Supporting Information

On the Alcoholysis of Alkyl-Aluminum(III) Alcoxy-NHC Derivatives: Reactivity of the Al-Carbene Lewis Pair *versus* Al-Alkyl

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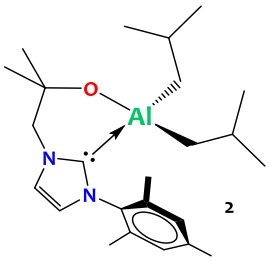
Content

A. Experimental section

General Considerations.

Unless otherwise noted, all reactions were performed either using standard Schlenk line techniques or in an MBraun inert atmosphere glovebox under an atmosphere of purified argon (<1 ppm O_2/H_2O). Glassware and cannulæ were stored in an oven at ~100 °C for at least 12 h prior to use. Toluene, *n*-pentane, Et_2O and THF were purified by passage through a column of activated alumina, dried over Na/benzophenone, vacuum-transferred to a storage flask and freeze-pump-thaw degassed prior to use. Deuterated solvents were dried over Na/benzophenone (THF-d_8 and C_6D_6) or CaH_2 ($CDCl_3$), vacuum-transferred to a storage flask and freeze-pump-thaw degassed prior to use. The NHC-OH ligand **1** and AlR(OAr) (R= ^{i}Bu, Me) were prepared according to the literature procedures.[1] All other reagents were acquired from commercial sources and used as received. NMR spectra were recorded on Bruker AV-300, AVQ-400 and AV-500 spectrometers. ^{1}H and ^{13}C chemical shifts were measured relative to residual solvent peaks, which were assigned relative to an external TMS standard set at 0.00 ppm. ^{11}B and ^{19}F chemical shifts are reported relative to $BF_3.OEt_2$ set at 0.00 ppm. ^{1}H and ^{13}C NMR assignments were routinely confirmed by ^{1}H–^{1}H COSY and ^{1}H–^{13}C HSQC and HMBC experiments. Samples for IR spectroscopy were prepared in a glovebox, sealed under argon in a DRIFT cell equipped with KBr windows and analyzed on a Nicolet 6700 FT-IR spectrometer. Elemental analyses were performed either at the School of Human Sciences, Science Center, London Metropolitan University or at Mikroanalytisches Labor Pascher, Germany. The X-ray structural determinations were performed at the Centre de Diffractométrie Henri Longchambon, UCBL, Villeurbanne. Details concerning X-ray diffraction analyses are provided in section C. The ^{13}C-labelled species were synthesized using the same procedures as for the unlabeled compounds.

Synthesis of Al(L)(^{i}Bu)$_2$ 2



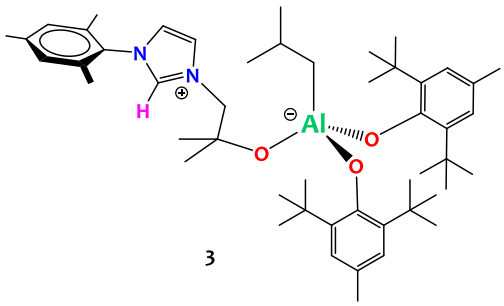
2

A cold (-40°C) orange-yellow THF suspension (20 mL) of the NHC-OH ligand **1** (205 mg, 0.79 mmol, 1 eq.) was added dropwise (in 2 minutes) to a 20 mL THF solution of triisobutylaluminium 1 M in hexanes (0.8 mL, 0.80 mmol, 1 eq.) at -40 °C. The resulting yellow solution was stirred at -40°C for 20 minutes and then stirred at r.t. for one hour. Volatiles were removed *in vacuo* yielding 310 mg (7.78 mmol, 99

%) of an orange oily residue. The crude compound was recrystallized upon dissolution in 1.5 mL of *n*-pentane and cooling at -40°C for 12 hours, yielding yellow crystals that were recovered by filtration and dried *in vacuo*. Single crystals suitable for X-ray diffraction were obtained similarly.

Alternative procedure: A 3 mL THF solution of neat triisobutylaluminum (177 mg, 0.89 mmol, 1 equiv.) was prepared and cooled to -40°C in the freezer inside the glovebox. A cold (-40°C) 15 mL orange THF suspension of the NHC-OH ligand **1** (232 mg, 0.89 mmol, 1 equiv.) was slowly added to the cold triisobutylaluminum THF solution. The resulting yellow solution was stirred for 1.5 h at room temperature. Volatiles were removed *in vacuo* and the resulting residue was dissolved in ~2 mL of pentane and stored in the glovebox freezer at -40°C for 14 hours yielding yellow-orange crystals that were recovered by filtration and dried *in vacuo* (348 mg, 98%). Single crystals suitable for X-ray diffraction were grown similarly. ^{1}H-NMR (300 MHz, C_6D_6, 293 K): δ = 6.68 (s, 2H, *m*-CH_{Mes}), 5.99 (d, 1H, CH_{imid}, $^{3}J_{H\text{-}H}$ = 1.6 Hz), 5.83 (d, 1H, CH_{imid}, $^{3}J_{H\text{-}H}$ = 1.6 Hz), 3.46 (s, 2H, NCH_2), 2.08 (m, 2H, β-CH_{iBu}), 2.03 (s, 3H, *p*-CH_{3Mes}), 1.89 (s, 6H, *o*-CH_{3Mes}), 1.27 (m, 12H, γ-$CH_{2\text{-}iBu}$), 1.24 (s, 6H, $C(CH_3)_2$), 0.03 (m, 4H, α-$CH_{2\text{-}iBu}$). ^{1}H-NMR (500 MHz, THF-d_8, 293 K): δ = 7.38 (d, 1H, CH_{imid}, $^{3}J_{H\text{-}H}$ = 1.6 Hz), 7.20 (d, 1H, CH_{imid}, $^{3}J_{H\text{-}H}$ = 1.6 Hz), 7.00 (s, 2H, *m*-CH_{Mes}), 4.01 (s, 2H, NCH_2), 2.32 (s, 3H, *p*-CH_{3Mes}), 2.00 (s, 6H, *o*-CH_{3Mes}), 1.58 (m, 2H, β-CH_{iBu}, $^{3}J_{H\text{-}H}$ = 6.6 Hz), 1.12 (s, 6H, $C(CH_3)_2$), 0.78 (d, 12H, γ-$CH_{2\text{-}iBu}$, $^{3}J_{H\text{-}H}$ = 6.6 Hz), -0.51 (d, 4H, α-$CH_{2\text{-}iBu}$, $^{3}J_{H\text{-}H}$ = 6.9 Hz). ^{13}C{^{1}H}-NMR (125 MHz, THF-d_8, 293 K): δ = 173.5 (C_{NHC}–Al), 139.8 (C_{Mes}), 135.9 (C_{Mes}), 135.6 (C_{Mes}), 129.6 (*m*-CH_{Mes}), 124.0 (CH_{imid}), 122.0 (CH_{imid}), 69.3 (O*C*$(CH_3)_2$), 62.6 (N*C*H_2), 29.5 (OC(*C*$H_3)_2$), 28.8 (γ-C_{iBu}), 28.5 (γ-C_{iBu}), 27.5 (β-C_{iBu}), 23.6 (br, α-C_{iBu}–Al), 20.9 (*p*-CH_{3Mes}), 17.6 (*o*-CH_{3Mes}). ^{13}C{^{1}H}-NMR (125 MHz, C_6D_6, 293 K): δ = 173.9 (C_{NHC}–Al). ^{27}Al-NMR (130 MHz, THF-d_8, 293 K): δ = 72.0 (br). Anal. calcd for $C_{24}H_{39}N_2OAl$: C, 72.32; H, 9.86; N, 7.03. Found: C, 72.34; H, 9.94; N, 6.89.

Synthesis of the zwitterion [HL][Al(^{i}Bu)(OAr)$_2$] 3

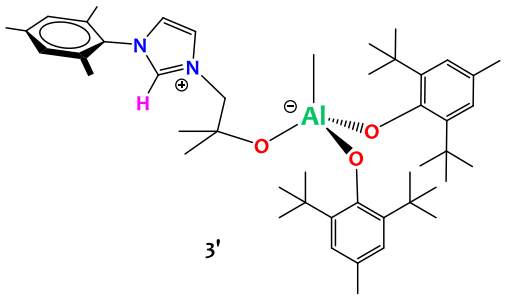


3

In a vial, a 6 mL toluene suspension of **1** (269 mg, 1.04 mmol, 1 eq.) was added onto Al(^{i}Bu)(OAr)$_2$ (544 mg, 1.04 mmol, 1 eq.). Instantly, the orange suspension became an orange solution. The reaction mixture was stirred for 1 hour at room temperature and turned from an orange solution to an off-white suspension. The solids were recovered by filtration, washed with 2x1mL toluene and dried *in vacuo* to give [HL][Al(^{i}Bu)(OAr)$_2$], **3** as a white powder (767 mg, 0.98 mmol 94 %). Single crystals suitable

for X-ray diffraction were grown from recrystallization in benzene. ^{1}H NMR (500 MHz, C_6D_6, 293 K) δ = 7.51 (t, 1H, CH_{imid}, $^{4}J_{HH}$ = 1.5 Hz), 7.19 (s, 4H, *m*-CH_{Ar}), 6.53 (s, 2H, *m*-CH_{Mes}), 6.27 (t, 1H, CH_{imid}, $^{4}J_{HH}$ = $^{3}J_{HH}$ = 1.5 Hz), 5.48 (t, 1H, CH_{imid}, $^{4}J_{HH}$ = $^{3}J_{HH}$ = 1.5 Hz), 3.53 (s, 2H, NCH_2), 2.33 (m, 1H, *β*-CH_{iBu}), 2.31 (s, 6H, *p*-CH_{3Ar}), 2.01 (s, 3H, p-CH_{3Mes}), 1.79 (s, 36H, *o*-$^{t}Bu_{Ar}$), 1.45 (s, 6H, *o*-CH_{3Mes}), 1.31 (d, 6H, *γ*-CH_{3iBu}, $^{3}J_{HH}$ = 6.0 Hz), 1.22 (s, 6H, $O(CH_3)_2$), 0.71 (d, 2H, *α*-CH_{2iBu}, $^{3}J_{HH}$ = 6.0 Hz). $^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6, 293 K) δ = 158.2 (C_{Ar}), 141.6 (C_{Ar}), 139.2 (C_{Ar}), 135.6 (CH_{imid}), 134.1 (C_{Ar}), 130.6 (C_{Ar}), 129.8 (m-CH_{Mes}), 126.2 (m-CH_{Ph}), 124.3 (C_{Ar}), 122.7 (CH_{imid}), 121.7 (CH_{imid}), 69.8 ($OC(CH_3)_2$), 64.1 (NCH_2), 35.9 ($(CH_3)_3CAr$), 33.0 ($(CH_3)_3CAr$), 29.7 (*γ*-C_{iBu}), 29.4 ($OC(CH_3)_2$), 27.0 (*β*-C_{iBu}), 21.5 (*p*-CH_{3Ar}), 20.9 (*p*-CH_{3Mes}), 17.0 (*o*-CH_{3Mes}). ^{27}Al NMR (130 MHz, C_6D_6, 293 K) δ = 78.0. Elemental analysis: Calculated for $C_{50}H_{77}O_3N_2Al$: C, 76.88; H, 9.94; N, 3.59. Found: C, 76.53; H, 10.05, N, 3.73.

