Dihydrogen activation by intermolecular rare-earth aryloxide/N-heterocyclic carbene Lewis pairs

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Supporting Information

General Procedures: All experiments were carried out under a dry Argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (including deuterated solvents used for NMR) were dried and distilled prior to use. NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts were reported as δ units with reference to the residual solvent resonance or an external standard. The assignments of NMR data were supported by 1D and 2D NMR experiments. Coupling constants J are given in Hz. Elemental analysis data was recorded on a Carlo-Erba EA-1110 instrument. Fourier transform infrared spectroscopy was measured with a Bruker VERTEX70. 1,3-Bis-(*t*-butyl)imidazolin-2-ylidene,[1] 1,3-bis-(2,4,6-trimethylphenyl)imidazolin-2-ylidene,[2] 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-ylidene[2] and $RE(OAr)_3$ (RE = La, Sm, Y; Ar = 2,6-^{t}Bu$_2$C$_6$H$_3$)[3] were synthesized by following the literature procedures.

References

[1] Arentsen, K.; Caddick, S.; Cloke, F. G. N. *Tetrahedron* **2005**, *61*, 9710-9715.

[2] Arduengo, A. J.; Krafczky, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523-14534.

[3] Lappert, M. F.; Singh, A.; Smith, R. G. *Inorg. Synth.* **1990**, *27*, 164-168.

General procedure for the stoichiometric reaction of RE(OAr)$_3$ (1) with NHC (2)

In a glove box, an oven-dried J-Young NMR tube was charged with RE(OAr)$_3$ (0.01 mmol), N-heterocyclic carbene (0.01 mmol) and 0.5 mL of C_6D_6. The tube was removed from the glove box and was gently shaken for a few minutes. The reaction was monitored by NMR spectroscopy after 1 h at room temperature.

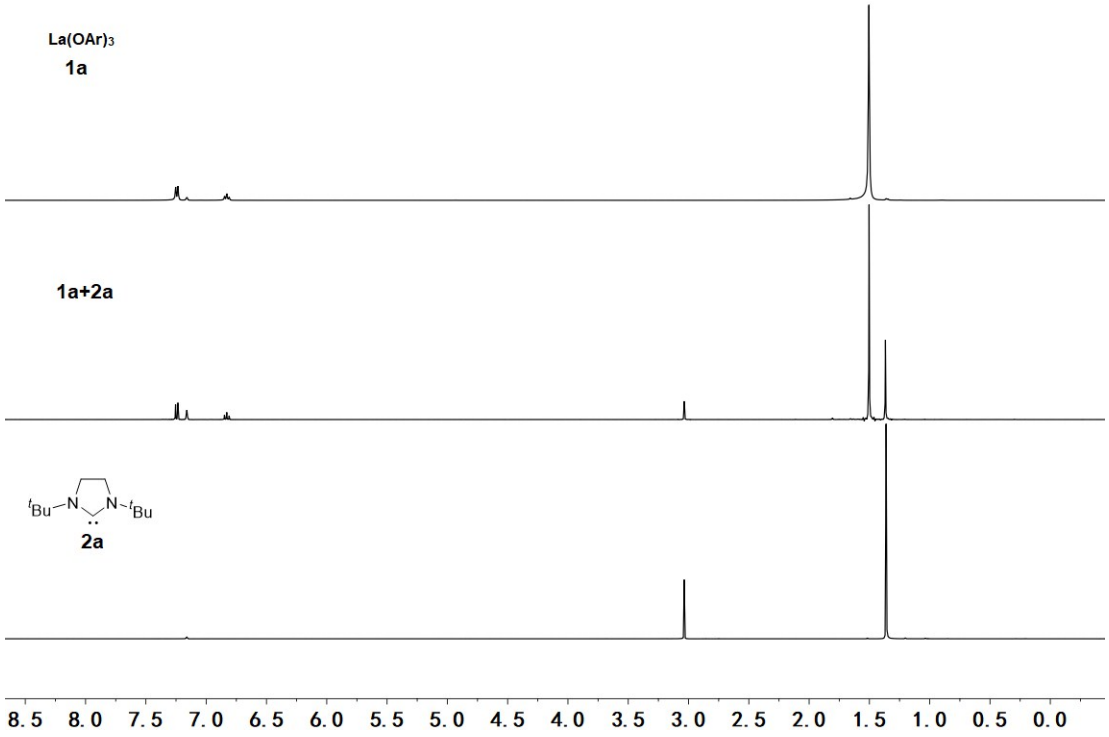


Fig. S1. ^{1}H NMR (400 MHz, C_6D_6, 298 K) of the reaction of La(OAr)$_3$ **1a** with NHC **2a** (middle). For a comparison, the **^{1}H NMR** spectra of La(OAr)$_3$ **1a** (top) and NHC **2a** (bottom) are also depicted.

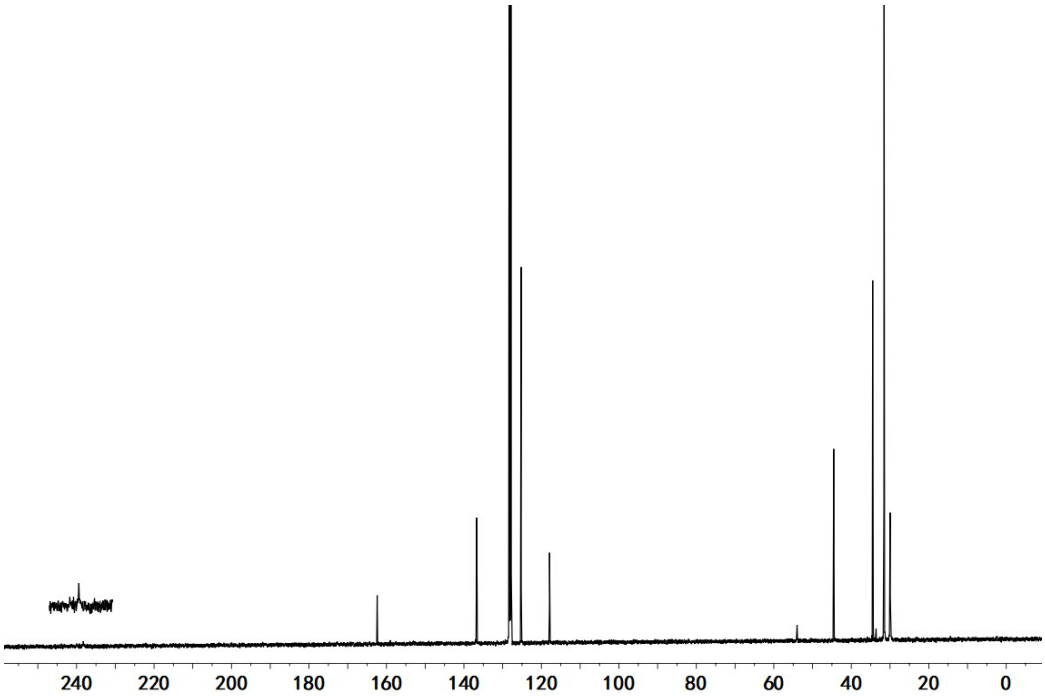


Fig. S2. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) of the reaction of $La(OAr)_3$ **1a** with NHC **2a**.

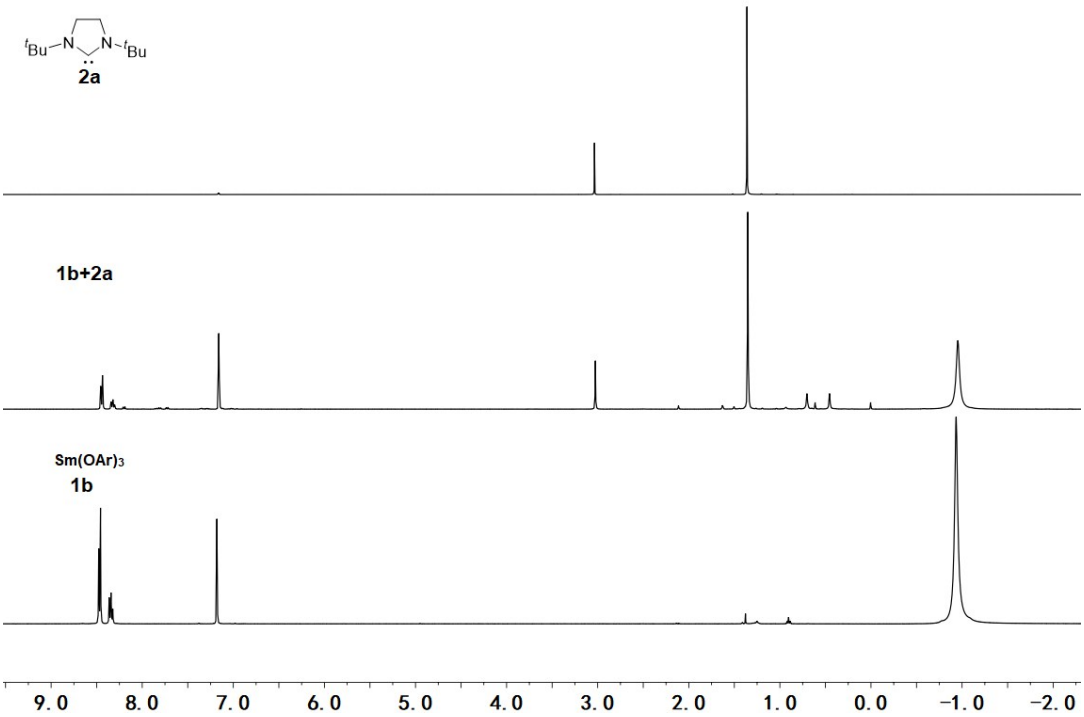


Fig. S3. ^1H NMR (400 MHz, C_6D_6, 298 K) of the reaction of $Sm(OAr)_3$ **1b** with NHC **2a** (middle). For a comparison, the **^1H NMR** spectra of $Sm(OAr)_3$ **1b** (bottom) and NHC **2a** (top) are also depicted.

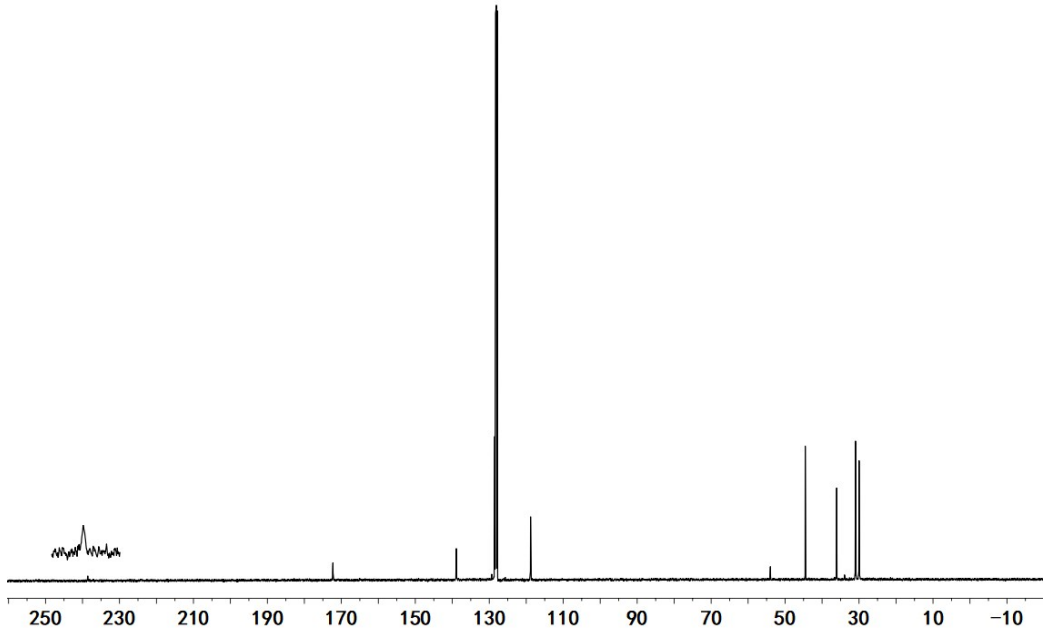


Fig. S4. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) of the reaction of $Sm(OAr)_3$ **1b** with NHC **2a**.

