Supplementary Information (SI) for Dalton Transactions.

General Remarks

All manipulations were carried out under an argon atmosphere using either Schlenk-line techniques or glove boxes. All solvents were purified by standard methods. Trace amounts of water and oxygen remaining in the solvents were thoroughly removed by bulb-to-bulb distillation from potassium mirror prior to use. All crystallizations were performed at room temperature unless otherwise indicated. ^{1}H, ^{13}C{^{1}H}, and ^{27}Al{^{1}H} NMR spectra were measured on a Bruker AVANCE-400 spectrometer (^{1}H: 400 MHz; ^{13}C: 101 MHz; ^{27}Al: 104 MHz) and a Bruker AVANCE-600 spectrometer (^{1}H: 600 MHz; ^{13}C{^{1}H}: 151 MHz). Signals arising from residual protons of C_6D_5H (7.16 ppm) and from ^{13}C nuclei in C_6D_6 (128.0 ppm) were used as the internal standards for the ^{1}H and ^{13}C NMR spectra, respectively. The signal arising from $Al(NO_3)_3$ (0.0 ppm) was used as an external standard for the ^{27}Al NMR spectra. High-resolution mass spectrometry (HRMS) data were obtained on a JEOL JMS-T100LP (DART) mass spectrometer. All melting points were determined on a Büchi Melting Point Apparatus M-565 and are uncorrected. The dimer of 1-Lithium-2,5-bis(3,5-di-*t*-butylphenyl)ferrocene ($(Fc^*Li)_2$) was prepared according to literature procedures.[S1] Fc*H was identified on the basis of the spectral data identical to those reported in the literature.[S1]

Experimental Procedure

・*Synthesis of Ferrocenyldichloroalumane THF complex* ***2a·(thf)***.

In a glovebox, $AlCl_3$ (7.0 mg, 0.052 mmol) was added to a benzene solution (2 mL) of $(Fc^*Li)_2$ (30 mg, 0.027 mmol) at room temperature (r.t.), where the reaction mixture was stirred for 1.5 h. After the reaction mixture became an orange suspension, the supernatant benzene solution was removed by decantation and the remaining orange solid was washed with benzene (*ca.* 10 mL). Then, THF (*ca.* 10 mL) was added to the resulting solid and the suspension was stirred at r.t. for 5 min, before the superfluous THF was removed under reduced pressure. Then, benzene (*ca.* 10 mL) was added to the resulting orange solid, and the thus obtained solution was filtered, before all volatiles were removed from the filtrate under reduced pressure, which provided **2a·(thf)** as an orange solid (25 mg) that was contaminated with Fc*H (53% NMR yield). **2a·(thf)**: orange solid, mp. 141 ºC (decomp.).**^{1}H NMR** (400 MHz, C_6D_6): δ [ppm] = 0.58 (br, THF-4H), 1.43 (s, *t*Bu-36H), 3.40 (br, THF-4H), 4.28 (s, Cp-5H), 4.86 (s, Cp-β-2H), 7.43 (t, *J* = 1.6 Hz, Dtp-*p*-2H), 7.86 (d, *J* = 1.6 Hz, Dtp-*o*-4H); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ [ppm] = 24.1 (CH_2), 31.9 (CH_3), 35.1 (C), 72.1 (CH), 72.3 (CH), 72.3(CH_2), 99.3(C), 120.8 (CH), 124.9 (C), 141.1 (C), 150.2(C) (signal from C_1 was not observed); **^{27}Al NMR** (104 MHz, C_6D_6): δ [ppm] = 101.2 (br). **HRMS(APCI)**, *m/z*: Found: 730.2988 ($[M]^+$), calcd. for $C_{42}H_{57}OAlCl_2Fe$ ($[M]^+$): 730.2953.

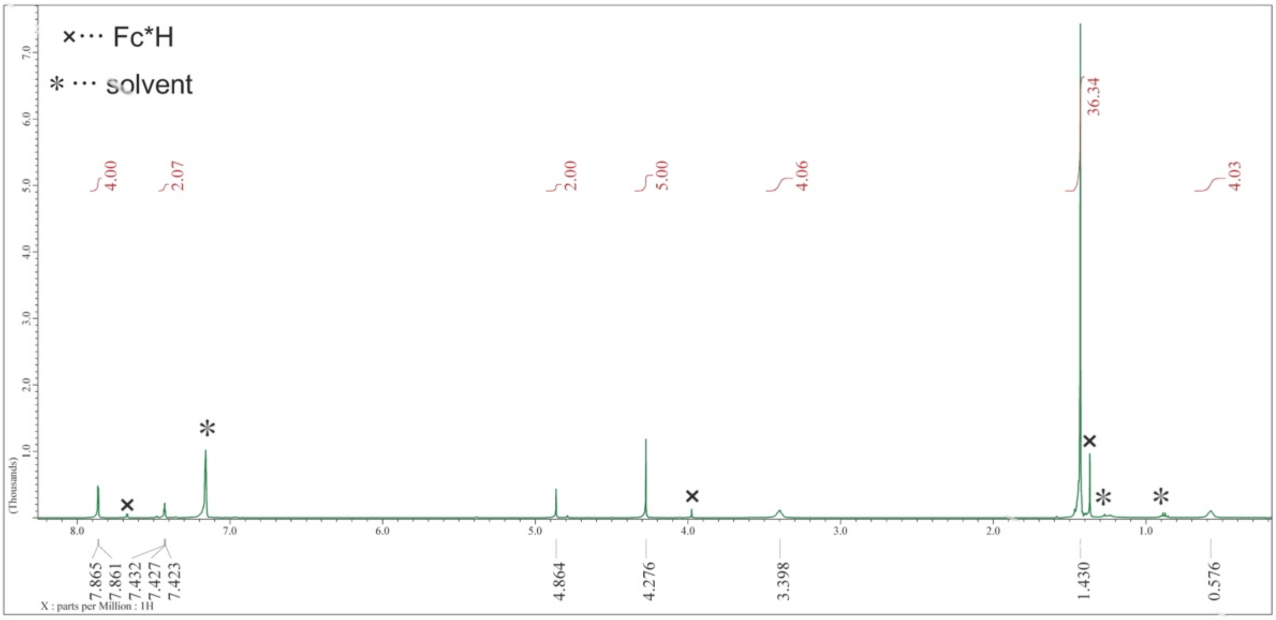


Figure S1. ^{1}H NMR (400 MHz, C_6D_6, r.t.) spectrum of **2a·(thf)**.

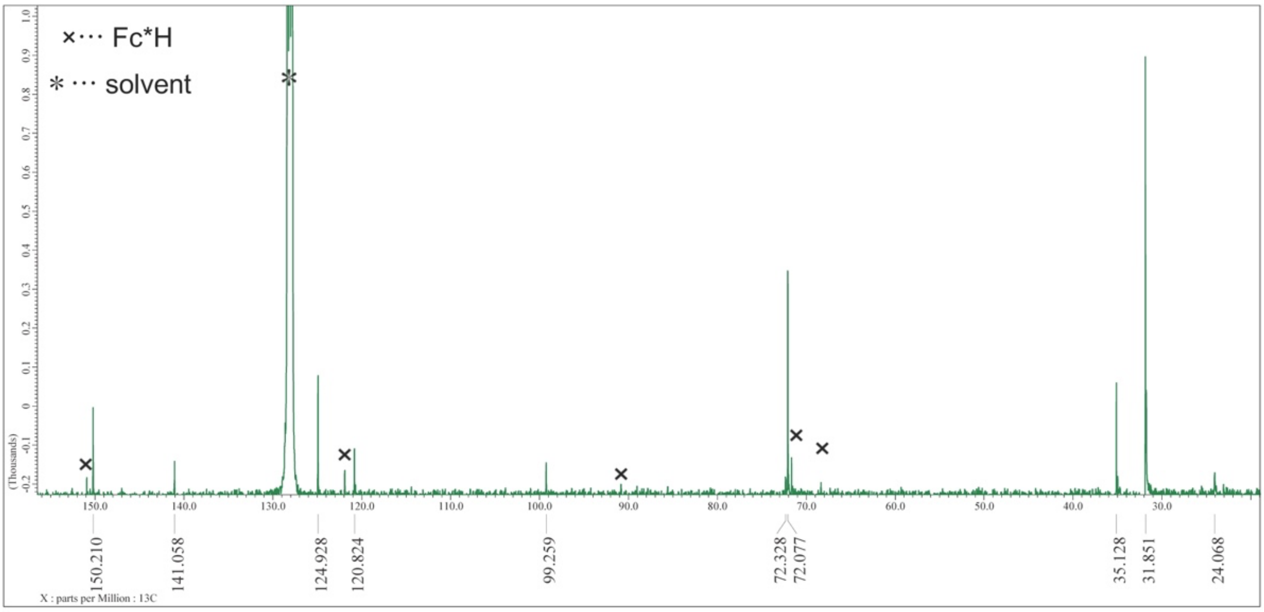


Figure S2. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, r.t.) spectrum of **2a·(thf)**.

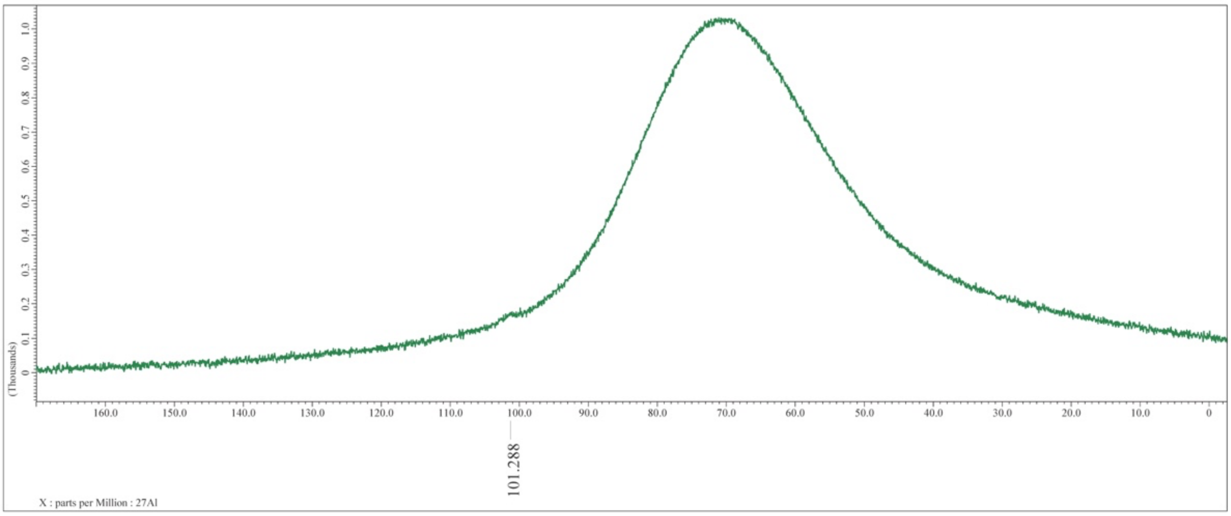


Figure S3. ^{27}Al NMR (104 MHz, C_6D_6, r.t.) spectrum of **2a·(thf)**.

