Bridged bis(amidinate) lanthanide aryloxides: Syntheses, structures, and catalytic activity for addition of amines to carbodiimides

Jing Tu, Wenbo Li, Mingqiang Xue,* Yong Zhang, and Qi Shen*

Key Laboratory of Organic Synthesis of Jiangsu Province, Department of Chemistry and Chemical Engineering, Dushu Lake Campus, Soochow University, Suzhou 215123, People's Republic of China

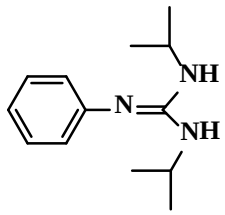
Supporting material

All manipulations and reactions were performed under a purified argon atmosphere using standard Schlenk techniques or glovebox techniques. Solvents were degassed and distilled from sodium benzophenone ketyl under argon prior to use. All nitriles and amines were predried, sublimed, recrystallized or redistilled before use. The IR spectra were recorded on a Magna-IR 550 spectrometer. Melting points were determined in sealed Ar-filled capillary tube, and uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Unity Inova-400 spectrometer. Chemical shifts (δ) were reported in ppm. Lanthanide analyses were performed by EDTA titration with a xylenol orange indicator and a hexamine buffer. Elemental analyses were performed by direct combustion using a Carlo-Erba EA 1110 instrument.

Procedures: General procedure for the synthesis of amidines from reaction of amines with nitriles catalyzed by 3 (Table 2, entry 3 as an example).

A 10 mL Schlenk flask under dried argon was charged with **3** (12.9 mg, 0.015 mmol). To the flask were added the aniline ($PhNH_2$) (0.27 ml, 10.96 M, 2.95 mmol), *N*, *N*-diisopropylcarbodiimide (^{i}PrNCN^{i}Pr) (0.45 ml, 6.418 M, 2.95 mmol). The resulting mixture was stirred at room temperature or 60 ^{o}C for the for 0.25h. After the reaction was completed, the reaction mixture was hydrolyzed by water, extracted with dichloromethane (3×10 mL), dried over anhydrous Na_2SO_4, and filtered. Then the solvent was removed under reduced pressure, and the final products were further purified by recrystallization from *n*-hexane (0.6147 g, 95% yield).

Analytical data:



***N*-phenyl-*N'*, *N"*-diisopropylguanidine (13):** Compound was obtained following the procedure catalyzed by catalysts **3**, isolated as a white solid in 99% yield. Known compound.[1] ^{1}H NMR ($CDCl_3$): δ = 7.22 (m, 2 H), 6.93 (m, 1 H), 6.85 (d, *J* = 7.6 Hz, 2 H) (aromatic C*H*), 3.77 (br, 2 H), 3.61 (m, 2 H) (C*H*Pr$^{i}_2$), 1.16 (d, *J* = 6.4 Hz, 12 H) (CH_3). ^{13}C NMR ($CDCl_3$): δ = 150.5, 150.4, 129.4, 123.7, 121.5, 43.6, 23.6.

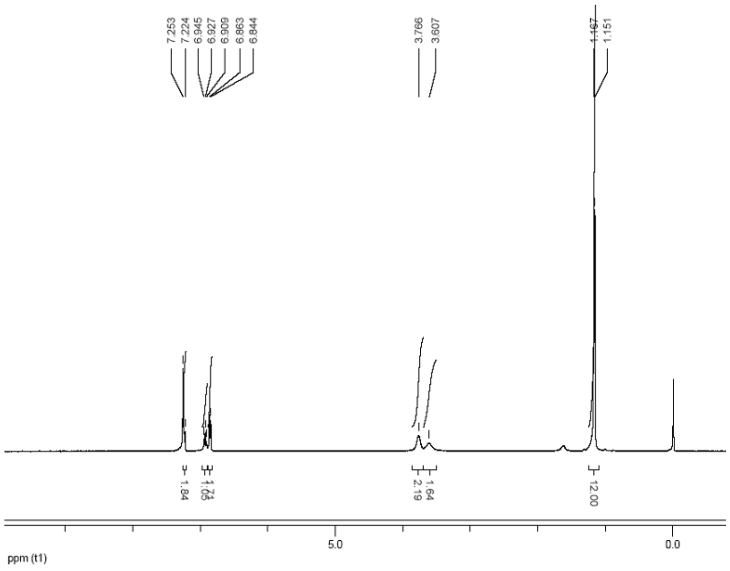
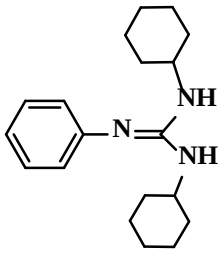


Figure S1 ^{1}H NMR spectrum of product **13**



***N*-phenyl-*N'*, *N"*-dicyclohexylguanidine (14):** Compound was obtained following the procedure catalyzed by catalysts **3**, isolated as a white solid in 99% yield. Known compound.[2] ^{1}H NMR ($CDCl_3$): δ = 7.25 (m, 2 H), 6.93 (m, 1 H), 6.86 (d, *J* = 8.0 Hz, 2 H) (aromatic C*H*), 3.64 (br, 2 H), 3.42 (m, 2 H), 2.03-1.05 (m, 20 H) (Cy). ^{13}C NMR ($CDCl_3$): δ = 150.7, 150.7, 129.5, 123.9, 121.6, 50.5, 34.1, 26.0, 25.2.

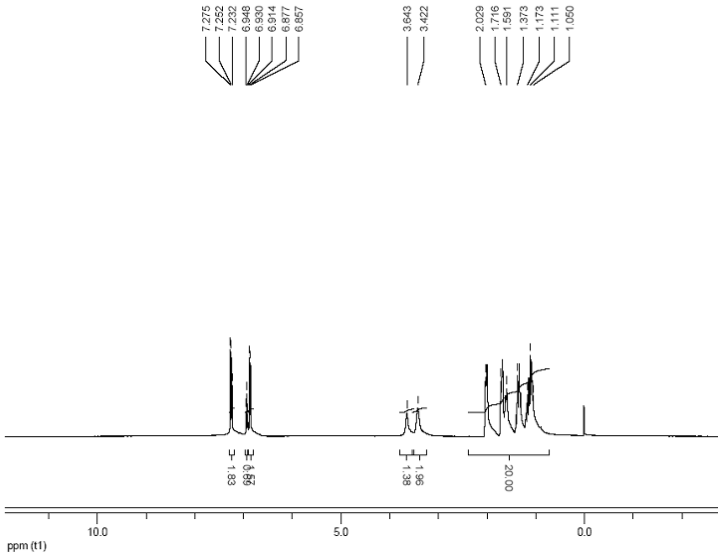
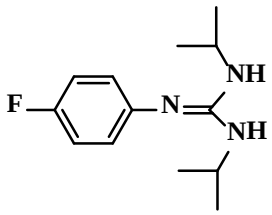


Figure S2 ^{1}H NMR spectrum of product **14**



***N*-*p*-flurophenyl-*N'*, *N"*-diisopropylguanidine (15):** Compound was obtained following the procedure catalyzed by catalysts **3**, isolated as a white solid in 99% yield. Known compound.[3] M.p.: 130-131 ^{o}C. ^{1}H NMR ($CDCl_3$): δ = 6.93 (m, 2 H), 6.76 (m, 2 H) (aromatic C*H*), 3.74 (br, 2 H), 3.52 (m, 2 H) (C*H*Pr^{i}_2), 1.15 (d, *J* = 6.0 Hz, 12 H) (CH_3). ^{13}C NMR ($CDCl_3$): δ = 148.0, 144.6, 141.8, 123.4, 122.5, 28.3, 24.2.

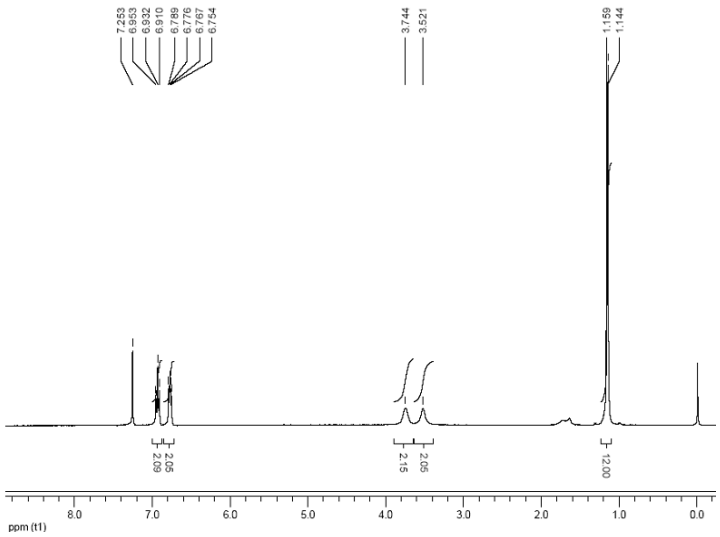
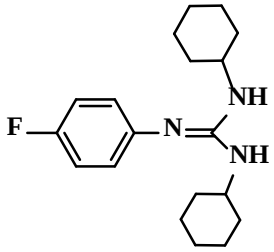


Figure S3 ^{1}H NMR spectrum of product **15**



***N*-*p*-flurophenyl-*N′*, *N″*-dicyclohexylguanidine (16):** Compound was obtained following the procedure catalyzed by catalysts **3**, isolated as a white solid in 99% yield. Known compound.[3] M.p.: 168-169 ^{o}C. ^{1}H NMR ($CDCl_3$): δ = 6.92 (m, 2 H), 6.76 (m, 2 H) (aromatic C*H*), 3.59 (br, 2 H), 3.38 (m, 2 H), 1.99-1.03 (m, 20 H) (Cy). ^{13}C NMR ($CDCl_3$): δ = 150.6, 124.9, 124.8, 116.1, 115.9, 50.4, 34.1, 25.9, 25.2.