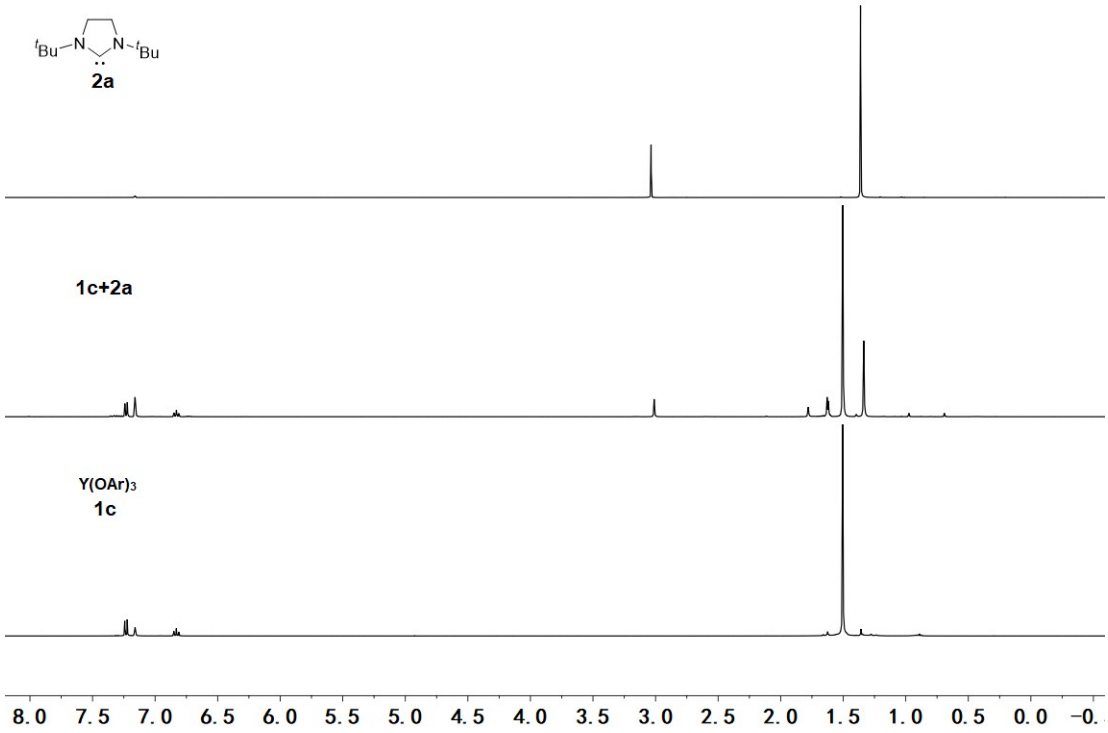


Fig. S5. ^1H NMR (400 MHz, C_6D_6, 298 K) of the reaction of $Y(OAr)_3$ **1c** with NHC **2a** (middle). For a comparison, the **^1H NMR** spectra of $Y(OAr)_3$ **1c** (bottom) and NHC **2a** (top) are also depicted.

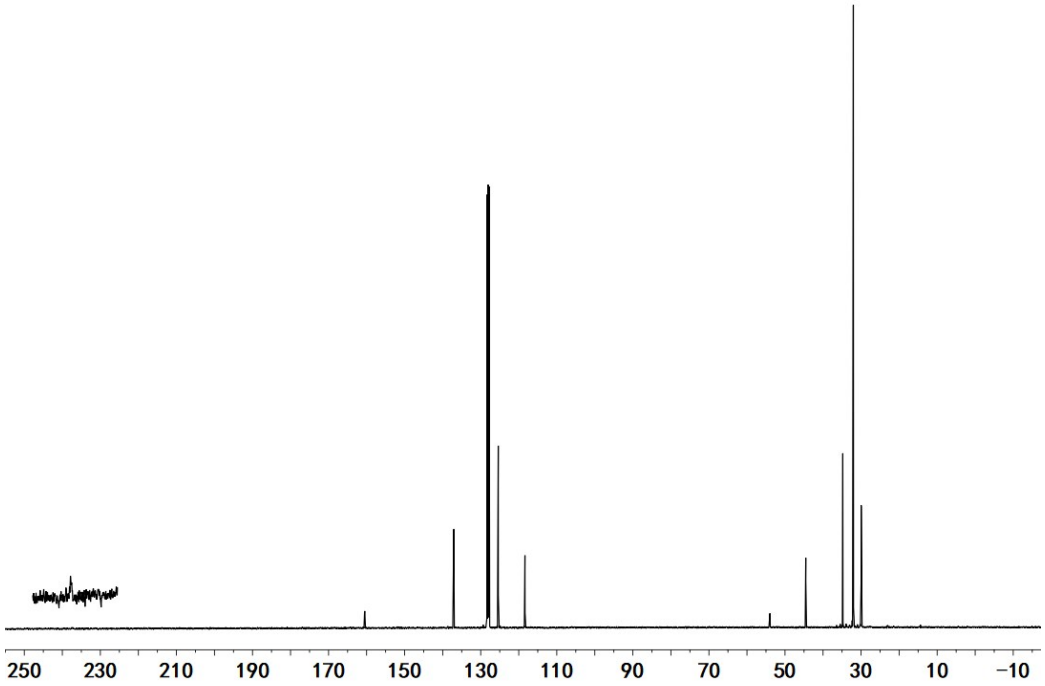


Fig. S6. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K) of the reaction of $Y(OAr)_3$ **1c** with NHC **2a**.

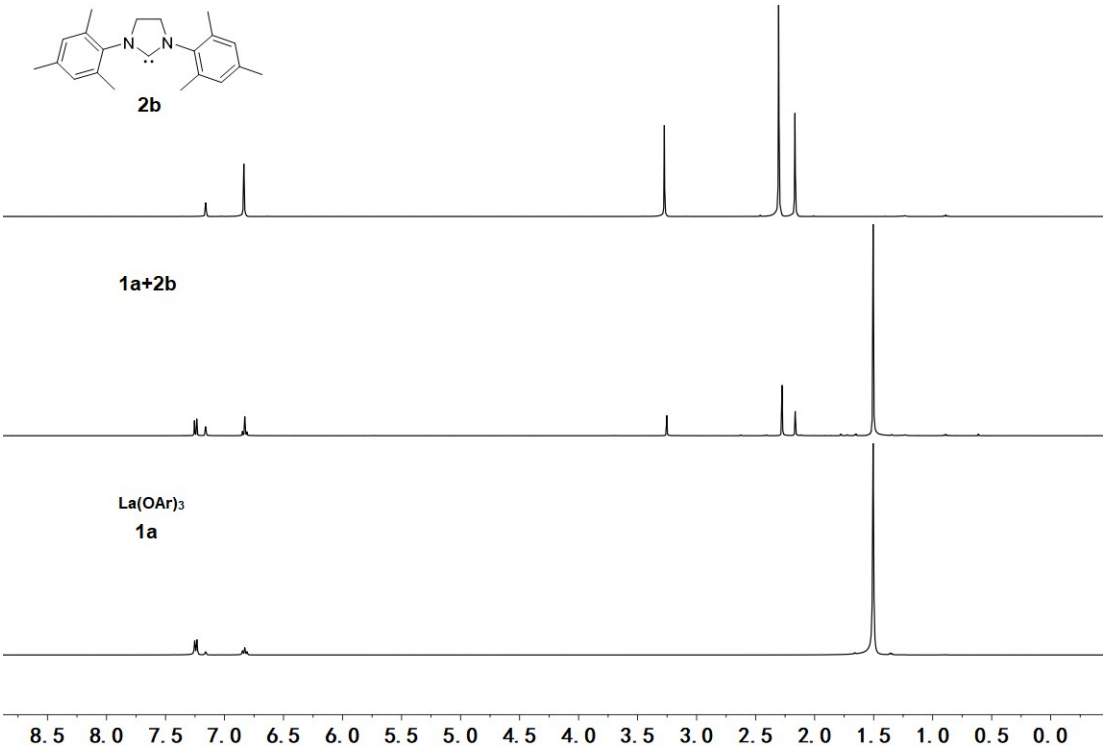


Fig. S7. ^{1}H NMR (400 MHz, C_6D_6, 298 K) of the reaction of $La(OAr)_3$ **1a** with NHC **2b** (middle). For a comparison, the **^{1}H NMR** spectra of $La(OAr)_3$ **1a** (bottom) and NHC **2b** (top) are also depicted.

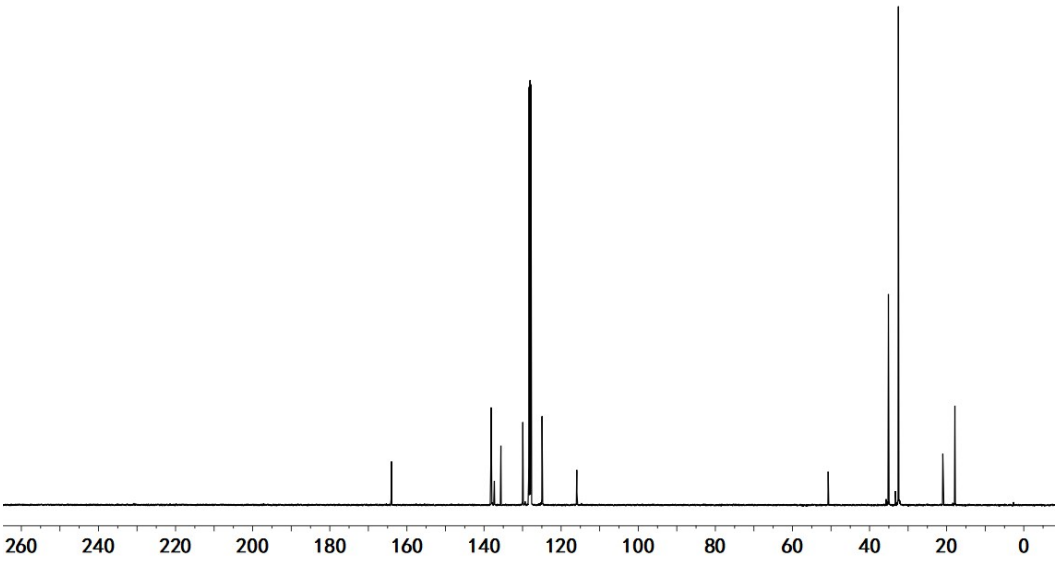


Fig. S8. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) of the reaction of $La(OAr)_3$ **1a** with NHC **2b**.

