Supporting Information

Amido Supported Rare-Earth Metal Methylidene Complexes with $Ln_3(\mu_3\text{-}CH_2)(\mu_3\text{-}Me)(\mu_2\text{-}Me)_3$ Core Structure

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Crystallographic data

NMR spectroscopic data

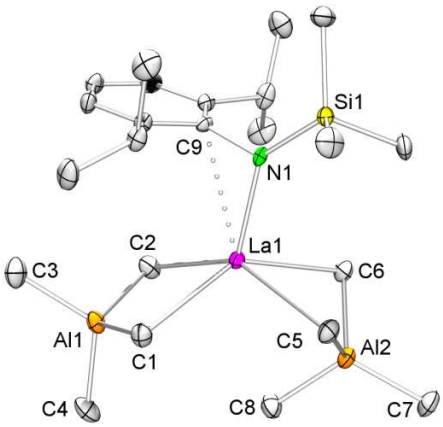

Figure S1. Molecular structure of [NSiMe$_3$(Ar)]La(AlMe$_4$)$_2$ (**5**-La). Atomic displacement parameters are set at the 30% level, hydrogen atoms have been omitted for clarity. La1−N1 2.295(4), La1−C1 2.712(5), La1−C2 2.716(5), La1−C5 2.837(5), La1−C6 2.717(5), Al1−C1 2.076(5), Al1−C2 2.072(5), Al1−C3 1.971(7), Al1−C4 1.968(6), Al2−C5 2.060(5), Al2−C6 2.077(5), Al2−C7 1.943(6), Al2−C8 1.992(6), La1···Al1 3.278(2), La1···Al2 3.013(1), La1···C9 2.779(4), La1−N1−C9 93.8(2), La1−C1−Al1−C2 −0.4(2), La1−C5−Al2−C6 45.5(2).

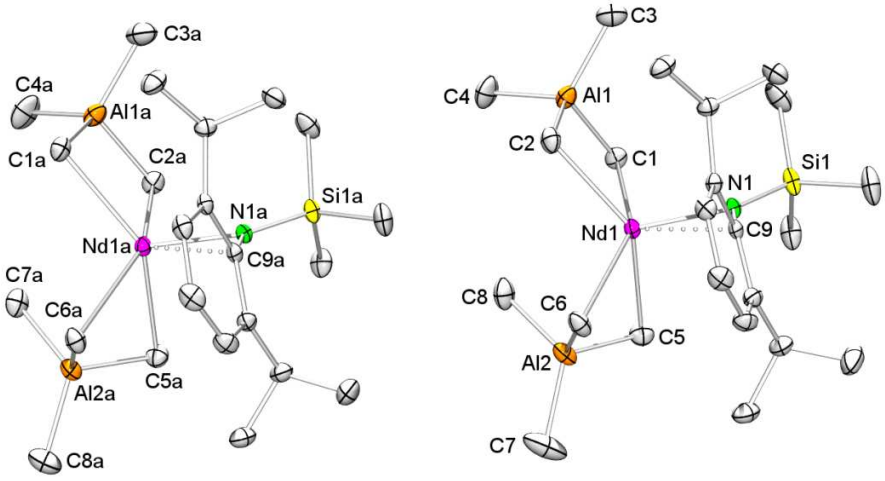

Figure S2. Molecular structure of [NSiMe$_3$(Ar)]Nd(AlMe$_4$)$_2$ (**5**-Nd). Atomic displacement parameters are set at the 30% level, hydrogen atoms have been omitted for clarity.

Table S1. Selected structural parameters [Å, °] of complex **5**-Nd.

	molecule 1		molecule 2
Nd1−N1	2.222(2)	Nd1a−N1a	2.234(2)
Nd1−C1	2.617(3)	Nd1a−C1a	2.638(3)
Nd1−C2	2.661(4)	Nd1a−C2a	2.637(3)
Nd1−C5	2.661(4)	Nd1a−C5a	2.685(4)
Nd1−C6	2.718(3)	Nd1a−C6a	2.730(3)
Al1−C1	2.072(4)	Al1a−C1a	2.065(4)
Al1−C2	2.074(4)	Al1a−C2a	2.082(4)
Al1−C3	1.970(5)	Al1a−C3a	1.969(5)
Al1−C4	1.984(4)	Al1a−C4a	1.969(5)
Al2−C5	2.069(4)	Al2a−C5a	2.071(4)
Al2−C6	2.072(4)	Al2a−C6a	2.067(4)
Al2−C7	1.941(5)	Al2a−C7a	1.983(4)
Al2−C8	1.979(4)	Al2a−C8a	1.943(4)
Nd1···Al1	3.194(1)	Nd1a···Al1a	3.188(1)
Nd1···Al2	2.976(1)	Nd1a···Al2a	2.973(1)
Nd1···C9	2.755(3)	Nd1a···C9a	2.720(3)
Nd1−N1−C9	95.7(2)	Nd1a−N1a−C9a	93.5(2)
Nd1−C1−Al1−C2	9.6(2)	Nd1a−C1a−Al1a−C2a	7.8(2)
Nd1−C5−Al2−C6	−40.0(1)	Nd1a−C5a−Al2a−C6a	42.5(1)

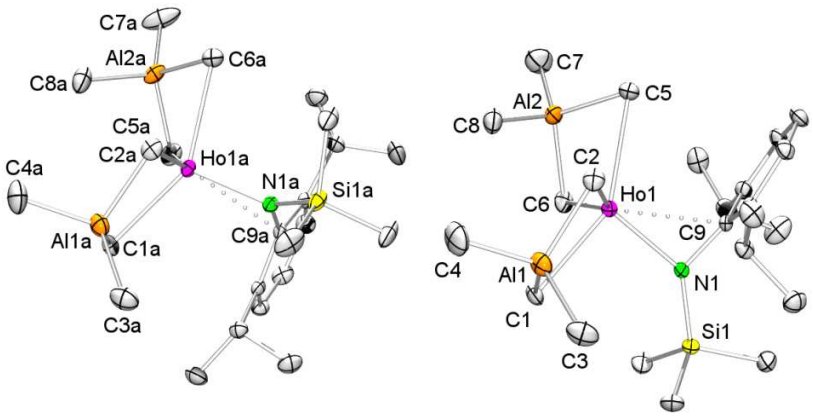

Figure S3. Molecular structure of [NSiMe$_3$(Ar)]Ho(AlMe$_4$)$_2$ (**5**-Ho). Atomic displacement parameters are set at the 30% level, hydrogen atoms have been omitted for clarity.

Table S2. Selected structural parameters [Å, °] of complex **5**-Ho.

	molecule 1		molecule 2
Ho1−N1	2.160(3)	Ho1a−N1a	2.154(3)
Ho1−C1	2.524(4)	Ho1a−C1a	2.523(4)
Ho1−C2	2.525(4)	Ho1a−C2a	2.503(4)
Ho1−C5	2.631(4)	Ho1a−C5a	2.616(4)
Ho1−C6	2.585(4)	Ho1a−C6a	2.569(4)
Al1−C1	2.085(4)	Al1a−C1a	2.076(4)
Al1−C2	2.069(4)	Al1a−C2a	2.065(4)
Al1−C3	1.964(5)	Al1a−C3a	1.967(5)
Al1−C4	1.965(5)	Al1a−C4a	1.966(5)
Al2−C5	2.059(4)	Al2a−C5a	2.069(4)
Al2−C6	2.077(4)	Al2a−C6a	2.065(4)
Al2−C7	1.941(5)	Al2a−C7a	1.946(5)
Al2−C8	1.975(4)	Al2a−C8a	1.985(5)
Ho1···Al1	3.078(1)	Ho1a···Al1a	3.0807(14)
Ho1···Al2	2.882(1)	Ho1a···Al2a	2.8903(14)
Ho1···C9	2.694(3)	Ho1a···C9a	2.750(3)
Ho1−N1−C9	95.4(2)	Ho1a−N1a−C9a	98.4(2)
Ho1−C1−Al1−C2	7.7(2)	Ho1a−C1a−Al1a−C2a	8.7(2)
Ho1−C5−Al2−C6	−40.4(2)	Ho1a−C5a−Al2a−C6a	−39.2(2)