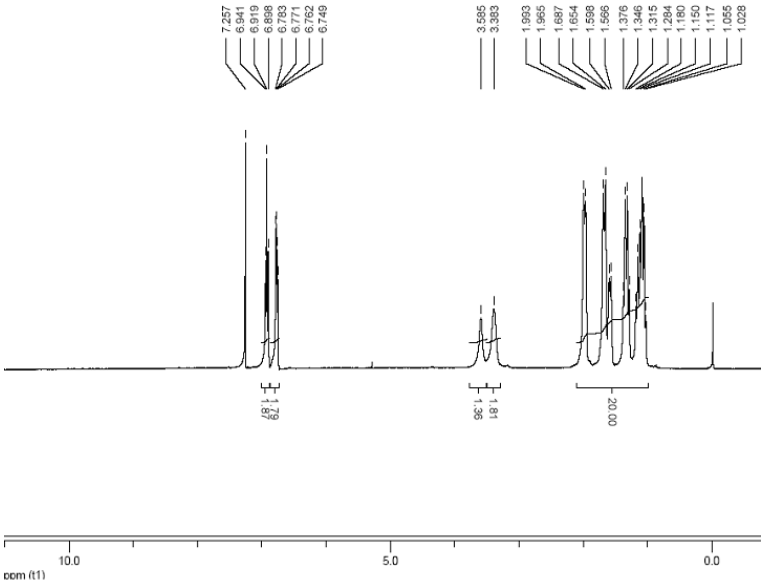
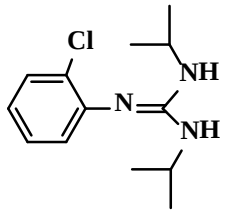


Figure S4 ^{1}H NMR spectrum of product **16**



***N*-*o*-chlorophenyl-*N'*, *N"*-diisopropylguanidine (17):** Compound was obtained following the procedure catalyzed by catalysts **3**, isolated as a white solid in 93% yield. Known compound.[3] M.p.: 137-138 ^{o}C. ^{1}H NMR ($CDCl_3$): δ = 7.34 (d, *J* = 8.0 Hz, 1 H), 7.13 (m, 1 H), 6.87 (m, 2 H) (aromatic C*H*), 3.78 (br, 2 H), 3.48 (m, 2 H) (C*H*Pr$^{i}_2$), 1.18 (m, 12 H) (CH_3). ^{13}C NMR ($CDCl_3$): δ = 150.1, 147.2, 130.1, 128.5, 127.8, 125.5, 122.7, 43.6, 23.6.

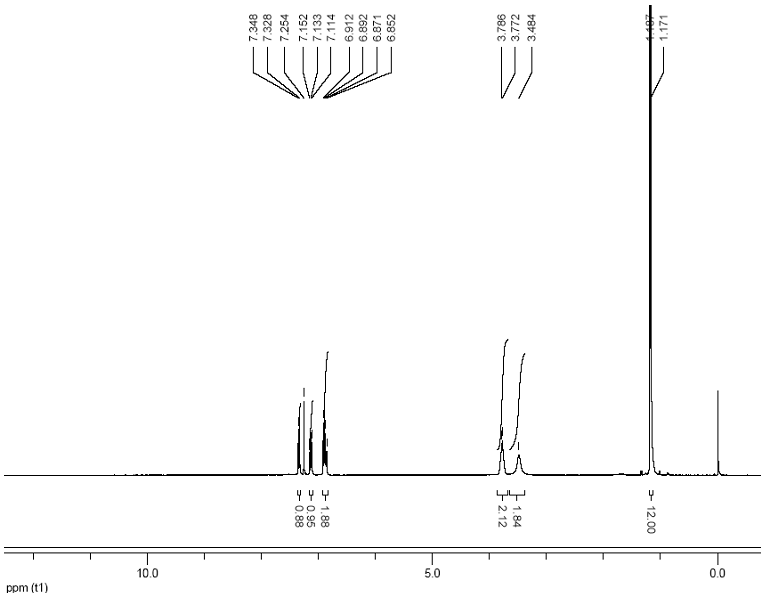
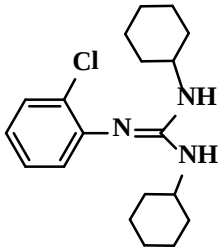


Figure S5 ^{1}H NMR spectrum of product **17**



***N*-*o*-chlorophenyl-*N'*, *N"*-dicyclohexylguanidine (18):** Compound was obtained following the procedure catalyzed by catalysts **3**, isolated as a white solid in 96% yield. Known compound.[3] M.p.: 137-138 ^{o}C. ^{1}H NMR ($CDCl_3$): δ = 7.34-7.33 (d, *J* = 7.6 Hz, 1 H), 7.15-7.11 (m, 1 H), 6.92-6.85 (m, 2 H) (aromatic C*H*), 3.55 (br, 2 H), 3.42 (m, 2 H), 2.05-1.06 (m, 20 H) (Cy). ^{13}C NMR ($CDCl_3$): δ = 150.1, 147.6, 130.1, 128.7, 127.8, 125.6, 122.6, 50.5, 34.1, 26.0, 25.2.

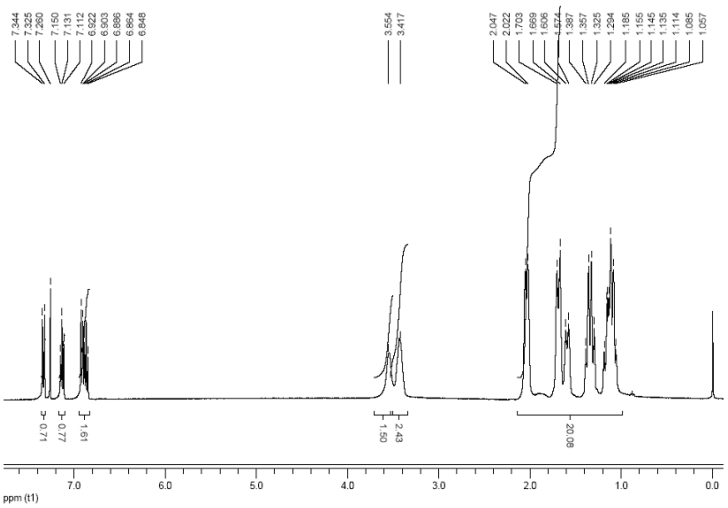
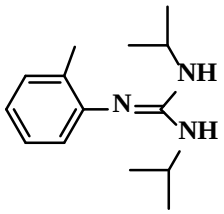


Figure S6 ^{1}H NMR spectrum of product **18**



***N*-*o*-methylphenyl-*N'*, *N''*-diisopropylguanidine (19):** Compound was obtained following the procedure catalyzed by catalysts **3**, isolated as a white solid in 90% yield. Known compound.[3] M.p.: 124-125 ^{o}C. ^{1}H NMR ($CDCl_3$): δ = 7.15 (m, 1 H), 7.08 (d, *J* = 7.6 Hz, 1 H), 6.90-6.86 (m, 1 H), 6.78 (d, *J* = 7.2 Hz, 1 H) (aromatic C*H*), 3.76 (br, 2 H), 3.46 (br 2 H) (C*H*Pr$^{i}_2$), 2.14 (m, 3 H), 1.17-1.15 (m, 12 H) (CH_3). ^{13}C NMR ($CDCl_3$): δ = 149.1, 148.6, 131.8, 130.6, 126.9, 123.4, 121.9, 43.4, 23.7, 18.4.

