

Supplementary Information

Mechanochemical Synthesis of Iron Aluminyl Complexes

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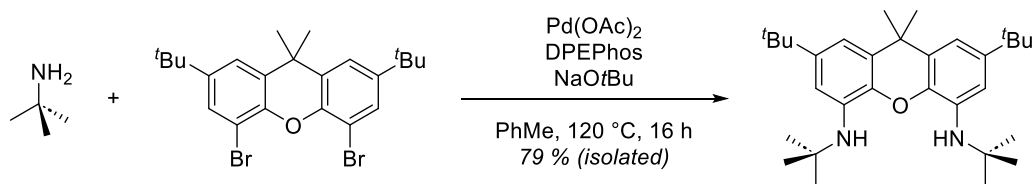
Materials and Methods

General considerations: All manipulations were performed under inert conditions using standard Schlenk and glovebox techniques. *n*-Hexane, toluene, tetrahydrofuran (thf) and diethyl ether were pre-dried using an MBraun solvent purification system, transferred to a Schlenk tube containing a sodium mirror, and sparged with Ar. Benzene and benzene- d_6 (C_6D_6) were refluxed over potassium and transferred to a Schlenk tube containing a sodium mirror for storage. Commercial *n*-butyl lithium was filtered and titrated against (-)-menthol/1,10-phenanthroline before use.^{S1} All other chemicals were used as received. $H_2(\text{DippNON})$,^{S2} $H_2(\text{TIPSNON})$,^{S3} $H_2(\text{DAS})$,^{S4} $K[\text{Fe}(\text{CO})_2\text{Cp}]$ ^{S5} (Cp = cyclopentadienyl) were synthesised according to literature.

NMR samples were prepared in a glovebox using Norell NMR tubes (5 mm) fitted with a J. Young Teflon valve. NMR spectra were recorded at 298 K (unless otherwise noted) using a Bruker Avance 800 MHz or a Bruker Avance 400 MHz spectrometer and ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra were referenced internally (^1H : 7.16 ppm (C_6D_5H), $^{13}\text{C}\{^1\text{H}\}$: 128.06 ppm). ^{29}Si NMR was referenced by adding a sealed capillary containing tetramethyl silane (TMS) in C_6D_6 to the NMR tube. Chemical shifts δ are reported in part per million (ppm), coupling constants are reported in Hertz (Hz) and coupling patterns are abbreviated as follows: m (multiplet), s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sex (sextet), sept (septet), or combinations thereof. GC-MS analysis was performed using an Agilent HP 6890 equipped with a HP5-MS column (30 m x 0.32 mm x 0.25 μm) and a 5973N inert MSD detector (EI, 70 eV). ATR IR spectra were obtained using a PerkinElmer Spectrum One. High-Resolution Mass Spectrometry was performed using a Thermo Orbitrap Elite system (Thermo Fisher Scientific, Delaware, USA) equipped with a HESI-II electron spray ionisation source (spray voltage: 2.5 kV, source heater: 300 °C) coupled to an Ultimate 3000 UHPLC (Thermo). The sample was delivered to the MS using an isocratic elution mode, the scan range was set to m/z 150-2000 at a resolution of 120 000, and the data was analysed using Thermo Freestyle software. Elemental analysis was performed by the Elemental Analysis Service of the Science Centre at London Metropolitan University, UK. Unfortunately, reliable elemental analysis results for $(\text{tBuDippNON})\text{Al-I}$ and the iron aluminyl compounds could not be obtained, possibly due to the high air and moisture sensitivity of the complexes.

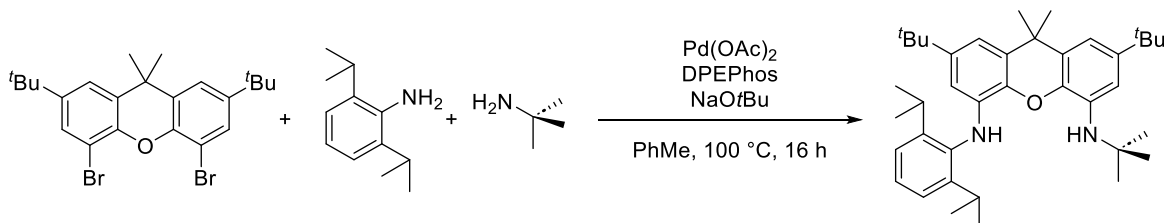
Synthetic and characterising data for new compounds

Synthesis of H₂(^tBuNON)



To a suspension of 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (9.60 g, 20.0 mmol), Pd(OAc)₂ (0.18 g, 0.80 mmol, 4 mol%), [Oxydi(2,1-phenylene)]bis(diphenylphosphane) (DPEPhos, 0.64 g, 1.2 mmol, 6 mol%), and sodium *tert*-butoxide (5.40 g, 56.0 mmol, 2.8 equiv.) in toluene (80 mL) was added *tert*-butylamine (8.4 mL, 80 mmol, 2 equiv.) in a Schlenk flask equipped with a Teflon J. Young valve under Ar. The flask was tightly sealed, and the mixture stirred at 120 °C overnight (**Caution**: pressure build-up). After cooling to room temperature, the reaction mixture was poured into water (100 mL) and extracted into toluene (3 x 150 mL). The organic phase was dried over MgSO₄, and the volatiles were removed *in vacuo* to give an amber solid, which was subsequently refluxed in methanol (100 mL) for 10 minutes. Upon cooling to 5 °C, the colourless solid was filtered off and dried to yield the titular compound. **Yield**: 79 % (7.31 g, 15.7 mmol) colourless solid. ¹H NMR (400 MHz, C₆D₆): δ = 7.12 (d, *J* = 2.2 Hz, 2H, Xanth-*p*-CH), 7.00 (d, *J* = 2.2 Hz, 2H, Xanth-*o*-CH), 4.22 (br, 2H, NH), 1.68 (s, 6H, CMe₂-CH₃), 1.38 (s, 18H, ^tBu-CH₃), 1.36 (s, 18H, ^tBu-CH₃) ppm. ¹³C{¹H} NMR (101 MHz, C₆D₆): δ = 145.3, 138.8, 135.1, 129.9, 112.4, 111.5 (Ar-C) 51.4 (N-C), 35.4 (CMe₂), 34.7 (CMe₃), 31.9 (C(CH₃)₃), 31.9 (C(CH₃)₂), 30.3 (C(CH₃)₃) ppm. **HRMS** (ESI⁺): *m/z* calcd. for [C₃₁H₄₈N₂O + H]⁺ 465.3839; found 465.3839.

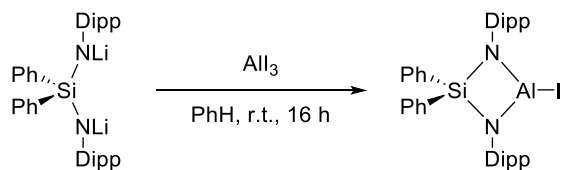
Synthesis of H₂(^tBuDippNON)



To a suspension of 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (9.60 g, 20.0 mmol), Pd(OAc)₂ (0.18 g, 0.80 mmol, 4 mol%), DPEPhos (0.64 g, 1.2 mmol, 6 mol%), and sodium *tert*-butoxide (5.40 g, 56.0 mmol, 2.8 equiv.) in toluene (80 mL) was added *tert*-butylamine (6.30 mL, 60.0 mmol, 3 equiv.) and 2,6-diisopropylaniline (3.8 mL, 20 mmol) under an argon atmosphere at

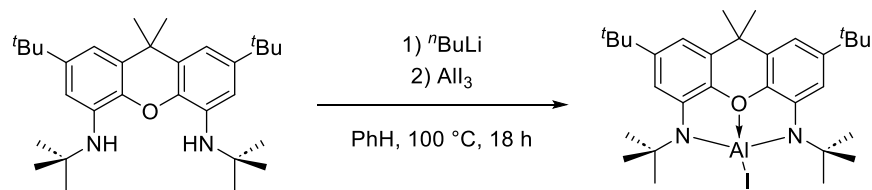
room temperature. The flask was tightly sealed, and the mixture stirred at 100 °C for 24 h (**Caution:** pressure build-up). After cooling to room temperature, the mixture was poured into water (100 mL) and extracted into toluene (3 x 100 mL). The organic layers were combined, dried over MgSO₄ and the solvent was evaporated. The crude product was purified *via* column chromatography (SiO₂, Ø 5 cm, 50 cm) using toluene and hexane (1:1). Yield: 55 % (6.30 g, 11.1 mmol) as a colourless solid. ¹H NMR (400 MHz, C₆D₆): δ = 7.30 – 7.14 (m, 4H, ArH), 7.01 (d, *J* = 2.2 Hz, 2H, Xanth-CH), 6.49 (d, *J* = 2.2 Hz, 1H, Xanth-CH), 5.93 (s, 1H, N(Dipp)H), 4.32 (br, 1H, N(^tBu)H), 3.40 (sept, *J* = 6.8 Hz, 2H, Dipp-ⁱPr-CH), 1.68 (s, 6H, CMe₂-CH₃), 1.37 (s, 9H, ^tBu-CH₃), 1.34 (s, 9H, ^tBu-CH₃), 1.24 (s, 9H, ^tBu-CH₃), 1.17 (d, *J* = 6.8 Hz, 6H, Dipp-CH₃), 1.12 (d, *J* = 6.9 Hz, 6H, Dipp-CH₃) ppm. ¹³C{¹H} NMR (101 MHz, C₆D₆): δ = 147.6, 146.1, 145.5, 139.0, 137.0, 136.3, 135.9, 135.3, 130.2, 130.1, 124.3, 112.7, 111.7, 111.5, 107.9 (Ar-C), 51.4 (N-C), 35.4 (CMe₂), 34.8, 34.8 (C(CH₃)₃), 31.9, 31.9, 31.8, 31.7, 30.3, 28.7, 25.2, 23.0 ppm. HRMS (ESI⁺): *m/z* calcd. for [C₃₉H₅₆N₂O + H]⁺ 569.4465; found 569.4467.

Synthesis of (DAS)Al-I



To a 25 mL Schlenk flask, Li₂[(NDipp)₂SiPh₂] (0.348 g, 0.64 mmol) and AlI₃ (0.147 g, 0.36 mmol) were charged. Following dissolution in benzene (10 mL), the colourless solution was stirred at room temperature for 16 h, giving a colourless precipitate. The precipitate was isolated via filtration, which was extracted with boiling benzene (10 mL). Volatiles from the light-yellow solution were removed *in vacuo* to give the title compound as a pale yellow powder. Yield: 44 % (199 mg, 0.29 mmol). ¹H NMR (800 MHz, C₆D₆, 343 K): δ = 7.54 (dd, ³*J*_{HH} = 8.1 Hz, 1.4 Hz, 4H, Ph-*o*-CH), 7.10 (d, ³*J*_{HH} = 7.6 Hz, 4H, Dipp-*m*-CH), 7.07 (tt, ³*J*_{HH} = 7.5 Hz, 1.4 Hz, 2H, Ph-*p*-CH), 7.02 (t, ³*J*_{HH} = 7.6 Hz, 4H, Ph-*m*-CH), 6.95 (t, ³*J*_{HH} = 7.6 Hz, 2H, Dipp-*p*-CH), 4.11 (h, ³*J*_{HH} = 6.7 Hz, 4H, Dipp-CH(CH₃)₂), 1.11 (d, ³*J*_{HH} = 6.8 Hz, 24H, Dipp-CH(CH₃)₂) ppm. ¹³C{¹H} NMR (201 MHz, C₆D₆): δ = 147.1, 143.4, 138.3, 136.5, 129.7, 127.5, 124.4, 122.7 (Ar-C), 28.9 (CH(CH₃)₂), 25.8 (CH(CH₃)₂) ppm. ²⁹Si NMR (79 MHz, C₆D₆): δ = -7.4 ppm (from ¹H/²⁹Si HMBC). ATR-IR (ν /cm⁻¹, nujol): 3050(w), 1591(w), 1426(m), 1368(w), 1314 (w), 1280(m), 1201(w), 1098(m), 1040(w), 929(m), 898(w), 826(m), 814(w), 793(s), 776(m), 741(m), 726(m), 704(s), 677(m), 623(w). 595(w), 540(w), 501(s), 487(m), 452(w), 432(w).

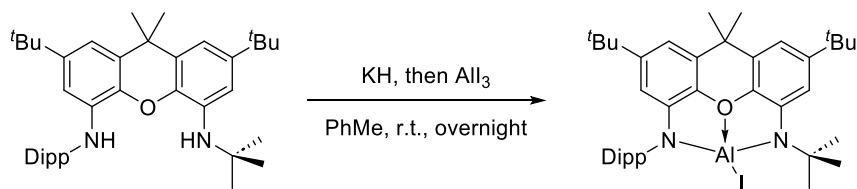
Synthesis of (^tBuNON)Al-I



Step 1) To a solution of H₂(^tBuNON) (3.32 g, 7.15 mmol) in benzene (50 mL) was added *n*-BuLi (4.5 mL, 7.2 mmol, 1.6 M in hexane) at room temperature. The suspension was stirred for one hour and the precipitate was collected by filtration. The colourless solid was dried under reduced pressure and used in the next step without further purification.

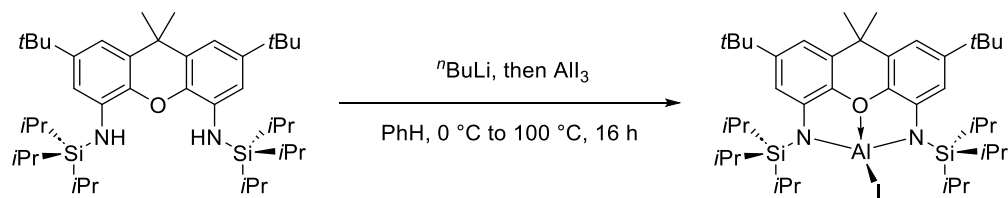
Step 2) A slurry of Li₂(^tBuNON) (3.40 g, 7.13 mmol) and AlI₃ (2.90 g, 7.11 mmol) in benzene (50 mL) was stirred for 18 h at 100 °C. After cooling to room temperature, the suspension was filtered, and the filtrate was dried *in vacuo*. The crude product was recrystallised from boiling hexane giving the titular compound as a microcrystalline colourless solid. **Yield:** 78 % (3.45 g, 5.59 mmol). X-ray quality crystals were obtained from a hot, saturated solution of the crude product in toluene, which was slowly cooled to room temperature. **¹H NMR** (400 MHz, C₆D₆): δ = 7.07 (d, *J* = 1.8 Hz, 2H, Xanth-*p*-CH), 6.61 (d, *J* = 1.7 Hz, 2H, Xanth-*o*-CH), 1.63 (s, 18H, ^tBu-CH₃), 1.52 (s, 3H, CMe₂-CH₃), 1.31 (s, 18H, ^tBu-CH₃), 1.30 (s, 3H, CMe₂-CH₃) ppm. **¹³C{¹H} NMR** (101 MHz, C₆D₆): δ = 149.6, 142.5, 140.7, 134.3, 111.8, 106.7 (Ar-C), 52.4 (N-C), 37.9 (CMe₂), 35.3 (C(CH₃)₃), 32.0, 31.1 (C(CH₃)₃), 30.6, 22.3 (CH(CH₃)₂) ppm. **Elemental Analysis** calcd. for C₃₁H₄₆AlN₂IO: C 60.39, H 7.52, N 4.54; found: C 59.65, H 7.53, N 4.39; **ATR-IR** (ν/cm⁻¹, solid): 2960 (s), 2866 (s), 1631 (s), 1574 (m), 1479 (s), 1464 (m), 1452 (m), 1415 (m), 1391 (m), 1362 (m), 1322 (m), 1299 (m), 1270 (w), 1234 (m), 1227 (m), 1208 (s), 1171 (s), 1136 (m), 1108 (m), 1047 (s), 940 (s), 855 (s), 837 (m), 802 (w), 775 (w), 745 (w), 707 (m), 696 (m), 665 (m), 638 (m), 614 (m), 606 (m), 569 (s), 518 (m), 509 (m), 489 (m), 457 (m), 431 (s).

Synthesis of (^tBuDippNON)Al-I



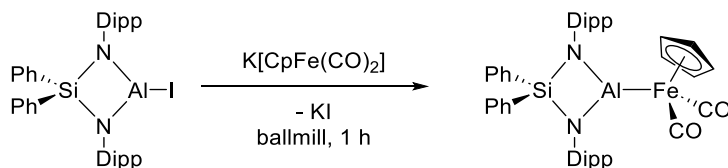
A slurry of H₂(^tBuDippNON) (2.00 g, 3.52 mmol) and KH (1.41 g, 35.2 mmol) in toluene (*ca.* 60 mL) was heated in a J. Young's flask at 120 °C for 1 h. Hydrogen was vented 3 times during this time under Ar (**Caution:** pressure build-up). Afterwards, the mixture was allowed to cool and settle for 30 min. The supernatant was filtered into a solution of AlI₃ (1.43 g, 3.52 mmol) in benzene (*ca.* 30 mL) and the mixture stirred overnight at room temperature. The solids were filtered off, and the solvent was removed from the filtrate *in vacuo*, yielding an off-white crude product (94 %, 2.39 g, 3.31 mmol). The crude product was recrystallised from hexane giving the titular compound as a colourless solid. **Yield:** 53 % (1.35 g, 1.87 mmol). Crystals suitable for single crystal X-ray diffraction were obtained from storing a saturated solution of (^tBuDippNON)Al-I in benzene for 10 days. ¹H NMR (400 MHz, C₆D₆): δ = 7.30 (dd, *J* = 7.6, 1.8 Hz, 1H, Dipp-*m*-CH), 7.23 (t, *J* = 7.6 Hz, 1H, Dipp-*p*-CH), 7.18 (d, *J* = 1.8 Hz, 1H, Dipp-*m*-CH)*, 7.09 (d, *J* = 1.8 Hz, 1H, Xanth-CH), 6.74 (d, *J* = 1.9 Hz, 1H, Xanth-CH), 6.56 (d, *J* = 1.8 Hz, 1H, Xanth-CH), 6.25 (d, *J* = 1.9 Hz, 1H, Xanth-CH), 3.93 (sept, *J* = 6.9 Hz, 1H, Dipp-ⁱPr-CH), 3.39 (sept, *J* = 6.8 Hz, 1H, Dipp-ⁱPr-CH), 1.58 (s, 9H, ^tBu-CH₃), 1.56 (d, *J* = 7.0 Hz, 3H, Dipp-ⁱPr-CH₃), 1.51 (s, 3H, CMe₂-CH₃), 1.36 (s, 3H, CMe₂-CH₃), 1.27 (s, 9H, ^tBu-CH₃), 1.20 (d, *J* = 7.0 Hz, 3H Dipp-ⁱPr-CH₃), 1.17 (s, 9H, ^tBu-CH₃), 1.14 (d, *J* = 6.8 Hz, 3H, Dipp-ⁱPr-CH₃), 0.66 (d, *J* = 6.6 Hz, 3H, Dipp-ⁱPr-CH₃) ppm. *Likely a doublet of doublets, signal overlaid by benzene ¹³C{¹H} NMR (101 MHz, C₆D₆): δ = 150.2, 149.9, 149.0, 147.3, 143.5, 142.8, 142.3, 140.4, 136.8, 134.8, 134.7, 127.7, 125.7, 124.2, 111.1, 110.2, 108.1, 107.1 (Ar-C), 51.9 (N-C), 38.4 (CMe₂), 35.3, 35.3 (C(CH₃)₃), 31.9, 31.7 (C(CH₃)₃), 30.5, 28.7, 28.4, 26.9, 26.2, 26.0, 23.9, 22.2 ppm; ATR-IR (ν /cm⁻¹, solid): 2960 (s, br), 2867 (m), 1619 (m), 1584 (m), 1498 (m), 1479 (m), 1463 (s), 1442 (s), 1415 (m), 1362 (s), 1212 (s, br), 1102 (m), 1044 (m), 1011 (w), 935 (w), 924 (w), 859 (w), 845 (m), 790 (w), 760 (w), 705 (w), 666 (w), 637 (w), 533 (m), 489 (m), 428 (m).

Synthesis of (^{TIPS}NON)Al-I



To a solution of $\text{H}_2(\text{TIPSNON})$ (1.00 g, 1.50 mmol) in benzene (15 mL) was added $n\text{-BuLi}$ (2.0 mL, 3.0 mmol, 1.5 M in hexane) at $0\text{ }^\circ\text{C}$. The mixture was left to warm to room temperature where it was stirred for a further 1 hour. A solution of aluminium iodide (0.611 g, 1.5 mmol) in benzene (20 mL) was then added at room temperature before heating the mixture to $100\text{ }^\circ\text{C}$ for 16 h. After allowing to cool to room temperature, volatiles were removed *in vacuo*, and the solid was extracted with hexane (25 mL). The solvent was removed under reduced pressure, and the compound was recrystallised from warm benzene (1.5 mL), yielding the title compound as colourless crystals suitable for single-crystal X-ray diffraction. **Yield:** 63 % (777 mg, 0.95 mmol). **^1H NMR** (400 MHz, C_6D_6): $\delta = 7.24$ (d, $J = 1.8$ Hz, 2H, Xanth-*p*-CH), 6.74 (d, $J = 1.7$ Hz, 2H, 2H, Xanth-*o*-CH), 1.65 – 1.52 (m, 6H, $\text{Si}^i\text{Pr}_3\text{-CH}$), 1.49 (s, 3H, $\text{CMe}_2\text{-CH}_3$), 1.41 – 1.34 (m, 18H, $\text{Si}^i\text{Pr}_3\text{-CH}_3$), 1.33 (s, 3H, $\text{CMe}_2\text{-CH}_3$), 1.32 (s, 18H, ${}^t\text{Bu-CH}_3$), 1.27 (d, $J = 7.5$ Hz, 18H, $\text{Si}^i\text{Pr}_3\text{-CH}_3$) ppm. **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, C_6D_6): $\delta = 149.6$, 144.2, 141.4, 134.8, 115.5, 109.8 (Ar-C), 37.8 (CMe_2) 35.4 ($\text{C}(\text{CH}_3)_3$), 32.0, 31.9, ($\text{C}(\text{CH}_3)_3$), 30.3, 22.2 ($\text{C}(\text{CH}_3)_2$), 20.1, 19.8, 19.7 ($\text{Si-CH}(\text{CH}_3)_2$), 16.6, 16.5 (Si-CH) ppm. **$^{29}\text{Si}\{^1\text{H}\}$ NMR** (79 MHz, C_6D_6 , TMS standard): $\delta = 8.3$ ppm. **Elemental Analysis** calcd. for $\text{C}_{41}\text{H}_{70}\text{AlN}_2\text{IO}\cdot\text{C}_6\text{H}_6$: C 63.06, H 8.56, N 3.13; found: C 63.28, H 9.03, N 3.15; **ATR-IR** (ν/cm^{-1} , solid): 2960 (m), 2948 (m), 2865 (m), 1624 (m), 1578 (w), 1476 (m), 1446 (m), 1412 (w), 1363 (m), 1303 (m, br), 1216 (m), 1172 (m), 1128 (w), 1099 (m), 1018 (s), 950 (w), 927 (w), 913 (w), 882 (s), 869 (s), 852 (s), 745 (w), 697 (s), 692 (s), 666 (m), 639 (s), 608 (w), 596 (m), 561 (m), 514 (s), 477 (m), 420 (s).

