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Supporting Information

Synthesis, structure and catalytic activity of new homoleptic Lanthanide(III) tris-(cyclopropylethinylamidinates).

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Crystallographic Data

Crystal Data Collection, Structure Solution, and Refinement

The intensity data of **2d** and **4** were collected on a Stoe IPDS 2T diffractometer with MoKα radiation. The data were collected with the Stoe XAREA[1] program using ω-scans. The space groups were determined with the XRED32[1] program.

The structures were solved by direct methods (SHELXS-97) and refined by full matrix least-squares methods on F^2 using SHELXL-97.[2]

1. Stoe, XAREA Program for Xray Crystal Data collection, (XRED32 included in XAREA) (Stoe, 2002)

2. (a) G. M. Sheldrick, *SHELXL-97 Program for Crystal Structure Refinement*, Universität Göttingen (Germany) **1997**; (b) G. M. Sheldrick, *SHELXS-97 Program for Crystal Structure Solution*, Universität Göttingen (Germany) **1997**.

NMR spectra (C_6D_6, 25 °C) of 2a

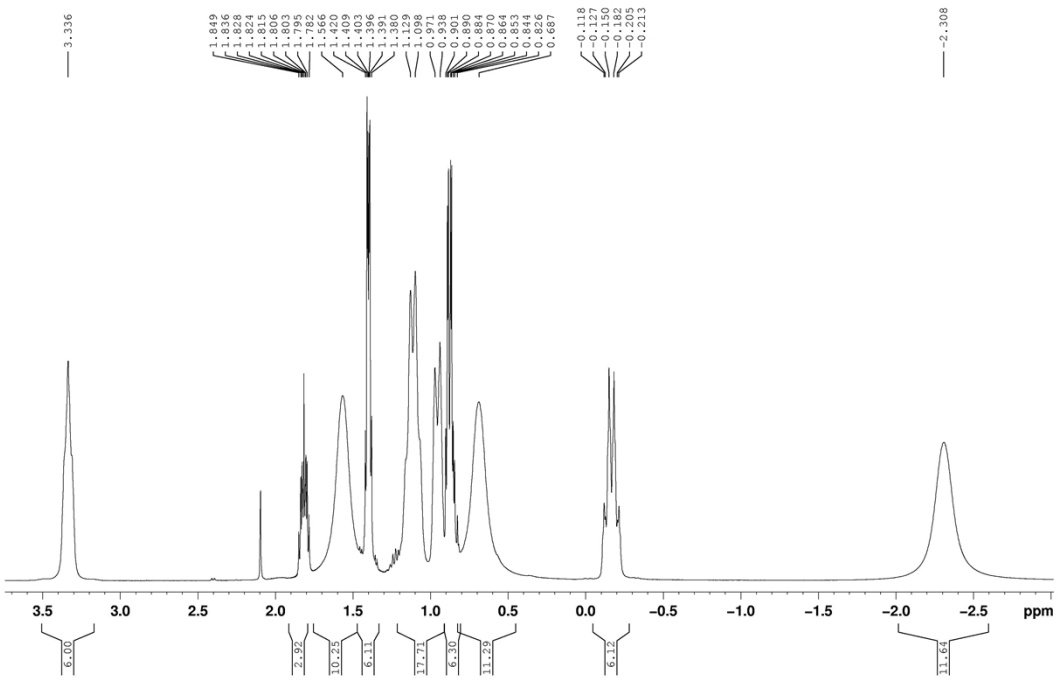

Fig. S1 ^{1}H NMR spectrum (C_6D_6, 25°C) of [*c*-C_3H_5-C≡CC(NCy)$_2$]$_3$Sm (**2a**)

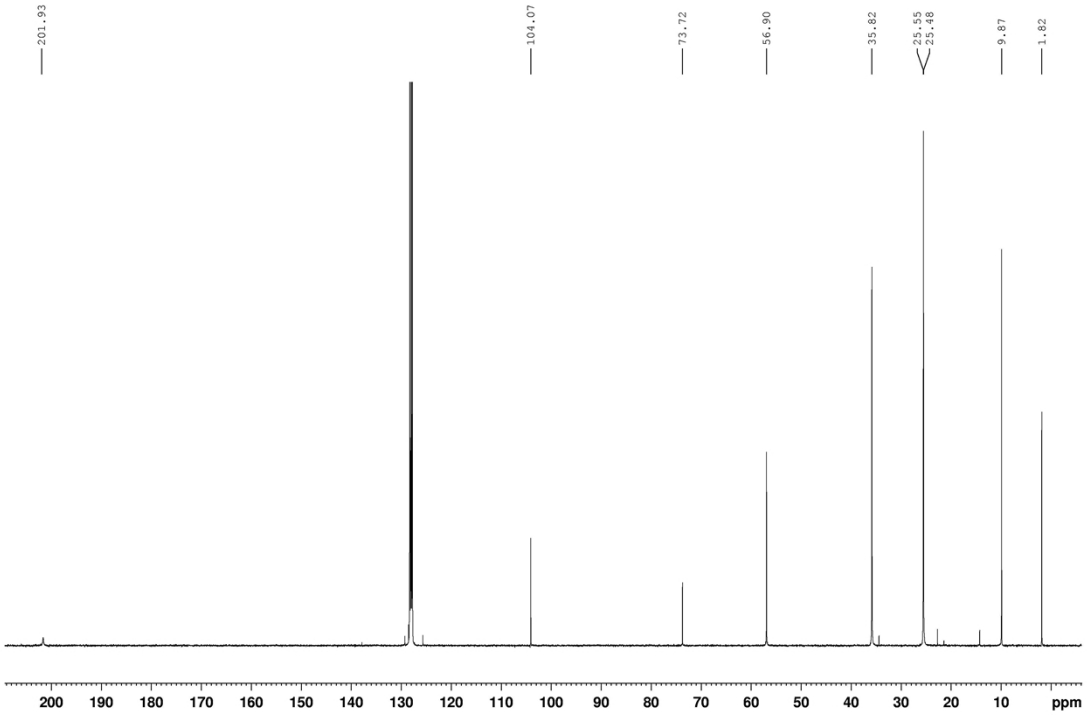

Fig. S2 ^{13}C NMR spectrum (C_6D_6, 25°C) of [*c*-C_3H_5-C≡CC(NCy)$_2$]$_3$Sm (**2a**)