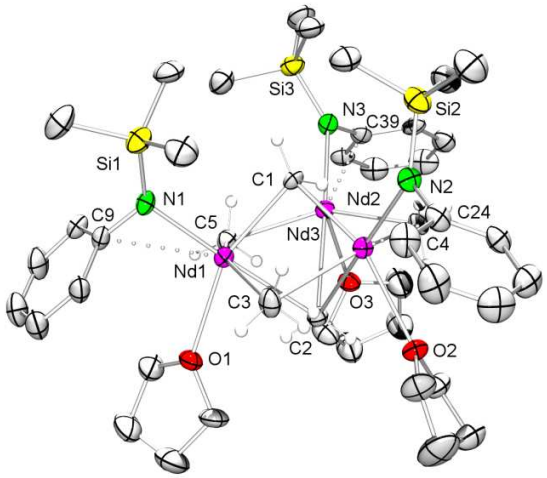

Figure S4. Molecular structure of **7**-Nd (atomic displacement parameters are set at the 30% level). Solvent molecules, isopropyl groups and hydrogen atoms have been omitted for clarity except for Nd−CH_2 and Nd−CH_3 moieties. Selected bond distances [Å] and angles [°]: Nd1−C1 2.425(7), Nd2−C1 2.505(8), Nd3−C1 2.494(8), Nd1−C2 2.811(8), Nd2−C2 2.805(8), Nd3−C2 2.835(8), Nd1−C3 2.626(8),

Nd1−C5 2.665(8), Nd2−C3 2.665(8), Nd2−C4 2.585(8), Nd3−C4 2.648(8), Nd3−C5 2.620(8), Nd1−N1 2.357(6), Nd2−N2 2.355(7), Nd3−N3 2.352(6), Nd1−O1 2.572(6), Nd2−O2 2.568(5), Nd3−O3 2.563(6), Nd1···C9 2.991(8), Nd2···C24 3.057(9), Nd3···C39 3.015(8), Nd1−C1−Nd2 90.8(2), Nd1−C1−Nd3 90.6(2), Nd2−C1−Nd3 91.3(2), Nd1−C2−Nd2 77.4(2), Nd1−C2−Nd3 76.6(2), Nd2−C2−Nd3 78.7(2), Nd1−C3−Nd2 83.1(2), Nd2−C4−Nd3 86.2(2), Nd1−C5−Nd3 82.9(2), N1−Nd1−O1 107.9(2), N2−Nd2−O2 105.8(2), N3−Nd3−O3 107.7(2).

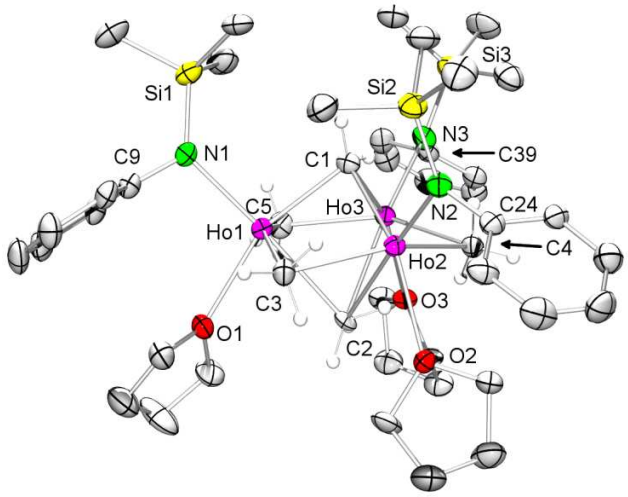

Figure S5. Molecular structure of **7**-Ho (atomic displacement parameters are set at the 30% level). Solvent molecules, isopropyl groups, disorder in two of the thf molecules and hydrogen atoms have been omitted for clarity except for Ho−CH_2 and Ho−CH_3 moieties. Selected bond distances [Å] and angles [°]: Ho1−C1 2.356(10), Ho2−C1 2.390(10), Ho3−C1 2.428(10), Ho1−C2 2.721(10), Ho2−C2 2.746(9), Ho3−C2 2.745(9), Ho1−C3 2.575(11), Ho1−C5 2.552(11), Ho2−C3 2.528(11), Ho2−C4 2.582(10), Ho3−C4 2.501(11), Ho3−C5 2.543(11), Ho1−N1 2.278(9), Ho2−N2 2.266(8), Ho3−N3 2.292(9), Ho1−O1 2.466(7), Ho2−O2 2.459(7), Ho3−O3 2.473(7), Ho1···C9 3.059(10), Ho2···C24 3.073(11), Ho3···C39 3.125(11), Ho1−C1−Ho2 87.9(3), Ho1−C1−Ho3 88.2(3), Ho2−C1−Ho3 89.4(3), Ho1−C2−Ho2 74.1(2), Ho1−C2−Ho3 75.1(2), Ho2−C2−Ho3 76.2(2), Ho1−C3−Ho2 80.4(3), Ho2−C4−Ho3 83.6(3), Ho1−C5−Ho3 81.6(3), N1−Ho1−O1 100.4(3), N2−Ho2−O2 100.8(3), N3−Ho3−O3 99.9(3).

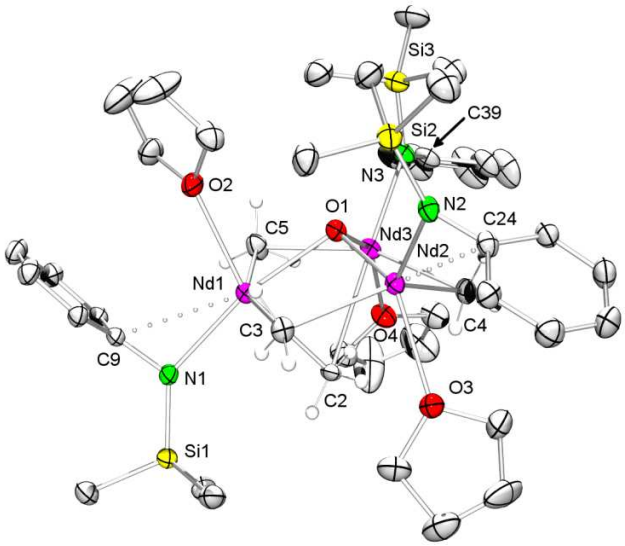

Figure S6. Molecular structure of **8**-Nd (atomic displacement parameters are set at the 30% level). Isopropyl groups and hydrogen atoms except for Nd−CH_3 moieties have been omitted for clarity. Selected bond distances [Å] and angles [°]: Nd1−O1 2.349(3), Nd2−O1 2.152(3). Nd3−O1 2.216(3), Nd1−C5 2.610(6), Nd1−C3 2.662(6), Nd1−C2 2.644(4), Nd2−C3 2.640(5), Nd2−C4 2.691(6), Nd3−C4 2.612(6), Nd3−C5 2.639(6), Nd3−C2 2.909(5), Nd1−N1 2.394(4), Nd2−N2 2.355(4), Nd3−N3 2.358(4), Nd1−O2 2.520(4), Nd2−O3 2.537(4), Nd3−O4 2.573(4), Nd1···C9 3.021(5), Nd2···C24 2.964(5), Nd3···C39 3.244(5), Nd1−O1−Nd2 104.79(4), Nd1−O1−Nd3 98.48(12), Nd2−O1−Nd3 108.78(14), Nd1−C2−Nd3 76.9(1), Nd1−C5−Nd3 82.45(17), Nd1−C3−Nd2 84.6(2), Nd2−C4−Nd3 84.1(2), N1−Nd1−O1 108.8(1), N2−Nd2−O2 109.7(1), N3−Nd3−O3 100.0(1).

