Supporting Information for

Schiff-base -Ate Derivatives with Main Group Metals: Generation of a Tripodal Aluminate Metalloligand

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1. ^{1}H NMR spectra the heterometallic '–*ate*' compounds

- [LiAlMe$_3$(L*a*)], (**1a**)

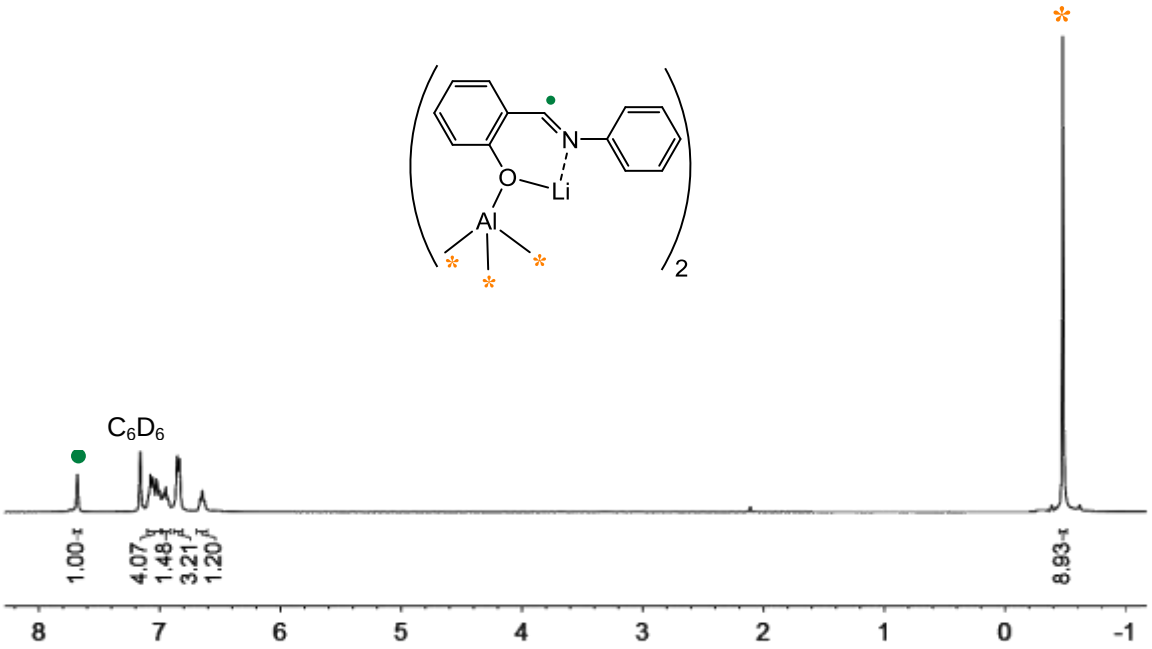

Figure S1 ^{1}H NMR spectrum of complex **1a** recorded in C_6D_6 at room temperature

- [LiAlMe$_3$(L*b*)], (**1b**)

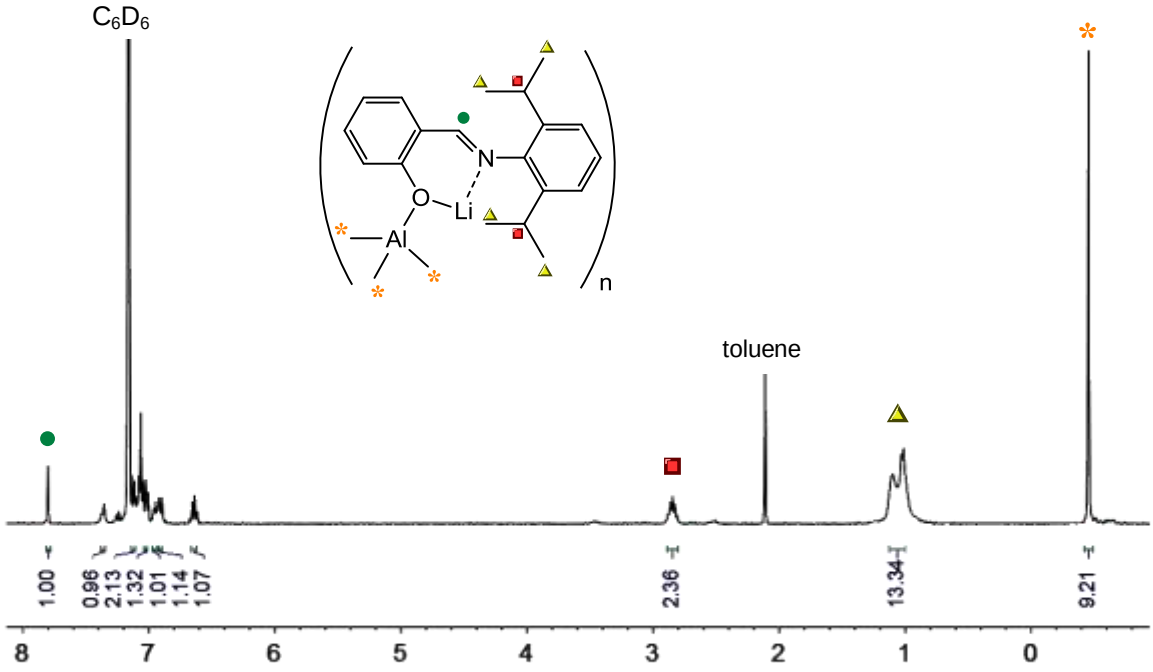

Figure S2 ^{1}H NMR spectrum of complex **1b** recorded in C_6D_6 at room temperature

- [KAlMe$_3$(L*a*)], (**2a**)

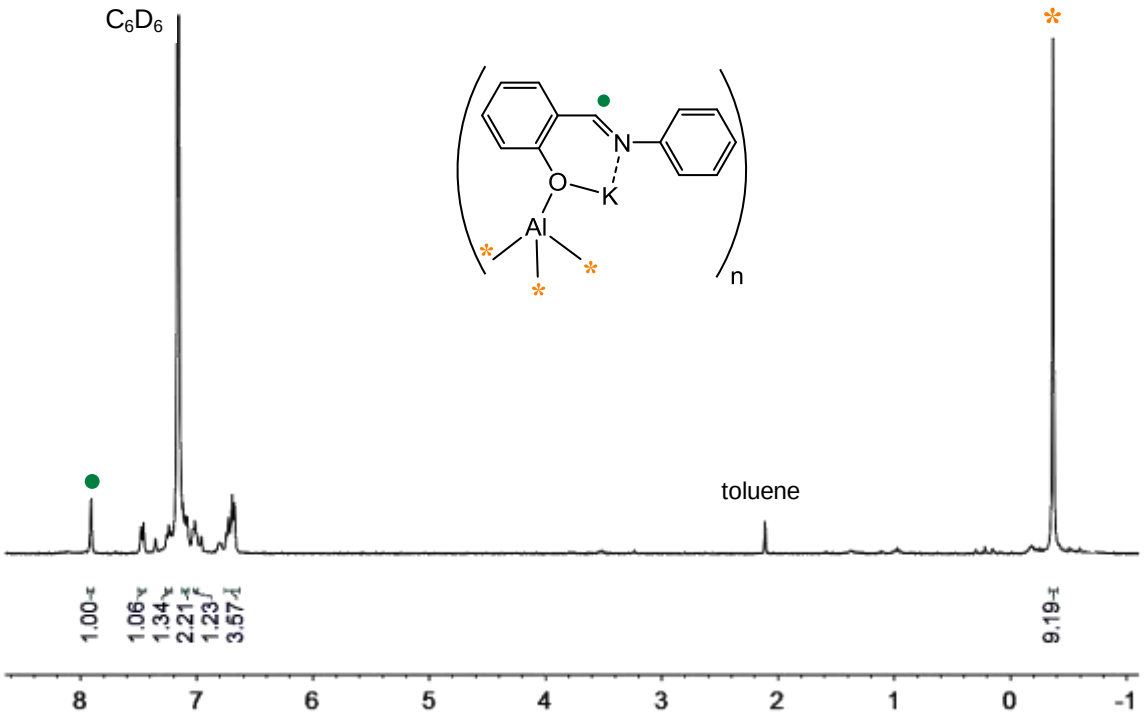

Figure S3 ^{1}H NMR spectrum of complex **2a** recorded in C_6D_6 at room temperature

- [NaAlMe$_2$(L*a*)$_2$], (**3a**)

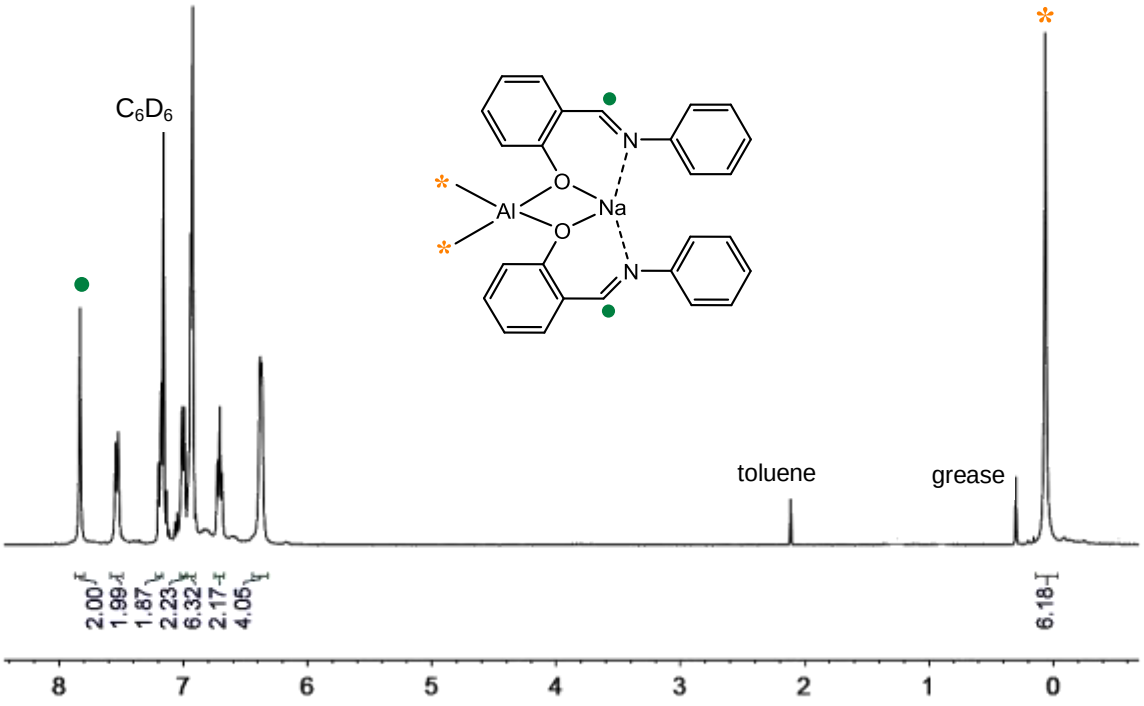

Figure S4 ^{1}H NMR spectrum of complex **3a** recorded in C_6D_6 at room temperature