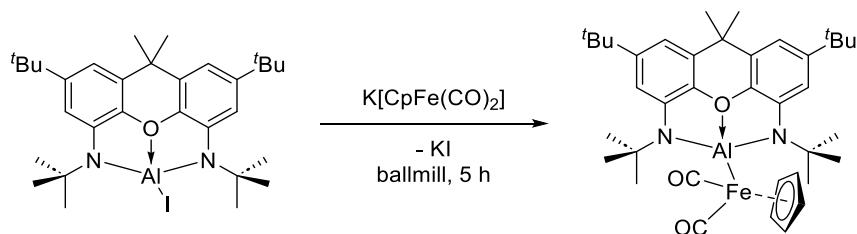
Synthesis of (DAS)AlFp



Mechanochemical synthesis: (DAS)Al-I (200 mg, 0.291 mmol) and K[CpFe(CO)₂] (0.630 g, 2.91 mmol) were charged into a 20 mL polypropylene vessel with stainless steel balls (30 pieces, diameter: 5 mm, weight per ball: 0.52 g). Milling was initiated on the highest setting (4000 rpm, 66.7 Hz) for 1 h using an IKA ULTRA-TURRAX® Tube Drive, which gave a light brown powder. Analysis of this powder by ¹H NMR Spectroscopy confirmed the quantitative preparation of (DAS)AlFp. Isolation of the powder from the polypropylene vessel, followed by extraction with benzene (3 x 4 mL) yielded a dark red solid. This solid was washed with cold hexane (3 x 3 mL), giving (DAS)AlFp as an off-white solid (0.146 g, 68%).

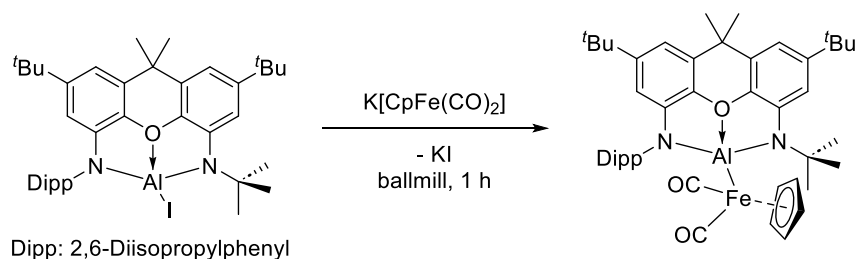
Solution phase synthesis: To a 25 mL Schlenk flask, (DAS)Al-I (200 mg, 0.29 mmol) and K[CpFe(CO)₂] (63 mg, 0.29 mmol) were charged. Following the addition of benzene (10 mL), the reaction mixture was stirred for 19 h at room temperature. A transparent brown-red solution was separated from a colourless precipitate *via* canular filtration. Volatiles from the filtrate were removed *in vacuo* yielding a brown-red foam-like solid. This solid was dissolved in cyclohexane (3 mL), and the resultant brown solution was concentrated under reduced pressure (*ca.* 0.5 mL) and left to stand at room temperature overnight, giving (DAS)AlFp as colourless blocks suitable for single crystal X-ray diffraction. Yield: 61% (0.131 g, 0.18 mmol). ¹H NMR (400 MHz, C₆D₆): δ = 7.50 (d, ³J_{HH} = 6.2 Hz, 4H, Ph-*o*-CH), 7.18 (d, ³J_{HH} = 7.4 Hz, 4H, Dipp-*m*-CH), 7.01 – 7.13 (m, 8H, Dipp-*p*-CH, Ph-*m*-CH, Ph-*p*-CH), 4.12 (s, 5H, CpH₅), 4.09 (h, ³J_{HH} = 6.8 Hz, 4H, Dipp-CH(CH₃)₂), 1.37 (d, ³J_{HH} = 6.9 Hz, 12H, Dipp-CH(CH₃)₂), 0.90 (d, ³J_{HH} = 6.7 Hz, 12H, Dipp-CH(CH₃)₂) ppm. ¹³C{¹H} NMR (101 MHz, C₆D₆): δ = 212.6 (CO), 144.8, 142.5, 138.1, 135.7, 129.6, 127.5, 123.8, 123.3 (Ar-C), 80.6 (Cp-C), 29.3 (CH(CH₃)₂), 25.6, 23.9 (CH(CH₃)₂) ppm. ²⁹Si{¹H} NMR (79 MHz, C₆D₆): δ = -29.5 ppm. ATR-IR (ν /cm⁻¹, nujol): 3070(w), 3051(w), 2001(s), 1957(s), 1943(s), 1785(w), 1588(w), 1427(m), 1381(w), 1312(m), 1251(m), 1203(m), 1100(m), 1041(w), 931(m), 827(s), 782(s), 740(w) 727(m), 708(m), 700(m), 682(w), 643(m), 587(s), 532(m), 501(s), 485(m), 456(m), 435(w).

Synthesis of (^tBuNON)AlFp



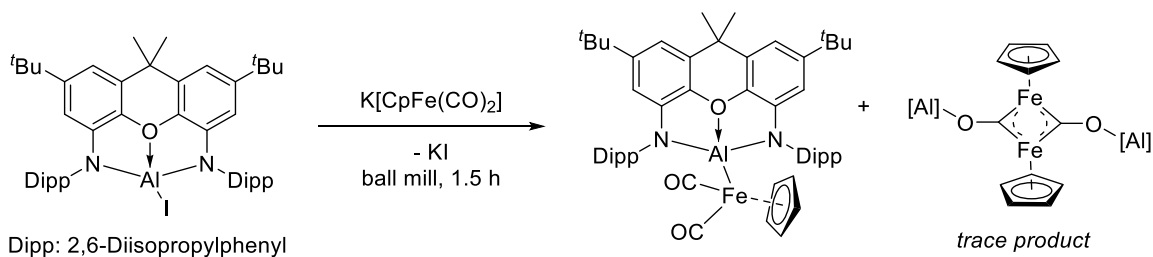
(^tBuNON)Al-I (0.205 g, 0.33 mmol), K[CpFe(CO)₂] (0.079 g, 0.36 mmol) and graphite (0.284 g) were combined in a 20 mL polypropylene vessel with stainless steel balls (30 pieces, diameter: 5 mm, weight per ball: 0.52 g). Milling was commenced for 5 h (4000 rpm, 66.7 Hz) using an IKA ULTRA-TURRAX® Tube Drive. Afterwards, the resultant powder was transferred to a Schlenk flask and extracted using toluene (20 mL). The suspension was filtered, and the volatiles were removed from the filtrate under reduced pressure. Hexane (7.5 mL) was added, and the powder was gently heated until fully dissolved. Storage of this solution at 5 °C led to the formation of (^tBuNON)AlFp as colourless crystals suitable for single-crystal X-ray diffraction. Further concentrating the supernatant gave the titular compound in a yield of 33 % (75 mg, 0.11 mmol). ¹H NMR (400 MHz, C₆D₆): δ = 7.08 (s, 2H, Xanth-*p*-CH), 6.62 (s, 2H, Xanth-*o*-CH), 4.33 (s, 5H, CpH), 1.69 (s, 21H, ^tBu-CH₃ and CMe₂-CH₃), 1.62 (s, 3H, CMe₂-CH₃), 1.32 (s, 18H, ^tBu-CH₃) ppm. ¹³C{¹H} NMR (101 MHz, C₆D₆): δ = 218.1 (CO), 149.1, 144.6, 142.5, 135.0, 111.4, 105.2 (Ar-C), 81.9 (Cp-C), 52.4 (N-C), 38.4 (CMe₂), 35.3 (C(CH₃)₃), 32.0, 31.4 (C(CH₃)₃), 30.9, 22.7 (C(CH₃)₂) ppm. ATR-IR (ν /cm⁻¹, solid): 2955 (m, br), 2866 (w), 1972 (s), 1909 (s), 1754 (m), 1623 (m), 1573 (m), 1477 (m), 1204 (m), 1169 (m), 1045 (m), 929 (m), 828 (m), 655 (m), 593 (s).

Synthesis of (^tBu^{Dipp}NON)AlFp



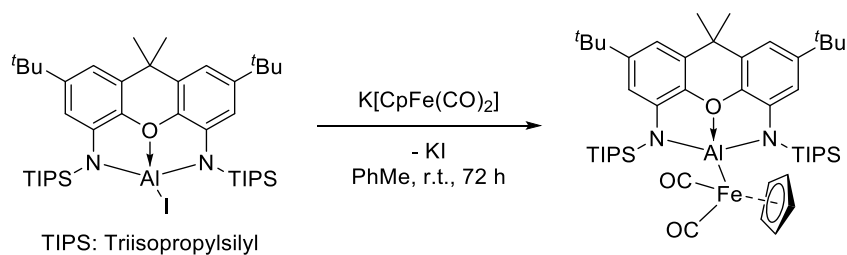
(^tBu^{Dipp}NON)Al-I (0.361 mg, 0.50 mmol) and K[CpFe(CO)₂] (0.108 g, 0.50 mmol) were combined in a 20 mL polypropylene vessel with stainless steel balls (30 pieces, diameter: 5 mm, weight per ball: 0.52 g). Milling was commenced for 1 h (4000 rpm, 66.7 Hz) using an IKA ULTRA-TURRAX® Tube Drive. Afterwards, the resultant powder (340 mg) was transferred to a Schlenk flask and extracted using toluene (20 mL). The suspension was filtered, and the volatiles were removed from the filtrate under reduced pressure. The residue was recrystallised from a 4:1 mixture of hexane and toluene (*ca.* 5mL), yielding (^tBu^{Dipp}NON)AlFp as a beige solid. Yield: 40% (0.156 g, 0.20 mmol). Single crystals suitable for X-ray diffraction were obtained by storing a concentrated solution in benzene at 5 °C overnight. ¹H NMR (400 MHz, C₆D₆): δ = 7.34 (t, *J* = 4.7 Hz, 1H, Dipp-*p*-CH), 7.24 (d, *J* = 4.7 Hz, 2H, Dipp-*m*-CH), 7.17 (d, *J* = 1.8 Hz, 1H, Xanth-CH), 6.74 (d, *J* = 1.9 Hz, 1H, Xanth-CH), 6.64 (d, *J* = 1.8 Hz, 1H, Xanth-CH), 6.17 (d, *J* = 1.8 Hz, 1H, Xanth-CH), 4.32 (s, 5H, CpH), 3.80 (sept, *J* = 6.7 Hz, 1H, Dipp-ⁱPr-CH), 3.63 (sept, *J* = 6.2 Hz, 1H, Dipp-ⁱPr-CH), 1.78 (s, 3H, CMe₂-CH₃), 1.71 (s, 3H, CMe₂-CH₃), 1.69 (s, 9H, ^tBu-CH₃), 1.55 (d, *J* = 6.8 Hz, 3H, Dipp-ⁱPr-CH₃), 1.34 – 1.30 (m, 12H, Dipp-ⁱPr-CH₃ and ^tBu-CH₃), 1.27 (d, *J* = 6.8 Hz, 3H, Dipp-ⁱPr-CH₃), 1.18 (s, 9H, ^tBu-CH₃), 0.66 (d, *J* = 6.5 Hz, 3H, Dipp-ⁱPr-CH₃) ppm. ¹³C{¹H} NMR (101 MHz, C₆D₆): δ = 216.7, 216.2 (CO), 149.5, 148.9, 148.4, 147.2, 144.8, 144.5, 143.8, 141.8, 140.9, 135.7, 134.8, 126.9, 125.2, 124.4, 110.9, 110.7, 106.8, 105.7 (Cp-C), 82.2 (Cp-C), 52.1 (N-C), 38.7 (CMe₂), 35.3, 35.3 (C(CH₃)₃), 32.0, 31.8 (C(CH₃)₃), 30.7, 30.3, 28.6, 28.1, 27.0, 26.6, 24.8, 24.4, 22.4 ppm. ATR-IR (ν /cm⁻¹, solid): 2963 (s, br), 2867 (m), 1962 (s), 1900 (s), 1621 (m), 1459 (m), 1441 (m), 1362 (m), 1212 (s), 846 (m), 656 (m), 590 (m), 425 (m).

Synthesis of (^{DippNON})AlFp



(^{DippNON})Al-I (0.825 g, 1.00 mmol) and K[CpFe(CO)₂] (0.216 g, 1.10 mmol) were combined in a 20 mL polypropylene vessel with stainless steel balls (30 pieces, diameter: 5 mm, weight per ball: 0.52 g). Milling was commenced for 1.5 h (4000 rpm, 66.7 Hz) using an IKA ULTRA-TURRAX® Tube Drive. Afterwards, the resultant powder (750 mg) was transferred to a Schlenk flask and extracted using pentane (40 mL). The suspension was filtered, and the volatiles were removed from the filtrate under reduced pressure. The residue was dissolved in minimal benzene and cooled to 5 °C overnight, giving (^{DippNON})AlFp as colourless crystals suitable for X-ray diffraction. **Yield:** 63 % (0.550 g, 0.63 mmol). N.B. Intense red crystals were observed in trace amounts upon storage of a more concentrated solution at 5 °C overnight, corresponding to the by-product shown in the scheme above. ¹H NMR (400 MHz, C₆D₆): δ = 7.19 (dd, *J* = 7.7, 1.9 Hz, 2H, Dipp-*p*-CH), 7.13 (d, *J* = 7.7 Hz, 2H, Dipp-*m*-CH), 7.07 (dd, *J* = 7.6, 1.9 Hz, 2H, Dipp-*m*-CH), 6.71 (d, *J* = 1.8 Hz, 2H, Xanth-*p*-CH), 6.44 (d, *J* = 1.9 Hz, 2H, Xanth-*o*-CH), 4.22 (s, 5H, CpH), 3.85 (sept, *J* = 6.9 Hz, 2H, Dipp-ⁱPr-CH), 2.71 (sept, *J* = 6.9 Hz, 2H), 1.78 (s, 3H, CMe₂-CH₃), 1.63 (s, 3H, CMe₂-CH₃), 1.36 (d, *J* = 6.6 Hz, 6H, Dipp-ⁱPr-CH₃), 1.27 (d, *J* = 6.9 Hz, 6H, Dipp-ⁱPr-CH₃), 1.16 (s, 18H, ^tBu-CH₃), 0.76 (d, *J* = 6.8 Hz, 6H, Dipp-ⁱPr-CH₃), 0.66 (s, 6H, Dipp-ⁱPr-CH₃) ppm. ¹³C{¹H} NMR (101 MHz, C₆D₆): δ = 215.2 (CO), 149.9, 147.7, 147.0, 145.7, 145.3, 142.8, 136.9, 125.8, 125.2, 124.5, 111.9, 108.2 (Ar-C), 80.8 (Cp-C), 39.7 (CMe₂), 35.2 (C(CH₃)₃), 31.7 (C(CH₃)₃), 30.3 (C(CH₃)₂), 29.0, 27.9, 26.2, 26.0, 24.6, 24.5 (Dipp-ⁱPr-C), 22.5 (C(CH₃)₂) ppm. ATR-IR (ν/cm⁻¹, Nujol): 2953 (s, br), 2855 (m), 1984 (s), 1927 (s), 1630 (m), 1459 (s), 1415 (m), 1380 (m), 1362 (m), 1324 (m, br), 1301 (m, br), 1200 (s), 1015 (s), 836 (m), 795 (m), 651 (m), 589 (m), 540 (m).

Synthesis of (^{TIPS}NON)AlFp



Solution phase synthesis: A suspension of (^{TIPS}NON)Al-I (1.00 g, 1.22 mmol) and K[CpFe(CO)₂] (0.270 g, 1.22 mmol) in benzene (30 mL) was stirred for 3 days at room temperature (an aliquot taken after 16 hours indicated approx. 50 % conversion via ¹H NMR analysis). After filtration, the volatiles were removed from the filtrate under reduced pressure giving a dark red, waxy solid. This solid was recrystallised from a mixture of 2:1 mixture of hexane and benzene (*ca.* 3 mL), giving (^{TIPS}NON)AlFp as colourless crystals suitable for X-ray diffraction. Yield: 41 % (0.435 g, 0.50 mmol).

Mechanochemical synthesis: (^{TIPS}NON)Al-I (0.204 g, 0.25 mmol), K[CpFe(CO)₂] (0.054 g, 0.25 mmol) and graphite (0.258 mg) were combined in a 20 mL polypropylene vessel with stainless steel balls (30 pieces, diameter: 5 mm, weight per ball: 0.52 g). Milling was commenced for 1 h (4000 rpm, 66.7 Hz) using an IKA ULTRA-TURRAX® Tube Drive. The resultant powder was transferred to a Schlenk flask and extracted using benzene (10 mL). The suspension was filtered, and the volatiles were removed from the filtrate under reduced pressure giving (^{TIPS}NON)AlFp as beige solid. Yield: 79 % (0.171 g, 0.20 mmol). ¹H NMR (400 MHz, C₆D₆): δ = 7.26 (d, *J* = 1.7 Hz, 2H, Xanth-*p*-CH), 6.77 (d, *J* = 1.7 Hz, 2H, Xanth-*o*-CH), 4.44 (s, 5H, CpH), 1.69 – 1.58 (m, 12H, Si^{*i*}Pr-CH and CMe₃-CH₃), 1.40 (d, *J* = 7.3 Hz, 18H, Si^{*i*}Pr-CH₃), 1.35 (s, 18H, ^{*t*}Bu-CH₃), 1.31 (d, *J* = 7.5 Hz, 18H, Si^{*i*}Pr-CH₃) ppm. ¹³C{¹H} NMR (101 MHz, C₆D₆): δ = 218.0 (CO), 148.9, 145.4, 143.6, 134.8, 116.1, 108.4 (Ar-C), 82.2 (Cp-C), 38.6 (CMe₂), 35.4 (C(CH₃)₃), 32.0 (C(CH₃)₃), 31.1, 22.6 (C(CH₃)₂), 20.6, 20.5 (SiCH(CH₃)₂), 17.9 (Si-CH) ppm. ²⁹Si{¹H} NMR (79 MHz, C₆D₆, TMS standard): δ = 6.7 ppm. ATR-IR (ν /cm⁻¹, solid): 2958 (s, br), 2865 (s), 1978 (s), 1922 (s), 1914 (s), 1623 (m), 1475 (m), 1304 (m), 1015 (s), 882 (m), 848 (m), 818 (m), 584 (s).

Attempted Synthesis of $[\text{Dipp}(\text{iPr}_3\text{Si})\text{N}]_2\text{AlFp}$

Mechanochemical synthesis attempt: $[\text{Dipp}(\text{iPr}_3\text{Si})\text{N}]_2\text{Al-I}$ (0.200 g, 0.291 mmol), $\text{K}[\text{CpFe}(\text{CO})_2]$ (0.630 g, 2.91 mmol), and graphite (0.440 g) were charged into a 20 mL polypropylene vessel with stainless steel balls (30 pieces, diameter: 5 mm, weight per ball: 0.52 g). Milling was initiated on the highest setting (4000 rpm, 66.7 Hz) for 60 mins using an IKA ULTRA-TURRAX® Tube Drive. The black powder was analysed *via* ^1H NMR spectroscopy (C_6D_6), which revealed that the major species was unreacted $[\text{Dipp}\{\text{iPr}_3\text{Si}\}\text{N}]_2\text{Al-I}$ with a small amount of pro-ligand $\text{Dipp}(\text{iPr}_3\text{Si})\text{NH}$ present. Consequential milling followed by ^1H NMR analysis at 2.5, 5, and 6 h increments identified the progressive generation of the pro-ligand *via* $[\text{Dipp}(\text{iPr}_3\text{Si})\text{N}]_2\text{Al-I}$ species degradation.

Solution phase synthesis attempt: A C_6D_6 (0.5 mL) solution of $[\text{Dipp}(\text{iPr}_3\text{Si})\text{N}]_2\text{Al-I}$ (40 mg, 0.058 mmol), $\text{K}[\text{CpFe}(\text{CO})_2]$ (10.5 mg, 0.058 mmol) was prepared in a J. Youngs NMR tube. Following a lack of reaction overnight at ambient temperature, the mixture was heated to $70\text{ }^\circ\text{C}$ for 48 h, lead to a gradual colour change toward dark-red/orange solution. Analysis of the reaction mixture *via* ^1H NMR spectroscopy revealed a mixture of $[(\text{Dipp})\text{Si}(\text{iPr})_3\text{N}]^-$ containing species in solution, but none of which matched those expected for the targeted $[\text{Dipp}(\text{iPr}_3\text{Si})\text{N}]_2\text{AlFp}$. Subsequent purification attempts were unable to separate the mixture of products, however, crystallisation afforded various decomposition products, including $[\text{Al}\{\text{N}(\text{Dipp})\text{Si}(\text{i-Pr})_2\text{CH}(\text{Me})\text{CH}_2\}\{\text{N}(\text{Dipp})\text{Si}(\text{i-Pr})_3\}]$ as colourless blocks and $[\text{CpFe}(\text{CO})(\mu\text{-CO})_2]$ as dark red plates.