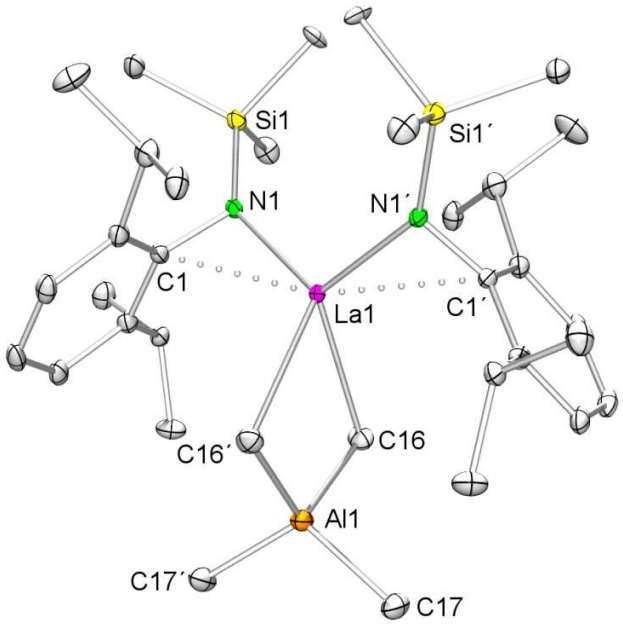

Figure S7. Molecular structure of $[NSiMe_3(Ar)]_2La(AlMe_4)$ (**9**-La). Atomic displacement parameters are set at the 30% level, hydrogen atoms have been omitted for clarity.

Table S3. Selected structural parameters [Å, °] of complexes **9**-Ln.

	9-La	**9**-Nd
Ln1−N1	2.356(3)	2.2968(8)
Ln1−C16	2.719(4)	2.650(1)
Al1−C16	2.072(4)	2.073(1)
Al1−C17	1.979(4)	1.980(1)
Ln1···Al1	3.296(2)	3.2302(4)
Ln1···C1	2.791(3)	2.7502(9)
N1−Ln1−C16	103.73(11)	103.10(3)
Ln1−N1−C1	91.95(18)	92.29(5)

Table S4. Summary of crystallographic data and structure refinement for compounds **4**-Lu, **5**-Y, **6**-La, **6**-Nd, and **6**-Ho.

	4-Lu	**5**-La	**5**-Nd	**5**-Ho	**6**-Y
Chemical	$C_{25}H_{48}NO_2SiLu$	$C_{23}H_{50}Al_2LaNSi$	$C_{23}H_{50}NAl_2SiNd$	$C_{23}H_{50}Al_2HoNSi$	$C_{23}H_{50}Ga_2NSiY$
M_r [g mol^{-1}]	597.71	561.60	566.93	587.62	597.08
Crystal	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	13.396(3)	9.3816(9)	12.2588(5)	12.201(3)	14.691(1)
b [Å]	14.122(2)	12.6128(8)	17.4136(7)	17.328(8)	12.3862(9)
c [Å]	14.991(3)	12.757(1)	28.1778(13)	28.104(8)	17.568(1)
β [°]	99.346(17)	94.340(8)	91.984(4)	91.70(2)	112.559(5)
V [Å^3]	2798.3(10)	1505.2(2)	6011.5(4)	5939(4)	2952.2(4)
Z	1	2	8	8	4
F(000)	1224	584	2360	2416	1240
T [K]	173(2)	173(2)	173(2)	173(2)	173(2)
$\rho_{\chi^{alcd}}$ [g cm^3]	1.419	1.239	1.253	1.314	1.343
μ [mm^{-1}]	3.590	1.526	1.834	2.773	3.811
R_1 (obsd.)[a]	0.0326	0.0278	0.0347	0.0433	0.0602
wR_2 (all)[b]	0.0544	0.0653	0.0729	0.0738	0.0996
S[c]	1.069	1.022	1.077	1.033	1.263

[a] $R^1 = \sum(|F_0| - |F_c|)/\sum|F_0|, F_0 > 4\sigma(F_0)$. [b] $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2]/[w(F_0^2)^2]\}^{1/2}$. [c] $S = \left[\sum w(F_0^2 - F_c^2)^2/(n_0 - np1/2\right.$.

Table S5. Summary of crystallographic data and structure refinement for compounds **7**-Nd, **7**-Ho, **8**-Nd, **9**-La and **9**-Nd.

	7-Nd	**7**-Ho	**8**-Nd	**9**-La	**9**-Nd
Chemical formula	$C_{62}H_{116}N_3Nd_3O_3Si_3 \cdot 0.5C_6H_{14}$	$C_{62}H_{116}Ho_3N_3O_3Si_3 \cdot C_6H_{14}$	$C_{61}H_{114}N_3Nd_3O_4Si_3$	$C_{34}H_{64}AlLaNSi_2$	$C_{34}H_{64}AlN_2NdSi_2$
M_r [g mol^{-1}]	1554.73	1616.80	1470.54	722.94	728.27
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$C2/c$	$C2/c$
a [Å]	11.7297(6)	11.4783(2)	14.4680(3)	18.056(1)	17.9545(6)
b [Å]	25.970(2)	26.0417(6)	25.6711(4)	17.873(1)	17.8184(6)
c [Å]	26.348(1)	26.4880(5)	19.6447(4)	12.2151(8)	12.2373(4)
β [°]	97.592(4)	97.637(1)	106.960(2)	104.133(1)	103.82
V [Å^3]	7955.7(8)	7847.4(3)	6978.9(2)	3822.6(4)	3801.5(2)
Z	4	4	4	4	4
F(000)	3120	3304	3020	1520	1532
T [K]	173(2)	153(2)	173(2)	103(2)	123(2)
ρ_{calcd} [g cm^3]	1.262	1.368	1.400	1.256	1.272
μ [mm^{-1}]	2.012	3.081	2.292	1.226	1.475
R_1 (obsd.)[a]	0.0681	0.0893	0.0570	0.0427	0.0141
wR_2 (all)[b]	0.1358	0.1360	0.0951	0.1107	0.0391
S[c]	1.035	1.417	1.317	1.193	1.113

[a] $R^1 = \sum(|F_0| - |F_c|)/\sum|F_0|, F_0 > 4\sigma(F_0)$. [b] $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2]/[w(F_0^2)^2]\}^{1/2}$. [c] $S = \left[\sum w(F_0^2 - F_c^2)^2/(n_0 - n_p)\right]^{1/2}$.