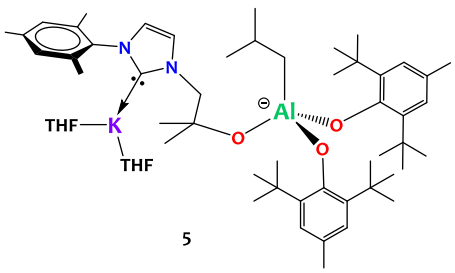
Formation of the zwitterion [HL][Al(Me)(OAr)$_2$] 3'



3'

A 0.7 mL C_6D_6 colorless solution of Al(Me)$(OAr)_2$ (30.2 mg, 0.06 mmol, 1 eq.) was added onto the ^{13}C-labelled NHC-OH ligand **1** (16.3 mg, 0.06 mmol, 1 eq.), yielding a white suspension. NMR monitoring of the reaction shows the clean formation of the imidazolium aluminate complex [HL][Al(Me)$(OAr)_2$], **3'**. ^{1}H NMR (300 MHz, C_6D_6, 293 K) δ = 8.40 (t, 1H, $^{13}CH_{imid}$, $^{1}J_{CH}$ = 226 Hz), 7.06 (s, 4H, *m*-CH_{Ar}), 6.48 (s, 2H, *m*-CH_{Mes}), 5.89 (t, 1H, CH_{imid}), 5.32 (t, 1H, CH_{imid}), 3.48 (s, 2H, NCH_2), 2.32 (s, 6H, *p*-CH_{3Ar}), 2.02 (s, 3H, p-CH_{3Mes}), 1.68 (s, 36H, *o*-$^{t}Bu_{Ar}$), 1.38 (s, 6H, *o*-CH_{3Mes}), 1.26 (s, 6H, $O(CH_3)_2$), 0.20 (s, 3H, Al-CH_3). $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6, 293 K) δ = 136.6 (CH_{imid}).

Synthesis of [K(THF)$_2$L][Al(^{i}Bu)(OAr)$_2$] 5



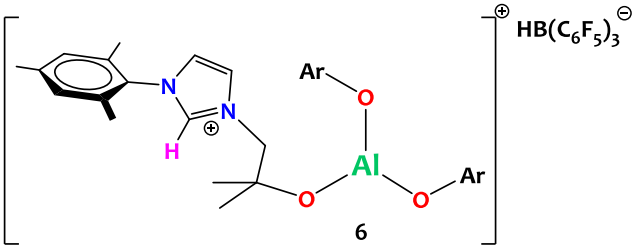
5

KHMDS (94 mg, 0.47 mmol, 1 eq.) was added to a 5 mL toluene suspension of the imidazolium aluminate **3** (365 mg, 0.47 mmol, 1 eq.). The reaction mixture was stirred overnight at room temperature. The volatiles were removed *in vacuo*. A minimum amount of THF (2mL) was added to

dissolve the off-white residue and the solution was layered with 10 mL pentane and kept at -40 °C for 3 days, yielding white crystals of [K(THF)$_2$L][Al(^{i}Bu)(OAr)$_2$] **5** that were recovered and dried *in vacuo* (324 mg, 0.34 mmol, 73%). Single crystals suitable for X-ray diffraction were grown from slow diffusion of pentane into a saturated THF solution of **5**. ^{1}H NMR (500 MHz, THF-d_8, 293 K) δ = 7.00 (d, 1H, CH$_{imid}$, $^3J_{HH}$ = 1.6 Hz), 6.94 (s, 2H, *m*-CH$_{Mes}$), 6.79 (s, 4H, *m*-CH$_{Ar}$), 6.77 (d, 1H, CH$_{imid}$, $^3J_{HH}$ = 1.6 Hz), 4.04 (s, 2H, NCH$_2$), 3.62 (m, 8H, THF), 2.29 (s, 3H, p-CH$_{3Mes}$), 2.11 (s, 6H, *p*-CH$_{3Ar}$), 1.06 (m, 1H, *β*-CH$_{iBu}$), 1.96 (s, 6H, *o*-CH$_{3Mes}$), 1.78 (m, 8H, THF); 1.46 (s, 36H, *o*-^{t}Bu$_{Ar}$), 1.18 (s, 6H, O(CH$_3$)$_2$), 0.83 (d, 6H, *γ*-CH$_{3iBu}$, $^3J_{HH}$ = 6.4 Hz), 0.23 (d, 2H, *α*-CH$_{2iBu}$, $^3J_{HH}$ = 6.4 Hz). ^{13}C{^{1}H} NMR (125 MHz, THF-d_8, 293 K) δ = 211.1 (C$_{NHC}$), 158.1 (C$_{Ar}$), 139.5 (C$_{Ar}$), 139.0 (C$_{Ar}$), 137.8 (C$_{Ar}$), 135.8 (C$_{Ar}$), 129.2 (m-CH$_{Mes}$), 125.6 (m-CH$_{Ph}$), 122.7 (C$_{Ar}$), 121.4 (CH$_{imid}$), 119.8 (CH$_{imid}$), 71.0 (O*C*(CH$_3$)$_2$), 68.0 (THF), 65.4 (N*C*H$_2$), 35.8 ((CH$_3$)$_3$*C*Ar), 32.9 ((*C*H$_3$)$_3$CAr), 30.2 (*γ*-C$_{iBu}$), 29.6 (OC(*C*H$_3$)$_2$), 27.0 (*β*-C$_{iBu}$), 26.2 (THF), 21.3 (*p*-CH$_{3Ar}$), 20.9 (*p*-CH$_{3Mes}$), 17.7 (*o*-CH$_{3Mes}$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 293 K) δ = 211.1 (C$_{NHC}$), ^{27}Al NMR (130 MHz, THF-d_8, 293 K) δ = 80.1. Anal. calcd for C$_{58}$H$_{92}$N$_2$O$_5$AlK: C, 72.31; H, 9.63; N, 2.91. Found: C, 72.19; H, 9.43; N, 2.79.

Note that upon heating (100°C for 2h in toluene), compound **5** is cleanly transformed into a new compound of unknown structure. Unfortunately, NMR data are ambiguous and thus insufficient to conclude on the precise structure of this thermal decomposition product, and attempts to crystallize it have failed in our hands to date.

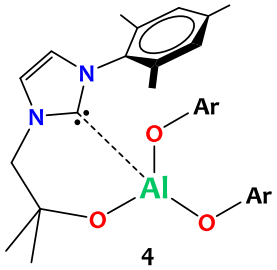
Alkyl abstraction from 3, formation of 6



6

A 0.5 mL C$_6$D$_6$ suspension of the ^{13}C-labelled imidazolium aluminate **3** (20.0 mg, 0.03 mmol 1eq.) was added onto *tris*(pentaflurorophenyl)borane (13.1 mg, 0.03 mmol, 1 eq.) at r.t., yielding a colorless solution. NMR monitoring of the reaction shows the quantitative formation of the imidazolium borate complex [(HL)Al(OAr)$_2$][HB(C$_6$F$_5$)$_3$], **6** and release of isobutene. ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K) δ = 7.66 (m, 1H, CH$_{imid}$), 7.08 (s, 4H, *m*-CH$_{Ar}$), 6.58 (s, 2H, *m*-CH$_{Mes}$), 6.20 (m, 1H, CH$_{imid}$), 5.90 (m, 1H, CH$_{imid}$), 4.75 (sept., *H*$_2$C=C(CH$_3$)$_2$), 4.01 (br, 1H, *H*B(C$_6$F$_5$)$_3^-$), 3.66 (s, 2H, NCH$_2$), 2.22 (s, 6H, *p*-CH$_{3Ar}$), 2.09 (s, 3H, p-CH$_{3Mes}$), 1.60 (t, 6H, H$_2$C=C(C*H*$_3$)$_2$), 1.54 (s, 6H, *o*-CH$_{3Mes}$), 1.53 (s, 36H, *o*-^{t}Bu$_{Ar}$), 0.82 (s, 6H, O(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 293 K) δ = 136.1 (CH$_{imid}$). ^{11}B NMR (96 MHz, C$_6$D$_6$, 293 K) δ = -24.3 (d, $^1J_{BH}$ = 79 Hz, H*B*(C$_6$F$_5$)$_3$). ^{19}F NMR (282 MHz, C$_6$D$_6$, 293 K) δ = -133.2 (d, 6F, *o*-C$_6$*F*$_5$), -162.8 (t, 3F, *m*-C$_6$*F*$_5$), -166.1 (t, 6F, *p*-C$_6$*F*$_5$).

Deprotonation of 6, formation of 4



4

NMR-scale reaction monitoring on the ^{13}C-labelled carbene derivative:

A 0.5 mL C_6D_6 suspension of the ^{13}C-labelled imidazolium aluminate **3** (20.0 mg, 0.03 mmol 1eq.) was added onto *tris*(pentaflurorophenyl)borane (13.1 mg, 0.03 mmol, 1 eq.) at r.t., yielding a colorless solution. This solution was then transferred onto KHMDS (5.1 mg, 0.03 mmol, 1 eq.). NMR monitoring of the reaction shows the quantitative formation of $Al(L)(OAr)_2$, **4**.

Isolation procedure:

A 8 mL toluene solution of tris(pentafluorophenyl)borane (615 mg, 0.79 mmol, 1 eq) was added dropwise onto the imidazolium aluminate zwitterion **3** (402 mg, 0.79 mmol, 1 eq). The resulting solution was stirred at room temperature for 10 minutes before addition of 157 mg of KHMS (0.79 mmol, 1.00 eq). The reaction mixture was stirred at room temperature for 18 hours yielding an off-white suspension. Volatiles were removed *in vacuo* yielding an off-white solid residue. The residue was washed with 18 mL of diethyl ether to remove the borate salt and the white solid was isolated by filtration (350 mg, 0.48 mmol, 61%). Single crystals suitable for X-ray diffraction were grown upon cooling to -40°C a saturated Et_2O solution of **4**. ^{1}H NMR (300 MHz, C_6D_6, 293 K) δ = 7.28 (s, 1H, CH_{Ar}), 7.20 (s, 1H, CH_{Ar}), 7.18 (s, 1H, CH_{Ar}), 6.89 (s, 1H, CH_{Ar}), 6.66 (s, 1H, CH_{Ar}), 6.37 (s, 1H, CH_{Ar}), 5.83 (d, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz, CH_{imid}), 5.71 (d, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz, CH_{imid}), 3.31 (d, 1H, $^2J_{H\text{-}H}$ = 12.6 Hz, NCH_2), 2.73 (d, 1H, $^2J_{H\text{-}H}$ = 12.6 Hz, NCH_2), 2.38 (s, 6H, *p*-CH_{3Ar}), 2.12 (m, 6H, *γ*-CH_{3iBu}), 1.95 (s, 3H, p-CH_{3Mes}), 1.54 (s, 6H, *o*-CH_{3Mes}), 1.76 (s, 18H, *o*-^{t}Bu_{Ar}), 1.40 (s, 18H, *o*-^{t}Bu_{Ar}), 0.98 (s, 3H, $O(CH_3)_2$), 0.78 (s, 3H, $O(CH_3)_2$). ^{1}H-NMR (500 MHz, THF-d_8, 293 K): δ = 7.35 (d, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz, CH_{imid}), 7.14 (d, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz, CH_{imid}), 6.93 (s, 1H, *m*-CH_{Mes}), 6.92 (s, 1H, *m*-CH_{Ar}), 6.86 (s, 1H, *m*-CH_{Ar}), 6.80 (s, 1H, *m*-CH_{Ar}), 6.58 (s, 1H, *m*-CH_{Ar}), 6.45 (s, 1H, *m*-CH_{Mes}), 3.66 (d, 1H, $^2J_{H\text{-}H}$ = 12.0 Hz, NCH_2), 3.36 (d, 1H, $^2J_{H\text{-}H}$ = 12.6 Hz, NCH_2), 2.27 (s, 3H, *p*-CH_{3Mes}), 2.22 (s, 3H, *o*-CH_{3Mes}), 2.18 (s, 3H, *o*-CH_{3Mes}), 2.11 (s, 3H, *p*-CH_{3Ar}) 1.59 (s, 3H, *p*-CH_{3Ar}), 1.42 (s, 9H, *o*-^{t}Bu_{Ar}), 1.38 (s, 9H, *o*-^{t}Bu_{Ar}), 1.20 (s, 9H, *o*-^{t}Bu_{Ar}), 1.07 (s, 9H, *o*-^{t}Bu_{Ar}), 0.81 (s, 6H, $O(CH_3)_2$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 293 K) δ = 167.7 (br, $C_{NHC\text{-}Al}$). ^{13}C{^{1}H}-NMR (125 MHz, THF-d_8, 293 K): δ = 157.0 (C_{Ar}), 155.4 (C_{Ar}), 140.3 (C_{Ar}), 139.4 (C_{Ar}), 139.1 (C_{Ar}), 136.0 (C_{Ar}), 135.8 (CH_{Ar}), 135.1 (C_{Ar}), 130.1 (CH_{Mes}), 129.7 (CH_{Mes}), 127.6 (CH_{Ar}), 125.9 (CH_{Ar}), 125.4 (CH_{Ar}), 124.7 (CH_{imid}), 124.3 (CH_{imid}), 69.8 ($OC(CH_3)_2$), 62.3 (NCH_2), 36.2 (($CH_3)_3CAr$), 35.8 (($CH_3)_3CAr$), 35.4 (($CH_3)_3CAr$), 35.2 (($CH_3)_3CAr$), 34.1

((CH_3)$_3$CAr), 32.8 ((CH_3)$_3$CAr), 32.5 ((CH_3)$_3$CAr), 30.5 ((CH_3)$_3$CAr), 29.5 (OC(CH_3)$_2$), 28.0 (OC(CH_3)$_2$), 21.2 (*p*-CH_{3Ar}), 20.8 (*p*-CH_{3Mes}), 18.7 (*o*-CH_{3Mes}). ^{27}Al-NMR (130 MHz, THF-d_8, 293 K): δ = 71.0 (br).