NMR spectra of new compounds

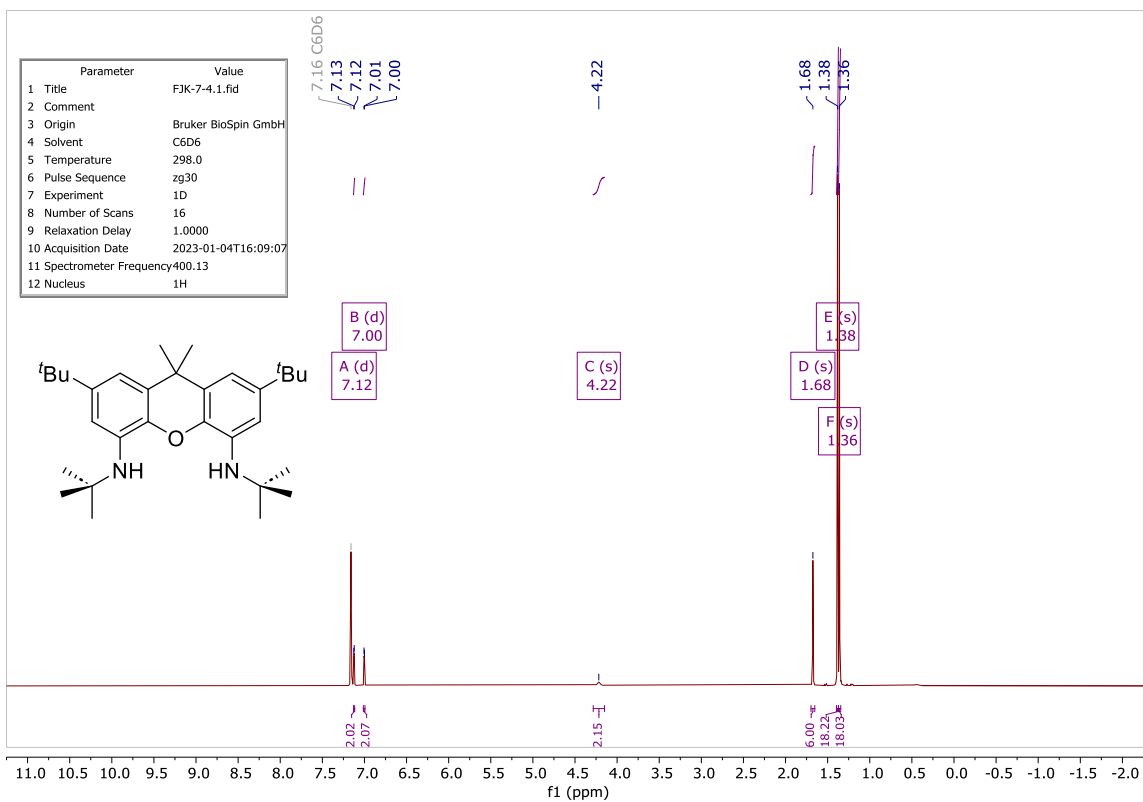


Figure S1: 1H NMR spectrum of $H_2(tBu)NON$ (400 MHz, C_6D_6 , 298 K)

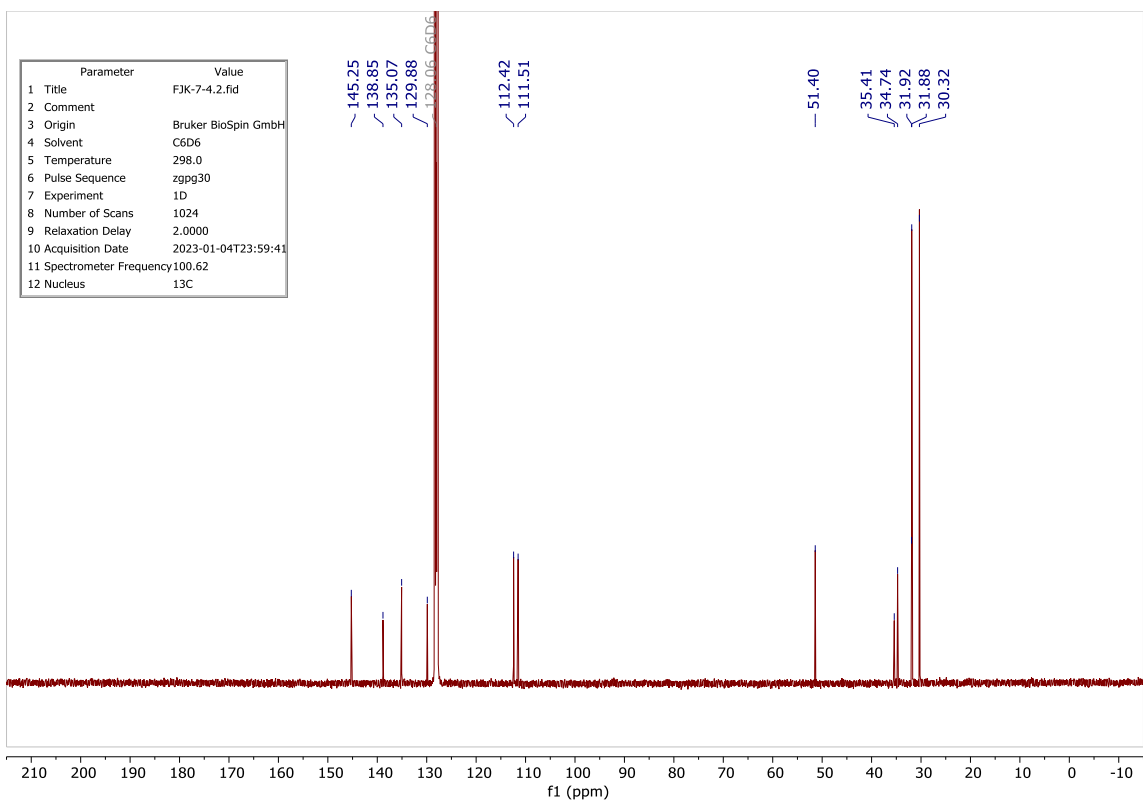


Figure S2: $^{13}C\{^1H\}$ NMR spectrum of $H_2(tBu)NON$ (101 MHz, C_6D_6 , 298 K)

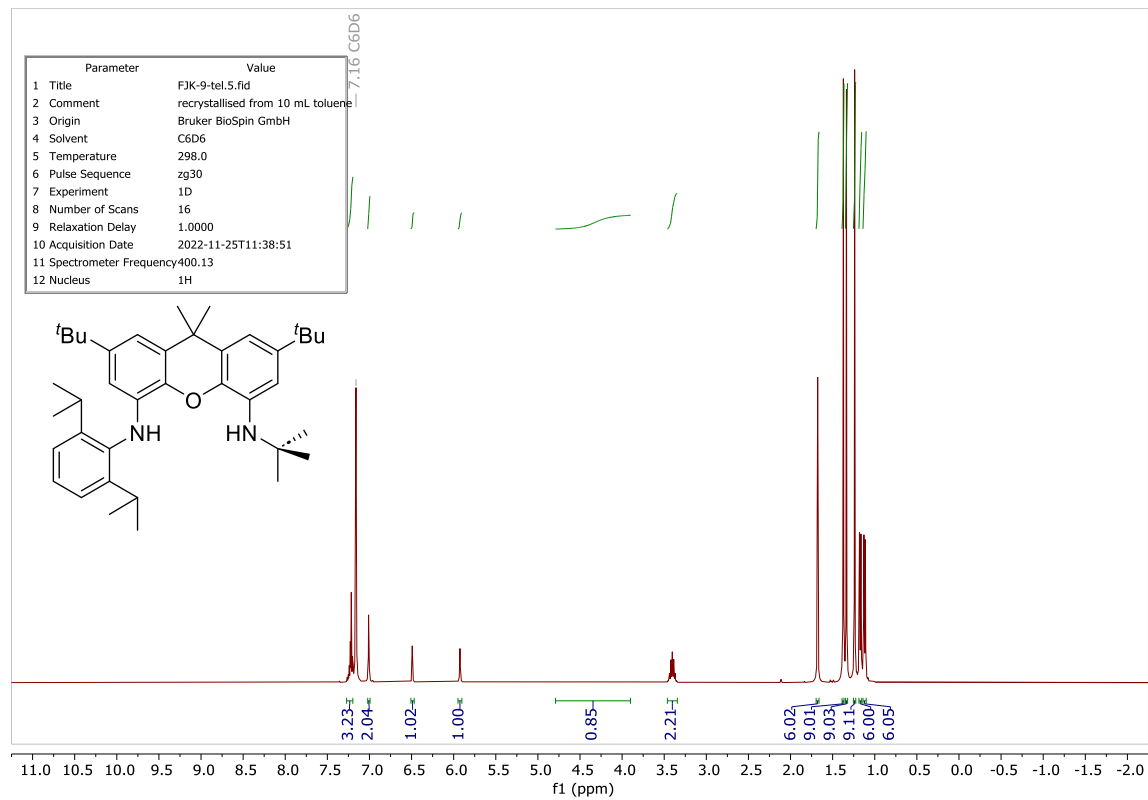


Figure S3: ^1H NMR spectrum of $\text{H}_2(\text{tBuDippNON})$ (400 MHz, C_6D_6 , 298 K)

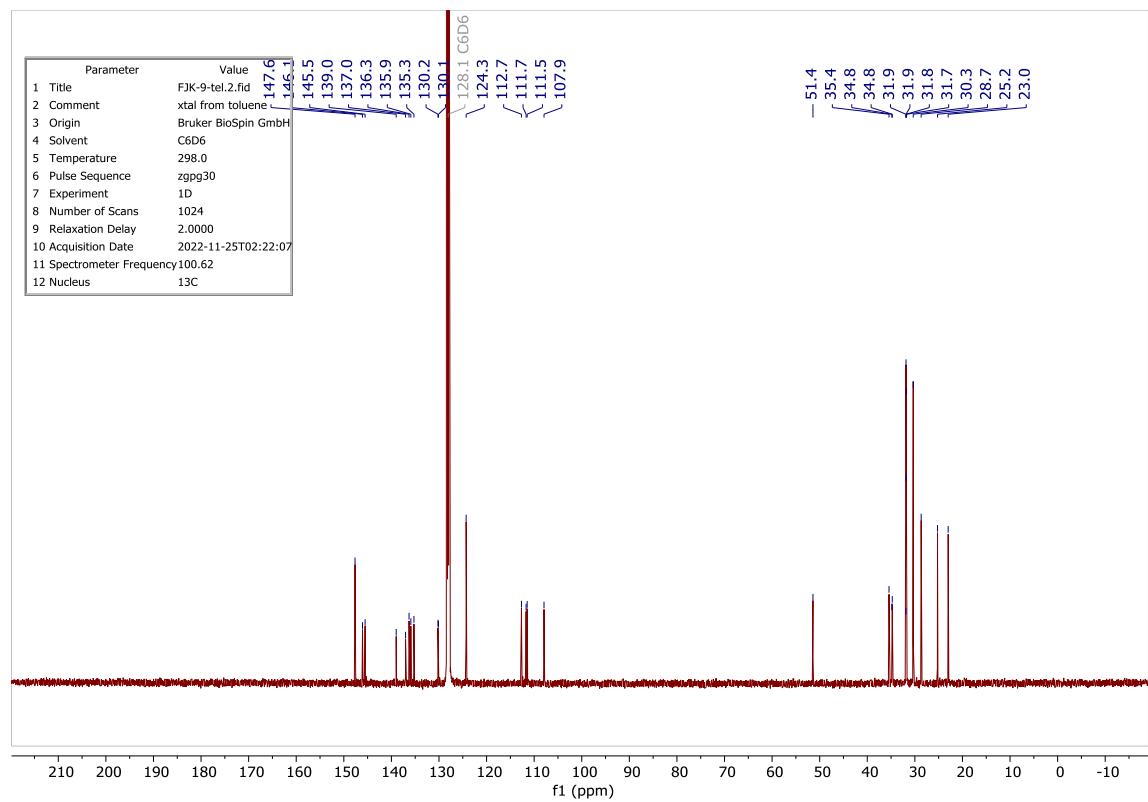


Figure S4: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{H}_2(\text{tBuNON})$ (101 MHz, C_6D_6 , 298 K)

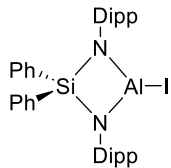
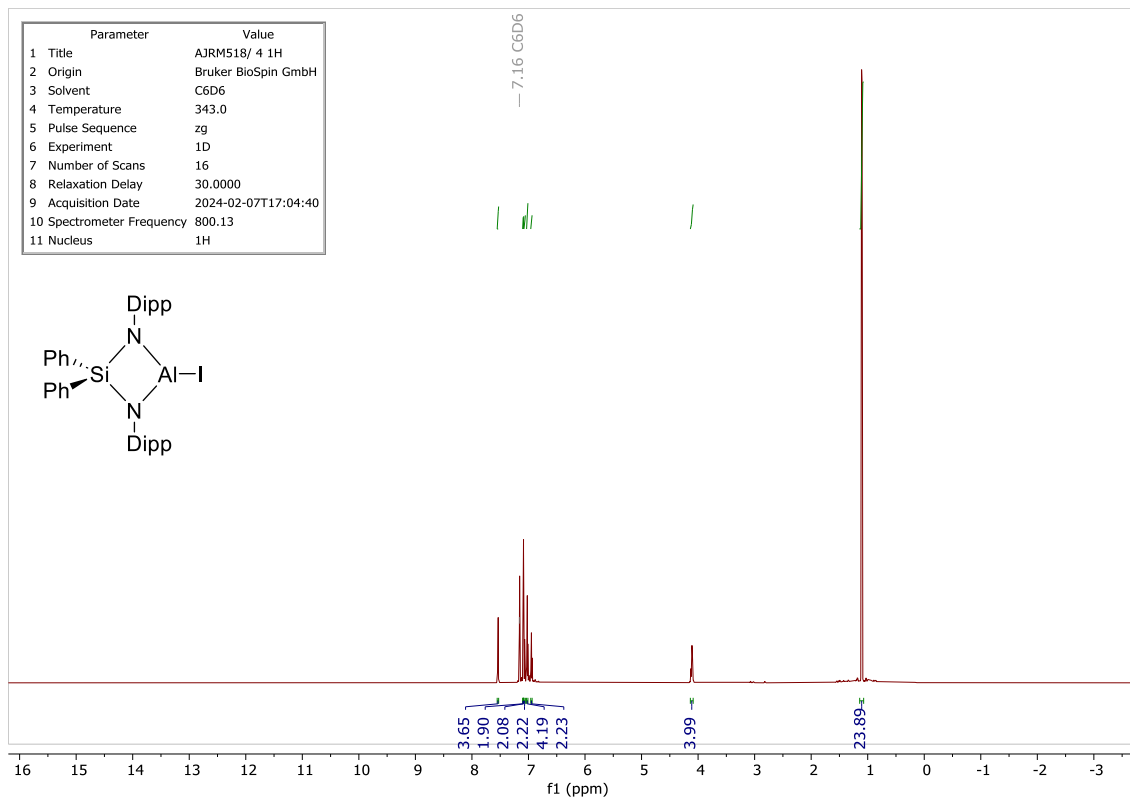


Figure S5: ^1H NMR spectrum of (DAS)Al-I (800 MHz, C_6D_6 , 298 K)

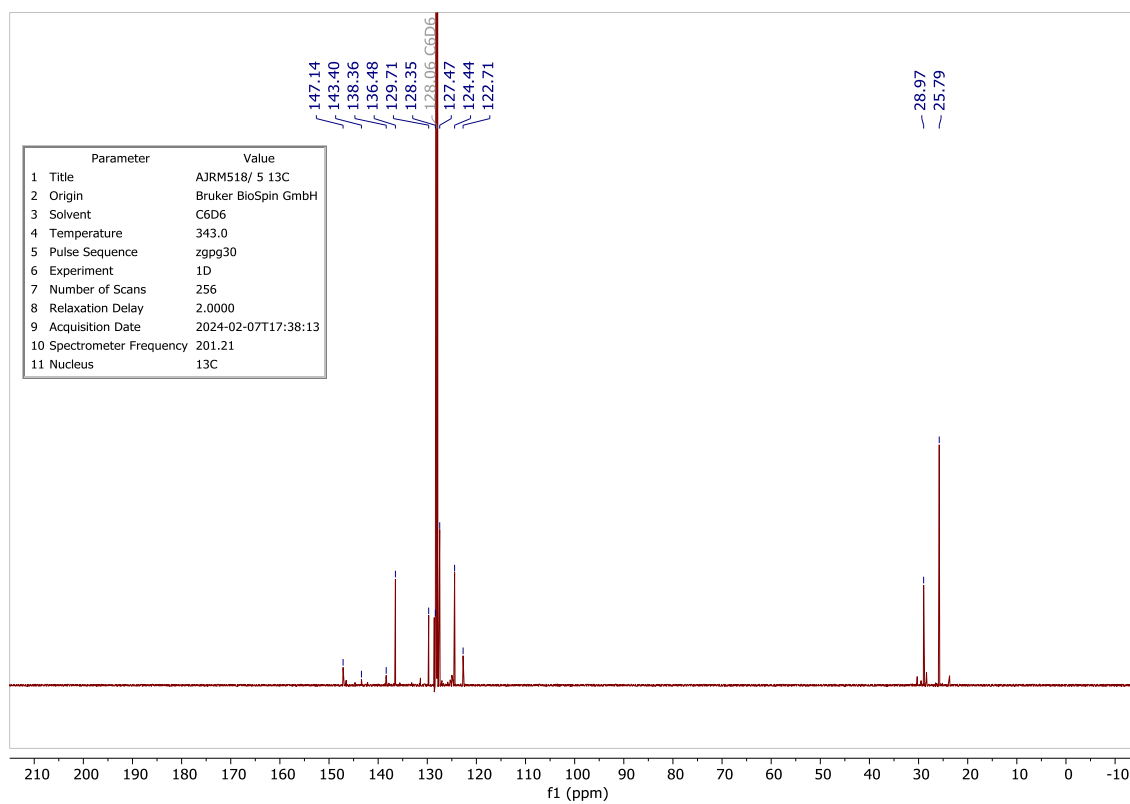
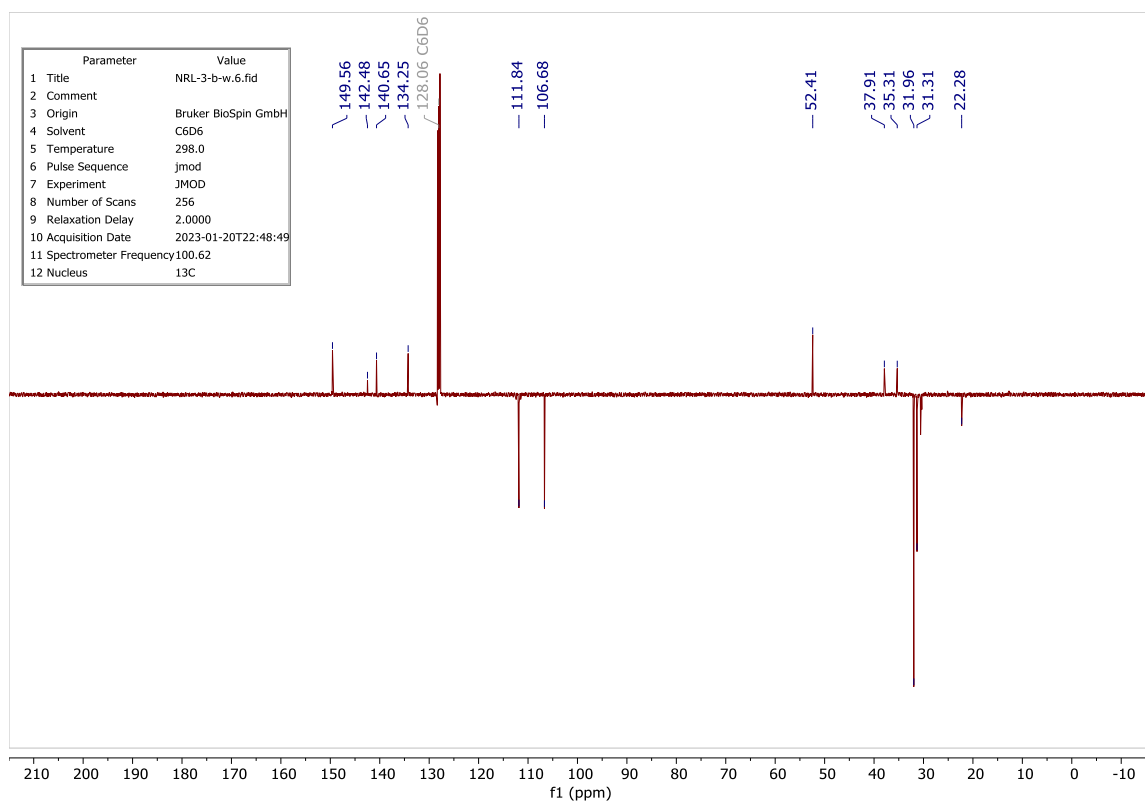
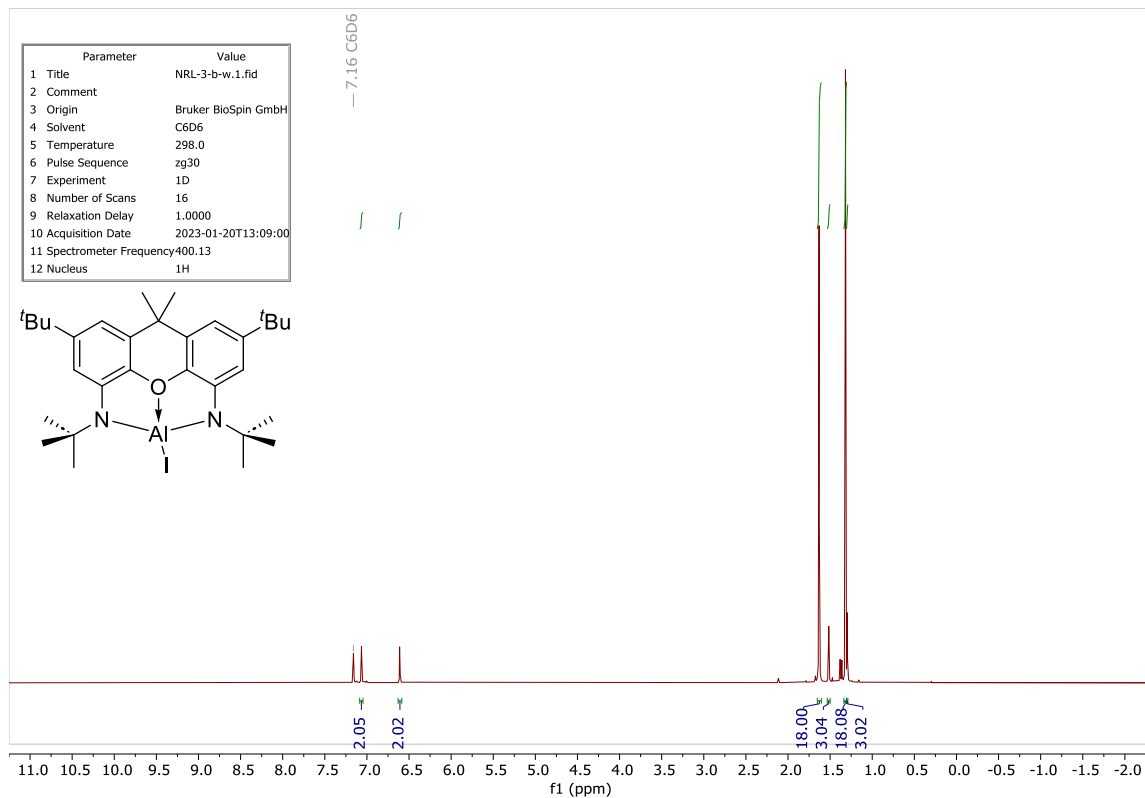


Figure S6: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (DAS)Al-I (201 MHz, C_6D_6 , 298 K)