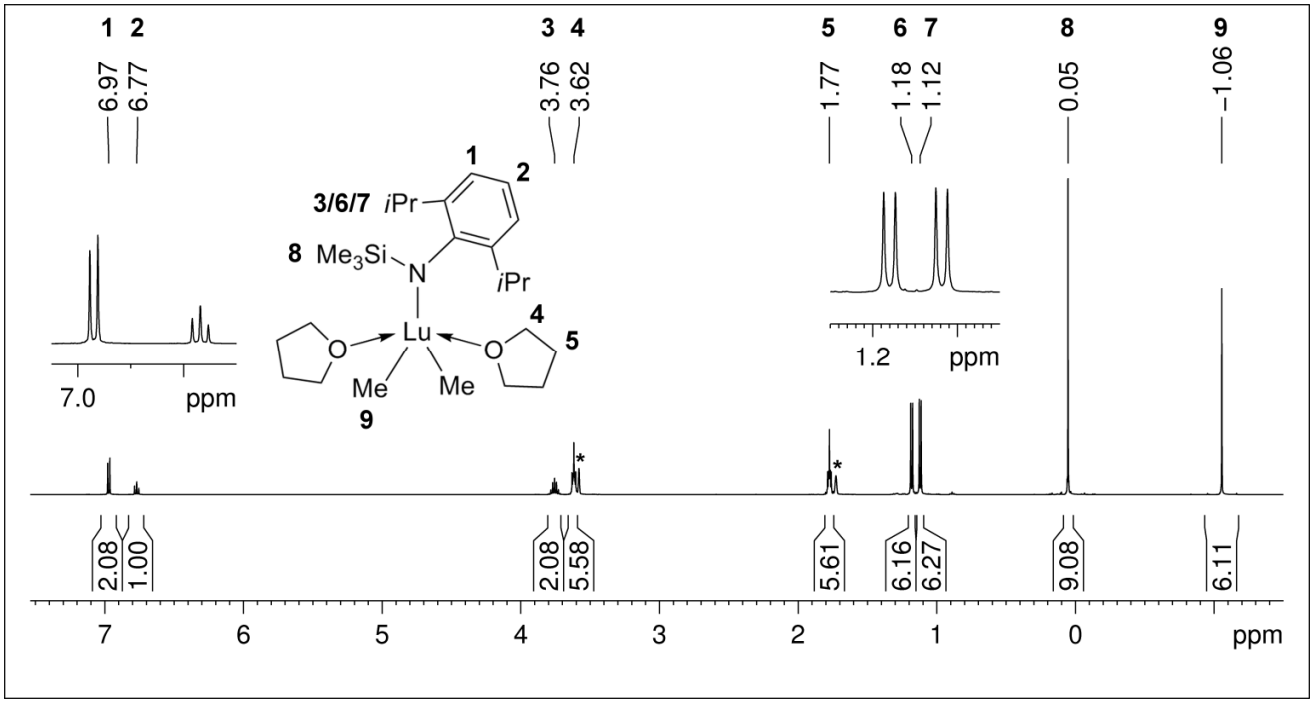

Figure S8. ^{1}H NMR spectrum (500 MHz) of **4**-Lu in thf-d_8 at 26 °C. The solvent residual peak is marked with an asterisk.

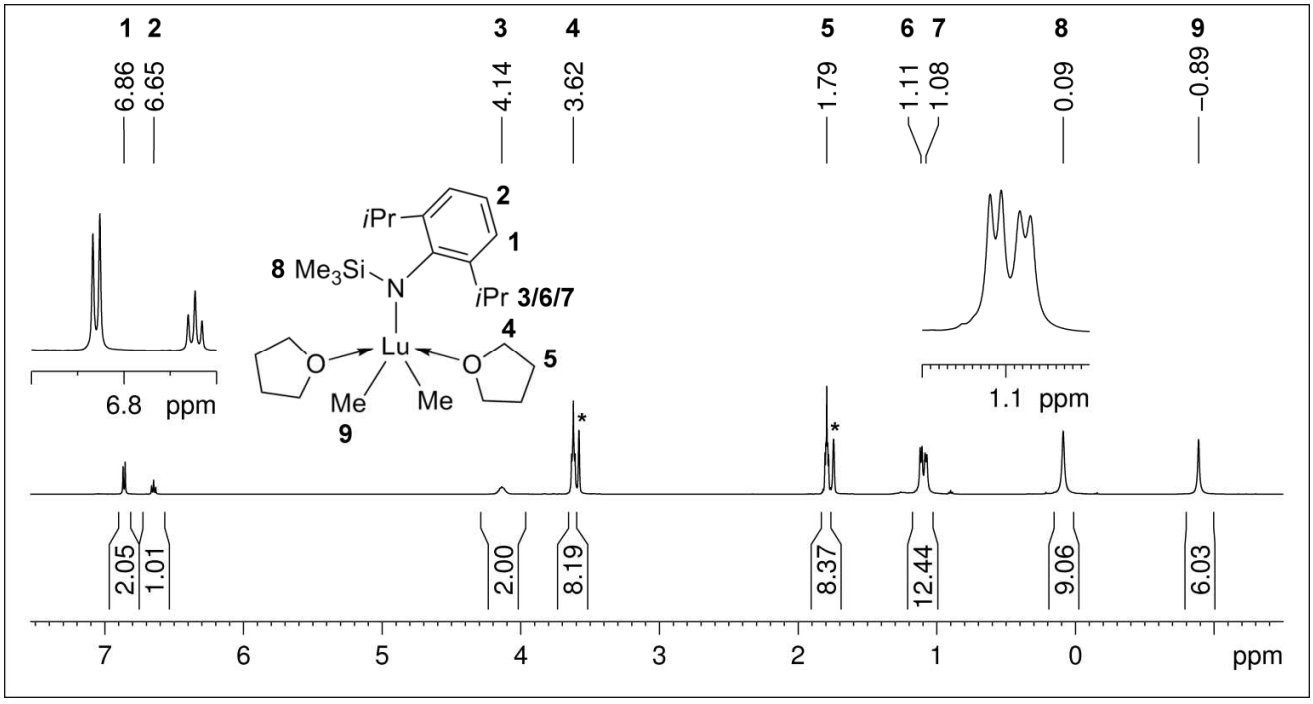

Figure S9. ^{1}H NMR spectrum (500 MHz) of **4**-Lu in thf-d_8 at −90 °C. The solvent residual peak is marked with an asterisk.

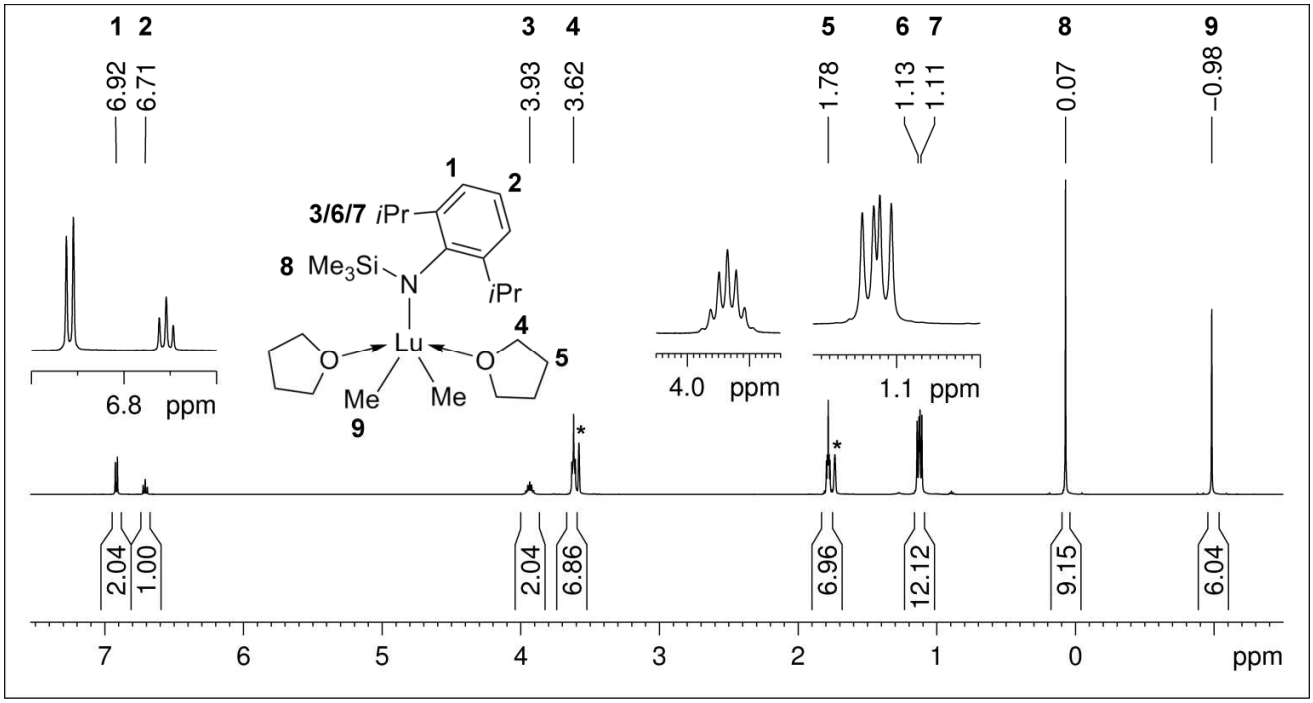

Figure S10. ^{1}H NMR spectrum (500 MHz) of **4**-Lu in thf-d_8 at −35 °C. The solvent residual peak is marked with an asterisk.