Reactivity of 4 with phenol

A 0.5 mL colorless C_6D_6 solution of the ^{13}C-labelled complex **4** (synthesized *in-situ*) was added onto phenol (4.8 mg, 0.05 mmol, 2 eq.). The colorless reaction mixture was sealed under argon in a J-Young NMR tube and heated at 75°C for 1h. ^{13}C NMR reaction monitoring (C_6D_6, 75 MHz, 293 K) showed the clean formation of an alcoxy-imidazolium zwiterrion species **7** with the diagnostic disappearance of the carbene resonance at δ = 167.7 ppm from **4** and the appearance of a characteristic imidazolium resonance at δ = 135.8 ppm (Fig. S14-d) for the ^{13}C-labelled carbon from the C_3N_2 heterocycle in **7**. A characteristic imidazolium resonance for **7** is also observed in the ^{1}H NMR spectrum δ = 7.31 (d, 1H, $^1J_{C\text{-}H}$ = 222.6 Hz, CH_{imid}). Data for **7**: ^{1}H NMR (300 MHz, C_6D_6, 293 K) δ = 7.31 (d, 1H, $^1J_{C\text{-}H}$ = 222.6 Hz, CH_{imid}), 7.12 (s, 4H, *m*-CH_{Ar}), 7.11-7.00 (m, 5H, CH_{Ph}), 6.54 (s, 2H, *m*-CH_{Mes}), 6.17 (m, 1H, CH_{imid}), 5.52 (m, 1H, CH_{imid}), 3.49 (s, 2H, NCH_2), 2.21 (s, 6H, *p*-CH_{3Ar}), 2.05 (s, 3H, p-CH_{3Mes}), 1.71 (s, 36H, *o*-^{t}Bu$_{Ar}$), 1.44 (s, 6H, *o*-CH_{3Mes}), 1.04 (s, 6H, O(CH_3)$_2$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 293 K) δ = 135.8 (CH_{imid}).

Reactivity of 2 with phenol

A 0.5 mL THF-d_8 solution of phenol (5.3 mg, 0.05 mmol, 1 eq.) was added slowly to a 0.5-mL the ^{13}C-labelled complex **2** (22.7 mg, 0.05 mmol, 1 eq.). The colorless reaction mixture is sealed under argon in a J-Young NMR tube and kept at r.t. for 3 days. ^{13}C NMR reaction monitoring (C_6D_6, 75 MHz, 293 K) shows the formation of an alcoxy-imidazolium zwiterrion species **8** with the diagnostic disappearance of the aluminum-bound carbene resonance at δ = 173.5 ppm from **2** and the appearance of a characteristic imidazolium resonance at δ = 139.4 ppm (Fig. S15) for the ^{13}C-labelled carbon from the C_3N_2 heterocycle in **8**. A characteristic imidazolium resonance for **8** is also observed in the ^{1}H NMR spectrum δ = 9.65 (d, 1H, $^1J_{C\text{-}H}$ = 225.9 Hz, CH_{imid}). Data for **8**: ^{1}H NMR (300 MHz, THF-d_8, 293 K) δ = 9.65 (d, 1H, $^1J_{C\text{-}H}$ = 225.9 Hz, CH_{imid}), 7.75 (m, 1H, CH_{imid}), 7.51 (m, 1H, CH_{imid}), 7.05 (s, 2H, *m*-CH_{Mes}), 6.76 (m, 2H, CH_{Ph}), 6.53 (m, 1H, CH_{Ph}), 6.34 (m, 2H, CH_{Ph}), 4.09 (s, 2H, NCH_2), 2.35 (s, 3H, *p*-CH_{3Mes}), 2.03 (s, 6H, *o*-CH_{3Mes}), 1.80 (m, 2H, β-CH_{iBu}, $^3J_{H\text{-}H}$ = 6.6 Hz), 1.17 (s, 6H, O(CH_3)$_2$), 0.84 (d, 12H, γ-$CH_{2\text{-}iBu}$, $^3J_{H\text{-}H}$ = 6.6 Hz), -0.22 (d, 4H, α-$CH_{2\text{-}iBu}$, $^3J_{H\text{-}H}$ = 6.9 Hz). ^{13}C{^{1}H} NMR (75 MHz, THF-d_8, 293 K) δ = 139.4 (CH_{imid}).

B. NMR spectroscopic data

Figure S1. ^{1}H NMR spectrum (500 MHz, THF-d_8, 293 K) of Al(L)(^{i}Bu)$_2$ **2**.

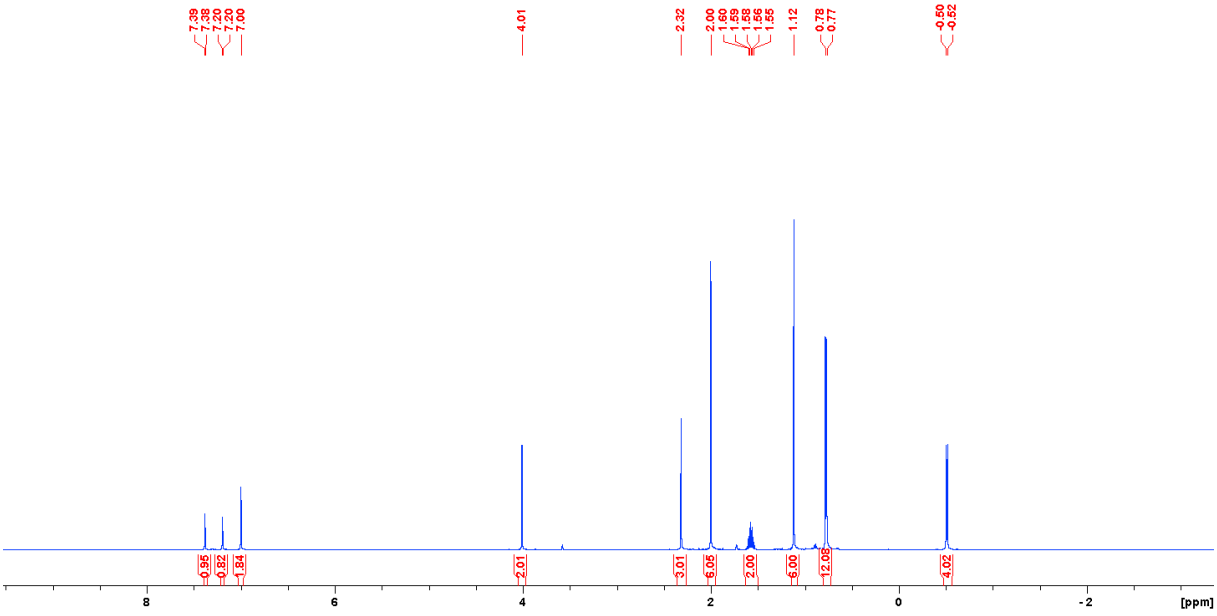


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, THF-d_8, 293 K) of Al(L)(^{i}Bu)$_2$ **2**.

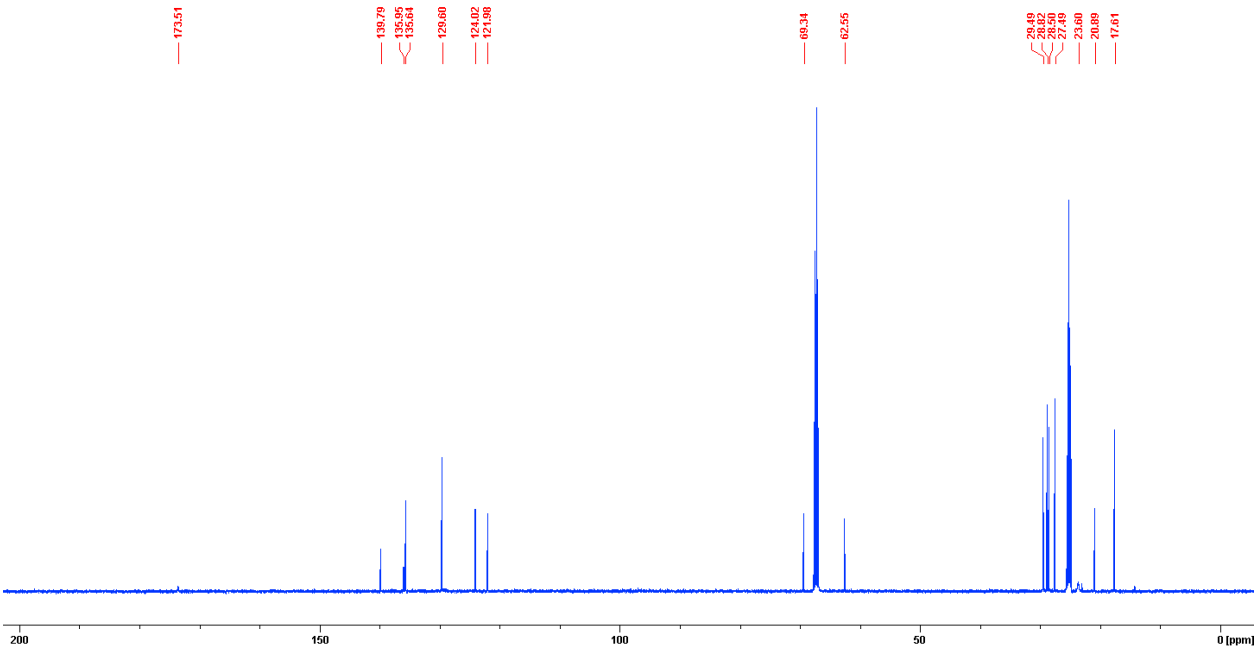


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, C_6D_6, 293 K) of the ^{13}C-labelled analogue of Al(L)(^{i}Bu)$_2$ **2** displaying a characteristic enhanced resonance at 173.9 ppm corresponding the imidazolium carbon.