- Complex [NaAlMe$_2$(L*b*)$_2$], (**3b**)

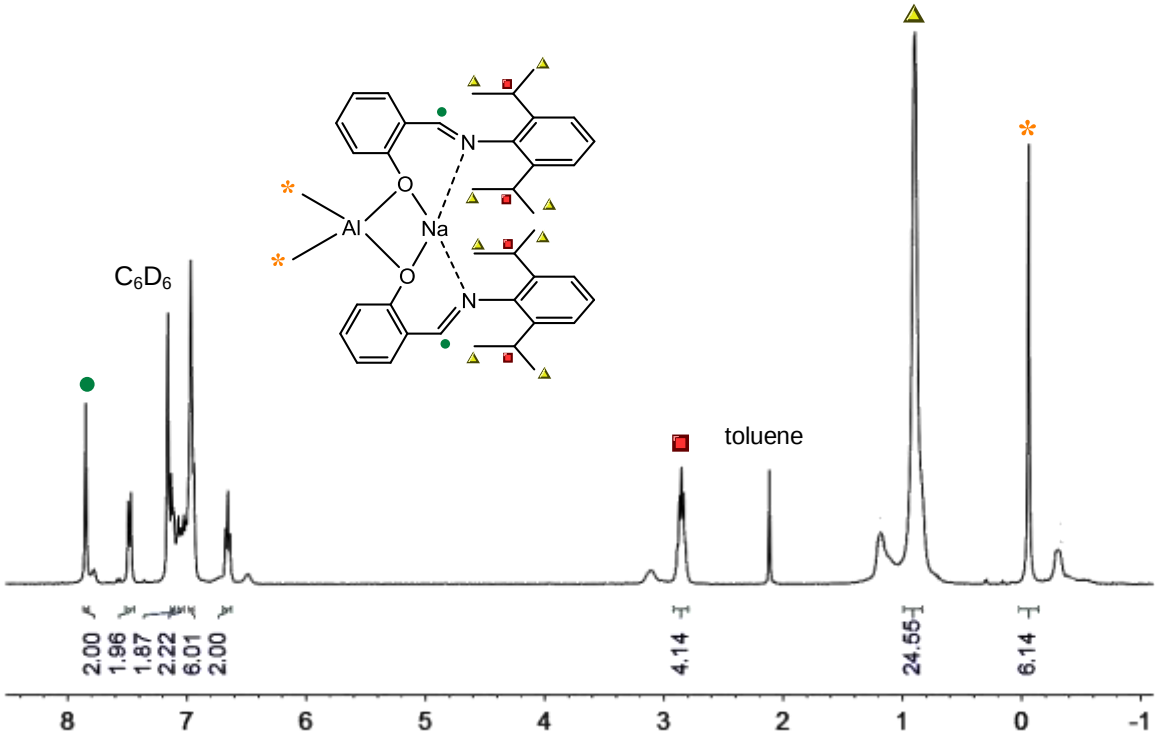

Figure S5 ^{1}H NMR spectrum of complex **3b** recorded in C_6D_6 at room temperature

- Complex [KAlMe$_2$(L*b*)$_2$], (**4b**)

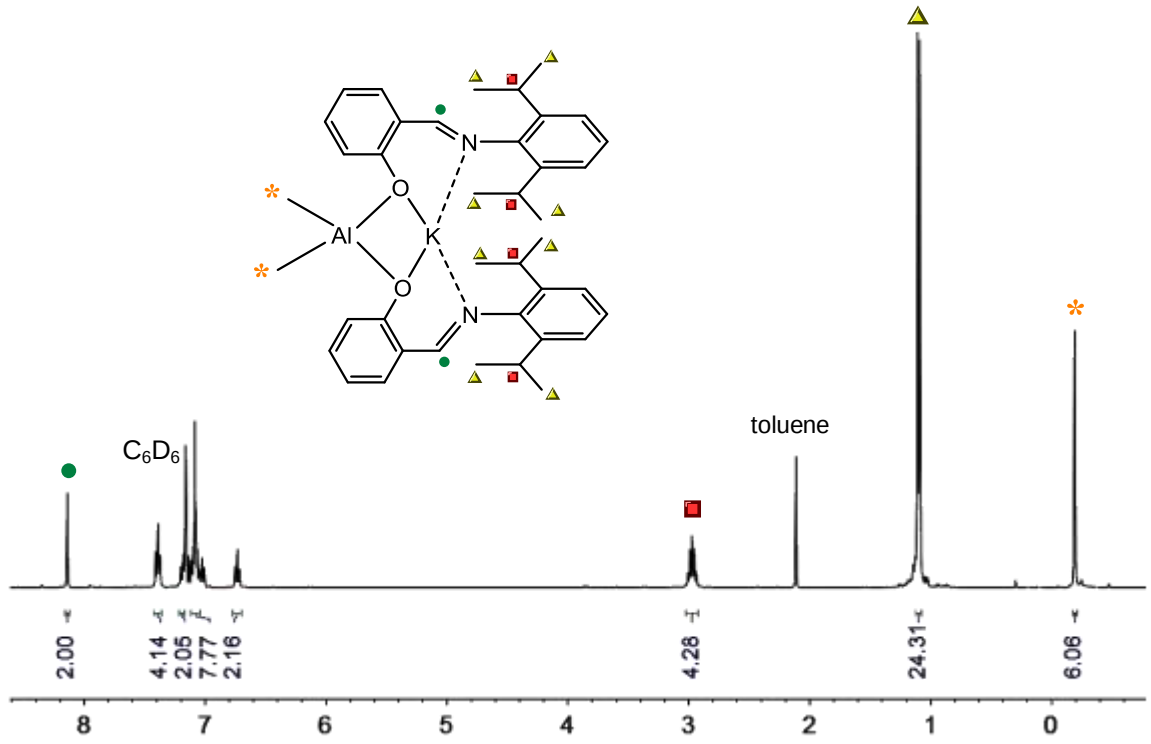

Figure S6 ^{1}H NMR spectrum of complex **4b** recorded in C_6D_6 at room temperature

- Complex [KAlMe(L*b*)$_3$], (**5b**)

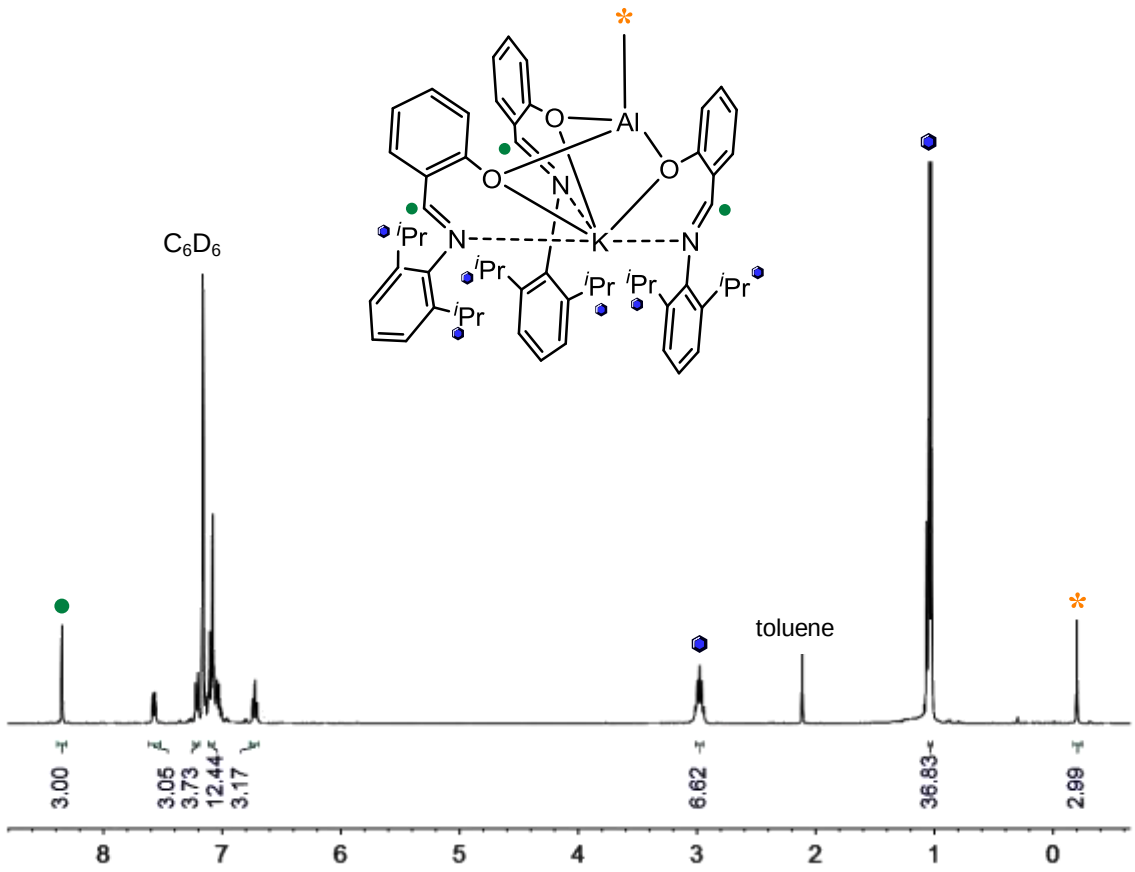

Figure S7 ^{1}H NMR spectrum of complex **5b** recorded in C_6D_6 at room temperature

1. ^{1}H NMR spectra for the reactions performed with a 2:1:1 ratio ([HL]/[M]/[Al]) (M = Na, K)

- Complex [$NaAlMe_2(La)_2$], (**3a**)

