Organolanthanide Complexes Supported by Thiazole-Containing Amidopyridinate Ligands: Synthesis, Characterization and Catalytic Activity in the Isoprene Polymerization

Lapo Luconi,[a] Dmitrii M. Lyubov,[b] Andrea Rossin,[a] Tatyana A. Glukhova,[b] Anton V. Cherkasov,[b] Giulia Tuci,[a] Georgy K. Fukin,[b] Alexander A. Trifonov*,[b,c] and Giuliano Giambastiani,*,[a,d]

[a] *Institute of Chemistry of OrganoMetallic Compounds*, ICCOM-CNR, Via Madonna del Piano, 10, 50019 Sesto Fiorentino, (Florence), Italy. Fax: +39 055 5225203.

Email: giuliano.giambastiani@iccom.cnr.it

[b] *G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences*, Tropinina 49, GSP-445, 603950 Nizhny Novgorod, Russia.

Email: trif@iomc.ras.ru

[c] *A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences*, 28 Vavilova str., 119991, Moscow,GSP-1, Russia

[d] *Kazan Federal University*, 420008 Kazan, Russian Federation

Contents:

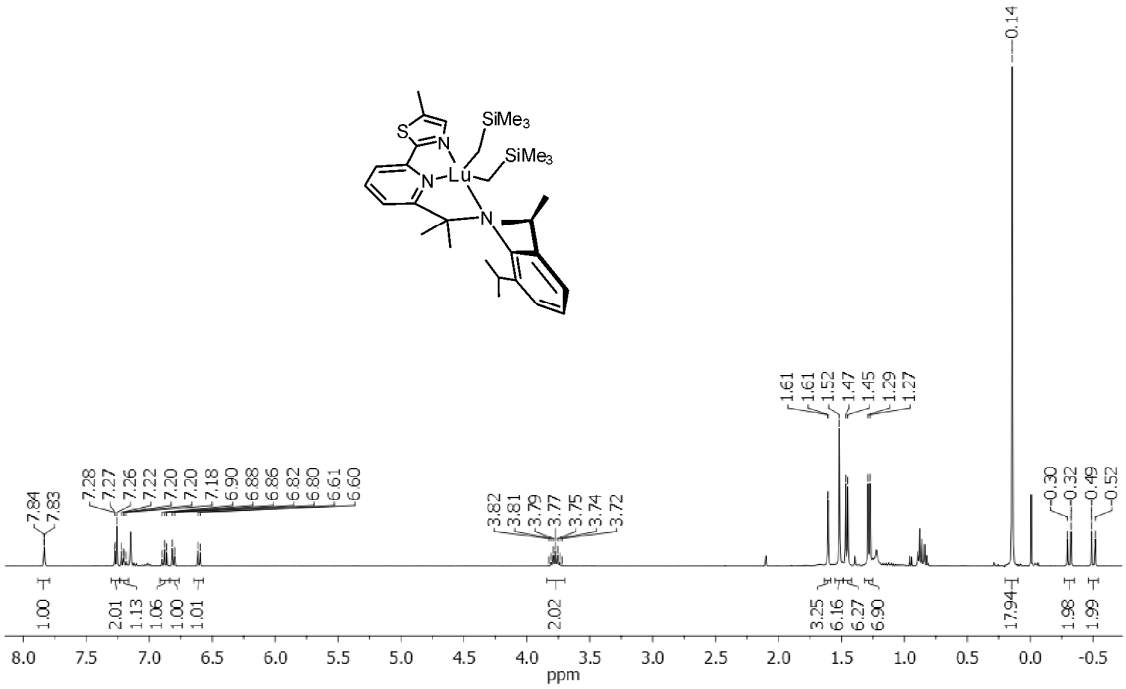

Fig. S1. ^{1}H NMR spectrum (400 MHz, C_6D_6, 293 K) of Lu(κ^3-N,N^{py},N$^-$)(CH_2SiMe_3)$_2$ **3.**

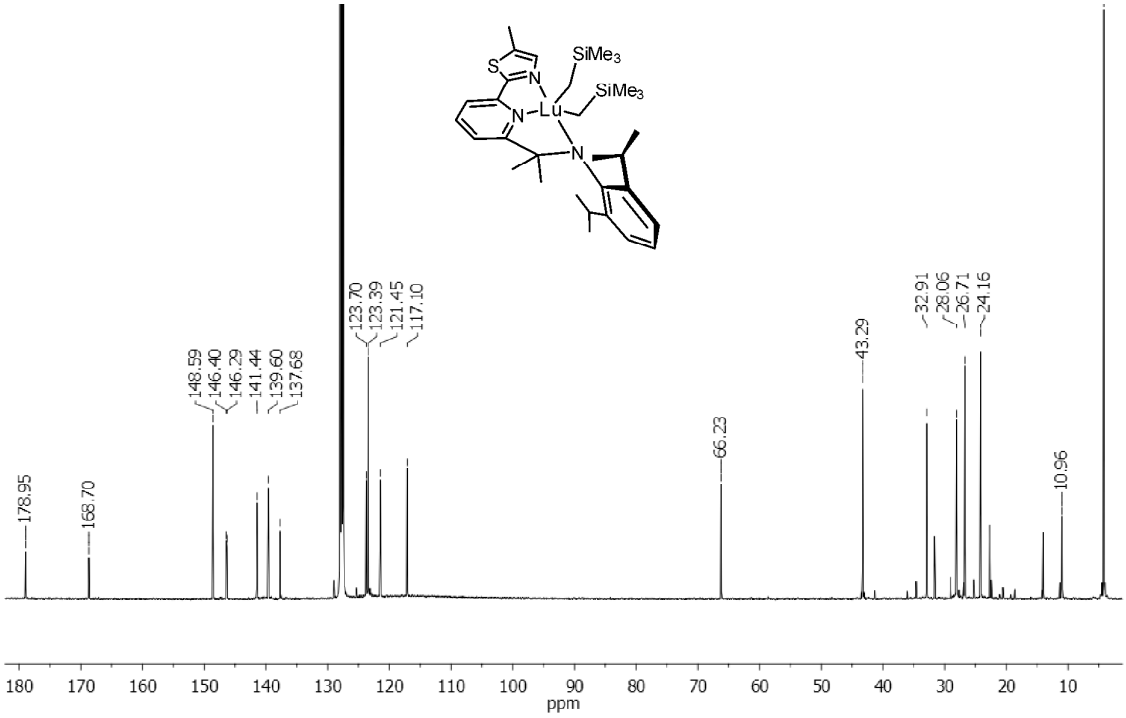

Fig. S2. ^{13}C{^{1}H} NMR spectrum (100 MHz, C_6D_6, 293 K) of Lu(κ^3-N,N^{py},N$^-$)(CH_2SiMe_3)$_2$ **3**.

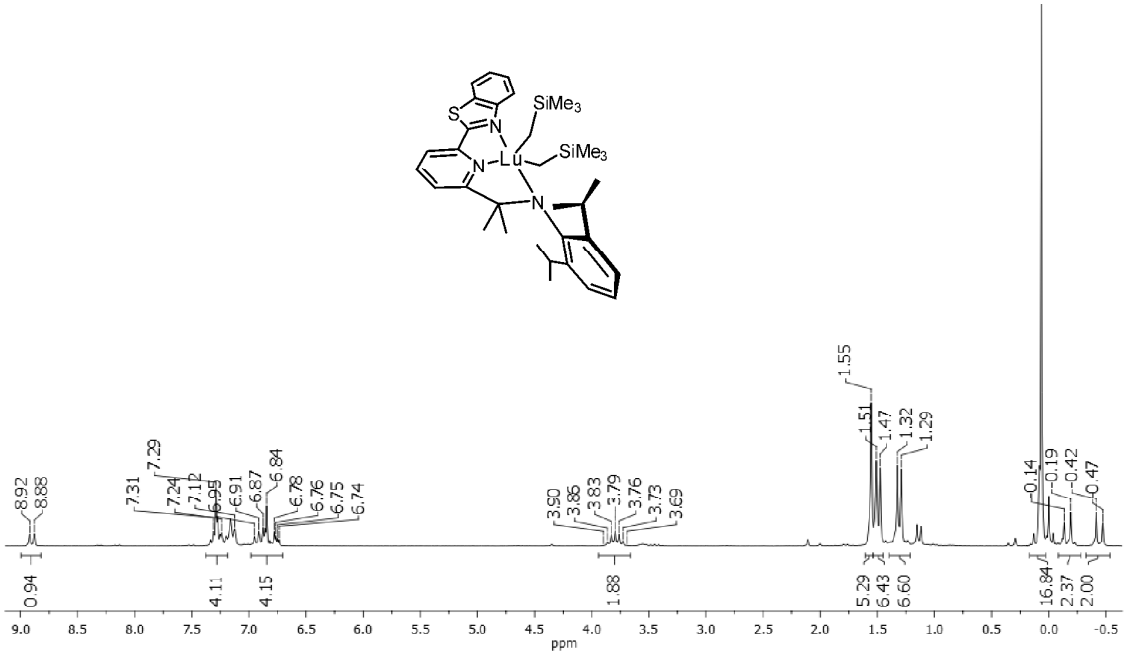

Fig. S3. ^{1}H NMR spectrum (400 MHz, C_6D_6, 293 K) of Lu(κ^3-N,N^{py},N$^-$)(CH_2SiMe_3)$_2$ **5**.