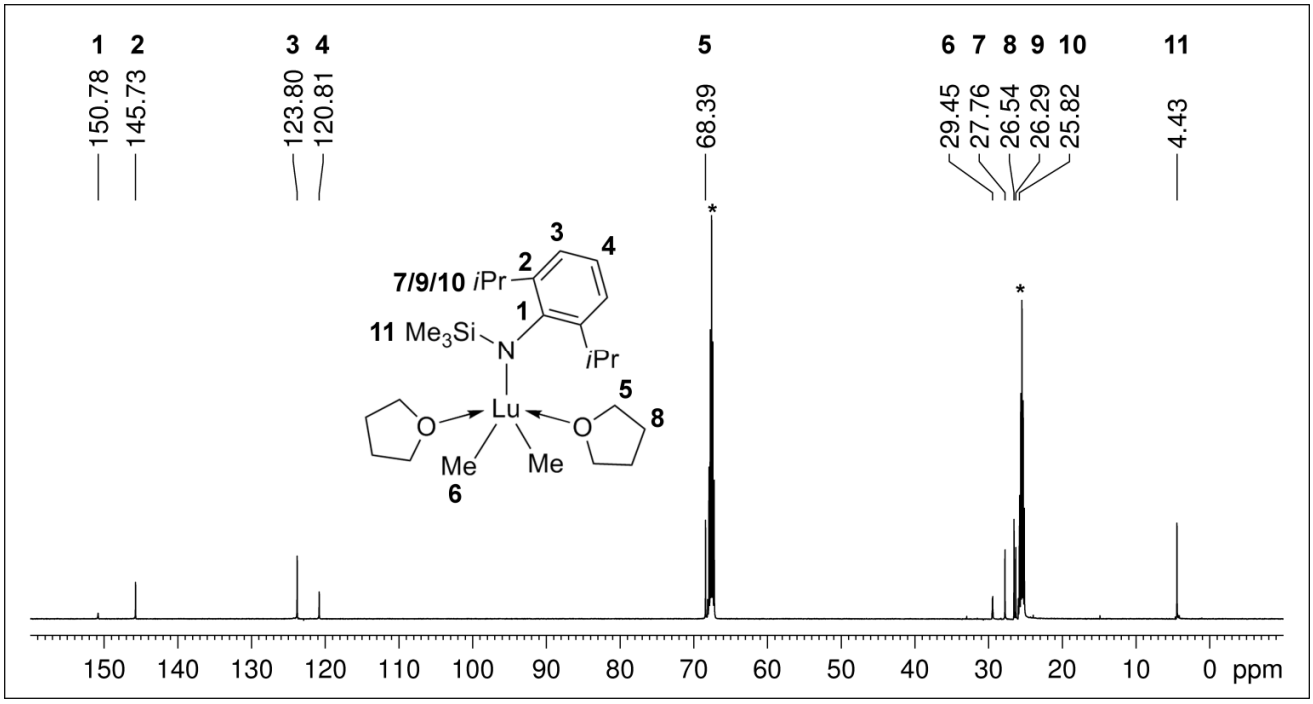

Figure S11. ^{13}C{^{1}H} NMR spectrum (126 MHz) of **4**-Lu obtained in thf-d_8 at −35 °C. The solvent residual peak is marked with an asterisk.

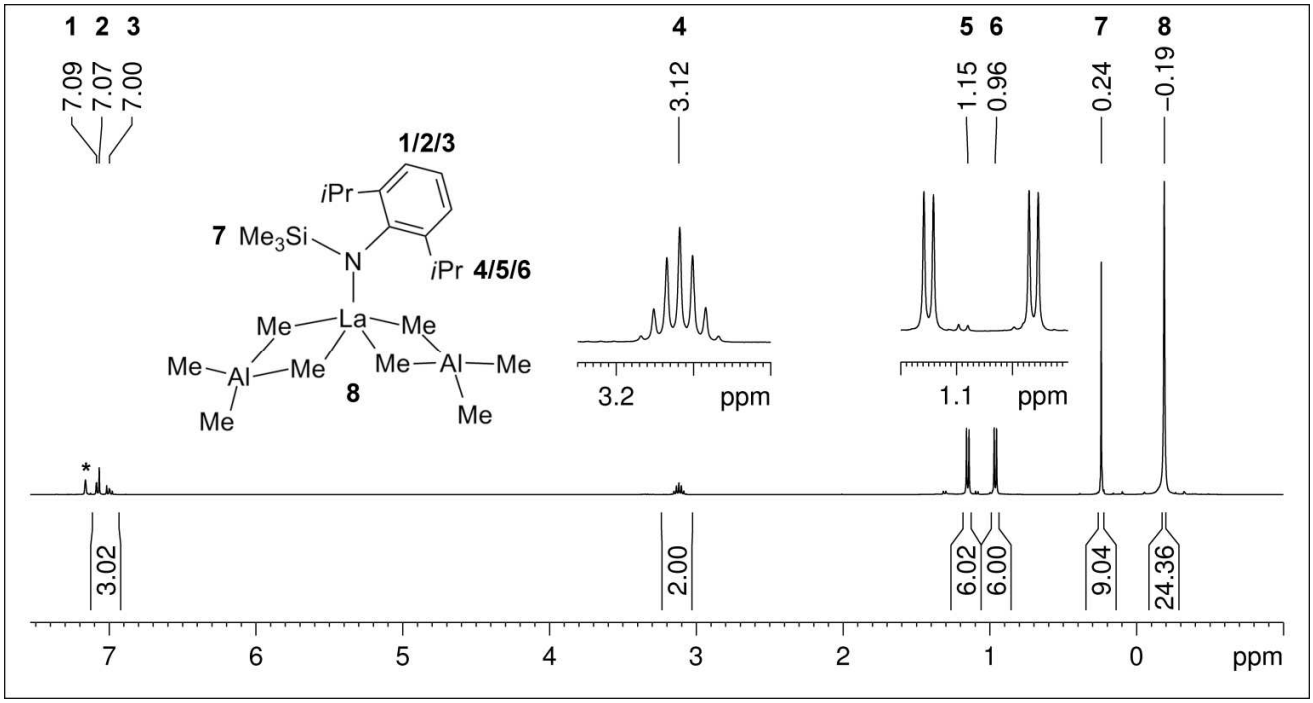

Figure S12. ^{1}H NMR spectrum (400 MHz) of **5**-La in C_6D_6 at 26 °C. The solvent residual peak is marked with an asterisk.