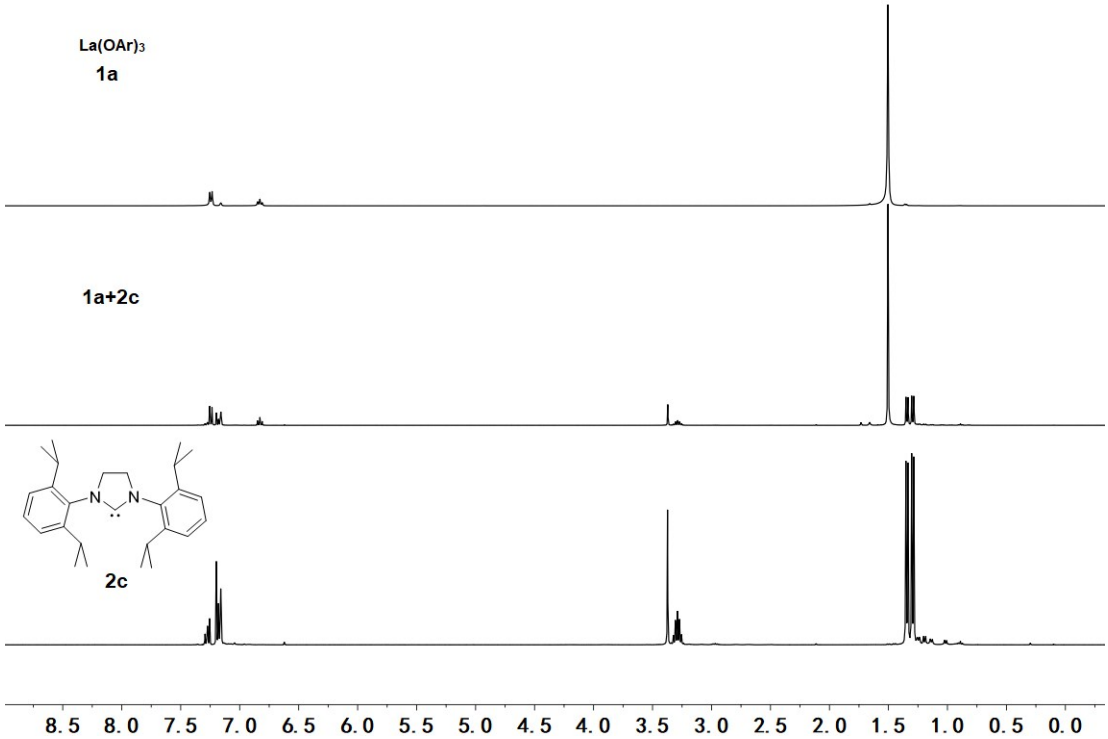


Fig. S9. ^1H NMR (400 MHz, C_6D_6, 298 K) of the reaction of $La(OAr)_3$ **1a** with NHC **2c** (middle). For a comparison, the **^1H NMR** spectra of $La(OAr)_3$ **1a** (top) and NHC **2c** (bottom) are also depicted.

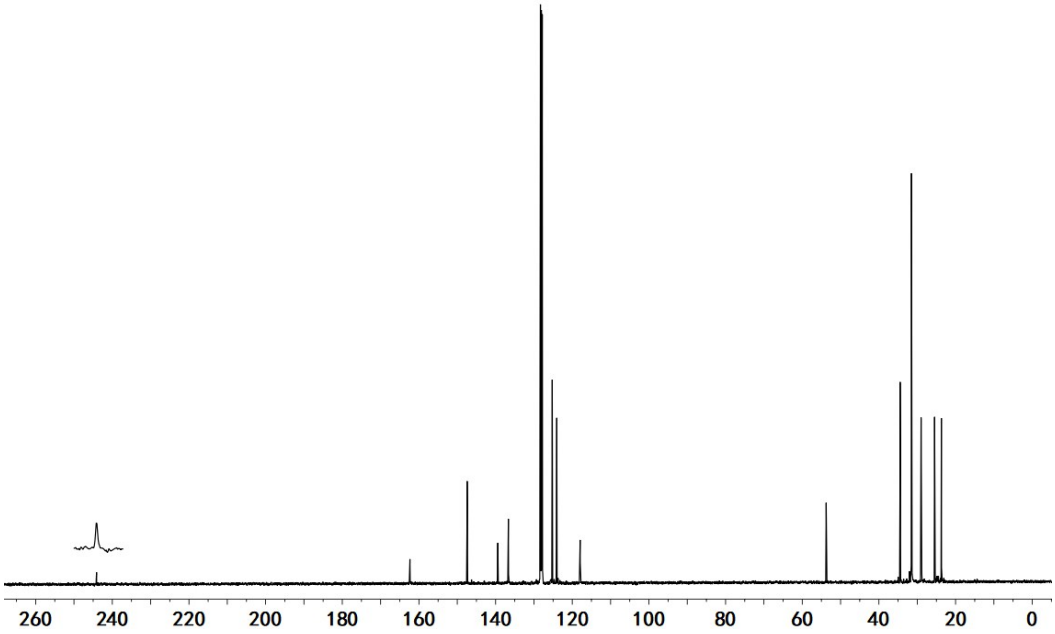


Fig. S10. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) of the reaction of $La(OAr)_3$ **1a** with NHC **2c**.

General procedure for H_2 activation by $RE(OAr)_3$/NHC Lewis pair

In a glove box, an oven-dried J-Young NMR tube was charged with $RE(OAr)_3$ (0.01 mmol), N-heterocyclic carbene (0.01 mmol) and 0.5 mL of C_6D_6. The tube was sealed and removed from the glove box. The mixture was degassed by a freeze-pump-thaw cycle and placed under 1 atm H_2 at room temperature. The tube was gently shaken for a few minutes at regular intervals. The reaction was monitored by ^1H NMR spectroscopy.

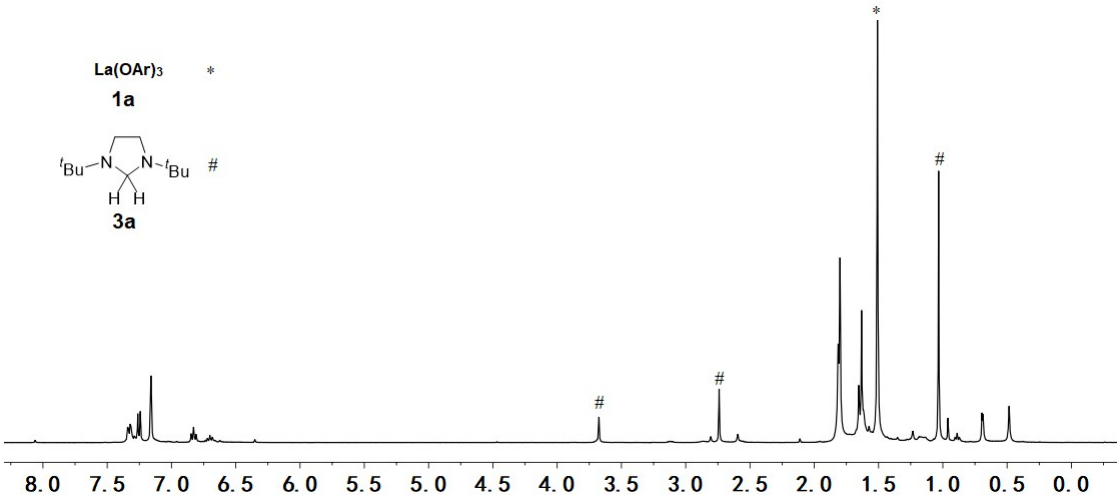


Fig. S11. ^1H NMR (400 MHz, C_6D_6, 298 K) of the H_2 activation reaction by $La(OAr)_3$ **1a** with NHC **2a**.

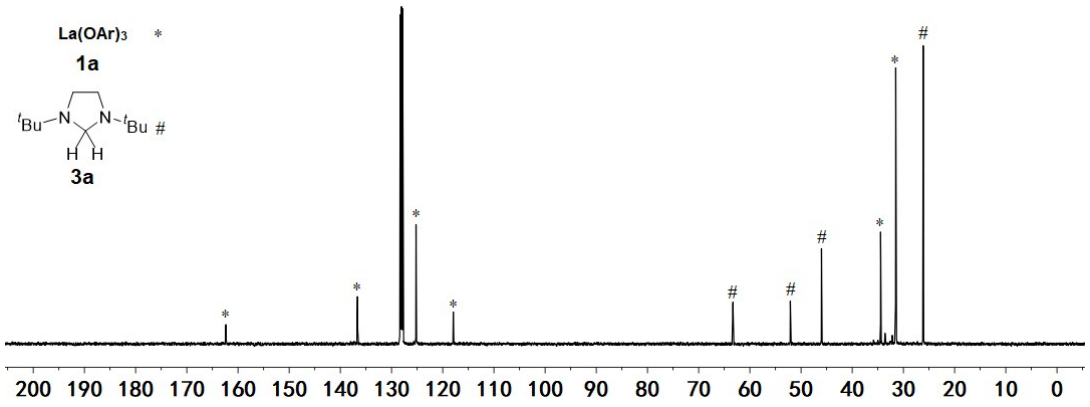


Fig. S12. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) of the H_2 activation reaction by $La(OAr)_3$ **1a** with NHC **2a**.

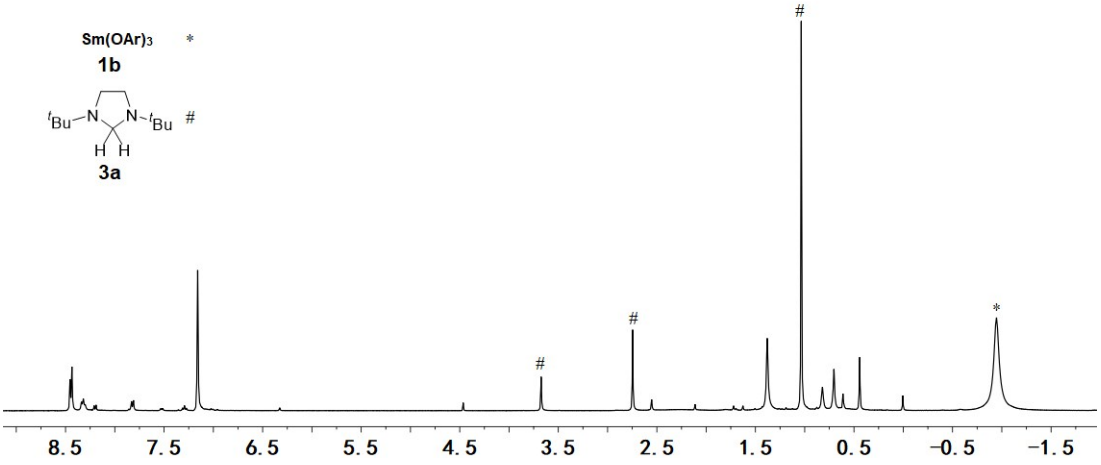


Fig. S13. ^{1}H NMR (400 MHz, C_6D_6, 298 K) of the H_2 activation reaction by $Sm(OAr)_3$ **1b** with NHC **2a**.