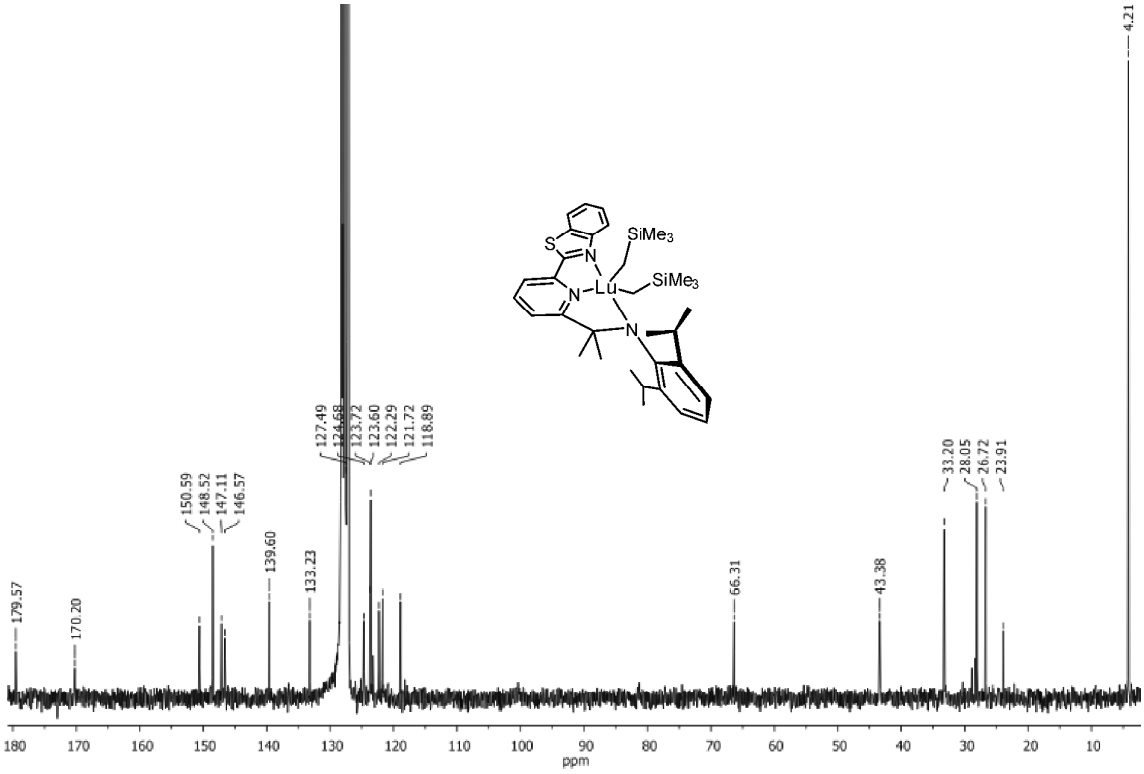

Fig. S4. ^{13}C{^{1}H} NMR spectrum (100 MHz, C_6D_6, 293 K) of Lu(κ^3-N,N^{py},N$^-$)(CH_2SiMe_3)$_2$ **5**.

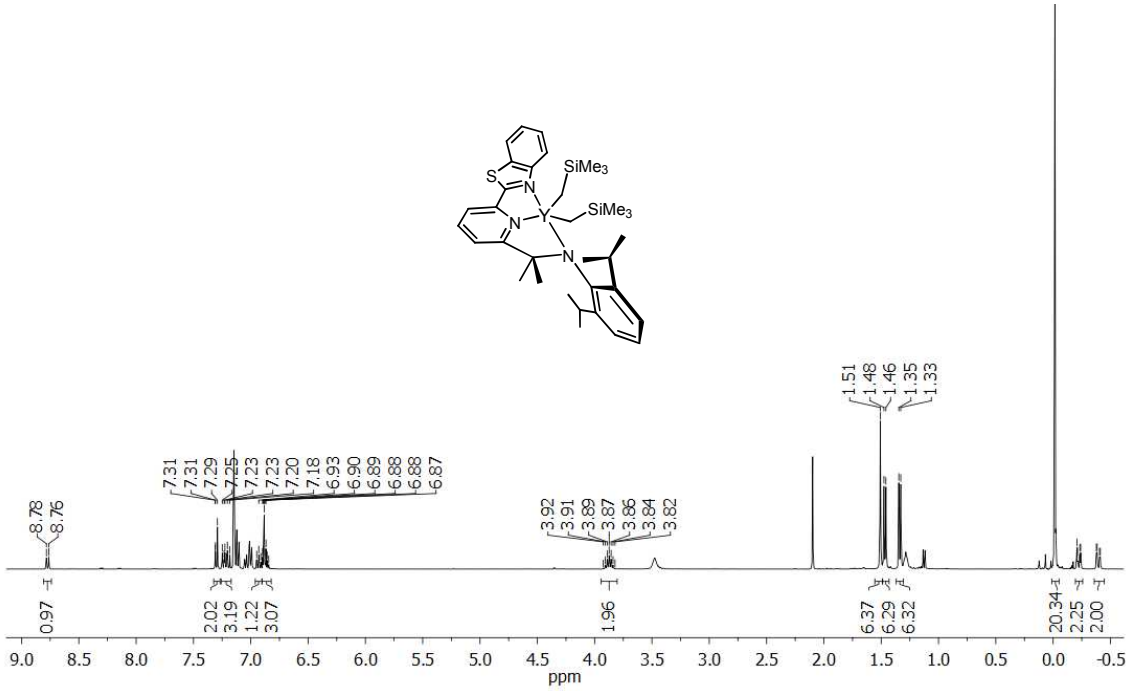

Figure S5. ^{1}H NMR spectrum (400 MHz, C_6D_6, 293 K) of Y(κ^3-N,N^{py},N$^-$)$(CH_2SiMe_3)_2$ **6**. (Reproduced with permission by © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Ref. *Chem.–Eur. J.*, **2014**, *20*, 3487–3499).

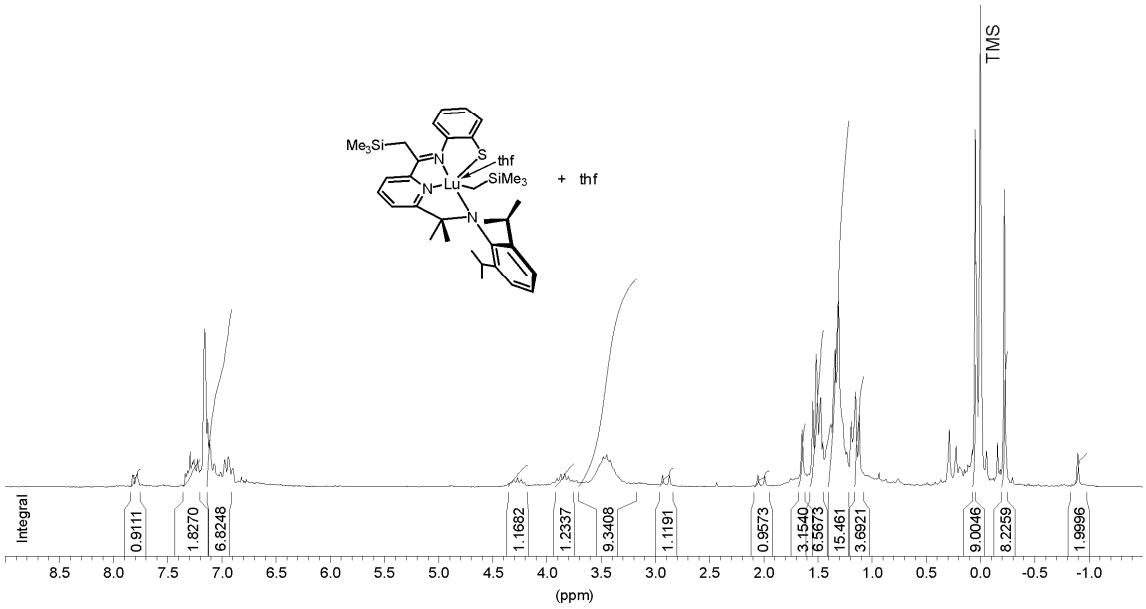

Fig. S6. ^{1}H NMR spectrum (200 MHz, C_6D_6, 293 K) of **9**.