· *Synthesis of Ferrocenyldibromoalumane THF complex **2b·(thf)***

In a glovebox, $AlBr_3$ (14 mg, 0.053 mmol) was added to a toluene solution (2 mL) of (Fc*Li)$_2$ (30 mg, 0.027 mmol) at r.t., where the reaction mixture was stirred for 1.5 h. After the reaction mixture became an orange suspension, the supernatant toluene solution was removed by decantation and the resulting orange solid was washed with toluene (*ca.* 10 mL). Then, THF (*ca.* 10 mL) was added to the resulting solid and the suspension was stirred at r.t. for 5 min, before the superfluous THF was removed under reduced pressure. Subsequently, toluene (*ca.* 10 mL) was added to the resulting orange solid, and the thus obtained solution was filtered, before all volatiles were removed from the filtrate under reduced pressure to generate **2b·(thf)** as an orange solid (35 mg) contaminated with Fc*H (74% ^{1}H NMR yield). Single crystals suitable for SC-XRD analysis were grown by slow evaporation of a saturated solution of **2b·(thf)** in C_6D_6 at r.t. **2b·(thf)**: orange solid, mp. 136 ºC (decomp.). **^{1}H NMR** (400 MHz, C_6D_6): δ [ppm] = 0.58 (br, THF-4H), 1.44 (s, *t*Bu-36H), 3.43 (br, THF-4H), 4.29 (s, Cp-5H), 4.84 (s, Cp-β-2H), 7.43 (d, *J* = 1.6 Hz, Dtp-*p*-2H), 7.87 (d, *J* = 1.6 Hz, Dtp-*o*-4H); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ [ppm] = 24.0 (CH_2), 31.9 (CH_3), 35.2 (C), 72.0 (CH), 72.2 (CH), 72.7 (CH_2), 99.2(C), 120.9 (CH), 125.9 (CH), 140.1 (C), 150.3(C) (signal from C_1 was not observed); **^{27}Al NMR** (104 MHz, C_6D_6): δ [ppm] = 93.8 (br). Despite several attempts of measurements, sufficient HRMS and MS data were not obtained, probably due to the lability of the compound.

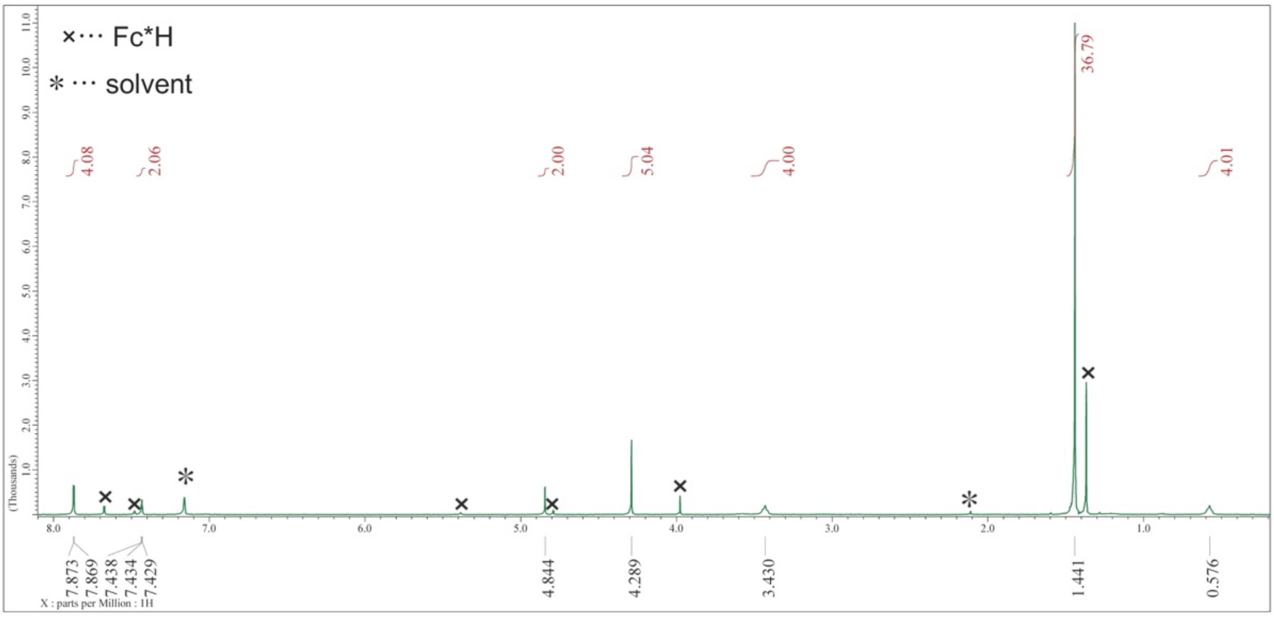


Figure S4. ^{1}H NMR (400 MHz, C_6D_6, r.t.) of **2b·(thf)**.

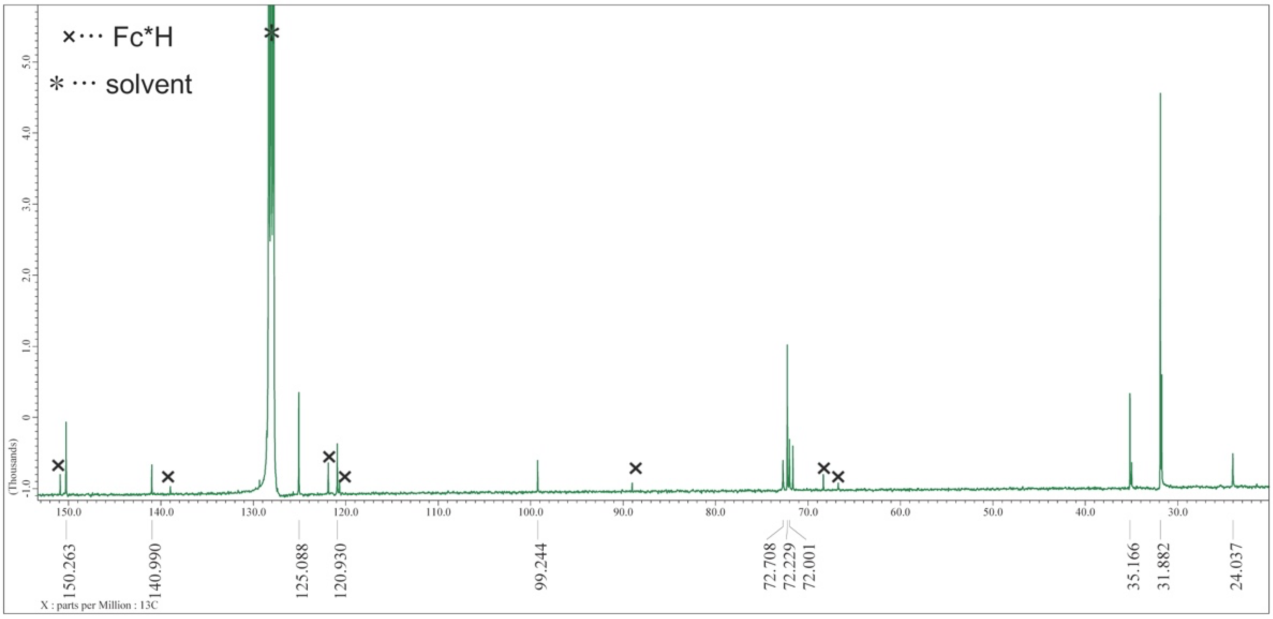


Figure S5. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, r.t.) of **2b·(thf)**.

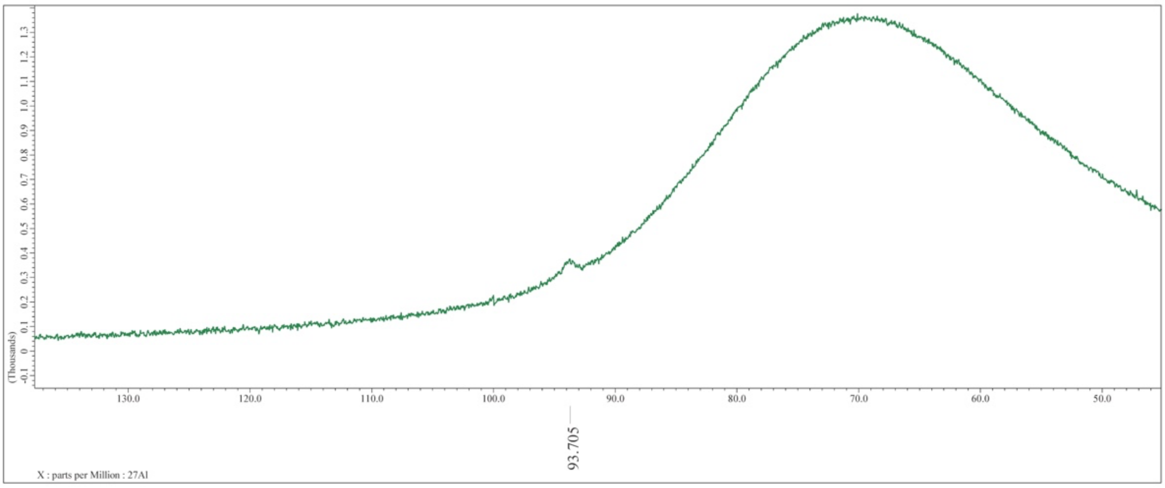


Figure S6. ^{27}Al NMR (104 MHz, C_6D_6, r.t.) of **2b·(thf)**.

・*Synthesis of Bis(ferrocenyl)chloroalumane* ***3a****.*

$AlCl_3$ (9.0 mg, 0.067 mmol) was added to a toluene solution (5 mL) of $(Fc^*Li)_2$ (73 mg, 0.064 mmol) in a Schlenk flask capped with a J-Young Teflon valve at r.t., and the reaction mixture was stirred at 60 ºC for 16 h. After the reaction mixture became an orange suspension, the reaction mixture was filtered and the remaining solid was extracted with toluene (3 × 3 mL). The combined filtrates were dried under reduced pressure, and the thus obtained solid was washed with hexane (*ca.* 10 mL). After evaporation to dryness, **3a** was obtained as a pale-yellow solid (70 mg) contaminated with Fc*H (63% ^{1}H NMR yield). Crystals suitable for SC-XRD analysis were obtained by slow evaporation of a saturated solution of **3a** in toluene at r.t. **3a**: orange solid, mp. 138 ºC (decomp.). **^{1}H NMR** (400 MHz, C_6D_6): δ [ppm] = 1.26 (s, *t*Bu-36H), 1.28 (s, *t*Bu-36H), 4.33 (s, Cp-5H), 4.83 (d, *J* = 2.0 Hz, Cp-β-2H), 4.89 (d, *J* = 2.0 Hz, Cp-β-2H), 7.38 (t, *J* = 1.8 Hz, Dtp-*p*-2H), 7.45 (t, *J* = 1.8 Hz, Dtp-*p*-2H), 7.57 (d, *J* = 1.8 Hz, Dtp-*o*-4H), 7.94 (d, *J* = 1.8 Hz, Dtp-*o*-4H); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ [ppm] = 31.8 (CH_3), 31.9 (CH_3), 34.9 (C), 35.1 (C), 72.4 (CH), 76.3 (CH), 76.4 (CH), 96.2 (C), 101.9 (C), 121.5 (CH), 121.9 (CH), 123.5 (CH), 125.1 (CH), 139.7 (C), 140.6 (C), 150.7 (C), 150.8 (C) (signal from C_1 was not observed). Despite several attempts of measurements, sufficient HRMS and MS data were not obtained, probably due to the lability of the compound.