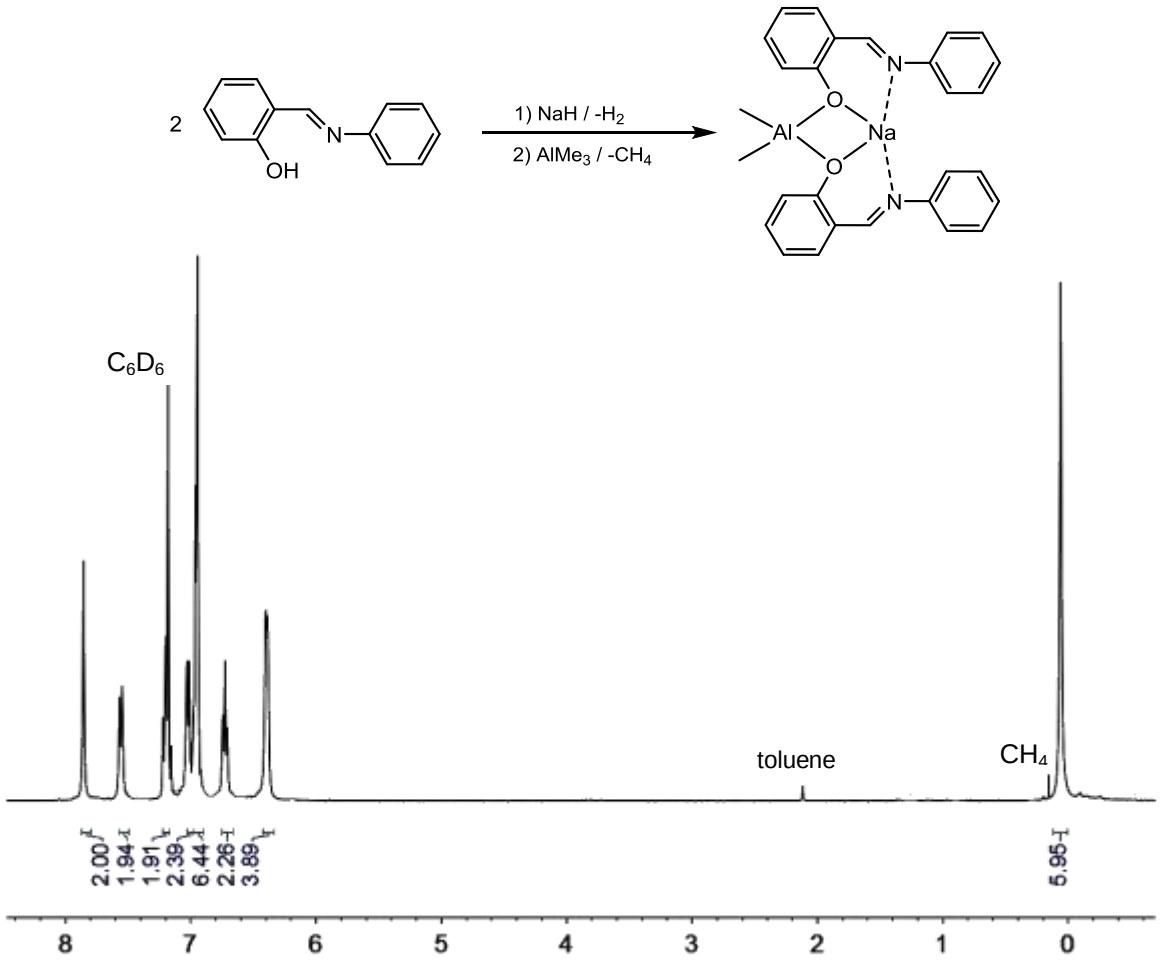

Figure S8 ^{1}H NMR spectrum of complex **3a** obtained using a [HL*a*]/[Na]/[Al] ratio of 2:1:1, and recorded in C_6D_6 at room temperature.

- Complex [KAlMe$_2$(L*b*)$_2$], (**4b**)

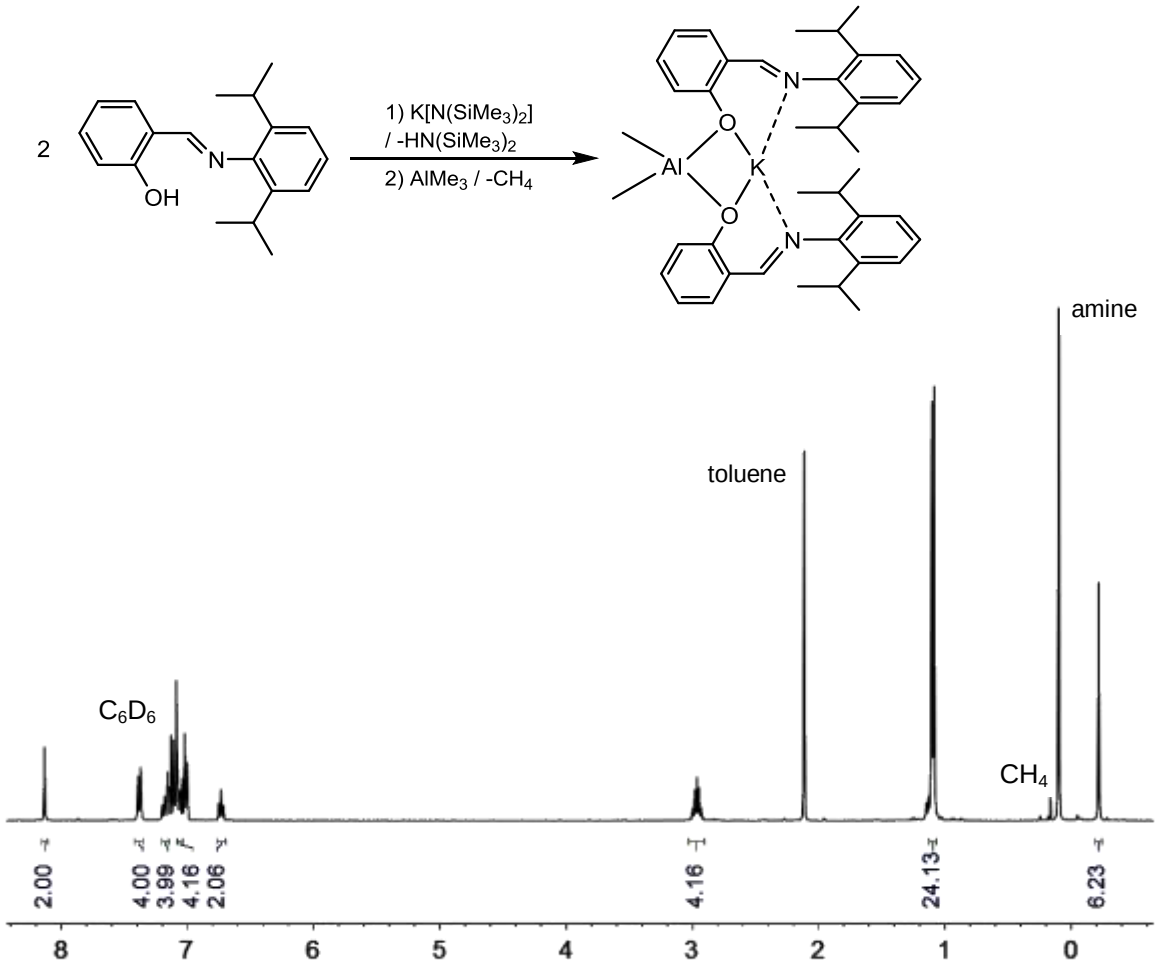

Figure S9 ^{1}H NMR spectrum of complex **4b** obtained using a [HL*b*]/[K]/[Al] ratio of 2:1:1, and recorded in C_6D_6 at room temperature.

3. ^{1}H NMR spectra for the reactions performed with a 1:1:1 ratio ([HL]/[M]/[Al]) (M = Na, K)

- Complex [$NaAlMe_2(La)_2$], (**3a**)

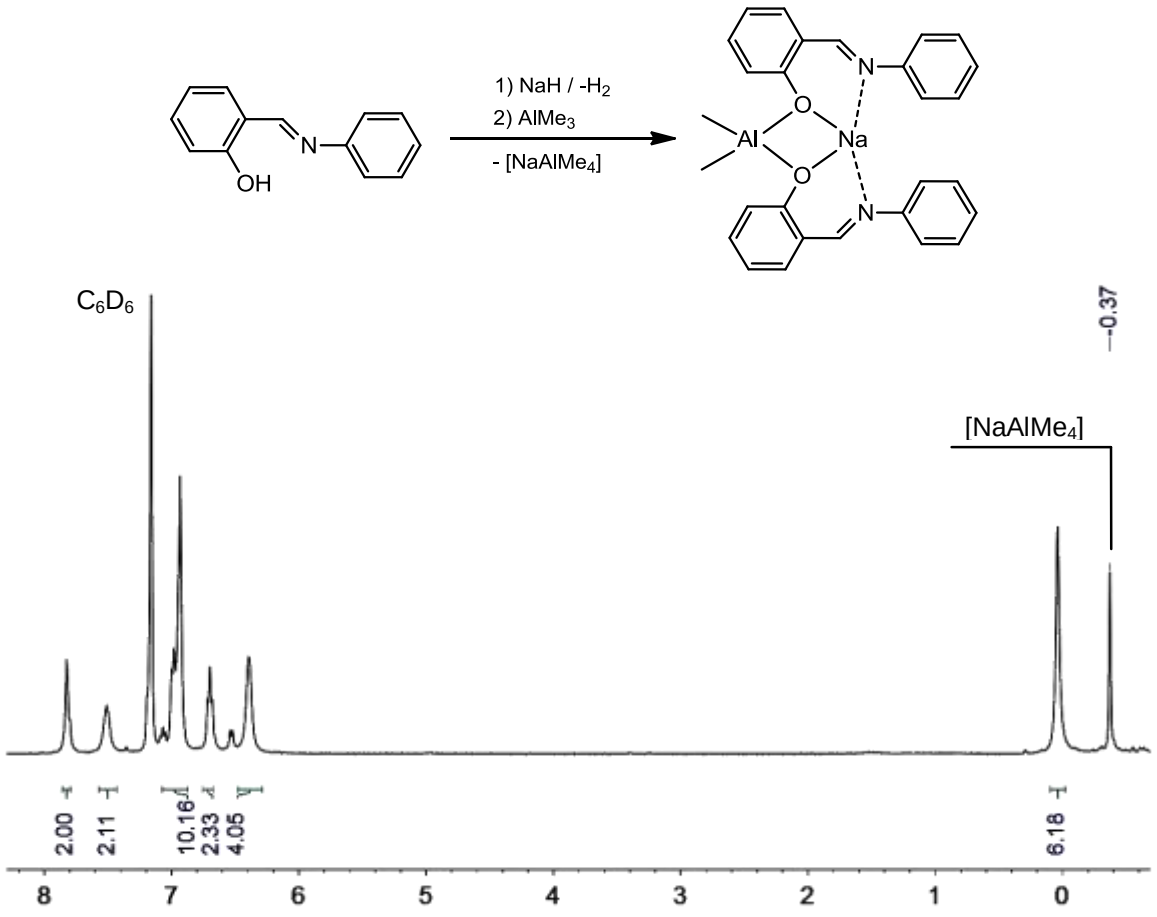

Figure S10 ^{1}H NMR spectrum of complex **3a** obtained in the stoichiometric reaction, and recorded in C_6D_6 at room temperature.