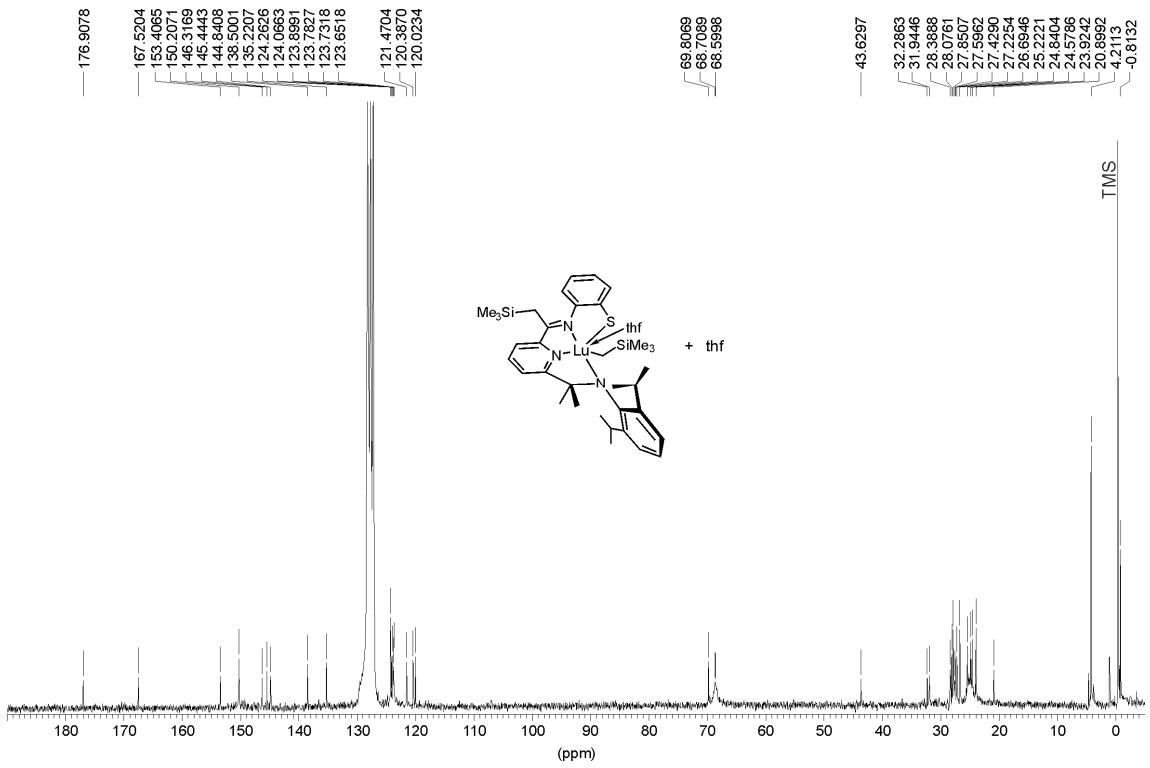

Fig. S7. $^{13}C\{^{1}H\}$ NMR spectrum (50 MHz, C_6D_6, 293 K) of **9**.

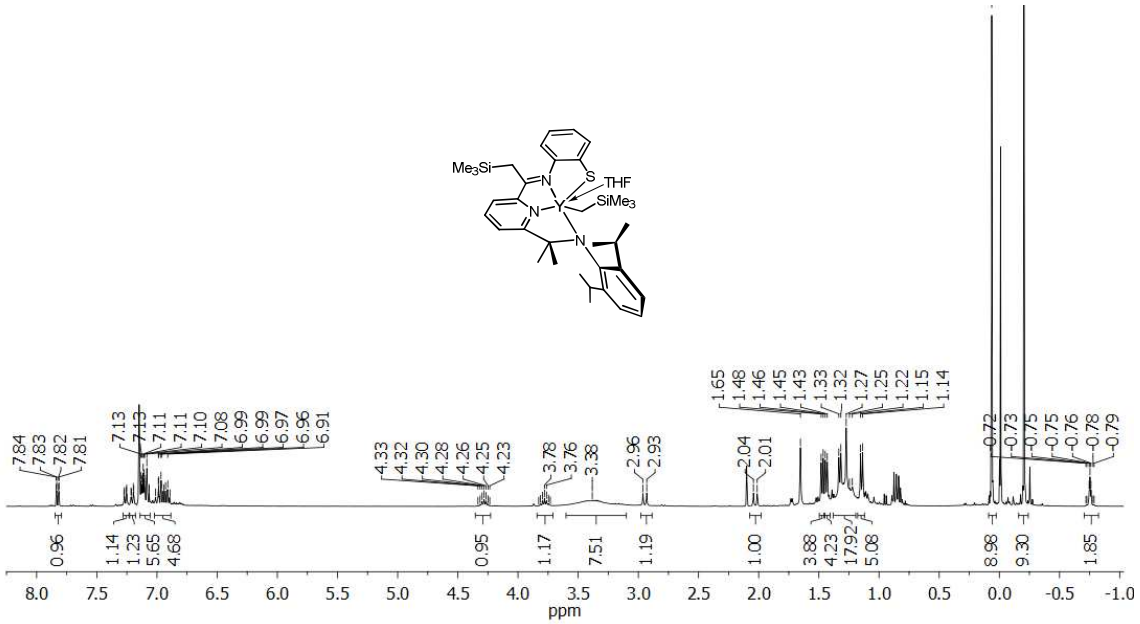

Fig. S8. ^{1}H NMR spectrum (400 MHz, C_6D_6, 293 K) of **10**. (Reproduced with permission by © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Ref. *Chem.–Eur. J.*, **2014**, *20*, 3487–3499).

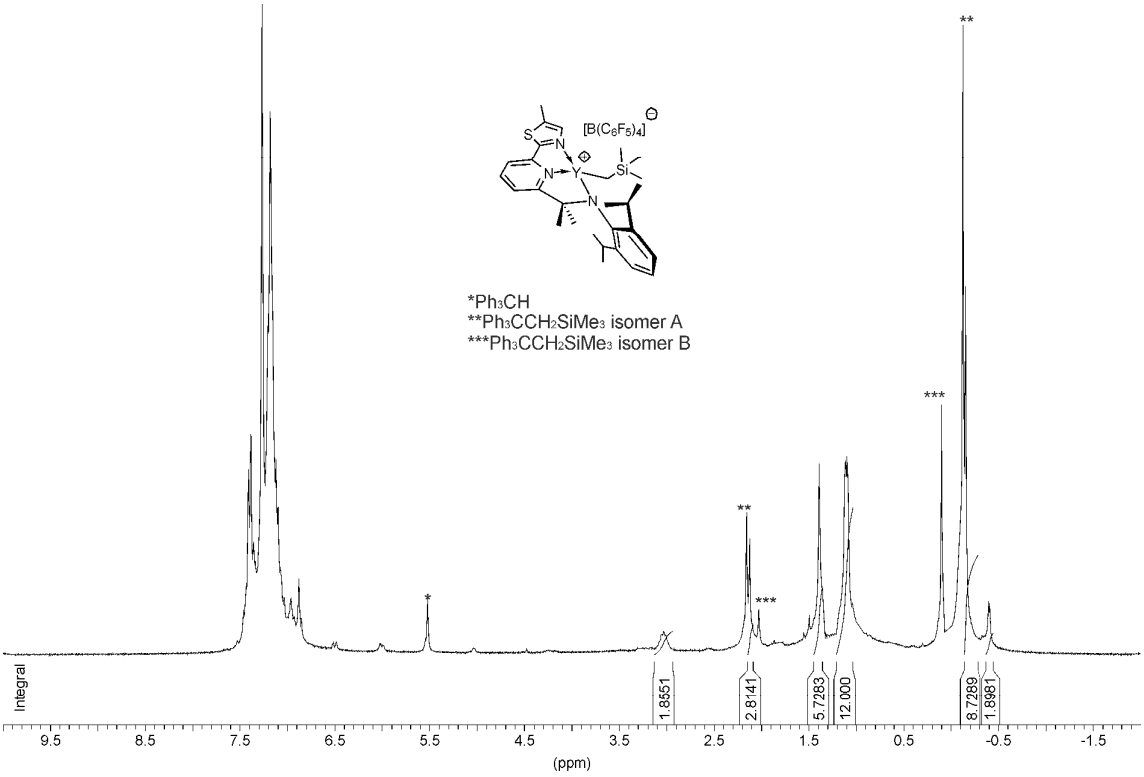

Fig. S9. ^{1}H-NMR spectrum (300 MHz, C_6D_6/C_6D_5Br 90:10/v:v, 293 K) of [Y(κ^3-N,N^{py},N-)CH_2SiMe_3][$B(C_6F_5)_4$] **4**/TB.