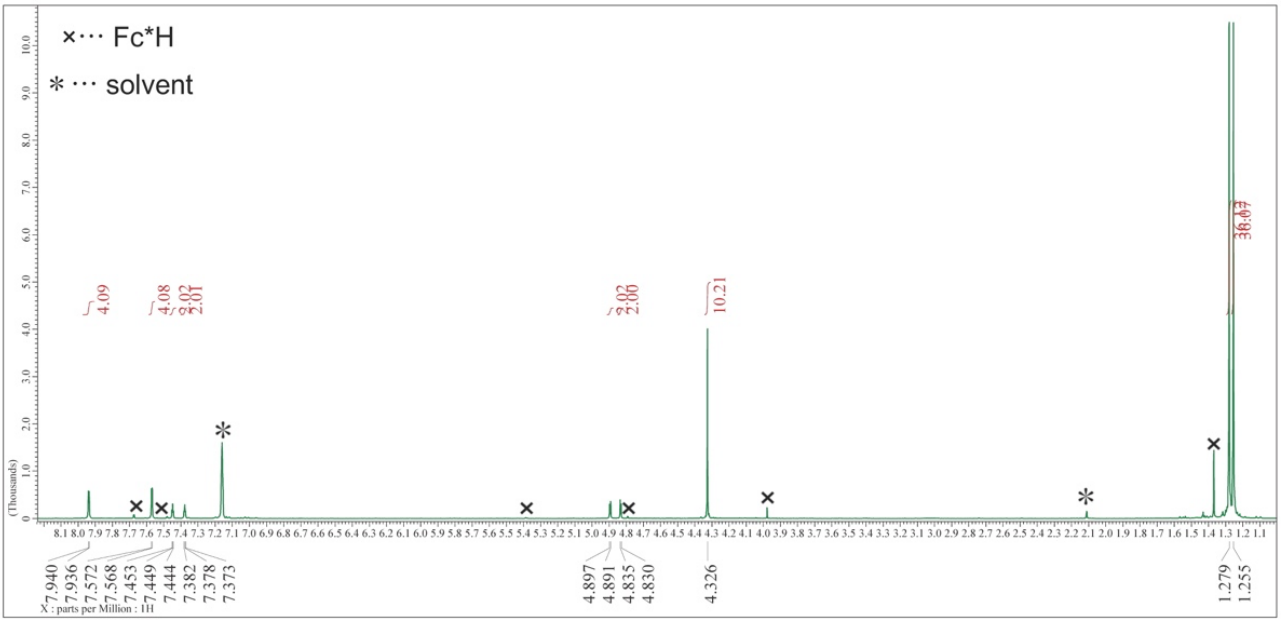


Figure S7. ^{1}H NMR (400 MHz, C_6D_6, r.t.) of **3a**.

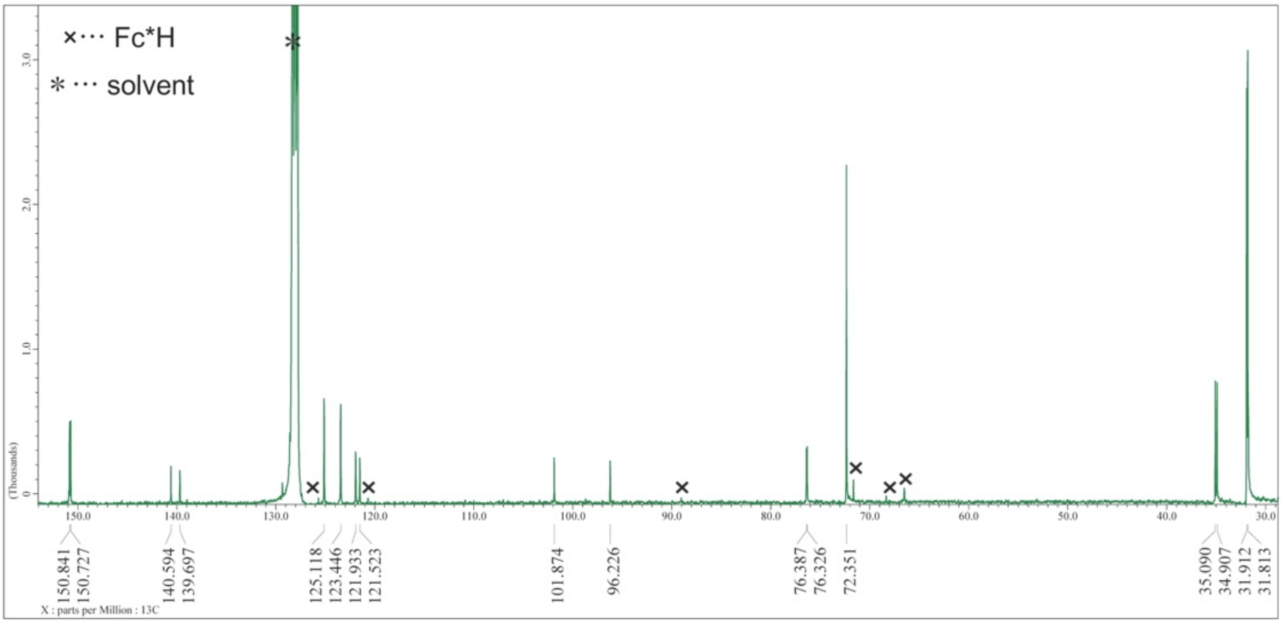


Figure S8. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, r.t.) of **3a**.

· *Synthesis of Bis(ferrocenyl)chloroalumane THF complex* ***3a·(thf)***

THF (5 mL) was added to **3a** and the obtained mixture was stirred for 5 min at r.t., before the excess THF was removed under reduced pressure to give **3a·(thf)** as an orange solid including a small amount of Fc*H. **3a(thf)**: orange solid. **^{1}H NMR** (400 MHz, C_6D_6): δ [ppm] = 0.72-0.75 (m, THF-4H), 1.19 (s, *t*Bu-18H), 1.39 (s, *t*Bu-18H), 1.47 (s, *t*Bu-18H), 1.55 (s, *t*Bu-18H), 3.77-3.79 (m, THF-2H), 3.91-3.93 (m, THF-2H), 4.04 (s, Cp-5H), 4.30 (s, Cp-5H), 4.43 (d, *J* = 2.0 Hz, Cp-β-1H), 4.56 (d, *J* = 2.0 Hz, Cp-β-1H), 4.65 (d, *J* = 2.0 Hz, Cp-β-1H), 4.74 (d, *J* = 2.0 Hz, Cp-β-1H), 7.22 (t, *J* = 1.8 Hz, Dtp-*p*-1H), 7.40 (t, *J* = 1.8 Hz, Dtp-*p*-1H), 7.50 (t, *J* = 1.8 Hz, Dtp-*p*-1H), 7.51 (t, *J* = 1.8 Hz, Dtp-*p*-1H), 7.54 (d, *J* = 1.8 Hz, Dtp-*o*-2H), 7.60 (d, *J* = 1.8 Hz, Dtp-*o*-2H), 7.76 (br, Dtp-*o*-2H), 8.24 (d, *J* = 1.8 Hz, Dtp-*o*-2H). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ [ppm] = 24.3 (CH_2), 31.9 (CH_3), 32.0 (CH_3), 32.3 (CH_3), 32.3 (CH_3), 34.9 (C), 35.1 (C), 35.1 (C), 35.4 (C), 71.2 (CH), 71.8 (CH), 72.9 (CH_2), 74.4 (CH), 75.3 (CH), 76.5 (CH), 77.2 (CH), 98.2 (C), 99.6 (C), 100.3 (C), 102.2 (C), 120.1 (CH), 121.2 (CH), 121.3 (CH), 121.9 (CH), 125.1 (CH), 126.1 (CH), 127.2 (CH), 141.1 (C), 141.9 (C), 142.0 (C), 142.3 (C), 148.9 (C), 149.3 (C), 149.3 (C), 149.4 (C), (signal from *o*-carbons of the Dtp group was not observed). **HRMS (DART)**, *m*/*z*: Found: 1257.6256 ([M+H]$^+$), calcd. for $C_{80}H_{106}OAlClFe$ ([M+H]$^+$): 1257.6525.

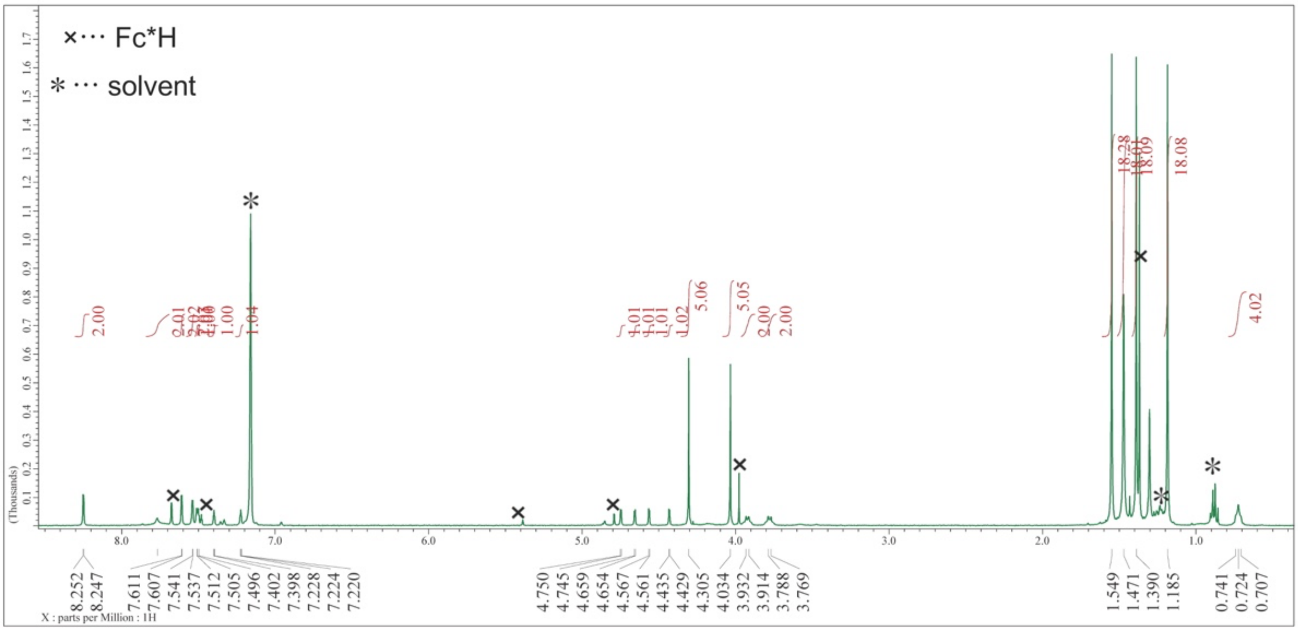


Figure S9. ^{1}H NMR (400 MHz, C_6D_6, r.t.) of **3a·(thf)**.