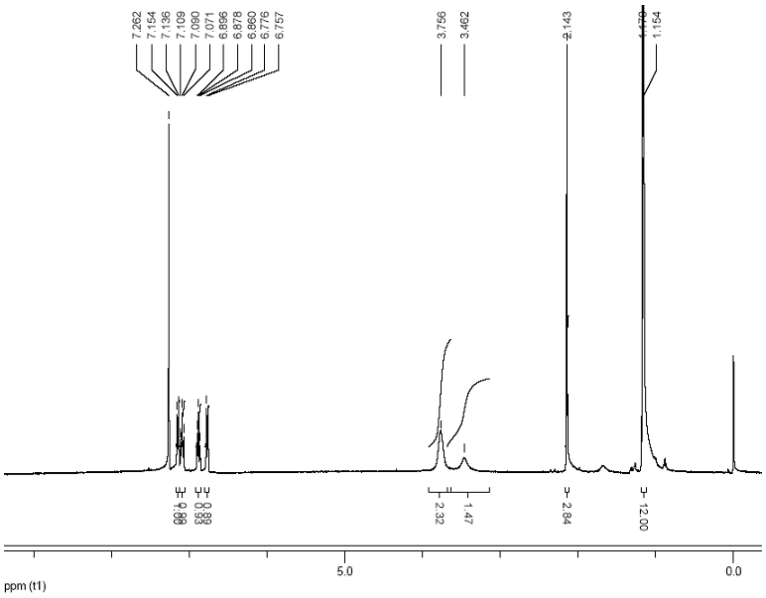
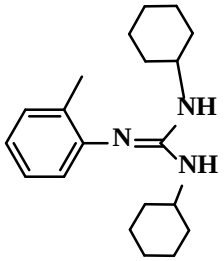


Figure S7 ^{1}H NMR spectrum of product **19**



***N*-*o*-methylphenyl-*N'*, *N"*-dicyclohexylguanidine (20):** Compound was obtained following the procedure catalyzed by catalysts **3**, isolated as a white solid in 93% yield. Known compound.[3] M.p.: 134-135 ^{o}C. ^{1}H NMR ($CDCl_3$): δ = 6.95-6.91 (m, 2 H), 6.80-6.76 (m, 2 H) (aromatic C*H*), 3.62 (br, 2 H), 3.40 (br, 2 H), 2.00 (m, 3 H), 1.97-1.03 (m, 20 H) (Cy). ^{13}C NMR ($CDCl_3$): δ = 148.9, 148.7, 131.9, 130.6, 126.8, 123.5, 121.9, 50.4, 34.2, 25.9, 25.2, 18.4.

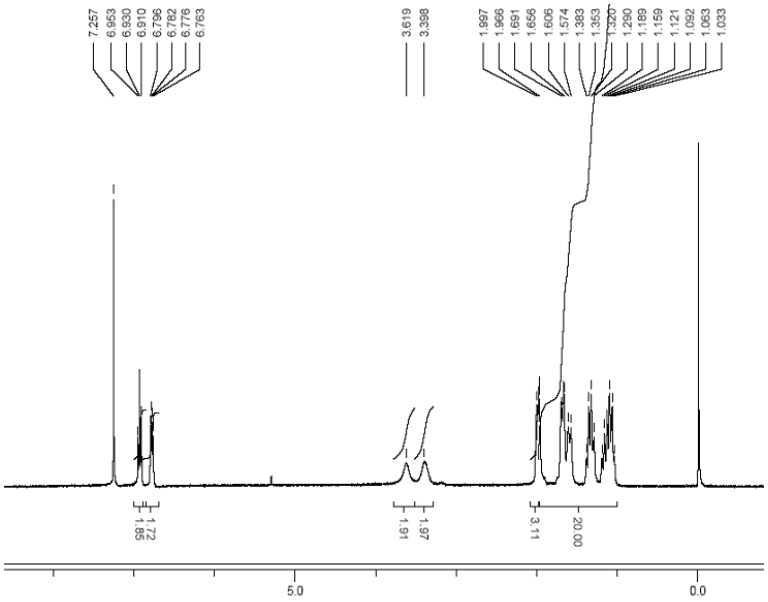
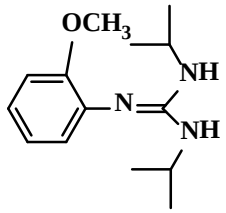


Figure S8 ^{1}H NMR spectrum of product **20**



***N*-*o*-methoxyphenyl-*N'*, *N"*-diisopropylguanidine (21):** Compound was obtained following the procedure catalyzed by catalysts **3**, isolated as a white solid in 92% yield. Known compound.[1] ^{1}H NMR ($CDCl_3$): δ = 6.94-6.86 (m, 4 H) (aromatic C*H*), 3.78 (m, 5 H), 3.55 (br, 2 H) (C*H*Pr$^{i}_2$), 1.17-1.16 (m, 12 H) (CH_3). ^{13}C NMR ($CDCl_3$): δ = 152.4, 150.7, 139.2, 124.7, 122.2, 121.3, 111.8, 55.6, 43.3, 23.4.

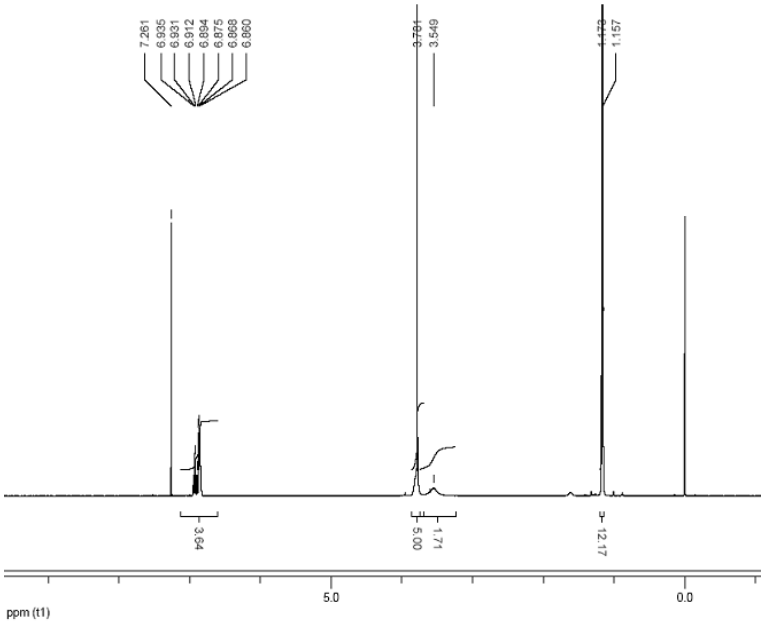
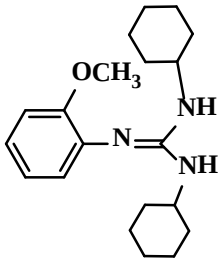


Figure S9 ^{1}H NMR spectrum of product **21**



***N*-*o*-methoxyphenyl-*N'*, *N"*-dicyclohexylguanidine (22)**: Compound was obtained following the procedure catalyzed by catalysts **3**, isolated as a white solid in 98% yield. Known compound.[3] M.p.: 122-123 ^{o}C. ^{1}H NMR ($CDCl_3$): δ = 6.96-6.85 (m, 4 H) (aromatic C*H*), 3.77 (m, 3 H), 3.60 (br, 2 H), 3.45 (br, 2 H), 2.02-1.03 (m, 20 H) (Cy). ^{13}C NMR ($CDCl_3$): δ = 152.6, 150.5, 139.3, 125.0, 122.4, 121.4, 111.9, 55.7, 50.4, 34.0, 25.9, 25.1.

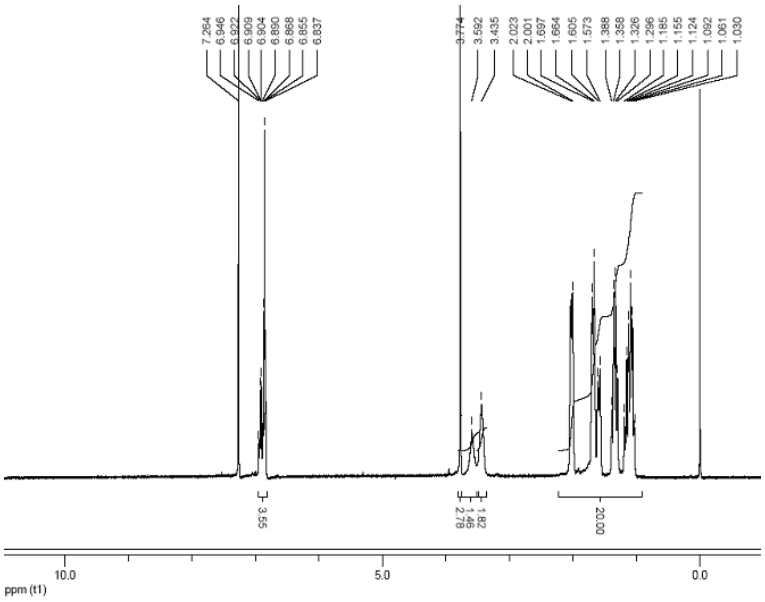
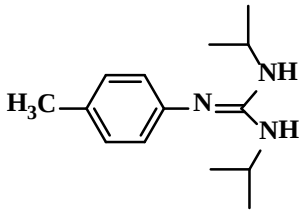


Figure S10 ^{1}H NMR spectrum of product **22**



***N*-*p*-methylphenyl-*N'*, *N''*-diisopropylguanidine (23):** Compound was obtained following the procedure catalyzed by catalysts **3**, isolated as a white solid in 99% yield. Known compound.[5] M.p.: 155-156 °C. ^{1}H NMR ($CDCl_3$): δ = 7.03 (d, *J* = 8.0 Hz, 2 H), 6.72 (d, *J* = 7.6 Hz, 2 H) (aromatic C*H*), 3.73 (br, 2 H), 3.53 (m, 2 H) (C*H*Pr^i_2), 2.26 (s, 3 H), 1.14-1.12 (m, 12 H) (CH_3). ^{13}C NMR ($CDCl_3$): δ = 150.6, 147.6, 130.7, 130.1, 123.5, 43.4, 23.6, 21.0.