(^{1}H-^{13}C) HSQC spectrum of 2a

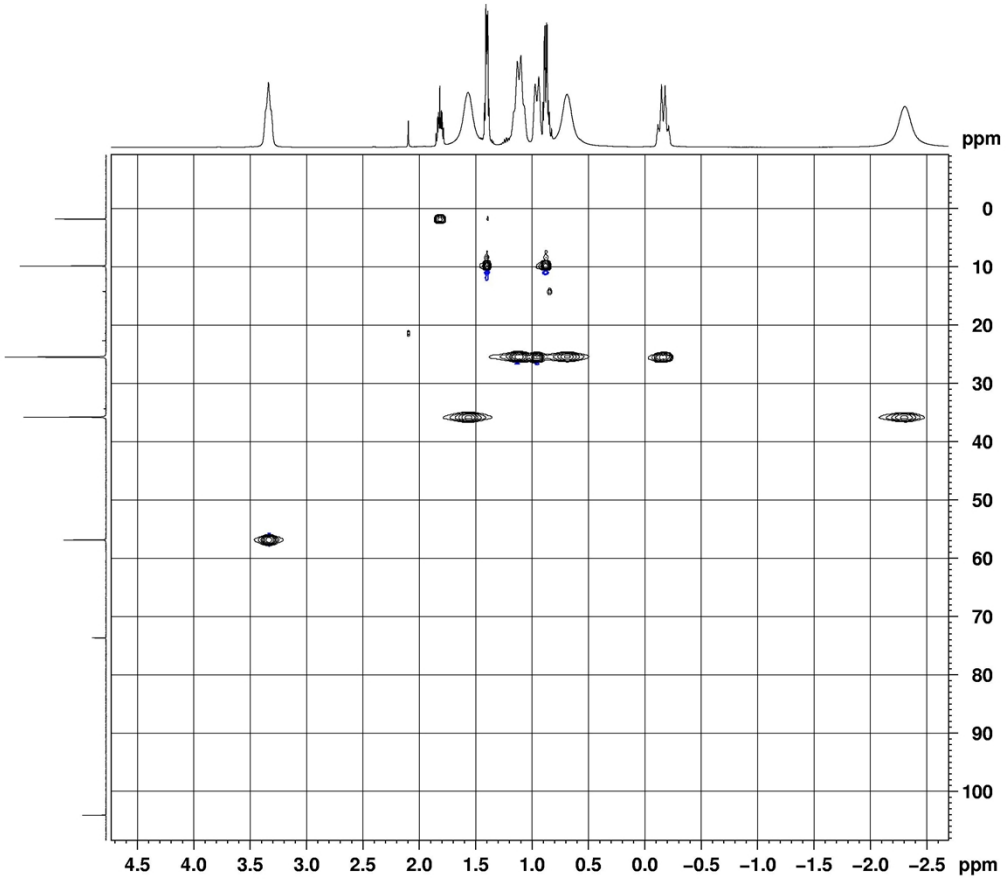

Fig. S3 2D (H, C- correlation via ^{1}J (C, H)) spectrum of [*c*-C_3H_5-C≡CC(NCy)$_2$]$_3$Sm (**2a**)

NMR spectra (C_6D_6, 25 °C) of 2b

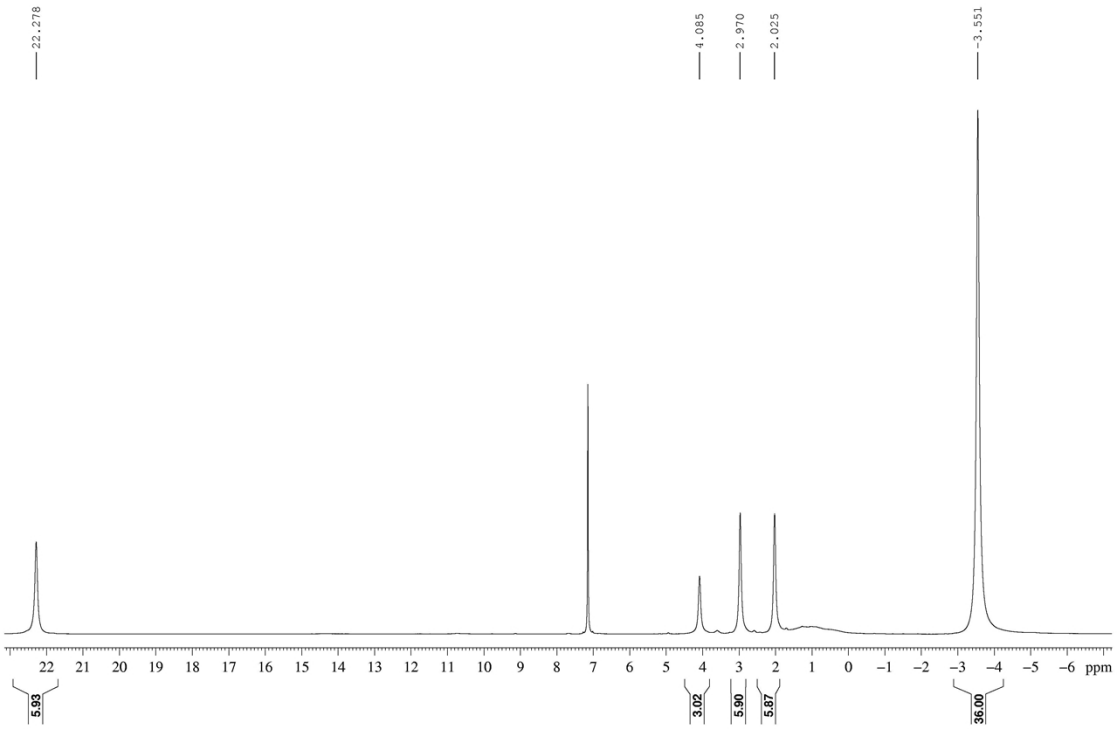

Fig. S4 ^{1}H NMR spectrum (C_6D_6, 25°C) of [*c*-C_3H_5-C≡CC(N^{i}Pr)$_2$]$_3$Nd (**2b**)