- Complex [$NaAlMe_2(Lb)_2$], (**3b**)

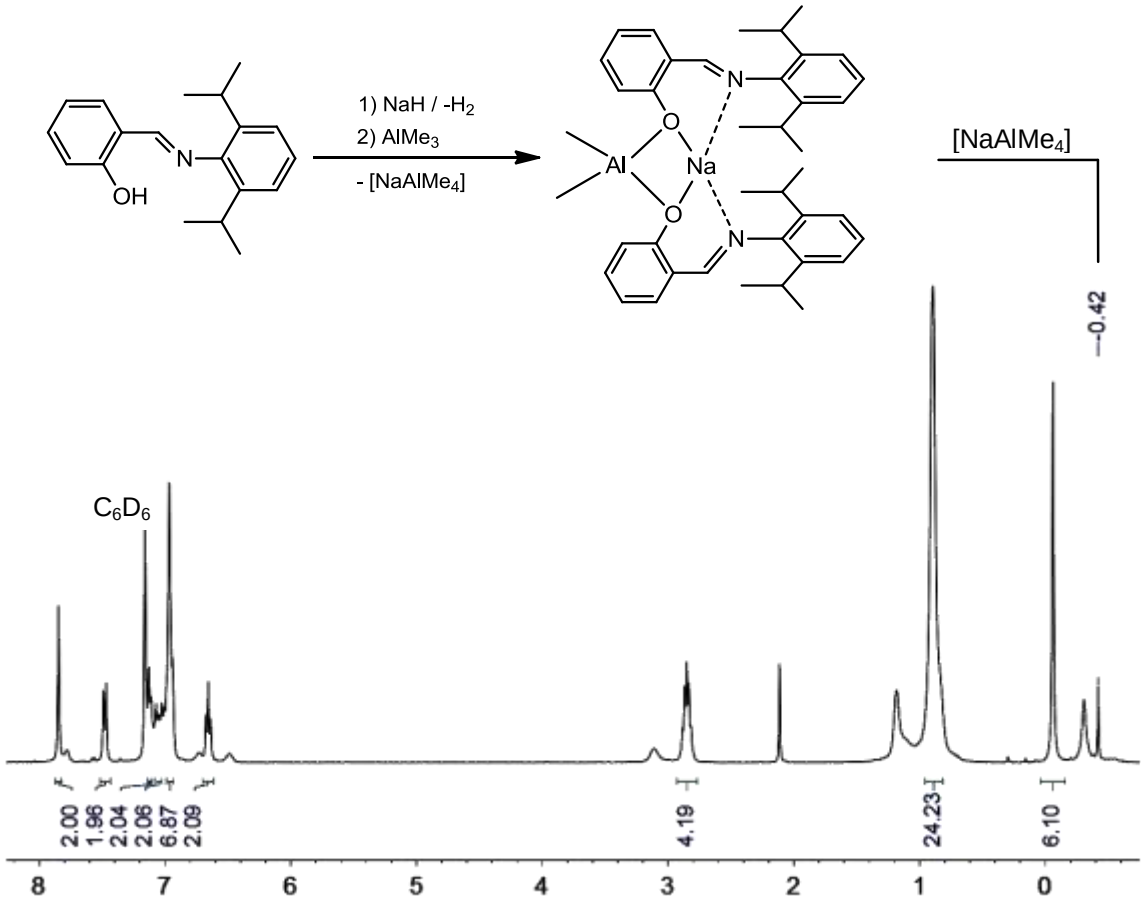

Figure S11 ^{1}H NMR spectrum of complex **3b** obtained in the stoichiometric reaction, and recorded in C_6D_6 at room temperature.

- Complex [KAlMe$_2$(L*b*)$_2$], (**4b**)

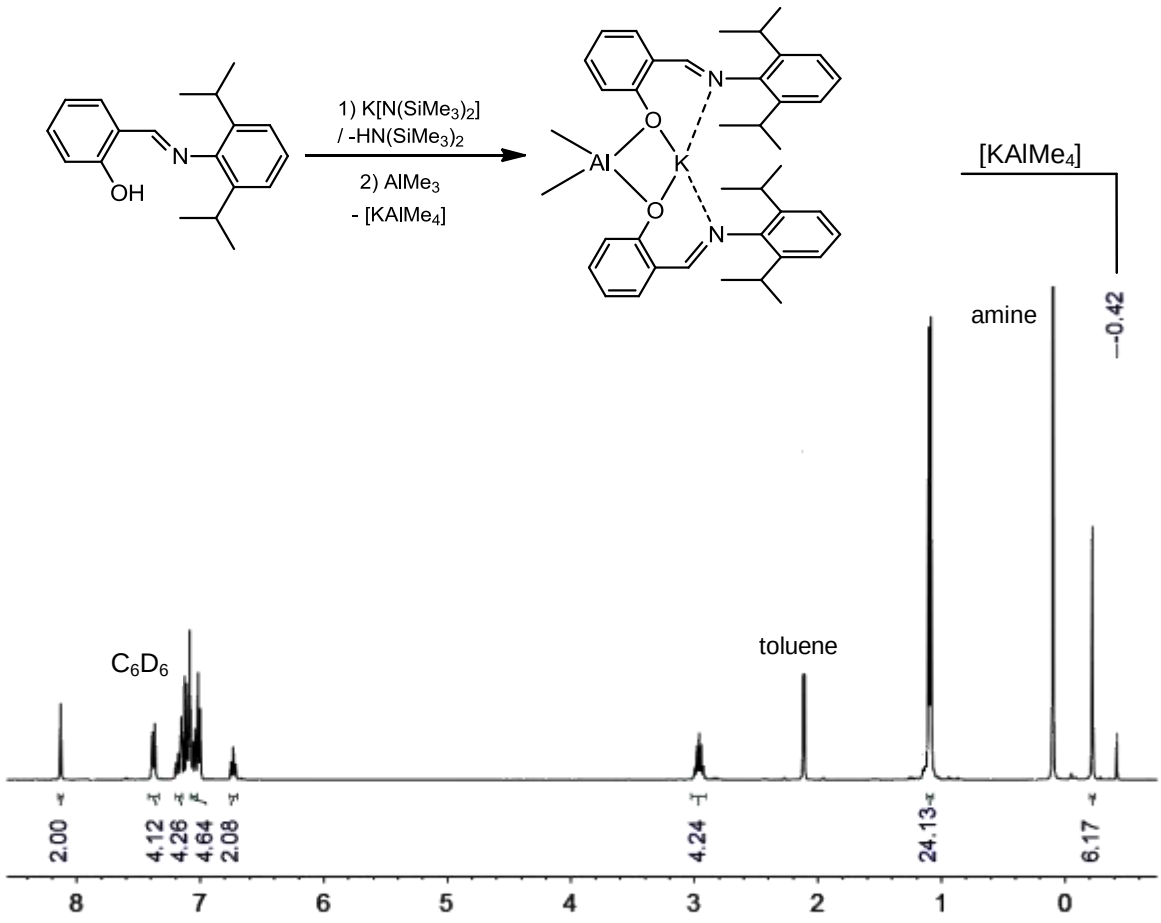

Figure S12 ^{1}H NMR spectrum of complex **4b** obtained in the stoichiometric reaction, and recorded in C_6D_6 at room temperature.

4. Comparative ^{1}H NMR Spectra for the synthesis of [KAl(L*b*)$_2$Me$_2$], (4b) using both stoichiometries

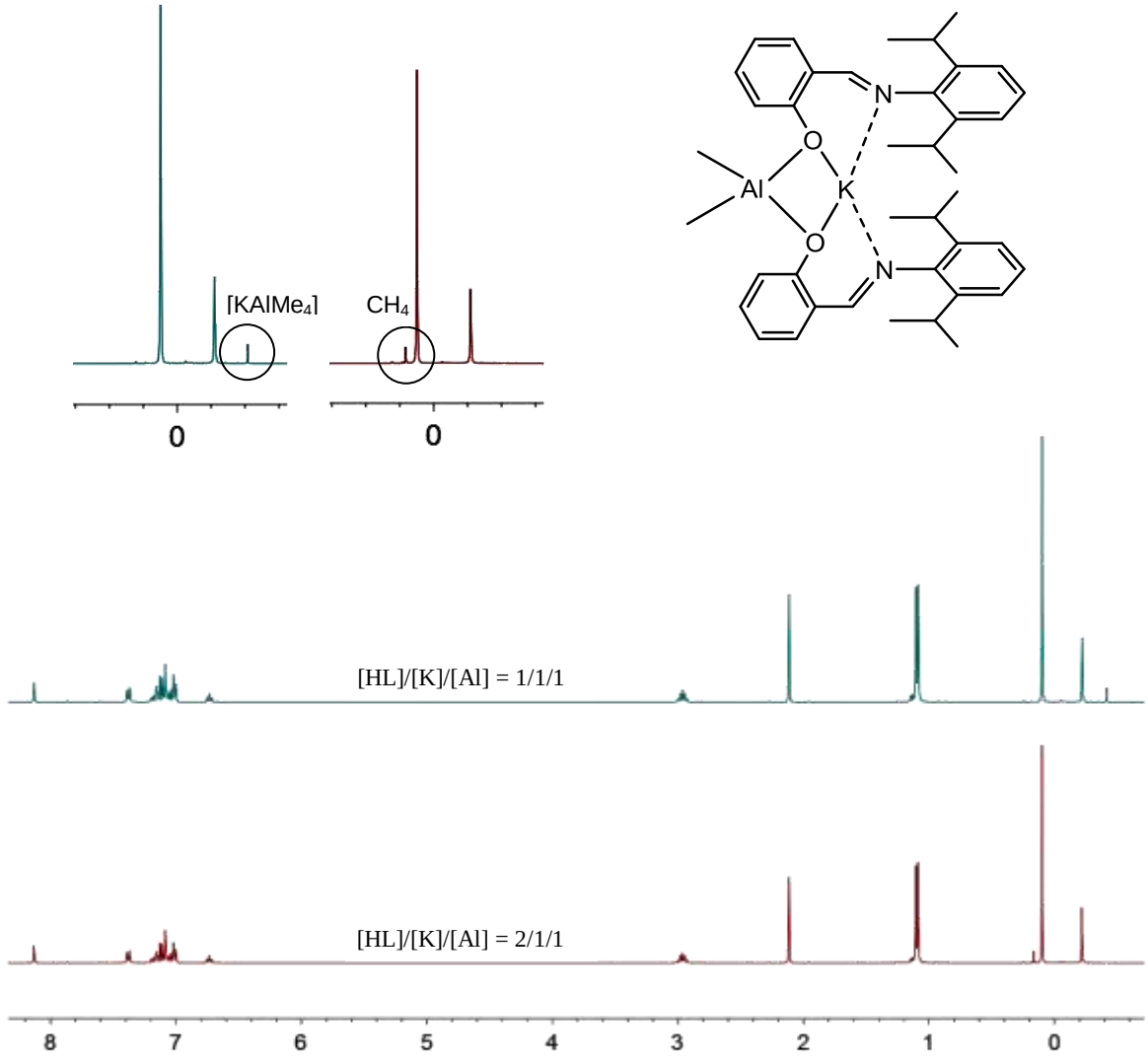

Figure S13 Comparative ^{1}H NMR spectra of complex [KAlMe$_2$(L*b*)$_2$] (**4b**), recorded in C_6D_6 at room temperature.