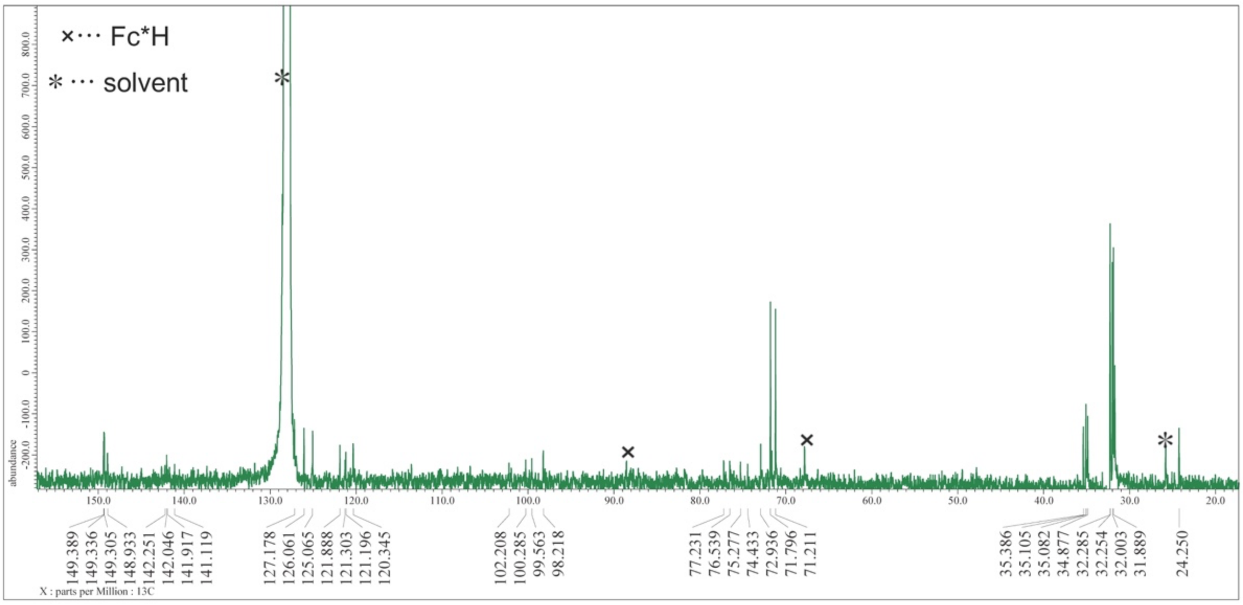


Figure S10. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, r.t.) of **3a·(thf)**.

・*Synthesis of Bis(ferrocenyl)bromoalumanes **3b** and **4b**.*

In a glovebox, AlBr$_3$ (36 mg, 0.14 mmol) was added to a toluene solution (3 mL) of (Fc*Li)$_2$ (150 mg, 0.132 mmol) in a vial (20 mL) at r.t., and the reaction mixture was stirred at r.t. for 2 h. The orange supernatant was removed by decantation and the orange precipitate was extracted with toluene (3 × 3 mL). All toluene fractions were combined and filtered, before the solvent was removed from the filtrate under reduced pressure to afford a mixture of bis(ferrocenyl)bromoalumane **3b** and **4b** (**3b**: 79%; **4b**: 13% as judged by the ^{1}H NMR spectrum) as orange solids (150 mg). The mixture of **3b** and **4b** was washed with hexane (*ca.* 10 mL) and after evaporation to dryness, **3b** was obtained as a pale-yellow solid (72 mg) contaminated with Fc*H (43% as judged by the ^{1}H NMR spectrum). The hexane fraction of the mixture of **3b** and **4b** was filtered and the solvent of the filtrated was evaporated over 2 weeks at r.t. to give a few single crystals of **4b**. **3b**: **^{1}H NMR** (400 MHz, C$_6$D$_6$): δ [ppm] = 1.24 (s, *t*Bu-36H), 1.28 (s, *t*Bu-36H), 4.39 (s, Cp-5H), 4.83 (d, *J* = 2.6 Hz, Cp-β-2H), 4.90 (d, *J* = 2.6 Hz, Cp-β-2H), 7.37 (t, *J* = 1.8 Hz, Dtp-*p*-2H), 7.46 (t, *J* = 1.8 Hz, Dtp-*p*-2H), 7.55 (d, *J* = 1.8 Hz, Dtp-*o*-4H), 7.95 (d, *J* = 1.8 Hz, Dtp-*o*-4H); **^{13}C{^{1}H} NMR** (101 MHz, C$_6$D$_6$): δ [ppm] = 31.8 (CH$_3$), 31.9 (CH$_3$), 34.9 (C), 35.1 (C), 72.5 (CH), 76.1 (CH), 76.7 (CH), 96.3 (C), 102.3 (C), 121.6 (CH), 122.1 (CH), 123.4 (CH), 125.2 (CH), 139.8 (C), 140.6 (C), 150.86 (C), 150.89 (C), (signal from C$_1$ was not observed). **4b**: **^{1}H NMR** (400 MHz, C$_6$D$_6$): δ [ppm] = 1.35 (s, *t*Bu-36H), 1.36 (s, *t*Bu-36H), 3.33 (t, *J* = 1.6 Hz, Fc*'-Cp1-α-2H), 4.13 (t, *J* = 1.6 Hz, Fc*'-Cp1-β-2H), 4.39 (s, Fc*-Cp-5H), 4.68 (d, *J* = 1.4 Hz, Fc*'-Cp2-2H), 4.95 (s, Fc*-β-2H), 5.45 (t, *J* = 1.4 Hz, Fc*'-Cp2-1H), 7.35 (t, *J* = 1.8 Hz, Fc*'-Dtp-*p*-2H), 7.40 (t, *J* = 1.8 Hz, Fc*-Dtp-*p*-2H), 7.44 (d, *J* = 1.8 Hz, Fc*'-Dtp-*o*-4H), 7.96 (d, *J* = 1.8 Hz, Fc*-Dtp-*o*-4H); **^{13}C{^{1}H} NMR** (101 MHz, C$_6$D$_6$): δ [ppm] = 31.7 (CH$_3$), 31.8 (CH$_3$), 35.0 (C), 35.2 (C), 66.5 (CH), 71.6 (CH), 72.0 (CH), 78.8 (CH), 79.5 (CH), 88.7 (C), 99.1 (C), 120.7 (CH), 121.5 (CH), 121.9 (CH), 123.7 (CH), 137.5 (C), 141.0 (C), 150.9 (C), 151.9 (C), (signals from C$_1$ and C$_{39}$ were not observed). Despite several attempts of measurements, sufficient HRMS and MS data were not obtained, probably due to the lability of the compound.

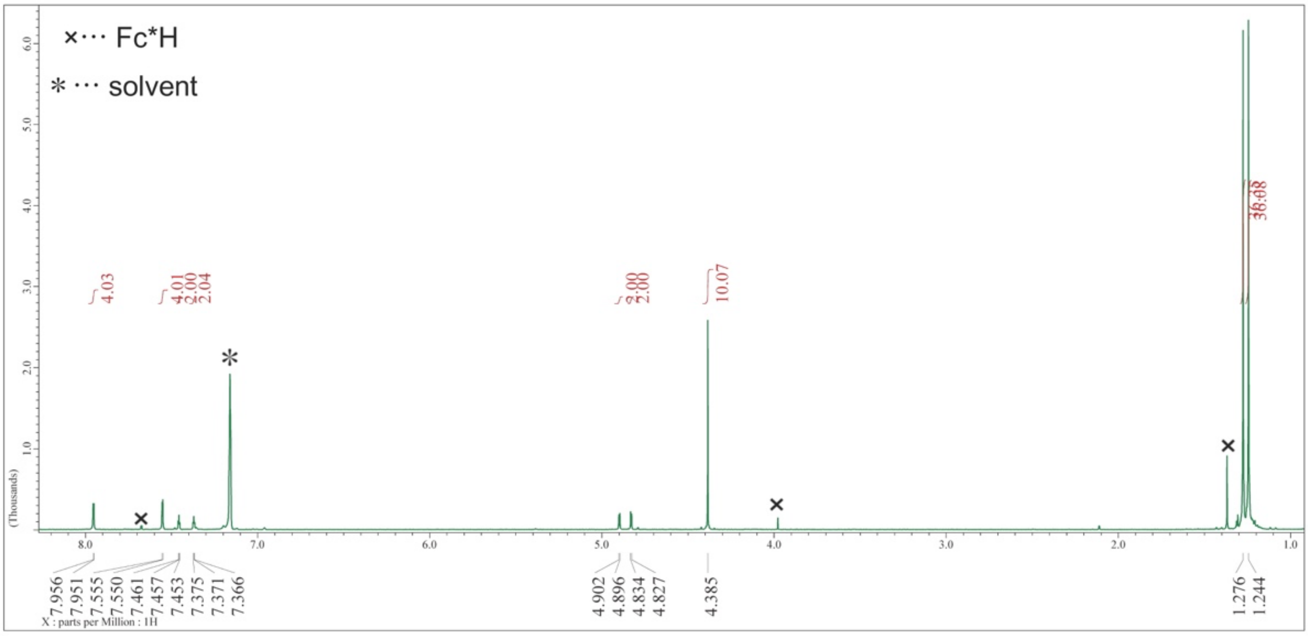


Figure S11. ^{1}H NMR (400 MHz, C$_6$D$_6$, r.t.) of **3b**.

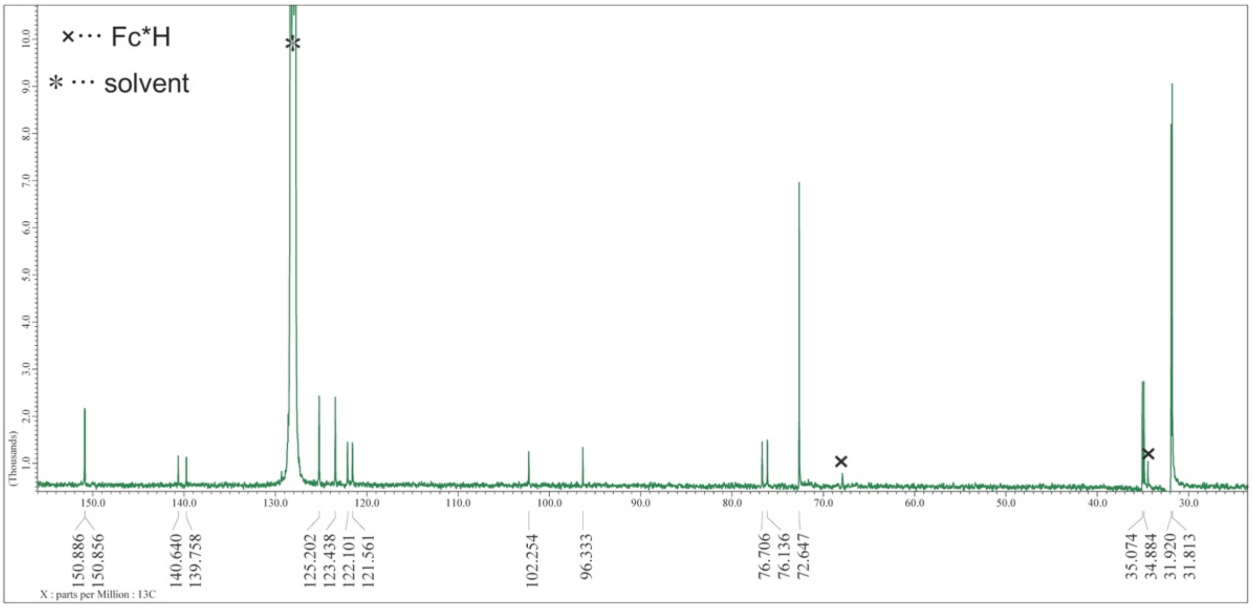


Figure S12. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, r.t.) of **3b**.