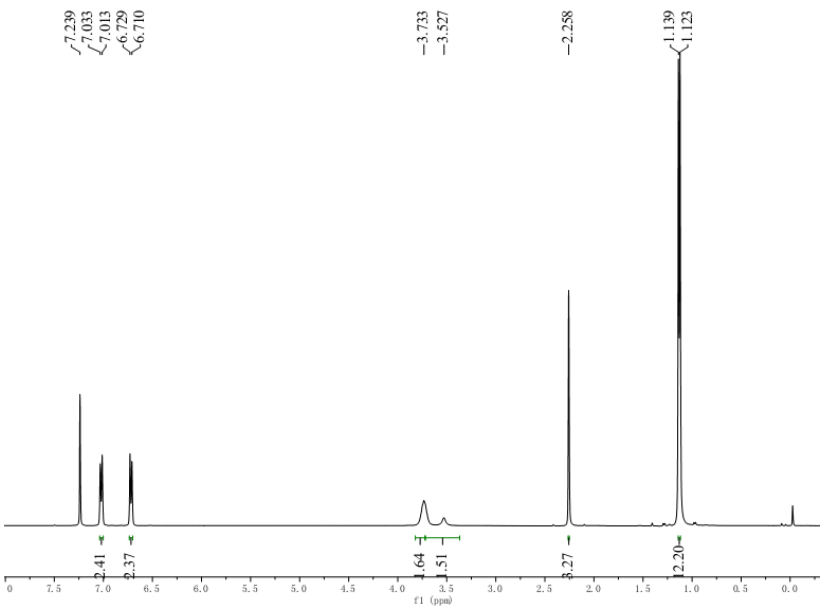
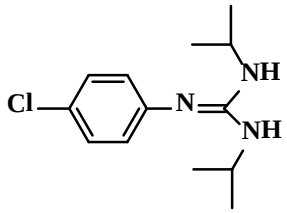


Figure S11 ^{1}H NMR spectrum of product **23**



***N*-*p*-chlorophenyl-*N'*, *N"*-diisopropylguanidine (24):** Compound was obtained following the procedure catalyzed by catalysts **3**, isolated as a white solid in 99% yield. Known compound.[5] ^{1}H NMR ($CDCl_3$): δ = 7.21 (d, *J* = 8.4 Hz, 2 H), 6.80 (d, *J* = 8.8 Hz, 2 H) (aromatic C*H*), 3.75 (br, 2 H), 3.61 (br, 2 H) (C*H*Pr^{i}_2), 1.17-1.16 (m, 12 H) (CH_3). ^{13}C NMR ($CDCl_3$): δ = 150.5, 149.2, 129.4, 126.4, 125.1, 43.5, 23.6.

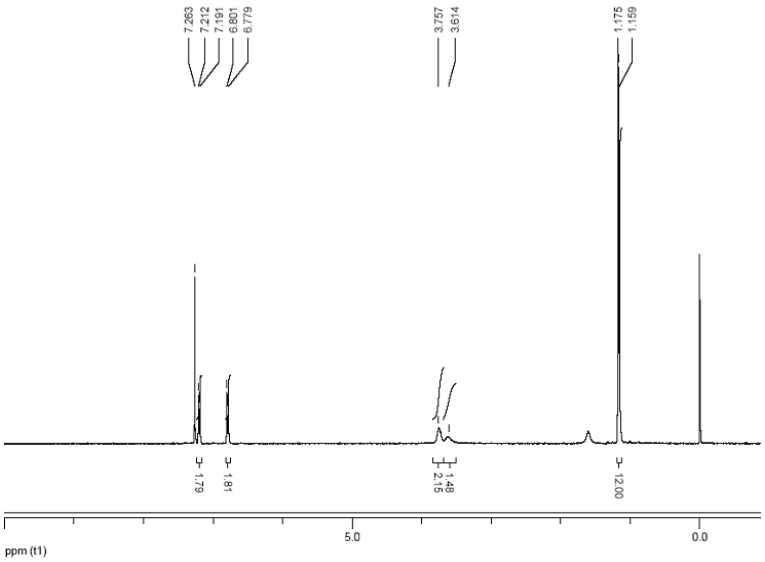
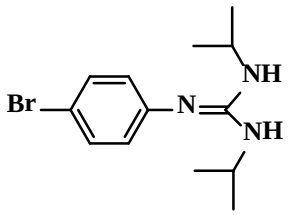


Figure S12 ^{1}H NMR spectrum of product **24**



***N*-*p*-bromophenyl-*N'*, *N"*-diisopropylguanidine (25):** Compound was obtained following the procedure catalyzed by catalysts **3**, isolated as a white solid in 99% yield. Known compound.[5] ^{1}H NMR ($CDCl_3$): δ = 7.40 (m, 2 H), 6.89 (d, *J* = 8.4 Hz, 2 H) (aromatic C*H*), 3.74 (m, 2 H) (C*H*Pr^{i}_2), 1.20-1.18 (m, 12 H) (CH_3). ^{13}C NMR ($CDCl_3$): δ = 150.4, 149.7, 132.4, 125.6, 114.0, 43.5, 23.6.

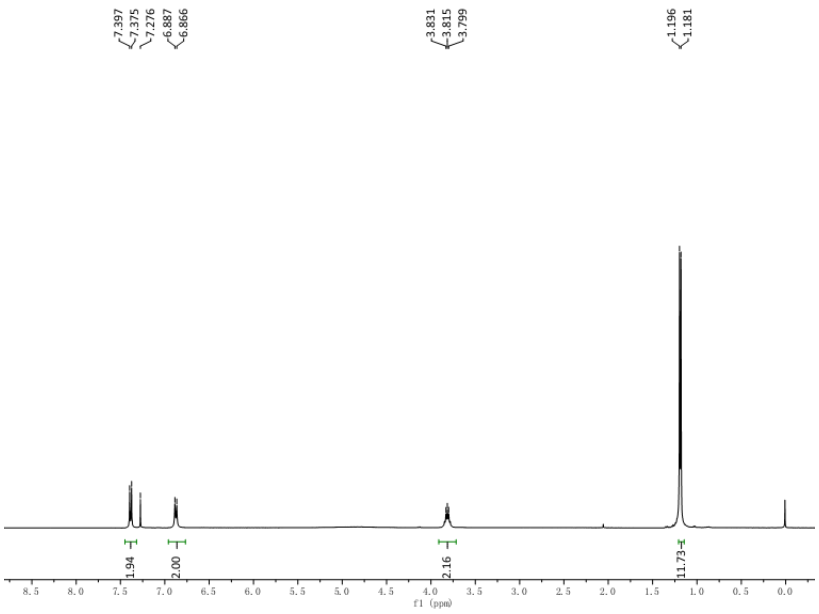
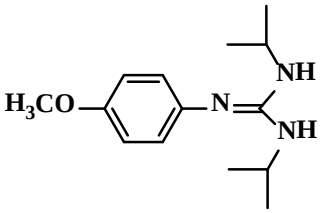


Figure S13 ^{1}H NMR spectrum of product **25**



***N*- p-methoxyphenyl- *N′*, *N″* –diisopropylguanidine (26):** Compound was obtained following the procedure catalyzed by catalysts **3**, isolated as a white solid in 95% yield. Known compound.[1] ^{1}H NMR ($CDCl_3$): δ = 6.84 (s, 4 H) (aromatic C*H*), 3.77 (m, 7 H) (OCH_3 and C*H*Pr^{i}_2), 1.18-1.17 (m, 12 H) (CH_3). ^{13}C NMR ($CDCl_3$): δ = 154.6, 150.8, 142.7, 124.2, 114.6, 55.4, 43.3, 23.3.