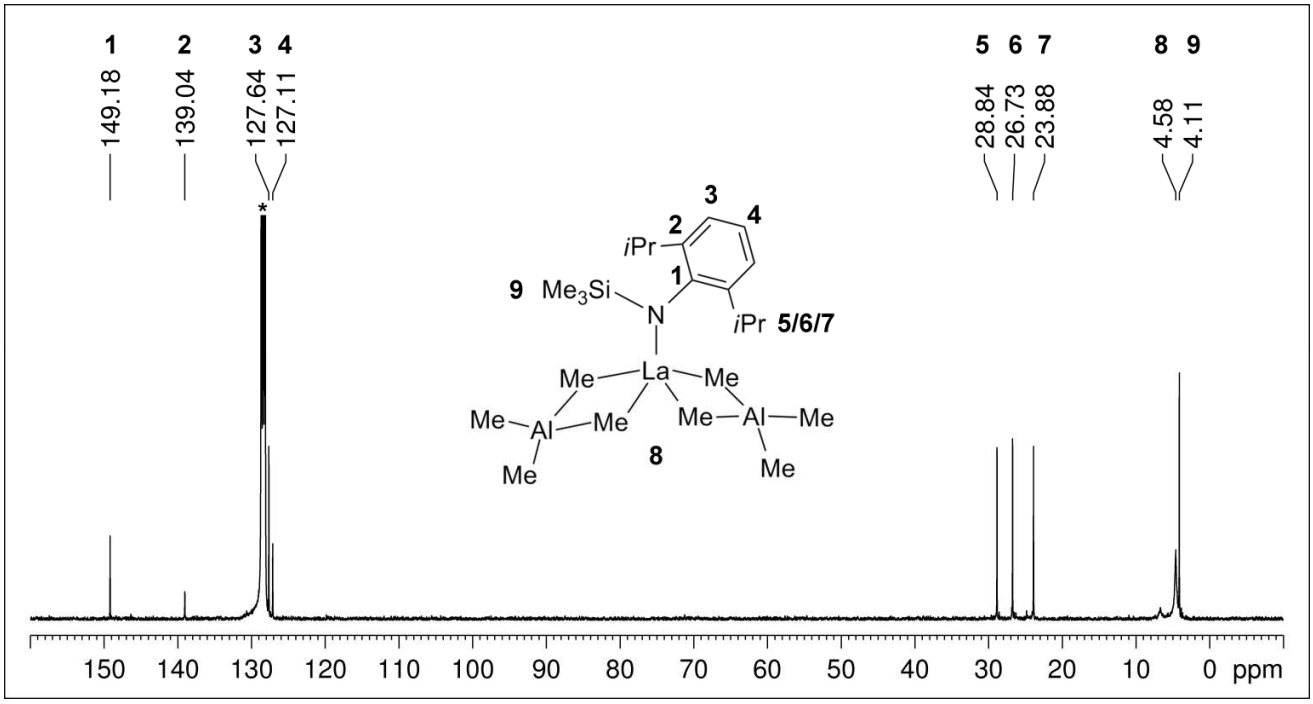

Figure S13. ^{13}C{^{1}H} NMR spectrum (101 MHz) of **5**-La in C_6D_6 at 26 °C. The solvent residual peak is marked with an asterisk.

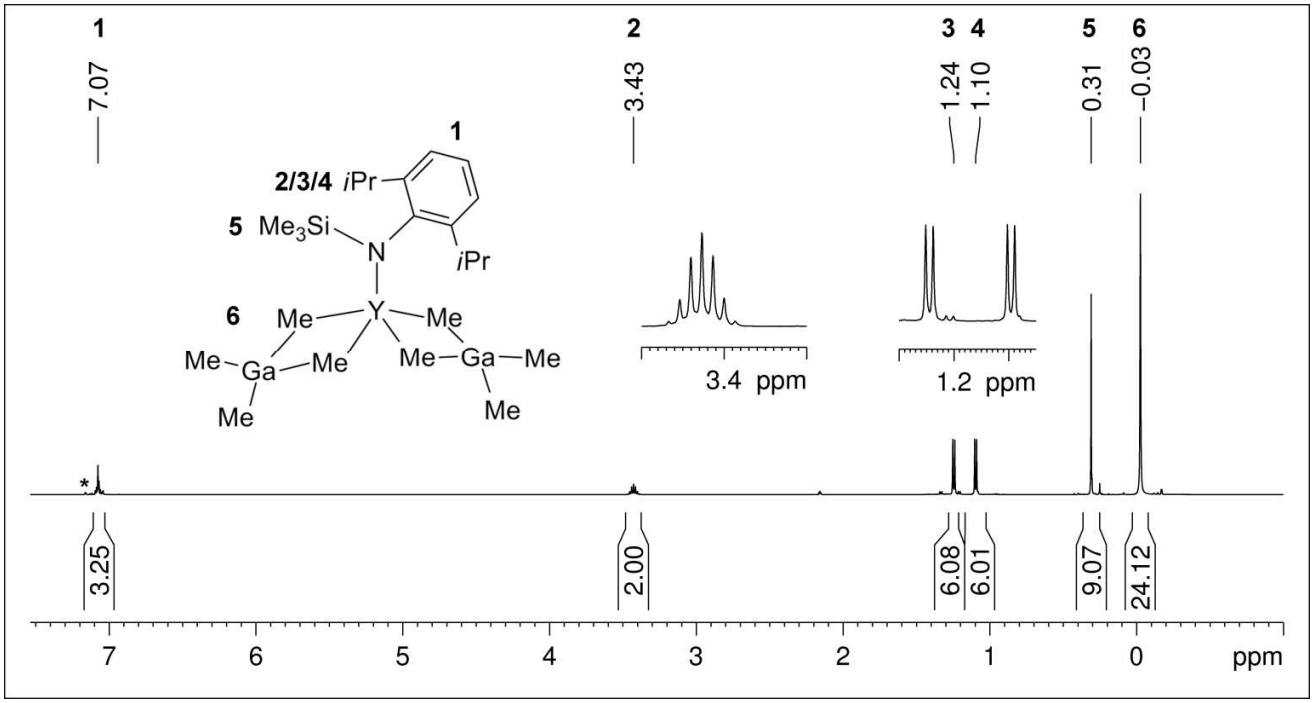

Figure S14. ^{1}H NMR spectrum (500 MHz) of **6**-Y in toluene-d_8 at 26 °C. The solvent residual peak is marked with an asterisk.

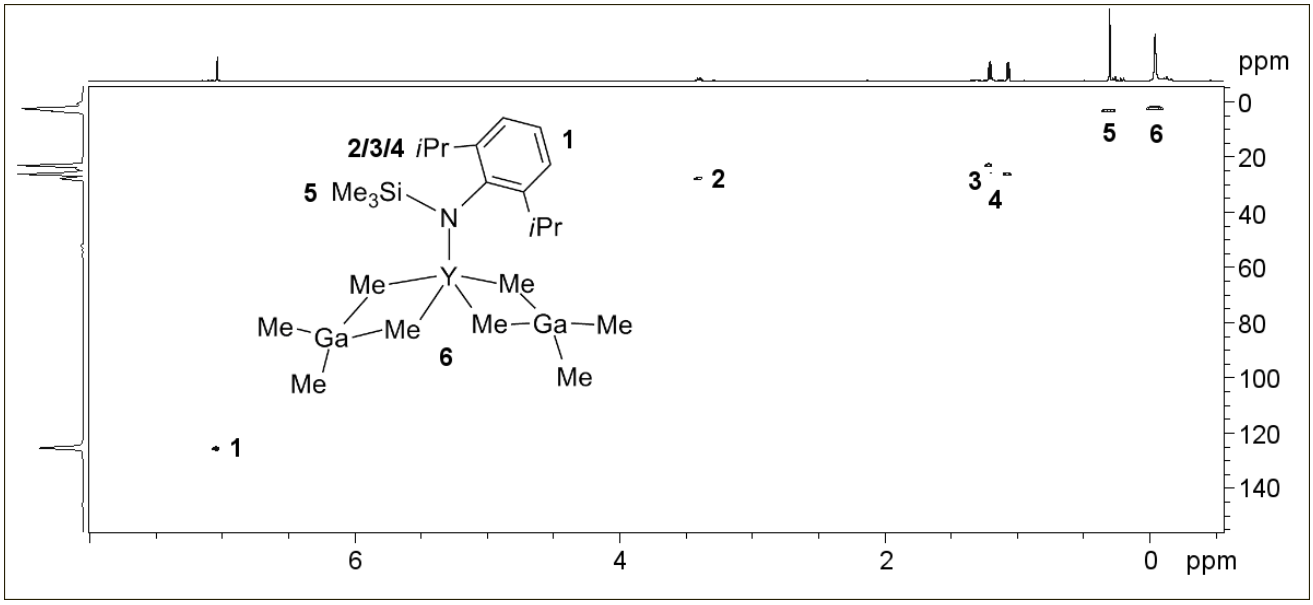

Figure S15. Two-dimensional ^{1}H-^{13}C HSQC NMR spectrum (500 MHz) of **6**-Y in toluene-d_8 at 26 °C.

