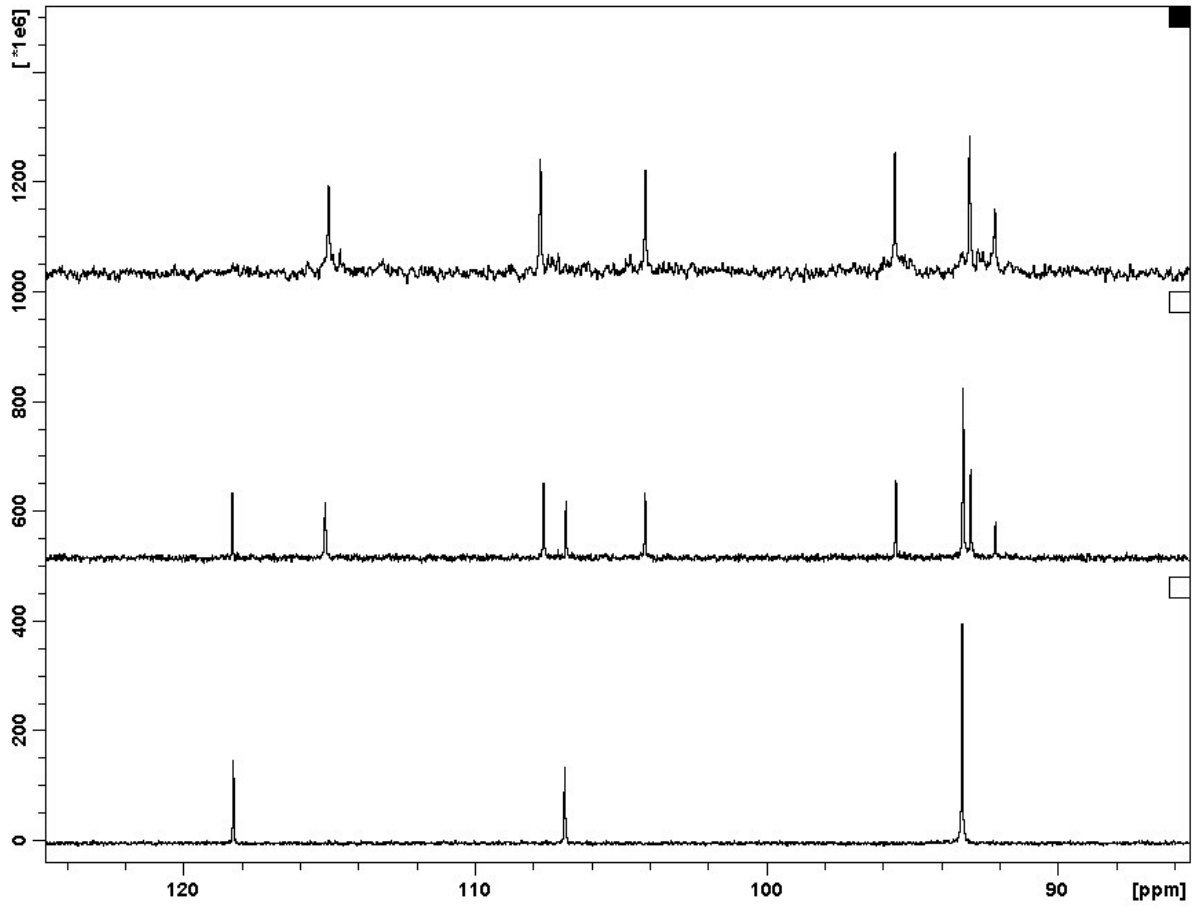

Figure S18. ^{13}C NMR (100.6 MHz, 300 K, $[D_8]$THF) spectra of an *in situ* reaction mixture of **1** and "LiTMP/*i*Bu_2AlTMP/THF" in 1:3 molar ratio under reflux conditions in methylcyclohexane for 3.5 h (top, full conversion to **4**), 1:2 molar ratio in methylcyclohexane under reflux conditions for 3.5 h (middle, mixture **3**:**4** in 0.4:0.6 ratio) and 1:1.2 molar ratio in *n*-hexane under reflux conditions overnight (bottom, full conversion to **3**).