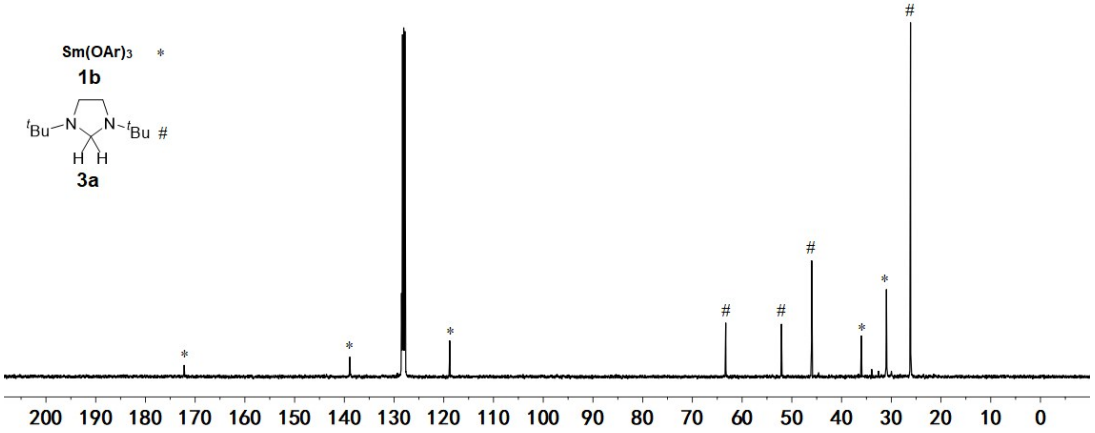


Fig. S14. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K) of the H_2 activation reaction by $Sm(OAr)_3$ **1b** with NHC **2a**.

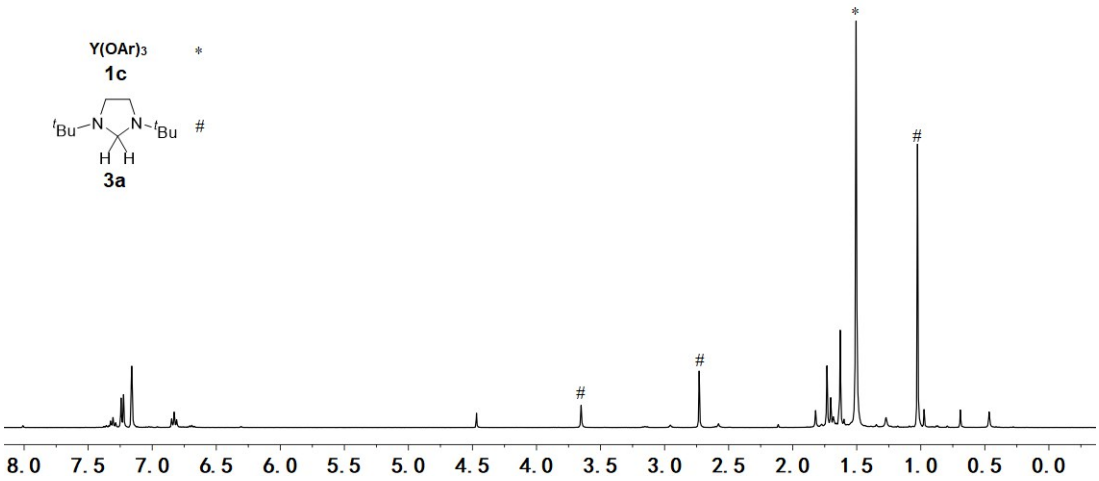


Fig. S15. ^{1}H NMR (400 MHz, C_6D_6, 298 K) of the H_2 activation reaction by $Y(OAr)_3$ **1c** with NHC **2a**.

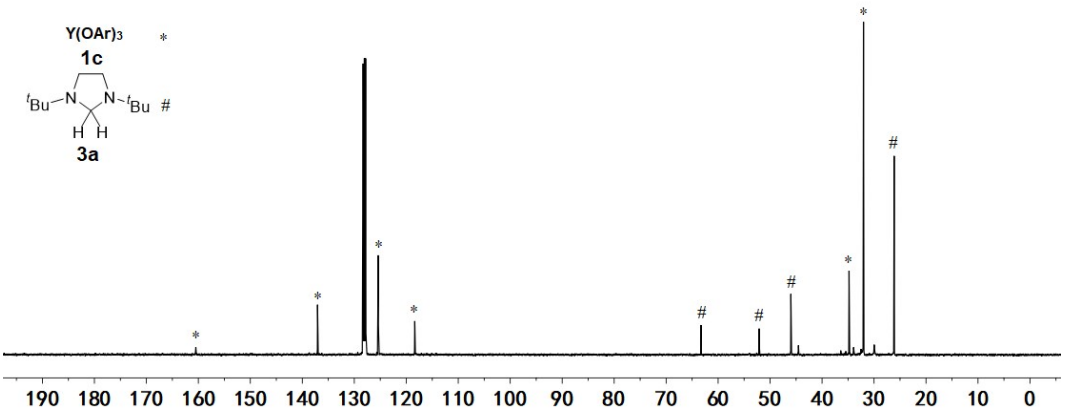


Fig. S16. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) of the H_2 activation reaction by $Y(OAr)_3$ **1c** with NHC **2a**.

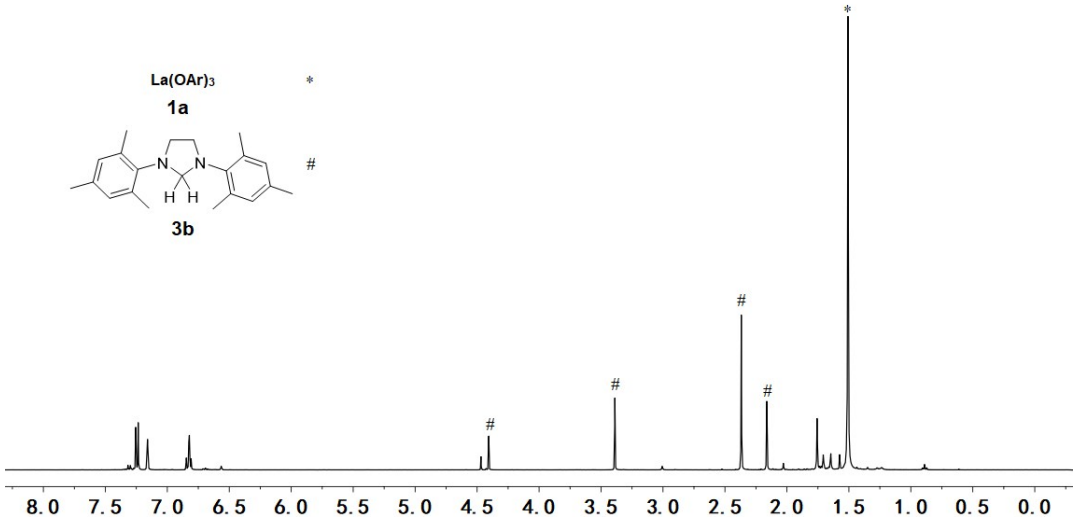


Fig. S17. ^1H NMR (400 MHz, C_6D_6, 298 K) of the H_2 activation reaction by $La(OAr)_3$ **1a** with NHC **2b**.

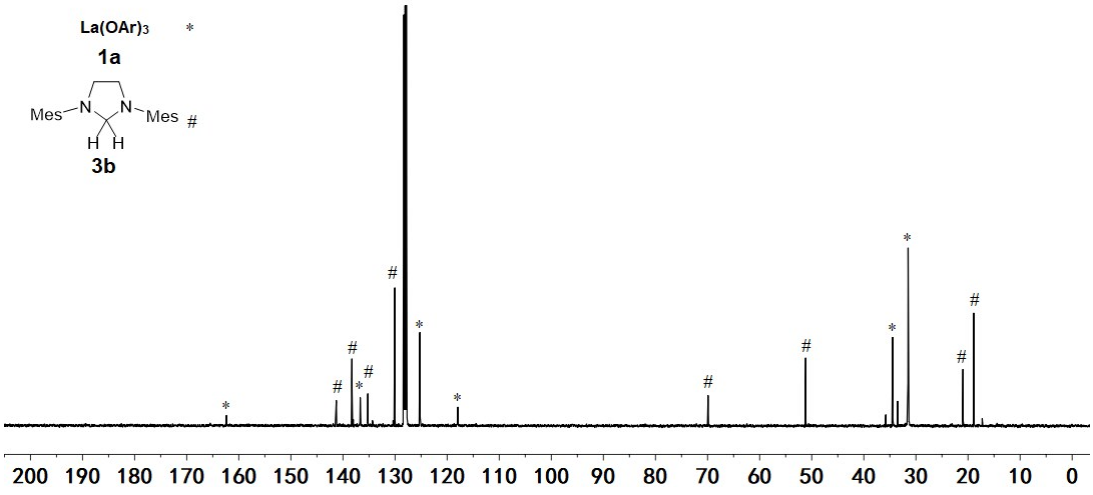


Fig. S18. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) of the H_2 activation reaction by $La(OAr)_3$ **1a** with NHC **2b**.

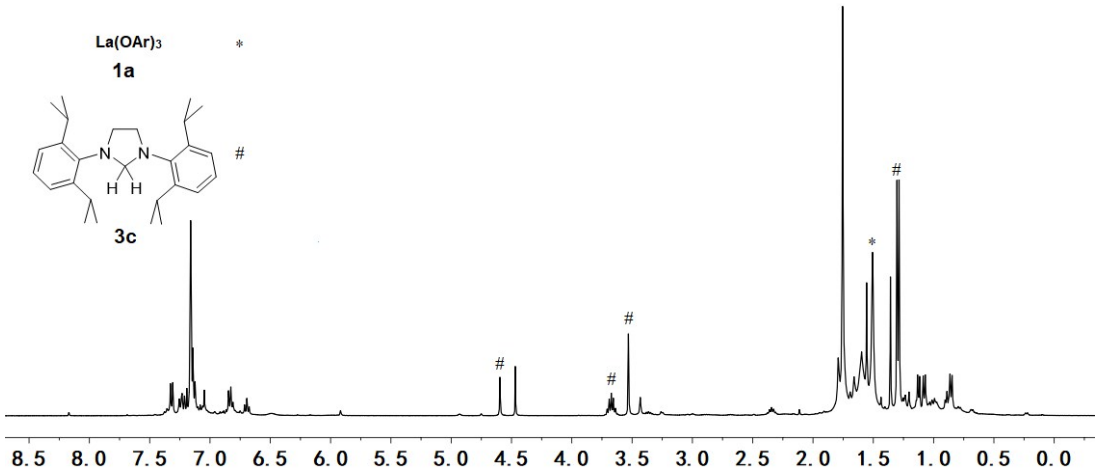


Fig. S19. ^{1}H NMR (400 MHz, C_6D_6, 298 K) of the H_2 activation reaction by $La(OAr)_3$ **1a** with NHC **2c**.