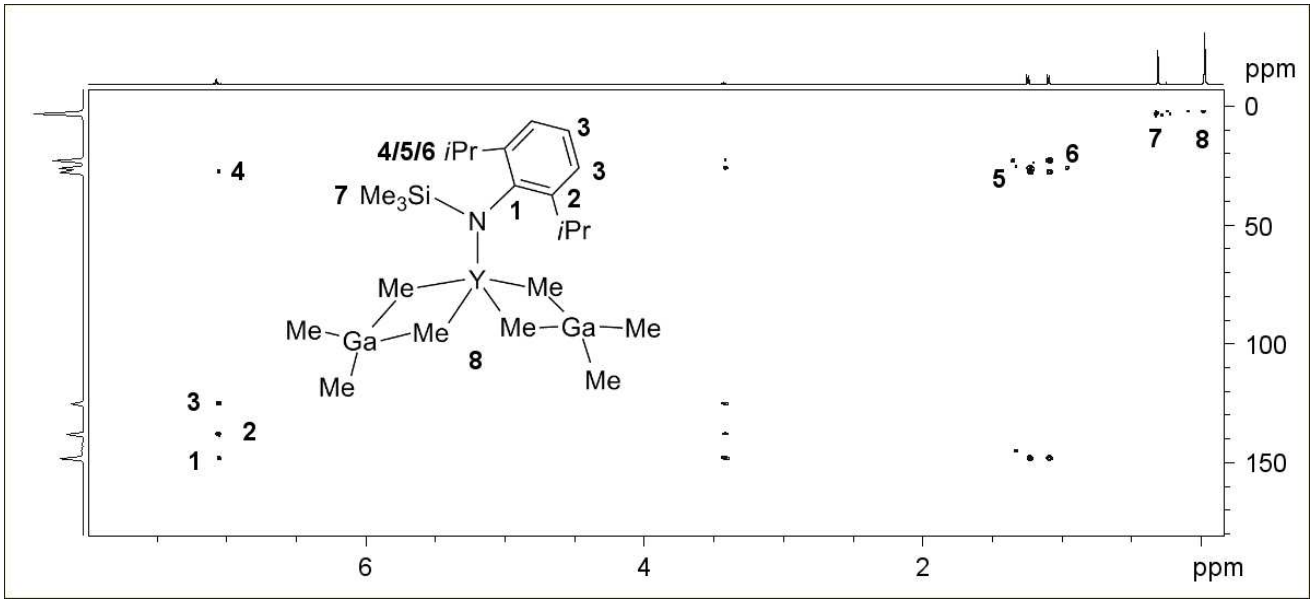

Figure S16. Two-dimensional $^{1}H^{13}C$ HMBC NMR spectrum (500 MHz) of **6**-Y in toluene-d_8 at 26 °C.

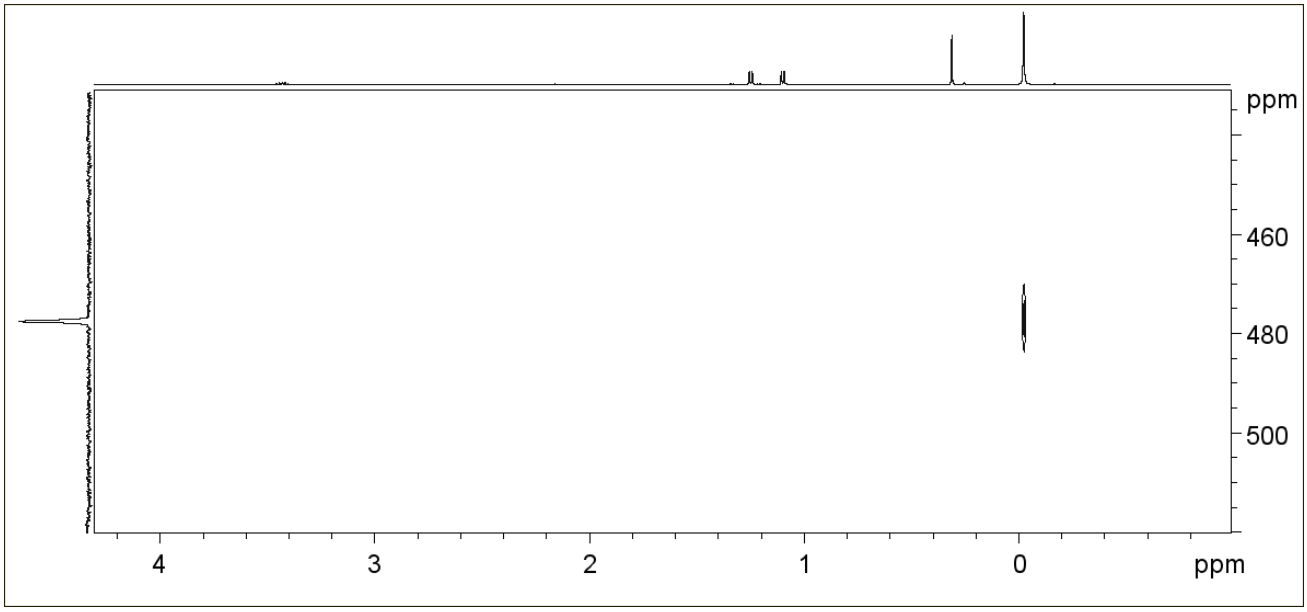

Figure S17. Two-dimensional $^{1}H^{89}Y$ HSQC NMR spectrum (500 MHz) of **6**-Y in toluene-d_8 at 26 °C. (1D ^{89}Y NMR spectrum (25 MHz) on the left edge of the contour plot, 1D ^{1}H NMR spectrum of the aliphatic region shown on the top).

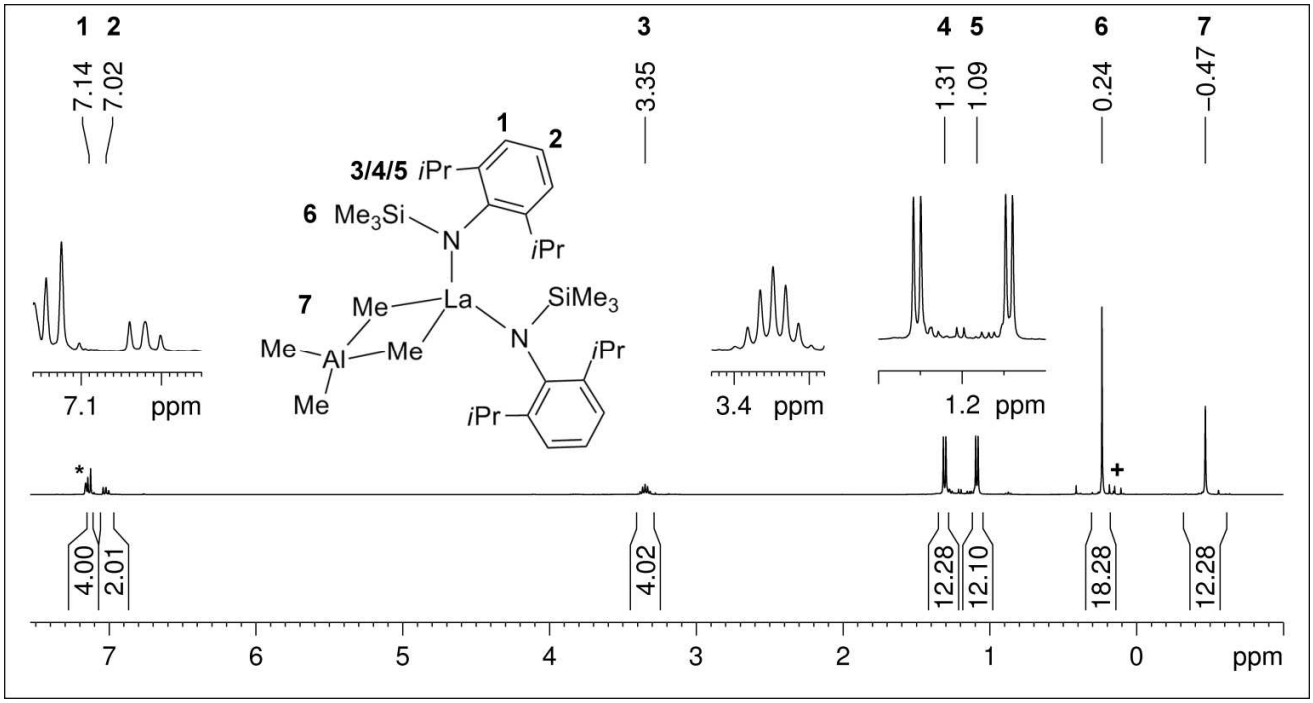

Figure S18. ^{1}H NMR spectrum (400 MHz) of **9**-La in C_6D_6 at 26 °C. The solvent residual peak is marked with an asterisk (+ minor impurities).