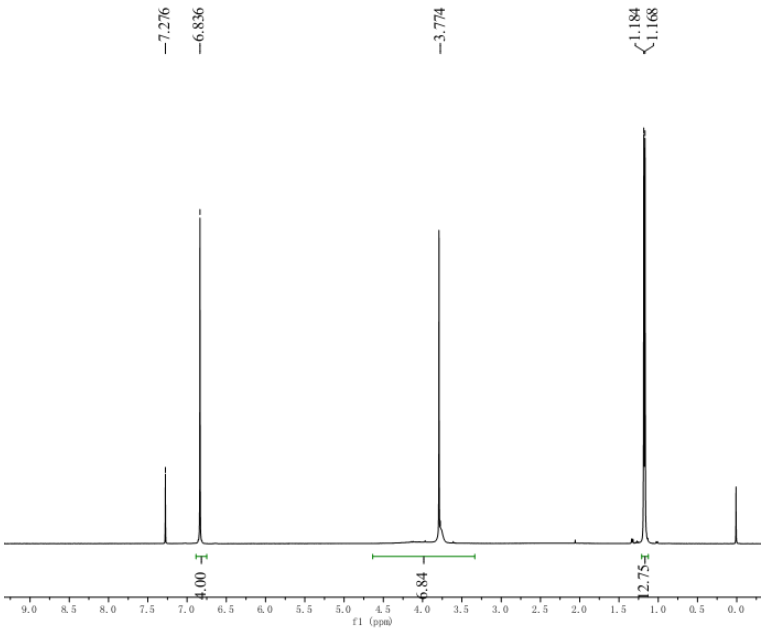
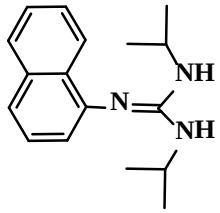


Figure S14 ^{1}H NMR spectrum of product **26**



***N*- (1-naphthyl)- *N′, N″* –diisopropylguanidine (27):** Compound was obtained following the procedure catalyzed by catalysts **3**, isolated as a white solid in 98% yield. Known compound.[5] ^{1}H NMR ($CDCl_3$): δ = 8.08 (d, *J* = 8.0 Hz, 1 H), 7.78 (d, *J* = 7.6 Hz, 1 H), 7.45 (m, 4 H), 6.91 (d, *J* = 7.2 Hz, 1 H) (aromatic C*H*), 3.88 (br, 2 H), 3.63 (m, 2 H) (C*H*Pr$^{i}_2$), 1.18 (m, 12 H) (CH_3). ^{13}C NMR ($CDCl_3$): δ = 150.2, 147.1, 135.1, 129.9, 128.1, 126.8, 126.1, 125.0, 124.7, 121.7, 118.1, 43.6, 23.7.

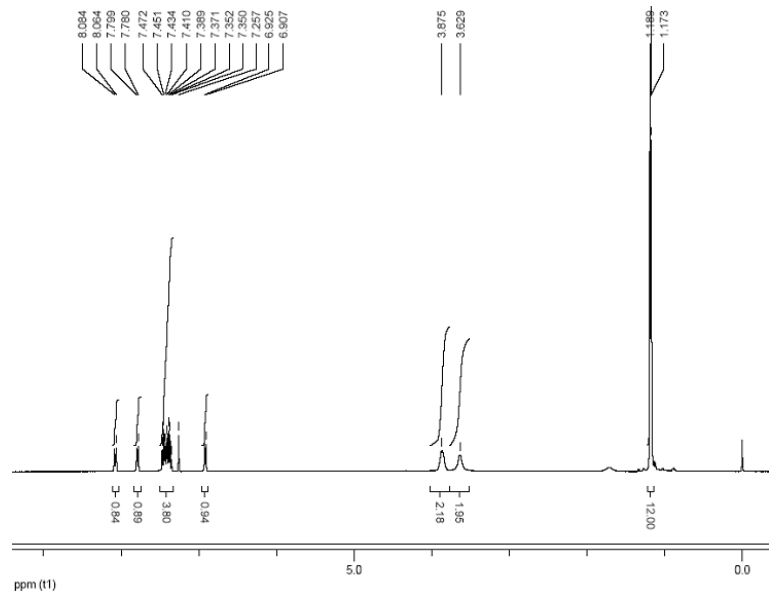
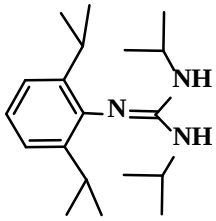


Figure S15 ^{1}H NMR spectrum of product **27**



***N*, *N''*-diisopropyl-*N'*-2, 6-diisopropylphenylguanidine (28):** Compound was obtained following the procedure catalyzed by catalysts **3**, isolated as a white solid in 80% yield. Known compound.[1] ^{1}H NMR ($CDCl_3$): δ = 7.07 (d, *J* = 7.2 Hz, 2 H), 6.98-6.94 (m, 1 H) (aromatic C*H*), 4.19(br, 2 H), 3.43-3.19 (m, 2 H), 3.11-3.04 (m, 2 H) (C*H*), 1.25-1.04 (m, 24 H) (CH_3). ^{13}C NMR ($CDCl_3$): δ = 147.7, 144.3, 141.6, 123.2, 122.3, 43.5, 42.7, 28.0, 23.9.

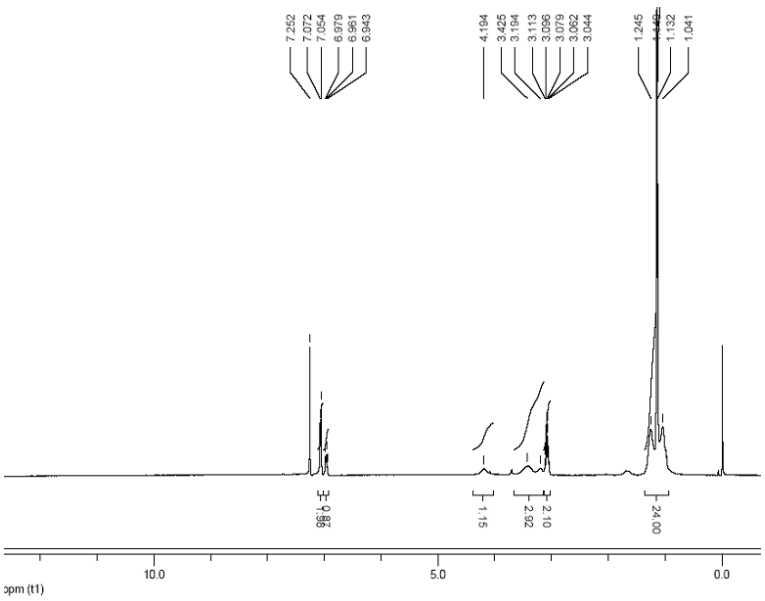
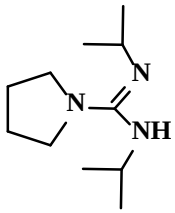


Figure S16 ^{1}H NMR spectrum of product **28**



***N, N'*-diisopropylpyrrolidine-1-carboximidamide (29)**: Compound was obtained following the procedure catalyzed by catalysts **3**. Colorless liquid. Yield: 95%. Known compound.[4] ^{1}H NMR ($CDCl_3$): δ = 3.38 (s, 2 H) (C*H*Pr$^{i}_2$), 3.26(m, 4 H) (CH_2), 1.80 (s, 4 H) (CH_2), 1.11 (m, 12 H) (CH_3). ^{13}C NMR ($CDCl_3$): δ = 153.7, 47.9, 43.6, 26.3, 24.8.

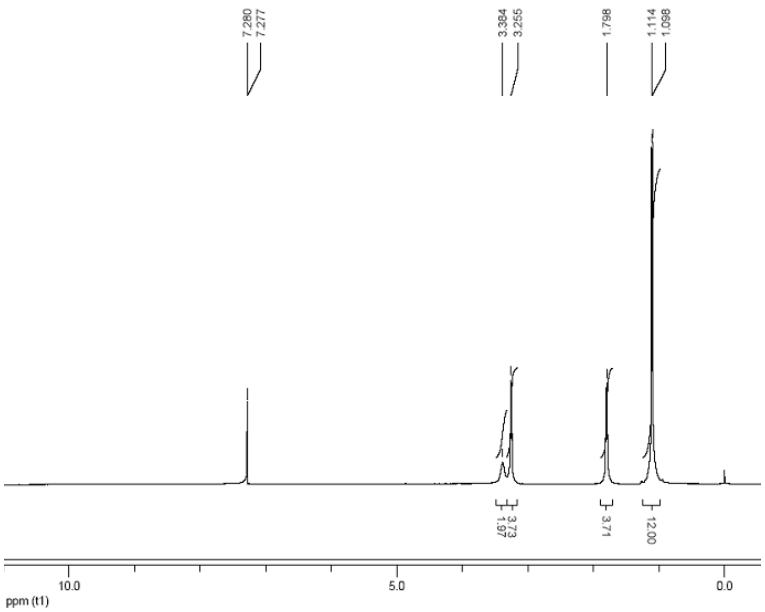
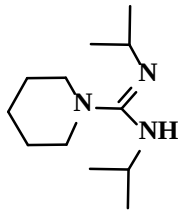


Figure S17 ^{1}H NMR spectrum of product **29**



***N, N'*-diisopropylpiperidine-1-carboximidamide (30)**: Compound was obtained following the procedure catalyzed by catalysts **3**. Colorless liquid. Yield: 92%. Known compound.[4] ^{1}H NMR ($CDCl_3$): δ = 3.36 (m, 2 H) (C*H*Pr$^{i}_2$), 3.04 (br, 4 H) (CH_2), 1.52 (br, 6 H) (CH_2), 1.09 (m, 12 H) (CH_3). ^{13}C NMR ($CDCl_3$): δ = 156.7, 49.1, 46.6, 26.0, 24.9, 24.0.