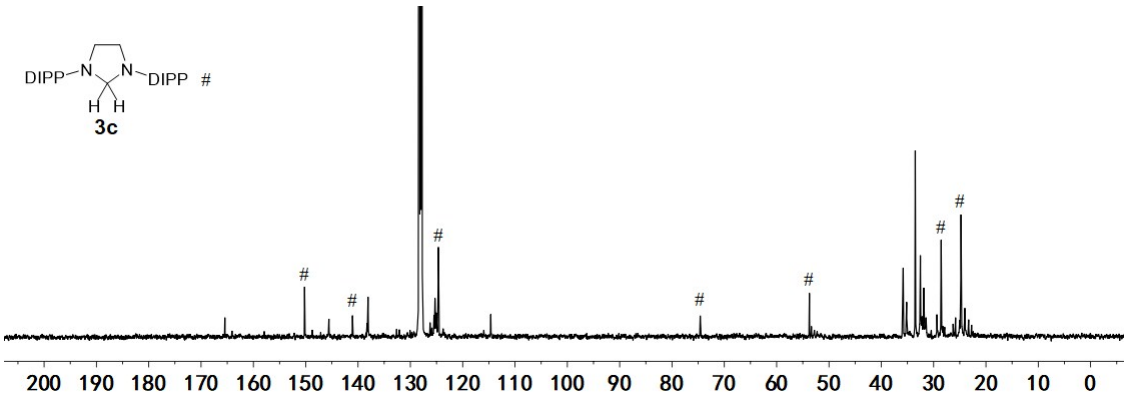


Fig. S20. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K) of the H_2 activation reaction by $La(OAr)_3$ **1a** with NHC **2c**.

The reaction of the La(OAr)$_3$/NHC Lewis pair with D$_2$

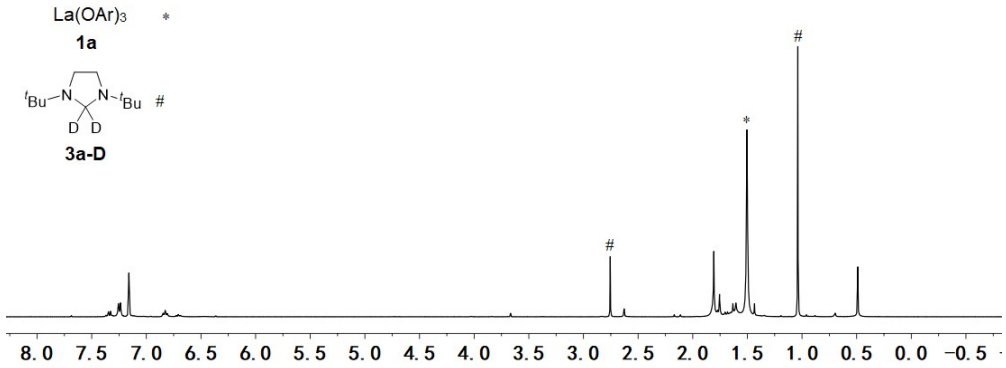
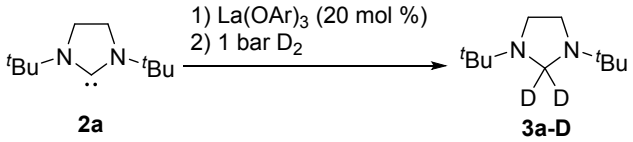


Fig. S21. ^{1}H NMR (400 MHz, C_6D_6, 298 K) of the reaction of the **1a**/**2a** Lewis pair with D_2.

Preparation of complex 3a-D



Scheme S1.

A solution of La(OAr)$_3$ **1a** (83 mg, 0.11 mmol) and NHC **2a** (100 mg, 0.55 mmol) in toluene was stirred for 1 h under 1 bar D_2 at room temperature. The volatiles were removed in vacuo and the residue was extracted by 2 mL of hexane to finally afford the product **3a-D** as colorless oil (86 mg, 84%).

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 2.75 (s, 4H, NCH_2), 1.04 (s, 18H, NC(CH_3)$_3$).

^{2}H NMR (92 MHz, C_6H_6 / C_6D_6 (100:1), 298 K): δ = 3.61 (s, NCD_2N).

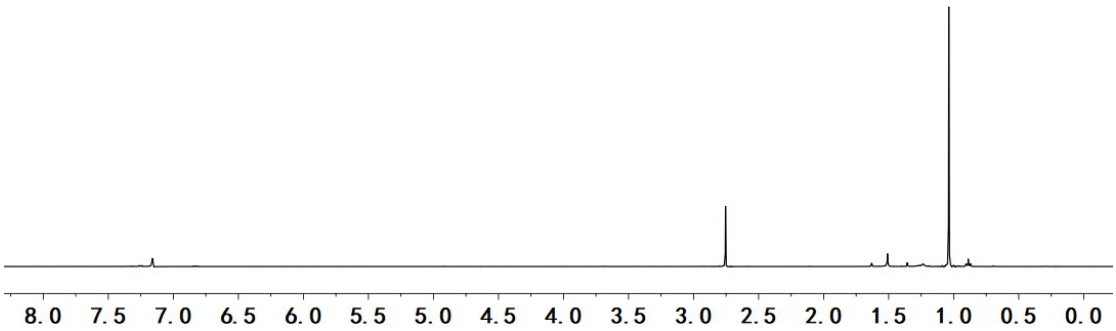


Fig. S22. ^{1}H NMR (400 MHz, C_6D_6, 298 K) of **3a-D**.

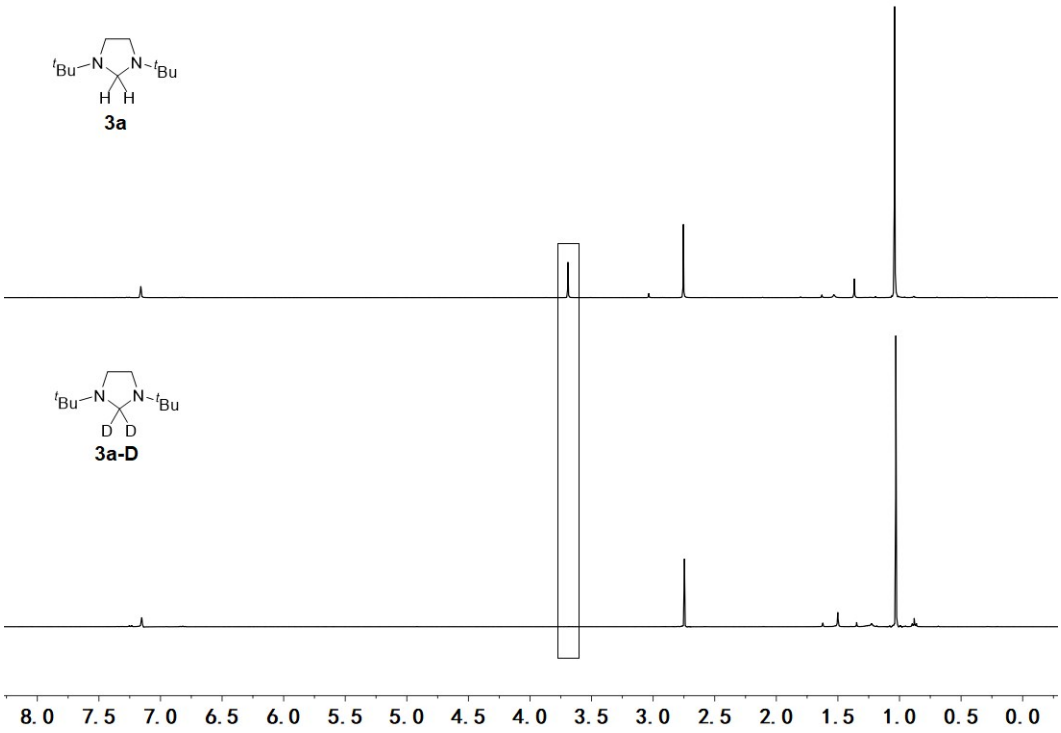


Fig. S23. Comparison of **^{1}H NMR** (400 MHz, C_6D_6, 298 K) of compounds **3a** and **3a-D**.

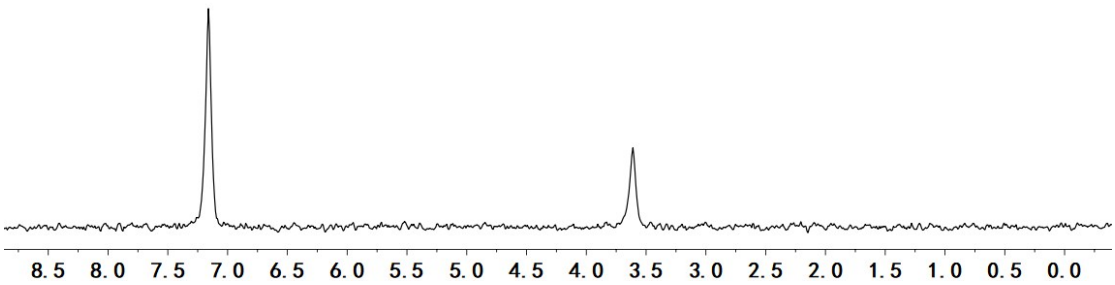


Fig. S24. ^{2}H NMR (92 MHz, C_6H_6 / C_6D_6 (100:1), 298 K) of **3a-D**.

General procedure for catalytic hydrogenation of NHC

In a glove box, an oven-dried J-Young NMR tube was charged with $RE(OAr)_3$ (0.005 mmol), N-heterocyclic carbene (0.1 mmol), and 0.1 mmol mesitylene or ferrocene as internal standard in 0.5 mL of C_6D_6. The tube was sealed and removed from the glove box. The mixture was degassed by a freeze-pump-thaw cycle and placed under 1 atm H_2 at room temperature. The tube was gently shaken for a few minutes at regular intervals. The reaction was monitored by ^1H NMR spectroscopy and the yield of product was determined with respect to the internal standard.

General procedure for the isolation of aminals 3

In a glove box, an oven-dried J-Young NMR tube was charged with $RE(OAr)_3$ (0.005 mmol), N-heterocyclic carbene (0.1 mmol) in 0.5 mL of C_6D_6. The tube was sealed and removed from the glove box. The mixture was degassed by a freeze-pump-thaw cycle and placed under 1 atm H_2 at room temperature. The tube was gently shaken for a few minutes at regular intervals. After the reaction was complete, all volatiles were removed in vacuo. The residue was dissolved in 2 mL of hexane and filtered through a short pad of celite to remove the catalyst. The solvent was removed in vacuo to afford aminal **3** (**3a**: 79%; **3b**: 86%**; 3c**: 46%). The analytical data of compounds are in accordance with literatures (Denk, M. K.; Gupta, S.; Brownie, J.; Tajammul, S.; Lough, A. J. *Chem. Eur. J.* **2001**, *7*, 4477-4486; Arduengo, A. J.; Krafczky, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523-14534).

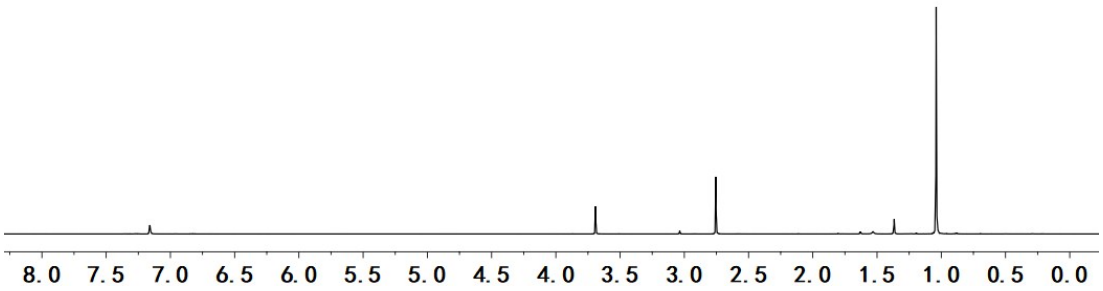


Fig. S25. ^1H NMR (400 MHz, C_6D_6, 298 K) of the aminal **3a**.