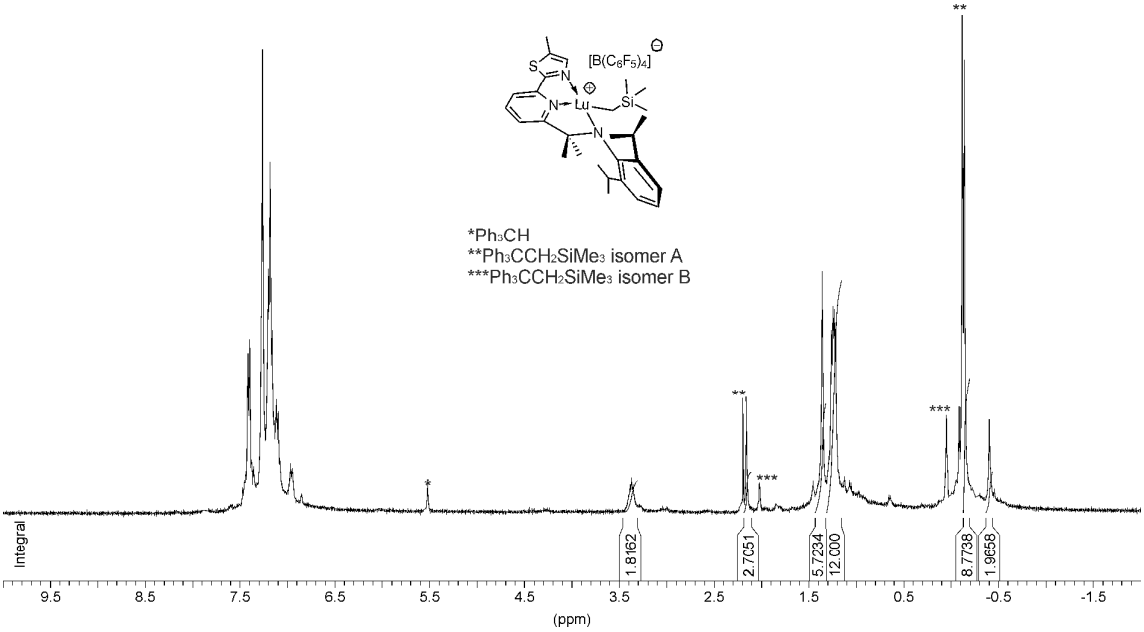

Fig. S10. ^{1}H-NMR spectrum (300 MHz, C_6D_6/C_6D_5Br 90:10/v:v, 293 K) of [Lu(κ^3-N,N^{py},N-)CH_2SiMe_3][$B(C_6F_5)_4$] **3**/TB.

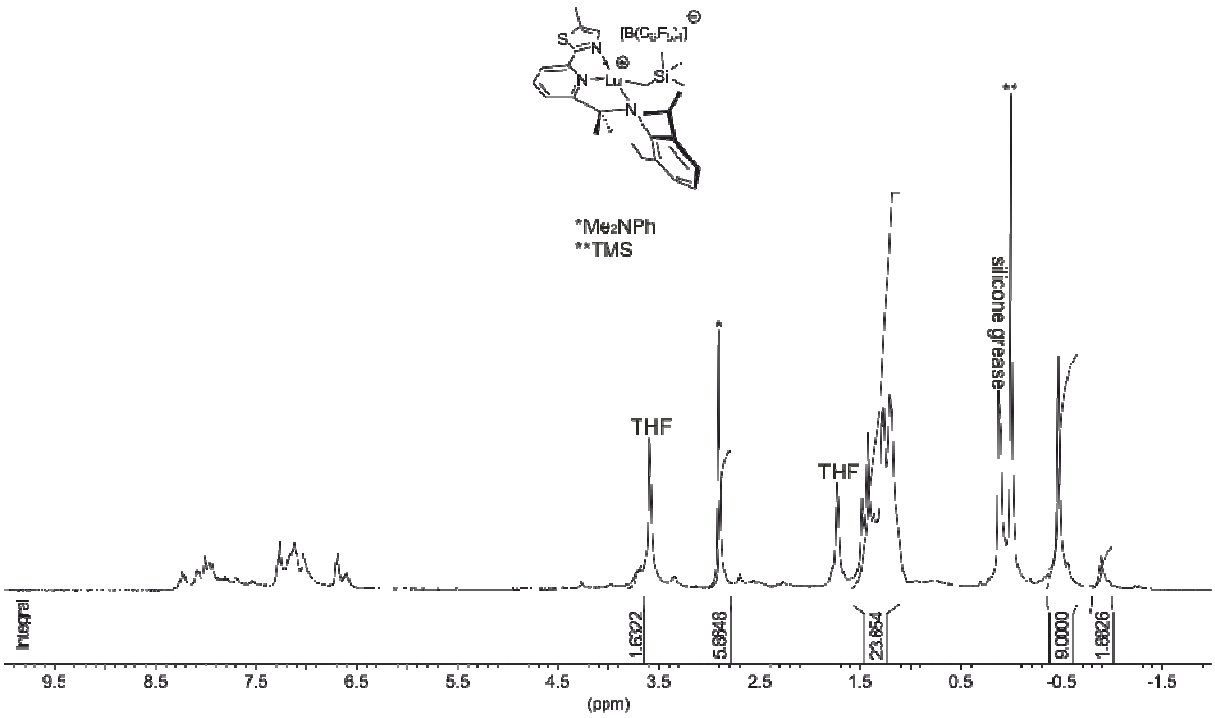

Fig. S11. ^{1}H-NMR spectrum (300 MHz, THF-d_8, 293 K) of [Lu(κ^3-N,N^{py},N$^-$)CH_2SiMe_3][$B(C_6F_5)_4$] **3**/HNB.

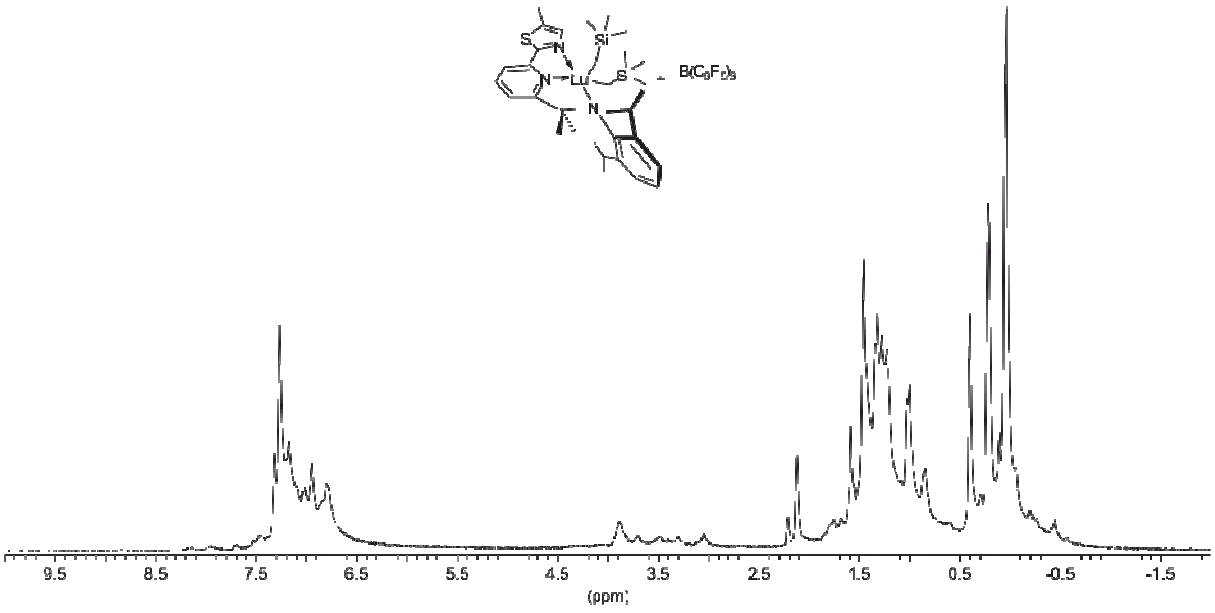

Fig. S12. ^{1}H-NMR spectrum (300 MHz, THF-d_8, 293 K) of [Lu(κ^3-N,N^{py},N$^-$)CH_2SiMe_3][$B(C_6F_5)_4$] **3**/BN.

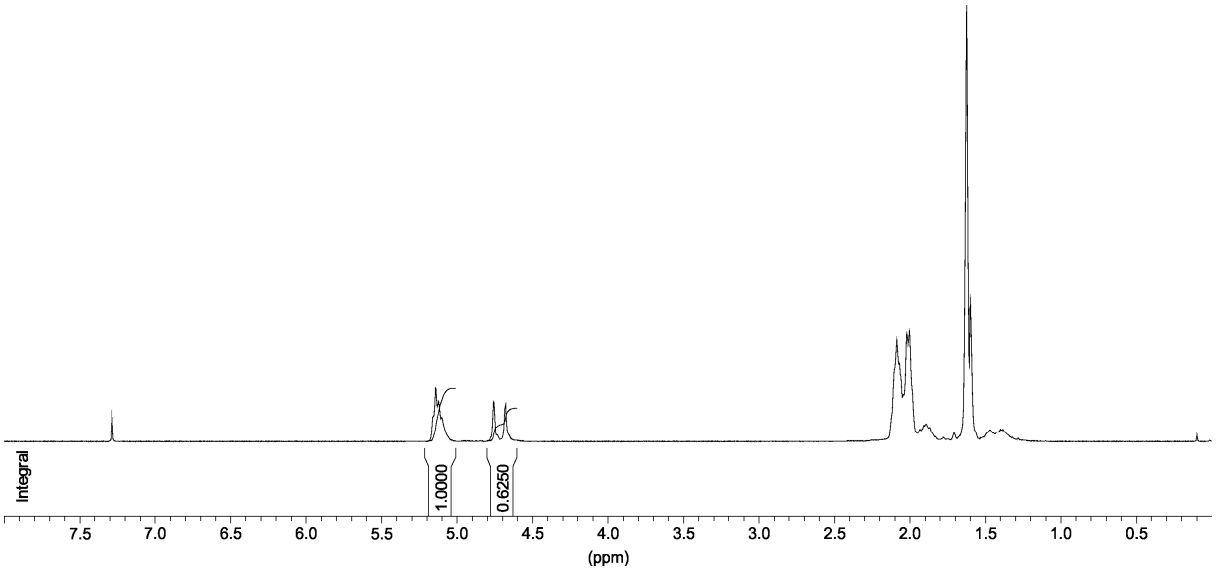

Fig. S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of PIP prepared by catalysis with **3**/$[Ph_3C][B(C_6F_5)_4]$ binary system (from Table 2, entry 7)**.**