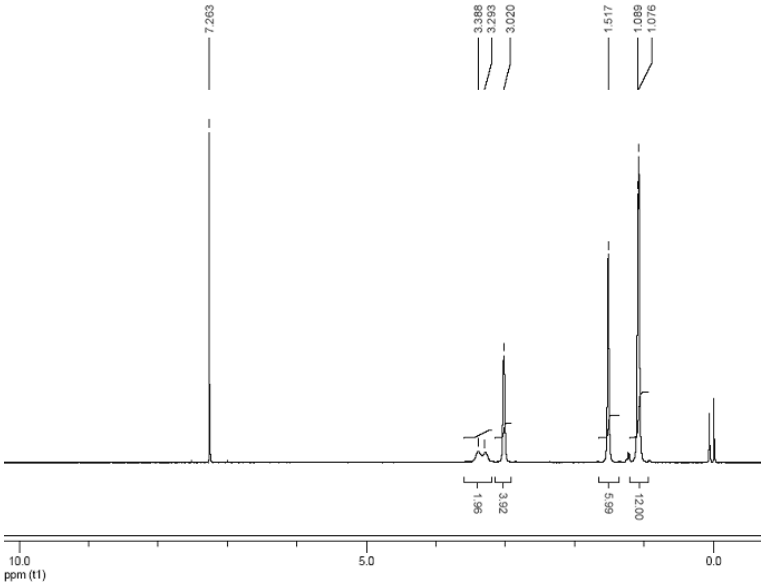
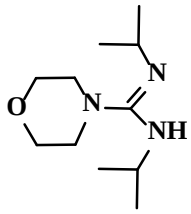


Figure S18 ^{1}H NMR spectrum of product **30**



***N, N'*-diisopropylmorpholine-4-carboximidamide (31)**: Compound was obtained following the procedure catalyzed by catalysts **3**. Colorless liquid. Yield: 91%. ^{1}H NMR ($CDCl_3$): δ = 3.69-3.67 (m, 4 H) (C*H*Pr$^{i}_2$ and CH_2), 3.42-3.39 (m, 1 H), 3.32-3.29 (m, 1 H) (CH_2), 3.08-3.06 (m, 4 H) (CH_2), 1.14-1.06 (m, 12 H) (CH_3). ^{13}C NMR ($CDCl_3$): δ = 155.5, 67.3, 48.9, 47.4, 46.6, 24.0, 23.8.

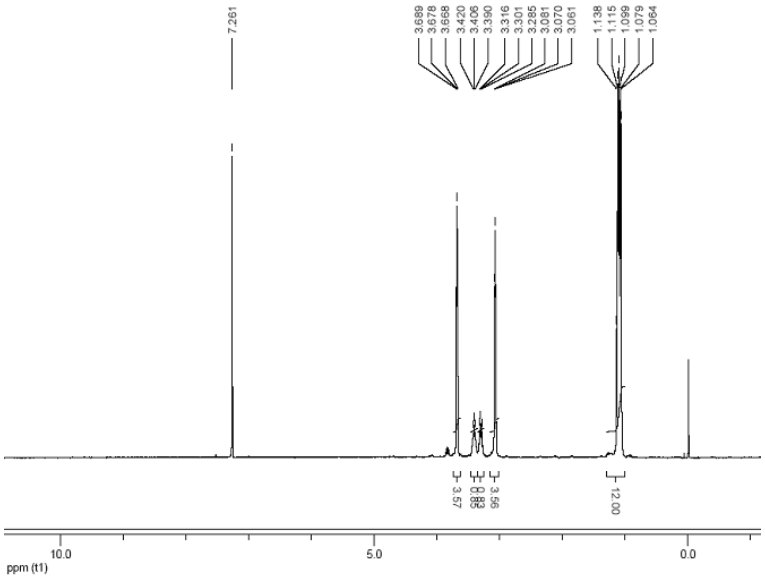


Figure S19 ^{1}H NMR spectrum of product **31**

The ORTEP drawing of the complexes 1, 2, 4-5 and 9 (Figure S20-S24).

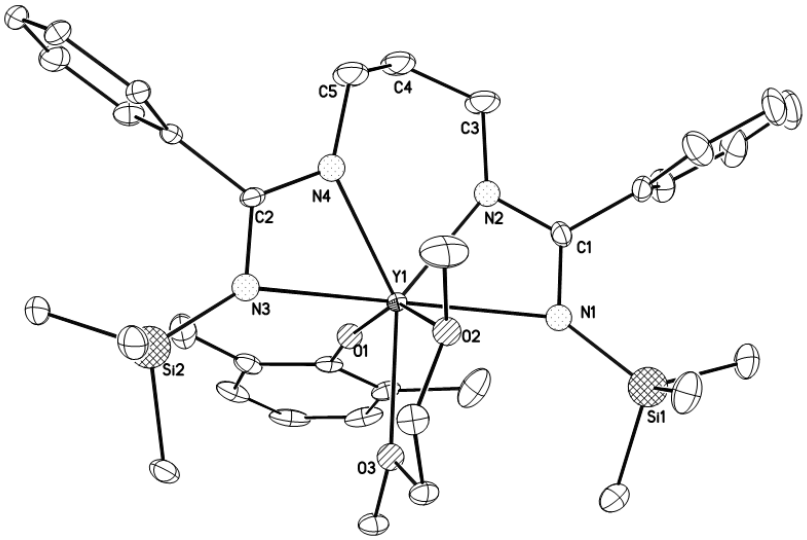


Figure S20 ORTEP diagram of the molecular structure of **1**. Thermal ellipsoids are drawn at 30 % probability level. All hydrogen atoms are omitted for clarity.

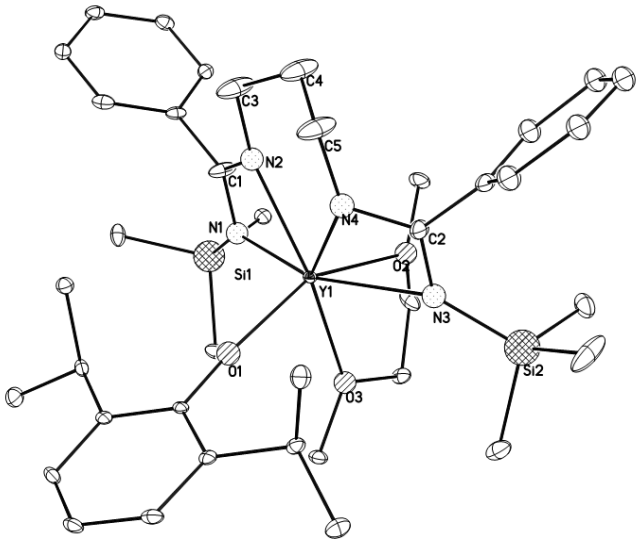


Figure S21 ORTEP diagram of the molecular structure of **2**. Thermal ellipsoids are drawn at 30 % probability level. All hydrogen atoms are omitted for clarity.

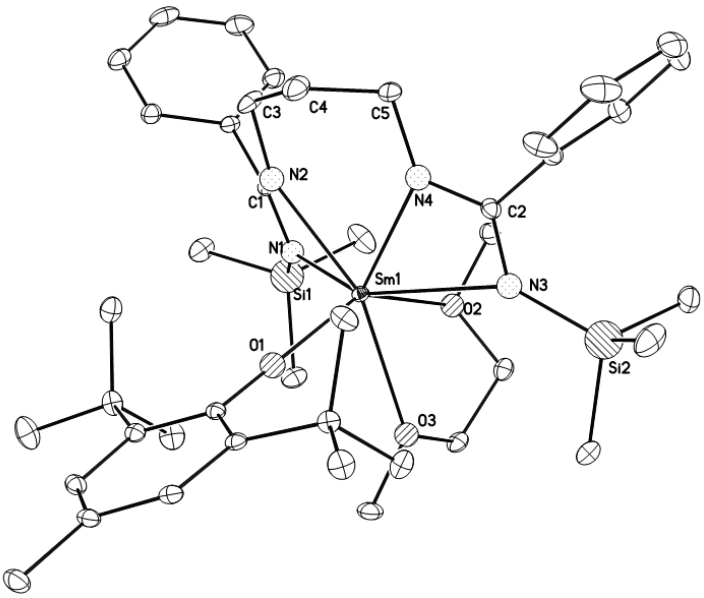


Figure S22 ORTEP diagram of the molecular structure of **4**. Thermal ellipsoids are drawn at 30 % probability level. All hydrogen atoms are omitted for clarity.