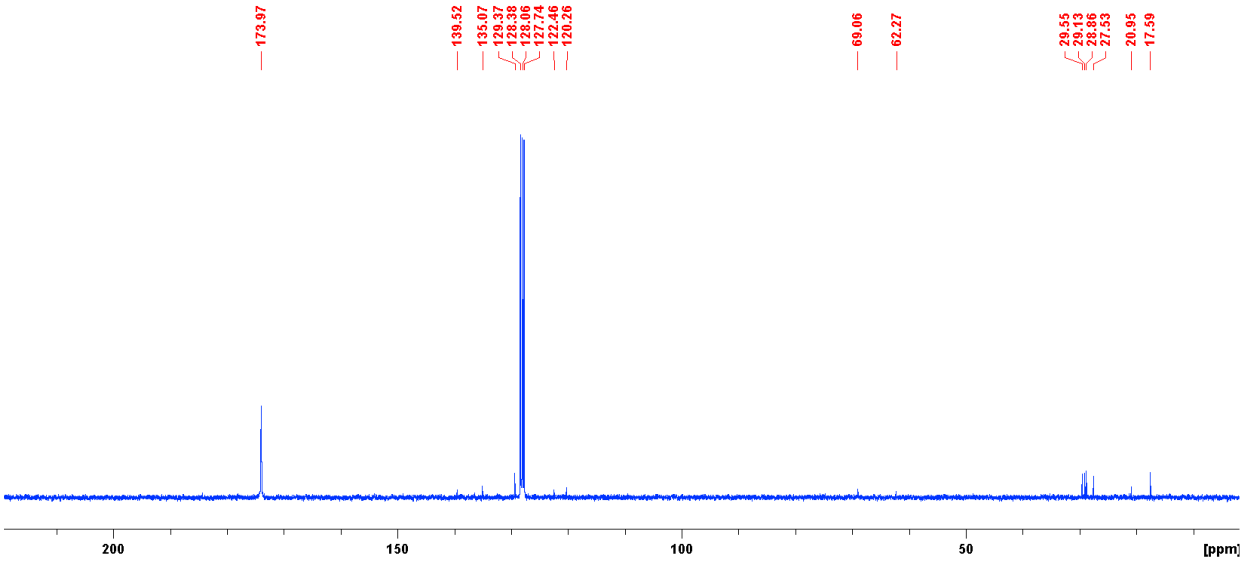


Figure S4. ^{27}Al-NMR spectrum (130 MHz, THF-d_8, 293 K) of Al(L)(^{i}Bu)$_2$ **2**.

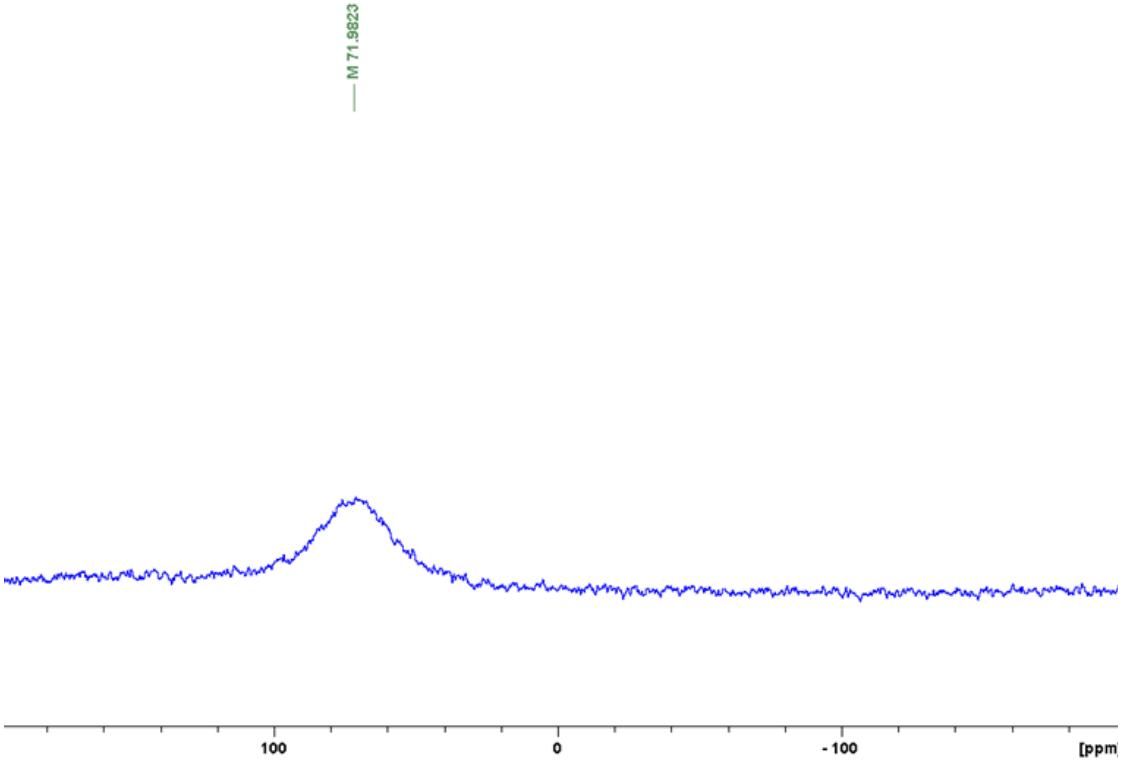


Figure S5. ^{1}H NMR spectrum (500 MHz, C_6D_6, 293 K) of [HL][Al(^{i}Bu)(OAr)$_2$] **3**.

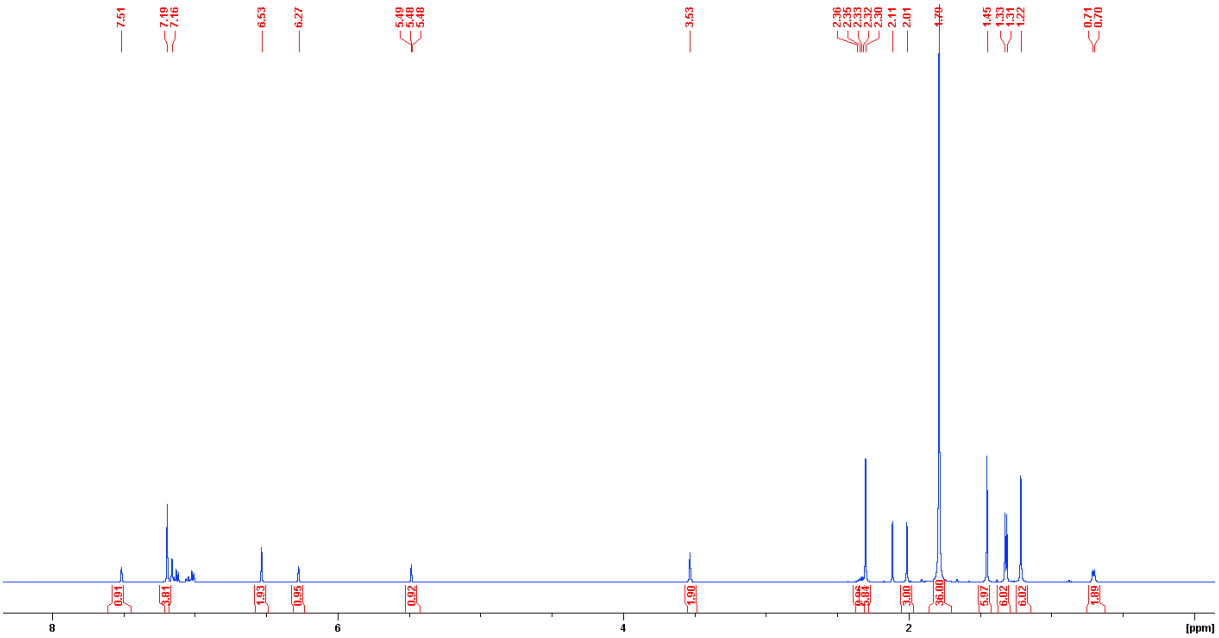


Figure S6. ^{13}C{^{1}H} NMR spectrum (125 MHz, C_6D_6, 293 K) of [HL][Al(^{i}Bu)(OAr)$_2$] **3**.

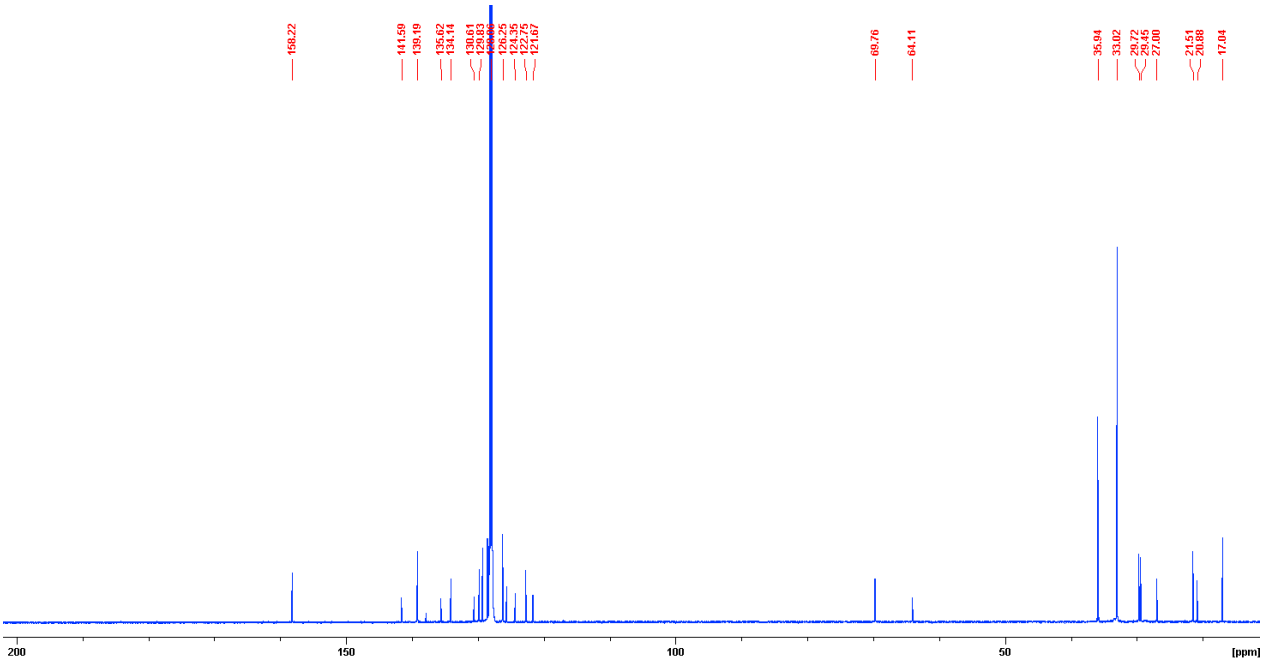


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, C_6D_6, 293 K) of the ^{13}C-labelled analogue of [HL][Al(^{i}Bu)(OAr)$_2$] **3** displaying a characteristic enhanced resonance at 135.6 ppm corresponding the imidazolium carbon.

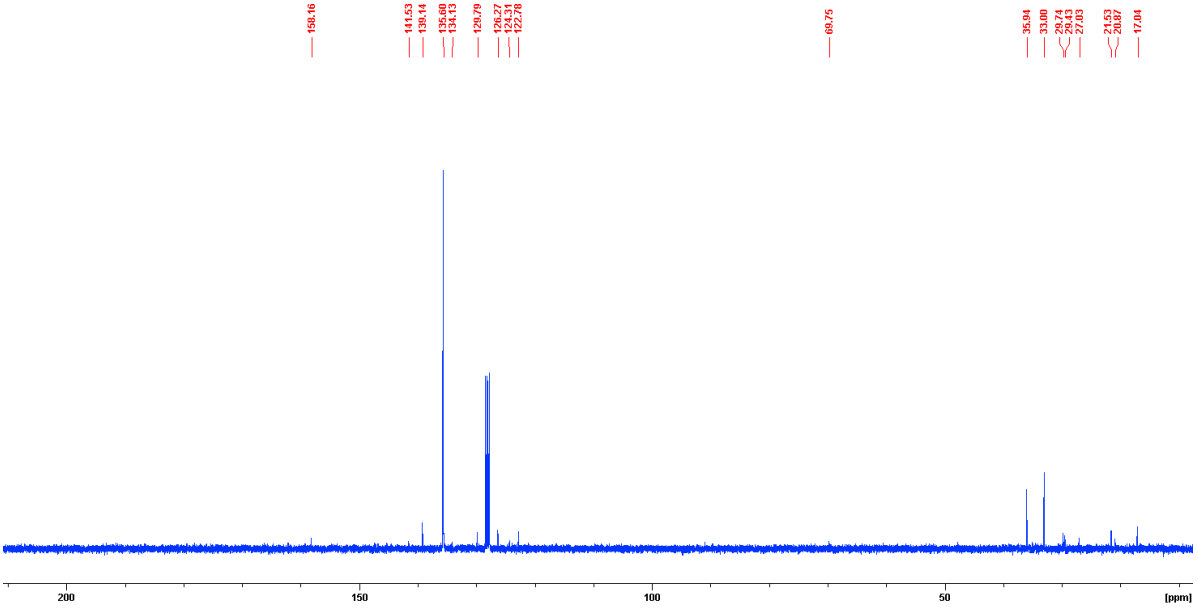


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, C_6D_6, 293 K) of the ^{13}C-labelled complex [HL][Al(Me)(OAr)$_2$] **3'** displaying a characteristic enhanced resonance at 136.6 ppm corresponding the imidazolium carbon.