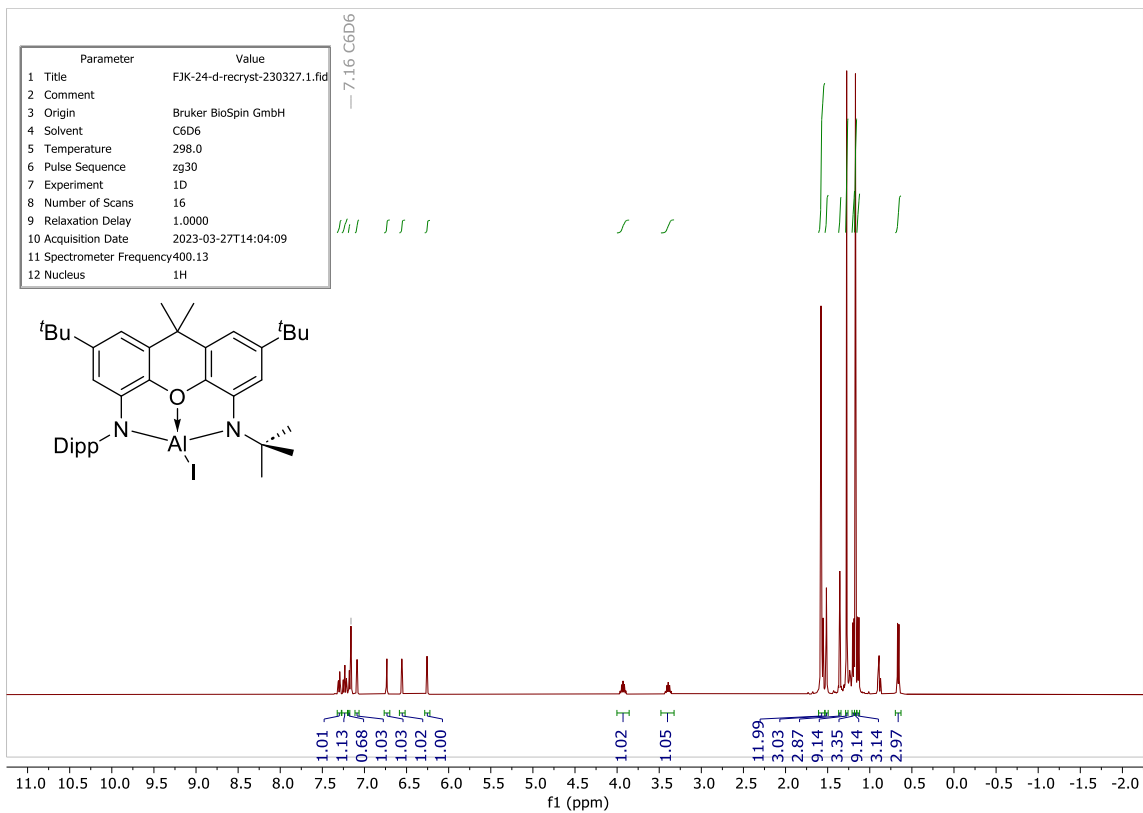


Figure S9: ^1H NMR spectrum of $(t\text{BuDippNON})\text{Al-I}$ (400 MHz, C_6D_6 , 298 K)

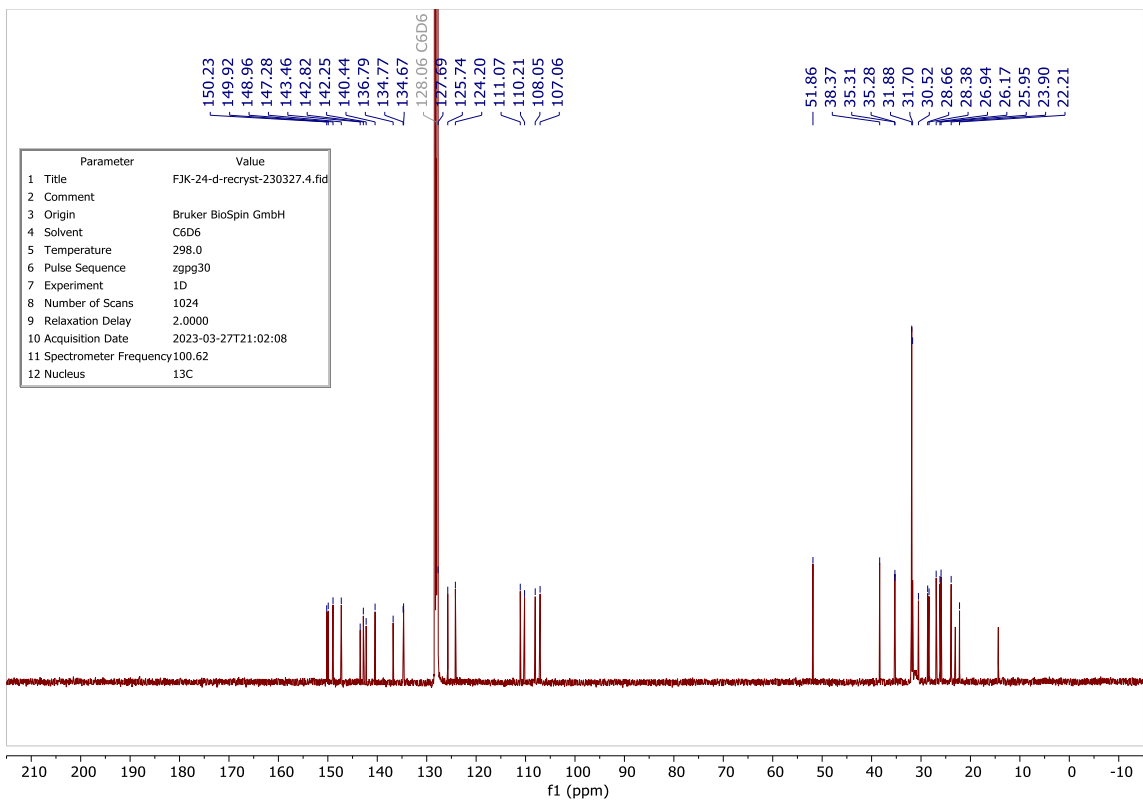


Figure S10: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $(t\text{BuDippNON})\text{Al-I}$ (101 MHz, C_6D_6 , 298 K)

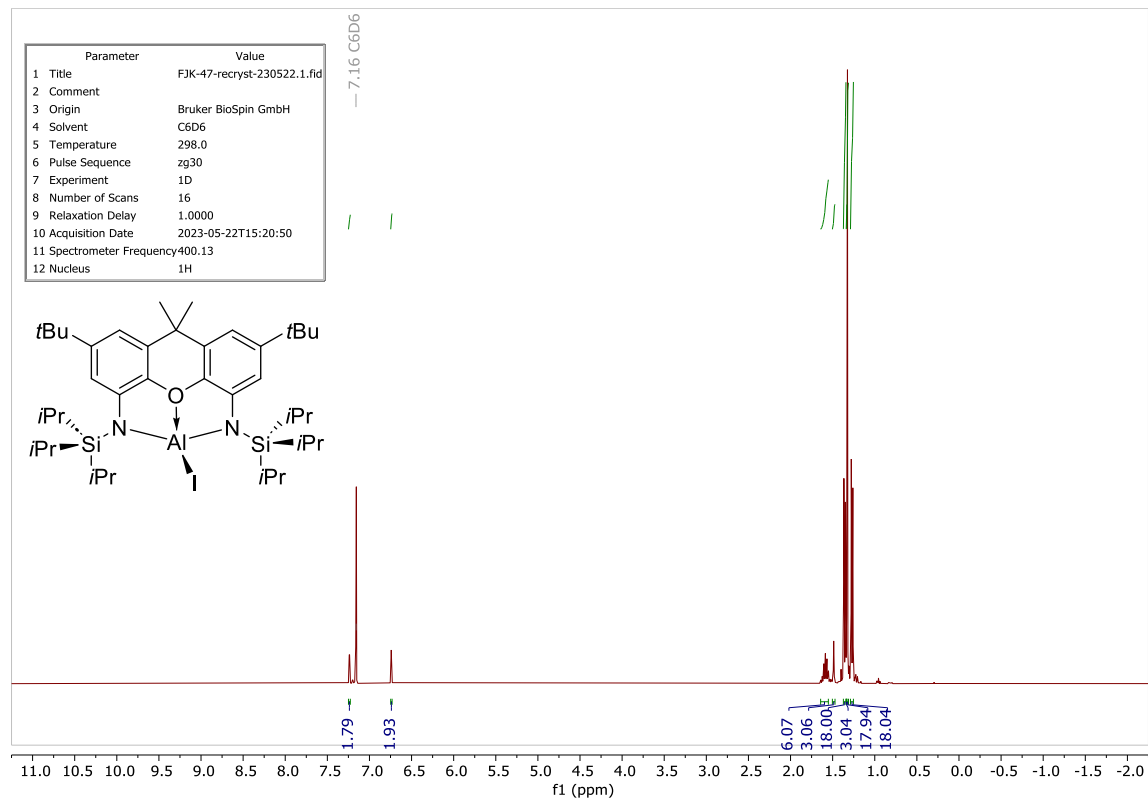


Figure S11: ¹H NMR spectrum of (^{TIPSON})Al-I (400 MHz, C₆D₆, 298 K)

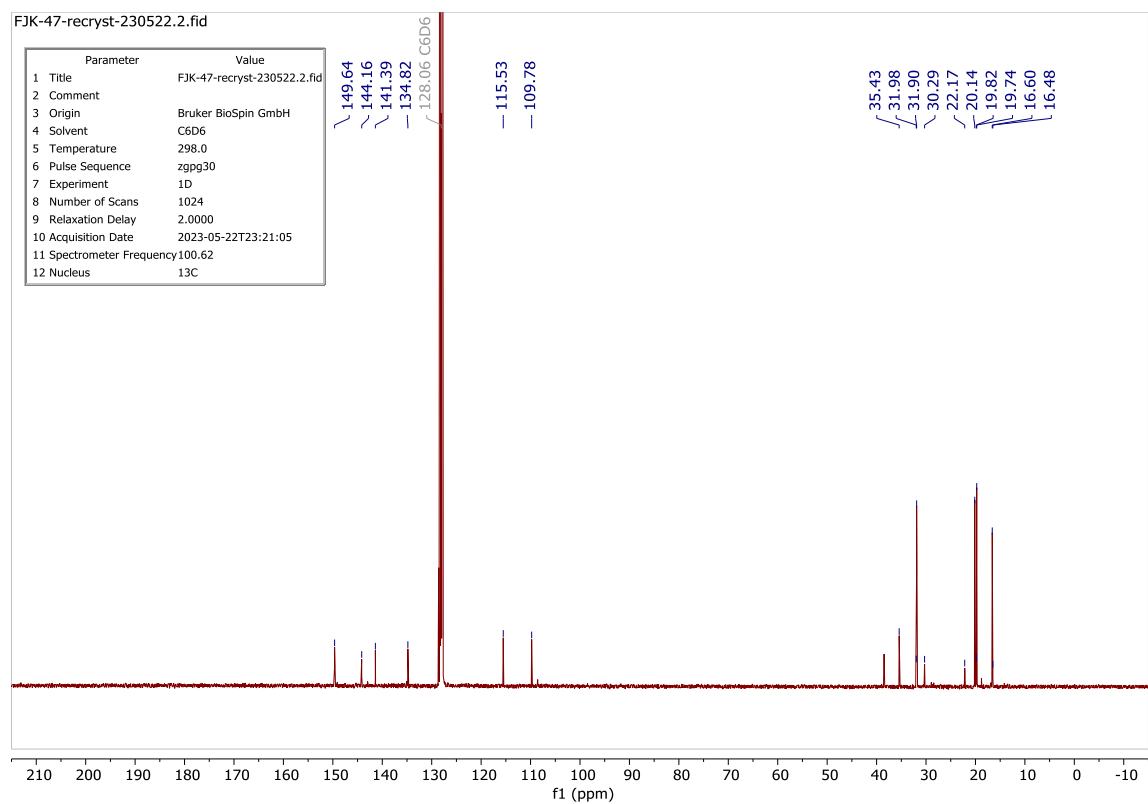


Figure S12: ¹³C{¹H} NMR spectrum of (^{TIPSON})Al-I (101 MHz, C₆D₆, 298 K)

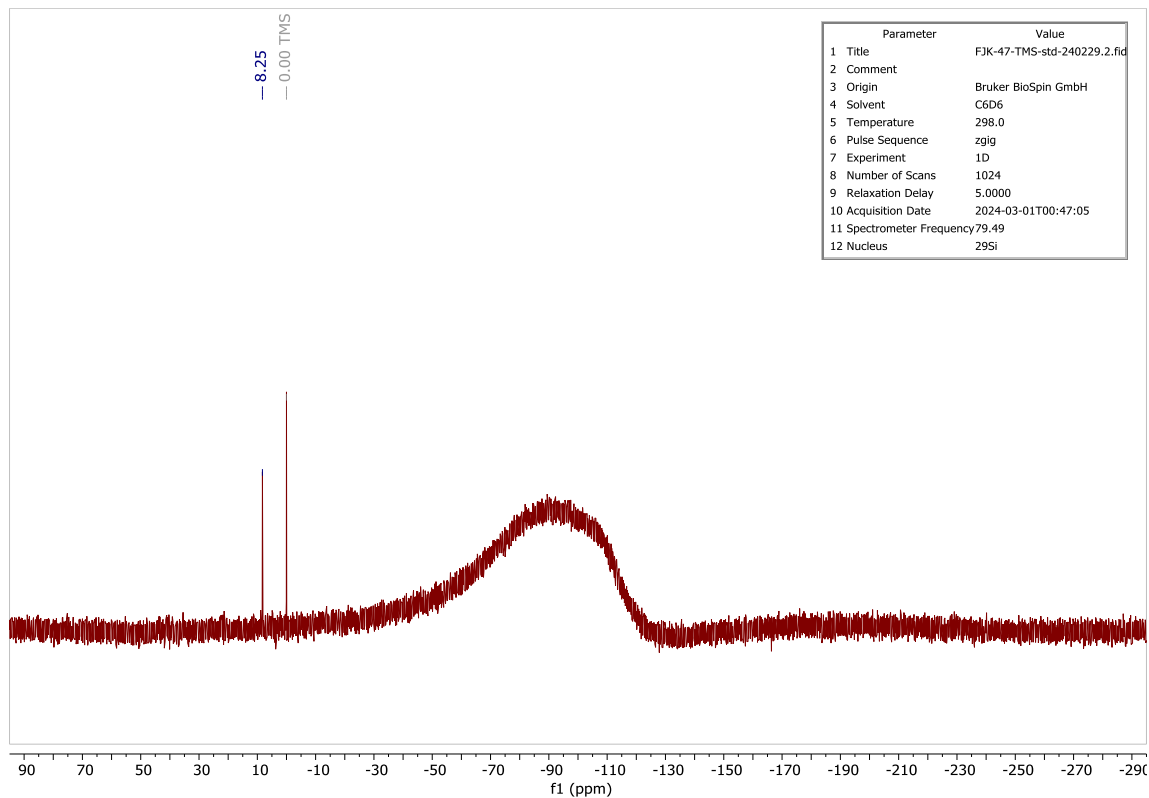


Figure S13: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of $(^{\text{TIPSON}}\text{Al-I})$ (80 MHz, C_6D_6 , 298 K)

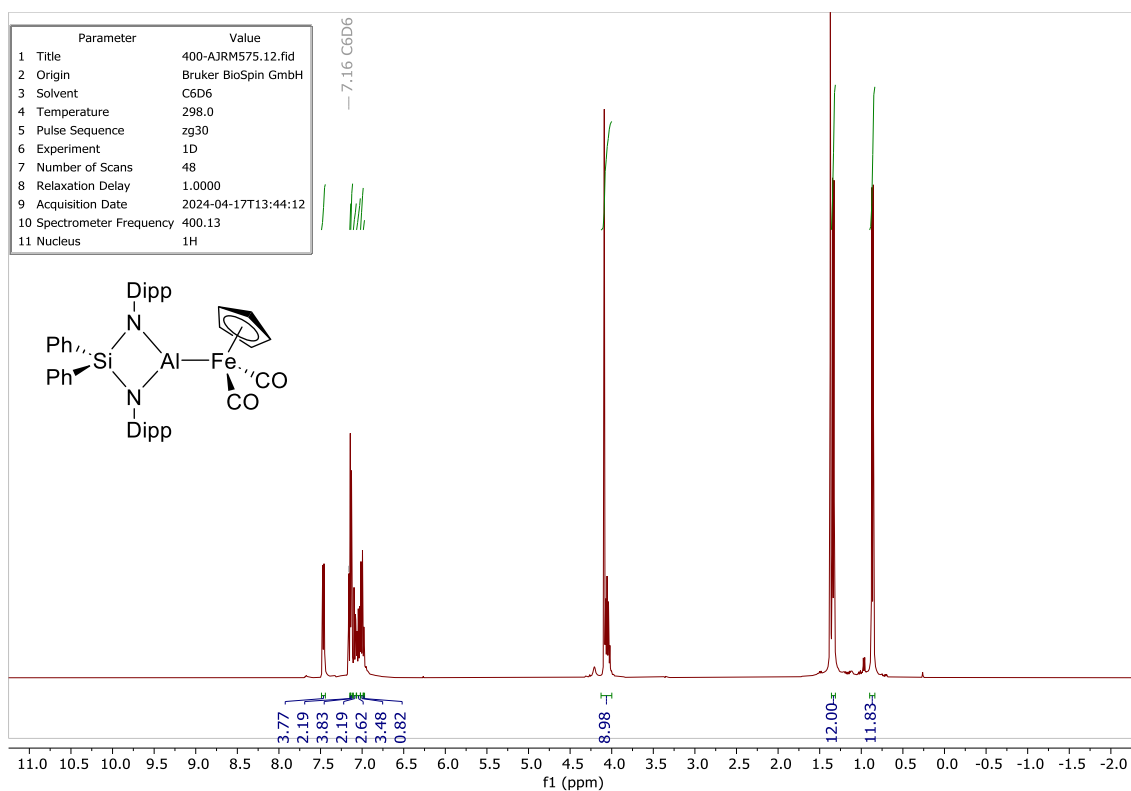


Figure S14: ^1H NMR spectrum of $(\text{DAS})\text{AlFp}$ (400 MHz, C_6D_6 , 298 K)

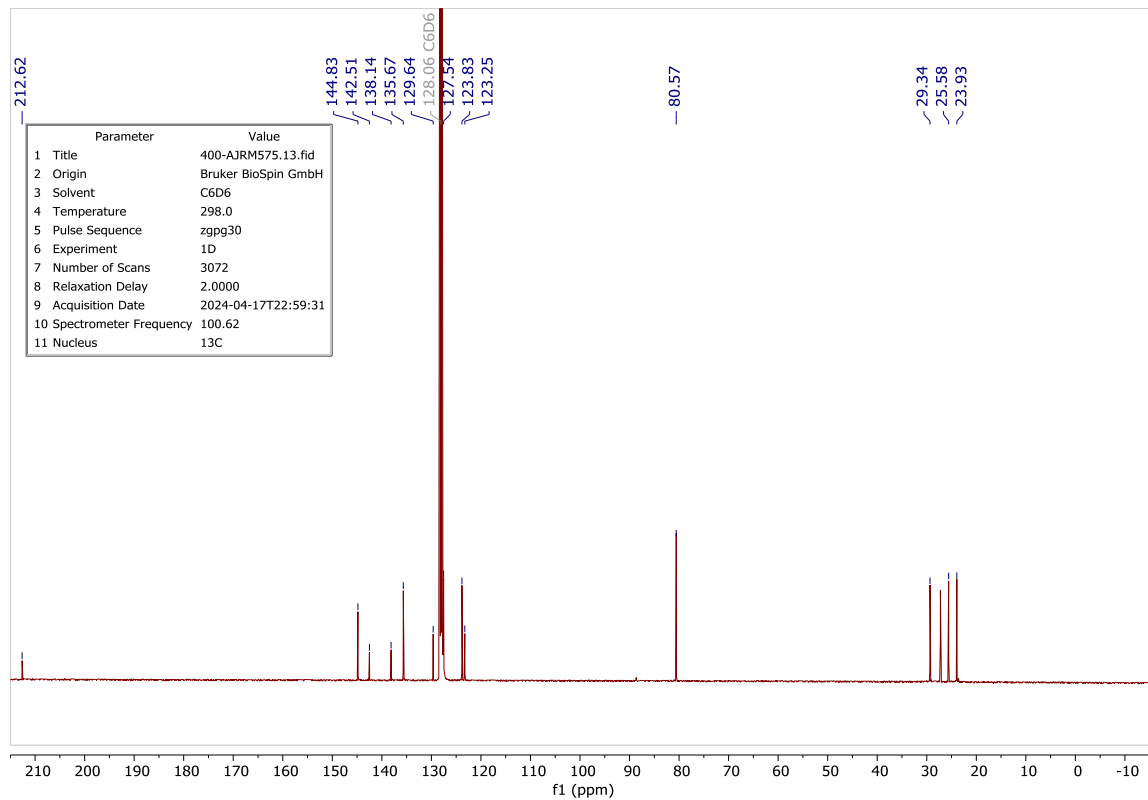


Figure S15: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (DAS)AlFp (101 MHz, C_6D_6 , 298 K)

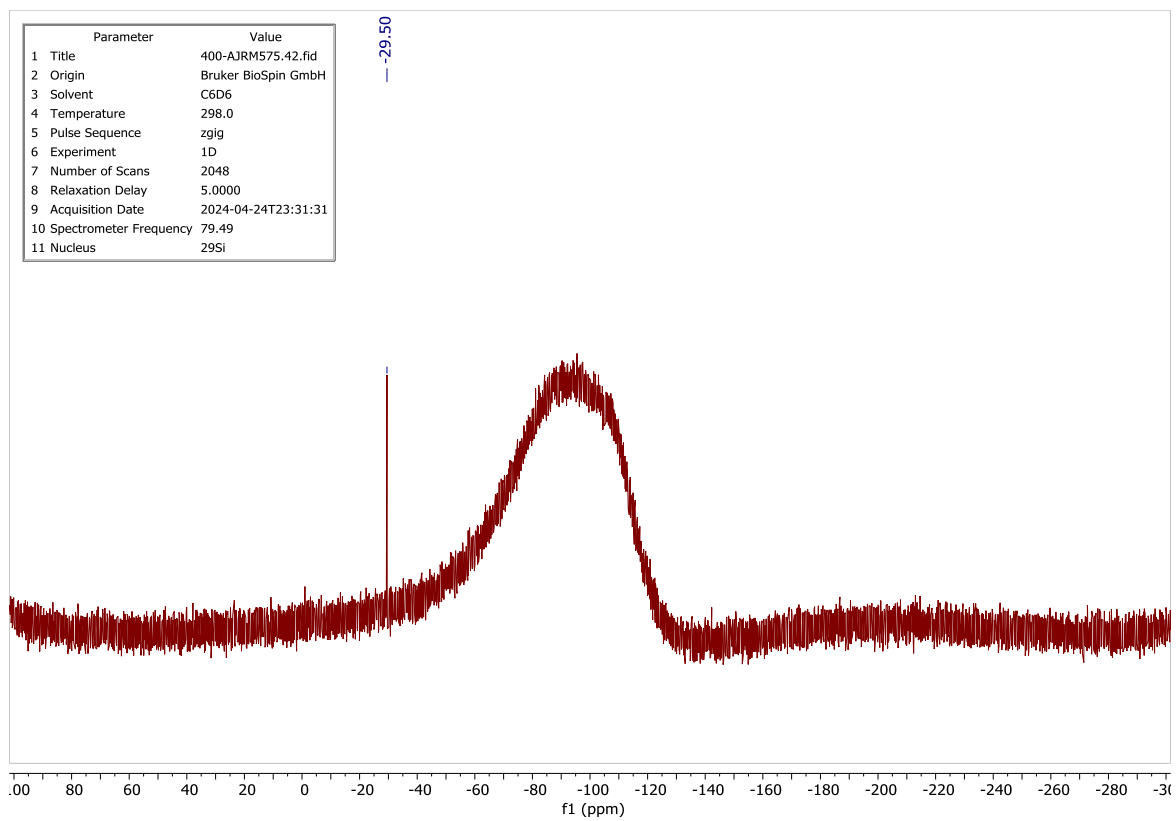


Figure S16: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of (DAS)AlFp (79 MHz, C_6D_6 , 298 K)