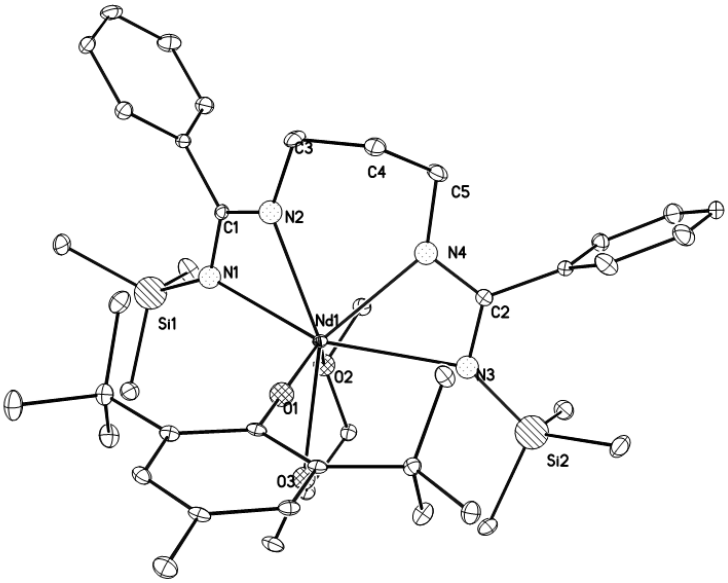


Figure S23 ORTEP diagram of the molecular structure of **5**. Thermal ellipsoids are drawn at 30 % probability level. All hydrogen atoms are omitted for clarity.

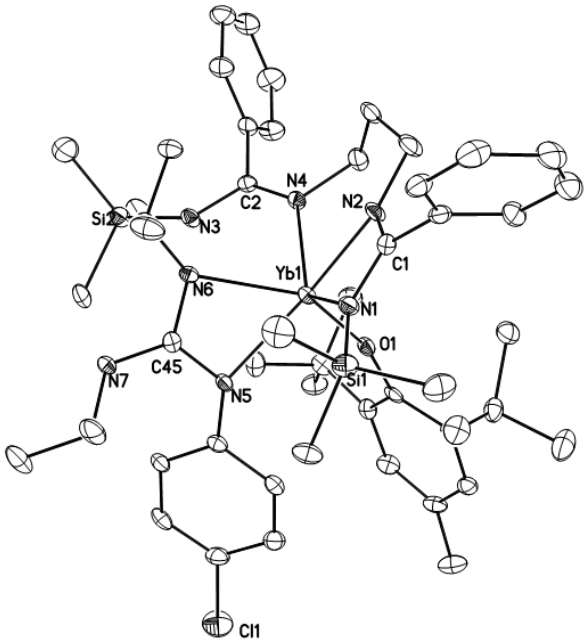


Figure S24 ORTEP diagram of the molecular structure of **9**. Thermal ellipsoids are drawn at 30 % probability level. All hydrogen atoms are omitted for clarity.

General procedure for the NMR tube reaction of 3 with $PhNH_2$ and $^{i}PrNCN^{i}Pr$.

i) In the glovebox, a J. Young valve NMR tube was charged with a solution of **3**

(10.3 mg, 0.0125 mmol) in d_8-THF (0.1 mL), a certain amount of aniline (1.14 uL, 10.96 M, 0.0125 mmol) in C_6D_6 (0.4 mL) was added to the tube. The tube was taken outside the glovebox and the reaction mixture was stirred at room temperature, which was easily monitored by ^{1}H NMR spectroscopy (Figure S25 in 15 min and Figure S26 in 2.5 h).

ii) In the glovebox, a J. Young valve NMR tube was charged with a solution of **3** (14.0 mg, 0.0170 mmol) in d_8-THF (0.1 mL), then a certain amount of aniline (1.55 uL, 10.96 M, 0.0170 mmol) and *N*, *N'*-diisopropylcarbodiimide (2.65 uL, 6.418M, 0.0170 mmol) in C_6D_6 (0.5 mL) was added to the tube. The tube was taken outside the glovebox and the reaction mixture was stirred at room temperature, which was easily monitored by ^{1}H NMR spectroscopy (Figure S27 in 15 min and Figure S28 in 20h).

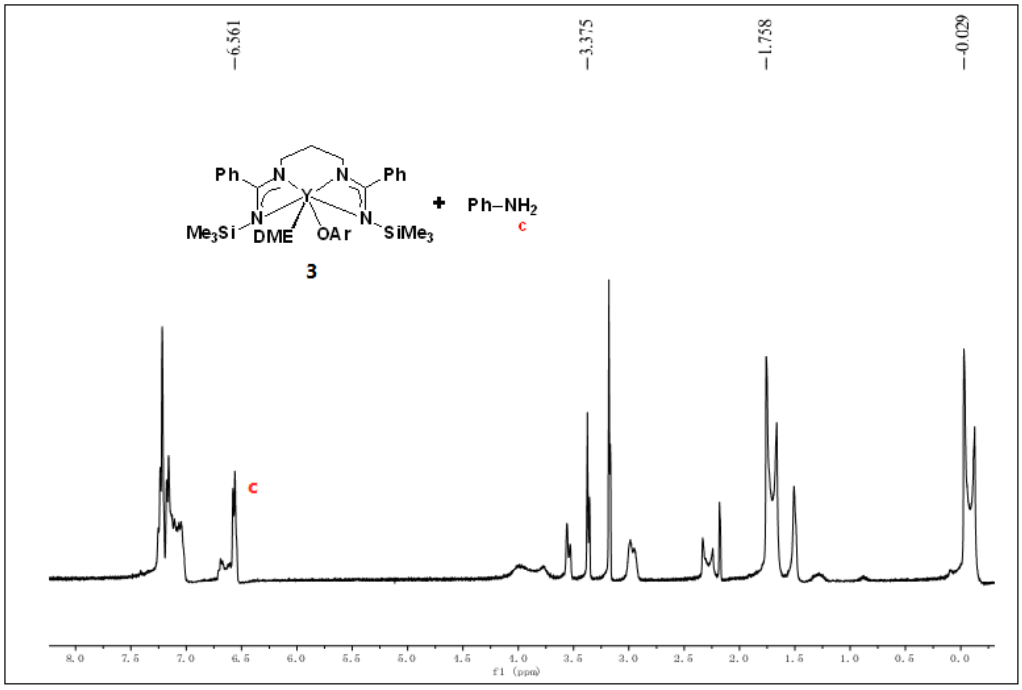


Figure S25 ^{1}H NMR spectrum of the reaction of **3** with 1 equiv of $PhNH_2$ in the mixture of C_6D_6 and d_8-THF at room temperature in 15 minutes.

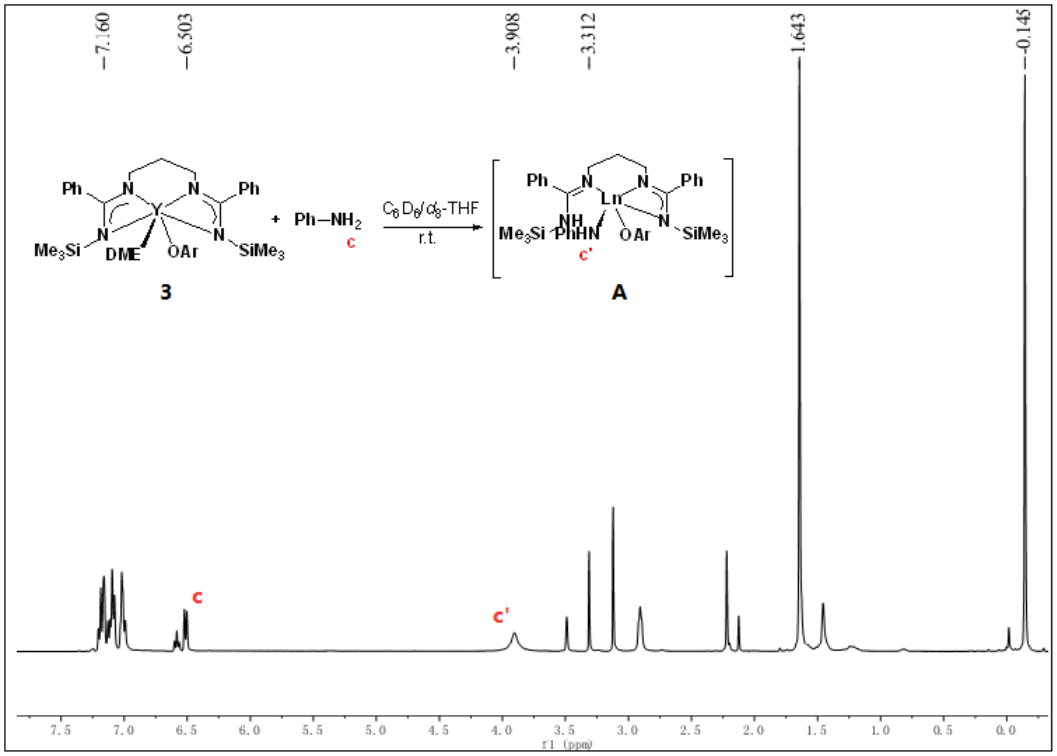


Figure S26 ^{1}H NMR spectrum of the reaction of **3** with 1 equiv of $PhNH_2$ in the mixture of C_6D_6 and d_8-THF at room temperature in 2.5h.