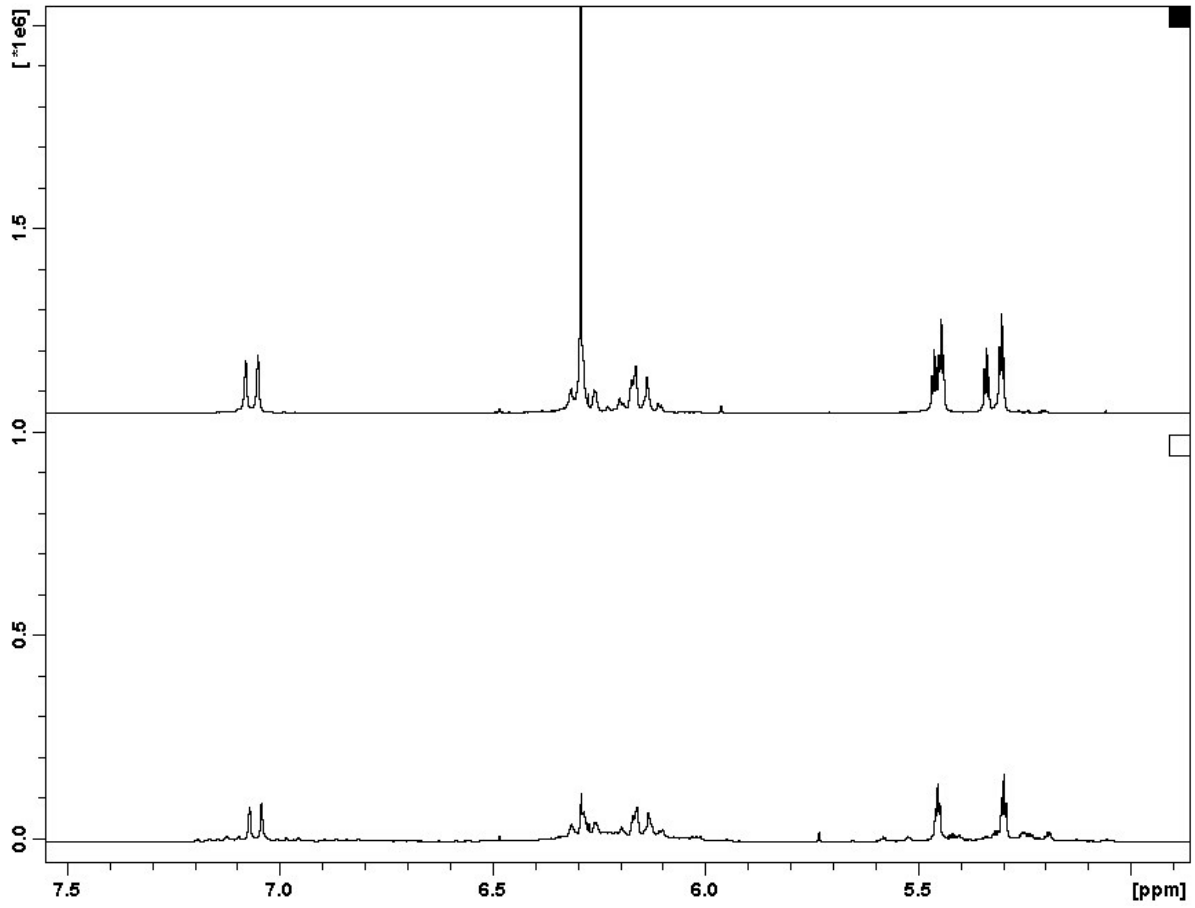

Figure S19. ^{1}H NMR (400.1 MHz, 300 K, [D_8]THF) spectra of an *in situ* reaction mixture of **1** and "LiTMP/*i*Bu_2AlTMP/THF" in 1:3 molar ratio under reflux conditions in *n*-hexane for 3.5 h (top, mixture **3**:**4** in 0.4:0.6 ratio) and in methylcyclohexane under reflux (bottom, full conversion to **4**).

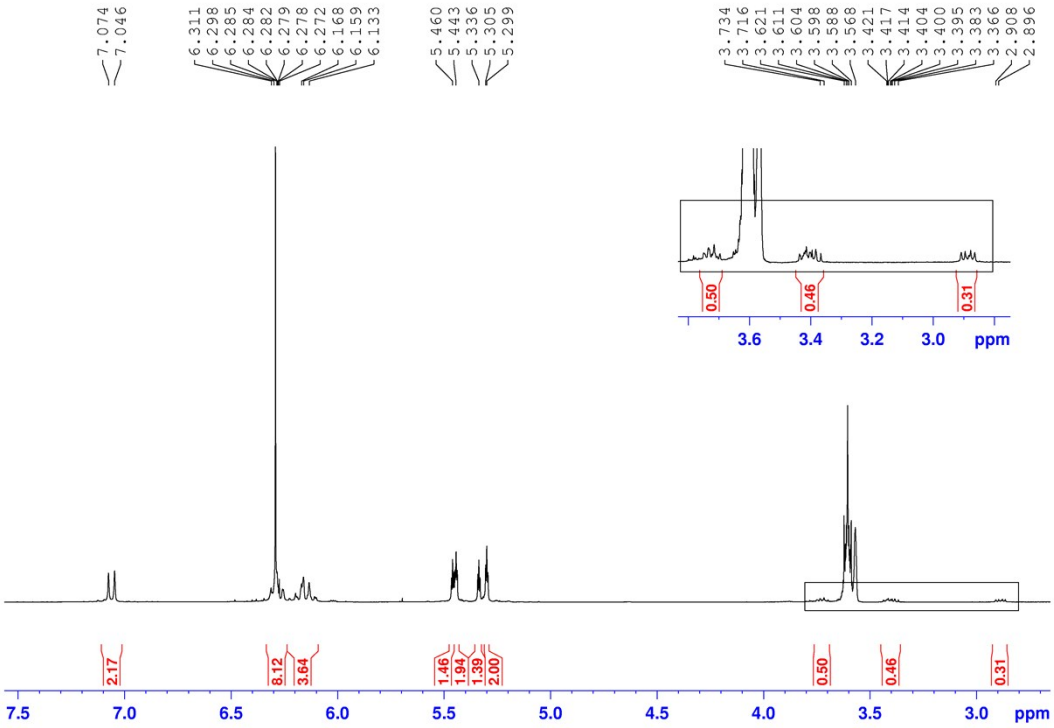

Figure S20. ^{1}H NMR (400.1 MHz, 300 K, [D_8]THF) spectra of an *in situ* reaction mixture of **1** and "LiTMP/*i*Bu_2AlTMP/THF" in 1:2 molar ratio under reflux conditions in methylcyclohexane for 3.5 h to give a 0.4:0.6 mixture of **3**:**4**. α-Metallation of THF (approximately 10%) is also detected (square box).

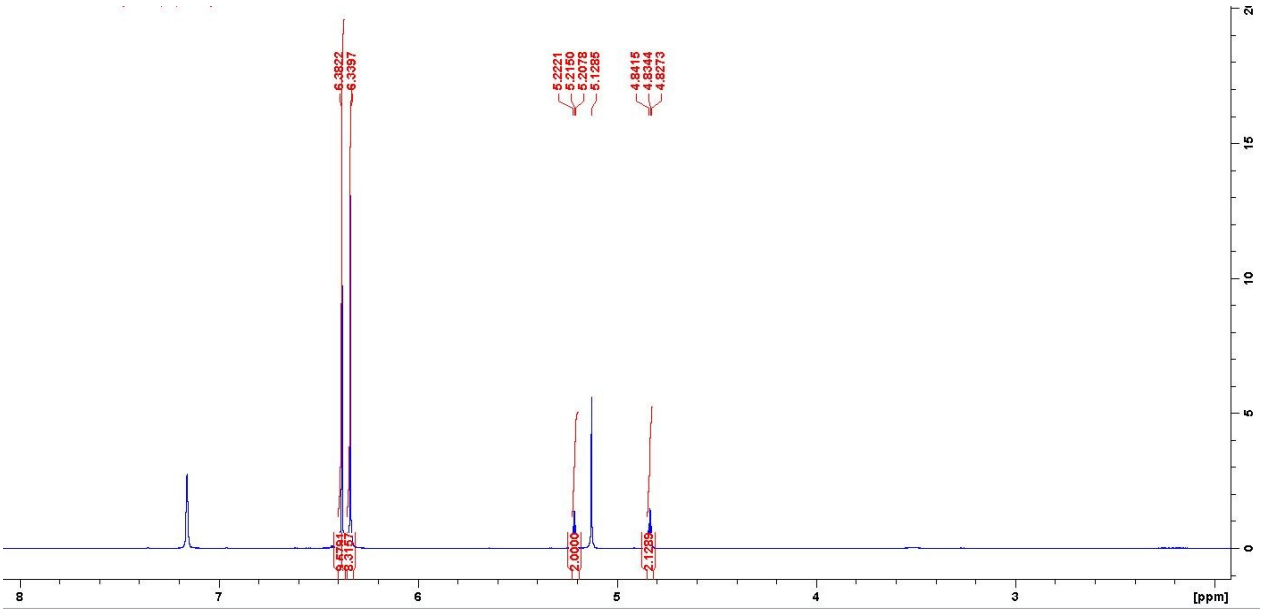

Figure S21. ^{1}H NMR (400.1 MHz, 300 K, C_6D_6) spectra of sublimed product of the reaction of **3** with 0.8 eq. I_2, showing a mixture of reprotonated **1** and a monosubstituted product.