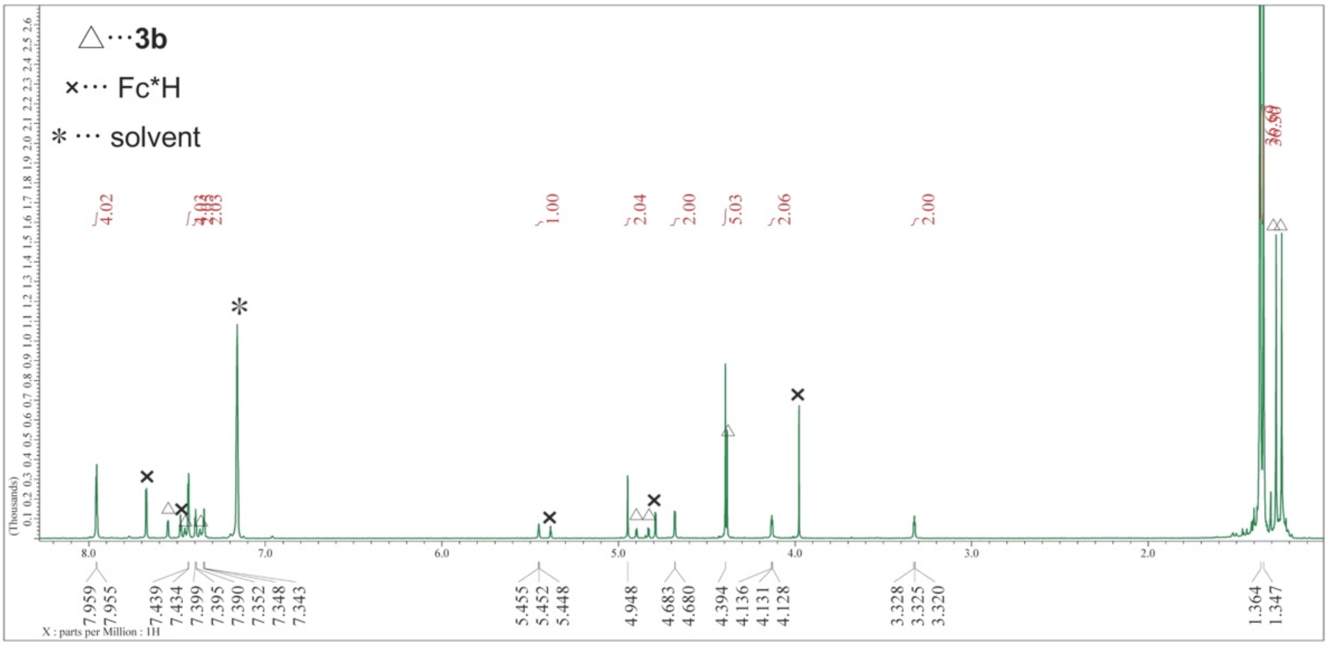


Figure S13. ^1H NMR (400 MHz, C_6D_6, r.t.) of the mixture of **3b** and **4b**.

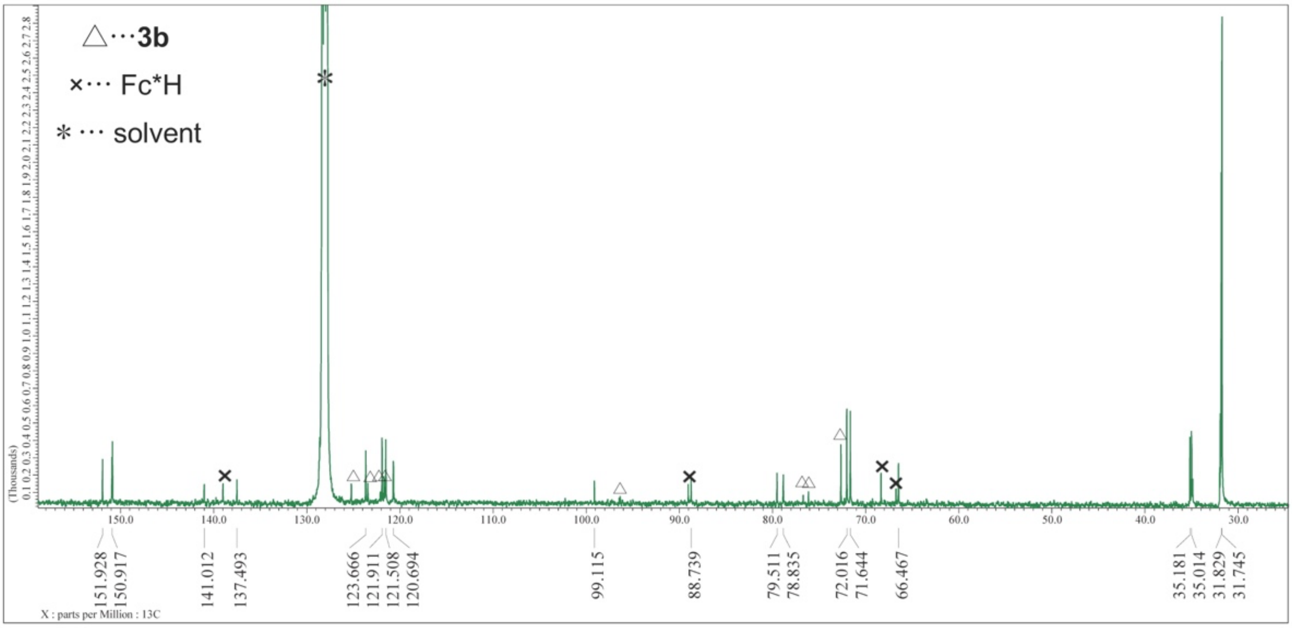


Figure S14. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, r.t.) of the mixture of **3b** and **4b**.

・*Synthesis of Bis(ferrocenyl)bromoalumane THF complex **3b·(thf)**.*

THF (5 mL) was added to **3b** and the obtained mixture was stirred for 5 min at r.t., before the excess THF was removed under reduced pressure to give **3b·(thf)** as an orange solid including a small amount of Fc*H. **3b·(thf)**: **^{1}H NMR** (400 MHz, C_6D_6): δ [ppm] = 0.74-0.80 (m, THF-4H), 1.22 (s, *t*Bu-18H), 1.38 (s, *t*Bu-18H), 1.46 (s, *t*Bu-18H), 1.56 (s, *t*Bu-18H), 3.83-3.88 (m, THF-2H), 3.92-3.97 (m, THF-2H), 4.10 (s, Cp-5H), 4.25 (s, Cp-5H), 4.45 (d, *J* = 2.4 Hz, Cp-β-1H), 4.60 (d, *J* = 2.4 Hz, Cp-β-1H), 4.63 (d, *J* = 2.4 Hz, Cp-β-1H), 4.72 (d, *J* = 2.4 Hz, Cp-β-1H), 7.22 (t, *J* = 1.6 Hz, Dtp-*p*-1H), 7.37 (t, *J* = 1.6 Hz, Dtp-*p*-1H), 7.47 (t, *J* = 1.6 Hz, Dtp-*p*-1H), 7.52 (t, *J* = 1.6 Hz, Dtp-*p*-1H), 7.53 (d, *J* = 1.6 Hz, Dtp-*o*-2H), 7.57 (d, *J* = 1.6 Hz, Dtp-*o*-2H), 7.77 (br, Dtp-*o*-2H), 8.18 (d, *J* = 1.6 Hz, Dtp-*o*-2H); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ [ppm] = 24.4 (CH_2), 31.9 (CH_3×2), 32.3 (CH_3×2), 34.9 (C), 35.1 (C), 35.1 (C), 35.4 (C), 71.6 (CH), 71.9 (CH), 73.3 (CH_2), 75.2 (CH), 75.6 (CH), 76.0 (CH), 76.8 (CH), 98.6 (C), 99.2 (C), 99.9 (C), 101.4 (C), 120.3 (CH), 120.6 (CH), 121.2 (CH), 121.2 (CH), 125.1 (CH), 125.7 (CH), 127.4 (CH), 141.1 (C), 141.8 (C), 141.9 (C), 142.34 (C), 149.2 (C), 149.3 (C×2) (a signal from the *o*-carbons of the Dtp group was not observed). Despite several attempts of measurements, sufficient HRMS and MS data were not obtained, probably due to the lability of the compound.

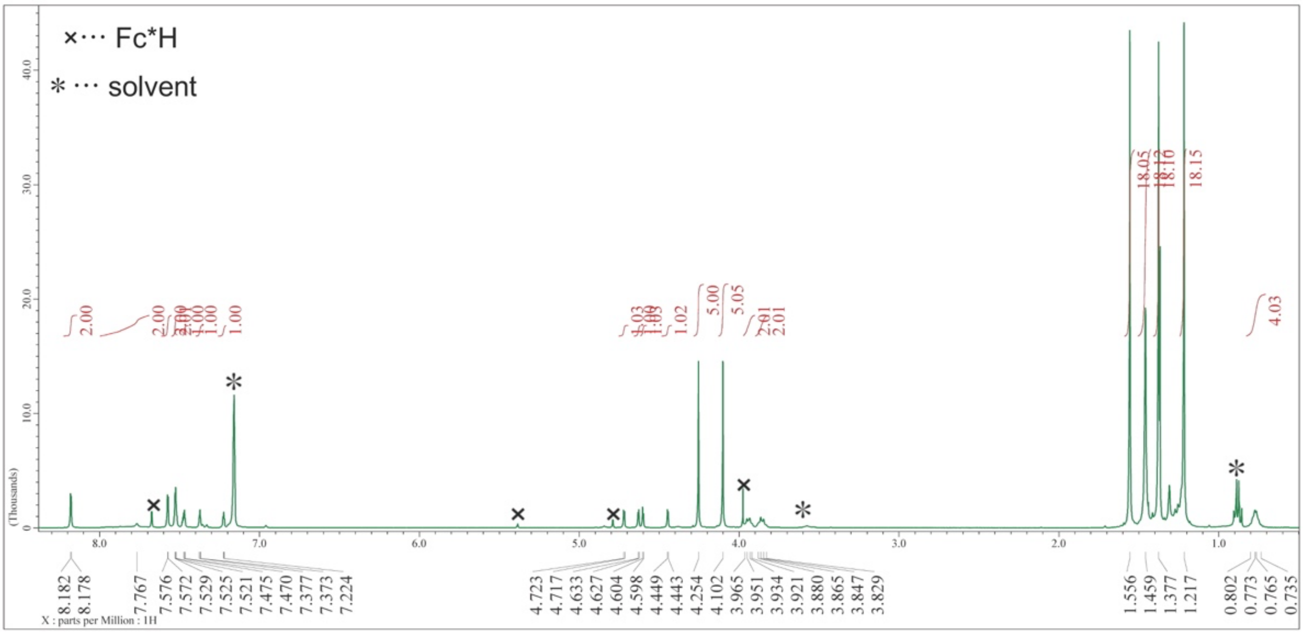


Figure S15. ^{1}H NMR (400 MHz, C_6D_6, r.t.) of **3b·(thf)**.