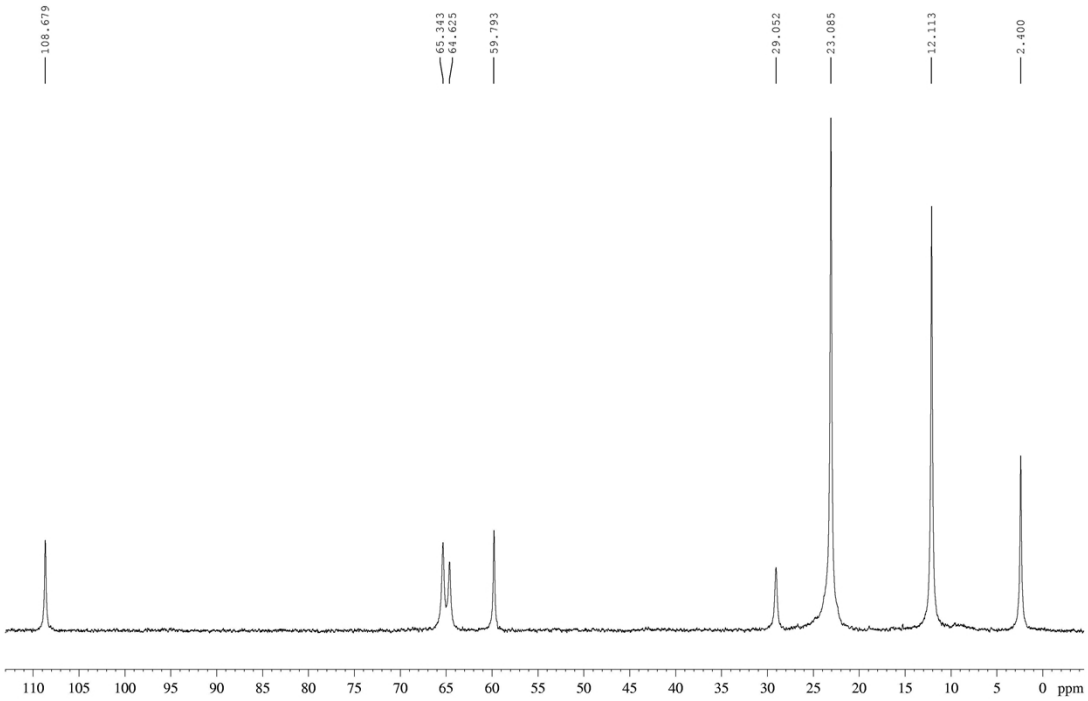

Fig. S5 ^{13}C NMR spectrum (C_6D_6, 25°C) of [*c*-C_3H_5-C≡CC(N^{i}Pr)$_2$]$_3$Nd (**2b**)

(^{1}H-^{13}C) HSQC spectrum of 2b

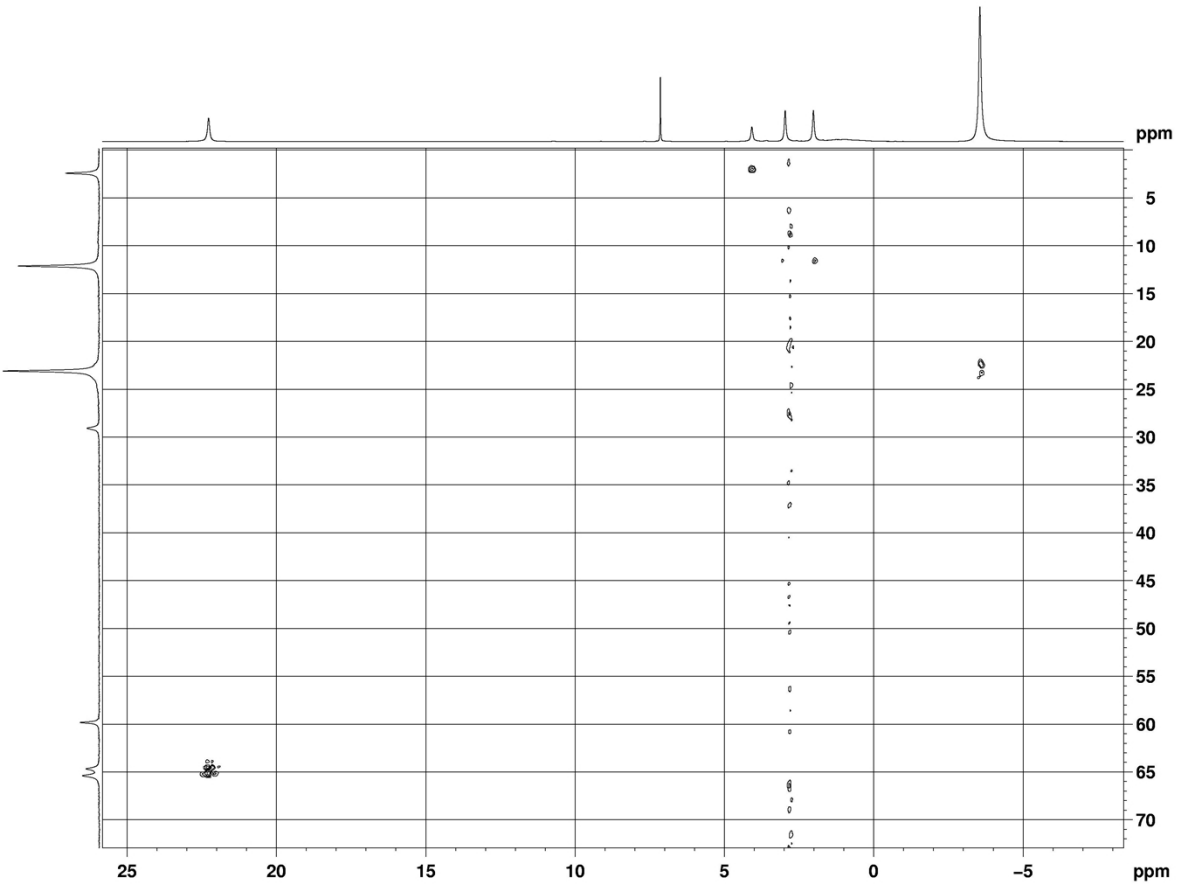

Fig. S6 2D (H, C- correlation via ^{1}J (C, H)) spectrum of [*c*-C_3H_5-C≡CC(N^{i}Pr)$_2$]$_3$Nd (**2b**)

NMR spectra (C_6D_6, 25 °C) of 2c

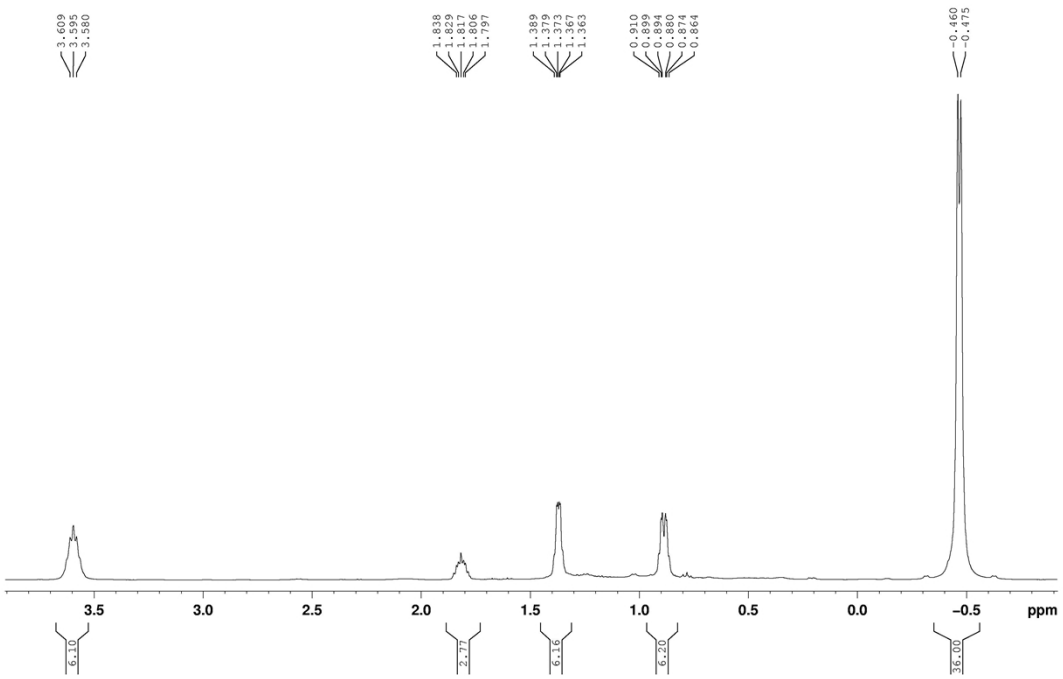

Fig. S7 ^{1}H NMR spectrum (C_6D_6, 25°C) of [*c*-C_3H_5-C≡CC(N^{i}Pr)$_2$]$_3$Sm (**2c**)