5. ^{1}H NMR Spectra of NaL and $AlMe_3$ reaction in a 1:2 molar ratio

- Reaction: NaL*a* + 2 $AlMe_3$

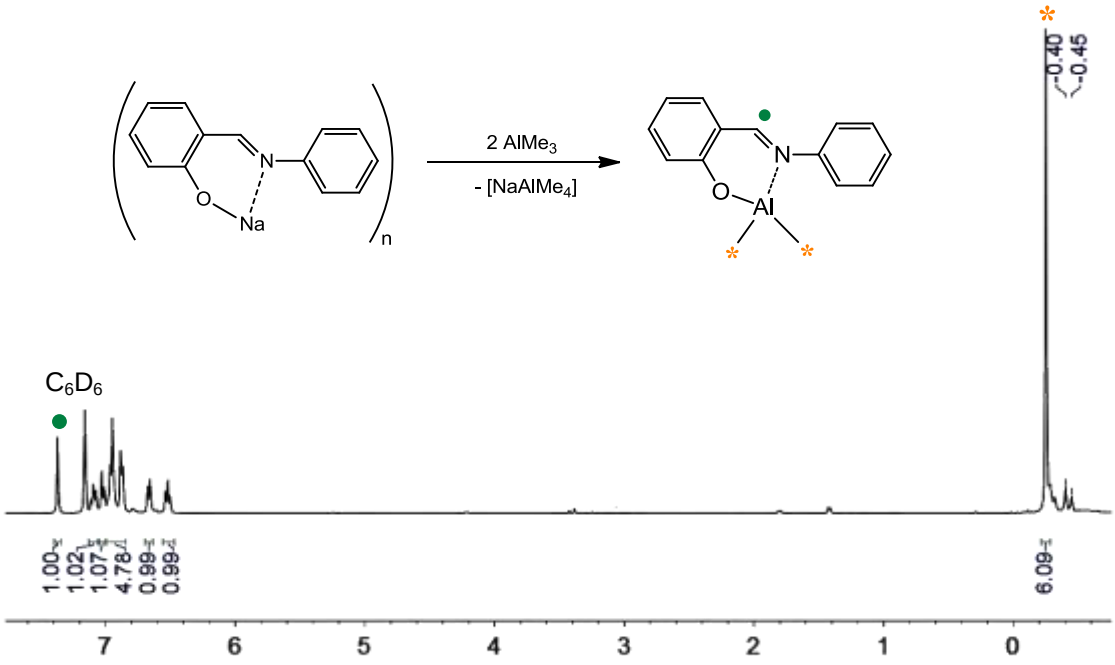

Figure S14 ^{1}H NMR spectrum of complex [$AlMe_2$(L*a*)] recorded in C_6D_6 at room temperature

- Reaction: NaL*b* + 2 $AlMe_3$

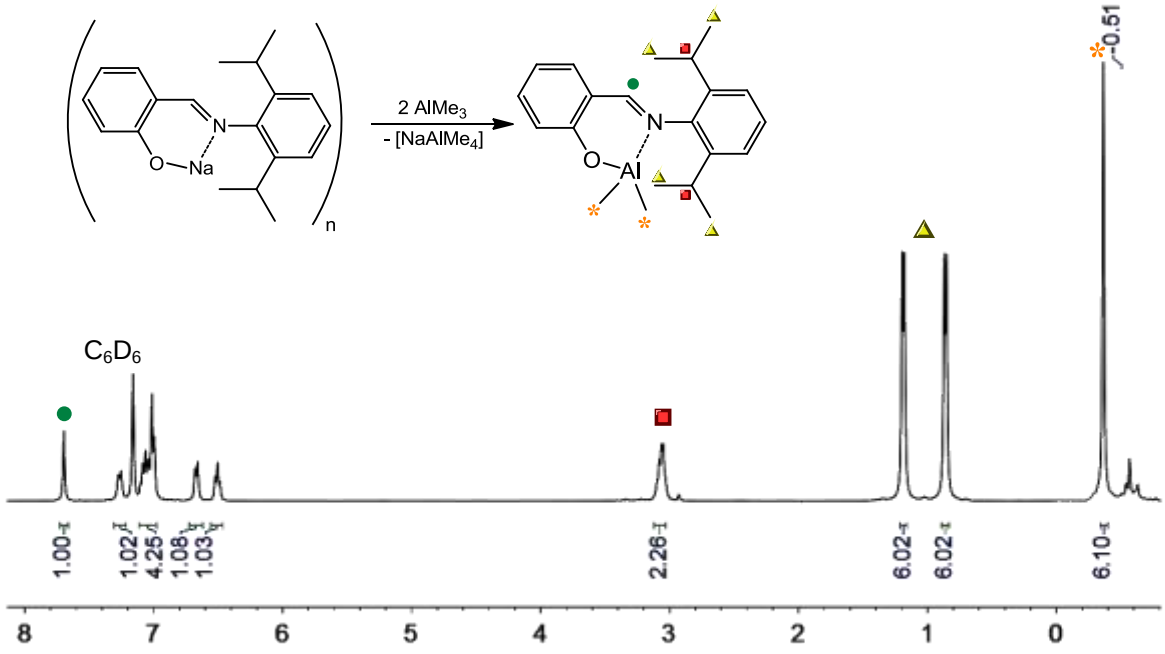

Figure S15 ^{1}H NMR spectrum of complex [$AlMe_2$(L*b*)] recorded in C_6D_6 at room temperature

6. Diffusion-Ordered SpectroscopY (^{1}H-DOSY) NMR experiments

The Diffusion-Ordered NMR SpectroscopY (DOSY) study of different complexes was carried out to know the true nature of this complex in solution. This technique allows to estimate the degree of aggregation and the molecular mass by determining the diffusion coefficient, D. As in previous works, we choose the internal references method described by Williard to obtain these values.[1-3] The internal reference standards chosen were N-benzylideneaniline (PhN=CHPh; M_w = 181.2), 1-phenylnaphtalene (PhN, M_w = 204.7), and 1,2,3,4-tetraphenylnaphthalene (TPhN, M_w = 432.6). The selected complexes for this study were **1a**, **3a**, **3b**, **4b**, and **5b**. However, only **4b** and **5b** could be determined by using this technique because **1a**, **3a**, and **3b** did not fulfil the conditions established by Williard.[4] As such, the corresponding signals for **1a**, and **3a** were completely overlapped with the references standards; and **3b** had not good solubility in the solvent used for the NMR study. Only **4b** and **5b** satisfied the established conditions. Once the results were obtained, a calibration curve of the standards was plotted (Log D *vs* Log M_w). Then, the molecular weight of **4b** and **5b** were obtained by interpolating or extrapolating the D values. For these complexes the solution structures were in agreement with the solid state ones and both are heterobimetallic in solution, [KAlMe$_2$(L)$_2$] (**4b**) and [KAlMe(L*b*)$_3$] (**5b**).

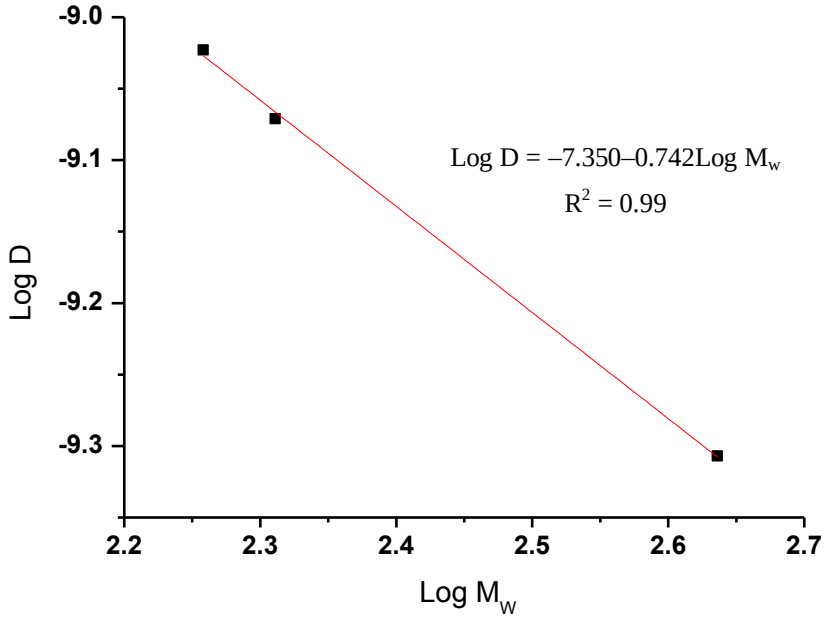

Figure S16 Calibration curve for determination of M_w of **5b** by ^{1}H DOSY NMR experiment using the internal references system.[1-4]

Table S1 M_w, Log M_w, D and Log D values of three patrons and **5b** in C_6D_6

Compound	M_w (g/mol)	Log M_w	D (m^2/s)	Log D	m* (g/mol)[b]	% error
PhN=CHPh	181.2	2.258	$9.484 \cdot 10^{-10}$	-9.023	--	--
PhN	204.7	2.311	$8.492 \cdot 10^{-10}$	-9.071	--	--
TPhN	432.6	2.636	$4.932 \cdot 10^{-10}$	-9.307	--	--
5b	922.3[a]	--	$2.958 \cdot 10^{-10}$	-9.529	864	6.3

[a] Predicted molecular mass. [b] Experimental molecular mass.