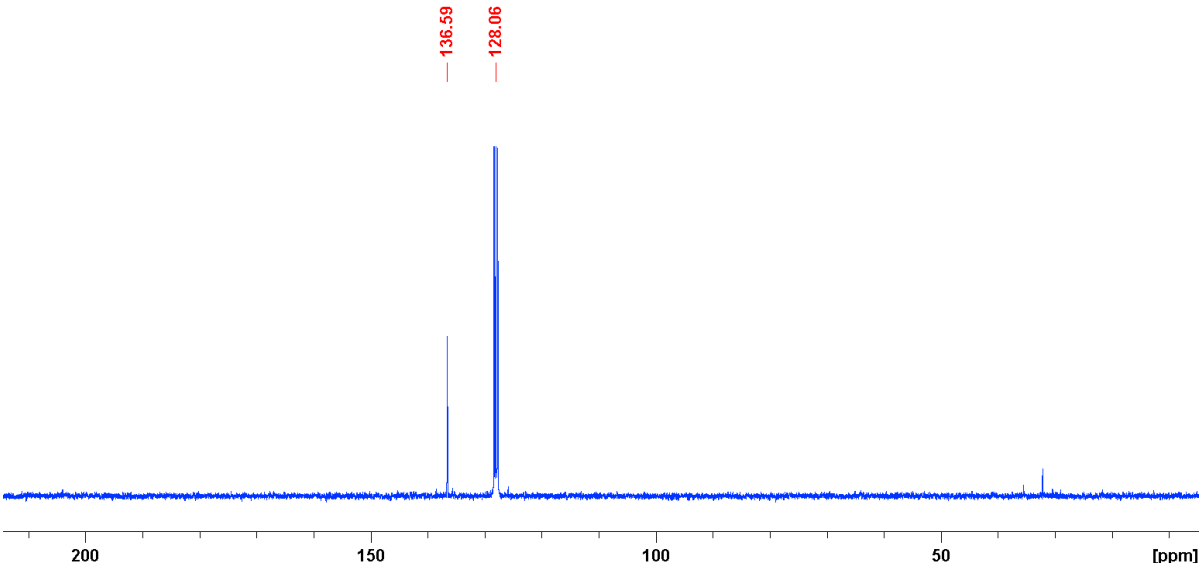


Figure S9. ^{1}H NMR spectrum (500 MHz, THF-d_8, 293 K) of [K(THF)$_2$L][Al(^{i}Bu)(OAr)$_2$] **5**.

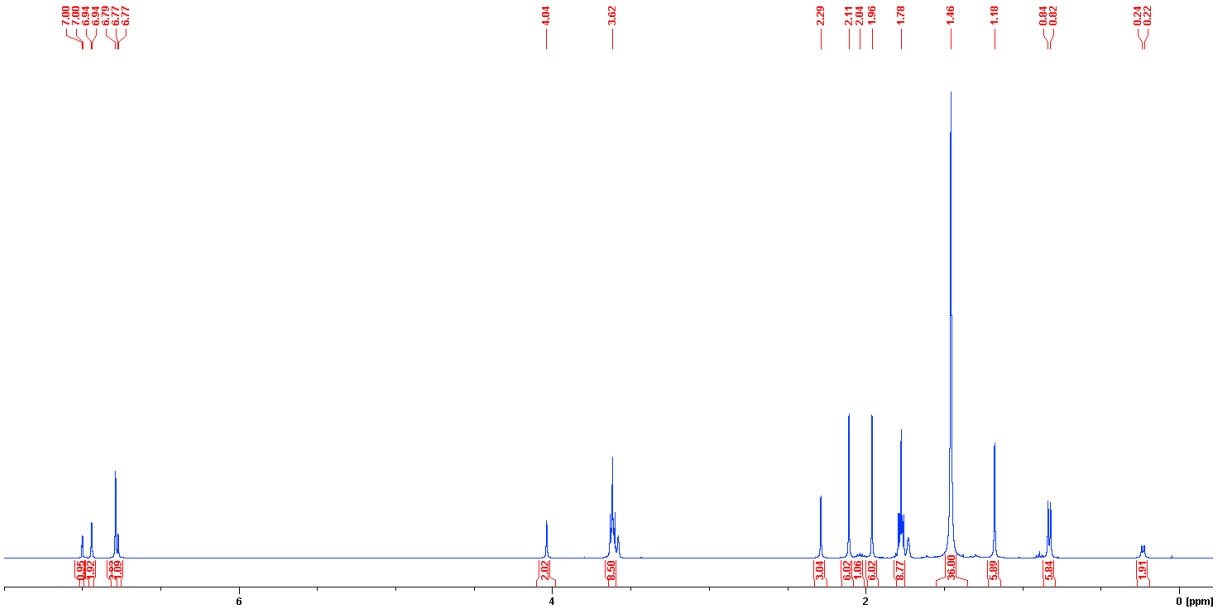


Figure S10. ^{13}C{^{1}H} NMR spectrum (125 MHz, THF-d_8, 293 K) of [K(THF)$_2$L][Al(^{i}Bu)(OAr)$_2$] **5**.

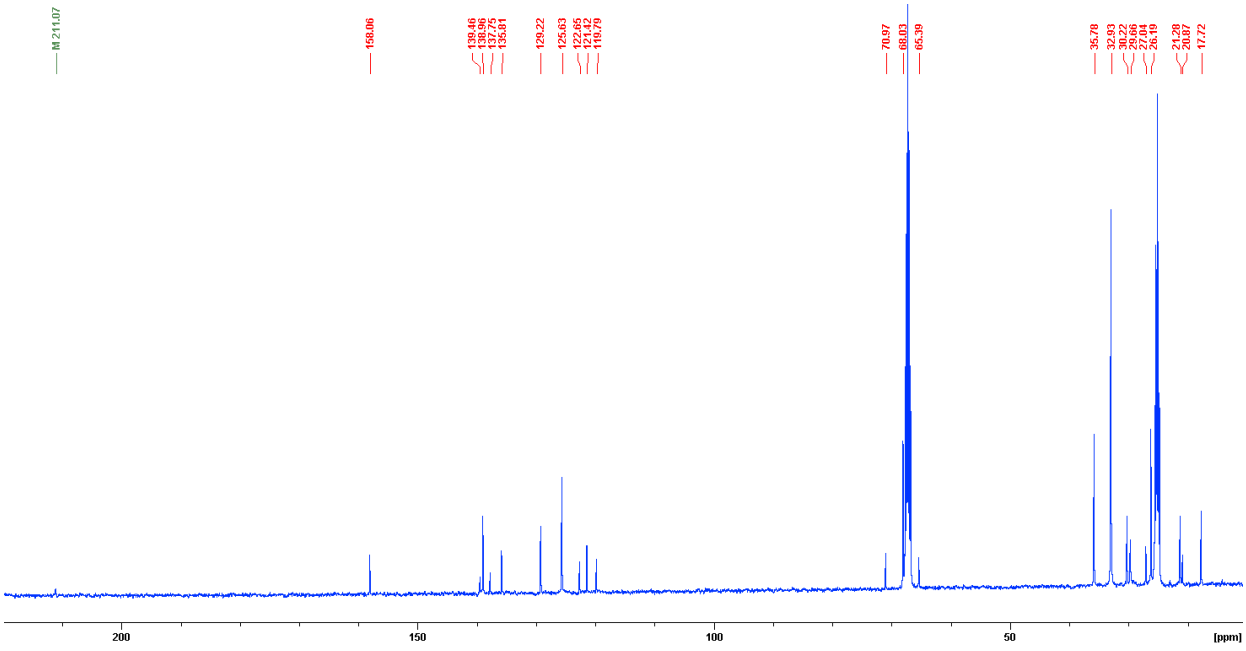


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, C_6D_6, 293 K) of the ^{13}C-labelled analogue of $[K(THF)_2L][Al(^{i}Bu)(OAr)_2]$ **5** displaying a characteristic enhanced resonance at 204.8 ppm corresponding to the carbenic carbon.

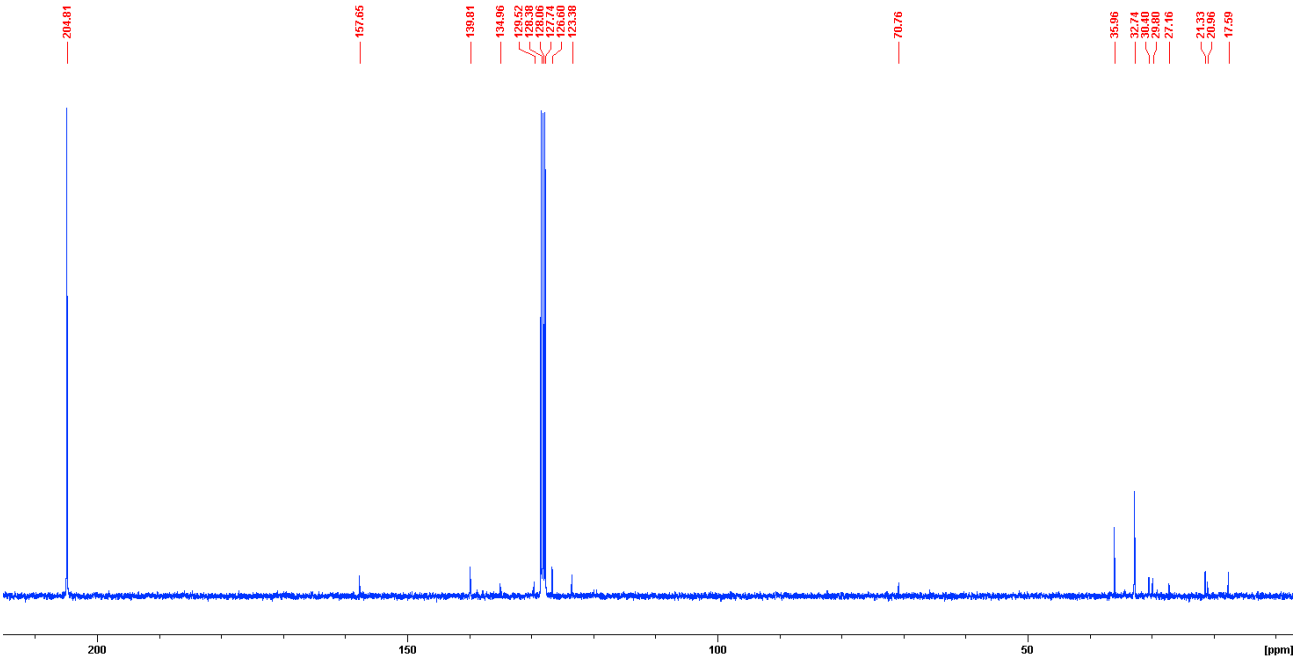


Figure S12. ^{1}H NMR reaction monitoring between **3** (^{13}C-labelled) and $B(C_6F_5)_3$ (300 MHz, C_6D_6, 293 K) showing the quantitative formation of $[(HL)Al(OAr)_2][HB(C_6F_5)_3]$ **6** together with release of isobutene (septuplet at δ = 4.75 ppm and a triplet at δ = 1.60 ppm).