4 ^{1}H DOSY NMR Analyses

4.1 General Considerations

The diffusion-ordered spectroscopy (DOSY) NMR experiments were performed on a Bruker AVANCE 400 MHz NMR spectrometer at 300 K operating at 400.1 MHz for ^{1}H under TopSpin (version 2.0, Bruker Biospin, Karlsruhe) and equipped with a BBFO-*z*-atm probe with actively shielded *z*-gradient coil capable of delivering a maximum gradient strength of 54 G cm^{-1}. Diffusion-ordered NMR data were acquired using the Bruker pulse program *dstegp3s* with a double stimulated echo with three spoiling gradients. Sine-shaped gradient pulses were used with a duration of 4 ms together with a diffusion period of 100 ms. Gradient recovery delays of 200 μs followed the application of each gradient pulse. Data were systematically accumulated by linearly varying the diffusion encoding gradients over a range from 2% to 95% of maximum for 64 gradient increment values. The signal decay dimension on the *pseudo*-2D data was generated by Fourier transformation of the time-domain data. DOSY plot were generated by use of the DOSY processing module of TopSpin. Parameters were optimized empirically to find the best quality of data for presentation purposes. Diffusion coefficients were calculated by fitting intensity data to the Stejskal-Tanner expression. For **3**, from the diffusion coefficients of the internal standards used (1,2,3,4-tetraphenylnaphthalene, 1-phenylnaphthalene and tetramethylsilane), linear calibration graphs were obtained by plotting *log*D versus *log*MW. Using the diffusion coefficients for the signals corresponding to the corresponding compound, an estimate of the MW of the species present in solution was obtained.[3] For **4**, from the diffusion coefficients of the internal 1-phenylnaphthalene and the linear calibration graphs obtained by using external calibration curves with normalized diffusion coefficients,[4] an estimate of the MW of the species present in solution was obtained.

4.2 DOSY NMR Sample Preparation

To an NMR tube containing the corresponding compound to be analysed (10 mg of **3** and 20 mg of **4**), the appropriate solvent (0.5 mL) was added to dissolve the compound. A series of solvent-soluble inert internal standards 1,2,3,4-tetraphenylnaphthalene (TPhN, 15 mg), 1-phenylnaphthalene (PhN, 13.2 μL) and tetramethylsilane (TMS, 19.1 μL) were then added to **3**, and (PhN, 4 μL) was added to **4**.

4.3 ^{1}H DOSY NMR Study of Compound 3 in [D_8]THF

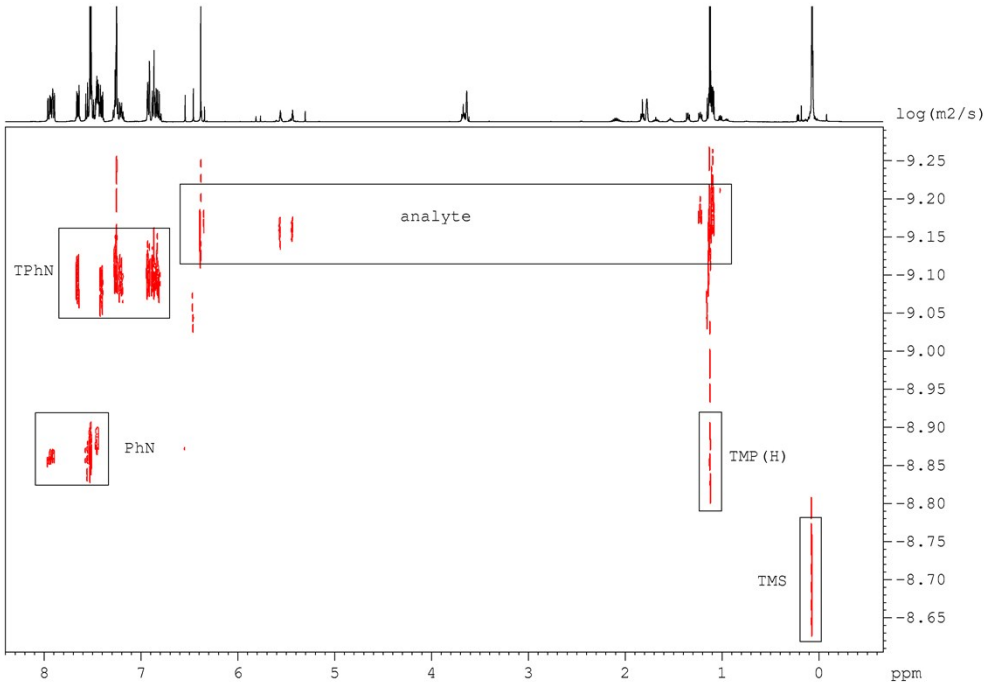

Figure S22. ^{1}H DOSY NMR plot of **3** in [D_8]THF solution (5 mg/mL, 400.1 MHz, 300 K). Small signals of TMP(H) were present due to unavoidable hydrolysis of **3**.

From the D values obtained for the internal standards a linear calibration graph of LogD versus LogMW was obtained (Figure S21), with formula logD = –0.5861 (logMW) – 7.5323. Using the D values for **3** and the calibration graph, the MW of species in solution is estimated (Table S2).

Table S2. Diffusion coefficients and MW of internal standards.

Standard	MW ($gmol^{-1}$)	logMW	D (m^2s^{-1})	logD
TPhN	432.55	2.636	8.13-10	–9.090
PhN	204.27	2.310	1.37E-9	–8.863
TMS	88.22	1.946	2.07E-9	–8.684

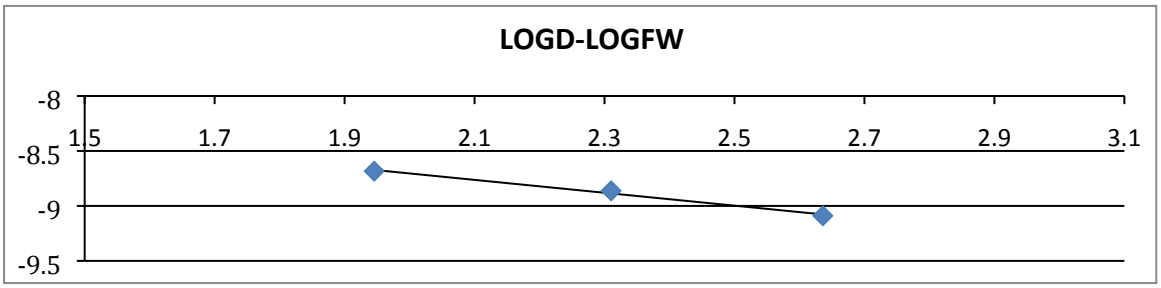

Figure S23. Calibration graph (logD = –0.5861 (logMW) – 7.5323, R^2 = 0.99) used to estimate of MW of compound of **3** in [D_8]THF solution.