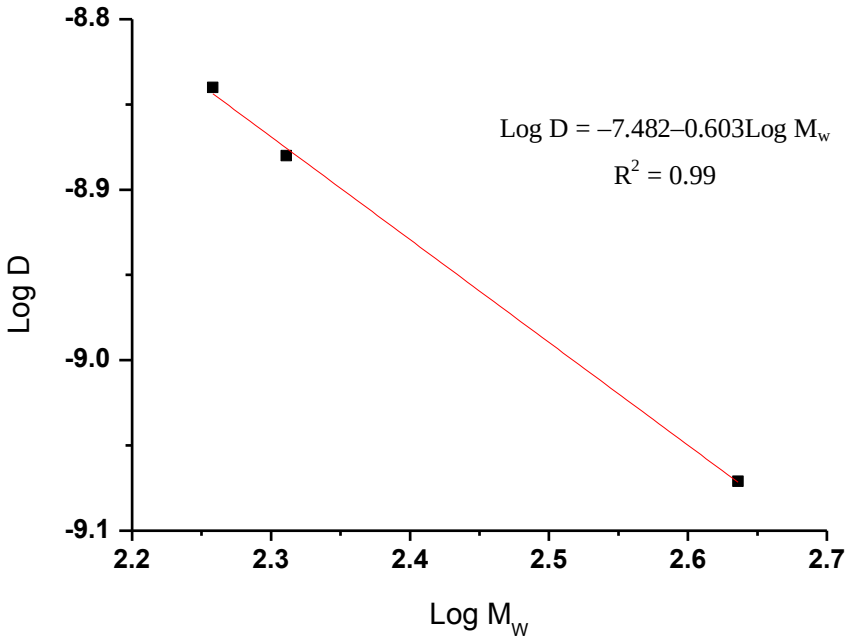

Figure S17 Calibration curve for determination of M_w of **4b** by ^{1}H DOSY NMR experiment using the internal references system.[1-4]

Table S2 M_w, Log M_w, D and Log D values of three patrons and **4b** in C_6D_6

Compound	M_w (g/mol)	Log M_w	D (m^2/s)	Log D	m* (g/mol)[b]	% error
PhN=CHPh	181.2	2.258	$1.445 \cdot 10^{-9}$	-8.840	--	--
PhN	204.7	2.311	$1.315 \cdot 10^{-9}$	-8.881	--	--
TPhN	432.6	2.636	$8.492 \cdot 10^{-10}$	-9.071	--	--
4b	656.9[a]	--	$6.471 \cdot 10^{-10}$	-9.189	677	-3.1

[a] Predicted molecular mass. [b] Experimental molecular mass.

7. Single-Crystal X-ray Data for (1a·C_7H_8), (4b·$2C_6H_6$) and (5b·C_6H_{14})

Table S3 Crystallographic data for **[$LiAlMe_3$(L*a*)·C_7H_8], (1a C_7H_8)**

	[$LiAlMe_3$(L*a*)·C_7H_8]
Empirical formula	$C_{39}H_{46}Al_2Li_2N_2O_2$ C_7H_8
Formula weight	734.75
Color, shape	Yellow/block
Crystal size (mm)	0.49 x 0.44 x 0.30
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	11.1067(12)
b (Å)	8.8238(11)
c (Å)	22.6234(19)
α (º)	90
β (º)	94.210(7)
γ (º)	90
V (Å^3)	2211.2(4)
Z	2
$\rho_{calcd.}$ (mg m^{-3})	1.104
F_{000}	784
μ (mm^{-1})	0.102
θ Range (°)	3.047 to 27.511
Reflns. Collected	9774
Indep. Reflns./R(int)	5085/0.0449
Data/restraints/param	5085/0/256
R_1/wR_2 (I > 2σ(I))[a]	0.0546/0.1401
R_1/wR_2 (all data)[a]	0.1097/0.1609
GOF	0.976
Max/min Δρ (e.Å^{-3})	0.400 and -0.265

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$

Table S4. Selected bond lengths (Å) and angles (°) for **[LiAlMe$_3$(L*a*)·C$_7$H$_8$], (1a C$_7$H$_8$)**.

Bond lengths (Å)		Angles (°)	
C(1)-Al(1)	1.969(2)	O(1)-LI(1)-O(1) #	198.03(19)
C(2)-Al(1)	1.965(2)	O(1)-LI(1)-N(1)	94.04(17)
C(3)-Al(1)	1.993(2)	O(1)#1-LI(1)-N(1)	125.4(2)
C(3)···Li(1)	2.409(4)	O(1)-Li(1)-C(3)	85.03(16)
C(4)-N(1)	1.269(2)	N(1)-Li(1)-C(3)	128.8(2)
C(4)-C(10)	1.460(3)	C(4)-N(1)-C(11)	118.14(19)
C(5)-O(1)	1.371(2)	C(4)-N(1)-Li(1)	123.6(2)
C(11)-N(1)	1.431(2)	Al(1)-O(1)-Li(1)	93.00(14)
LI(1)-O(1)	1.936(3)	Al(1)-C(3)-Li(1)	77.44(13)
LI(1)-O(1)#1	1.961(4)	O(1)-Al(1)-C(3))	99.02(10)
LI(1)-N(1)	1.986(3)		
O(1)-Al(1)	1.890(1)		

Symmetry transformations used to generate equivalent atoms: [a] #1 –x + 2, -y + 1, -z.

Table S5 Bond lengths (Å) and angles (°) for **[LiAlMe$_3$(L*a*)·C$_7$H$_8$], (1a C$_7$H$_8$)**

Bond lengths (Å)			
C(1)-Al(1)	1.969(2)	C(7)-C(8)	1.373(4)
C(1D)-C(2D)	1.505(5)	C(8)-C(9)	1.365(3)
C(2)-Al(1)	1.965(2)	C(9)-C(10)	1.406(3)
C(2D)-C(3D)	1.377(5)	C(11)-C(12)	1.377(3)
C(2D)-C(7D)	1.381(5)	C(11)-C(16)	1.385(3)
C(3)-Al(1)	1.993(2)	C(11)-N(1)	1.431(2)
C(3)-Li(1)	2.409(4)	C(12)-C(13)	1.372(3)
C(3D)-C(4D)	1.355(5)	C(13)-C(14)	1.379(3)
C(4)-N(1)	1.269(2)	C(14)-C(15)	1.359(4)
C(4)-C(10)	1.460(3)	C(15)-C(16)	1.382(3)
C(4D)-C(5D)	1.357(5)	Li(1)-O(1)	1.936(3)
C(5)-O(1)	1.371(2)	Li(1)-O(1)#1	1.961(4)
C(5)-C(6)	1.379(3)	Li(1)-N(1)	1.986(3)
C(5)-C(10)	1.401(3)	Li(1)-Li(1)#1	2.558(7)
C(5)-Li(1)#1	2.764(4)	Li(1)-C(5)#1	2.764(4)
C(5D)-C(6D)	1.351(4)	Li(1)-Al(1)	2.777(3)
C(6)-C(7)	1.380(3)	O(1)-Al(1)	1.8903(14)
C(6D)-C(7D)	1.391(4)	O(1)-Li(1)#1	1.961(4)
Angles (°)			
C(3D)-C(2D)-C(7D)	118.6(3)	N(1)-Li(1)-C(3)	128.77(19)
C(3D)-C(2D)-C(1D)	119.2(4)	O(1)-Li(1)-Li(1)#1	49.42(11)
C(7D)-C(2D)-C(1D)	122.1(4)	O(1)#1-Li(1)-Li(1)#1	48.55(12)
Al(1)-C(3)-Li(1)	77.59(11)	N(1)-Li(1)-Li(1)#1	119.8(2)
C(4D)-C(3D)-C(2D)	120.9(3)	C(3)-Li(1)-Li(1)#1	97.65(17)
N(1)-C(4)-C(10)	127.06(17)	O(1)-Li(1)-C(5)#1	113.15(15)

C(3D)-C(4D)-C(5D)	120.8(4)	O(1)#1-Li(1)-C(5)#1	27.63(7)
O(1)-C(5)-C(6)	118.88(17)	N(1)-Li(1)-C(5)#1	140.78(16)
O(1)-C(5)-C(10)	121.17(17)	C(3)-Li(1)-C(5)#1	83.39(12)
C(6)-C(5)-C(10)	119.94(18)	Li(1)#1-Li(1)-C(5)#1	67.55(14)
O(1)-C(5)-Li(1)#1	41.56(11)	O(1)-Li(1)-Al(1)	42.82(7)
C(6)-C(5)-Li(1)#1	98.31(16)	O(1)#1-Li(1)-Al(1)	116.98(14)
C(10)-C(5)-Li(1)#1	126.39(14)	N(1)-Li(1)-Al(1)	107.47(14)
C(6D)-C(5D)-C(4D)	119.8(3)	C(3)-Li(1)-Al(1)	44.50(8)
C(7)-C(6)-C(5)	120.9(2)	Li(1)#1-Li(1)-Al(1)	78.04(14)
C(5D)-C(6D)-C(7D)	120.7(3)	C(5)#1-Li(1)-Al(1)	111.68(11)
C(6)-C(7)-C(8)	120.1(2)	C(4)-N(1)-C(11)	118.21(16)
C(2D)-C(7D)-C(6D)	119.2(3)	C(4)-N(1)-Li(1)	123.68(16)
C(9)-C(8)-C(7)	119.7(2)	C(11)-N(1)-Li(1)	117.99(15)
C(8)-C(9)-C(10)	121.9(2)	C(5)-O(1)-Al(1)	117.88(11)
C(9)-C(10)-C(5)	117.51(19)	C(5)-O(1)-Li(1)	126.44(14)
C(9)-C(10)-C(4)	116.86(18)	Al(1)-O(1)-Li(1)	93.07(12)
C(5)-C(10)-C(4)	125.62(17)	C(5)-O(1)-Li(1)#1	110.80(15)
C(12)-C(11)-C(16)	118.94(19)	Al(1)-O(1)-Li(1)#1	121.64(11)
C(12)-C(11)-N(1)	118.08(17)	Li(1)-O(1)-Li(1)#1	82.03(16)
C(16)-C(11)-N(1)	122.91(19)	O(1)-Al(1)-C(1)	106.65(8)
C(13)-C(12)-C(11)	120.8(2)	O(1)-Al(1)-C(2)	107.04(9)
C(12)-C(13)-C(14)	120.0(2)	C(1)-Al(1)-C(2)	115.51(11)
C(15)-C(14)-C(13)	119.6(2)	O(1)-Al(1)-C(3)	98.95(9)
C(14)-C(15)-C(16)	120.8(2)	C(1)-Al(1)-C(3)	112.52(12)
C(15)-C(16)-C(11)	119.8(2)	C(2)-Al(1)-C(3)	114.31(11)
O(1)-Li(1)-O(1)#1	97.97(16)	O(1)-Al(1)-Li(1)	44.11(8)
O(1)-Li(1)-N(1)	93.84(14)	C(1)-Al(1)-Li(1)	106.08(10)
O(1)#1-Li(1)-N(1)	125.59(18)	C(2)-Al(1)-Li(1)	135.89(11)
O(1)-Li(1)-C(3)	84.88(13)	C(3)-Al(1)-Li(1)	57.91(10)
O(1)#1-Li(1)-C(3)	105.17(15)		