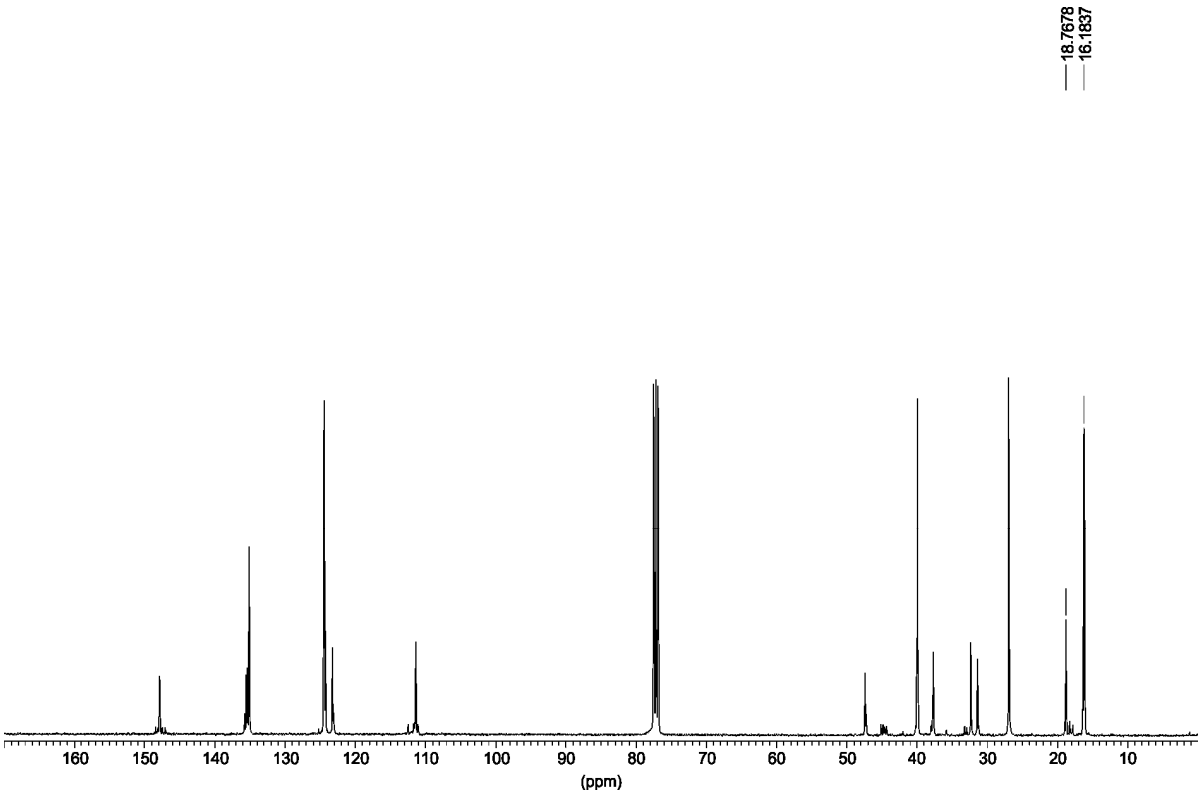

Fig. S14. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 293 K) of PIP prepared by catalysis with **3**/$[Ph_3C][B(C_6F_5)_4]$ binary system (from Table 2, entry 7)**.**

Table S1. Crystal data and structure refinement for complexes **3, 7** and **8**.

	3	**7**	**8**
CCDC number	1021045	1021046	1021047
Empirical formula	$C_{32}H_{52}N_3SSi_2Lu$	$C_{32}H_{52}N_3SSi_2Er$	$C_{32}H_{52}N_3SSi_2Yb$
FW	741.98	734.27	740.05
T, K	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P n*	*P n*	*P n*
Unit cell dimensions	a [Å] = 9.36415(7) b [Å] = 11.51241(8) c [Å] = 16.74418(12) α [°] = 90 β [°] = 92.3218(7) γ [°] = 90	a [Å] = 9.38846(17) b [Å] = 11.5607(3) c [Å] = 16.7385(3) α [°] = 90 β [°] = 92.0783(17) γ [°] = 90	a [Å] = 9.36372(12) b [Å] = 11.54210(14) c [Å] = 16.75309(18) α [°] = 90 β [°] = 92.1653(11) γ [°] = 90
V, Å^3	1803.61(2)	1815.55(6)	1809.33(4)
Z	2	2	2
D_{calc}, g/cm^3	1.366	1.343	1.358
Abs coeff, mm^{-1}	2.884	2.458	2.732
F(000)	760	754	758
Crystal size, mm	0.30×0.30×0.20	0.40 × 0.10 × 0.10	0.40 × 0.20 × 0.04
θ range for data collection, [°]	3.01–28.00	3.01–28.00	3.01–27.00
Index ranges	–12 ≤ h ≤ 12 –15 ≤ k ≤ 15 –22≤ l ≤ 22	–12 ≤ h ≤ 12 –15 ≤ k ≤ 15 –22 ≤ l ≤ 22	–11 ≤ h ≤ 11 –14 ≤ k ≤ 14 –21 ≤ l ≤ 21
Reflns collected	31271	31012	29533
Independent reflns	8685	8753	7852
R_{int}	0.0282	0.0247	0.0395
Completeness to θ	99.8	99.8	99.8
Data / restraints / parameters	8685 / 16 / 376	8753 / 4 / 370	7852 / 9 / 365
GOF on F^2	1.021	1.020	1.033
Final *R* indices *[I>2σ(I)]*	R_1 = 0.0184 wR_2 = 0.0394	R_1 = 0.0174 wR_2 = 0.0399	R_1 = 0.0214 wR_2 = 0.0421
R indices (all data)	R_1 = 0.0202 wR_2 = 0.0398	R_1 = 0.0183 wR_2 = 0.0402	R_1 = 0.0242 wR_2 = 0.0429
Largest diff peak and hole, [e Å^3]	0.338 and –0.511	0.430 / –0.427	0.495/ –0.451

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Lu(1)	-2478(1)	-1855(1)	-2503(1)	12(1)
S(1)	2023(1)	-3620(1)	-1589(1)	19(1)
Si(1)	-3525(1)	-3184(1)	-4501(1)	18(1)
Si(2)	-3557(1)	-4266(1)	-1139(1)	20(1)
N(1)	-169(2)	-2874(1)	-2393(1)	15(1)
N(2)	-1010(2)	-1242(1)	-1384(1)	15(1)
N(3)	-3102(2)	-118(1)	-2104(1)	15(1)
C(1)	2490(2)	-5243(2)	-2806(1)	25(1)
C(2)	1609(2)	-4267(2)	-2500(1)	20(1)
C(3)	425(2)	-3752(2)	-2831(1)	18(1)
C(4)	578(2)	-2712(2)	-1717(1)	15(1)
C(5)	174(2)	-1834(1)	-1140(1)	15(1)
C(6)	918(2)	-1593(2)	-428(1)	21(1)
C(7)	413(2)	-703(2)	41(1)	25(1)
C(8)	-777(2)	-82(2)	-213(1)	25(1)
C(9)	-1489(2)	-364(2)	-940(1)	18(1)
C(10)	-2855(2)	233(2)	-1256(1)	20(1)
C(11)	-2696(3)	1555(2)	-1126(1)	34(1)
C(12)	-4055(2)	-208(2)	-721(1)	33(1)
C(13)	-3750(2)	760(1)	-2612(1)	14(1)

C(14)	-5249(2)	819(2)	-2743(1)	18(1)
C(15)	-5848(2)	1727(2)	-3199(1)	22(1)
C(16)	-4999(2)	2571(2)	-3525(1)	22(1)
C(17)	-3529(2)	2485(2)	-3431(1)	19(1)
C(18)	-2882(2)	1586(1)	-2990(1)	15(1)
C(19)	-6243(2)	-104(2)	-2423(1)	22(1)
C(20)	-7445(2)	430(2)	-1947(1)	35(1)
C(21)	-6841(3)	-863(2)	-3111(1)	33(1)
C(22)	-1262(2)	1488(2)	-2960(1)	20(1)
C(23)	-493(2)	2658(2)	-2821(1)	33(1)
C(24)	-756(2)	956(2)	-3744(1)	29(1)
C(25)	-2679(2)	-1991(2)	-3919(1)	19(1)
C(26)	-3494(2)	-2983(2)	-5617(1)	24(1)
C(27)	-5451(2)	-3387(2)	-4262(1)	29(1)
C(28)	-2608(3)	-4607(2)	-4277(1)	32(1)
C(29)	-3976(2)	-3269(2)	-1976(1)	20(1)
C(30)	-3166(7)	-3479(4)	-170(2)	43(2)
C(30')	-3832(8)	-3516(4)	-163(2)	46(2)
C(31)	-1800(2)	-4987(2)	-1264(2)	54(1)
C(32)	-4844(2)	-5512(2)	-1056(2)	46(1)

Table S3. Bond lengths [A] and angles [deg] for **3**.