Table S3. Diffusion coefficients and corresponding calculated MW_{DOSY} for components present in [D_8]THF solution for **3**.

Component of spectrum	D ($m^2\ s^{-1}$)	MW_{DOSY}[a] ($g\ mol^{-1}$)
3	6.92E-10	598.2

[a] MW from [logD = –0.5861 (logMW) – 7.5323, R^2 = 0.99]

The MW_{DOSY} value obtained was compared to the actual MW of various species which may be present in the solution. The error of the MW_{DOSY} values with respect to these species was also determined. The results are shown in Table S4.

Table S4. Comparison of MW_{DOSY} to the MW of possible species.

Possible Species	MW[a]	MW_{DOSY}[b]	Error (%) in MW_{DOSY}
[([D_8]THF)·Li(*μ*-TMP){*μ*-(C_5H_4)Sc(C_8H_8)}Al(*i*Bu)$_2$]	581.7	598.2	3

[a] Real MW ($g\ mol^{-1}$), [b] MW ($g\ mol^{-1}$) from [logD = –0.5861 (logMW) – 7.5323, R^2 = 0.99]

The ^{1}H DOSY signals of **3** in [D_8]THF solution gave a D value in correlation with a MW_{DOSY} which is in agreement with the empirical formula [([D_8]THF)Li(μ-TMP){μ-{(η^5-C_5H_4)Sc(η^8-C_8H_8)}}Al(*i*Bu)$_2$] (Figure S21 and Table S4, MW 581.7 $g\ mol^{-1}$; MW_{DOSY} 598.2 $g\ mol^{-1}$; error 3%). The data could be consistent with a single species [([D_8]THF)Li(μ-TMP){μ-{(η^5-C_5H_4)Sc(η^8-C_8H_8)}}Al(*i*Bu)$_2$] existing in a [D_8]THF solution of **3**.

4.4 ^{1}H DOSY NMR Study of Compound 4 in [D_8]THF

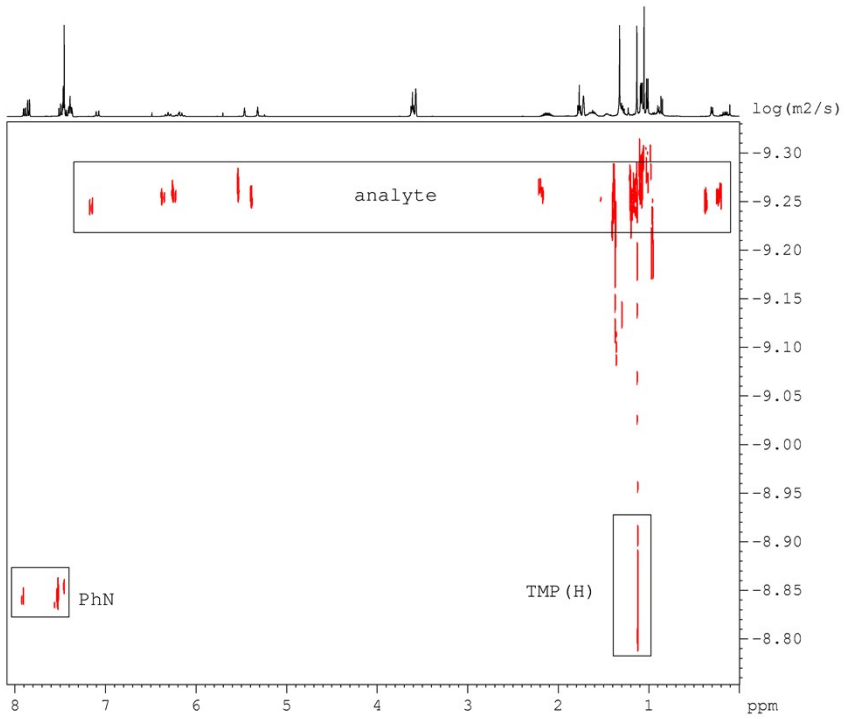

Figure S24. ^{1}H DOSY NMR plot of **3** in [D_8]THF solution (10 mg/mL, 400.1 MHz, 300 K). Small signals of TMP(H) were present due to unavoidable hydrolysis of **4**.

From the D values obtained for the internal standard 1-phenylnaphthalene and **4**, and using the use of the reported external calibration curves in [D_8]THF solution[4] the MW of species in solution is estimated. The MW_{DOSY} value obtained was compared to the actual MW of various species which may be present in the solution. The error of the MW_{DOSY} values with respect to these species was also determined. The results are shown in Table S5.

Table S5. Comparison of MW_{DOSY} to the MW of possible species.

Possible Species	MW[a]	MW_{DOSY}[b]	Error (%) in MW_{DOSY}
[{([D_8]THF)·Li(*μ*-TMP)Al(*i*Bu)$_2$}$_2${*μ*-{(C_5H_4)Sc(C_8H_7)}}]	949.3	993.0	-5

The ^{1}H DOSY signals of **4** in [D_8]THF solution gave a D value in correlation with a MW_{DOSY} which is in agreement with the empirical formula [{([D_8]THF)·Li(μ-TMP)Al(*i*Bu)$_2$}$_2${μ-{(C_5H_4)Sc(C_8H_7)}}], MW 949.3 g mol^{-1}; MW_{DOSY} 993.0 g mol^{-1}; error -5%). The data could be consistent with a single species [{([D_8]THF)Li(μ-TMP)Al(*i*Bu)$_2$}$_2${μ-{(η^5-C_5H_4)Sc(η^8-C_8H_7)}}] existing in a [D_8]THF solution of **4**.

5 X-ray Crystallography

Single-crystal data collection details

Single-crystal data crystal for **3** and **4** were recorded at 123(2) K on an Oxford Diffraction Gemini diffractometer Cu Kα (λ = 1.54184 Å) radiation. Structures were refined to convergence on *F*2 against all independent reflections by the full-matrix least-squares method using the SHELXL programs.[5] All non-hydrogen atoms were refined using anisotropic thermal parameters. The structure of monometallated **3** was refined as a two-component twin. For **4**, the geometries of the disordered groups were restrained to approximate typical values. In addition, for **4** the SQUEEZE routine within PLATON[6] was used to remove approximately 291 electron equivalents from 759 Å^5 of "void" space per unit cell. This corresponds to approximately five molecules of methylcyclohexane per unit cell. Selected crystallographic details and refinement details are given in Table S6. CCDC 1909622 (**3**) and 1909623 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from http://www.ccdc.cam.ac.uk.

Table S6. Selected crystallographic and refinement data for **3** and **4**.