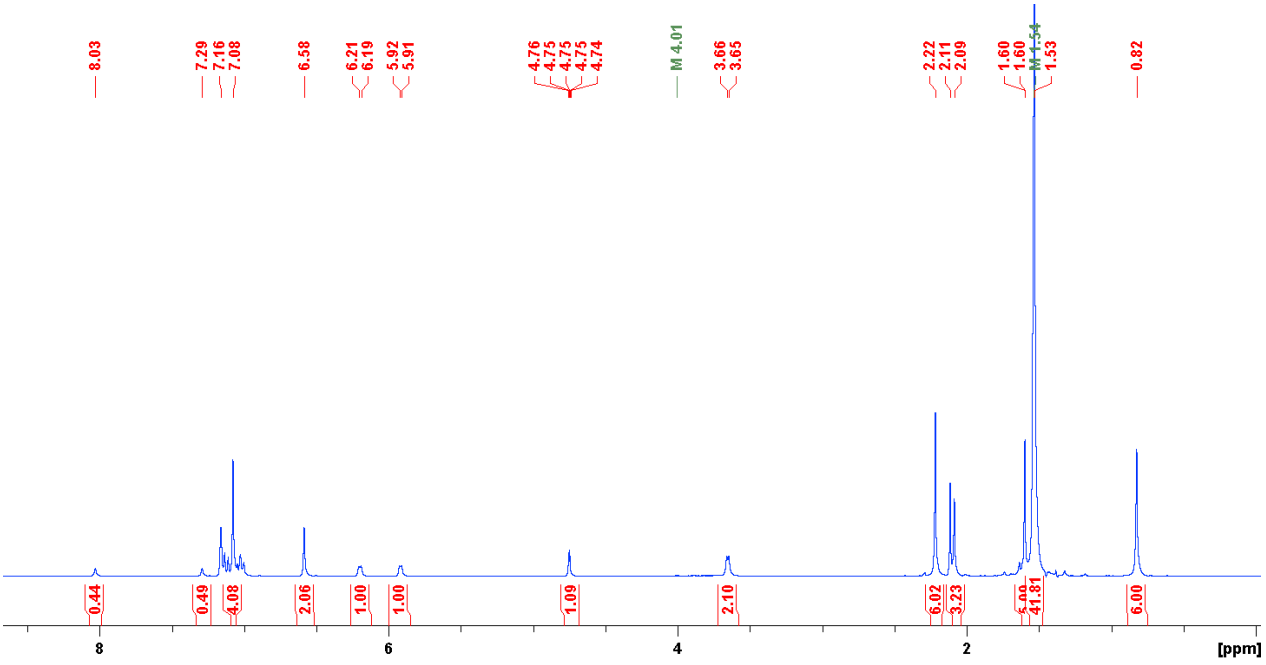


Figure S13. Top: ^{19}F NMR spectrum of $B(C_6F_5)_3$ (282 MHz, C_6D_6, 293 K). Bottom: ^{19}F NMR spectrum after reaction between **3** and $B(C_6F_5)_3$ (282 MHz, C_6D_6, 293 K), showing the quantitative conversion of $B(C_6F_5)_3$ into $[HB(C_6F_5)_3]^-$ (fluorobenzene (6 eq.) was used as a ^{19}F NMR internal standard).

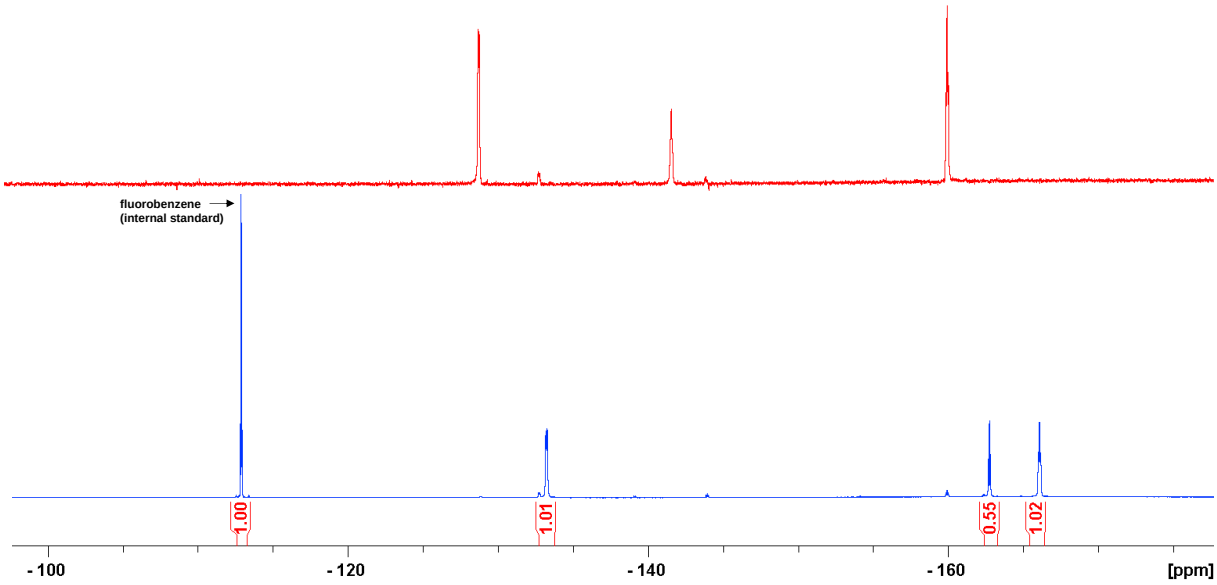


Figure S14. ^{11}B NMR spectrum after reaction between **3** and $B(C_6F_5)_3$ (282 MHz, C_6D_6, 293 K), showing the formation of $[HB(C_6F_5)_3]^-$.

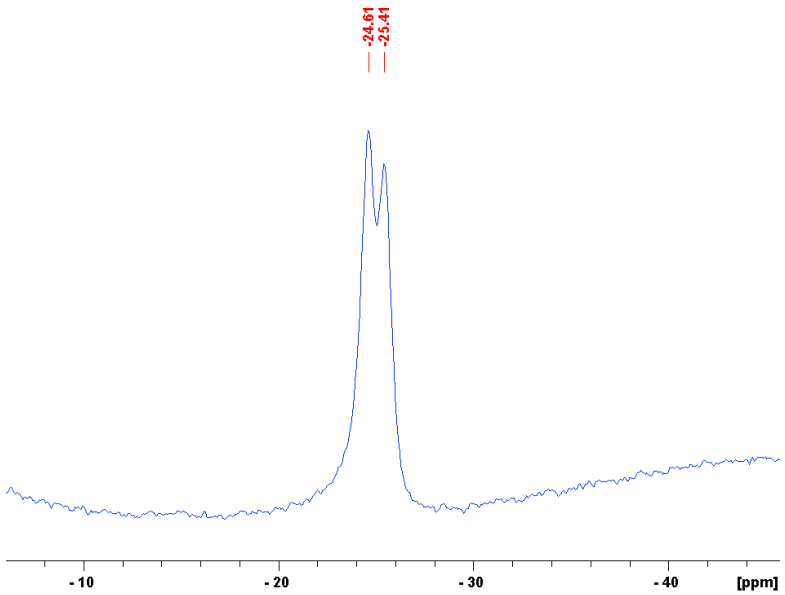


Figure S15. ^{1}H NMR reaction monitoring between [(HL)Al(OAr)$_2$][B(^{i}Bu)(C$_6$F$_5$)$_3$] **6** and KHMDS (300 MHz, C$_6$D$_6$, 293 K) showing the quantitative formation of Al(L)(OAr)$_2$ **4**

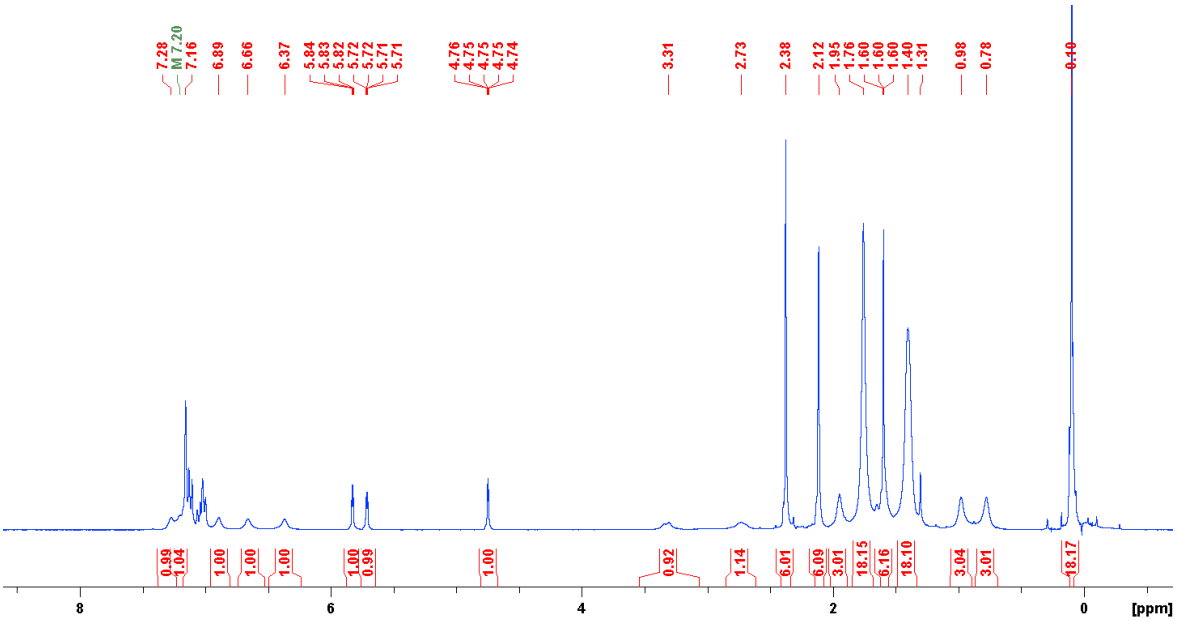


Figure S16. ^{1}H NMR spectrum (500 MHz, THF-d$_8$, 293 K) of Al(L)(OAr)$_2$, **4**.

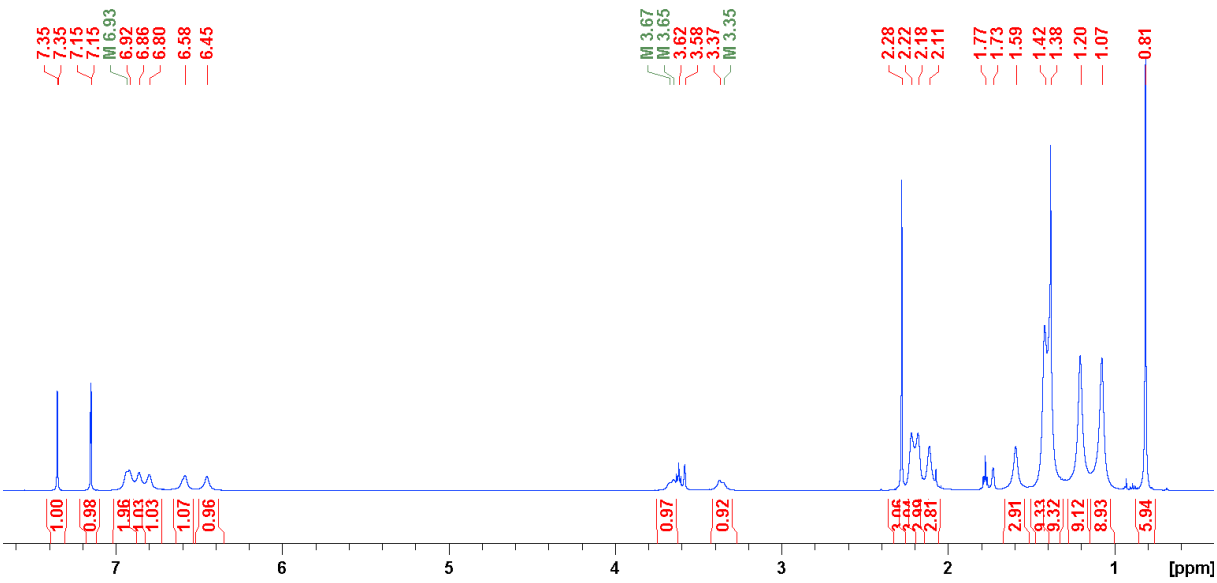


Figure S17. ^{27}Al-NMR spectrum (130 MHz, THF-d_8, 293 K) of Al(L)$(OAr)_2$, **4**.