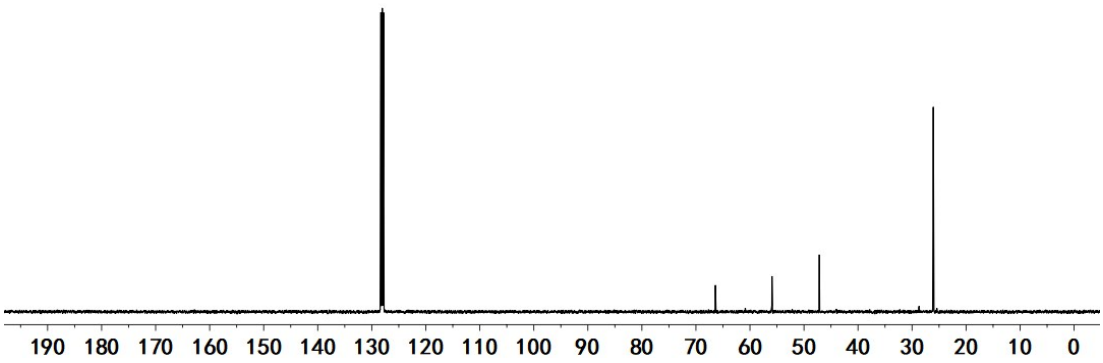


Fig. S26. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K) of the aminal **3a**.

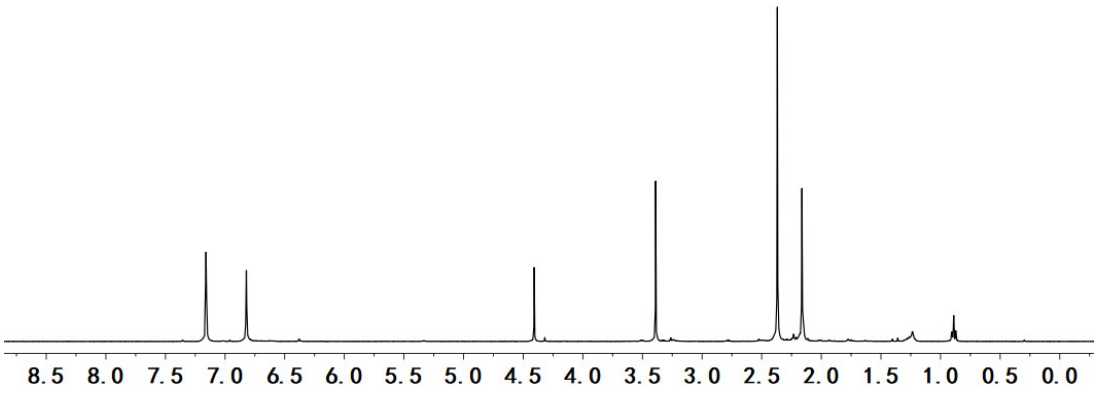


Fig. S27. ^{1}H NMR (400 MHz, C_6D_6, 298 K) of the aminal **3b**.

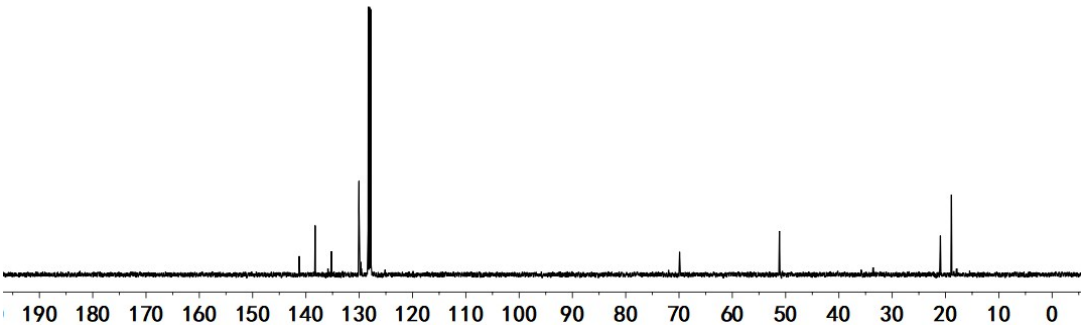


Fig. S28. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K) of the aminal **3b**.

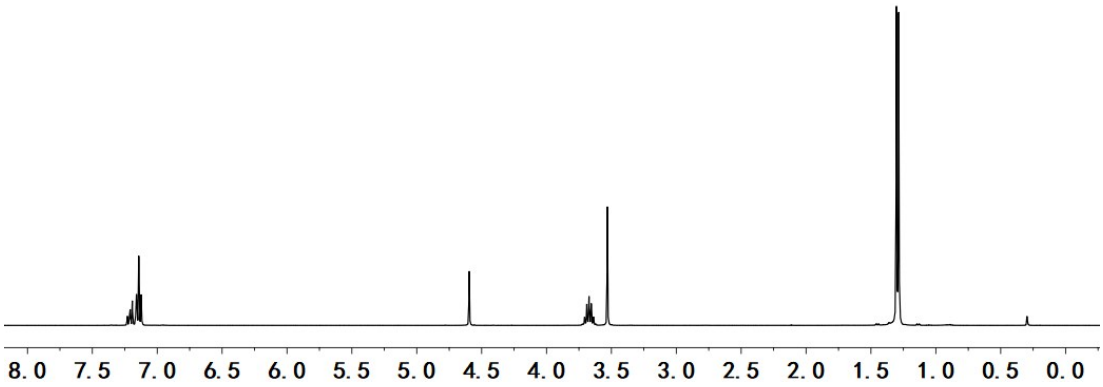


Fig. S29. ^{1}H NMR (400 MHz, C_6D_6, 298 K) of the aminal **3c**.

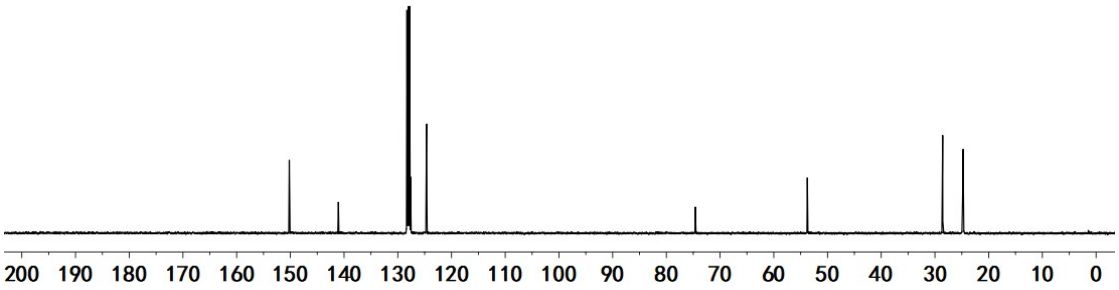
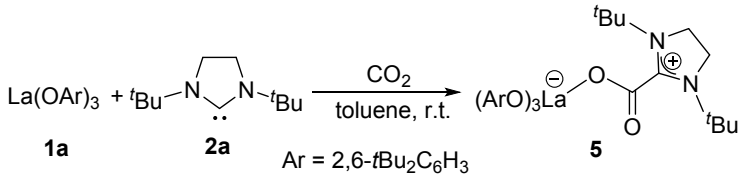


Fig. S30. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K) of the aminal **3c**.

Preparation of complex 5



Scheme S2.

CO_2 (3.7 mL, 0.15 mmol) was slowly added to a solution of $La(OAr)_3$ **1a** (113 mg, 0.15 mmol) and NHC **2a** (27 mg, 0.15 mmol) in toluene (2 mL) using an injector at room temperature. The reaction mixture was stirred for 30 minutes and then all volatiles were removed in vacuo. The residue was washed with hexane (3×2 mL) to eventually give complex **5** as a white crystalline solid (130 mg, 88%). Crystals of **5** suitable for analysis by single crystal X-ray diffraction were obtained by a layered toluene / hexane (v/v: 1:1) solution at room temperature.

Elemental Analysis: calcd. for $C_{54}H_{85}O_5N_2La \cdot C_7H_8$: C, 68.26; H, 8.73; N, 2.61. Found: C, 68.37; H, 8.57; N, 2.32.

IR (KBr, cm^{-1}): ν = 1633 (C=O).

^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (5:1), 298 K): δ = 7.32 (6H, *m*), 6.77 (3H, *p*) (each m, O*Ar*), 2.52 (s, 4H, NCH_2), 1.72 (s, 54H, $C(CH_3)_3$), 0.94 (s, 18H, $NC(CH_3)_3$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6 / C_6D_5Br (5:1), 298 K): δ = 164.0 (*i*), 137.8 (*o*), 125.1 (*m*), 116.2 (*p*) (O*Ar*), 161.4 (N*C*N), 160.4 (CO_2), 59.3 ($NC(CH_3)_3$), 44.4 (NCH_2), 35.3 ($C(CH_3)_3$), 32.8 ($C(CH_3)_3$), 28.1 ($NC(CH_3)_3$).

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / C_6D_5Br (5:1), 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.32 / 6.77 (*m*-O*Ar* / *p*-O*Ar*).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5:1), 298 K): δ ^{1}H / δ ^{13}C = 7.32 / 125.1 (*m*-O*Ar*), 6.77 / 116.2 (*p*-O*Ar*), 2.52 / 44.4 (NCH_2), 1.72 / 32.8 ($C(CH_3)_3$), 0.94 / 28.1 ($NC(CH_3)_3$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5:1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.32 / 164.0, 125.1, 35.3 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, $C(CH_3)_3$), 6.77 / 137.8 (*p*-O*Ar* / *o*-O*Ar*), 2.52 / 161.4, 44.4 (NCH_2 / N*C*N, N*C*H_2), 1.72 / 137.8, 35.3 ($C(CH_3)_3$ / *o*-O*Ar*, $C(CH_3)_3$), 0.94 / 59.3 ($NC(CH_3)_3$ / $NC(CH_3)_3$).