Compound	**3**	**4**
Formula	$C_{34}H_{56}AlLiNOSc$	$C_{55}H_{99}Al_2Li_2N_2O_2Sc$
Fw	573.67	933.16
Cryst. System	Monoclinic	Tetragonal
Space Group	*P2$_1$/n*	*P4$_2$/mbc*
Wavelength/Å	1.54184	1.54184
a/Å	11.11866(14)	20.6285(4)
b/Å	15.1374(2)	20.6285(4)
c/Å	19.5596(3)	14.8136(5)
α/°	90	90
β/°	97.9689(14)	90
γ/°	90	90
Volume/Å^3	3260.26(8)	6303.7(3)
Z	4	4
Temp./*K*	123(2)	123(2)
Refls. Collect.	22387	22083
$2\theta_{max}$	146.9	140
R_{int}	0.0339	0.0577

Refls. Unique	22387	3105
Reflns. Obs.	19031	2072
Goodness of fit	1.041	1.044
$R[F^2>2\sigma]$, F	0.0463	0.0900
R_w (all data), F^2	0.1266	0.2919
CCDC Nr.	1909622	1909623

6 Computational Details

The geometry optimizations of **1**, **3** and **4** were carried out starting from the experimental molecular structures characterized in the solid state by X-ray diffraction studies. We performed Density Functional Theory calculations using B3LYP as functional and a double-zeta quality Pople 6-31+G* basis set with diffuse and polarization functions for optimizing the geometries. Stability tests on the single-determinant wavefunctions at the optimized structures were also performed, and no internal instabilities were found. We observed only small deviations between the optimized geometries and the X-ray diffraction molecular structures. Hessian calculations and thermochemical analysis were obtained at the same level of theory. The optimized geometries were characterized as minimum energy structures in their respective potential energy surfaces, as all vibrational frequencies were found to be real. We then performed single-point calculations at the DFT/6-311++G** level with the B3LYP, M06L and TPSSH functionals in order to obtain the frontier Molecular Orbitals. The calculated orbitals were found to be similar irrespective of the DFT functional, and therefore we focused our analysis on the FMOs obtained at the B3LYP/6-311++G** level. All calculations were done with the Gaussian 16 program package.[7]

6.1 Cartesian Coordinates (B3LYP/6-31+G*)

1

Sc	-2.760233000	1.481266000	-0.166943000
C	-0.485393000	0.531375000	0.068920000
C	-0.688397000	1.385233000	1.186547000
H	-0.747801000	1.074548000	2.223098000
C	-0.800459000	2.718002000	0.706316000
H	-0.960596000	3.602071000	1.312305000
C	-0.666544000	2.687898000	-0.708109000
H	-0.706451000	3.545064000	-1.370028000
C	-4.222506000	-0.167972000	0.814197000
H	-4.055694000	-1.010508000	1.480680000
C	-0.471994000	1.336426000	-1.102068000

H	-0.337337000	0.981970000	-2.117328000
C	-4.151565000	1.560953000	-2.136099000
H	-3.943606000	1.726832000	-3.190201000
C	-4.054841000	-0.518072000	-0.548265000
H	-3.791322000	-1.564939000	-0.676512000
C	-4.025794000	0.198151000	-1.770491000
H	-3.745025000	-0.431014000	-2.611428000
C	-4.554796000	2.406496000	1.153443000
H	-4.582376000	3.065195000	2.017863000
C	-4.525893000	3.122532000	-0.068489000
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C	-4.358105000	2.772429000	-1.431098000
H	-4.271642000	3.644671000	-2.074149000
C	-4.428838000	1.043389000	1.519178000
H	-4.383456000	0.907219000	2.596784000
H	-0.362587000	-0.544818000	0.103573000

3

Sc	-2.739707122	1.385134896	-0.136016023
C	-0.396594288	0.540180278	0.068684183
Al	0.318237021	-1.419599480	0.043334424
C	-0.622703375	1.448010826	1.165393085
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H	-1.281465903	-1.544585843	-1.923654409
H	0.155883943	-2.332188448	-2.504175573
C	-4.334255458	-0.145229728	0.854131684
H	-4.234467488	-0.980263219	1.540564409

C	-0.486336092	1.387863164	-1.100318323
H	-0.390637046	1.045622673	-2.125787360
C	3.125329199	-1.146841004	1.222965707
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H	0.462958404	-2.503333943	2.518064528
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H	3.691623321	-2.723482415	2.636322911
H	3.942008008	-3.182001378	0.953689154
H	2.310590105	-3.155023223	1.618752374
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C	5.317283543	-0.960022967	-0.119304394
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H	4.415953048	0.536961923	-1.349022417
C	3.011852731	3.518150071	-1.108541245
H	2.078256696	3.745329462	-1.637502653
H	3.653008368	2.911396421	-1.754247060
C	2.815452813	3.537792236	1.267025920
H	3.693427445	3.184502720	1.821902583
H	1.918858402	3.384767611	1.873509144

C	-1.988654346	-4.089495962	2.671149648
H	-1.322042966	-4.366934010	3.499857350
H	-1.871798044	-4.846345394	1.885669156
H	-3.023274911	-4.143819886	3.039487997
C	2.988370099	4.976644856	0.778093723
H	2.011266577	5.453661093	0.638618513
H	3.567947586	5.584248068	1.479910938
C	3.689300979	4.780776268	-0.576292122
H	4.763077988	4.610165433	-0.433609401
H	3.566441368	5.632293605	-1.252634130
Li	1.759205795	1.021713212	0.005578754

4

Sc	0.037800000	0.660099000	-0.090230000
C	-2.399887000	0.052736000	0.004236000
Al	-4.123110000	1.217130000	0.100849000
C	-1.712295000	-0.705492000	1.020402000
H	-1.871448000	-0.604571000	2.089324000
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H	-2.909105000	2.440041000	-1.765233000
H	-4.542591000	2.306442000	-2.346355000
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H	-0.264646000	3.371391000	1.709418000
C	-1.838747000	-0.446715000	-1.231013000
H	-2.102693000	-0.091139000	-2.221809000
C	-6.233910000	-0.756690000	1.091905000
C	1.218104000	1.483784000	-2.008694000
H	1.125236000	1.277778000	-3.073420000