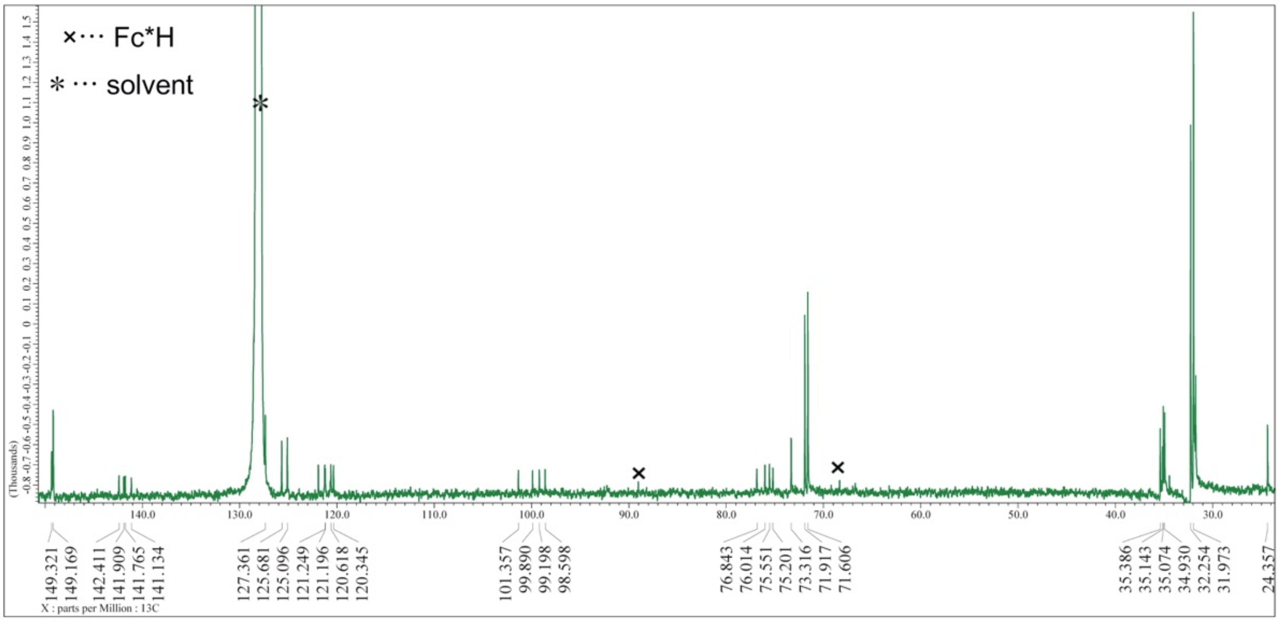


Figure S16. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, r.t.) of **3b(thf)**.

・Synthesis of Bis(ferrocenyl)iodoalumanes ***3c*** *and* ***4c****.*

In a glovebox, AlI_3 (43 mg, 0.11 mmol) was added to a toluene solution (3 mL) of (Fc*Li)$_2$ (114 mg, 0.100 mmol) in a vial (20 mL) at r.t., and the reaction mixture was stirred at r.t. for 19 h. The orange supernatant was removed by decantation and the orange precipitate was extracted with toluene (3 × 3 mL). All toluene fractions were combined and filtered, before the solvent was removed from the filtrate under reduced pressure to afford a mixture of bis(ferrocenyl)bromoalumane **3c** and **4c** (**3c**: 39%; **4c**: 59%

as judged by the ^{1}H NMR spectrum) as orange solids (149 mg). Recrystallization of a pentane solution (3 mL) of the mixture of **3c** and **4c** over 2 weeks at r.t. gave a few single crystals of **4c**. **3c**: **^{1}H NMR** (400 MHz, C_6D_6): δ [ppm] = 1.23 (s, *t*Bu-36H), 1.27 (s, *t*Bu-36H), 4.45 (s, Cp-5H), 4.83 (d, *J* = 2.2 Hz, Cp-β-2H), 4.89 (d, *J* = 2.2 Hz, Cp-β-2H), 7.36 (t, *J* = 1.6 Hz, Dtp-*p*-2H), 7.46 (t, *J* = 1.8 Hz, Dtp-*p*-2H), 7.52 (d, *J* = 1.6 Hz, Dtp-*o*-4H), 7.96 (d, *J* = 1.8 Hz, Dtp-*o*-4H); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ [ppm] = 31.8 (CH_3), 31.9 (CH_3), 34.8 (C), 35.0 (C), 73.0 (CH), 75.8 (CH), 77.0 (CH), 96.5 (C), 102.6 (C), 121.6 (CH), 122.3 (CH), 123.4 (CH), 125.3 (CH), 139.7 (C), 140.7 (C), 150.9 (C), 151.0 (C), (signal from C_1 was not observed). **4c:** orange solids, mp. 136 ºC (decomp.). **^{1}H NMR** (400 MHz, C_6D_6): δ [ppm] = 1.35 (s, *t*Bu-36H), 1.37 (s, *t*Bu-36H), 3.32 (t, *J* = 1.6 Hz, Fc*'-Cp1-α-2H), 4.15 (t, *J* = 1.6 Hz, Fc*'-Cp1-β-2H), 4.43 (s, Fc*-Cp-5H), 4.74 (d, *J* = 1.6 Hz, Fc*'-Cp2-2H), 4.92 (s, Fc*-β-2H), 5.45 (t, *J* = 1.6 Hz, Fc*'-Cp2-1H), 7.35 (t, *J* = 1.6 Hz, Fc*'-Dtp-*p*-2H), 7.40 (t, *J* = 1.6 Hz, Fc*-Dtp-*p*-2H), 7.43 (d, *J* = 1.6 Hz, Fc*'-Dtp-*o*-4H), 7.95 (d, *J* = 1.6 Hz, Fc*-Dtp-*o*-4H); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ [ppm] = 31.8 (CH_3), 31.9 (CH_3), 35.0 (C), 35.2 (C), 66.5 (CH), 66.6 (CH), 72.0 (CH), 72.1 (CH), 79.0 (CH), 79.7 (CH), 88.8 (C), 99.5 (C), 120.7 (CH), 121.6 (CH), 121.7 (CH), 124.0 (CH), 137.4 (C), 140.8 (C), 150.9 (C), 151.9 (C) (signals from C_1 and C_{39} were not observed). Despite several attempts of measurements, sufficient HRMS and MS data were not obtained, probably due to the lability of the compound.

The results of other entries of the similar reactions are summarized in Table S1.

Table S1. Reactions of ferrocenyl lithium dimer **1** with AlI_3.

entry	Ratio of the reactants **1** : AlI_3	Solvent	Temp. (˚C)	Time (h)	Ratio of the products (**3c** : **4c**)
1	1.0:1.0	toluene	60	19	1.0:0.65
2	1.0:1.0	toluene	60	69	1.0:0.50
3	1.0:1.0	toluene	r.t.	2.0	1.0:1.7
4	1.0:1.1	C_6D_6	r.t.	1.5	1.0:2.5
5	1.0:0.9	C_6D_6	r.t.	1.5	1.0:0.34

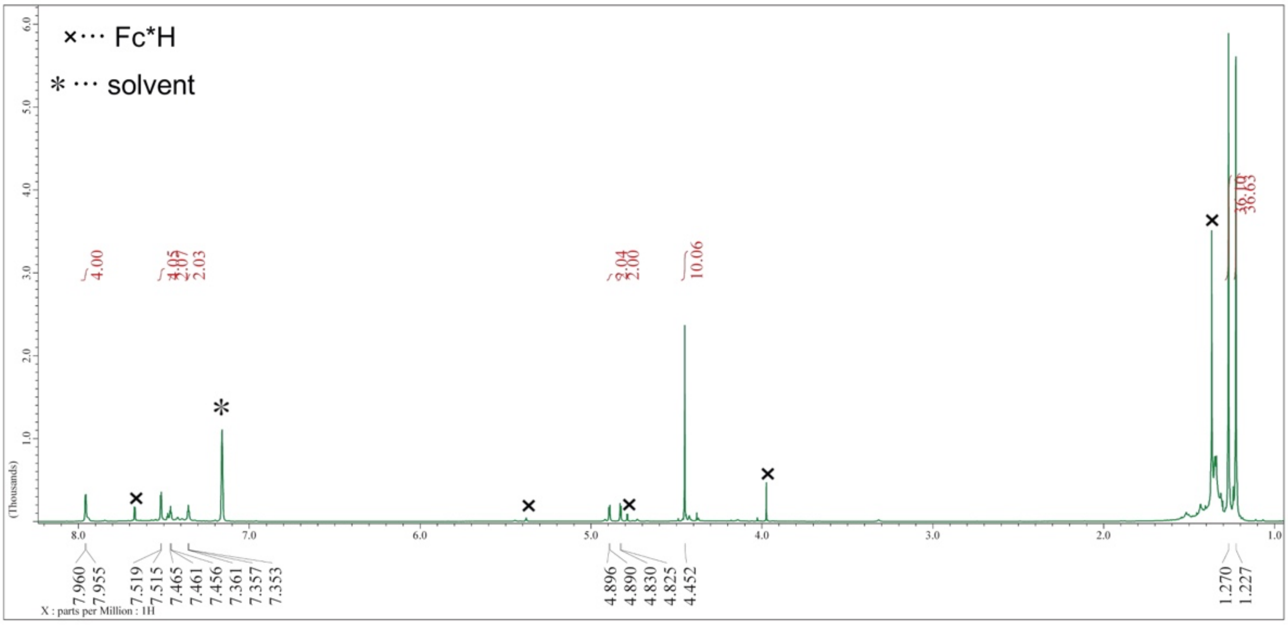


Figure S17. ^{1}H NMR (400 MHz, C_6D_6, r.t.) of **3c**.

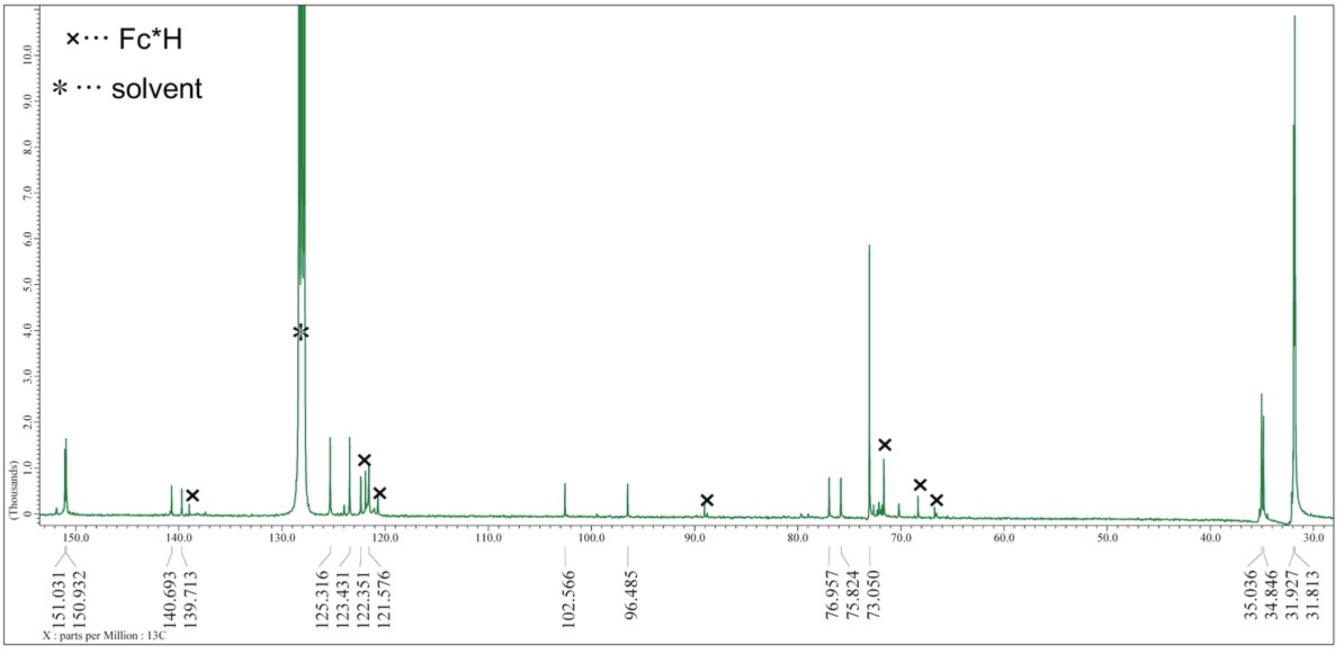


Figure S18. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, r.t.) of **3c**.