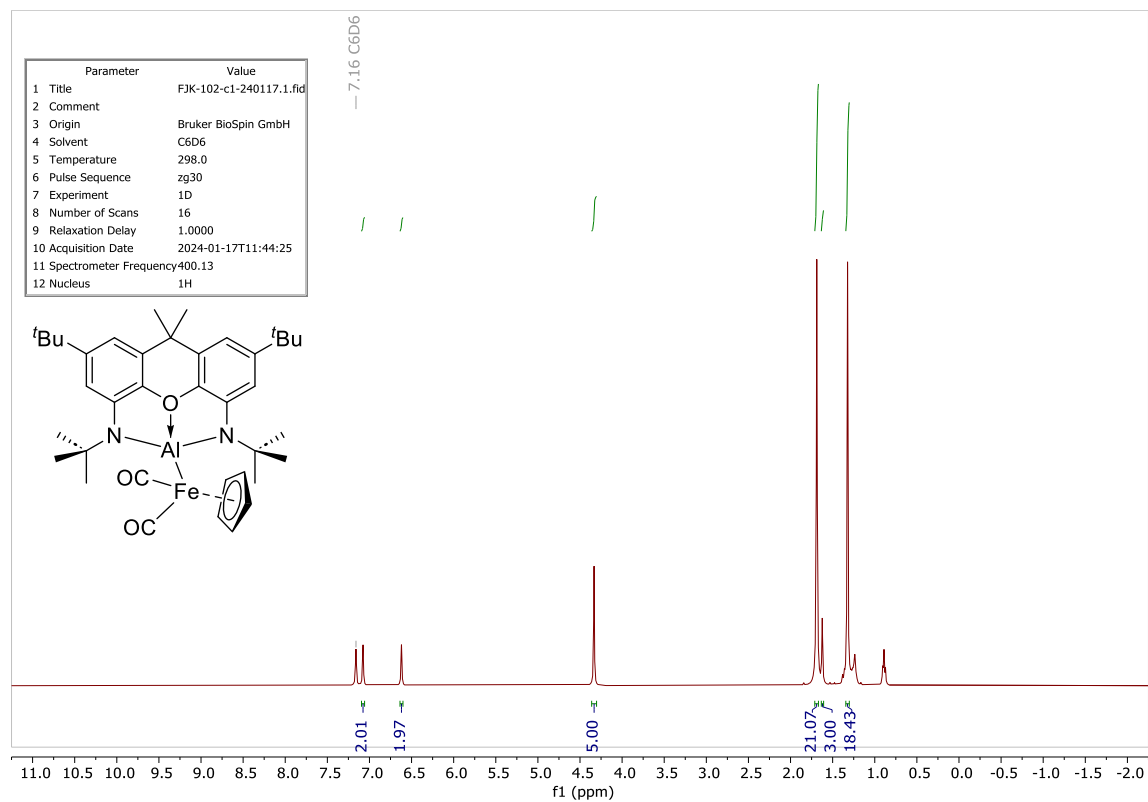


Figure S17: ^1H NMR spectrum of $(t\text{BuNON})\text{AlFp}$ (400 MHz, C_6D_6 , 298 K)

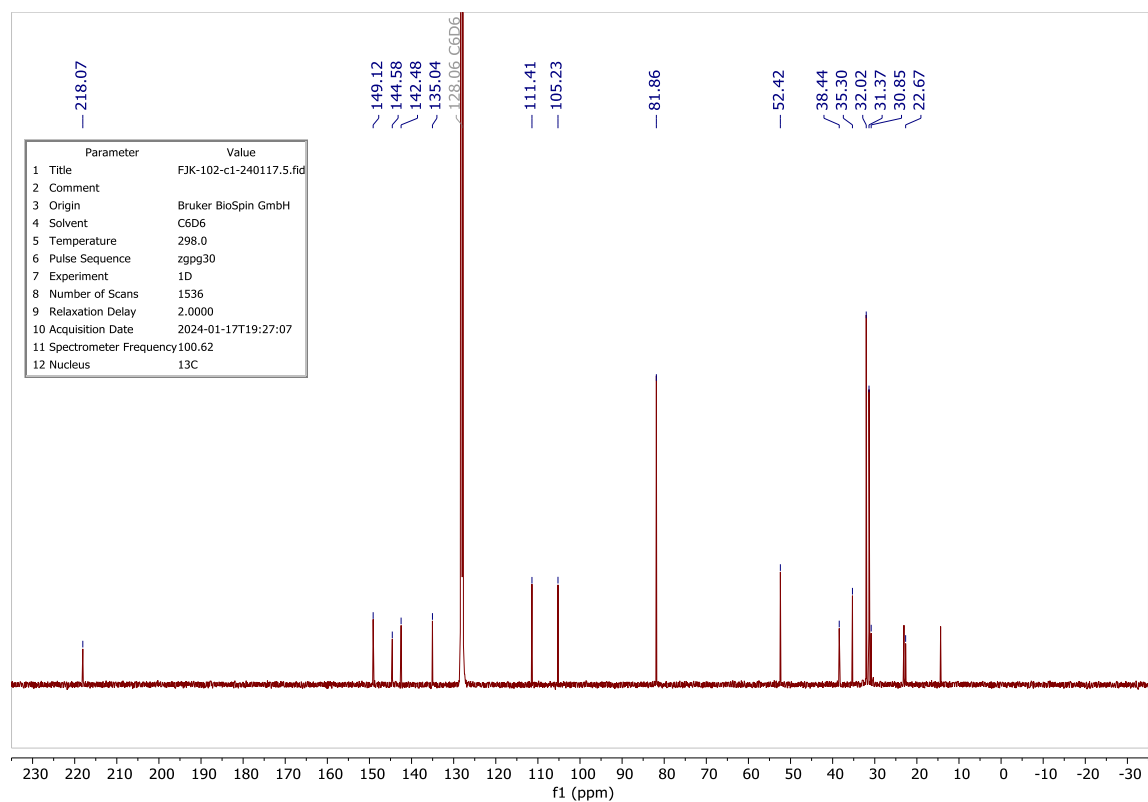


Figure S18: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $(t\text{BuNON})\text{AlFp}$ (101 MHz, C_6D_6 , 298 K)

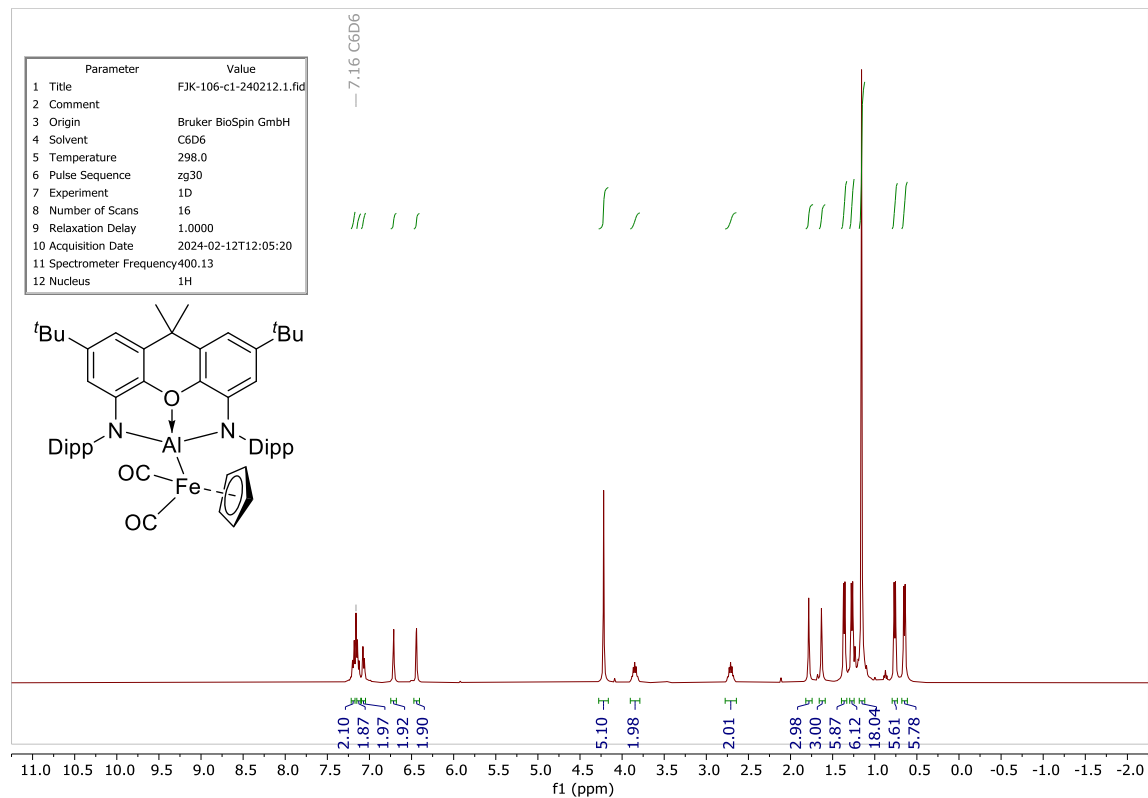


Figure S21: ^1H NMR spectrum of $(\text{DippNON})\text{AlFp}$ (400 MHz, C_6D_6 , 298 K)

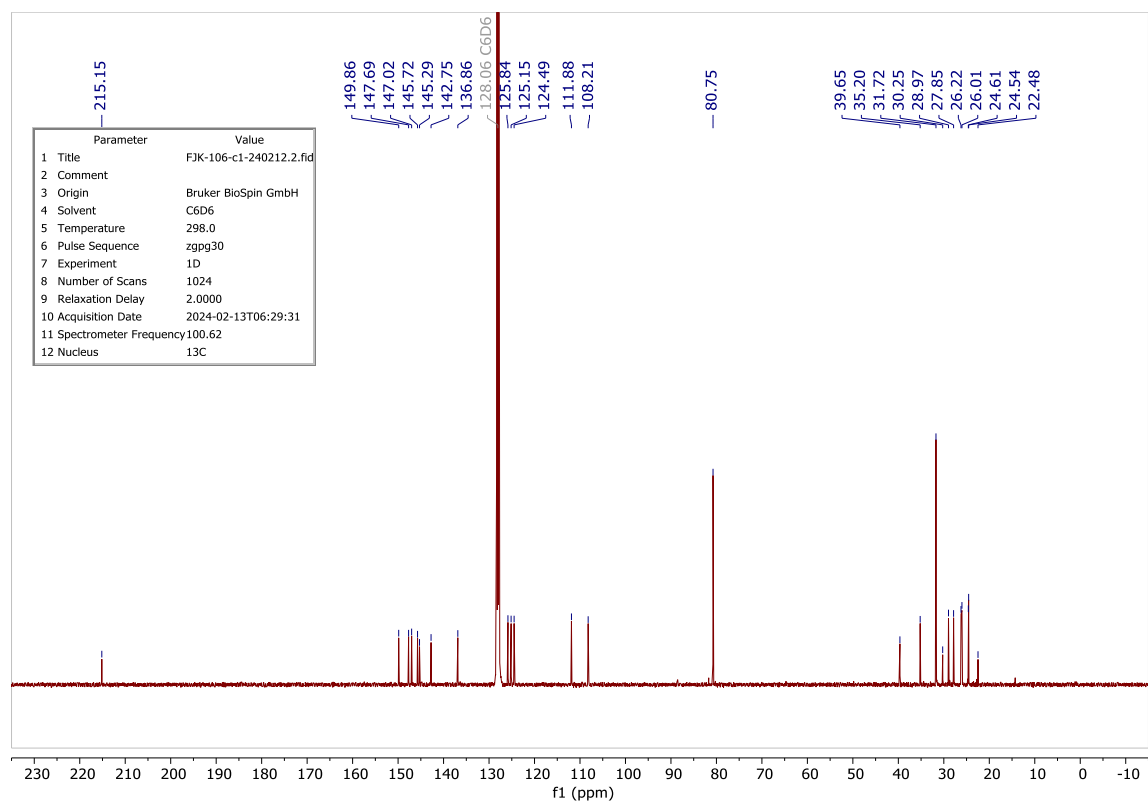
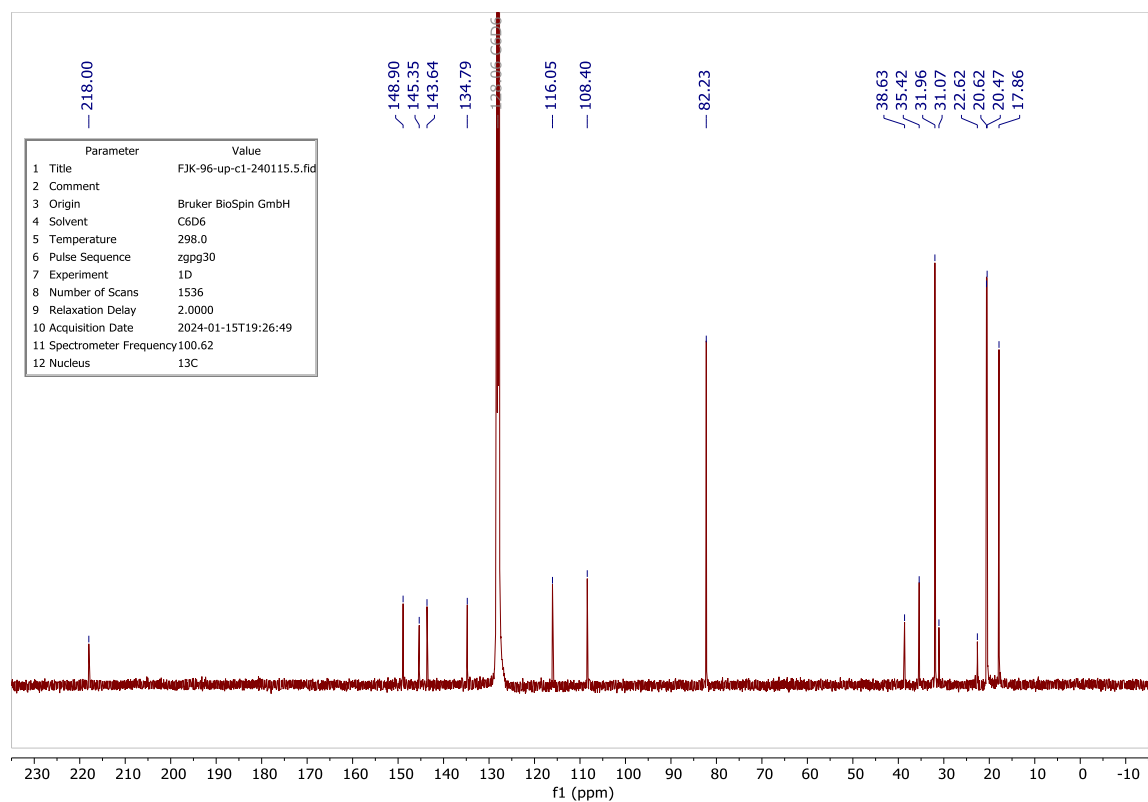
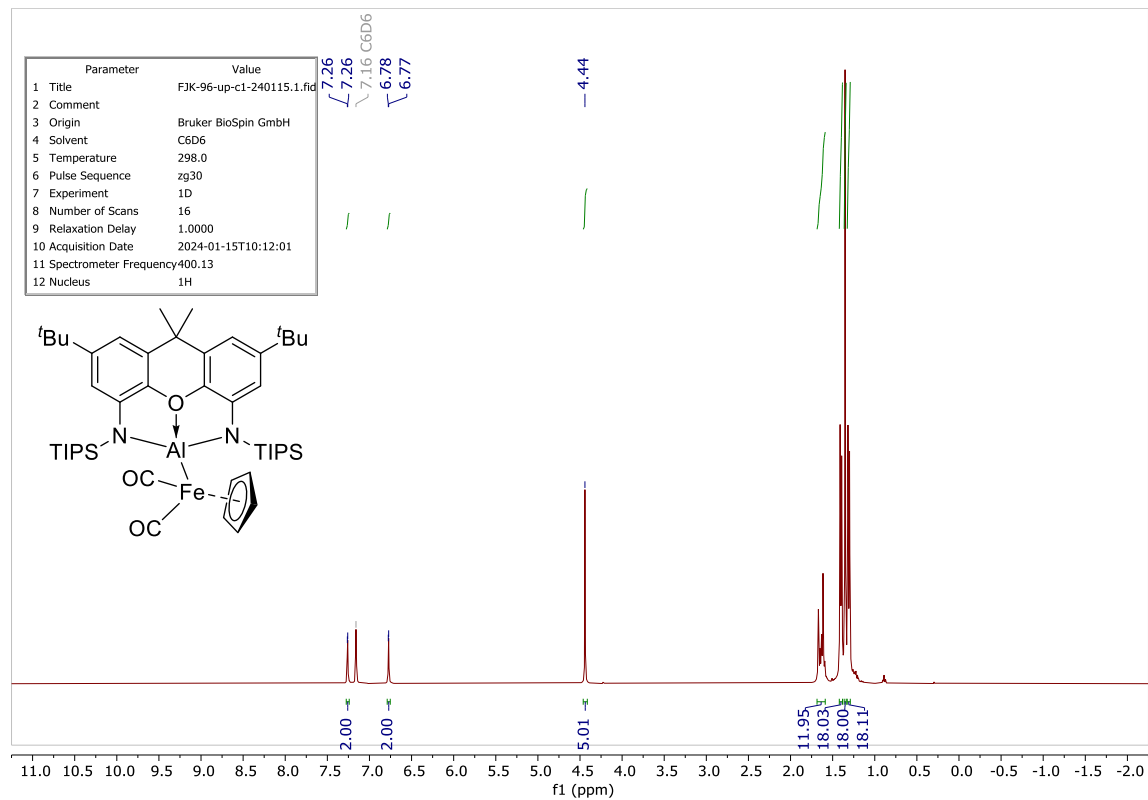


Figure S22: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $(\text{DippNON})\text{AlFp}$ (101 MHz, C_6D_6 , 298 K)



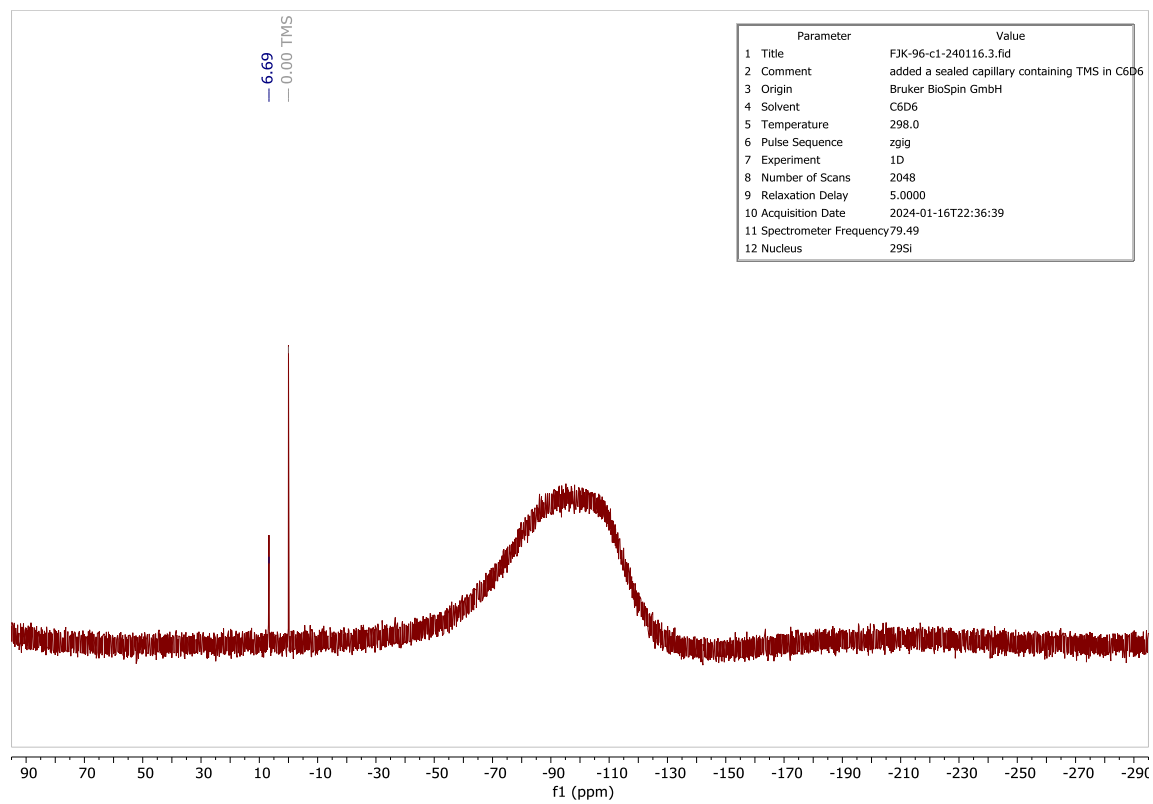


Figure S25: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of $(\text{TIPSON})\text{AlFp}$ (79 MHz, C_6D_6 , 298 K)

Crystallographic Details

X-ray diffraction experiments were performed using a Rigaku Supernova dual-source diffractometer using Cu K α radiation equipped with a Rigaku Hybrid Pixel 2-dimensional detector (HyPix-6000HE). X-ray diffraction of (^tBuNON)Al-I was performed using a Rigaku Xcalibur equipped with an Atlas detector using Mo K α radiation. Crystals were suspended in immersion oil, mounted on Micromount loops, and quench-cooled to 150 K using an Oxford Cryostream N₂ cooler. Data was processed using the CrysAlisPro package,^{S5} solved using the SHELX software package,^{S7} refined using Olex2,^{S8} and visualised using Mercury.^{S9}