C	-4.421138000	2.310506000	1.803848000
H	-5.211661000	3.007357000	1.476141000
H	-4.882601000	1.764824000	2.638667000
C	-4.198669000	4.065309000	-1.175520000
H	-3.762267000	4.331416000	-0.201407000
C	-7.228962000	0.320031000	1.605347000
H	-7.608397000	0.045783000	2.599016000
H	-8.096671000	0.423619000	0.949150000
H	-6.757312000	1.299609000	1.686614000
C	-5.234407000	-1.075446000	2.228226000
H	-4.595066000	-0.229181000	2.480971000
H	-4.587668000	-1.924497000	1.964989000
H	-5.774872000	-1.367111000	3.137188000
C	-3.277697000	3.165033000	2.411491000
H	-2.602728000	3.501205000	1.609124000
C	-6.180175000	-0.450250000	-1.451231000
C	-0.003126000	3.079614000	-0.338992000
H	-0.812136000	3.800621000	-0.422165000
C	0.364902000	2.533372000	-1.592492000
H	-0.227595000	2.937346000	-2.409896000
C	-7.032312000	-2.071169000	0.869741000
H	-6.323073000	-2.908075000	0.780613000
H	-7.635788000	-2.266066000	1.766849000
C	-7.902705000	-2.053863000	-0.382093000
H	-8.699022000	-1.303274000	-0.300210000
H	-8.406401000	-3.021678000	-0.510831000
C	-5.143074000	-0.519145000	-2.595525000
H	-4.501572000	0.360590000	-2.641343000
H	-5.655683000	-0.605294000	-3.561771000
H	-4.499867000	-1.405416000	-2.501567000
C	2.042258000	0.816762000	1.226906000
H	2.421949000	0.278505000	2.091787000
C	2.425922000	0.201987000	-0.006627000
C	2.054556000	0.535426000	-1.350361000

H	2.419147000	-0.190353000	-2.073303000
C	-5.695342000	4.413584000	-1.116985000
H	-6.224082000	3.826385000	-0.357910000
H	-6.175709000	4.213577000	-2.085400000
H	-5.850803000	5.475727000	-0.884479000
C	1.184115000	1.871998000	1.653339000
H	1.075029000	1.901645000	2.735716000
C	-7.124150000	0.746287000	-1.737647000
H	-7.985331000	0.763969000	-1.065310000
H	-7.512808000	0.693810000	-2.763809000
H	-6.596629000	1.695316000	-1.626826000
C	-3.512096000	4.952761000	-2.232549000
H	-3.672425000	6.022593000	-2.035480000
H	-3.904745000	4.734187000	-3.235720000
H	-2.428633000	4.776248000	-2.258773000
C	-2.439455000	2.351747000	3.410637000
H	-3.067036000	2.007031000	4.244629000
H	-1.624843000	2.951392000	3.839969000
H	-1.992281000	1.470490000	2.940193000
C	-6.999114000	-1.765702000	-1.575419000
H	-7.578353000	-1.725723000	-2.507942000
H	-6.298818000	-2.608823000	-1.679724000
C	-3.418234000	-4.224540000	-1.625061000
H	-2.529439000	-3.796396000	-2.103847000
H	-4.290008000	-4.051940000	-2.262791000
C	-3.273201000	-4.378476000	0.749647000
H	-4.195713000	-4.677011000	1.263086000
H	-2.653214000	-3.791091000	1.431925000
C	-3.816286000	4.431225000	3.104723000
H	-4.506156000	4.161521000	3.916678000
H	-4.368233000	5.064911000	2.399445000
H	-3.007001000	5.036187000	3.539088000
C	-2.545736000	-5.575299000	0.136162000
H	-1.476427000	-5.360390000	0.029868000

H	-2.653541000	-6.479194000	0.743590000
C	-3.211391000	-5.690520000	-1.244973000
H	-4.175294000	-6.207739000	-1.167161000
H	-2.595936000	-6.223553000	-1.976068000
Li	-3.861442000	-1.599603000	-0.225824000
N	5.510015000	-0.165784000	-0.046598000
Al	3.834338000	-1.356896000	0.140674000
C	3.403592000	-2.674764000	-1.377534000
C	3.764291000	-2.463403000	1.864600000
O	4.275675000	3.322621000	-0.383548000
C	4.142060000	4.006143000	-1.662744000
C	4.013291000	4.248530000	0.709302000
Li	4.245071000	1.408291000	-0.190252000
C	6.343859000	0.056212000	1.200112000
C	6.286401000	-0.234112000	-1.346580000
H	2.360237000	-2.411361000	-1.629712000
H	3.954616000	-2.505921000	-2.315580000
C	3.424588000	-4.204376000	-1.119861000
C	7.027871000	-1.226423000	1.744326000
C	5.434113000	0.614875000	2.317111000
C	7.439303000	1.139951000	0.999864000
H	4.499315000	-3.250541000	1.621495000
H	4.180546000	-1.989034000	2.764821000
C	2.456290000	-3.186211000	2.296577000
H	2.936810000	-4.409666000	-0.157253000
C	4.847971000	-4.778882000	-1.039047000
C	2.627325000	-4.969113000	-2.195502000
H	7.483619000	-1.029014000	2.724072000
H	7.823274000	-1.582966000	1.085568000
H	6.310295000	-2.038760000	1.868994000
H	4.629931000	-0.068103000	2.588622000
H	4.984488000	1.575446000	2.029573000
H	6.025558000	0.805101000	3.221271000
H	1.821785000	-3.360544000	1.412901000

C	1.633846000	-2.353585000	3.294115000
C	2.749192000	-4.567296000	2.914871000
C	5.333717000	0.068372000	-2.524805000
C	6.931865000	-1.616548000	-1.617976000
C	7.390441000	0.855185000	-1.442066000
H	6.952163000	2.122116000	0.898252000
H	8.048784000	1.187298000	1.912468000
C	8.310468000	0.915217000	-0.229507000
H	8.898714000	-0.006511000	-0.134447000
H	9.035693000	1.732932000	-0.339753000
H	4.535197000	-0.665912000	-2.623472000
H	5.896828000	0.069334000	-3.466438000
H	4.873824000	1.061783000	-2.432839000
H	5.440812000	-4.296879000	-0.253625000
H	5.379259000	-4.639776000	-1.991035000
H	4.829872000	-5.856564000	-0.827360000
H	7.740289000	-1.844434000	-0.919233000
H	7.357274000	-1.650322000	-2.630270000
H	6.189841000	-2.412318000	-1.539507000
H	2.619180000	-6.052233000	-2.005518000
H	3.064175000	-4.807548000	-3.191171000
H	1.584777000	-4.626345000	-2.234662000
H	2.215752000	-2.164884000	4.207223000
H	0.716143000	-2.879042000	3.593161000
H	1.341817000	-1.384570000	2.878319000
H	7.963059000	0.685121000	-2.363863000
H	6.907965000	1.839064000	-1.551948000
H	3.226056000	3.645987000	-2.143845000
H	5.006886000	3.737819000	-2.277083000
C	4.065743000	5.495529000	-1.325029000
H	4.969850000	4.478149000	1.196252000
H	3.350256000	3.748691000	1.419670000
C	3.391405000	5.482235000	0.056677000
H	3.385270000	-4.461533000	3.804722000

H	3.278166000	-5.216916000	2.206737000
H	1.826955000	-5.082428000	3.221136000
H	2.308838000	5.349151000	-0.044455000
H	3.576556000	6.392963000	0.634994000
H	5.071088000	5.929332000	-1.260137000
H	3.499437000	6.057392000	-2.074181000

6.2 Hessian Calculations (B3LYP/6-31+G*)

Table S7. Harmonic frequencies (cm^{-1}), Reduced masses (amu), force constants (mDyne $Å^{-1}$) and IR intensities (km mol^{-1}) for the nine lowest vibrational frequency modes.