Lu(1)-N(3)	2.1949(14)
Lu(1)-C(29)	2.3443(19)
Lu(1)-C(25)	2.3764(18)
Lu(1)-N(2)	2.3856(14)
Lu(1)-N(1)	2.4607(15)
S(1)-C(4)	1.7160(18)
S(1)-C(2)	1.7281(19)
Si(1)-C(25)	1.8433(18)
Si(1)-C(27)	1.877(2)
Si(1)-C(28)	1.880(2)
Si(1)-C(26)	1.8857(19)
Si(2)-C(29)	1.8422(19)
Si(2)-C(31)	1.862(2)
Si(2)-C(30')	1.874(3)
Si(2)-C(30)	1.880(3)
Si(2)-C(32)	1.883(2)
N(1)-C(4)	1.320(2)
N(1)-C(3)	1.379(2)
N(2)-C(9)	1.342(2)
N(2)-C(5)	1.351(2)
N(3)-C(13)	1.439(2)
N(3)-C(10)	1.487(2)
C(1)-C(2)	1.497(3)
C(2)-C(3)	1.356(2)
C(4)-C(5)	1.459(2)
C(5)-C(6)	1.384(3)

C(6)-C(7)	1.386(3)
C(7)-C(8)	1.377(3)
C(8)-C(9)	1.401(3)
C(9)-C(10)	1.528(3)
C(10)-C(11)	1.543(3)
C(10)-C(12)	1.550(3)
C(13)-C(14)	1.414(3)
C(13)-C(18)	1.417(2)
C(14)-C(15)	1.399(3)
C(14)-C(19)	1.524(3)
C(15)-C(16)	1.381(3)
C(16)-C(17)	1.383(3)
C(17)-C(18)	1.396(2)
C(18)-C(22)	1.521(3)
C(19)-C(21)	1.533(3)
C(19)-C(20)	1.534(3)
C(22)-C(24)	1.540(3)
C(22)-C(23)	1.540(3)
N(3)-Lu(1)-C(29)	110.33(6)
N(3)-Lu(1)-C(25)	110.64(6)
C(29)-Lu(1)-C(25)	107.76(7)
N(3)-Lu(1)-N(2)	69.12(5)
C(29)-Lu(1)-N(2)	104.14(6)
C(25)-Lu(1)-N(2)	145.43(6)
N(3)-Lu(1)-N(1)	130.98(5)
C(29)-Lu(1)-N(1)	100.28(6)
C(25)-Lu(1)-N(1)	94.40(6)
N(2)-Lu(1)-N(1)	66.79(5)
C(4)-S(1)-C(2)	90.27(9)
C(25)-Si(1)-C(27)	112.10(9)

C(25)-Si(1)-C(28)	111.11(9)
C(27)-Si(1)-C(28)	106.51(10)
C(25)-Si(1)-C(26)	114.13(9)
C(27)-Si(1)-C(26)	106.26(9)
C(28)-Si(1)-C(26)	106.23(9)
C(29)-Si(2)-C(31)	110.73(10)
C(29)-Si(2)-C(30')	110.13(17)
C(31)-Si(2)-C(30')	117.2(2)
C(29)-Si(2)-C(30)	112.59(15)
C(31)-Si(2)-C(30)	99.8(2)
C(30')-Si(2)-C(30)	19.2(3)
C(29)-Si(2)-C(32)	114.43(10)
C(31)-Si(2)-C(32)	103.88(11)
C(30')-Si(2)-C(32)	100.1(2)
C(30)-Si(2)-C(32)	113.98(19)
C(4)-N(1)-C(3)	110.41(15)
C(4)-N(1)-Lu(1)	115.46(11)
C(3)-N(1)-Lu(1)	133.00(11)
C(9)-N(2)-C(5)	120.09(15)
C(9)-N(2)-Lu(1)	117.58(11)
C(5)-N(2)-Lu(1)	121.85(11)
C(13)-N(3)-C(10)	114.79(13)
C(13)-N(3)-Lu(1)	124.85(10)
C(10)-N(3)-Lu(1)	120.36(10)
C(3)-C(2)-C(1)	129.89(17)
C(3)-C(2)-S(1)	108.84(14)
C(1)-C(2)-S(1)	121.26(14)
C(2)-C(3)-N(1)	116.36(16)
N(1)-C(4)-C(5)	121.56(16)
N(1)-C(4)-S(1)	114.13(13)

C(5)-C(4)-S(1)	124.31(13)
N(2)-C(5)-C(6)	122.52(16)
N(2)-C(5)-C(4)	112.44(15)
C(6)-C(5)-C(4)	125.02(16)
C(5)-C(6)-C(7)	117.69(17)
C(8)-C(7)-C(6)	119.97(17)
C(7)-C(8)-C(9)	119.89(17)
N(2)-C(9)-C(8)	119.81(17)
N(2)-C(9)-C(10)	116.16(15)
C(8)-C(9)-C(10)	123.96(16)
N(3)-C(10)-C(9)	107.71(14)
N(3)-C(10)-C(11)	114.37(15)
C(9)-C(10)-C(11)	108.68(16)
N(3)-C(10)-C(12)	112.00(16)
C(9)-C(10)-C(12)	105.57(15)
C(11)-C(10)-C(12)	108.09(17)
C(14)-C(13)-C(18)	118.85(15)
C(14)-C(13)-N(3)	121.17(15)
C(18)-C(13)-N(3)	119.98(15)
C(15)-C(14)-C(13)	119.60(17)
C(15)-C(14)-C(19)	118.42(17)
C(13)-C(14)-C(19)	121.94(15)
C(16)-C(15)-C(14)	121.13(18)
C(15)-C(16)-C(17)	119.43(17)
C(16)-C(17)-C(18)	121.42(17)
C(17)-C(18)-C(13)	119.35(17)
C(17)-C(18)-C(22)	118.90(16)
C(13)-C(18)-C(22)	121.69(15)
C(14)-C(19)-C(21)	110.05(16)
C(14)-C(19)-C(20)	112.00(17)

C(21)-C(19)-C(20)	111.48(17)
C(18)-C(22)-C(24)	110.03(15)
C(18)-C(22)-C(23)	113.57(16)
C(24)-C(22)-C(23)	108.61(17)
Si(1)-C(25)-Lu(1)	126.26(9)
Si(2)-C(29)-Lu(1)	127.36(10)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for **3**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Lu(1)	13(1)	11(1)	12(1)	0(1)	-1(1)	1(1)
S(1)	14(1)	20(1)	22(1)	0(1)	-3(1)	2(1)
Si(1)	26(1)	14(1)	14(1)	1(1)	-4(1)	-1(1)
Si(2)	22(1)	19(1)	19(1)	7(1)	2(1)	2(1)
N(1)	15(1)	14(1)	16(1)	0(1)	-1(1)	0(1)
N(2)	18(1)	12(1)	15(1)	1(1)	-2(1)	-3(1)
N(3)	22(1)	11(1)	11(1)	3(1)	-3(1)	3(1)
C(1)	20(1)	24(1)	31(1)	-4(1)	1(1)	5(1)
C(2)	17(1)	22(1)	22(1)	-2(1)	2(1)	-2(1)
C(3)	15(1)	23(1)	17(1)	-2(1)	1(1)	0(1)

C(4)	11(1)	16(1)	20(1)	3(1)	-1(1)	-1(1)
C(5)	17(1)	13(1)	15(1)	1(1)	-2(1)	-4(1)
C(6)	24(1)	17(1)	20(1)	2(1)	-9(1)	-3(1)
C(7)	37(1)	19(1)	17(1)	-2(1)	-13(1)	-3(1)
C(8)	42(1)	16(1)	17(1)	-3(1)	-5(1)	2(1)
C(9)	26(1)	13(1)	15(1)	1(1)	0(1)	-1(1)
C(10)	28(1)	16(1)	16(1)	0(1)	-1(1)	8(1)
C(11)	58(1)	21(1)	22(1)	-7(1)	-13(1)	14(1)
C(12)	34(1)	50(1)	16(1)	0(1)	4(1)	10(1)
C(13)	19(1)	11(1)	13(1)	0(1)	-1(1)	3(1)
C(14)	19(1)	16(1)	19(1)	3(1)	3(1)	3(1)
C(15)	18(1)	22(1)	26(1)	4(1)	2(1)	7(1)
C(16)	27(1)	16(1)	22(1)	5(1)	-1(1)	8(1)
C(17)	28(1)	11(1)	19(1)	3(1)	2(1)	-1(1)
C(18)	19(1)	12(1)	16(1)	-3(1)	-1(1)	0(1)
C(19)	17(1)	23(1)	26(1)	6(1)	5(1)	2(1)
C(20)	24(1)	40(1)	41(1)	10(1)	13(1)	2(1)
C(21)	35(1)	27(1)	36(1)	4(1)	2(1)	-10(1)
C(22)	17(1)	16(1)	28(1)	3(1)	-4(1)	-3(1)
C(23)	29(1)	24(1)	44(1)	0(1)	-9(1)	-9(1)
C(24)	19(1)	31(1)	38(1)	-5(1)	4(1)	-2(1)
C(25)	25(1)	14(1)	16(1)	1(1)	-3(1)	0(1)
C(26)	31(1)	24(1)	16(1)	-1(1)	-2(1)	1(1)
C(27)	31(1)	35(1)	21(1)	2(1)	-3(1)	-8(1)
C(28)	50(1)	15(1)	29(1)	1(1)	-14(1)	1(1)
C(29)	16(1)	20(1)	24(1)	5(1)	-1(1)	0(1)
C(30)	64(4)	43(3)	24(2)	12(2)	5(2)	3(2)
C(30')	70(4)	40(3)	29(2)	0(2)	14(2)	-2(3)
C(31)	27(1)	49(1)	86(2)	49(1)	13(1)	15(1)
C(32)	27(1)	36(1)	75(2)	33(1)	1(1)	2(1)