Finalised CIFs for all X-ray diffraction structures (2359911-2359919) have been deposited at the Cambridge Crystallographic Data Centre. These can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table S1. Crystallographic and refinement parameters for (^{TIPS}NON)Al-I, (^{tBu}NON)Al-I and (^{tBuDipp}NON)Al-I

	(^{TIPS} NON)Al-I ·C ₆ H ₆	(^{tBu} NON)Al-I	(^{tBuDipp} NON)Al-I
Formula	C ₄₇ H ₇₆ AlIN ₂ OSi ₂	C ₃₁ H ₄₆ AlIN ₂ O	C ₃₉ H ₅₄ AlIN ₂ O
M	895.15	616.58	720.72
Cell setting	triclinic	monoclinic	monoclinic
Space group	P $\bar{1}$	P2 ₁ /c	P2 ₁ /n
a [Å]	12.4360(4)	13.8403(8)	11.4074(2)
b [Å]	13.9695(5)	18.5282(9)	17.6989(2)
c [Å]	14.6880(6)	12.5670(6)	19.0286(2)
α [°]	86.848(3)	90	90
β [°]	83.768(3)	103.509(6)	105.1050(10)
γ [°]	72.693(3)	90	90
V [Å ³]	2421.05(16)	3133.5(3)	3709.11(9)
Z	2	4	4
Unique / I > 2σI	10093/8548	8871/ 6283	7750/6493
R _{int}	0.0573	0.0398	0.0502
Parameters	713	386	412
R1 (all data / I > 2σI)	0.0615/0.0535	0.0785/0.0475	0.0428/0.0341
wR2 (all data / I > 2σI)	0.1492/0.1430	0.1019/0.0892	0.0840/0.0799
GooF	1.063	1.014	1.059
Residual max / min	0.796/-1.890	0.545/-0.557	0.451/-0.662
T [K]	150.00(10)	150.01(10)	150.00(10)
CCDC Deposition No.	2359911	2359912	2359913

Table S2. Crystallographic and refinement parameters for (^tIPsNON)AlFp, (^tBuNON)AlFp and (^tBuDippNON)AlFp

	(^t IPsNON)AlFp ·C ₆ H ₆	(^t BuNON)AlFp ·C ₆ H ₁₄	(^t BuDippNON)AlFp ·2C ₆ H ₆
Formula	C ₅₄ H ₈₁ AlFeN ₂ O ₃ Si ₂	C ₄₄ H ₆₅ AlFeN ₂ O ₃	C ₅₈ H ₇₁ AlFeN ₂ O ₃
M	945.21	752.81	926.99
Cell setting	triclinic	triclinic	triclinic
Space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$
a [Å]	11.9890(2)	10.4105(4)	10.71570(10)
b [Å]	15.0157(2)	11.6341(5)	13.6963(2)
c [Å]	16.5211(3)	18.7132(7)	18.2912(2)
α [°]	96.1280(10)	85.068(3)	80.7550(10)
β [°]	97.6050(10)	76.654(4)	77.6870(10)
γ [°]	113.366(2)	71.928(4)	77.1070(10)
V [Å ³]	2664.49(8)	2096.23(16)	2538.56(5)
Z	2	2	2
Unique / I > 2σI	10909/9167	10687/9022	10571/9985
R _{int}	0.0565	-	0.0279
Parameters	576	477	663
R1 (all data / I > 2σI)	0.0677/0.0564	0.1101/0.0953	0.0403/0.0382
wR2 (all data / I > 2σI)	0.1455/0.1393	0.2424/0.2351	0.0994/0.1006
GooF	1.045	1.118	1.059
Residual max / min	0.718/-0.505	0.964/-0.602	0.641/-0.436
T [K]	150.01(10)	150.00(10)	150.00(10)
CCDC Deposition No.	2359914	2359915	2359916

Table S3. Crystallographic and refinement parameters for (DippNON)AlFp, (DAS)AlFp and $[\{(DippNON)AlOC(\mu-FeCp)\}_2]$

	(DippNON)AlFp	(DAS)AlFp ·C ₆ H ₁₂	$[\{(DippNON)AlOC(\mu-FeCp)\}_2]$ ·5C ₆ H ₆
Formula	C ₅₄ H ₆₇ AlFeN ₂ O ₃	C ₉₂ H ₁₁₀ Al ₂ Fe ₂ N ₄ O ₄ Si ₂	C ₁₃₆ H ₁₆₄ Al ₂ Fe ₂ N ₄ O ₄
M	874.92	1557.67	2084.36
Cell setting	monoclinic	orthorhombic	monoclinic
Space group	P2 ₁ /c	Pbca	C2/c
a [Å]	11.10740(10)	19.4527(2)	24.70547(11)
b [Å]	18.5869(2)	19.4412(2)	19.02701(8)
c [Å]	23.6162(2)	44.6082(6)	25.22918(9)
α [°]	90	90	90
β [°]	92.6500(10)	90	94.0477(4)
γ [°]	90	90	90
V [Å ³]	4870.40(8)	16870.1(3)	11829.92(9)
Z	4	8	4
Unique / I > 2σI	10185/9027	17462/14131	12597/11977
R _{int}	0.0454	0.0528	0.0625
Parameters	597	1017	705
R1 (all data / I > 2σI)	0.0451/0.0387	0.0611/0.0464	0.0461/0.0441
wR2 (all data / I > 2σI)	0.0949/0.0920	0.1204/0.1126	0.1187/0.1202
GooF	1.041	1.028	1.033
Residual max / min	0.297/-0.341	0.734/-0.310	0.599/-0.577
T [K]	150.00(10)	150.00(10)	150.00(10)
CCDC Deposition No.	2359917	2359918	2359919

Investigation into the steric properties of the ligands

Percent buried volume (%BV) was calculated using SambVca 2.1,^{S10} pruning the complex of the Cp and CO moieties to leave just the (NON)Al or (DAS)Al “ligand” coordinated to the Fe centre. The conventionally reported %BV uses a radial cut-off of 3.5 Å, however this is because it is most often used when the majority of the steric bulk is geminal to the atom at the centre of the sphere. In the case of the complexes presented, the steric bulk provides kinetic protection to the Fe centre but is further away due to its vicinal relation. As such, the 3.5 Å radial cut-off was deemed potentially inappropriate and we have presented the %uBV at several cut-off distances for each complex in order to elucidate appropriate radial cut-offs (Figures S26-S29).

The expected behaviour of the %BV when radially encountering steric bulk is, initially, to increase as the integration volume engulfs the encountered atoms. Once the engulfing sphere expands into the empty space beyond the atoms, the integrated volume increases but maintains the integrated quantity, leading to a decrease in the %BV. As such, the size of the steric protection can be proxied *via* the magnitude of %BV, and the location of (or rather the distance to) the steric bulk is indicated by the critical points in %BV. Additionally, presented herein is actually percent *unburied* volume (%uBV), found by simply subtracting the %BV from 100%, as this is more directly compatible with percent accessible surface area (a larger %BV is more protecting, as is a smaller accessible surface area).

Atom Access^{S11} was also used for comparison, calculating the accessible surface area of a sphere at different radii using ray tracing. The complexes were pruned identically as for %BV, removing the Cp and CO moieties. Atom Access calculates a similar parameter to %BV, however instead of the integral over the volume of the sphere, it is the (proxy for the) integral over the *surface* of the sphere. Poignantly, this value can never decrease with cut-off radius- once at a cut-off radius that blocks a ray from the surface, the object blocking it remains blocking said ray at any subsequent distance. The expected qualification of steric bulk is thus to have a gradient as the sphere engulfs the full extent of the object providing steric bulk, then plateau until another object is encountered. Thus, the start of the plateaus in the graphs is where the steric bulk is, and the change in accessible surface area from one plateau to the next is an appropriate proxy for the magnitude.

Interestingly, no clear relation between the steric distance or magnitude, calculated using either %BV or accessible surface area, and any of the Al-Fe σ -bonding orbital energy, Al-Fe bond distance, and experimental or calculated CO stretching frequencies was elucidated.

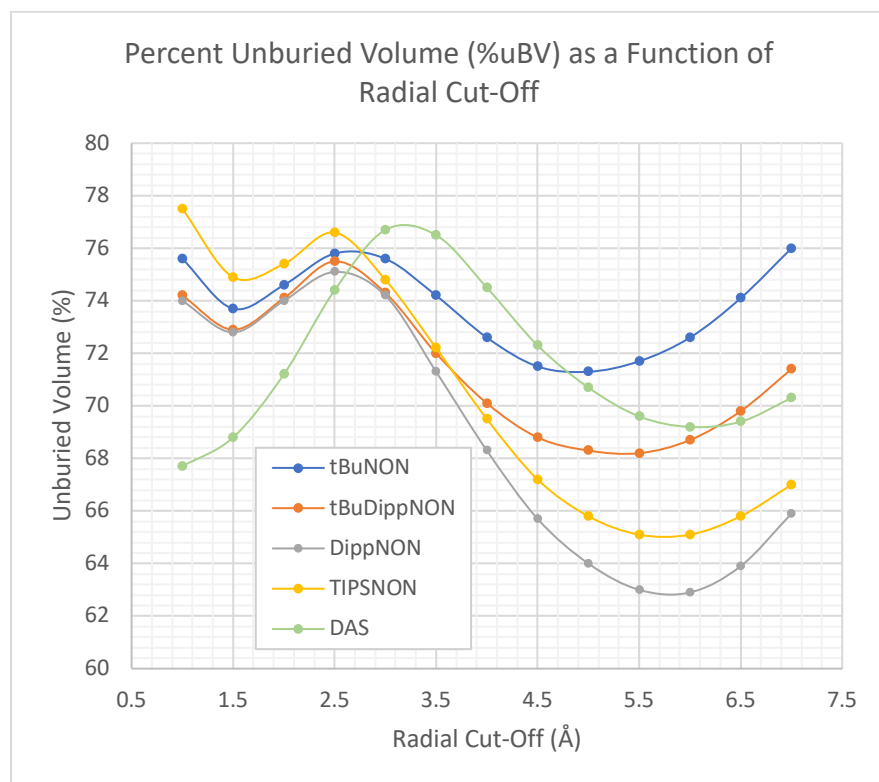


Figure S26: Percent unburied volume as a function of radial cut-off for the 5 reported complexes. Unburied volume (%uBV, i.e. 100% - %BV) was used for ready comparison with accessible surface area (*vide supra*). The minima in the 4.8-6.2 Å range are due to the associated ligands, with approximate minima abscissae shown from the numerical derivative (*vide adpositus*). The magnitude of the associated ordinates is qualitatively reflective of the steric protection afforded by the indicated moiety, leading to the relative size of the ligand substituents to be $t\text{BuNON} < \text{DAS} < t\text{BuDippNON} < \text{TIPSNON} < \text{DippNON}$.

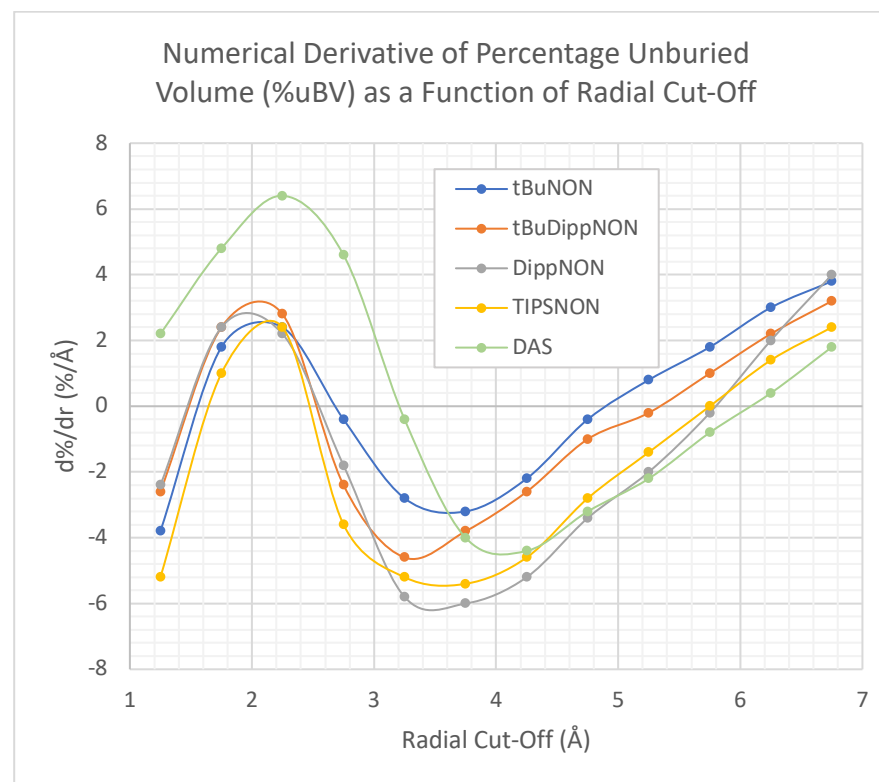


Figure S27: The numerical derivative of the %uBV with respect to radial cut-off shows the location of the maxima, evidently where the gradient is 0 and thus where this graph crosses the axis. The zeroes before 3.5 Å are due to the iron and aluminium atoms themselves. The zeroes between 4.8 and 6.2 Å show the location of the ligand-based steric bulk. As each of the ligands are similar, the small number of data points and single geometries taken, rather than appropriate conformationally sampled distributions, we stress that only a qualitative comparison of the systems can be drawn. A qualitative set of zeroes we propose is: $t\text{BuNON}$, 4.9 Å; $t\text{BuDippNON}$, 5.4 Å; TIPSNON , 5.8 Å; DippNON , 5.8 Å; DAS , 6.1 Å.

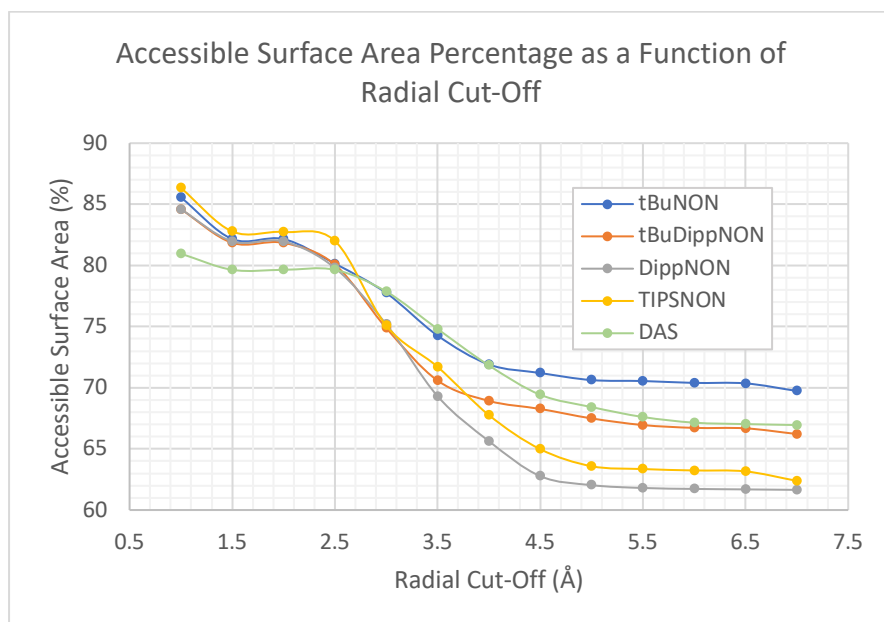


Figure S28: Accessible surface area as a function of radial cut-off for the 5 reported complexes. The magnitude of the accessible surface area percentage at the plateaus gives a qualitative relative measure of the steric protection afforded by the associated ligands (*vide infra*). It is difficult to quantify a plateau due to only the centre of such a feature possessing a true turning point, empirically evident from the numerical derivative (*vide adpositus*). Consequently, where the plateau begins, and thus the distance to the steric bulk, is far more difficult to quantify in the accessible surface area model than for %BV. However, as all the compared ligands appear at similar distances from the Fe centre, a qualitative ranking of their sizes is possible by comparing the heights of the plateaus in the 4.5-7.0 Å region. Encouragingly, this is the same ordering established by %BV: $t\text{BuNON} < \text{DAS} < t\text{BuDippNON} < \text{TIPSNON} < \text{DippNON}$.

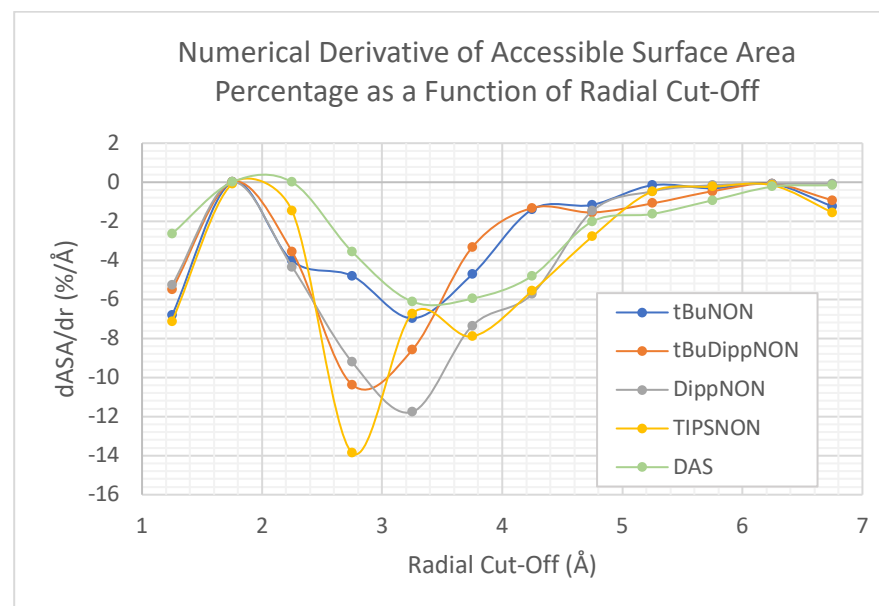


Figure S29: Numerical derivative of accessible surface area percentage as a function of radial cut-off. As for %uBV above, the derivative is used here to indicate the location of turning points. However, as the critical points in the parent graph are inflections rather than stationary points, the zeroes are more difficult to quantify, and the location of the critical points in the parent graph are less important to the interpretation of the data. Consequently, the interpretability of a graph such as that above is limited.

Computational Details

Methodology: Density functional theory (DFT) calculations for geometry optimisation were performed using the Gaussian 16 program^{S12} using the PBE0 hybrid density functional approximation^{S13} and Grimme's D3 dispersion correction with Becke-Johnson dampening,^{S14} Stuttgart-Dresden effective core potentials and associated basis sets^{S15} for Fe and Al ($\zeta_d = 0.190$), with listed additional polarisation function, and Pople's 6-31G** basis set^{S16} for all other atoms (BS1), and the ultrafine integration grid.

A hybrid density functional may seem excessively computationally expensive for geometry optimisations of such large species, however recent benchmarking in our group^{S17} suggests the presented method to reproduce experimental data more accurately for low-valent main group species than other more inexpensive methods. Additionally, the relatively small admixture of Hartree-Fock exchange in the PBE0 hybrid (25%) makes it *a priori* more appropriate for a 3d-metal containing species,^{S18} although this effect is minimal for closed-shell low-spin 3d⁶ pseudo-octahedral complexes like the presented iron complexes.

Starting geometries were taken from solid-state structures from X-ray diffraction, removing errant solvent molecules and taking only one part of modelled disorder, corresponding to the most symmetrical structure. In the case of the DAS alumanyl, only one of the two isostructural molecules (in this case, the un-disordered one) in the unit cell. The geometries were confirmed as minima on the potential energy surface *via* analytical frequency calculations, yielding no imaginary eigenmodes. Thermochemical properties were calculated at a pressure of 1.0 atmospheres, unscaled frequencies, and a temperature of 298.15 K. Single point calculations were performed on the optimised geometries using at the PBE0-D3BJ level of theory, with the cc-pVTZ basis^{S19} and conductor-like polarisable continuum model^{S20} solvation correction (CPCM) with benzene as the solvent. Gibb's free energies were obtained by adding the thermal contribution to Gibb's free energy calculated at the PBE0-D3BJ/BS1 level of theory to the electronic energy calculated at PBE0-D3BJ-(CPCM=benzene)/cc-pVTZ level, which was also used to calculate the presented molecular orbitals.

Natural bond orbital (NBO) analysis

(^tIPSNON)AlFp, (^tBuNON)AlFp, (^tBuDippNON)AlFp, (^DippNON)AlFp and (DAS)AlFp were analysed using the NBO7 program^{S21} to elucidate common structure and bonding motifs, principally in terms of their relative π -acidities. Each of the structures presented is strongly delocalised and poorly described in terms of simple doubly occupied, 2-centre – 2-electron bonds is designed by the NBO basis.

It should be noted that for the silicon-substituted amides the bonds were considered quite N->Si dative in NBO, and consequently the nitrogen atoms are far more negatively charged than the carbon-substituted amides. Wiberg bond indices^{S22} in the Natural Atomic Orbitals (NAO) basis are also each very similar, varying by less than 0.04. Occupancy of the Al-Fe σ -bonding NBOs is somewhat complicated. For ligands without the Dipp moiety have occupancies between 1.59 and 1.62, significantly less than the desired 2-electrons and are thus indicative of a structure departed from a simple Lewis diagram. Additionally, those with Dipp moieties did not possess an Al-Fe bonding NBO at all, instead possessing a fourth Fe lone pair (using any basis set or the wB97X-D density functional), and a minimally occupied aluminium orbital. Finally, the hybridisation of the orbitals involved is very similar to that described by Tokitoh and co-workers^{S23} (0.85 Fe sd^{2.8} 0.52 Al sp^{0.3}), for both the categorised NBOs and the Fe LP – Al LV combinations (Table S4).

Table S4: Summary of the key results obtained from NBO analysis.

Complex	Natural Charge			Al-Fe Natural Wiberg Bond Index	σ (Al-Fe) NBO Occupancy*	σ (Fe-Al) NBO hybridisation*
	Fe	Al	N, N'			
(^t IPSNON)AlFp	-0.443	1.821	-1.413, -1.418	0.373	1.604	0.873 Fe sd ^{3.15} 0.488 Al sp ^{0.23}
(^t BuNON)AlFp	-0.447	1.816	-0.957, -0.956	0.357	1.591	0.882 Fe sd ^{3.50} 0.471 Al sp ^{0.25}
(^t BuDippNON)AlFp	-0.430	1.841	-0.952, -0.961	0.350	1.310 +	0.885 Fe sd ^{3.39} +
(^D ippNON)AlFp	-0.468	1.881	-0.970, -0.972	0.349	0.630	0.617 Al sp ^{0.25}
(^D ippNON)AlFp	-0.468	1.881	-0.970, -0.972	0.349	1.341 +	Fe sd ^{3.51} +
(DAS)AlFp	-0.466	1.733	-1.469, -1.472	0.393	0.636	Al sp ^{0.21}
(DAS)AlFp	-0.466	1.733	-1.469, -1.472	0.393	1.624	0.859 Fe sd ^{3.19} 0.513 Al sp ^{0.17}

*(^tBuDippNON)AlFp and (^DippNON)AlFp are shown as a combination of the donor Fe (LP) NBO and the acceptor Al (LV) NBO as no Al-Fe bonding NBO was naturally assigned.