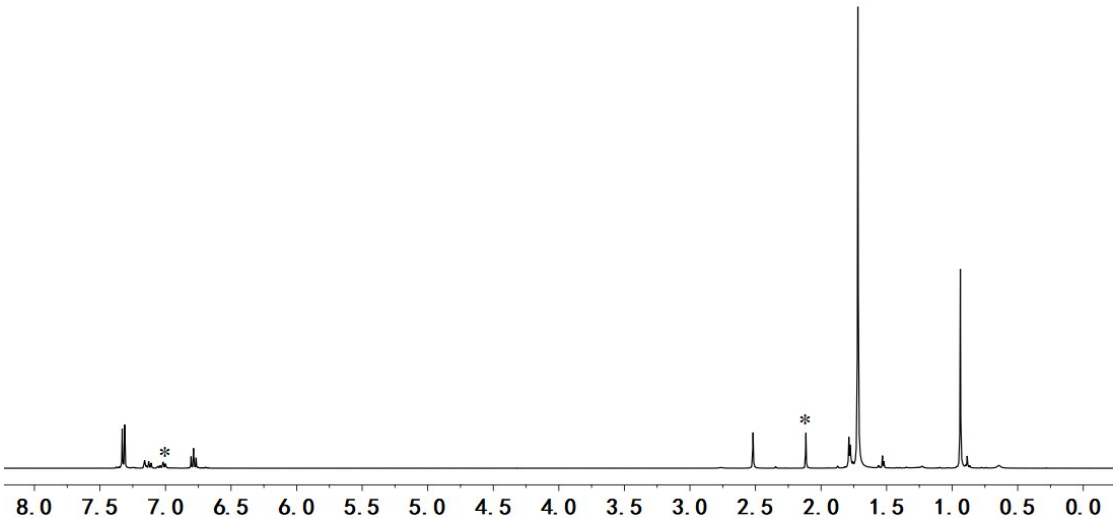


Fig. S31. ^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (5:1), 298 K) [*: Toluene].

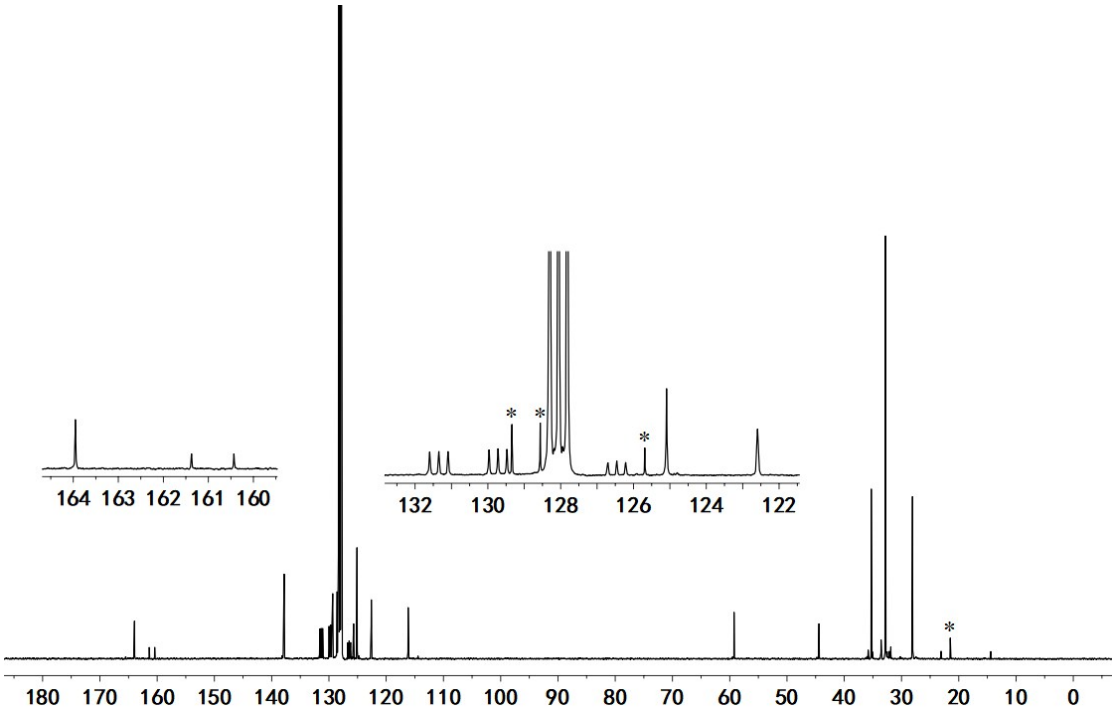


Fig. S32. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6 / C_6D_5Br (5:1), 298 K) [*: Toluene].

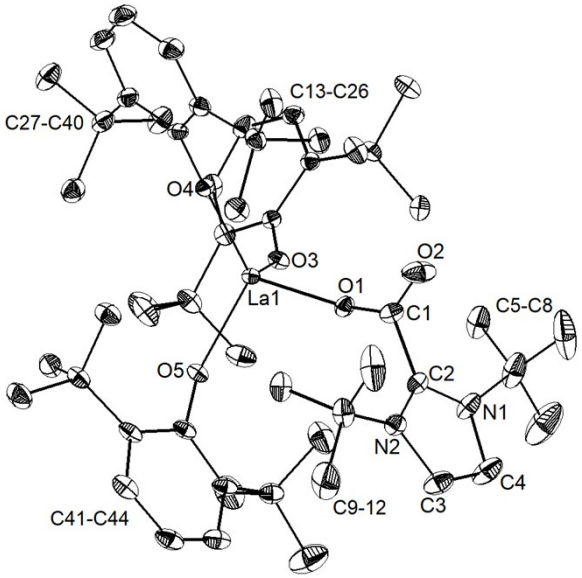
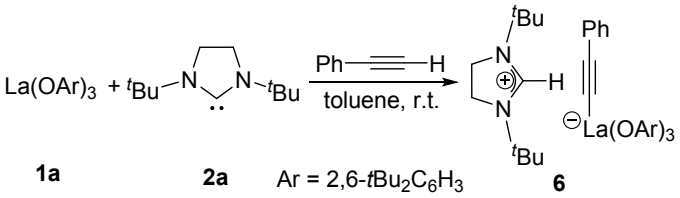


Fig. S33. Molecular structure of complex **5**.

X-ray crystal structure analysis of complex 5: formula $2(C_{54}H_{85}LaN_2O_5)\cdot C_3H_7$, M = 2005.39 gmol^{-1}, colourless, 0.25 x 0.20 x 0.10 mm, Monoclinic, space group $P2_1/c$, a = 21.2202(11), b = 12.7080(6), c = 22.4553(12) Å, β = 110.496(2)°, V = 5672.1(5) Å^3, ρ_{calc} = 1.174 gcm^{-3}, μ = 0.797 mm^{-1}, empirical absorption correction ($0.826 \leq T \leq 0.923$), Z = 2, λ = 0.71073 Å, T = 150(2) K, 91078 reflections collected ($-27 \leq h \leq 27$, $-16 \leq k \leq 16$, $-29 \leq l \leq 29$), 13064 independent (R_{int} = 0.0801) and 10344 observed reflections [$I>2\sigma(I)$], 611 refined parameters, the final R_1 was 0.0402 ($I > 2\sigma(I)$) and wR_2 was 0.1200 (all data). max. (min.) residual electron density 1.360 (-1.197) e.Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

Preparation of complex 6



Scheme S3.

A solution of phenylacetylene (10 mg, 0.10 mmol, in 1 mL of toluene) was added to a solution of La(OAr)$_3$ **1a** (76 mg, 0.10 mmol) and NHC **2a** (18 mg, 0.10 mmol) in toluene (2 mL). The reaction mixture was stirred at room temperature for 30 minutes and then all volatiles were removed in vacuo. The residue was washed with hexane (3×2 mL) to eventually give complex **6** as a white crystalline solid (94 mg, 90%). Crystals of **6** suitable for analysis by single crystal X-ray diffraction were obtained by a layered toluene / hexane (v/v: 1:1) solution at room temperature.

Elemental Analysis: calcd. for $C_{61}H_{91}O_3N_2La \cdot C_7H_8$: C, 72.19; H, 8.82; N, 2.48. Found: C, 71.85; H, 8.68; N, 2.30.

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 7.42 (s, 1H, NC*H*N), 7.35 (2H, *o*), 7.21 (2H, *m*), 7.12 (1H, *p*) (each m, *Ph*C≡C), 7.05 (6H, *m*), 6.44 (3H, *p*) (each m, O*Ar*), 3.82 (s, 4H, NCH_2), 1.52 (s, 54H, C(CH_3)$_3$), 1.36 (s, 18H, NC(CH_3)$_3$).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K): δ = 164.9 (*i*), 138.5 (*o*), 124.4 (*m*), 114.3 (*p*) (O*Ar*), 150.7 (N*C*HN), 131.6 (*o*), 128.7 (*i*), 128.1 (*m*), 125.2 (*p*) (*Ph*C≡C), 103.9 (Ph*C*≡C), n.o. (PhC≡*C*), 57.8 (N*C*(CH$_3$)$_3$), 45.6 (N*C*H$_2$), 35.0 (*C*(CH$_3$)$_3$), 31.8 (C(*C*H$_3$)$_3$), 28.2 (NC(*C*H$_3$)$_3$). [n.o.: not observed]

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, CD_2Cl_2, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.42 / 3.82 (NC*H*N / NCH_2), 7.35 / 7.21 (*o*-*Ph*C≡C / *m*-*Ph*C≡C), 7.05 / 6.44 (*m*-O*Ar* / *p*-O*Ar*).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, CD_2Cl_2, 298 K): δ ^{1}H / δ ^{13}C = 7.42 / 150.7 (N*CH*N), 7.35 / 131.6 (*o*-*Ph*C≡C), 7.21 / 128.1 (*m*-*Ph*C≡C), 7.12 (*p*-*Ph*C≡C), 7.05 / 124.4 (*m*-O*Ar*), 6.44 / 114.3 (*p*-O*Ar*), 3.82 / 45.6 (NCH_2), 1.52 / 31.8 (C(*C*H$_3$)$_3$), 1.36 / 28.2 (NC(*C*H$_3$)$_3$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, CD_2Cl_2, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.42 / 57.8, 45.6 (NC*H*N / N*C*(CH$_3$)$_3$, N*C*H$_2$), 7.35 / 131.6, 125.2, 103.9 (*o*-

*Ph*C≡C / *o*-*Ph*C≡C, *p*-*Ph*C≡C, Ph*C*≡C), 7.21 / 128.7 (*m*-*Ph*C≡C / *i*-*Ph*C≡C), 7.12 / 131.6 (*p*-*Ph*C≡C / *o*-*Ph*C≡C), 7.05 / 164.9, 124.4, 35.0 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*$(CH_3)_3$), 6.44 / 138.5 (*p*-O*Ar* / *o*-O*Ar*), 3.82 / 150.7, 45.6 (NCH_2 / N*C*HN, N*C*H_2), 1.52 / 138.5, 35.0 (C(CH_3)$_3$ / *o*-O*Ar*, *C*$(CH_3)_3$), 1.36 / 57.8 (NC(CH_3)$_3$ / N*C*$(CH_3)_3$).