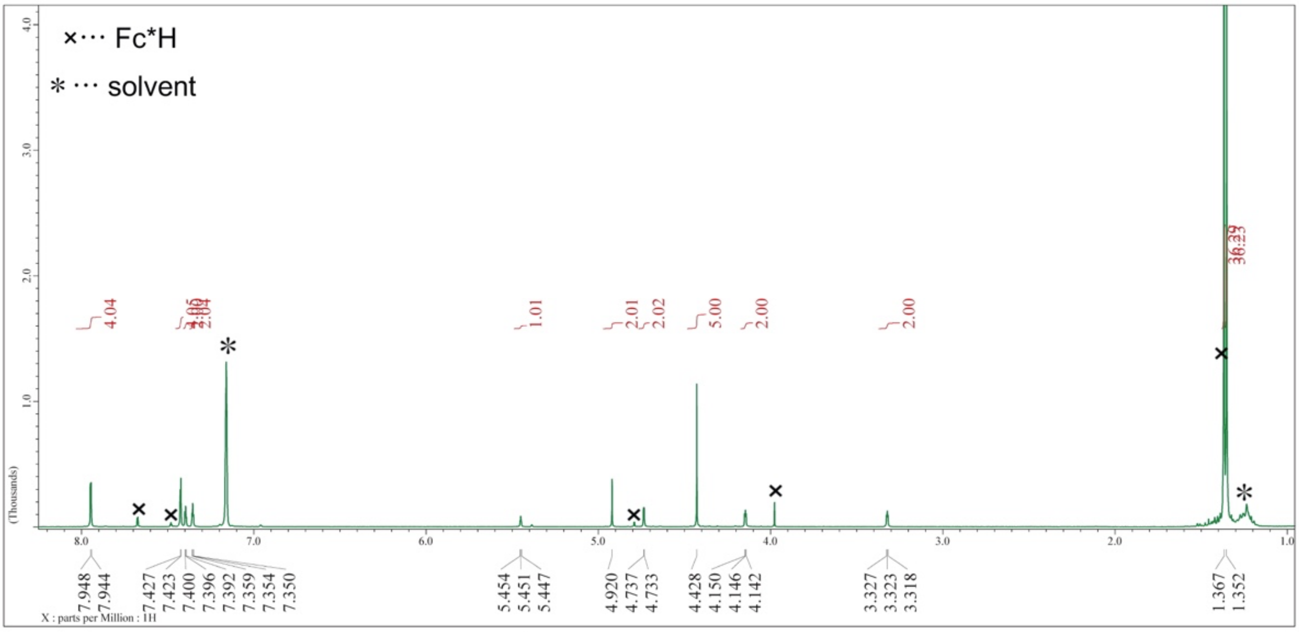


Figure S19. ${}^{1}H$ NMR (400 MHz, C_6D_6, r.t.) of **4c**.

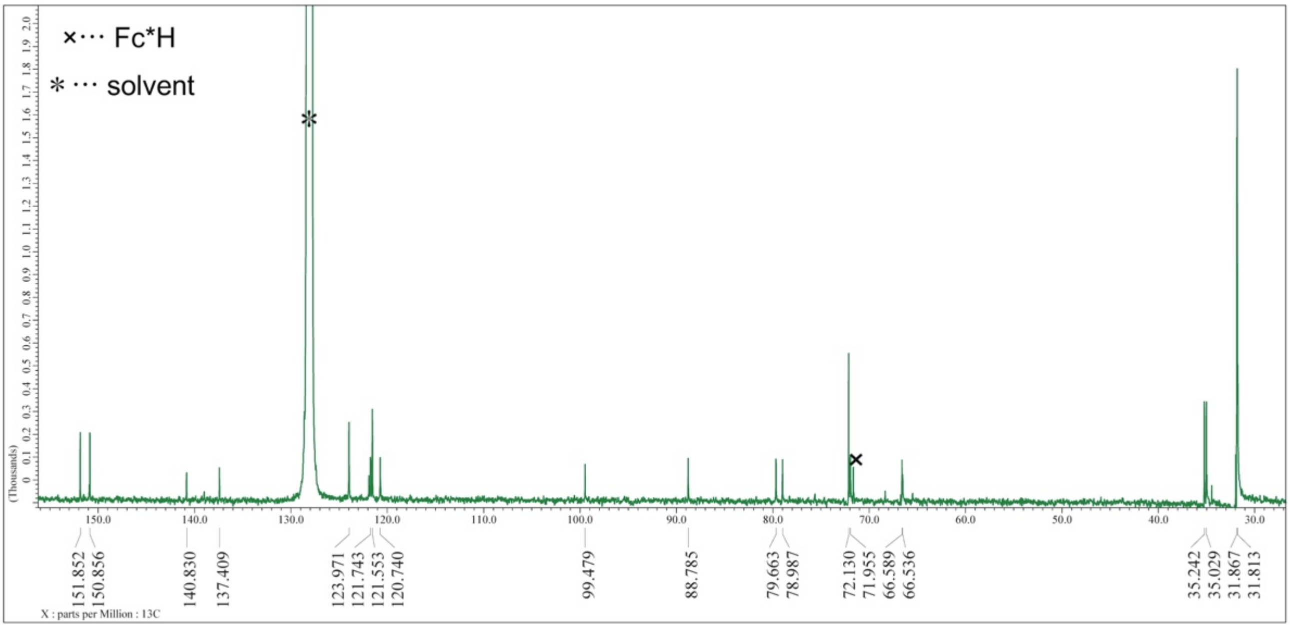


Figure S20. ${}^{13}C\{{}^{1}H\}$ NMR (101 MHz, C_6D_6, r.t.) of **4c**.

・*Reaction of Bis(ferrocenyl)bromoalumane **3b** with AlBr₃.*

In a glovebox, **3b** (19 mg, 0.015 mmol) and $AlBr_3$ (4.0 mg, 0.015 mmol) were dissolved in a J. Young NMR tube and dissolved in C_6D_6 (0.5 mL). The reaction mixture was shaken a few times and monitored for 6 days, leading to the predominant formation of ferrocenyldibromoalumane dimer $Fc^{*\prime}AlBr_2)_2$ (**5b**). A hexane solution containing **5b** was cooled at –30 °C for 2 days to obtain a small amount of red single crystals of **5b**. **${}^{1}H$ NMR** (400 MHz, C_6D_6): δ [ppm] = 1.35 (s, *t*Bu-36H), 4.40 (br, Cp-α-2H), 4.80 (br, Cp-β-

2H), 5.17 (br, Cp-1H), 5.36 (br, Cp-2H), 7.47 (br, Dtp-*p*-2H), 7.61 (br, Dtp-*o*-4H); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ [ppm] = 31.7 (CH_3), 35.0 (C), 65.3 (CH), 72.21 (CH), 81.9 (CH), 88.4 (CH), 121.8 (CH), 122.0 (CH), 150.9 (C), 151.3(C) (a signal from C_1 and was not observed). Despite several attempts of measurements, sufficient HRMS and MS data were not obtained, probably due to the lability of the compound.

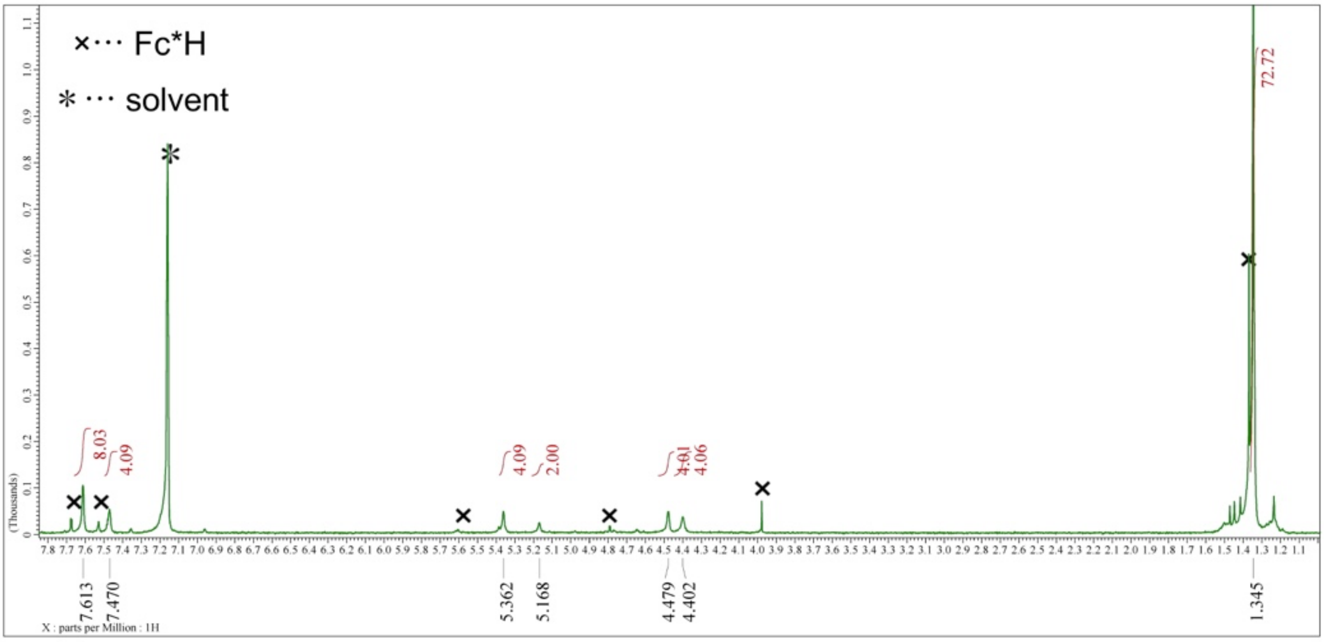


Figure S21. ^{1}H NMR (400 MHz, C_6D_6, r.t.) of **5b**.