Table S6 Crystallographic data for **[KAlMe$_2$(L*b*)$_2$·2C$_6$H$_6$], (4b·2C$_6$H$_6$)**

	[KAlMe$_2$(L*b*)$_2$·2C$_6$H$_6$]
Empirical formula	$C_{40}H_{50}AlKN_2O_2 \cdot 2C_6H_6$
Formula weight	813.11
Color, shape	Yellow/block
Crystal size (mm)	0.49 x 0.49 x 0.42
Crystal system	Monoclinic
Space group	*P2$_1$/c*
a (Å)	20.053(3)

b (Å)	11.5534(14)
c (Å)	20.4001(16)
α (º)	90
β (º)	90.391(10)
γ (º)	90
V (Å^3)	4726.1(11)
Z	4
$\rho_{calcd.}$ (mg m^{-3})	1.143
F_{000}	1744
μ (mm^{-1})	0.171
θ Range (°)	3.048 to 27.507
Reflns. Collected	33758
Indep. Reflns./R(int)	10658/0.0563
Data/restraints/param	10658/468/529
R_1/wR_2 (I > 2σ(I)) [a]	0.0528/0.1317
R_1/wR_2 (all data)[a]	0.0971/0.1540
GOF	1.059
Max/min Δρ (e.Å^{-3})	0.467 and -0.415

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$

Table S7. Selected bond lengths (Å) and angles (°) for **[KAlMe$_2$(L*b*)$_2$·2C$_6$H$_6$], (4b·2C$_6$H$_6$)**.

Bond lengths (Å)		**Angles (°)**	
K(1)-O(2)	2.657(2)	O(2)-K(1)-O(1)	59.96(5)
K(1)-O(1)	2.660(2)	O(2)-K(1)-N(1)	93.02(7)
K(1)-N(1)	2.781(2)	N(1)-K(1)-N(2)	155.16(6)
K(1)-N(2)	2.784(3)	O(1)-Al(1)-O(2)	95.18(7)
Al(1)-O(1)	1.809(2)	O(2)-Al(1)-C(1)	116.62(13)
Al(1)-O(2)	1.790(2)	C(1)-Al(1)-C(2)	113.22(12)
Al(1)-C(1)	1.965(3)	C(10)-N(1)-C(30)	118.5(2)
Al(1)-C(2)	1.964(3)	C(10)-N(1)-K(1)	129.88(17)
N(1)-C(10)	1.262(4)	C(30)-N(1)-K(1)	110.24(16)
N(1)-C(30)	1.431(3)	Al(1)-O(2)-K(1)	102.11(8)
N(2)-C(20)	1.272(4)		
N(2)-C(40)	1.439(3)		
O(1)-C(12)	1.344(3)		
O(2)-C(22)	1.343(3)		
C(10)-C(11)	1.466(4)		

Symmetry transformations used to generate equivalent atoms: #1 –x + 2, -y + 1, -z.

Table S8 Bond lengths (Å) and angles (°) for **[KAlMe$_2$(L*b*)$_2$·2C$_6$H$_6$], (4b·2C$_6$H$_6$)**

Bond lengths (Å)			
K(1)-O(2)	2.657(2)	C(27)-C(45)	1.516(5)
K(1)-O(1)	2.660(2)	C(27)-C(28)	1.515(5)
K(1)-N(1)	2.781(2)	C(27)-C(29)	1.528(5)
K(1)-N(2)	2.784(3)	C(30)-C(35)	1.417(4)
K(1)-Al(1)	3.5162(8)	C(30)-C(31)	1.392(4)
K(1)-C(50)	3.556(4)	C(31)-C(32)	1.390(4)
Al(1)-O(1)	1.809(2)	C(31)-C(36)	1.523(4)
Al(1)-O(2)	1.790(2)	C(32)-C(33)	1.387(4)
Al(1)-C(1)	1.965(3)	C(33)-C(34)	1.362(5)
Al(1)-C(2)	1.964(3)	C(34)-C(35)	1.397(4)
N(1)-C(10)	1.262(4)	C(36)-C(37)	1.514(5)
N(1)-C(30)	1.431(3)	C(36)-C(38)	1.513(5)
N(2)-C(20)	1.272(4)	C(40)-C(41)	1.402(4)
N(2)-C(40)	1.439(3)	C(40)-C(45)	1.402(4)
O(1)-C(12)	1.344(3)	C(41)-C(42)	1.401(4)
O(2)-C(22)	1.343(3)	C(41)-C(46)	1.526(4)
C(10)-C(11)	1.466(4)	C(42)-C(43)	1.384(5)
C(11)-C(16)	1.404(4)	C(43)-C(44)	1.373(5)
C(11)-C(12)	1.408(4)	C(44)-C(45)	1.398(4)
C(12)-C(13)	1.390(4)	C(46)-C(48)	1.524(5)
C(13)-C(14)	1.388(4)	C(46)-C(47)	1.507(5)
C(14)-C(15)	1.376(5)	C(50)-C(51)	1.292(6)
C(15)-C(16)	1.374(4)	C(50)-C(55)	1.318(7)
C(17)-C(18)	1.518(5)	C(51)-C(52)	1.274(7)
C(17)-C(19)	1.509(6)	C(52)-C(53)	1.313(7)
C(17)-C(35)	1.514(4)	C(53)-C(54)	1.408(8)
C(20)-C(21)	1.461(4)	C(54)-C(55)	1.462(8)
C(21)-C(26)	1.397(4)	C(60)-C(61)	1.298(7)
C(21)-C(22)	1.411(4)	C(60)-C(65)	1.311(6)
C(22)-C(23)	1.394(4)	C(61)-C(62)	1.334(7)
C(23)-C(24)	1.386(5)	C(62)-C(63)	1.481(8)
C(24)-C(25)	1.378(5)	C(63)-C(64)	1.389(8)
C(25)-C(26)	1.375(4)	C(64)-C(65)	1.318(7)

Angles (°)			
O(2)-K(1)-O(1)	59.96(5)	C(18)-C(17)-C(35)	113.3(3)
O(2)-K(1)-N(1)	93.02(7)	C(19)-C(17)-C(35)	110.5(3)
O(1)-K(1)-N(1)	64.89(6)	N(2)-C(20)-C(21)	126.8(3)
O(2)-K(1)-N(2)	64.81(7)	C(26)-C(21)-C(22)	118.0(3)
O(1)-K(1)-N(2)	92.99(7)	C(26)-C(21)-C(20)	116.3(2)
N(1)-K(1)-N(2)	155.16(6)	C(22)-C(21)-C(20)	125.6(3)
O(2)-K(1)-Al(1)	29.77(5)	O(2)-C(22)-C(23)	119.7(3)
O(1)-K(1)-Al(1)	30.19(4)	O(2)-C(22)-C(21)	121.8(2)
N(1)-K(1)-Al(1)	77.77(5)	C(23)-C(22)-C(21)	118.5(3)
N(2)-K(1)-Al(1)	77.40(5)	C(24)-C(23)-C(22)	121.8(3)
O(2)-K(1)-C(50)	124.00(9)	C(25)-C(24)-C(23)	119.9(3)
O(1)-K(1)-C(50)	70.23(10)	C(24)-C(25)-C(26)	118.8(3)
N(1)-K(1)-C(50)	87.57(10)	C(25)-C(26)-C(21)	122.9(3)
N(2)-K(1)-C(50)	95.63(10)	C(45)-C(27)-C(28)	109.5(3)
Al(1)-K(1)-C(50)	97.49(9)	C(45)-C(27)-C(29)	113.5(3)
O(1)-Al(1)-O(2)	95.18(7)	C(28)-C(27)-C(29)	110.2(3)
O(1)-Al(1)-C(1)	106.48(13)	C(35)-C(30)-C(31)	121.2(2)
O(2)-Al(1)-C(1)	116.62(13)	C(35)-C(30)-N(1)	120.0(3)
O(1)-Al(1)-C(2)	117.36(14)	C(31)-C(30)-N(1)	118.7(2)
O(2)-Al(1)-C(2)	107.06(13)	C(30)-C(31)-C(32)	118.9(3)
C(1)-Al(1)-C(2)	113.22(12)	C(30)-C(31)-C(36)	121.6(2)
O(1)-Al(1)-K(1)	47.69(6)	C(32)-C(31)-C(36)	119.5(3)
O(2)-Al(1)-K(1)	47.48(6)	C(33)-C(32)-C(31)	120.4(3)
C(1)-Al(1)-K(1)	122.98(11)	C(34)-C(33)-C(32)	120.3(3)
C(2)-Al(1)-K(1)	123.80(11)	C(33)-C(34)-C(35)	121.8(3)
C(10)-N(1)-C(30)	118.5(2)	C(30)-C(35)-C(34)	117.3(3)
C(10)-N(1)-K(1)	129.88(17)	C(30)-C(35)-C(17)	122.1(2)
C(30)-N(1)-K(1)	110.24(16)	C(34)-C(35)-C(17)	120.5(3)
C(20)-N(2)-C(40)	117.7(2)	C(31)-C(36)-C(37)	110.4(3)
C(20)-N(2)-K(1)	129.54(18)	C(31)-C(36)-C(38)	112.5(3)
C(40)-N(2)-K(1)	111.64(18)	C(37)-C(36)-C(38)	110.2(3)
C(12)-O(1)-Al(1)	125.12(17)	C(41)-C(40)-C(45)	121.6(2)
C(12)-O(1)-K(1)	129.14(16)	C(41)-C(40)-N(2)	117.9(2)
Al(1)-O(1)-K(1)	102.11(8)	C(45)-C(40)-N(2)	120.3(3)
C(22)-O(2)-Al(1)	126.42(18)	C(42)-C(41)-C(40)	118.5(3)
C(22)-O(2)-K(1)	127.76(17)	C(42)-C(41)-C(46)	118.7(3)
Al(1)-O(2)-K(1)	102.75(9)	C(40)-C(41)-C(46)	122.8(2)
N(1)-C(10)-C(11)	127.4(3)	C(43)-C(42)-C(41)	120.4(3)
C(16)-C(11)-C(12)	118.9(2)	C(42)-C(43)-C(44)	120.2(3)
		C(45)-C(44)-C(43)	121.8(3)
		C(44)-C(45)-C(40)	117.6(3)
		C(44)-C(45)-C(27)	120.2(3)
		C(40)-C(45)-C(27)	122.1(2)
		C(48)-C(46)-C(47)	110.1(3)
		C(48)-C(46)-C(41)	111.7(3)
		C(47)-C(46)-C(41)	111.1(3)