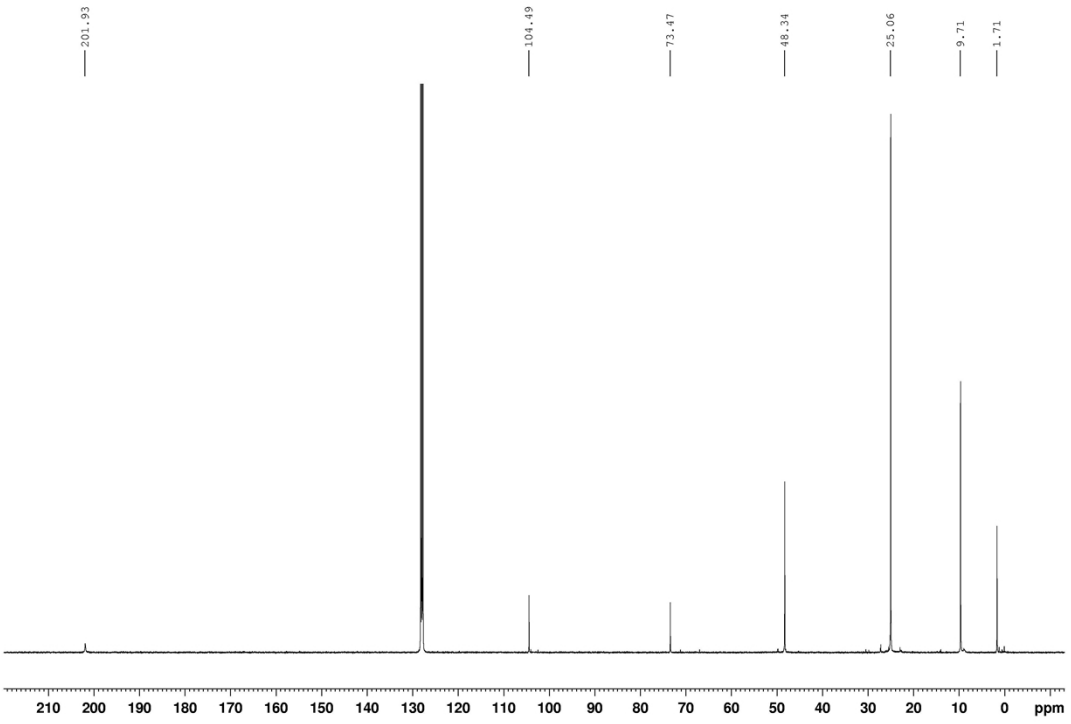

Fig. S8 ^{13}C NMR spectrum (C_6D_6, 25°C) of [*c*-C_3H_5-C≡CC(N^{i}Pr)$_2$]$_3$Sm (**2c**)

(^{1}H-^{13}C) HSQC spectrum of 2c

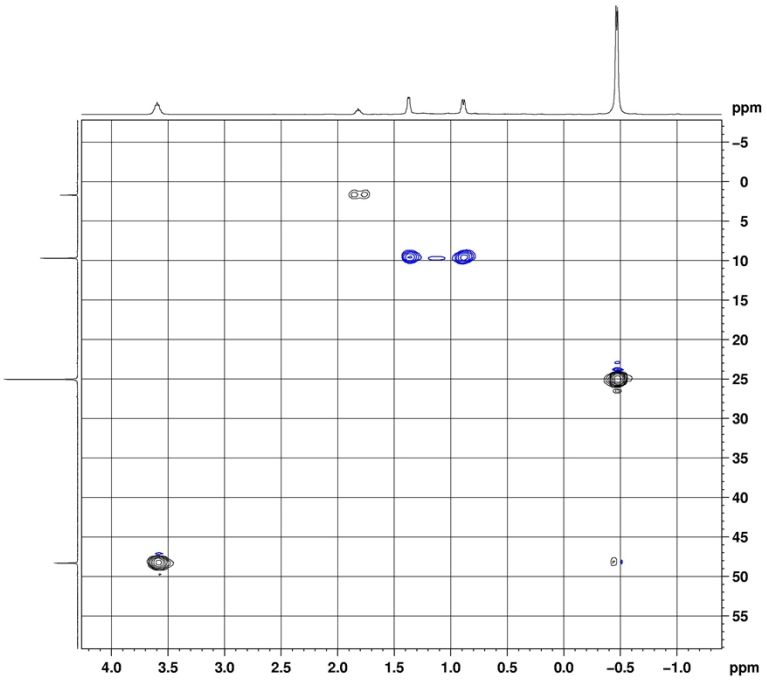

Fig S9 2D (H, C- correlation via ^{1}J (C, H)) spectrum of [*c*-C_3H_5-C≡CC(N^{i}Pr)$_2$]$_3$Sm (**2c**)