Model Complexes

Due to the difficulties encountered in assessing the π -donating abilities of the N donors in the NON-Al coordination complexes, three model complexes were additionally analysed by DFT. These model complexes are shown in Figure S30.

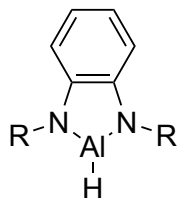


Figure 30: Structure of the model complexes calculated, where R = ^tBu, Dipp, TIPS.

The series of model complexes were chosen because a) they possess the same R groups as the NON-ligands used in this study, b) the R(Ar)N⁻ nitrogen donors are similar to those in the NON-ligands, and c) the geometry of the Al centre and ligand is the same across all three complexes. As such, any changes in the orbital energies should be a direct consequence of the change in R groups.

Initial conformation for representative species was initially constructed from chemical intuition and optimised at the PBE0-D3BJ/BS1 level of theory, as established for the experimental complexes. The Dipp- and ^tBu- complexes possessed C_{2v} symmetry, and the TIPS complex C_s. Each of these possess mirror symmetry with respect to the nitrogen lone pairs, producing in-phase and out-of-phase daughters. Single-point calculations were performed at the PBE0-D3BJ/cc-pVTZ level of theory in an attempt to fully capture polarisation and delocalisation into the R-groups. The in-phase combination has significant delocalisation into the vacant aluminium *p*-orbital which is, as expected, absent in the out-of-phase combination.

To assess the π -donating ability of the three ligands, the energy levels of the HOMO and the HOMO-1 were compared. These are the out-of-phase and in-phase combinations of nitrogen lone-pair *p* orbitals. If the R groups are relatively more π -acidic, the energy of the HOMO and HOMO-1 should be lowered. Results of this study are shown in Table S5.

Table S5 Summary of the relevant nitrogen-based molecular orbitals in the three model complexes.

Complex	HOMO energy (eV)	HOMO-1 energy (eV)
R = ^t Bu	-5.144	-5.990
R = TIPS	-5.407	-6.215
R = Dipp	-5.465	-6.259

The ^tBu complex has the highest energy HOMO and HOMO-1 orbitals, signifying that the ^tBu(Ar)N⁻ are the strongest π -donors. The TIPS and Dipp complexes have similar, lower energy HOMO and HOMO-1 orbitals, meaning that the TIPS(Ar)N⁻ and Dipp(Ar)N⁻ are significantly weaker π -donors. This is due to the π -acidity of both the TIPS and Dipp groups, which withdraw π -electron density from the N donors.

Energetic Data and Optimised xyz Coordinates

(D^{pp}NON)AlFp

SCF (PBE0-D3BJ-CPCM(C₆H₆)/cc-pVTZ)

Energy =

-3937.45154951 Eh

Thermal Gibb's Corr. = 1.007133 Eh

Gibb's Free Energy= -3936.4444165 Eh

Lowest Frequency = 26.2849 cm⁻¹

Second Frequency = 28.3824 cm⁻¹

Fe	1.33880	-2.56950	-1.95565
Al	0.46461	-0.97614	-0.50349
O	-0.38018	0.57520	-1.43561
O	1.66376	-0.29288	-3.70064
O	-1.39888	-2.96027	-2.78369
N	1.60251	0.34588	0.24185
N	-1.27830	-1.18284	0.24990
C	0.12610	1.78345	-0.92634
C	1.17633	1.64202	-0.01796
C	1.63172	2.83298	0.55657
H	2.43840	2.77669	1.28131
C	1.03271	4.06432	0.24841
C	-0.03603	4.11603	-0.65663
H	-0.51201	5.06211	-0.87824
C	-0.51930	2.95090	-1.26300
C	-1.70824	2.82759	-2.22998
C	-2.51282	1.61833	-1.73826
C	-3.88758	1.56250	-1.50861
H	-4.51839	2.37548	-1.84937
C	-4.45794	0.48931	-0.80202
C	-3.63096	-0.48765	-0.24056
H	-4.03383	-1.24535	0.42061
C	-2.24089	-0.44680	-0.43005
C	-1.77989	0.52962	-1.31067
C	1.53846	5.31955	0.96626
C	3.04074	5.50029	0.70632
H	3.40619	6.40293	1.20842
H	3.24274	5.59995	-0.36499
H	3.62408	4.65439	1.08140
C	1.29927	5.16199	2.47598
H	1.81495	4.28475	2.87754
H	0.23183	5.04778	2.69002
H	1.66421	6.04395	3.01430
C	0.82003	6.58681	0.49869
H	1.22411	7.45404	1.03040
H	-0.25425	6.54482	0.70550
H	0.95962	6.75880	-0.57365
C	-1.17017	2.56226	-3.65005
H	-0.56811	3.41207	-3.98645
H	-2.00367	2.42670	-4.34633
H	-0.54463	1.66724	-3.68301
C	-2.55692	4.09342	-2.23994

H	-2.95945	4.31626	-1.24751
H	-3.39212	3.98665	-2.93797
H	-1.96184	4.94753	-2.57538
C	-5.97777	0.44550	-0.62658
C	-6.62480	0.30430	-2.01286
H	-6.36233	1.14334	-2.66403
H	-7.71657	0.27232	-1.92355
H	-6.29289	-0.61608	-2.50359
C	-6.46949	1.74077	0.03691
H	-6.01201	1.87416	1.02199
H	-7.55693	1.70818	0.16618
H	-6.23446	2.62393	-0.56383
C	-6.42966	-0.73337	0.23762
H	-6.12989	-1.69242	-0.19675
H	-7.52132	-0.73106	0.31790
H	-6.02357	-0.67386	1.25303
C	2.91057	0.12647	0.74748
C	3.08122	-0.47651	2.01309
C	4.37239	-0.78766	2.44753
H	4.50331	-1.25958	3.41776
C	5.48551	-0.48214	1.67950
H	6.48261	-0.72260	2.03690
C	5.31296	0.14305	0.45086
H	6.18434	0.38671	-0.15118
C	4.04307	0.44281	-0.04432
C	1.91825	-0.72224	2.95269
H	0.99547	-0.48927	2.41334
C	1.81812	-2.16506	3.44606
H	1.72226	-2.87676	2.62201
H	0.93384	-2.28210	4.07845
H	2.69811	-2.45505	4.03045
C	2.01050	0.22549	4.15311
H	2.89510	-0.00053	4.75893
H	1.12519	0.12269	4.78872
H	2.08410	1.26944	3.83447
C	3.93376	1.06392	-1.42532
H	2.87805	1.08545	-1.70555
C	4.67030	0.24003	-2.48426
H	4.48128	0.65348	-3.47957
H	4.33620	-0.79969	-2.48575
H	5.75298	0.24610	-2.32011
C	4.45280	2.50349	-1.43468
H	5.51428	2.53834	-1.16429
H	3.89999	3.12890	-0.73184
H	4.34569	2.94063	-2.43308
C	-1.56042	-1.55069	1.59568
C	-1.80835	-0.56025	2.57727
C	-1.99405	-0.96734	3.90070
H	-2.17734	-0.21259	4.66132
C	-1.94650	-2.30559	4.26389
H	-2.08831	-2.59740	5.30059
C	-1.72702	-3.27122	3.28948
H	-1.70474	-4.31775	3.57515
C	-1.53904	-2.91652	1.95336

C	-1.91999	0.92322	2.26308	H	0.11030	4.64950	-1.60499
H	-1.75488	1.06814	1.19521	C	-0.37813	2.56722	-1.40655
C	-0.87486	1.77148	2.98457	C	-1.77523	2.51981	-2.03544
H	-0.94502	1.66912	4.07287	C	-2.62738	1.63337	-1.11758
H	-1.01906	2.82760	2.73475	C	-3.93401	1.89210	-0.69008
H	0.13504	1.49892	2.67722	H	-4.45598	2.76052	-1.06877
C	-3.32771	1.43501	2.58279	C	-4.54831	1.04573	0.23639
H	-4.08984	0.82202	2.09666	C	-3.83925	-0.03252	0.78752
H	-3.44515	2.46559	2.23148	H	-4.32765	-0.63020	1.54394
H	-3.51768	1.42340	3.66183	C	-2.51003	-0.31576	0.42529
C	-1.38481	-3.97493	0.87917	C	-2.02684	0.50743	-0.60415
H	-0.66261	-3.59301	0.15029	C	2.51362	4.83911	-0.36816
C	-0.86767	-5.31114	1.40334	C	2.94219	5.34593	-1.75327
H	0.06689	-5.19929	1.96334	H	2.07764	5.58831	-2.37830
H	-0.68814	-6.00073	0.57188	H	3.53124	4.58656	-2.27748
H	-1.59621	-5.79984	2.05915	H	3.55429	6.24988	-1.65753
C	-2.70719	-4.16714	0.13026	C	3.77387	4.57979	0.46004
H	-3.49125	-4.50236	0.81845	H	4.34258	5.50983	0.56007
H	-2.60012	-4.91877	-0.65939	H	4.43005	3.84196	-0.01266
H	-3.03062	-3.23634	-0.34031	H	3.53203	4.22786	1.46823
C	2.25847	-4.39073	-2.42126	C	1.69325	5.92342	0.34672
H	2.06457	-4.96306	-3.31752	H	2.29652	6.82803	0.48220
C	1.54659	-4.48995	-1.18985	H	1.36985	5.57622	1.33325
H	0.72015	-5.15708	-0.99017	H	0.79969	6.20067	-0.21965
C	2.09801	-3.55039	-0.27271	C	-2.37236	3.91483	-2.18018
H	1.81368	-3.43269	0.76312	H	-2.46407	4.41526	-1.21202
C	3.15399	-2.86229	-0.93959	H	-3.36280	3.86219	-2.64103
H	3.77458	-2.08725	-0.51126	H	-1.74530	4.52975	-2.83192
C	3.24415	-3.38524	-2.26224	C	-1.67568	1.86356	-3.42735
H	3.93113	-3.04860	-3.02725	H	-1.04700	2.47187	-4.08492
C	1.53727	-1.19346	-2.98206	H	-2.67116	1.77669	-3.87431
C	-0.30853	-2.78199	-2.44113	H	-1.23522	0.86526	-3.36516

(DipptBuNON)AlFp

SCF (PBE0-D3BJ-CPCM(C₆H₆)/cc-pVTZ)

Energy =

-3628.01140763 Eh

Thermal Gibb's Corr. = 0.874729 Eh

Gibb's Free Energy= -2246.525029 Eh

Lowest Frequency = 19.9318 cm⁻¹

Second Frequency = 25.9537 cm⁻¹

Fe	0.43258	-3.10364	-1.44646	H	0.11030	4.64950	-1.60499
Al	0.05242	-1.28249	-0.00778	C	-0.37813	2.56722	-1.40655
O	-0.70502	0.23774	-0.98896	C	-1.77523	2.51981	-2.03544
O	2.46422	-3.72109	0.51182	C	-2.62738	1.63337	-1.11758
O	1.69725	-1.11932	-3.10797	C	-3.93401	1.89210	-0.69008
N	1.47177	-0.05140	0.39457	H	-4.45598	2.76052	-1.06877
N	-1.61093	-1.23592	0.93396	C	-4.54831	1.04573	0.23639
C	0.10812	1.37997	-0.90630	C	-3.83925	-0.03252	0.78752
C	1.26463	1.20406	-0.15404	H	-4.32765	-0.63020	1.54394
C	2.05852	2.35403	-0.00727	C	-2.51003	-0.31576	0.42529
H	2.96865	2.27292	0.57359	C	-2.02684	0.50743	-0.60415
C	1.65669	3.58218	-0.54144	C	2.51362	4.83911	-0.36816
C	0.43550	3.68617	-1.22900	C	2.94219	5.34593	-1.75327
				H	2.07764	5.58831	-2.37830
				H	3.53124	4.58656	-2.27748
				H	3.55429	6.24988	-1.65753
				C	3.77387	4.57979	0.46004
				H	4.34258	5.50983	0.56007
				H	4.43005	3.84196	-0.01266
				H	3.53203	4.22786	1.46823
				C	1.69325	5.92342	0.34672
				H	2.29652	6.82803	0.48220
				H	1.36985	5.57622	1.33325
				H	0.79969	6.20067	-0.21965
				C	-2.37236	3.91483	-2.18018
				H	-2.46407	4.41526	-1.21202
				H	-3.36280	3.86219	-2.64103
				H	-1.74530	4.52975	-2.83192
				C	-1.67568	1.86356	-3.42735
				H	-1.04700	2.47187	-4.08492
				H	-2.67116	1.77669	-3.87431
				H	-1.23522	0.86526	-3.36516
				C	-5.98698	1.27676	0.70877
				C	-5.99838	1.51581	2.22630
				H	-5.38790	2.38628	2.48612
				H	-5.60609	0.65613	2.77771
				H	-7.02106	1.69642	2.57582
				C	-6.63249	2.48814	0.03292
				H	-7.66064	2.60314	0.39052
				H	-6.66965	2.37205	-1.05510
				H	-6.09648	3.41454	0.26350
				C	-6.83404	0.03856	0.37849
				H	-7.86879	0.18494	0.70801
				H	-6.44955	-0.85901	0.87194
				H	-6.84117	-0.15020	-0.69974
				C	2.65651	-0.23578	1.16882
				C	3.90099	-0.44544	0.53589
				C	5.03257	-0.65760	1.32583
				H	5.98939	-0.83018	0.83998
				C	4.95799	-0.64969	2.70974
				H	5.84737	-0.82505	3.30832
				C	3.74064	-0.39447	3.32597
				H	3.69181	-0.35721	4.40958
				C	2.58335	-0.16908	2.57881
				C	4.06306	-0.40677	-0.96935
				H	3.07582	-0.24863	-1.40273

C	4.62728	-1.71582	-1.52586	O	-0.00926	0.23332	-0.65146
H	5.65586	-1.87994	-1.18606	N	-1.83050	-0.75274	0.90534
H	4.63905	-1.68627	-2.62023	N	1.50063	-0.76747	1.18964
H	4.03736	-2.57915	-1.21176	O	2.85544	-2.50232	-1.28859
C	4.94339	0.76800	-1.40638	O	0.25631	-5.03962	1.00344
H	4.52337	1.72244	-1.07957	C	-2.08822	0.51968	0.41690
H	5.02399	0.79318	-2.49828	C	0.16218	2.69876	-1.79911
H	5.95611	0.68169	-0.99710	C	-1.11931	1.06055	-0.44212
C	1.30163	0.23321	3.28220	C	1.20630	0.90392	-0.45075
H	0.46638	-0.06120	2.63671	C	2.03516	0.31224	0.51270
C	1.12529	-0.43228	4.64628	C	-1.08463	2.32306	-0.98677
H	1.24549	-1.51873	4.59201	C	1.36771	2.13470	-1.03957
H	0.13014	-0.21881	5.04816	C	4.92687	2.81504	0.22785
H	1.84834	-0.05172	5.37526	C	3.55444	2.17466	-0.00183
C	1.22507	1.75773	3.42866	C	-3.22658	2.67782	0.08332
H	2.05949	2.12488	4.03719	C	3.27256	0.96729	0.65423
H	0.29061	2.04950	3.92106	H	4.02340	0.55471	1.31326
H	1.26725	2.25527	2.45690	C	0.27671	4.20852	-1.98228
C	-1.91491	-2.05019	2.11792	H	-0.58948	4.59474	-2.52692
C	-2.24953	-1.17492	3.33439	H	1.16396	4.45480	-2.57215
H	-2.33026	-1.79346	4.23410	H	0.34388	4.72543	-1.02094
H	-3.18815	-0.63128	3.21708	C	-3.16836	1.39302	0.64440
H	-1.46075	-0.43674	3.49192	H	-3.97403	1.09145	1.29769
C	-3.04422	-3.06120	1.86741	C	-2.18407	3.14504	-0.72060
H	-2.76782	-3.76373	1.07721	H	-2.21146	4.14779	-1.12516
H	-3.97814	-2.58140	1.56869	C	2.58916	2.77794	-0.81330
H	-3.24198	-3.63897	2.77621	H	2.77488	3.74546	-1.25980
C	-0.64379	-2.84227	2.43322	C	-0.45214	-2.21332	-2.96357
H	0.21139	-2.17539	2.59686	H	0.06516	-1.34711	-3.35193
H	-0.39862	-3.52798	1.61679	C	-4.44837	3.54528	0.40269
H	-0.76555	-3.43677	3.34321	C	-2.83647	-1.45864	1.71344
C	-1.13338	-3.24556	-2.81153	C	5.08809	4.13188	-0.53431
H	-1.42552	-2.45556	-3.49026	H	4.97936	3.98941	-1.61436
C	-1.63069	-3.43352	-1.49527	H	6.08658	4.54177	-0.35164
H	-2.37539	-2.82460	-1.00301	H	4.35832	4.88070	-0.20922
C	-0.96465	-4.56398	-0.94276	C	-0.12285	-3.57823	-3.23808
H	-1.11484	-4.97555	0.04549	H	0.69455	-3.92055	-3.85784
C	-0.06741	-5.08097	-1.92885	C	2.14319	-1.29062	2.40200
H	0.59827	-5.92344	-1.79964	C	-2.33171	-2.87768	1.97153
C	-0.16826	-4.26989	-3.08034	H	-2.21460	-3.42980	1.03653
H	0.40573	-4.37816	-3.99034	H	-3.04143	-3.42251	2.60100
C	1.24635	-1.89653	-2.37670	H	-1.37263	-2.87817	2.49697
C	1.66803	-3.42845	-0.27887	C	2.38125	-0.18393	3.44105

(^tBuNON)AlFp

SCF (PBE0-D3BJ-CPCM(C₆H₆)/cc-pVTZ)

Energy =

-1938.04282005 Eh

Thermal Gibb's Corr. = 0.744185 Eh

Gibb's Free Energy= -1937.298635 Eh

Lowest Frequency = 22.4226 cm⁻¹

Second Frequency = 23.2337 cm⁻¹

Fe 0.05210 -3.18020 -1.19080

Al -0.10822 -1.42428 0.38208

O	-0.00926	0.23332	-0.65146	O	-0.00926	0.23332	-0.65146
N	-1.83050	-0.75274	0.90534	N	-1.83050	-0.75274	0.90534
N	1.50063	-0.76747	1.18964	N	1.50063	-0.76747	1.18964
O	2.85544	-2.50232	-1.28859	O	2.85544	-2.50232	-1.28859
O	0.25631	-5.03962	1.00344	O	0.25631	-5.03962	1.00344
C	-2.08822	0.51968	0.41690	C	-2.08822	0.51968	0.41690
C	0.16218	2.69876	-1.79911	C	0.16218	2.69876	-1.79911
C	-1.11931	1.06055	-0.44212	C	-1.11931	1.06055	-0.44212
C	1.20630	0.90392	-0.45075	C	1.20630	0.90392	-0.45075
C	2.03516	0.31224	0.51270	C	2.03516	0.31224	0.51270
C	-1.08463	2.32306	-0.98677	C	-1.08463	2.32306	-0.98677
C	1.36771	2.13470	-1.03957	C	1.36771	2.13470	-1.03957
C	4.92687	2.81504	0.22785	C	4.92687	2.81504	0.22785
C	3.55444	2.17466	-0.00183	C	3.55444	2.17466	-0.00183
C	-3.22658	2.67782	0.08332	C	-3.22658	2.67782	0.08332
C	3.27256	0.96729	0.65423	C	3.27256	0.96729	0.65423
H	4.02340	0.55471	1.31326	H	4.02340	0.55471	1.31326
C	0.27671	4.20852	-1.98228	C	0.27671	4.20852	-1.98228
H	-0.58948	4.59474	-2.52692	H	-0.58948	4.59474	-2.52692
H	1.16396	4.45480	-2.57215	H	1.16396	4.45480	-2.57215
H	0.34388	4.72543	-1.02094	H	0.34388	4.72543	-1.02094
C	-3.16836	1.39302	0.64440	C	-3.16836	1.39302	0.64440
H	-3.97403	1.09145	1.29769	H	-3.97403	1.09145	1.29769
C	-2.18407	3.14504	-0.72060	C	-2.18407	3.14504	-0.72060
H	-2.21146	4.14779	-1.12516	H	-2.21146	4.14779	-1.12516
C	2.58916	2.77794	-0.81330	C	2.58916	2.77794	-0.81330
H	2.77488	3.74546	-1.25980	H	2.77488	3.74546	-1.25980
C	-0.45214	-2.21332	-2.96357	C	-0.45214	-2.21332	-2.96357
H	0.06516	-1.34711	-3.35193	H	0.06516	-1.34711	-3.35193
C	-4.44837	3.54528	0.40269	C	-4.44837	3.54528	0.40269
C	-2.83647	-1.45864	1.71344	C	-2.83647	-1.45864	1.71344
C	5.08809	4.13188	-0.53431	C	5.08809	4.13188	-0.53431
H	4.97936	3.98941	-1.61436	H	4.97936	3.98941	-1.61436
H	6.08658	4.54177	-0.35164	H	6.08658	4.54177	-0.35164
H	4.35832	4.88070	-0.20922	H	4.35832	4.88070	-0.20922
C	-0.12285	-3.57823	-3.23808	C	-0.12285	-3.57823	-3.23808
H	0.69455	-3.92055	-3.85784	H	0.69455	-3.92055	-3.85784
C	2.14319	-1.29062	2.40200	C	2.14319	-1.29062	2.40200
C	-2.33171	-2.87768	1.97153	C	-2.33171	-2.87768	1.97153
H	-2.21460	-3.42980	1.03653	H	-2.21460	-3.42980	1.03653
H	-3.04143	-3.42251	2.60100	H	-3.04143	-3.42251	2.60100
H	-1.37263	-2.87817	2.49697	H	-1.37263	-2.87817	2.49697
C	2.38125	-0.18393	3.44105	C	2.38125	-0.18393	3.44105
H	3.09203	0.57477	3.11304	H	3.09203	0.57477	3.11304
H	2.76222	-0.62140	4.36962	H	2.76222	-0.62140	4.36962
H	1.43579	0.32218	3.65966	H	1.43579	0.32218	3.65966
C	0.07251	2.03019	-3.18516	C	0.07251	2.03019	-3.18516
H	-0.01913	0.94558	-3.09151	H	-0.01913	0.94558	-3.09151
H	0.97181	2.24998	-3.76896	H	0.97181	2.24998	-3.76896
H	-0.80125	2.40206	-3.72956	H	-0.80125	2.40206	-3.72956
C	-1.02148	-4.39651	-2.51689	C	-1.02148	-4.39651	-2.51689
H	-1.01597	-5.47754	-2.48831	H	-1.01597	-5.47754	-2.48831
C	0.18442	-4.26478	0.14173	C	0.18442	-4.26478	0.14173
C	-1.91073	-3.54383	-1.79252	C	-1.91073	-3.54383	-1.79252
H	-2.71359	-3.87094	-1.14661	H	-2.71359	-3.87094	-1.14661
C	-3.02400	-0.78145	3.07938	C	-3.02400	-0.78145	3.07938