Vibrational Mode	Frequencies	Reduced Masses	Force Constants	IR Intensities
*Sc sandwich **1***				
1	5.3798	3.5410	0.0001	0.0000
2	87.4667	4.9302	0.0222	1.0750
3	88.2041	4.9395	0.0226	1.0705
4	203.8507	5.5777	0.1366	0.0674
5	237.8808	3.8912	0.1297	0.0652
6	238.2104	3.8949	0.1302	0.0663
7	241.9608	3.5286	0.1217	0.0003
8	242.1249	3.5277	0.1218	0.0003
9	331.5292	9.5469	0.6182	0.4284
Monometallated Sc sandwich **3**				
1	17.0637	4.1577	0.0007	0.1028
2	22.0522	4.0784	0.0012	0.0234
3	22.4098	3.3631	0.0010	0.5087
4	29.8381	4.4146	0.0023	0.0069
5	33.3102	3.0559	0.0020	0.0482
6	35.3185	3.2328	0.0024	0.0396
7	47.8124	3.2273	0.0043	0.0405
8	50.1695	3.4172	0.0051	0.1573
9	60.6200	3.3725	0.0073	0.1715
Dimetallated Sc sandwich **4**				
1	5.3798	3.5410	0.0001	0.0000

2	87.4667	4.9302	0.0222	1.0750
3	88.2041	4.9395	0.0226	1.0705
4	203.8507	5.5777	0.1366	0.0674
5	237.8808	3.8912	0.1297	0.0652
6	238.2104	3.8949	0.1302	0.0663
7	241.9608	3.5286	0.1217	0.0003
8	242.1249	3.5277	0.1218	0.0003
9	331.5292	9.5469	0.6182	0.4284

6.3 Thermochemical Analysis

Table S8. Thermochemical analysis of **1**, **3**, and **4**. All values are in hartree. Except for E(Single-point - RB3LYP/6-311++G**), all other entries are related to B3LYP/6-31+G* calculations.

	1	**3**	**4**
E(RB3LYP/6-31+G*)	-1263.959644	-2470.152084	-3676.343960
Zero-point correction	0.219859	0.834688	1.449627
Thermal correction to Energy	0.232017	0.880673	1.529449
Thermal correction to Enthalpy	0.232961	0.881618	1.530393
Thermal correction to Gibbs Free Energy	0.179959	0.755230	1.329887
Sum of electronic and zero-point Energies	-1263.739785	-2469.317396	-3674.894333
Sum of electronic and thermal Energies	-1263.727628	-2469.271411	-3674.814511
Sum of electronic and thermal Enthalpies	-1263.726684	-2469.270467	-3674.813567
Sum of electronic and thermal Free Energies	-1263.779686	-2469.396855	-3675.014074
E(Single-point - RB3LYP/6-311++G**)	-1264.110499	-2470.563748	-3677.015576

6.4 Frontier Molecular Orbitals

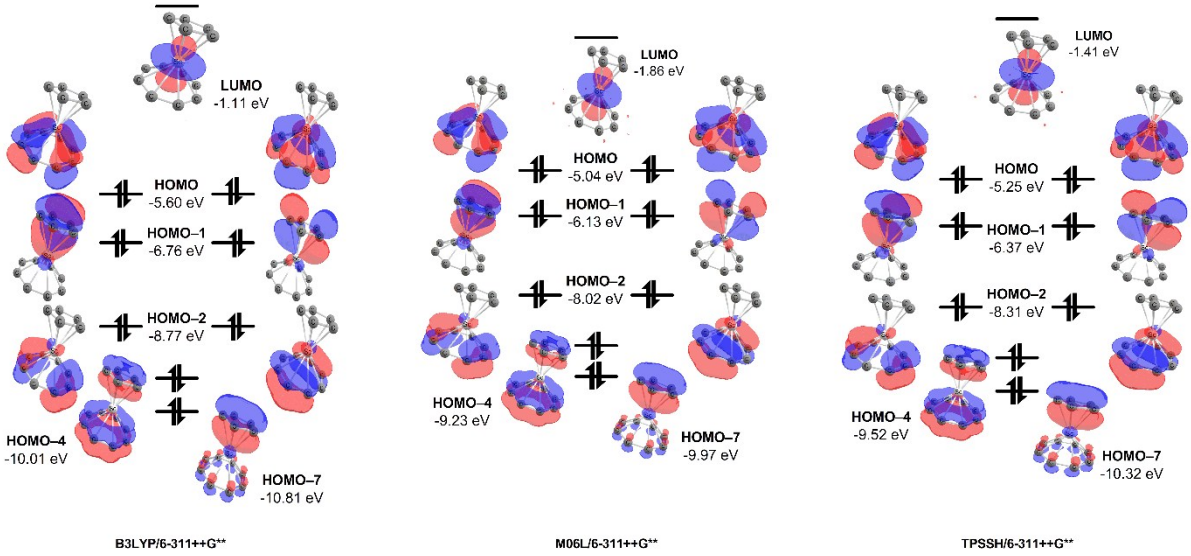

Figure S25. Selected Molecular Orbitals of **1**. Hydrogen atoms are omitted for clarity. Surface isovalue: ±0.04 [e a_0^{-3}]$^{1/2}$. From top to bottom (energies in eV): LUMO (-1.11); HOMO (-5.60); HOMO-1 (-5.60); HOMO-2 (-6.76); HOMO-3 (-6.76); HOMO-4 (-8.77); HOMO-5 (-8.77); HOMO-8 (-10.01); HOMO-13 (-10.81).