(^{13}C NMR) spectrum (C_6D_6, 25 °C) of 2d

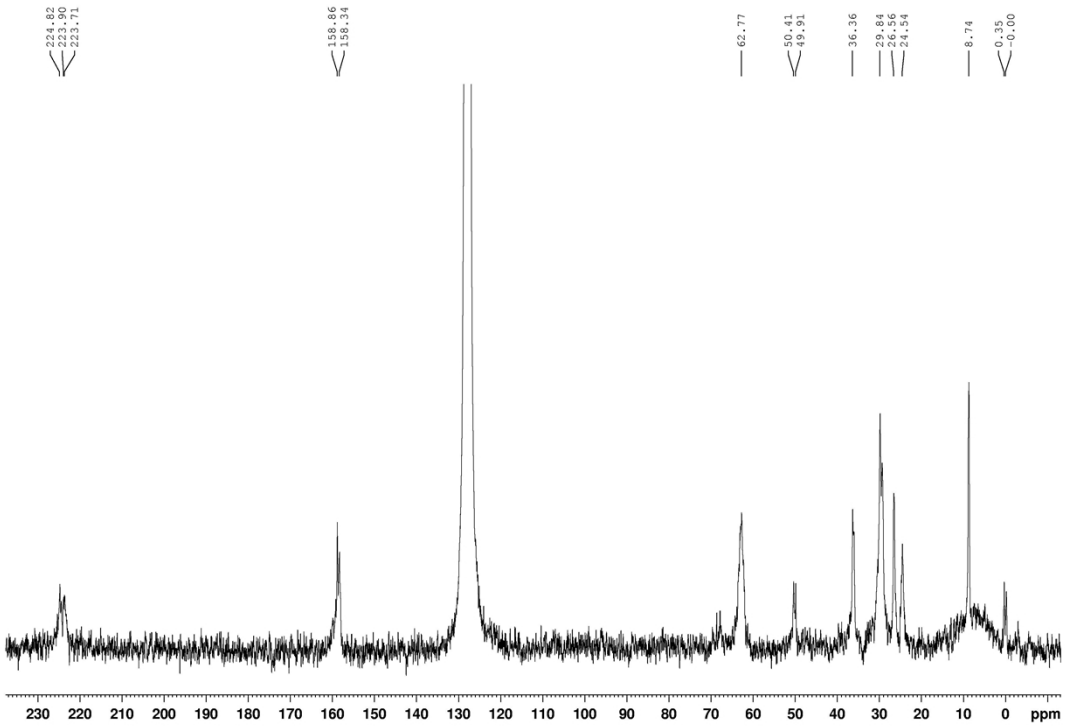

Fig. S10 ^{13}C NMR spectrum (C_6D_6, 25°C) of [*c*-C_3H_5-C≡CC(N^{i}Pr)$_2$]$_3$Ho (**2d**)

Table S1 Crystal data and structure refinement of **2d**

Identification code	ip298	
Empirical formula	$C_{36}H_{57}HoN_6$	
Formula weight	738.81	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.776(2) Å	α= 101.28(3)°
	b = 13.149(3) Å	β= 105.35(3)°
	c = 16.983(3) Å	γ = 108.19(3)°
Volume	1905.6(7) $Å^3$	
Z	2	
Density (calculated)	1.288 Mg/m^3	
Absorption coefficient	2.106 mm^{-1}	
F(000)	764	
Crystal size	0.40 x 0.40 x 0.20 mm^3	
Theta range for data collection	2.31 to 29.21°	
Index ranges	-13<=h<=13, -18<=k<=18, -19<=l<=23	
Reflections collected	21302	
Independent reflections	10209 [R(int) = 0.0600]	
Completeness to theta = 29.21°	98.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10209 / 38 / 461	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0343, wR2 = 0.0890	
R indices (all data)	R1 = 0.0379, wR2 = 0.0907	
Extinction coefficient	0.0091(7)	
Largest diff. peak and hole	2.496 and -1.758 $e.Å^{-3}$	

Table S2 Bond lengths [Å] and angles [°] of **2d**

Ho-N(5)	2.342(2)	C(7)-C(8)	1.513(11)
Ho-N(3)	2.348(2)	C(7)-C(9)	1.529(11)
Ho-N(2)	2.351(3)	C(7')-C(9')	1.530(14)
Ho-N(4)	2.353(3)	C(7')-C(8')	1.536(13)
Ho-N(1)	2.359(3)	C(10)-C(11)	1.508(6)
Ho-N(6)	2.383(3)	C(10)-C(12)	1.517(6)
Ho-C(13)	2.755(3)	C(13)-C(14)	1.449(4)
Ho-C(1)	2.756(3)	C(14)-C(15)	1.185(4)
Ho-C(25)	2.773(3)	C(15)-C(16)	1.443(5)
N(1)-C(1)	1.312(4)	C(16)-C(18)	1.469(7)
N(1)-C(7')	1.42(3)	C(16)-C(17)	1.492(5)
N(1)-C(7)	1.481(14)	C(17)-C(18)	1.445(7)
N(2)-C(1)	1.327(4)	C(19)-C(21)	1.510(5)
N(2)-C(10)	1.460(4)	C(19)-C(20)	1.521(6)
N(3)-C(13)	1.333(4)	C(22)-C(23)	1.503(13)
N(3)-C(19)	1.458(4)	C(22)-C(24)	1.514(13)
N(4)-C(13)	1.331(4)	C(22')-C(23')	1.506(12)
N(4)-C(22')	1.44(2)	C(22')-C(24')	1.518(11)
N(4)-C(22)	1.472(18)	C(25)-C(26)	1.453(4)
N(5)-C(25)	1.333(4)	C(26)-C(27)	1.184(5)
N(5)-C(31)	1.461(3)	C(27)-C(28)	1.446(5)
N(6)-C(25)	1.324(3)	C(28)-C(29)	1.441(12)
N(6)-C(34)	1.461(4)	C(28)-C(30)	1.496(10)
C(1)-C(2)	1.461(5)	C(29)-C(30)	1.416(16)
C(2)-C(3)	1.182(6)	C(31)-C(33)	1.513(5)
C(3)-C(4)	1.496(7)	C(31)-C(32)	1.528(5)
C(4)-C(6)	1.441(8)	C(34)-C(36)	1.514(5)
C(4)-C(5)	1.470(7)	C(34)-C(35)	1.520(6)
C(5)-C(6)	1.440(9)		
N(5)-Ho-N(3)	153.11(10)	N(3)-Ho-N(1)	100.01(11)
N(5)-Ho-N(2)	98.77(10)	N(2)-Ho-N(1)	57.08(9)
N(3)-Ho-N(2)	103.76(10)	N(4)-Ho-N(1)	101.28(11)
N(5)-Ho-N(4)	106.03(10)	N(5)-Ho-N(6)	57.14(8)
N(3)-Ho-N(4)	57.74(9)	N(3)-Ho-N(6)	101.51(9)
N(2)-Ho-N(4)	150.92(10)	N(2)-Ho-N(6)	107.47(10)
N(5)-Ho-N(1)	104.51(10)	N(4)-Ho-N(6)	98.74(11)