C(16)-C(11)-C(10)	115.7(2)	C(51)-C(50)-C(55)	122.1(5)
C(12)-C(11)-C(10)	125.4(2)	C(51)-C(50)-K(1)	109.8(3)
O(1)-C(12)-C(13)	119.4(2)	C(55)-C(50)-K(1)	91.6(3)
O(1)-C(12)-C(11)	122.0(2)	C(52)-C(51)-C(50)	122.9(5)
C(13)-C(12)-C(11)	118.6(3)	C(51)-C(52)-C(53)	123.1(5)
C(14)-C(13)-C(12)	121.4(3)	C(52)-C(53)-C(54)	118.1(5)
C(13)-C(14)-C(15)	120.0(3)	C(53)-C(54)-C(55)	116.6(4)
C(16)-C(15)-C(14)	119.7(3)	C(50)-C(55)-C(54)	117.0(5)
C(15)-C(16)-C(11)	121.3(3)	C(61)-C(60)-C(65)	122.0(5)
C(18)-C(17)-C(19)	110.8(3)	C(60)-C(61)-C(62)	122.8(5)
		C(61)-C(62)-C(63)	116.5(5)
		C(64)-C(63)-C(62)	116.7(4)
		C(65)-C(64)-C(63)	119.8(5)
		C(60)-C(65)-C(64)	122.1(5)

Table S9 Crystallographic data for **[KAlMe(L*b*)$_3$·C$_6$H$_{14}$], (5b·C$_6$H$_{14}$)**

	[KAlMe(L*b*)$_3$·C$_6$H$_{14}$]
Empirical formula	$C_{58}H_{69}AlKN_3O_3 \cdot C_6H_{14}$
Formula weight	1008.41
Color, shape	Yellow/block
Crystal size (mm)	0.49 x 0.46 x 0.43
Crystal system	Trigonal
Space group	*R-3*
a (Å)	13.4310(11)
b (Å)	13.4310(11)
c (Å)	57.550(4)
α (º)	90
β (º)	90
γ (º)	120
V (Å^3)	8990.6(16)
Z	6
$\rho_{calcd.}$ (mg m^{-3})	1.117
F_{000}	3264
μ (mm^{-1})	0.148
θ Range (°)	3.033 to 27.500
Reflns. Collected	13711
Indep. Reflns./R(int)	4615/0.0274

Data/restraints/param	4615 / 0 / 198
R_1/wR_2 (I > 2σ(I)) [a]	0.0618/0.1805
R_1/wR_2 (all data)[a]	0.0901/0.1995
GOF	1.039
Max/min Δρ (e.Å^{-3})	0.980 and -0.435

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$

Table S10. Selected bond lengths (Å) and angles (°) for [**KAlMe(L*b*)$_3$·C$_6$H$_{14}$], (5b·C$_6$H$_{14}$)**

Bond lengths (Å)		**Angles (°)**	
Al(2)-O(1)	1.7625(16)	O(1)#1-Al(2)-O(1)	99.29(7)
Al(2)-C(1)	1.943(4)	O(1)#1-Al(2)-C(1)	118.37(6)
Al(2)-K(1)	3.1740(13)	C(1)-Al(2)-K(1)	180.0
K(1)-O(1)	2.8045(17)	O(1)-K(1)-N(1)	97.03(5)
K(1)-N(1)	2.9101(19)	O(1)-K(1)-Al(2)	33.57(3)
N(1)-C(8)	1.277(3)	C(8)-N(1)-C(9)	114.3(2)
N(1)-C(9)	1.435(3)	C(8)-N(1)-K(1)	133.43(15)
O(1)-C(2)	1.332(3)	Al(2)-O(1)-K(1)	84.79(6)
C(2)-C(3)	1.401(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x, -y, -z.

Table S11 Bond lengths (Å) and angles (°) for **[KAlMe(L*b*)$_3$·C$_6$H$_{14}$], (5b·C$_6$H$_{14}$)**

Bond lengths (Å)			
Al(2)-O(1)	1.7625(16)	C(5)-C(6)	1.372(4)
Al(2)-O(1)#1	1.7625(16)	C(6)-C(7)	1.402(3)
Al(2)-O(1)#2	1.7625(16)	C(7)-C(8)#2	1.462(3)
Al(2)-C(1)	1.943(4)	C(9)-C(14)	1.400(3)
Al(2)-K(1)	3.1740(13)	C(9)-C(10)	1.403(3)
K(1)-O(1)#1	2.8045(17)	C(10)-C(11)	1.392(4)
K(1)-O(1)#2	2.8046(16)	C(10)-C(18')	1.521(5)
K(1)-O(1)	2.8046(16)	C(10)-C(18)	1.522(2)
K(1)-N(1)#1	2.9101(19)	C(11)-C(12)	1.377(4)
K(1)-N(1)#2	2.9102(19)	C(12)-C(13)	1.376(4)
K(1)-N(1)	2.9102(19)	C(13)-C(14)	1.390(3)
N(1)-C(8)	1.277(3)	C(14)-C(15)	1.521(3)
N(1)-C(9)	1.435(3)	C(15)-C(16)	1.503(5)
O(1)-C(2)	1.332(3)	C(15)-C(17)	1.510(5)
C(2)-C(3)	1.401(3)	C(20)-C(18)	1.248(13)
C(2)-C(7)	1.408(3)	C(18)-C(19)	1.461(6)
C(3)-C(4)	1.374(3)	C(20')-C(18')	1.572(7)
		C(18')-C(19')	1.473(12)

C(4)-C(5)1.384(4)			
Angles (°)			
O(1)-Al(2)-O(1)#1	99.29(7)	C(2)-O(1)-K(1)	136.38(13)
O(1)-Al(2)-O(1)#2	99.29(7)	Al(2)-O(1)-K(1)	84.79(6)
O(1)#1-Al(2)-O(1)#2	99.29(7)	O(1)-C(2)-C(3)	121.7(2)
O(1)-Al(2)-C(1)	118.36(6)	O(1)-C(2)-C(7)	120.04(19)
O(1)#1-Al(2)-C(1)	118.37(6)	C(3)-C(2)-C(7)	118.3(2)
O(1)#2-Al(2)-C(1)	118.36(6)	C(4)-C(3)-C(2)	121.6(2)
O(1)-Al(2)-K(1)	61.64(6)	C(3)-C(4)-C(5)	120.6(2)
O(1)#1-Al(2)-K(1)	61.63(6)	C(6)-C(5)-C(4)	118.6(2)
O(1)#2-Al(2)-K(1)	61.64(6)	C(5)-C(6)-C(7)	122.5(2)
C(1)-Al(2)-K(1)	180.0	C(6)-C(7)-C(2)	118.4(2)
O(1)#1-K(1)-O(1)#2	57.23(5)	C(6)-C(7)-C(8)#2	115.6(2)
O(1)#1-K(1)-O(1)	57.23(5)	C(2)-C(7)-C(8)#2	126.0(2)
O(1)#2-K(1)-O(1)	57.23(5)	N(1)-C(8)-C(7)#1	128.1(2)
O(1)#1-K(1)-N(1)#1	97.03(5)	C(14)-C(9)-C(10)	121.4(2)
O(1)#2-K(1)-N(1)#1	60.98(5)	C(14)-C(9)-N(1)	119.0(2)
O(1)-K(1)-N(1)#1	117.33(5)	C(10)-C(9)-N(1)	119.6(2)
O(1)#1-K(1)-N(1)#2	117.33(5)	C(11)-C(10)-C(9)	117.7(2)
O(1)#2-K(1)-N(1)#2	97.04(5)	C(11)-C(10)-C(18')	121.5(3)
O(1)-K(1)-N(1)#2	60.98(5)	C(9)-C(10)-C(18')	120.8(3)
N(1)#1-K(1)-N(1)#2	119.854(5)	C(11)-C(10)-C(18)	121.2(2)
O(1)#1-K(1)-N(1)	60.98(5)	C(9)-C(10)-C(18)	121.13(19)
O(1)#2-K(1)-N(1)	117.33(5)	C(12)-C(11)-C(10)	121.5(2)
O(1)-K(1)-N(1)	97.04(5)	C(13)-C(12)-C(11)	120.0(2)
N(1)#1-K(1)-N(1)	119.852(5)	C(12)-C(13)-C(14)	121.0(2)
N(1)#2-K(1)-N(1)	119.851(5)	C(13)-C(14)-C(9)	118.3(2)
O(1)#1-K(1)-Al(2)	33.57(3)	C(13)-C(14)-C(15)	120.4(2)
O(1)#2-K(1)-Al(2)	33.57(3)	C(9)-C(14)-C(15)	121.2(2)
O(1)-K(1)-Al(2)	33.57(3)	C(16)-C(15)-C(17)	110.0(3)
N(1)#1-K(1)-Al(2)	92.21(4)	C(16)-C(15)-C(14)	111.7(3)
N(1)#2-K(1)-Al(2)	92.21(4)	C(17)-C(15)-C(14)	112.2(3)
N(1)-K(1)-Al(2)	92.21(4)	C(19)-C(18)-C(20)	126.6(7)
C(8)-N(1)-C(9)	114.24(19)	C(19)-C(18)-C(10)	113.4(3)
C(8)-N(1)-K(1)	133.43(15)	C(20)-C(18)-C(10)	119.7(6)
C(9)-N(1)-K(1)	111.88(13)	C(19')-C(18')-C(10)	110.8(6)
C(2)-O(1)-Al(2)	135.03(14)	C(19')-C(18')-C(20')	102.4(6)
		C(10)-C(18')-C(20')	112.2(4)

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