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **7**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Er(1)	2479(1)	1839(1)	2504(1)	12(1)
S(1)	-2027(1)	3615(1)	1574(1)	19(1)
Si(1)	3531(1)	3198(1)	4506(1)	18(1)
Si(2)	3558(1)	4260(1)	1126(1)	21(1)
N(1)	140(1)	2864(1)	2385(1)	17(1)
N(2)	984(1)	1222(1)	1372(1)	15(1)
N(3)	3082(1)	96(1)	2079(1)	15(1)
C(1)	-2502(2)	5243(2)	2788(1)	24(1)
C(2)	-1626(2)	4261(1)	2488(1)	20(1)
C(3)	-454(2)	3744(1)	2823(1)	19(1)
C(4)	-595(2)	2710(1)	1705(1)	15(1)
C(5)	-193(2)	1822(1)	1132(1)	16(1)
C(6)	-934(2)	1594(2)	417(1)	22(1)
C(7)	-445(2)	706(2)	-57(1)	25(1)
C(8)	747(2)	79(2)	194(1)	24(1)
C(9)	1450(2)	352(1)	922(1)	17(1)
C(10)	2806(2)	-251(1)	1226(1)	19(1)

C(11)	2648(2)	-1571(2)	1098(1)	32(1)
C(12)	4008(2)	177(2)	685(1)	32(1)
C(13)	3721(2)	-777(1)	2582(1)	14(1)
C(14)	5219(2)	-837(1)	2716(1)	18(1)
C(15)	5814(2)	-1742(1)	3174(1)	23(1)
C(16)	4954(2)	-2582(1)	3505(1)	22(1)
C(17)	3492(2)	-2490(1)	3414(1)	19(1)
C(18)	2847(2)	-1593(1)	2968(1)	16(1)
C(19)	6211(2)	82(2)	2389(1)	23(1)
C(20)	7411(2)	-452(2)	1914(1)	34(1)
C(21)	6798(2)	842(2)	3068(1)	33(1)
C(22)	1231(2)	-1494(2)	2946(1)	20(1)
C(23)	455(2)	-2654(2)	2825(1)	30(1)
C(24)	736(2)	-935(2)	3719(1)	30(1)
C(25)	2671(2)	2004(1)	3943(1)	18(1)
C(26)	3506(2)	3030(2)	5627(1)	24(1)
C(27)	5461(2)	3379(2)	4255(1)	30(1)
C(28)	2632(2)	4616(2)	4259(1)	33(1)
C(29)	3993(2)	3258(1)	1955(1)	21(1)
C(30)	3844(9)	3507(5)	153(3)	52(2)
C(30')	3133(7)	3484(4)	151(2)	52(2)
C(31)	1826(2)	4996(2)	1283(2)	57(1)
C(32)	4847(2)	5491(2)	1020(2)	50(1)

Table S6. Bond lengths [A] and angles [deg] for **7**.

Er(1)-N(3)	2.2165(13)
Er(1)-C(29)	2.3771(17)

Er(1)-C(25)	2.4171(17)
Er(1)-N(2)	2.4239(13)
Er(1)-N(1)	2.4970(14)
S(1)-C(4)	1.7114(16)
S(1)-C(2)	1.7306(17)
Si(1)-C(25)	1.8408(17)
Si(1)-C(28)	1.8833(19)
Si(1)-C(26)	1.8859(18)
Si(1)-C(27)	1.886(2)
Si(2)-C(29)	1.8424(18)
Si(2)-C(31)	1.863(2)
Si(2)-C(30)	1.873(5)
Si(2)-C(32)	1.881(2)
Si(2)-C(30')	1.892(4)
N(1)-C(4)	1.321(2)
N(1)-C(3)	1.384(2)
N(2)-C(9)	1.340(2)
N(2)-C(5)	1.353(2)
N(3)-C(13)	1.4326(19)
N(3)-C(10)	1.495(2)
C(1)-C(2)	1.499(2)
C(2)-C(3)	1.356(2)
C(4)-C(5)	1.464(2)
C(5)-C(6)	1.388(2)
C(6)-C(7)	1.387(2)
C(7)-C(8)	1.385(3)
C(8)-C(9)	1.402(2)
C(9)-C(10)	1.522(2)
C(10)-C(11)	1.548(2)
C(10)-C(12)	1.554(3)

C(13)-C(14)	1.417(2)
C(13)-C(18)	1.421(2)
C(14)-C(15)	1.402(2)
C(14)-C(19)	1.526(2)
C(15)-C(16)	1.391(2)
C(16)-C(17)	1.379(2)
C(17)-C(18)	1.402(2)
C(18)-C(22)	1.521(2)
C(19)-C(21)	1.524(3)
C(19)-C(20)	1.533(3)
C(22)-C(24)	1.533(3)
C(22)-C(23)	1.536(2)
N(3)-Er(1)-C(29)	109.86(5)
N(3)-Er(1)-C(25)	112.42(5)
C(29)-Er(1)-C(25)	107.86(6)
N(3)-Er(1)-N(2)	68.23(5)
C(29)-Er(1)-N(2)	103.79(5)
C(25)-Er(1)-N(2)	145.33(5)
N(3)-Er(1)-N(1)	129.78(5)
C(29)-Er(1)-N(1)	100.25(5)
C(25)-Er(1)-N(1)	94.34(5)
N(2)-Er(1)-N(1)	66.07(4)
C(4)-S(1)-C(2)	90.34(8)
C(25)-Si(1)-C(28)	110.83(8)
C(25)-Si(1)-C(26)	114.29(8)
C(28)-Si(1)-C(26)	106.62(9)
C(25)-Si(1)-C(27)	112.09(9)
C(28)-Si(1)-C(27)	106.29(9)
C(26)-Si(1)-C(27)	106.23(9)
C(29)-Si(2)-C(31)	110.56(10)

C(29)-Si(2)-C(30)	109.1(2)
C(31)-Si(2)-C(30)	119.3(3)
C(29)-Si(2)-C(32)	114.87(9)
C(31)-Si(2)-C(32)	103.60(10)
C(30)-Si(2)-C(32)	99.1(2)
C(29)-Si(2)-C(30')	112.72(16)
C(31)-Si(2)-C(30')	100.4(2)
C(30)-Si(2)-C(30')	20.4(3)
C(32)-Si(2)-C(30')	113.22(19)
C(4)-N(1)-C(3)	110.35(14)
C(4)-N(1)-Er(1)	115.80(10)
C(3)-N(1)-Er(1)	132.60(11)
C(9)-N(2)-C(5)	119.89(14)
C(9)-N(2)-Er(1)	117.90(10)
C(5)-N(2)-Er(1)	121.66(10)
C(13)-N(3)-C(10)	115.25(12)
C(13)-N(3)-Er(1)	123.88(10)
C(10)-N(3)-Er(1)	120.86(9)
C(3)-C(2)-C(1)	129.92(16)
C(3)-C(2)-S(1)	108.86(12)
C(1)-C(2)-S(1)	121.21(12)
C(2)-C(3)-N(1)	116.17(15)
N(1)-C(4)-C(5)	121.29(14)
N(1)-C(4)-S(1)	114.27(12)
C(5)-C(4)-S(1)	124.44(12)
N(2)-C(5)-C(6)	122.52(15)
N(2)-C(5)-C(4)	113.11(14)
C(6)-C(5)-C(4)	124.37(15)
C(7)-C(6)-C(5)	117.89(16)
C(8)-C(7)-C(6)	119.62(16)

C(7)-C(8)-C(9)	119.79(16)
N(2)-C(9)-C(8)	120.27(15)
N(2)-C(9)-C(10)	116.26(13)
C(8)-C(9)-C(10)	123.38(14)
N(3)-C(10)-C(9)	108.06(13)
N(3)-C(10)-C(11)	114.18(13)
C(9)-C(10)-C(11)	109.26(14)
N(3)-C(10)-C(12)	111.48(14)
C(9)-C(10)-C(12)	106.00(13)
C(11)-C(10)-C(12)	107.55(15)
C(14)-C(13)-C(18)	118.78(14)
C(14)-C(13)-N(3)	121.27(14)
C(18)-C(13)-N(3)	119.95(14)
C(15)-C(14)-C(13)	119.77(15)
C(15)-C(14)-C(19)	118.60(15)
C(13)-C(14)-C(19)	121.61(14)
C(16)-C(15)-C(14)	120.88(16)
C(17)-C(16)-C(15)	119.47(15)
C(16)-C(17)-C(18)	121.64(15)
C(17)-C(18)-C(13)	119.20(15)
C(17)-C(18)-C(22)	118.68(15)
C(13)-C(18)-C(22)	122.05(14)
C(21)-C(19)-C(14)	110.05(15)
C(21)-C(19)-C(20)	111.51(15)
C(14)-C(19)-C(20)	112.03(15)
C(18)-C(22)-C(24)	110.15(14)
C(18)-C(22)-C(23)	113.93(14)
C(24)-C(22)-C(23)	108.84(15)
Si(1)-C(25)-Er(1)	125.81(8)
Si(2)-C(29)-Er(1)	127.29(9)