N(1)-Ho-N(6)	156.20(10)	C(22)-N(4)-Ho	144.0(9)
N(5)-Ho-C(13)	131.91(10)	C(25)-N(5)-C(31)	121.1(2)
N(3)-Ho-C(13)	28.89(9)	C(25)-N(5)-Ho	93.91(17)
N(2)-Ho-C(13)	129.31(10)	C(31)-N(5)-Ho	143.8(2)
N(4)-Ho-C(13)	28.85(9)	C(25)-N(6)-C(34)	120.5(3)
N(1)-Ho-C(13)	101.97(10)	C(25)-N(6)-Ho	92.33(17)
N(6)-Ho-C(13)	101.78(9)	C(34)-N(6)-Ho	146.68(19)
N(5)-Ho-C(1)	102.01(9)	N(1)-C(1)-N(2)	117.0(3)
N(3)-Ho-C(1)	104.81(10)	N(1)-C(1)-C(2)	120.9(3)
N(2)-Ho-C(1)	28.74(9)	N(2)-C(1)-C(2)	122.0(3)
N(4)-Ho-C(1)	127.90(11)	N(1)-C(1)-Ho	58.75(16)
N(1)-Ho-C(1)	28.39(9)	N(2)-C(1)-Ho	58.43(16)
N(6)-Ho-C(1)	133.32(10)	C(2)-C(1)-Ho	176.1(2)
C(13)-Ho-C(1)	119.61(10)	C(3)-C(2)-C(1)	176.1(5)
N(5)-Ho-C(25)	28.66(8)	C(2)-C(3)-C(4)	175.2(6)
N(3)-Ho-C(25)	128.45(9)	C(6)-C(4)-C(5)	59.3(4)
N(2)-Ho-C(25)	104.65(9)	C(6)-C(4)-C(3)	117.8(5)
N(4)-Ho-C(25)	104.39(10)	C(5)-C(4)-C(3)	116.0(5)
N(1)-Ho-C(25)	131.54(10)	C(6)-C(5)-C(4)	59.3(4)
N(6)-Ho-C(25)	28.49(8)	C(5)-C(6)-C(4)	61.4(4)
C(13)-Ho-C(25)	119.97(9)	N(1)-C(7)-C(8)	110.0(9)
C(1)-Ho-C(25)	120.41(9)	N(1)-C(7)-C(9)	112.1(9)
C(1)-N(1)-C(7')	116.5(8)	C(8)-C(7)-C(9)	108.6(9)
C(1)-N(1)-C(7)	124.7(6)	N(1)-C(7')-C(9')	107.4(13)
C(7')-N(1)-C(7)	13.6(9)	N(1)-C(7')-C(8')	108.1(15)
C(1)-N(1)-Ho	92.86(19)	C(9')-C(7')-C(8')	105.3(13)
C(7')-N(1)-Ho	150.4(8)	N(2)-C(10)-C(11)	111.0(3)
C(7)-N(1)-Ho	141.5(5)	N(2)-C(10)-C(12)	108.6(3)
C(1)-N(2)-C(10)	120.7(3)	C(11)-C(10)-C(12)	112.2(4)
C(1)-N(2)-Ho	92.83(18)	N(4)-C(13)-N(3)	116.9(3)
C(10)-N(2)-Ho	145.6(2)	N(4)-C(13)-C(14)	122.0(3)
C(13)-N(3)-C(19)	120.9(3)	N(3)-C(13)-C(14)	121.1(3)
C(13)-N(3)-Ho	92.74(18)	N(4)-C(13)-Ho	58.56(15)
C(19)-N(3)-Ho	144.9(2)	N(3)-C(13)-Ho	58.37(15)
C(13)-N(4)-C(22')	120.3(7)	C(14)-C(13)-Ho	178.0(2)
C(13)-N(4)-C(22)	122.4(9)	C(15)-C(14)-C(13)	177.7(4)
C(22')-N(4)-C(22)	4.7(14)	C(14)-C(15)-C(16)	177.5(3)
C(13)-N(4)-Ho	92.59(18)	C(15)-C(16)-C(18)	120.0(4)
C(22')-N(4)-Ho	146.9(7)	C(15)-C(16)-C(17)	118.5(3)

C(18)-C(16)-C(17)	58.4(3)	N(5)-C(25)-Ho	57.43(15)
C(18)-C(17)-C(16)	60.0(3)	C(26)-C(25)-Ho	177.5(2)
C(17)-C(18)-C(16)	61.6(3)	C(27)-C(26)-C(25)	172.3(3)
N(3)-C(19)-C(21)	109.5(3)	C(26)-C(27)-C(28)	176.0(4)
N(3)-C(19)-C(20)	109.8(3)	C(29)-C(28)-C(27)	120.1(6)
C(21)-C(19)-C(20)	110.2(4)	C(29)-C(28)-C(30)	57.6(7)
N(4)-C(22)-C(23)	110.4(13)	C(27)-C(28)-C(30)	118.2(5)
N(4)-C(22)-C(24)	109.6(13)	C(30)-C(29)-C(28)	63.1(7)
C(23)-C(22)-C(24)	109.0(13)	C(29)-C(30)-C(28)	59.2(6)
N(4)-C(22')-C(23')	109.6(12)	N(5)-C(31)-C(33)	108.2(3)
N(4)-C(22')-C(24')	108.8(13)	N(5)-C(31)-C(32)	110.2(3)
C(23')-C(22')-C(24')	108.7(12)	C(33)-C(31)-C(32)	110.7(3)
N(6)-C(25)-N(5)	116.6(3)	N(6)-C(34)-C(36)	109.0(3)
N(6)-C(25)-C(26)	123.3(3)	N(6)-C(34)-C(35)	109.3(3)
N(5)-C(25)-C(26)	120.1(2)	C(36)-C(34)-C(35)	110.0(3)
N(6)-C(25)-Ho	59.18(15)		

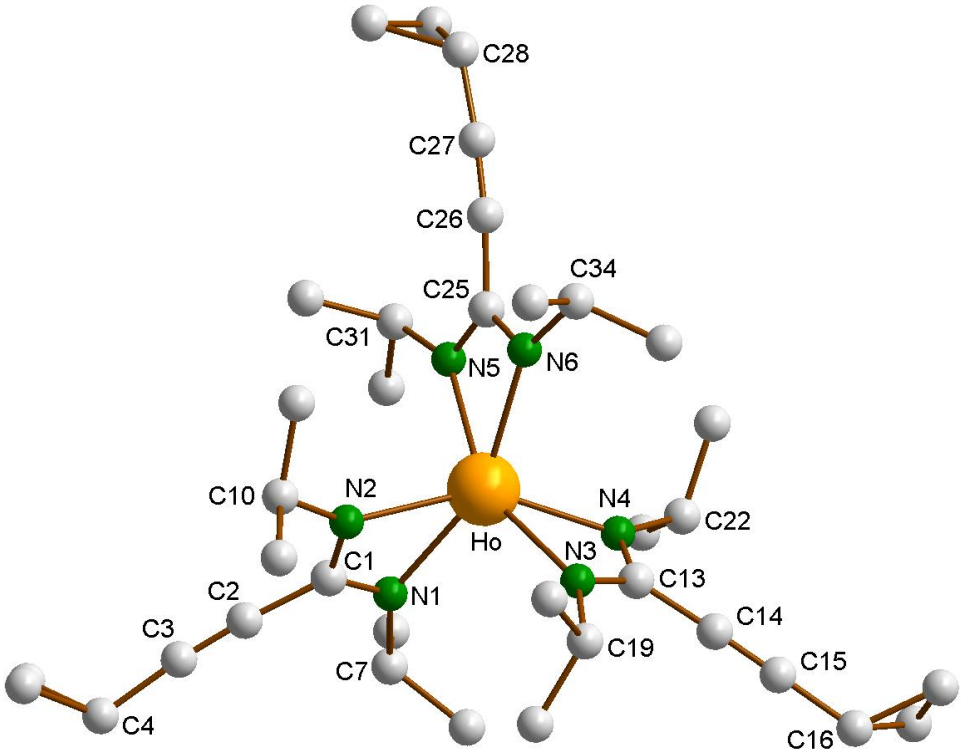

Fig. S11 Molecular structure of complex [*c*-C_3H_5-C≡CC(N^{i}Pr)$_2$]$_3$Ho (**2d**)