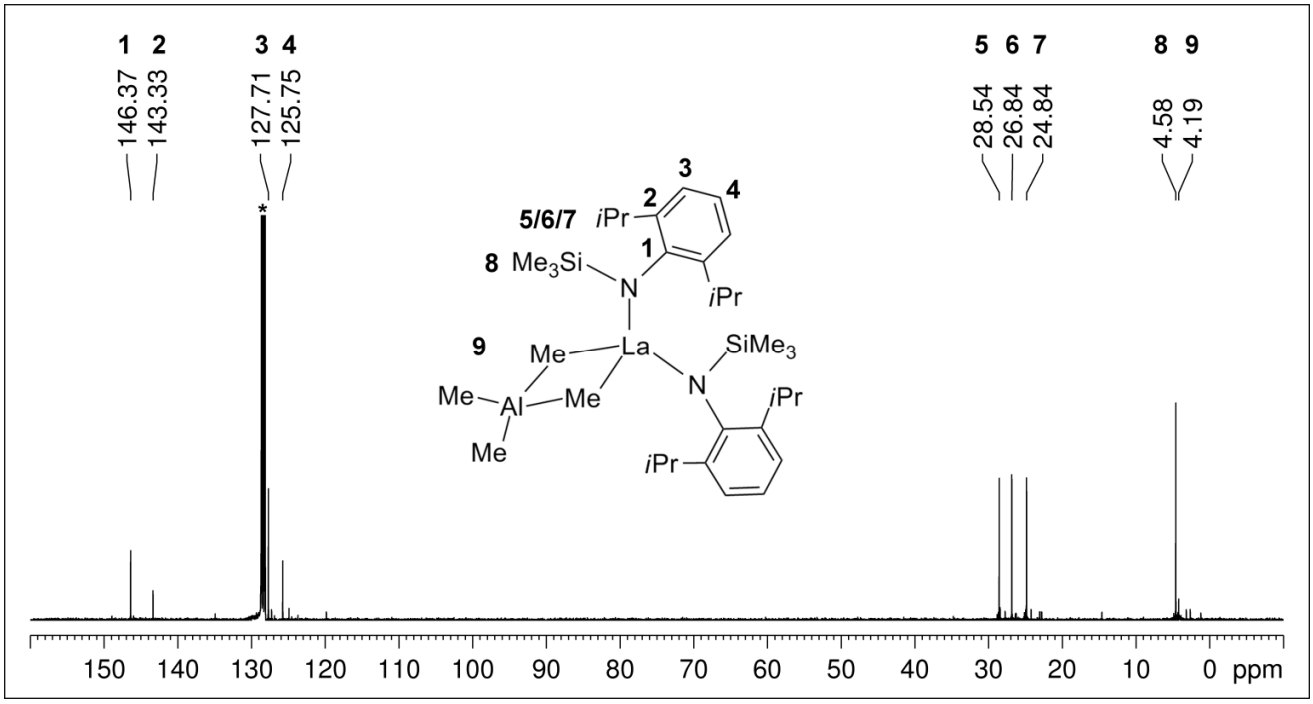

Figure S19. ^{13}C{^{1}H} NMR spectrum (101 MHz) of **9**-La in C_6D_6 at 26 °C. The solvent residual peak is marked with an asterisk.

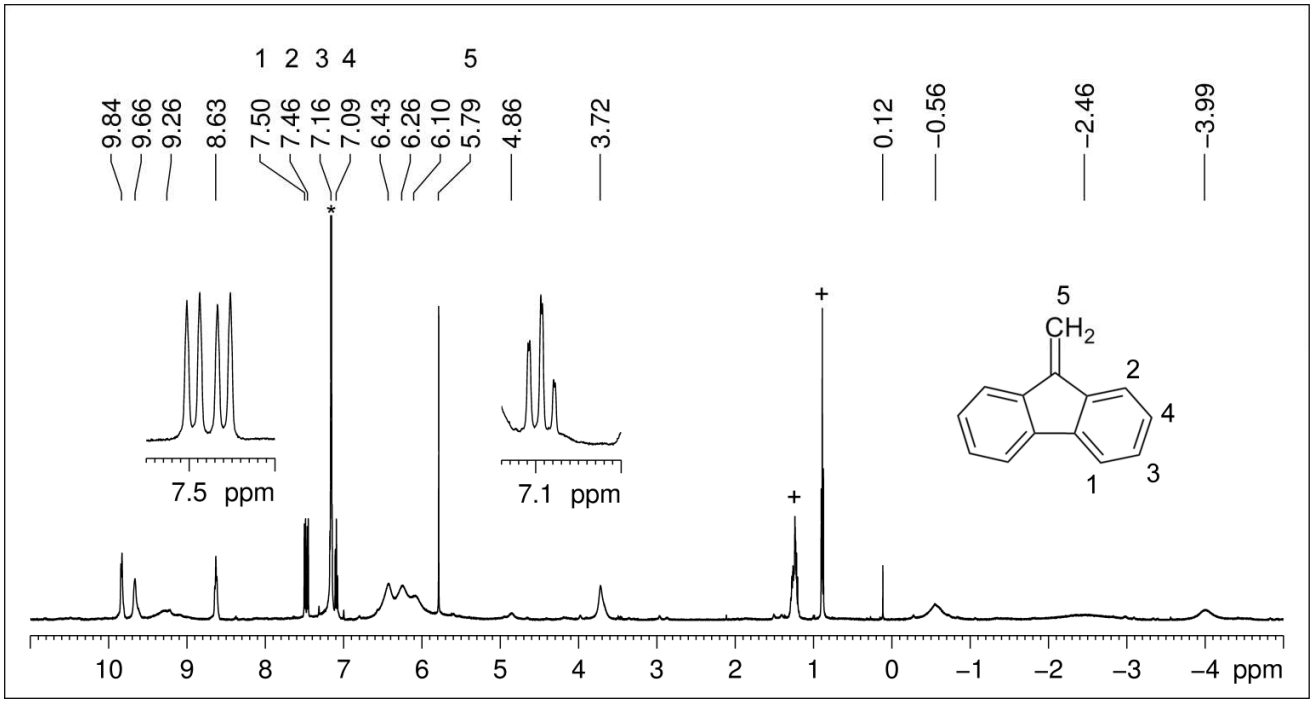

Figure S20. Insitu ^{1}H NMR spectrum (500 MHz) of **7**-Nd and 5 equiv. 9-fluorenone in C_6D_6 at 26 °C. The solvent residual peak is marked with an asterisk (+ *n*-hexane).

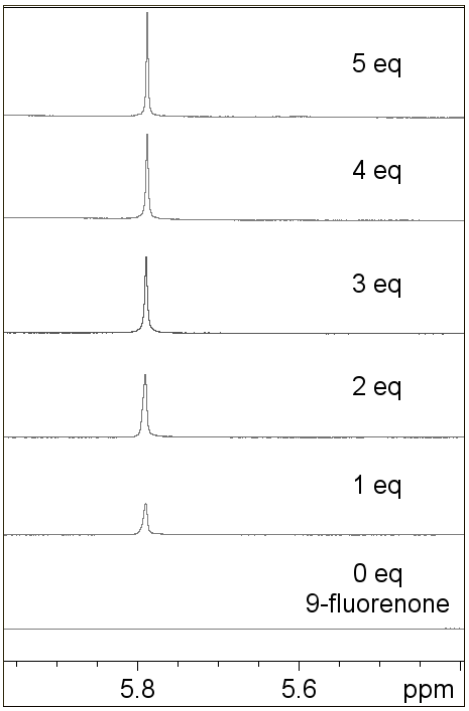

Figure S21. ^{1}H NMR spectra (500.13 MHz) of the terminal alkene resonances of 9-methylidene-fluorene after adding 0-5 equivalents 9-fluorenone to **7**-Nd in C_6D_6.