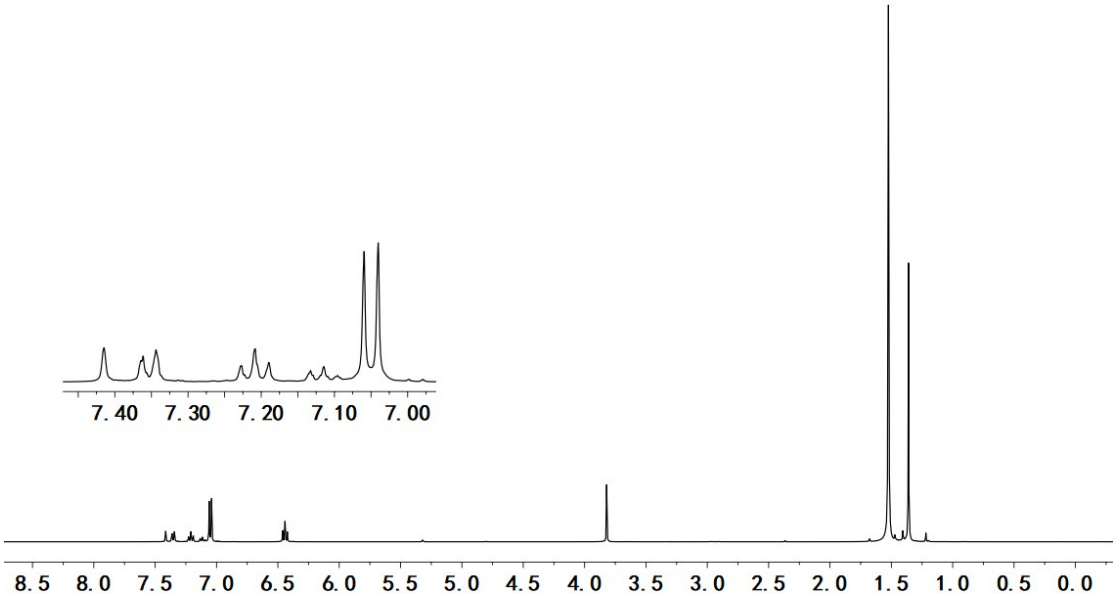


Fig. S34. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K).

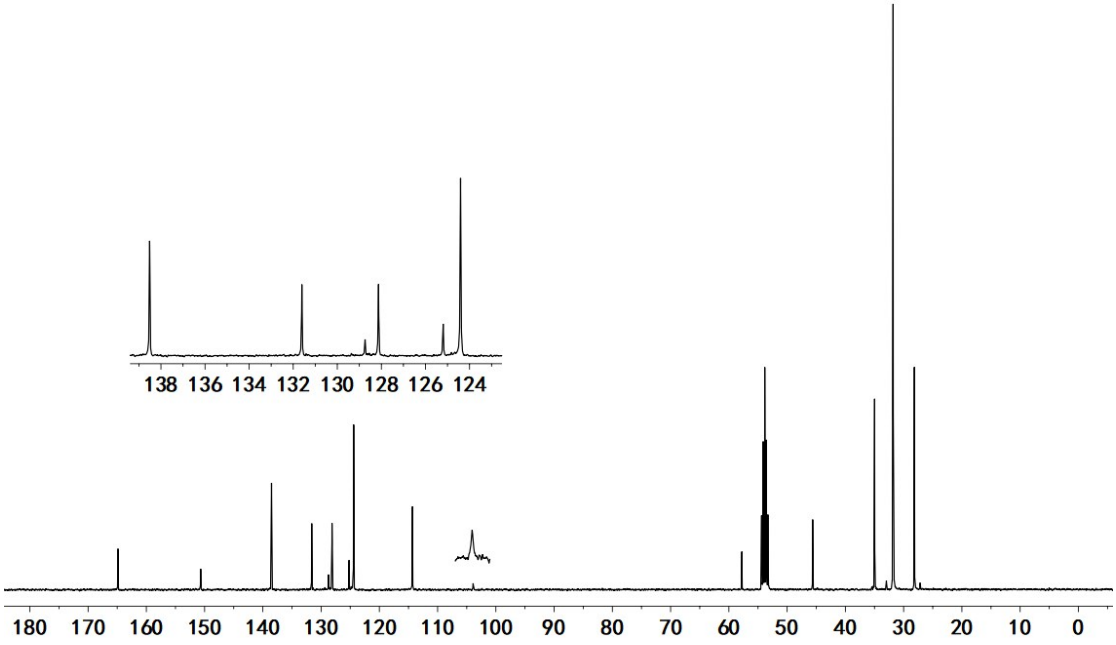


Fig. S35. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K).

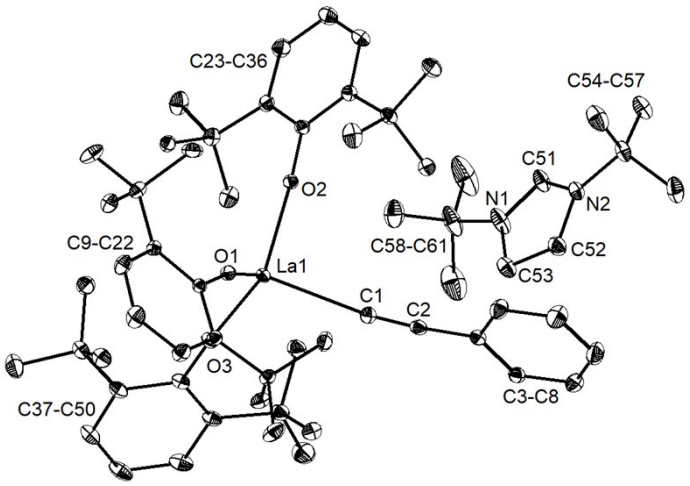
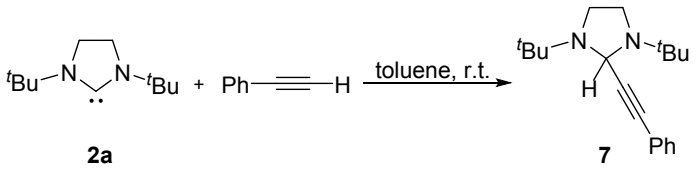


Fig. S36. Molecular structure of complex **6**.

X-ray crystal structure analysis of complex 6: formula $C_{61}H_{91}LaN_2O_3$, M = 1039.27 gmol^{-1}, colourless, 0.25 x 0.20 x 0.15 mm, Monoclinic, space group $P2_1/c$, a = 21.6284(7), b = 14.1604(5), c = 20.9678(7) Å, β = 113.3270(10)°, V = 5896.8(3) Å^3, ρ_{calc} = 1.171 gcm^{-3}, μ = 0.766 mm^{-1}, empirical absorption correction (0.832 ≤ T ≤ 0.891), Z = 4, λ = 0.71073 Å, T = 120(2) K, 97817 reflections collected (-28 ≤ h ≤ 28, -18 ≤ k ≤ 18, -27 ≤ l ≤ 26), 13552 independent (R_{int} = 0.0722) and 11017 observed reflections [I>2σ(I)], 628 refined parameters, the final R_1 was 0.0313 (I > 2σ(I)) and wR_2 was 0.0770 (all data). max. (min.) residual electron density 0.877 (-0.728) e.Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

Control reaction of NHC 2a with phenylacetylene



2a **7**

Scheme S4.

A solution of phenylacetylene (20 mg, 0.20 mmol, in 1 mL of toluene) was added to a solution of NHC **2a** (36 mg, 0.20 mmol, in 2 mL of toluene). The reaction mixture was stirred at room temperature for 30 minutes and then all volatiles were removed in vacuo to eventually give complex **7** as a colorless oil (50 mg, 88%).

Elemental Analysis: calcd. for $C_{19}H_{28}N_2$: C, 80.23; H, 9.92; N, 9.85. Found: C, 80.07; H, 9.84; N, 10.11.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.42 (2H, *o*), 6.94 (3H, *m*, *p*) (each m, *Ph*), 4.95 (s, 1H, NC*H*N), 2.98 (2H), 2.74 (2H) (each m, NCH_2), 1.23 (s, 18H, $NC(CH_3)_3$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 131.6 (*o*), 128.5 (*m*), 127.8 (*p*), 124.7 (*i*) (*Ph*), 94.3 (PhC≡*C*), 84.5 (Ph*C*≡C), 65.0 (N*C*HN), 52.9 ($C(CH_3)_3$), 44.8 (NCH_2), 27.3 ($C(CH_3)_3$).

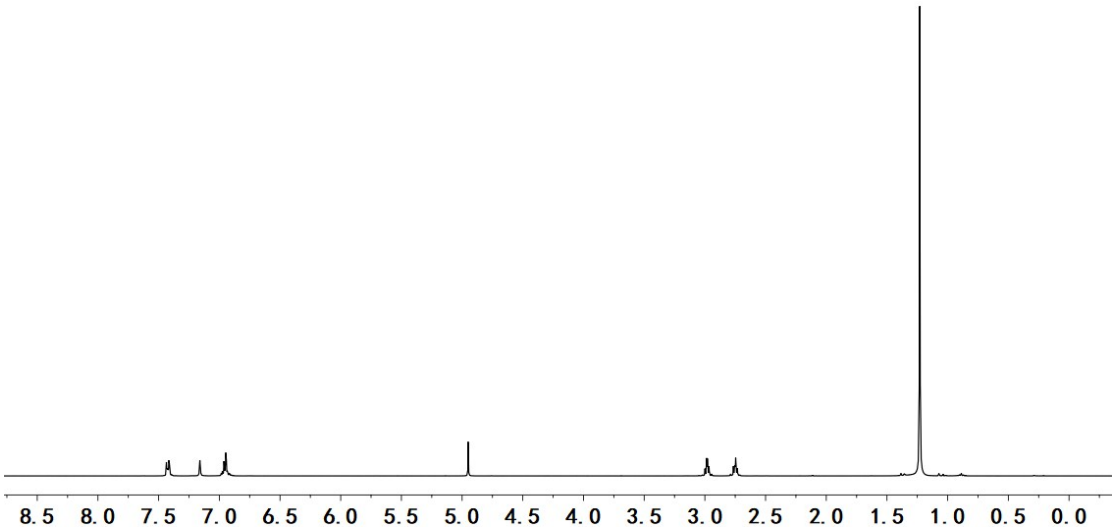


Fig. S37. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

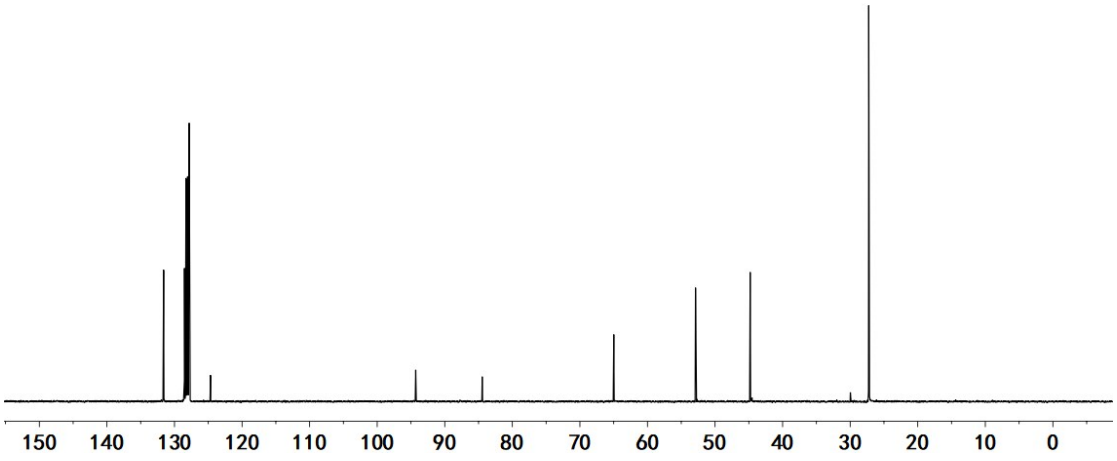


Fig. S38. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K).