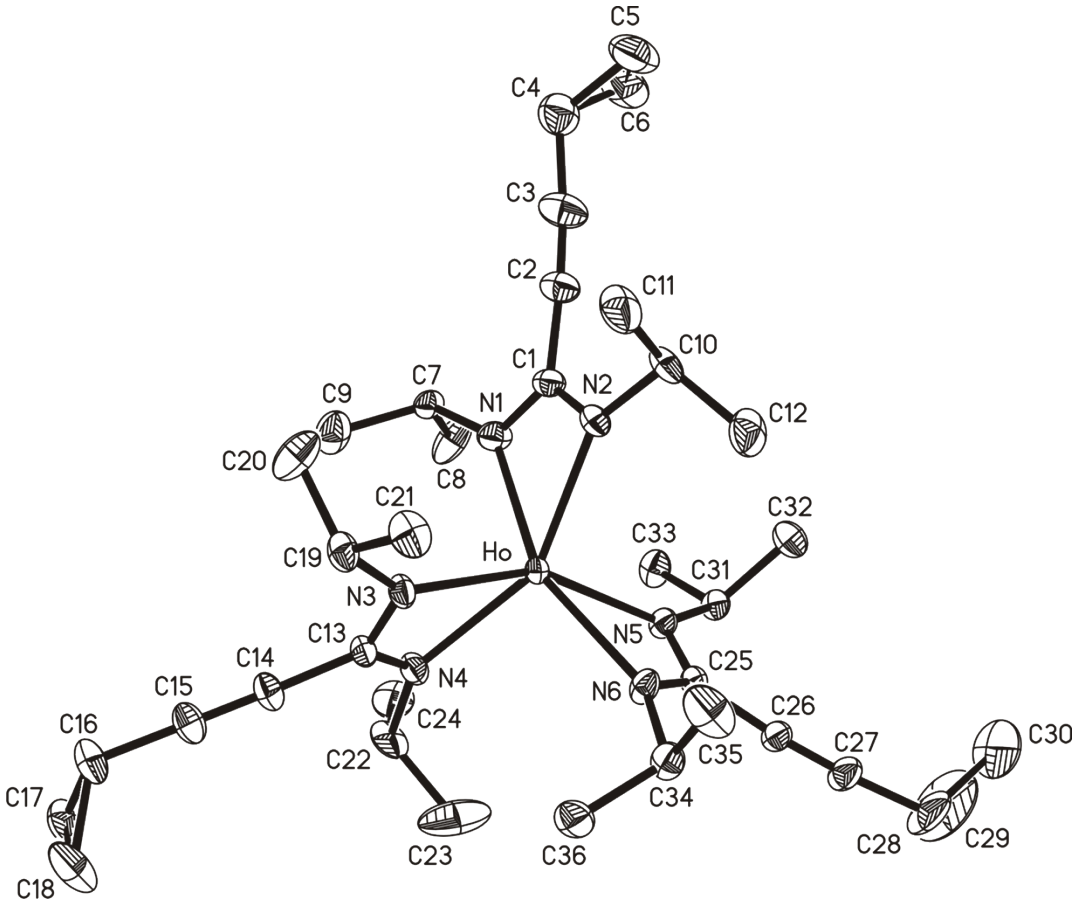

Fig. S12 ORTEP drawing of the molecular structure of [*c*-C_3H_5-C≡CC(N^{i}Pr)$_2$]$_3$Ho (**2d**)

Table S3 Crystal data and structure refinement of **4**

Identification code	ip376	
Empirical formula	$C_{21}H_{28}N_2$	
Formula weight	308.45	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.7257(19) Å	α= 70.77(3)°
	b = 10.383(2) Å	β= 65.92(3)°
	c = 10.558(2) Å	γ = 70.83(3)°
Volume	895.5(3) $Å^3$	
Z	2	
Density (calculated)	1.144 Mg/m^3	
Absorption coefficient	0.067 mm^{-1}	
F(000)	336	
Crystal size	0.34 x 0.23 x 0.22 mm^3	
Theta range for data collection	2.13 to 26.37°	
Index ranges	-12<=h<=11, -12<=k<=12, -13<=l<=12	
Reflections collected	7657	
Independent reflections	3625 [R(int) = 0.0479]	
Completeness to theta = 26.37°	99.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3625 / 157 / 267	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0535, wR2 = 0.1411	
R indices (all data)	R1 = 0.0717, wR2 = 0.1512	
Largest diff. peak and hole	0.198 and -0.223 $e.Å^{-3}$	

Table S4. Bond lengths [Å] and angles [°] of **4**

N(1)-C(1)	1.364(2)	C(13)-C(14)	1.516(4)
N(1)-C(10)	1.451(3)	C(14)-C(15)	1.521(3)
C(1)-N(2)	1.275(2)	N(2)-C(16)	1.457(7)
C(1)-C(2)	1.451(2)	N(2)-C(16')	1.513(11)
C(2)-C(3)	1.195(3)	C(16)-C(21)	1.505(8)
C(3)-C(4)	1.436(2)	C(16)-C(17)	1.519(7)
C(4)-C(5)	1.393(3)	C(17)-C(18)	1.528(4)
C(4)-C(9)	1.394(2)	C(18)-C(19)	1.525(8)
C(5)-C(6)	1.379(3)	C(19)-C(20)	1.510(9)
C(6)-C(7)	1.381(3)	C(20)-C(21)	1.683(8)
C(7)-C(8)	1.379(3)	C(16')-C(17')	1.506(11)
C(8)-C(9)	1.381(3)	C(16')-C(21')	1.537(11)
C(10)-C(11)	1.515(3)	C(17')-C(18')	1.529(7)
C(10)-C(15)	1.515(3)	C(18')-C(19')	1.480(11)
C(11)-C(12)	1.518(4)	C(19')-C(20')	1.399(12)
C(12)-C(13)	1.508(4)	C(20')-C(21')	1.491(11)
C(1)-N(1)-C(10)	125.79(15)	C(10)-C(15)-C(14)	111.94(18)
N(2)-C(1)-N(1)	121.93(17)	C(1)-N(2)-C(16)	117.4(4)
N(2)-C(1)-C(2)	125.55(17)	C(1)-N(2)-C(16')	118.2(6)
N(1)-C(1)-C(2)	112.52(15)	C(16)-N(2)-C(16')	14.3(6)
C(3)-C(2)-C(1)	176.65(18)	N(2)-C(16)-C(21)	111.0(6)
C(2)-C(3)-C(4)	179.07(18)	N(2)-C(16)-C(17)	106.2(5)
C(5)-C(4)-C(9)	119.58(16)	C(21)-C(16)-C(17)	112.1(6)
C(5)-C(4)-C(3)	120.70(16)	C(16)-C(17)-C(18)	109.3(4)
C(9)-C(4)-C(3)	119.72(16)	C(19)-C(18)-C(17)	110.3(4)
C(6)-C(5)-C(4)	119.82(17)	C(20)-C(19)-C(18)	103.8(6)
C(5)-C(6)-C(7)	120.42(18)	C(19)-C(20)-C(21)	100.9(6)
C(8)-C(7)-C(6)	120.03(18)	C(16)-C(21)-C(20)	101.2(5)
C(7)-C(8)-C(9)	120.30(17)	C(17')-C(16')-N(2)	116.6(9)
C(8)-C(9)-C(4)	119.84(17)	C(17')-C(16')-C(21')	108.6(8)
N(1)-C(10)-C(11)	110.35(17)	N(2)-C(16')-C(21')	105.5(8)
N(1)-C(10)-C(15)	111.42(16)	C(16')-C(17')-C(18')	113.8(6)
C(11)-C(10)-C(15)	110.87(17)	C(19')-C(18')-C(17')	114.6(7)
C(10)-C(11)-C(12)	111.7(2)	C(20')-C(19')-C(18')	113.3(10)
C(13)-C(12)-C(11)	111.5(2)	C(19')-C(20')-C(21')	128.1(10)
C(12)-C(13)-C(14)	111.3(2)	C(20')-C(21')-C(16')	116.4(8)
C(13)-C(14)-C(15)	111.1(2)		