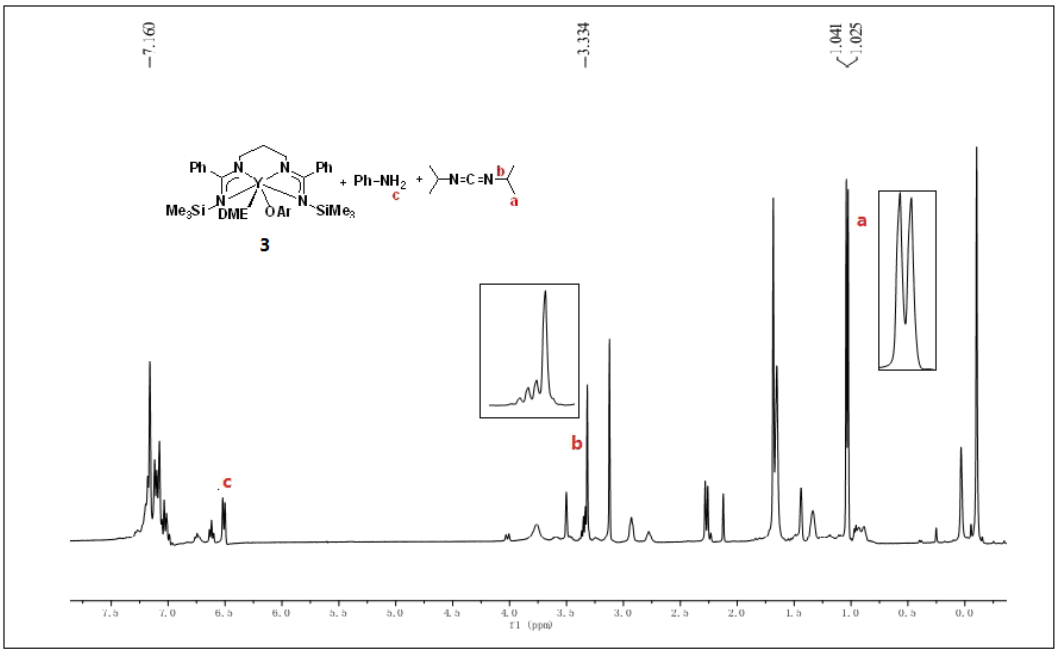


Figure S27 ^{1}H NMR spectrum of the reaction of **3** with 1 equiv of $PhNH_2$ and ^{i}PrNCN^{i}Pr in the mixture of C_6D_6 and d_8-THF at room temperature in 15 minutes.

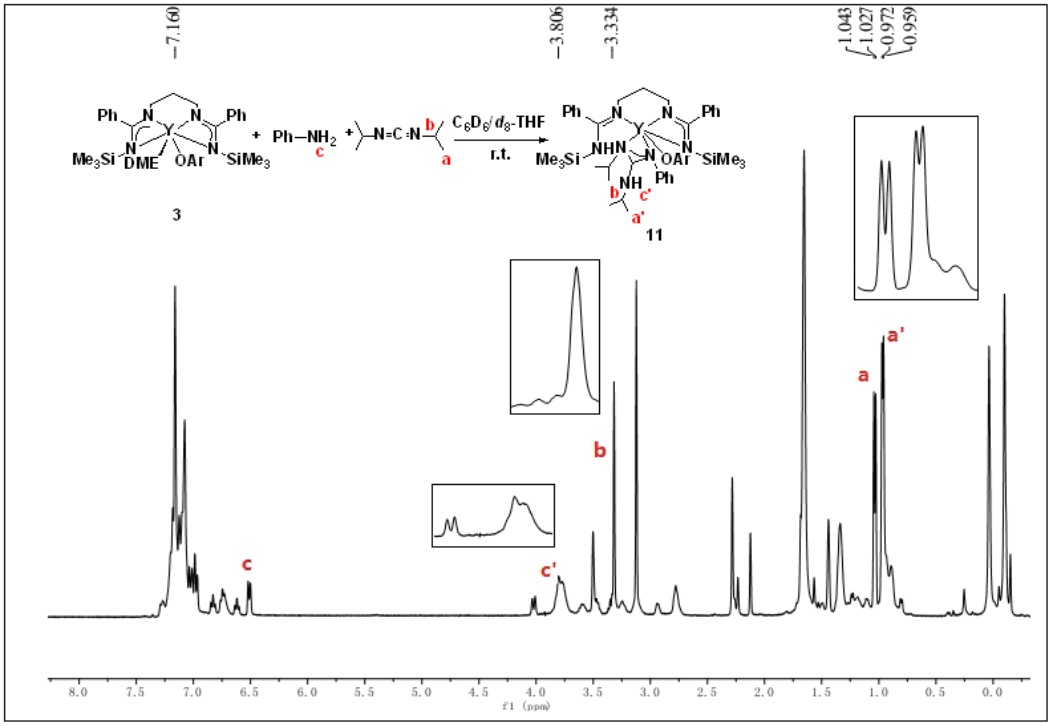


Figure S28 ^{1}H NMR spectrum of the reaction of **3** with 1 equiv of $PhNH_2$ and $^{i}PrNCN^{i}Pr$ in the mixture of C_6D_6 and d_8-THF at room temperature in 20h.

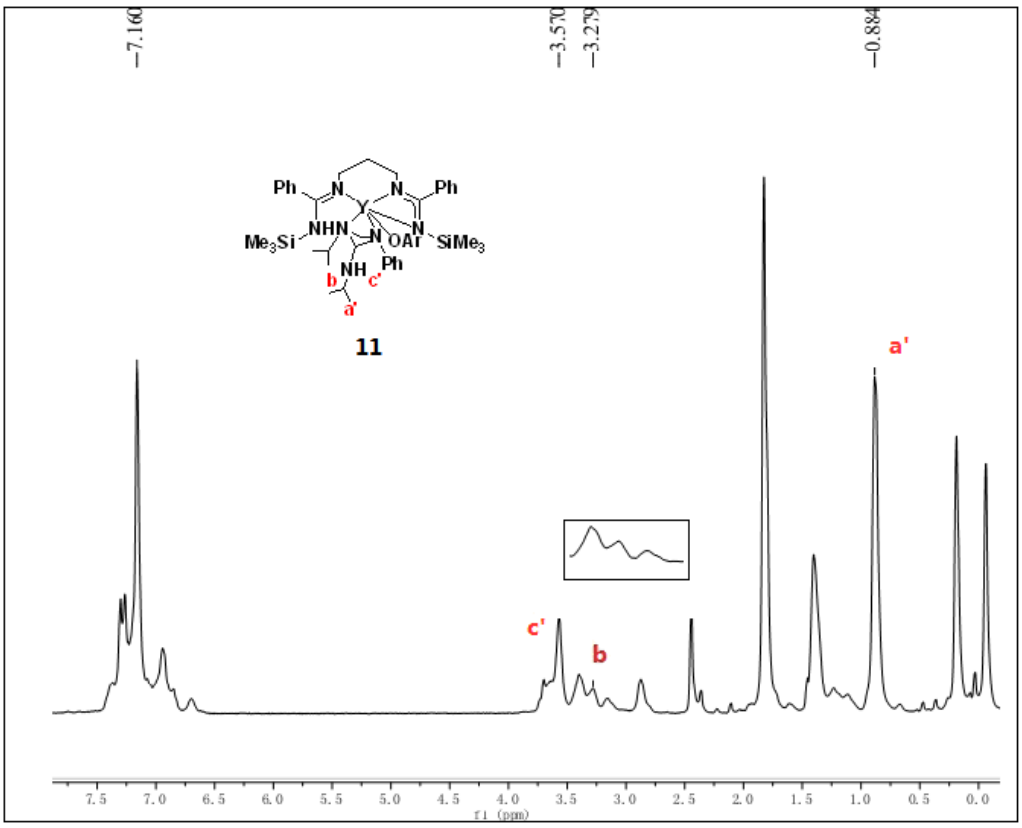


Figure S29 ^{1}H NMR spectrum of complex **11** in C_6D_6.

References

1 T. G. Ong, G. P. A. Yap and D. S. Richeson, *J. Am. Chem. Soc.* 2003, **125**, 8100.

2 A. R. Katritzky, N. M. Khashab and S. Bobrov, *Helv. Chim. Acta*. 2005, **88**, 1664.

3 X. M. Zhang, C. Y. Wang, C. W. Qian, F. B. Han, F. Xu and Q. Shen, *Tetrahedron* 2011, **67**, 8790.

4 E. W. Thomas, E. E. Nishizawa, D. C. Zimmermann and D. J. Williams, *J. Med. Chem.* 1989, **32**, 228.

5 Q. H. Li, S. W. Wang, S. L. Zhou, G. S. Yang, X. C. Zhu and Y. Y. Liu, *J. Org. Chem.* 2007, **72**, 6763.