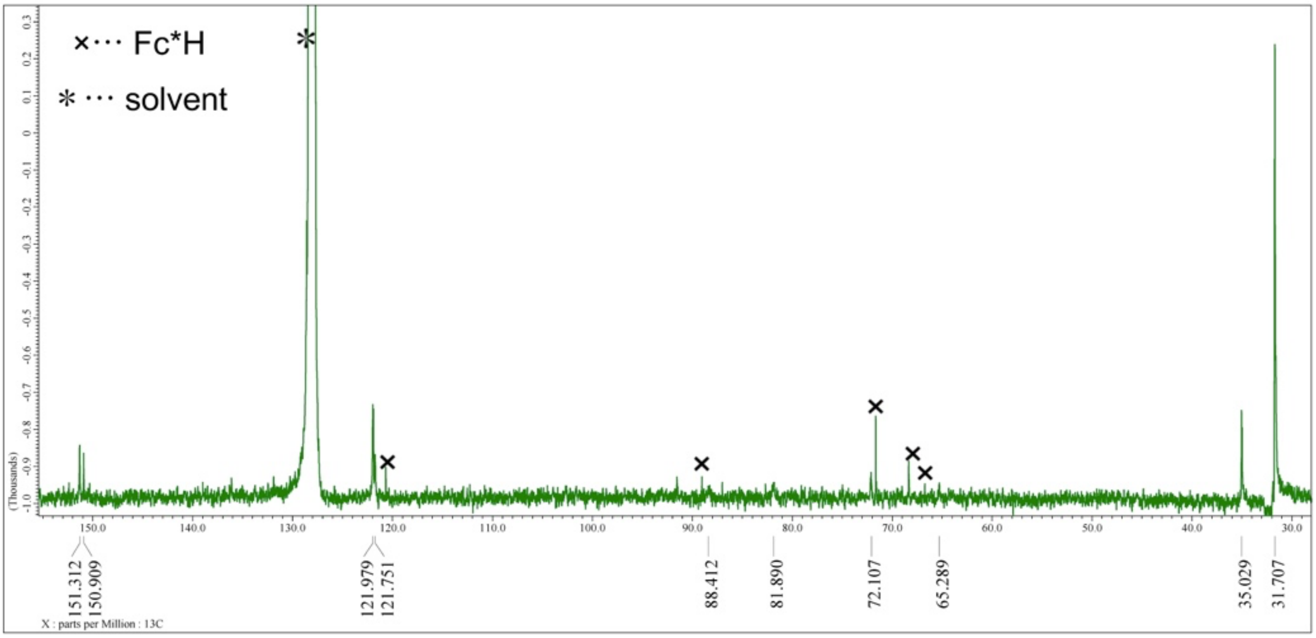


Figure S22. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, r.t.) of **5b**.

X-Ray Crystallographic Analyses

Single crystals of **2b·(thf)**, **3a**, **4b**, **4c**, and **5b** were obtained as described in the previous section (*vide supra*). Intensity data of **2b·(thf)**, **4b**, **4c**, and **5b** were collected on a Bruker APEX-II system using Mo-Kα radiation (λ = 0.71073 Å), while those of **3a** were collected on the BL02B1 beamline of SPring-8 (proposal numbers: 2023A1539, 2023A1771, 2023A1785, 2023A1794, 2023A1859, 2023A1925, 2023B1675, 2023B1806, 2023B1878, and 2024A1857) on a PILATUS3 X CdTe 1M camera using synchrotron radiation (λ = 0.4132 Å). The structures were solved using SHELXT-2018[S2] and refined by a full-matrix least-squares method (LSQ) on F^2 for all reflections using SHELXL-2018[S3] and the Yadokari-XG software package.[S4] All non-hydrogen atoms were refined anisotropically, while the positions of all hydrogen atoms were calculated geometrically and refined as riding models. Supplementary crystallographic data were deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC-2401680 (**2b·(thf)**), 2401681 (**3a**), 2401682 (**4b**), 2401683 (**4c**) and 2403232 (**5b**); these can be obtained free of charge via www.ccdc.cam.ac.uk/data_request.cif.

Table S1. Crystal data and data collection of **2b·(thf)**, **3a**, **4b**, **4c** and **5b**.

Compound	**2b·(thf)**	**3a**	**4b**	**4c**	**5b**
Formula	$C_{51}H_{66}AlBr_2FeO$	$C_{76}H_{98}AlClFe_2$	$C_{79}H_{105}AlBrFe_2$	$C_{79}H_{105}AlIFe_2$	$C_{38}H_{49}AlBrFe_2$
Molecular Weight	937.68	1185.67	1273.21	1320.20	748.42
Temperature / K	103	103	103	103	103
λ (Å)	0.71073	0.4139	0.71073	0.71073	0.71073
Crystal size / mm^3	0.20×0.12×0.10	0.10×0.10×0.10	0.15×0.10×0.07	0.10×0.08×0.04	0.10×0.08×0.04
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*P*-1 (#2)	$P2_1/c$ (#14)	*C*2 (#5)	*C*2 (#5)	*P*-1 (#2)
a /Å	9.8469(2)	27.6731(12)	30.2977(8)	41.545(6)	9.6531(6)
b /Å	14.9905(3)	22.0774(6)	11.2247(2)	11.2552(4)	13.4278(9)
c /Å	16.4903(3)	11.0682(3)	24.8238(6)	24.773(3)	14.0646(9)
α /deg	103.731(2)	90	90	90	89.361(5)
β / deg	90.9670(10)	100.582(3)	122.980(4)	142.79(3)	81.596(5)
γ / deg	92.201(2)	90	90	90	85.812(5)
V /Å^3	2361.97(8)	6647.1(4)	7081.8(4)	7006(3)	1798.7(2)
Z	2	4	4	4	2
μ / mm^{-1}	2.064	0.130	1.027	0.909	2.689
$D_{calcd.}$ / g·cm^{-3}	1.318	1.185	1.194	1.252	1.382
θ_{max}	28.641	15.591	28.702	29.144	26.373
Refl./restr./param.	11275/0/517	15228/0/805	17050/73/824	17624/115/803	7331/66/407
Completeness	99.9	99.9	99.9	99.9	99.8
GOF	1.017	1.124	1.025	1.503	1.126
R_1 (I>2σ(I))	0.0262	0.0832	0.0345	0.0807	0.1355
wR_2 (I>2σ(I))	0.0659	0.1609	0.0744	0.1311	0.2051
R_1 (all data)	0.0290	0.1349	0.0417	0.1404	0.2521
wR_2 (all data)	0.0673	0.1827	0.0771	0.1511	0.2467
Largest diff. peak and hole /e·Å^{-3}	0.754, –0.423	0.836, –0.891	0.402, –0.275	1.351, –0.940	1.017, –0.650
CCDC number	2401680	2401681	2401682	2401683	2403232

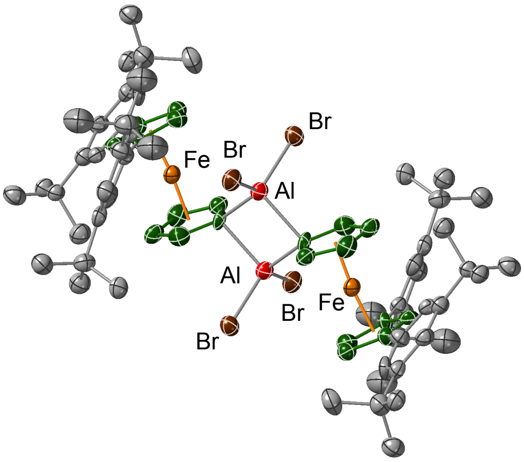


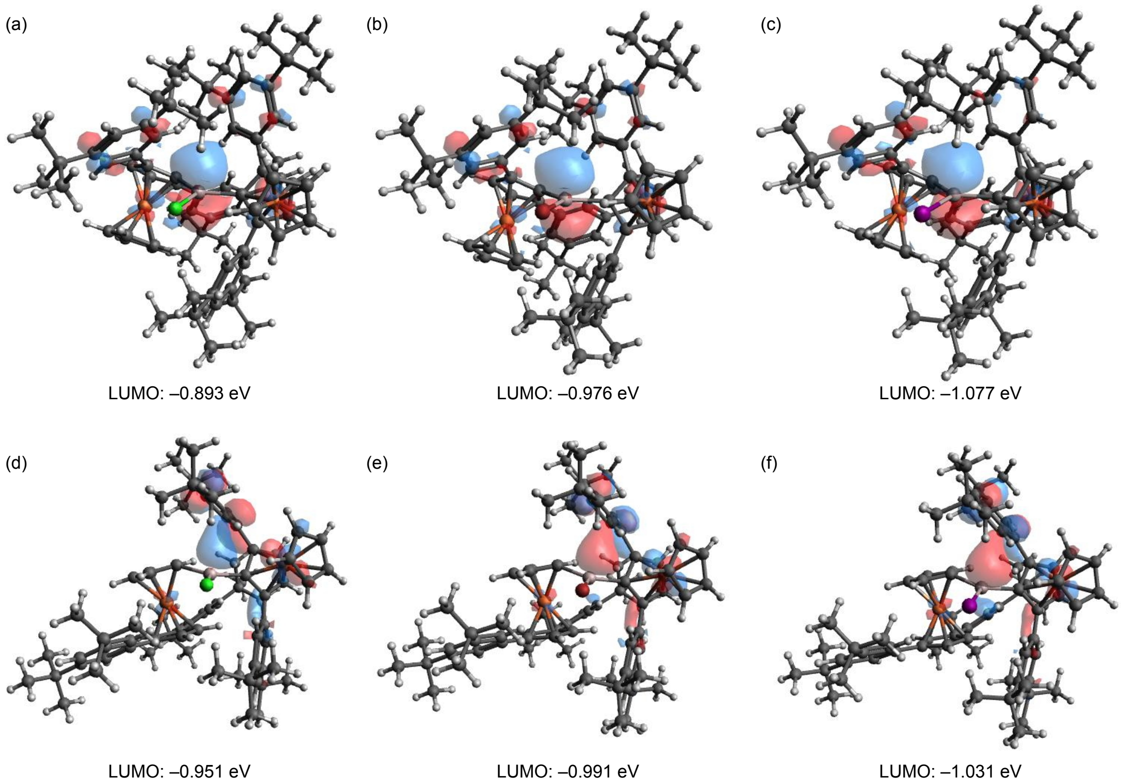
Figure S23 Molecular structure of **5b** in the crystalline state with thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity.

Theoretical Calculations

Theoretical calculations for the geometry optimizations and frequency calculations of **3a**-**c** and **4a**-**c** were carried out using the Gaussian 16 (Revision C.01) program package.[S5] Geometry optimizations were performed at the B3PW91-D3(BJ) level using basis sets described in the text. Minimum energies for the optimized structures were confirmed by frequency calculations. Energies were corrected for the zero-point energy (ZPE) term at the optimization level (E_{zero}). Computational time was generously provided by the Supercomputer Laboratory at the Institute for Chemical Research (Kyoto University). Computations were also carried out using resources of the Research Center for Computational Science, Okazaki, Japan (Projects: 24-IMS-C377/24-IMS-C397). The coordinates of the optimized structures are included in the corresponding .xyz files as supporting information.

· Estimation of the electrophilicity of the bis(ferrocenyl)haloalumanes.

The theoretically calculated LUMO levels of **3a-c** and **4a-c** (Figure S24) are highly negative, indicating their expected electrophilicity.



(a) LUMO: –0.893 eV

(b) LUMO: –0.976 eV

(c) LUMO: –1.077 eV

(d) LUMO: –0.951 eV

(e) LUMO: –0.991 eV

(f) LUMO: –1.031 eV

Figure S24 KS-LUMOs [B3PW91-D3(BJ)/def2TZVPP] of (a) **3a**, (b) **3b**, (c) **3c**, (d) **4a**, (e) **4b**, (f) **4c**.

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[S2] I. Usón and G. M. Sheldrick, *Acta Cryst. Sect. D.* 2018**, 74**, 106-116.

[S3] (a) G. M. Sheldrick, *Acta Cryst.,* 2015, A71, 3-8. (b) G. M. Sheldrick, *Acta Cryst.,* 2015, C71, 3-8.

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