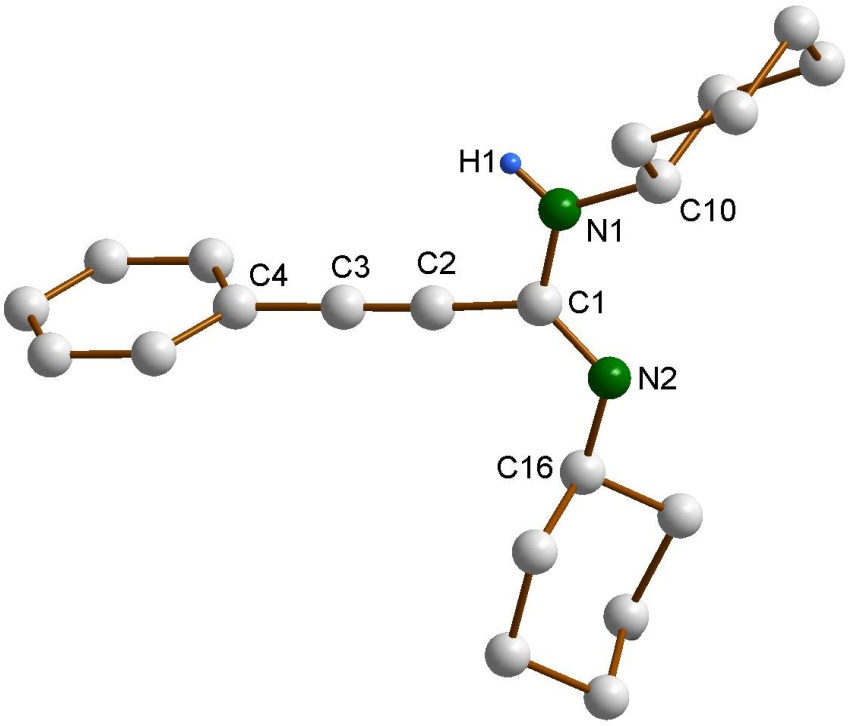

Fig. S13 Molecular structure of C_6H_5–C≡C–C(NHCy)(NCy) (**4**)

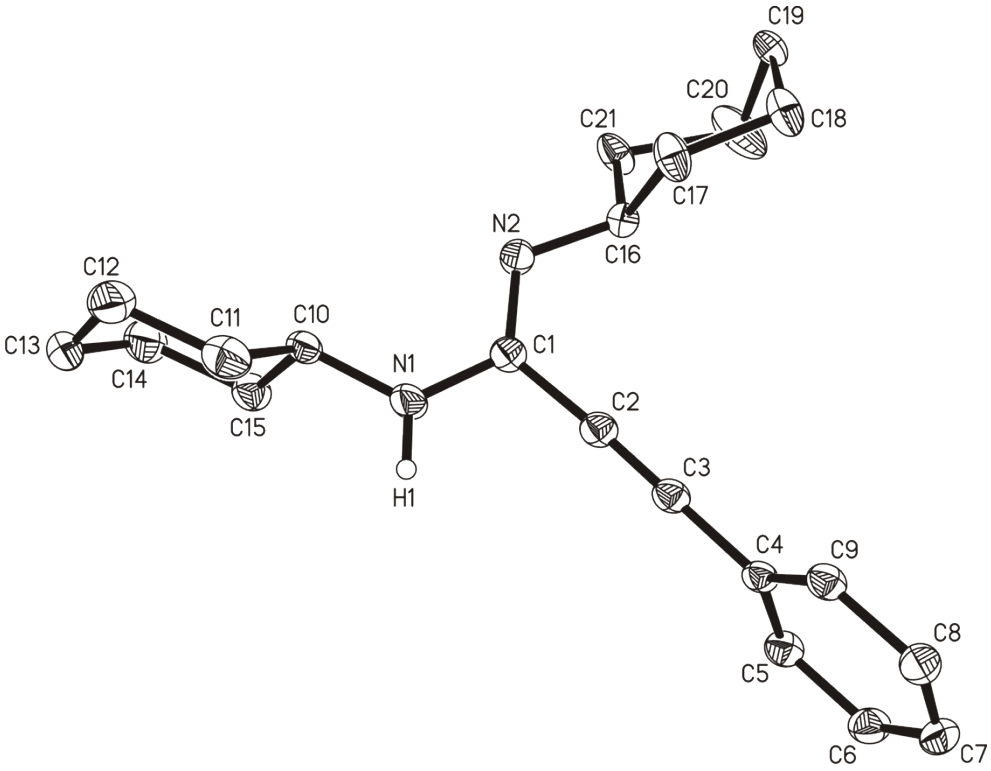

Fig. S14 ORTEP drawing of the molecular structure of C_6H_5–C≡C–C(NHCy)(NCy) (**4**)

NMR data of the propiolamidinates 3-5:

Ph-C≡C-C(N^{i}Pr)(NH^{i}Pr) (3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ = 7.45 – 7.54 (m, 2H), 7.31 – 7.38 (m, 3H), 3.96 (sept, 2H), 1.17 (d, *J* = 6.5 Hz, 12H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ = 179.7, 141.8, 131.9, 129.4, 128.5, 121.4, 88.9, 23.9.

Ph-C≡C-C(NCy)(NHCy) (4). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): *δ* = 7.23 – 7.62 (m, 5H), 3.61 (m, 2H), 0.93 – 2.00 (m, 20H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): *δ* = 141.9, 132.1, 129.4, 126.6, 121.5, 79.8, 34.9, 26.0, 25.2.

***c*-C_3H_5-C≡C-C(NCy)(NHCy) (5)**. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ = 3.39 – 3.48 (m, 2H), 1.54 – 1.84 (m, 10H), 1.35 – 1.49 (m, 1H), 1.10 – 1.34 (m, 10H), 0.89 – 0.94 (m, 2H), 0.76 – 0.81 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ = 141.9, 97.3, 77.3, 66.2, 34.2, 25.8, 24.9, 8.7, –0.4.