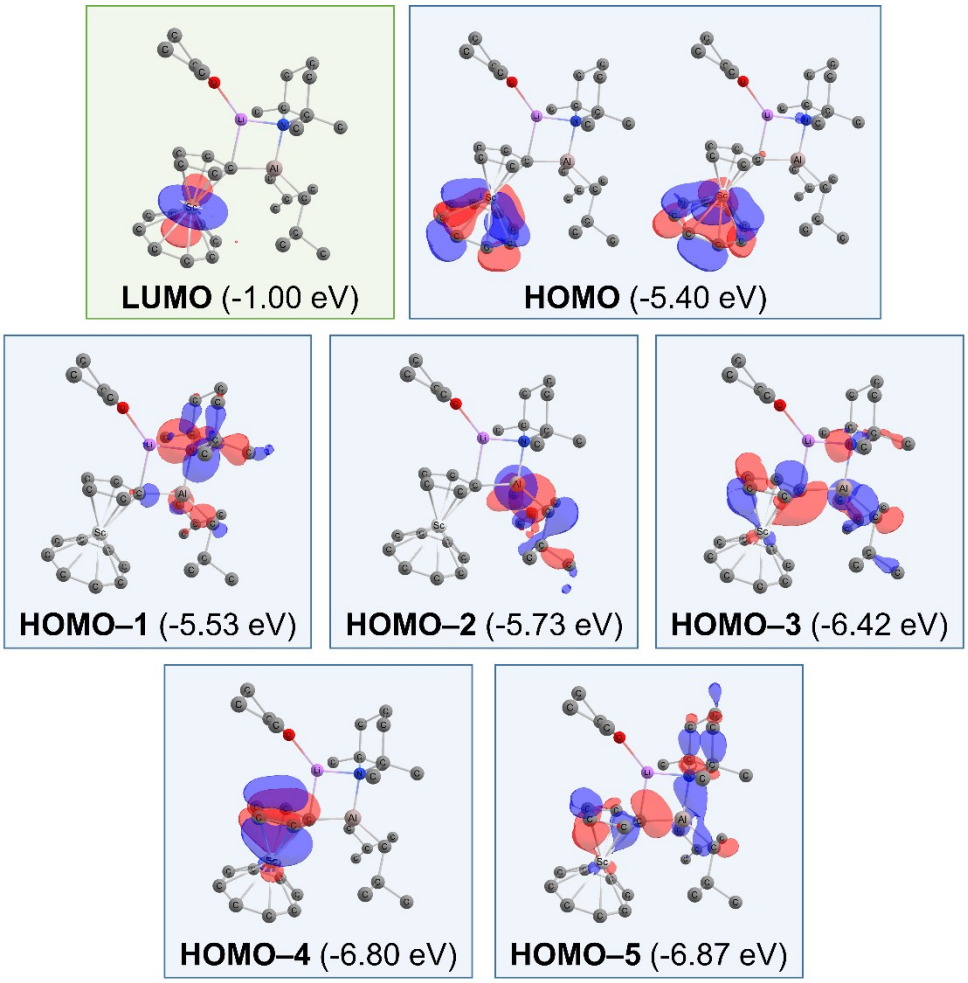

Figure S26. Selected Molecular Orbitals of **3** at the B3LYP/6-311++G** level. Orbital energies are in eV. Hydrogen atoms are omitted for clarity.

Surface isovalue: ±0.04 $[e\ a_0^3]^{1/2}$.

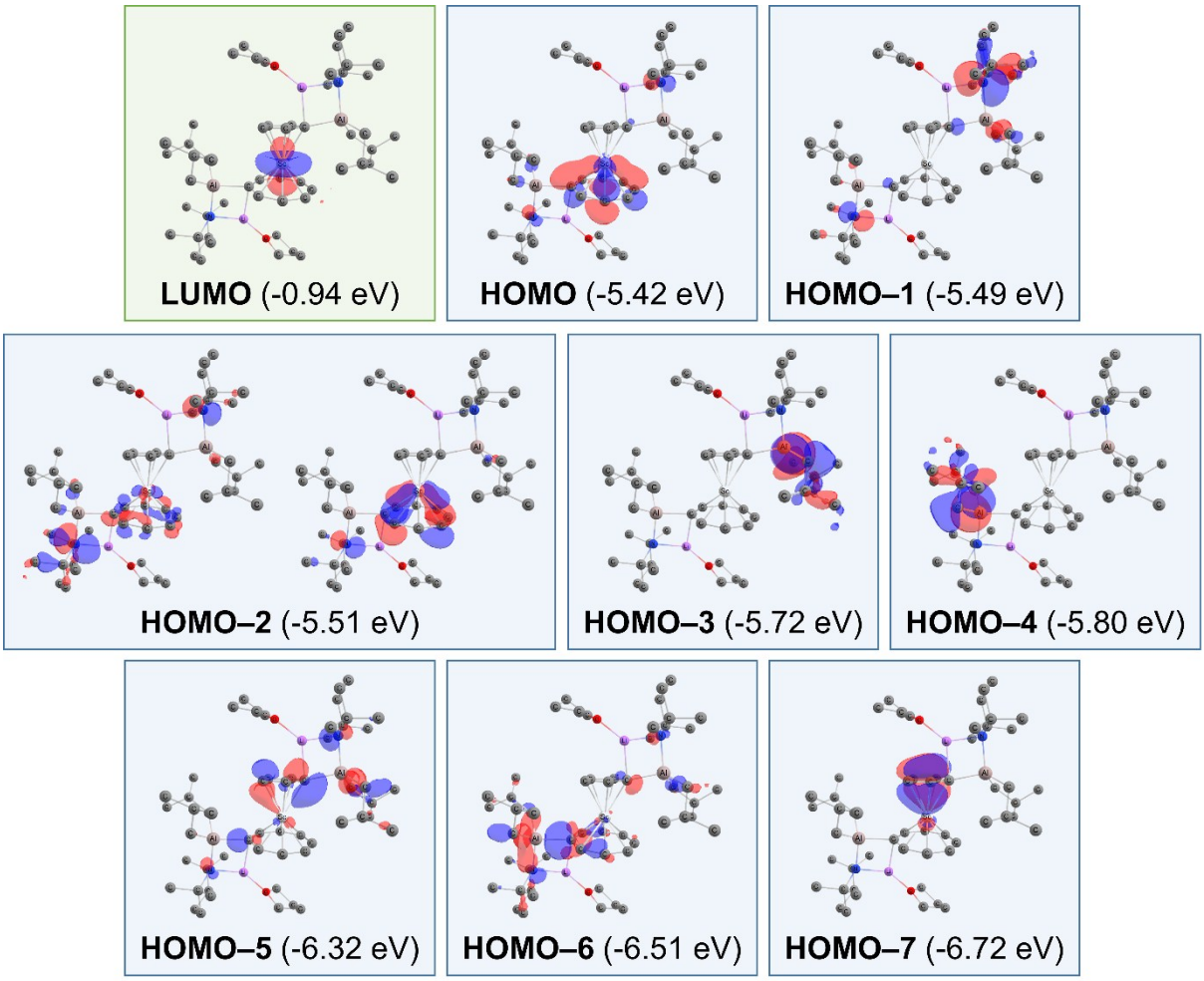

Figure S27. Selected Molecular Orbitals of **4** at the B3LYP/6-311++G** level. Orbital energies are in eV. Hydrogen atoms are omitted for clarity. Surface isovalue: ±0.04 [e a_0^{-3}]$^{1/2}$.

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