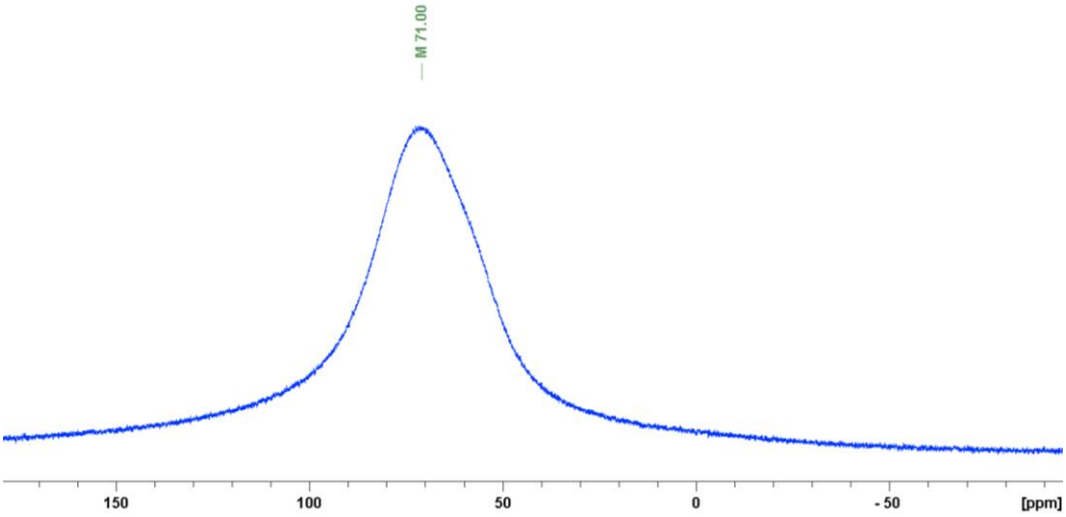
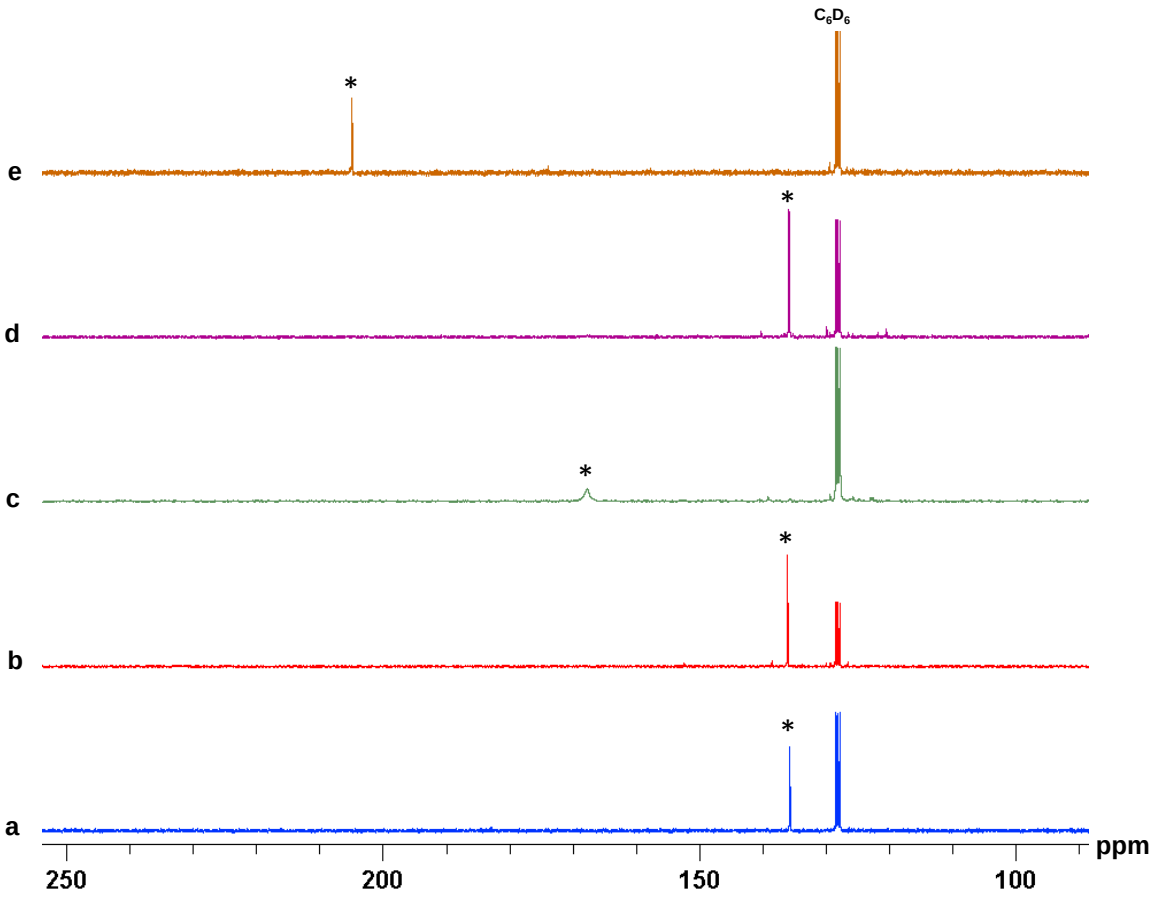


Figure S18. ^{13}C NMR reaction monitoring in C_6D_6 solution (75 MHz, 293 K). The * denotes the resonance for the ^{13}C-labelled carbon from the C_3N_2 heterocycle. (a) imidazolium-aluminate zwitterion **3** (b) after de-alkylation of **3** with $B(C_6F_5)_3$ yielding **6** (c) after subsequent deprotonation of **6** with KHMDS yielding **4**; (d) after reaction of **6** with PhOH yielding **7** and (e) deprotonation of **3** with KBenzyl yielding **5**.



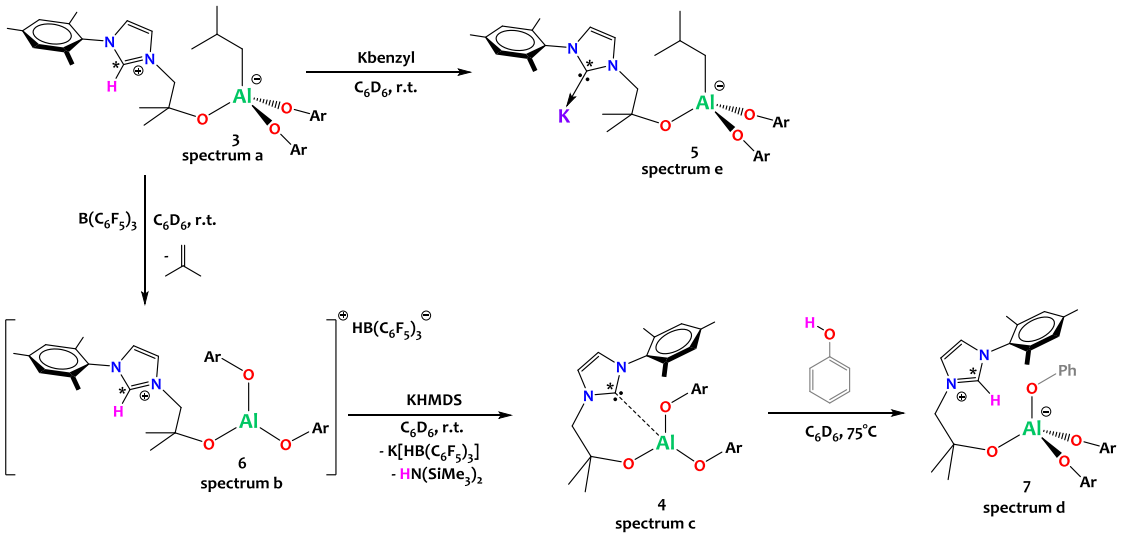


Figure S19. ^{13}C NMR reaction monitoring in THF-d_8 solution (75 MHz, 293 K) of the reaction between **2** and 1 eq. PhOH yielding an alcoxy-imidazolium zwiterrion species **8** as shown with the disappearance of the aluminum-bound carbene resonance at δ = 173.5 ppm from **2** (bottom spectrum – blue line) and the appearance of a characteristic imidazolium resonance at δ = 139.4 ppm for **8** (top spectrum – red line) corresponding to the ^{13}C-labelled carbon from the C_3N_2 heterocycle.

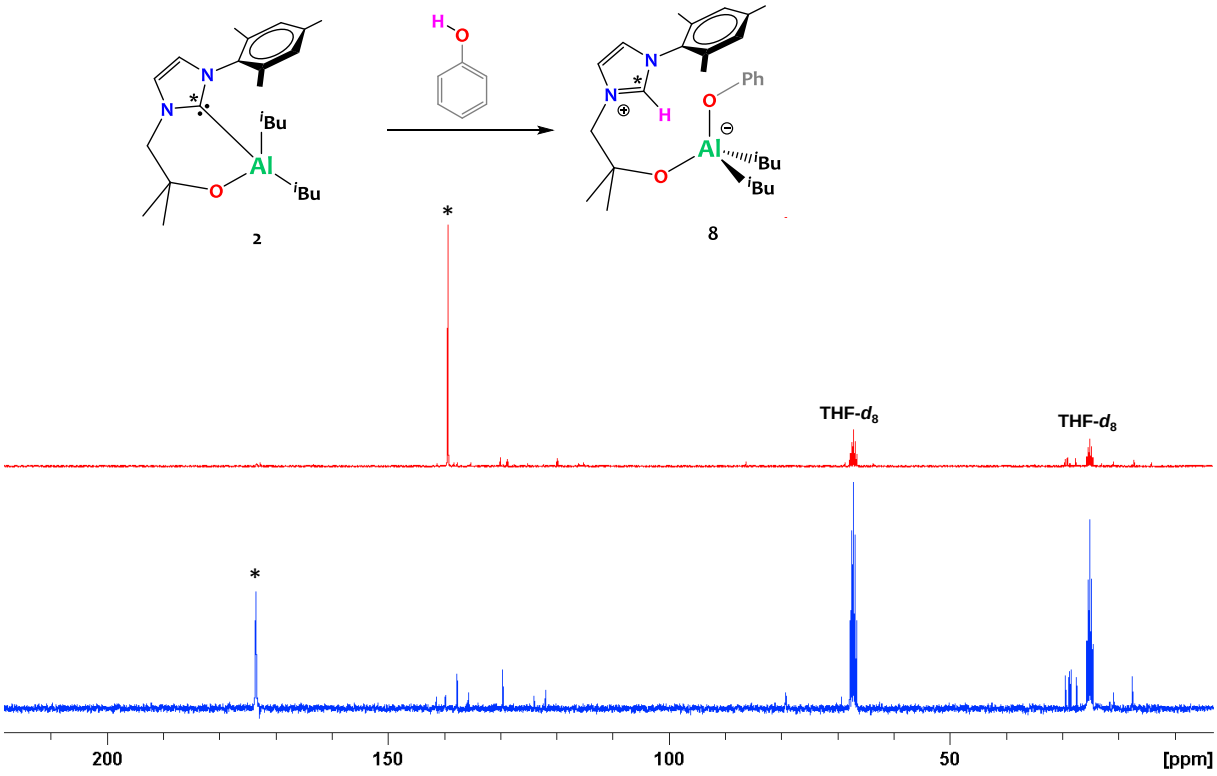


Figure S20. ^{13}C NMR reaction monitoring in C_6D_6 solution (75 MHz, 293 K) of the reaction between **2** and 1 eq. 2-naphtalenethiol yielding a mixture of two imidazolium species, as shown with the disappearance of the aluminum-bound carbene resonance at δ = 173.5 ppm from **2** (bottom spectrum – blue line) and the appearance of 2 characteristic imidazolium resonance at δ = 138.6 and 137.6 ppm (top spectrum – red line) corresponding to the ^{13}C-labelled carbon from the C_3N_2 heterocycle.