H	-2.07588	-0.79047	3.62625	N	-1.76165	-0.15902	-0.03106
H	-3.76945	-1.31697	3.67678	N	1.55150	-0.69955	-0.36953
H	-3.34042	0.25955	2.99646	C	-0.75192	1.86052	0.77323
C	6.02068	1.84881	-0.25136	C	-1.82316	1.22572	0.13693
H	5.98529	0.89767	0.28764	C	-2.82370	2.12380	-0.27028
H	7.01277	2.28755	-0.09543	H	-3.69748	1.73781	-0.77480
H	5.90505	1.63077	-1.31772	C	-2.71999	3.50854	-0.08496
C	1.16002	-2.27053	3.03755	C	-1.56994	4.05350	0.49502
H	0.23838	-1.74984	3.32075	H	-1.46497	5.12531	0.59832
H	1.58317	-2.71404	3.94365	C	-0.54134	3.21350	0.92780
H	0.92351	-3.10001	2.36287	C	0.80222	3.64955	1.52933
C	-4.17021	-1.60677	0.96310	C	1.87535	2.74117	0.91853
H	-4.64112	-0.65542	0.71532	C	3.14105	3.11367	0.46904
H	-4.87820	-2.18461	1.56570	H	3.47666	4.13686	0.59482
H	-4.00610	-2.14383	0.02354	C	3.98050	2.17540	-0.15456
C	1.73211	-2.76202	-1.20027	C	3.51057	0.88446	-0.41246
C	3.43551	-2.05401	2.08166	H	4.14180	0.18145	-0.93767
H	3.21376	-2.92104	1.45327	C	2.21132	0.48102	-0.04700
H	3.91030	-2.40959	3.00233	C	1.52675	1.42082	0.72303
H	4.15878	-1.44047	1.54126	C	-3.88433	4.38683	-0.55200
C	-1.56283	-2.19289	-2.07549	C	-5.16202	3.96641	0.19030
H	-2.07483	-1.31390	-1.70737	H	-5.41820	2.92071	-0.00434
C	5.11844	3.10506	1.72419	H	-6.00882	4.58519	-0.12742
H	4.33858	3.77965	2.09152	H	-5.03879	4.08188	1.27179
H	6.09166	3.57735	1.89922	C	-4.09070	4.20931	-2.06340
H	5.08054	2.19142	2.32477	H	-3.18475	4.47929	-2.61516
C	-4.53740	3.76721	1.92025	H	-4.91015	4.84706	-2.41334
H	-4.64594	2.82431	2.46434	H	-4.34109	3.17595	-2.31954
H	-5.40270	4.39396	2.16355	C	-3.63766	5.87124	-0.27604
H	-3.63681	4.26561	2.29234	H	-3.49925	6.06632	0.79241
C	-4.37968	4.91608	-0.27355	H	-4.50062	6.45519	-0.61143
H	-3.51053	5.49071	0.06266	H	-2.75827	6.24290	-0.81231
H	-5.27524	5.49373	-0.02352	C	0.75423	3.42901	3.05436
H	-4.33484	4.82774	-1.36395	H	0.50550	2.39192	3.29188
C	-5.71980	2.83572	-0.08695	H	-0.01148	4.06977	3.50235
H	-5.67668	2.66379	-1.16715	H	1.72279	3.66828	3.50474
H	-6.60435	3.44561	0.12840	C	1.09543	5.11902	1.24591
H	-5.85677	1.86581	0.40046	H	2.04890	5.41172	1.69474

(TIPS^{NON})AlFp

SCF (PBE0-D3BJ-CPCM(C₆H₆)/cc-pVTZ)

Energy =

-2341.01579929 Eh

Thermal Gibb's Corr. = 1.050677 Eh

Gibb's Free Energy= -2339.965123 Eh

Lowest Frequency = 16.4254 cm⁻¹

Second Frequency = 24.9833 cm⁻¹

Fe	0.11863	-2.02251	2.73763	H	6.27119	4.03736	-1.95974
Si	-3.04792	-1.07613	-0.88727	H	4.73335	4.58005	-1.27024
Si	2.06773	-1.62940	-1.79616	C	6.14228	3.15215	0.64288
Al	-0.08792	-0.87370	0.65192	H	5.63637	4.01589	1.08332
O	0.27375	0.99548	1.16772	H	7.15181	3.46643	0.35565
O	-2.38037	-0.67505	3.24450	H	6.23045	2.38471	1.41854
O	-0.80400	-4.57040	1.76609	C	6.20410	1.45213	-1.16162
				H	6.30698	0.62917	-0.44637
				H	7.20991	1.80525	-1.41026
				H	5.75900	1.05782	-2.08062
				C	-4.83221	-0.48441	-0.46825
				H	-4.98207	0.40701	-1.09635
				C	-5.03822	-0.07655	0.99186

H -4.96732 -0.94120 1.65777
H -6.03510 0.36102 1.13366
H -4.29908 0.65370 1.33061
C -5.91487 -1.47981 -0.90465
H -5.80879 -1.79743 -1.94465
H -6.90795 -1.02488 -0.80016
H -5.91556 -2.38027 -0.28494
C -2.76097 -0.87241 -2.77901
H -1.80048 -1.38403 -2.94937
C -2.59188 0.59249 -3.18763
H -3.54250 1.13094 -3.09665
H -2.28420 0.66958 -4.23837
H -1.85355 1.12272 -2.58265
C -3.80078 -1.51905 -3.69760
H -3.99652 -2.56840 -3.46593
H -3.46932 -1.46900 -4.74281
H -4.75387 -0.98127 -3.64514
C -2.74756 -2.88998 -0.34257
H -1.67105 -2.91728 -0.10575
C -3.49686 -3.27009 0.93628
H -3.32057 -2.56548 1.75198
H -3.19124 -4.26336 1.28020
H -4.57546 -3.30681 0.76546
C -2.97650 -3.95030 -1.41807
H -4.03426 -4.01472 -1.69714
H -2.68190 -4.93922 -1.04494
H -2.40170 -3.75344 -2.32764
C 3.81415 -2.39863 -1.60302
H 4.50919 -1.56831 -1.79442
C 4.08408 -3.44493 -2.68737
H 3.45021 -4.32916 -2.56365
H 5.12552 -3.78857 -2.65242
H 3.90388 -3.04974 -3.69351
C 4.12344 -2.93016 -0.20574
H 3.96448 -2.16121 0.55666
H 5.16598 -3.26513 -0.13243
H 3.48992 -3.78662 0.04696
C 2.07025 -0.56285 -3.39060
H 1.92611 -1.31090 -4.18529
C 0.85711 0.36369 -3.39174
H -0.07097 -0.18330 -3.21075
H 0.75142 0.88916 -4.34931
H 0.94124 1.12099 -2.60417
C 3.34344 0.20958 -3.73477
H 3.50218 1.03934 -3.03980
H 3.26925 0.63956 -4.74178
H 4.23861 -0.42176 -3.71771
C 0.69005 -2.94671 -1.96399
H -0.22071 -2.40366 -1.65745
C 0.44501 -3.44456 -3.38849
H 0.13083 -2.63959 -4.05997
H -0.34069 -4.21009 -3.40172
H 1.34470 -3.90058 -3.81639
C 0.88072 -4.12032 -1.00303
H 1.69921 -4.76843 -1.33324
H -0.02189 -4.73948 -0.94487

H 1.11502 -3.78787 0.01219
C 0.85382 -1.76806 4.67910
H 0.22120 -1.66102 5.54972
C 1.31089 -0.70644 3.83698
H 1.10712 0.34616 3.97286
C 2.08130 -1.27402 2.78612
H 2.59634 -0.72915 2.00908
C 2.08535 -2.68258 2.96281
H 2.57628 -3.39911 2.31960
C 1.33245 -2.98455 4.14264
H 1.13336 -3.97383 4.53203
C -1.39675 -1.23012 2.98689
C -0.49024 -3.50332 2.09057

(DAS)AlFp

SCF (PBE0-D3BJ-CPCM(C₆H₆)/cc-pVTZ)
Energy =
-2055.94569701 Eh
Thermal Gibb's Corr. = 0.739650 Eh
Gibb's Free Energy= -2055.206047 Eh
Lowest Frequency = 16.5159 cm⁻¹
Second Frequency = 24.5843 cm⁻¹

Fe 2.67241 2.15065 0.59907
Si -1.06995 -0.84303 0.10841
Al 0.85819 0.88415 0.02798
N 0.69009 -0.95715 0.09721
C 1.54191 3.43263 0.90176
N -0.97187 0.92003 -0.03979
C -2.83624 2.39743 0.58448
C -2.25412 2.06304 -1.76746
C -1.32960 1.48617 -2.81968
H -0.97727 0.51987 -2.44401
C -2.99193 -2.20294 1.76823
H -3.42489 -2.55749 0.83636
O 3.12011 2.96365 -2.13767
C -4.12484 3.48262 -1.16455
H -4.94454 4.13046 -1.46181
C -2.60796 2.17063 2.06259
H -1.74328 1.50844 2.14968
C 1.16065 -3.12426 1.97914
H 0.67290 -2.15903 2.12601
C -1.42852 -2.95598 -1.78396
H -0.47879 -3.33566 -1.41464
C 4.32937 2.44576 1.83660
H 4.82176 3.39598 1.98764
C -1.86708 -1.37186 1.73349
C -3.17842 -1.29841 -1.77059
H -3.60483 -0.37234 -1.39233
C 2.87095 0.66480 2.05905
H 2.10778 -0.00324 2.43709
C -2.10531 -3.66303 -2.77498
H -1.68380 -4.58556 -3.16416
C -1.95051 -1.75918 -1.27235
C 3.06567 -3.02286 -1.87251

H 3.55893 -3.00470 -2.84099
 C 2.90689 2.62169 -1.05511
 C 3.74270 0.38667 0.96167
 H 3.72370 -0.50822 0.35300
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 H -4.51246 3.69142 0.93226
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 H -2.87656 0.59786 -4.06184
 H -1.28854 0.70966 -4.83265
 H -2.28271 2.15640 -4.67114
 C 2.03373 -0.84367 -2.52357
 H 1.47952 -0.03126 -2.02874
 C -3.56352 -2.58803 2.98018
 H -4.43824 -3.23223 2.98622
 C 3.23464 1.93460 2.59192
 H 2.74646 2.43489 3.41772
 C 3.36231 -0.25667 -2.99898
 H 3.98907 0.04847 -2.15551
 H 3.19166 0.62141 -3.62872
 H 3.92996 -0.98327 -3.58887
 C -3.80064 1.47313 2.71790
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 H -3.59462 1.26899 3.77369
 H -4.01894 0.51867 2.23126
 C -1.33079 -0.93923 2.95433
 H -0.45826 -0.28766 2.95356
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 H 1.68685 -3.23669 4.07785
 H 2.95767 -2.52810 3.06074
 H 2.68235 -4.27353 3.05210
 C -3.30693 2.90123 -2.12729
 H -3.49430 3.10166 -3.17789
 C -2.27380 3.47808 2.78407
 H -1.41042 3.97237 2.33053
 H -2.04914 3.28579 3.83943
 H -3.11524 4.17906 2.74982
 C -3.31752 -3.18612 -3.26672
 H -3.84480 -3.73621 -4.04108
 C -3.01116 -2.15212 4.18002
 H -3.45312 -2.45383 5.12542
 C -0.11148 2.39849 -2.97790
 H -0.40589 3.36786 -3.39427
 H 0.64646 1.95805 -3.63486
 H 0.35532 2.60645 -2.00818
 C 4.63614 1.48826 0.83239
 H 5.40395 1.58886 0.07662
 C 2.65071 -4.11258 0.21564
 H 2.82099 -4.94380 0.89544
 C 0.07636 -4.20086 2.04646
 H 0.51253 -5.20170 1.94816
 H -0.65740 -4.07548 1.24510
 H -0.46175 -4.15022 2.99889
 C -1.88828 -1.32456 4.16695
 H -1.45426 -0.97975 5.10145
 C 3.27750 -4.09963 -1.02249
 H 3.92966 -4.91528 -1.32035

C -3.85468 -2.00386 -2.76229
 H -4.80158 -1.62969 -3.14161
 C 1.80682 -3.07634 0.61402
 C 2.22206 -1.96695 -1.52242
 C 1.17508 -1.28312 -3.71081
 H 1.03883 -0.45649 -4.41662
 H 0.19010 -1.62561 -3.38508
 H 1.65810 -2.10776 -4.24654
 O 0.81794 4.30455 1.12374
 C -2.01691 1.79758 -0.39397
 C 1.55713 -1.99623 -0.26728

[(N,N'-bis-tert-butyl-1,2-diamido)AlFp]

SCF (PBE0-D3BJ/cc-pVTZ) Energy =
 -658.198476702 Eh
 Thermal Gibb's Corr. = 0.303564 Eh
 Gibb's Free Energy= -657.894912 Eh
 Lowest Frequency = 44.2571 cm⁻¹
 Second Frequency = 59.6039 cm⁻¹

C -0.00000 1.38636 -2.03904
 C -0.00000 0.71938 -0.80936
 C -0.00000 -0.71938 -0.80936
 C -0.00000 -1.38636 -2.03904
 C 0.00000 -0.69311 -3.24611
 C 0.00000 0.69311 -3.24611
 H -0.00000 2.46690 -2.06957
 H -0.00000 -2.46690 -2.06957
 H 0.00000 -1.24775 -4.17951
 H 0.00000 1.24775 -4.17951
 N -0.00000 1.31556 0.45738
 N -0.00000 -1.31556 0.45738
 Al -0.00000 0.00000 1.71078
 H -0.00000 0.00000 3.28395
 C -0.00000 2.76429 0.68826
 C -0.00000 -2.76429 0.68826
 C 1.27333 3.42229 0.13825
 H 1.38450 3.30007 -0.93935
 H 1.27089 4.49427 0.36038
 H 2.15183 2.97422 0.61286
 C -1.27333 3.42229 0.13825
 H -1.27089 4.49427 0.36038
 H -1.38450 3.30007 -0.93935
 H -2.15183 2.97422 0.61286
 C -1.27333 -3.42229 0.13825
 H -1.38450 -3.30007 -0.93935
 H -1.27089 -4.49427 0.36038
 H -2.15183 -2.97422 0.61286
 C 1.27333 -3.42229 0.13825
 H 1.27089 -4.49427 0.36038
 H 1.38450 -3.30007 -0.93935
 H 2.15183 -2.97422 0.61286
 C -0.00000 2.97564 2.20375
 H -0.89066 2.53283 2.66617
 H 0.89066 2.53283 2.66617

H -0.00000 4.04322 2.44122
 C -0.00000 -2.97564 2.20375
 H 0.89066 -2.53283 2.66617
 H -0.89066 -2.53283 2.66617
 H -0.00000 -4.04322 2.44122

[(N,N'-bis-triisopropylsilyl-1,2-diamido)AlFp]

SCF (PBE0-D3BJ/cc-pVTZ) Energy =
 -1059.01531618 Eh
 Thermal Gibb's Corr. = 0.441234 Eh
 Gibb's Free Energy= -1058.574082 Eh
 Lowest Frequency = 9.4971 cm⁻¹
 Second Frequency = 11.9142 cm⁻¹

C -3.51552 -0.25665 -2.10733
 C -4.⁹⁹⁶⁶⁷ 0.16642 -0.72420
 C -4.99667 0.16642 0.72420
 C -3.51552 -0.25665 2.10733
 C -0.14969 1.31461 0.69731
 C -0.14969 1.31461 -0.69731
 H -3.17473 0.18071 -3.12167
 H -3.17473 0.18071 3.12167
 H 2.53496 2.04550 0.95774
 H 2.53496 2.04550 -0.95774
 N -0.32434 -0.69418 -1.31597
 N -0.32434 -0.69418 1.31597
 Al 0.80410 -1.18633 -0.00000
 H 2.25331 -1.79925 -0.00000
 C -0.42851 -1.14150 -4.42648
 H 0.49784 -1.38013 -5.00468
 C -0.14475 1.70858 -3.11746
 H -1.19907 1.73940 -3.48649
 C -0.14475 1.70858 3.11746
 H -1.19907 1.73940 3.48649
 C -0.42851 -1.14150 4.42648
 H 0.49784 -1.38013 5.00468
 C 2.16778 -0.42600 -2.86347
 H 2.52304 0.01810 -3.82858
 C 2.16778 -0.42600 2.86347
 H 2.52304 0.01810 3.82858
 Si 0.26072 -0.15005 -2.90927
 Si 0.26072 -0.15005 2.90927
 C -1.28410 -0.29988 -5.39323
 H -0.61679 0.48126 -5.87133
 H -1.72867 -0.92998 -6.22284
 H -2.16104 0.24460 -4.99766
 C -1.12001 -2.49152 -4.04316
 H -0.45751 -3.10856 -3.40555
 H -2.05774 -2.35189 -3.45799
 H -1.38614 -3.07160 -4.96980
 C 2.55551 -1.90670 -2.89064
 H 2.10053 -2.43894 -3.75812
 H 3.66118 -2.01569 -2.95958
 H 2.22742 -2.43383 -1.96444
 C 2.83723 0.34518 -1.68750

H 3.78192 -0.12329 -1.35419
 H 3.08206 1.38301 -1.96768
 H 2.16117 0.38979 -0.79114
 C -0.07531 2.49301 -1.77514
 H -0.39303 3.53226 -1.92588
 H -0.73562 2.04917 -0.99337
 H 0.96514 2.53364 -1.37464
 C 0.76082 2.36170 -4.20701
 H 0.44697 3.39263 -4.41209
 H 1.82574 2.41279 -3.87743
 H 0.72874 1.81838 -5.17949
 C -1.12001 -2.49152 4.04316
 H -2.05774 -2.35189 3.45799
 H -0.45751 -3.10856 3.40555
 H -1.38614 -3.07160 4.96980
 C -1.28410 -0.29988 5.39323
 H -1.72867 -0.92998 6.22284
 H -0.61679 0.48126 5.87133
 H -2.16104 0.24460 4.99766
 C 2.55551 -1.90670 2.89064
 H 3.66118 -2.01569 2.95958
 H 2.10053 -2.43894 3.75812
 H 2.22742 -2.43383 1.96444
 C 2.83723 0.34518 1.68750
 H 3.08206 1.38301 1.96768
 H 3.78192 -0.12329 1.35419
 H 2.16117 0.38979 0.79114
 C -0.07531 2.49301 1.77514
 H -0.73562 2.04917 0.99337
 H -0.39303 3.53226 1.92588
 H 0.96514 2.53364 1.37464
 C 0.76082 2.36170 4.20701
 H 1.82574 2.41279 3.87743
 H 0.44697 3.39263 4.41209
 H 0.72874 1.81838 5.17949

[(N,N'-bis-diisopropylphenyl-1,2-diamido)AlFp]

SCF (PBE0-D3BJ/cc-pVTZ) Energy =
 -1276.90004332 Eh
 Thermal Gibb's Corr. = 0.553096 Eh
 Gibb's Free Energy= -1276.346947 Eh
 Lowest Frequency = 8.6971 cm⁻¹
 Second Frequency = 13.4880 cm⁻¹

C 0.00000 1.40116 -2.24302
 C 0.00000 0.71076 -1.03255
 C -0.00000 -0.71076 -1.03255
 C -0.00000 -1.40116 -2.24302
 C 0.00000 -0.69592 -3.44595
 C 0.00000 0.69592 -3.44595
 H 0.00000 2.48700 -2.23289
 H -0.00000 -2.48700 -2.23289
 H 0.00000 -1.24174 -4.38456
 H 0.00000 1.24174 -4.38456
 N 0.00000 1.30208 0.23706

N	-0.00000	-1.30208	0.23706	H	4.26474	2.56602	-1.03698
Al	0.00000	0.00000	1.50164	C	-3.33190	-3.13228	-0.94569
H	0.00000	0.00000	3.07315	H	-2.74678	-2.97256	-1.85580
C	0.00000	2.71807	0.34666	H	-3.59078	-4.19527	-0.88939
C	-1.22565	3.40815	0.39748	H	-4.26474	-2.56602	-1.03698
C	1.22565	3.40815	0.39748				
C	-1.20168	4.79627	0.54194				
C	1.20168	4.79627	0.54194				
C	0.00000	5.48836	0.61902				
H	-2.14024	5.34239	0.59068				
H	2.14024	5.34239	0.59068				
H	0.00000	6.56872	0.73196				
C	-0.00000	-2.71807	0.34666				
C	1.22565	-3.40815	0.39748				
C	-1.22565	-3.40815	0.39748				
C	1.20168	-4.79627	0.54194				
C	-1.20168	-4.79627	0.54194				
C	-0.00000	-5.48836	0.61902				
H	2.14024	-5.34239	0.59068				
H	-2.14024	-5.34239	0.59068				
H	-0.00000	-6.56872	0.73196				
C	-2.54977	2.68038	0.28891				
H	-2.32761	1.61599	0.16095				
C	2.54977	2.68038	0.28891				
H	2.32761	1.61599	0.16095				
C	2.54977	-2.68038	0.28891				
H	2.32761	-1.61599	0.16095				
C	-2.54977	-2.68038	0.28891				
H	-2.32761	-1.61599	0.16095				
C	3.37905	-2.83730	1.56478				
H	2.82893	-2.48317	2.44302				
H	3.64238	-3.88559	1.74261				
H	4.31153	-2.26751	1.49236				
C	-3.37905	2.83730	1.56478				
H	-2.82893	2.48317	2.44302				
H	-3.64238	3.88559	1.74261				
H	-4.31153	2.26751	1.49236				
C	3.37905	2.83730	1.56478				
H	3.64238	3.88559	1.74261				
H	2.82893	2.48317	2.44302				
H	4.31153	2.26751	1.49236				
C	-3.37905	-2.83730	1.56478				
H	-3.64238	-3.88559	1.74261				
H	-2.82893	-2.48317	2.44302				
H	-4.31153	-2.26751	1.49236				
C	3.33190	-3.13228	-0.94569				
H	3.59078	-4.19527	-0.88939				
H	2.74678	-2.97256	-1.85580				
H	4.26474	-2.56602	-1.03698				
C	-3.33190	3.13228	-0.94569				
H	-3.59078	4.19527	-0.88939				
H	-2.74678	2.97256	-1.85580				
H	-4.26474	2.56602	-1.03698				
C	3.33190	3.13228	-0.94569				
H	2.74678	2.97256	-1.85580				
H	3.59078	4.19527	-0.88939				

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