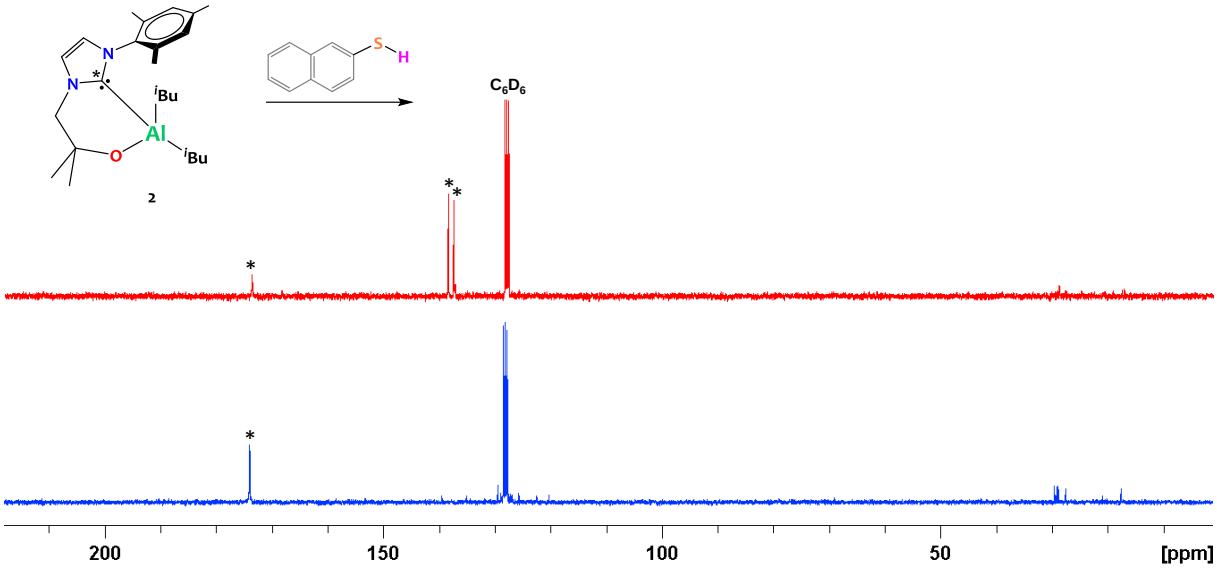
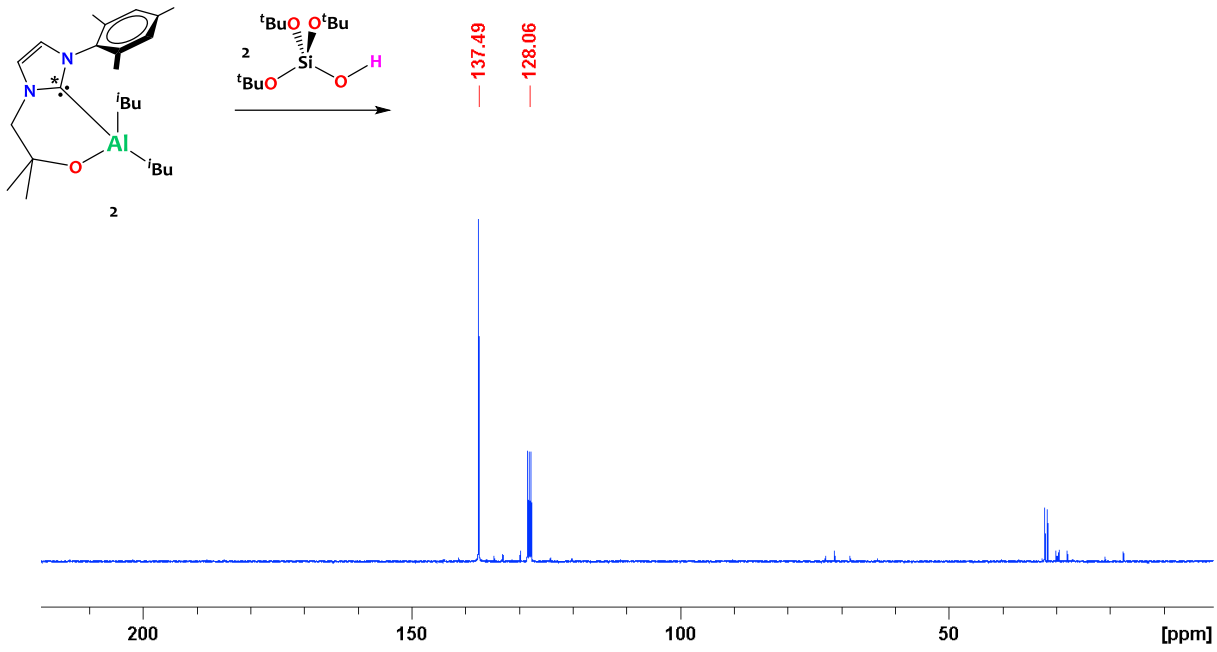


Figure S21. ^{13}C NMR reaction monitoring in C_6D_6 solution (75 MHz, 293 K) of the reaction between **2** and 2 eq. $HOSi(O^tBu)_3$ yielding cleanly an imidazolium species as shown with the disappearance of the aluminum-bound carbene resonance at δ = 173.5 ppm from **2** and the appearance of a characteristic imidazolium resonance at δ = 137.5 ppm corresponding to the ^{13}C-labelled carbon from the C_3N_2 heterocycle.



C. X-ray crystallography

X-ray structural determinations were performed at the Centre de Diffractométrie Henri Longchambon, Université de Lyon. Suitable crystals coated in Fomblin were selected and mounted on a Gemini kappa-geometry diffractometer (Rigaku Oxford Diffraction) equipped with an Atlas CCD detector and using Mo radiation (λ= 0.71073 Å). Intensities were collected at 150 K by means of the CrysalisPro software.[2] Reflection indexing, unit-cell parameters refinement, Lorentz-polarization correction, peak integration and background determination were carried out with the CrysalisPro software.[2] An analytical absorption correction was applied using the modeled faces of the crystal.[3] The resulting set of hkl was used for structure solution and refinement. The structures were solved by direct methods with SIR97[4] and the least-square refinement on F^2 was achieved with the CRYSTALS software.[5] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were all located in a difference map, and then were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C---H in the range 0.93--0.98 Å) and Uiso(H) (in the range 1.2-1.5 times Ueq of the parent atom), after which the positions were refined with riding constraints. The absolute structure of compound **5** was determined by refining the Flack parameter[6] to a value of 0.015(7). The refined Flack parameter of 0.5(3) for compound **2** tends to suggest the presence of a racemic twin. Compound **5** displayed residual electronic density corresponding to solvent molecules that could not be modelled. The contribution of this disordered solvent was removed using the SQUEEZE algorithm.[7] CCDC 1836205-1836207 and 1850906 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

Table S1. Crystallographic parameters for compounds **2**, **3**, **4** and **5**.

Compound	**2**	**3**	**4**	**5**
CCDC #	1836207	1836205	1850906	1836206
Formula	$2(C_{24}H_{39}Al_1N_2O_1)$	$2(C_{50}H_{77}Al_1N_2O_3).3(C_6H_6)$	$C_{46}H_{67}Al_1N_2O_3$	$C_{66}H_{108}Al_1K_1N_2O_7$
cryst syst	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
space group	P c a 2_1	$P2_1/c$	$P2_1/c$	Cc
volume ($Å^3$)	4878.2(7)	10950(3)	4329.6(9)	7558.6(20)
a (Å)	16.3437(11)	25.392(5)	11.5882(11)	23.374(3)
b (Å)	9.6410(8)	21.778(2)	9.9069(14)	14.3114(9)
c (Å)	30.959(3)	21.355(4)	38.069(4)	26.926(3)
α (deg)	90	90	90	90
β (deg)	90	111.99(2)	97.839(9)	122.947(17)
γ (deg)	90	90	90	90
Z	8	4	4	4
formula weight (g/mol)	797.14	1796.65	723.03	2213.33
density (g cm^{-3})	1.085	1.090	1.109	0.972
absorption coefficient (mm^{-1})	0.099	0.080	0.087	0.125
F(000)	1744	3928	1576	2420
$2\theta_{max}$ (°)	29.573	29.706	29.749	29.651
temp (K)	150.0(1)	150.0(1)	150.0(1)	150.0(1)
total no. reflections	46949	111871	43850	67904
unique reflections [R(int)]	11928 [0.084]	27442[0.068]	10796 [0.15]	18429 [0.047]
no. refined parameters	506	1171	470	694
Final R indices [I > 2σ(I)]	R1 = 0.102, wR2 = 0.192	R1 = 0.065, wR2 = 0.120	R1 = 0.080, wR2 = 0.115	R1 = 0.053, wR2 = 0.109
Largest diff. peak and hole ($e.A^{-3}$)	1.97 and -1.06	0.69 and -0.80	1.24 and -1.22	0.33 and -0.41
GoF	1.00	0.98	1.07	0.94

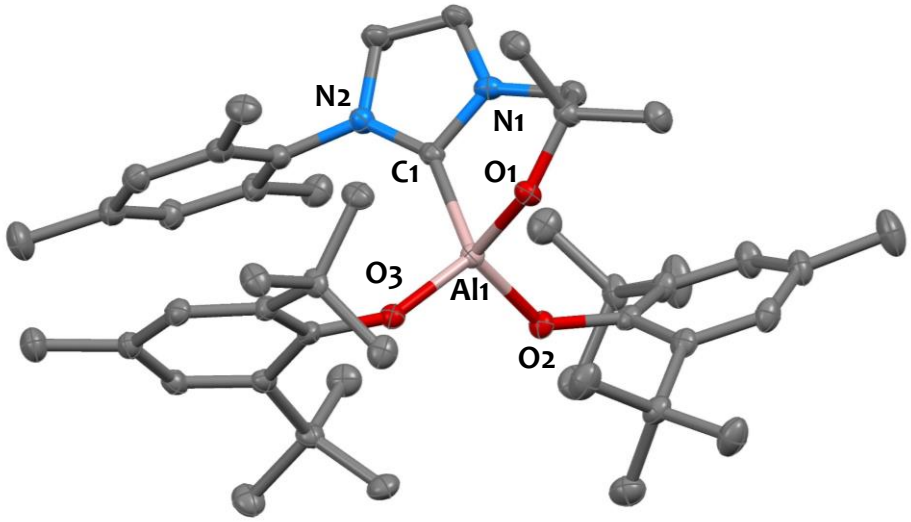


Figure 22. Solid-state molecular structures of **4** (30% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and angles [°]: Al1-O1 1.732(3) Al1-O2 1.766(3); Al1-O3 1.728(3); Al1-C1 2.055(2); N1-C1 1.362(5); N2-C1 1.374(5); N1-C1-N2 102.7(4); C1-Al1-O1 94.2(16); Al1-C1-N1 113.7(3); Al1-C1-N2 143.1(3).

D. References

[1] Synthesis of **1**: R. Srivastava, R. Moneuse, J. Petit, P. A. Pavard, V. Dardun, M. Rivat, P. Schiltz, M. Solari, E. Jeanneau, L. Veyre, C. Thieuleux, E. A. Quadrelli and C. Camp, *Chem. - A Eur. J.*, 2018, **24**, 4361–4370; Synthesis of AlR(OAr) (R= ^{i}Bu, Me): A. P. Shreve, R. Mulhauot, W. Fultz, J. Calabrese, W. Robbins and S. D. Ittel, *Organometallics*, 1988, **7**, 409–416.

[2] CrysAlisPro 1.171.38.43, Rigaku Oxford Diffraction, 2015

[3] R. C. Clark & J. S. Reid, *Acta Cryst. A* 1995, **51**, 887-897.

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[5] P.W. Betteridge, J.R. Carruthers, R.I. Cooper, K. Prout, D.J. Watkin, *J. Appl. Cryst.* 2003, **36**, 1487-1487.

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[7] P. v.d. Sluis & A.L. Spek, *Acta Cryst.* 1990, **A46**, 194-201.