Symmetry transformations used to generate equivalent atoms:

Table S7. Anisotropic displacement parameters (A^2 x 10^3) for **7**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Er(1)	13(1)	12(1)	12(1)	0(1)	-2(1)	1(1)
S(1)	14(1)	21(1)	22(1)	1(1)	-3(1)	3(1)
Si(1)	26(1)	14(1)	14(1)	1(1)	-4(1)	-2(1)
Si(2)	23(1)	20(1)	19(1)	7(1)	3(1)	3(1)
N(1)	15(1)	18(1)	17(1)	0(1)	-1(1)	-1(1)
N(2)	18(1)	13(1)	14(1)	1(1)	-3(1)	-1(1)
N(3)	20(1)	14(1)	12(1)	1(1)	-2(1)	4(1)
C(1)	19(1)	25(1)	29(1)	-4(1)	3(1)	4(1)
C(2)	18(1)	20(1)	21(1)	-1(1)	3(1)	-1(1)
C(3)	19(1)	22(1)	17(1)	-3(1)	2(1)	-1(1)
C(4)	13(1)	15(1)	18(1)	1(1)	-2(1)	-1(1)
C(5)	17(1)	15(1)	16(1)	3(1)	-2(1)	-3(1)
C(6)	23(1)	20(1)	20(1)	1(1)	-8(1)	-2(1)
C(7)	38(1)	19(1)	17(1)	0(1)	-11(1)	-4(1)
C(8)	41(1)	17(1)	15(1)	-2(1)	-5(1)	2(1)
C(9)	24(1)	13(1)	13(1)	0(1)	-2(1)	0(1)

C(10)	28(1)	17(1)	13(1)	-1(1)	-2(1)	7(1)
C(11)	56(1)	19(1)	19(1)	-6(1)	-11(1)	13(1)
C(12)	33(1)	48(1)	17(1)	0(1)	5(1)	7(1)
C(13)	17(1)	11(1)	14(1)	0(1)	1(1)	3(1)
C(14)	18(1)	17(1)	20(1)	1(1)	4(1)	4(1)
C(15)	18(1)	25(1)	26(1)	4(1)	1(1)	6(1)
C(16)	27(1)	16(1)	23(1)	6(1)	0(1)	7(1)
C(17)	25(1)	13(1)	19(1)	2(1)	1(1)	0(1)
C(18)	19(1)	14(1)	14(1)	-3(1)	0(1)	1(1)
C(19)	18(1)	24(1)	27(1)	5(1)	4(1)	2(1)
C(20)	25(1)	39(1)	38(1)	7(1)	13(1)	2(1)
C(21)	32(1)	32(1)	35(1)	5(1)	2(1)	-10(1)
C(22)	18(1)	15(1)	28(1)	3(1)	-3(1)	-3(1)
C(23)	27(1)	23(1)	41(1)	0(1)	-6(1)	-9(1)
C(24)	20(1)	34(1)	37(1)	-6(1)	5(1)	-2(1)
C(25)	23(1)	16(1)	16(1)	-1(1)	-4(1)	0(1)
C(26)	31(1)	25(1)	16(1)	-1(1)	-2(1)	0(1)
C(27)	31(1)	36(1)	21(1)	2(1)	-3(1)	-11(1)
C(28)	52(1)	15(1)	30(1)	0(1)	-16(1)	2(1)
C(29)	17(1)	22(1)	24(1)	6(1)	-3(1)	-2(1)
C(30)	91(5)	44(1)	20(1)	5(1)	3(2)	3(2)
C(30')	91(5)	44(1)	20(1)	5(1)	3(2)	3(2)
C(31)	30(1)	51(1)	91(2)	48(1)	16(1)	17(1)
C(32)	24(1)	42(1)	84(2)	42(1)	-1(1)	1(1)

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **8**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Yb(1)	7521(1)	8168(1)	7496(1)	12(1)
S(1)	12028(1)	6388(1)	8422(1)	19(1)
Si(1)	6496(1)	6816(1)	5501(1)	18(1)
Si(2)	6453(1)	5740(1)	8869(1)	20(1)
N(1)	9847(2)	7138(2)	7613(1)	15(1)
N(2)	8994(2)	8770(2)	8626(1)	14(1)
N(3)	6908(2)	9900(2)	7904(1)	16(1)
C(1)	12505(2)	4770(2)	7208(1)	25(1)
C(2)	11619(2)	5742(2)	7508(1)	20(1)
C(3)	10447(2)	6263(2)	7176(1)	18(1)
C(4)	10583(2)	7293(2)	8291(1)	16(1)
C(5)	10174(2)	8165(2)	8867(1)	16(1)
C(6)	10911(2)	8404(2)	9582(1)	21(1)
C(7)	10416(3)	9285(2)	10051(1)	25(1)
C(8)	9225(3)	9928(2)	9798(1)	24(1)
C(9)	8523(2)	9638(2)	9072(1)	18(1)
C(10)	7167(3)	10255(2)	8761(1)	21(1)
C(11)	7338(3)	11566(2)	8888(2)	35(1)
C(12)	5947(3)	9824(2)	9290(1)	32(1)
C(13)	6257(2)	10774(2)	7404(1)	15(1)
C(14)	4755(2)	10834(2)	7271(1)	18(1)
C(15)	4164(2)	11738(2)	6818(1)	21(1)

C(16)	5013(3)	12583(2)	6485(1)	22(1)
C(17)	6482(2)	12491(2)	6582(1)	19(1)
C(18)	7123(2)	11598(2)	7022(1)	15(1)
C(19)	3768(2)	9903(2)	7591(1)	22(1)
C(20)	2553(3)	10426(3)	8066(2)	33(1)
C(21)	3180(3)	9146(2)	6906(2)	34(1)
C(22)	8749(2)	11506(2)	7049(1)	20(1)
C(23)	9512(3)	12671(2)	7184(2)	32(1)
C(24)	9253(3)	10967(2)	6267(2)	29(1)
C(25)	7334(3)	8013(2)	6079(1)	19(1)
C(26)	6514(3)	7010(2)	4385(1)	24(1)
C(27)	4569(3)	6617(2)	5750(2)	29(1)
C(28)	7406(3)	5395(2)	5728(2)	31(1)
C(29)	6055(2)	6733(2)	8030(1)	20(1)
C(30)	6501(5)	6527(3)	9847(2)	70(1)
C(31)	8229(3)	5033(3)	8759(2)	54(1)
C(32)	5173(3)	4500(3)	8958(2)	47(1)

Table S9. Bond lengths [A] and angles [deg] for **8**.

Yb(1)-N(3)	2.1952(18)
Yb(1)-C(29)	2.349(2)
Yb(1)-C(25)	2.381(2)
Yb(1)-N(2)	2.4014(17)
Yb(1)-N(1)	2.4823(18)
S(1)-C(4)	1.717(2)
S(1)-C(2)	1.733(2)
Si(1)-C(25)	1.845(2)

Si(1)-C(27)	1.881(3)
Si(1)-C(28)	1.881(2)
Si(1)-C(26)	1.884(2)
Si(2)-C(29)	1.842(2)
Si(2)-C(31)	1.868(3)
Si(2)-C(30)	1.872(3)
Si(2)-C(32)	1.876(3)
N(1)-C(4)	1.319(3)
N(1)-C(3)	1.380(3)
N(2)-C(9)	1.335(3)
N(2)-C(5)	1.356(3)
N(3)-C(13)	1.433(3)
N(3)-C(10)	1.505(3)
C(1)-C(2)	1.494(3)
C(2)-C(3)	1.352(3)
C(4)-C(5)	1.456(3)
C(5)-C(6)	1.387(3)
C(6)-C(7)	1.377(3)
C(7)-C(8)	1.392(3)
C(8)-C(9)	1.401(3)
C(9)-C(10)	1.529(3)
C(10)-C(11)	1.535(3)
C(10)-C(12)	1.553(3)
C(13)-C(14)	1.417(3)
C(13)-C(18)	1.418(3)
C(14)-C(15)	1.393(3)
C(14)-C(19)	1.528(3)
C(15)-C(16)	1.388(3)
C(16)-C(17)	1.383(3)
C(17)-C(18)	1.391(3)

C(18)-C(22)	1.526(3)
C(19)-C(21)	1.529(4)
C(19)-C(20)	1.536(3)
C(22)-C(23)	1.535(3)
C(22)-C(24)	1.541(3)
N(3)-Yb(1)-C(29)	111.10(8)
N(3)-Yb(1)-C(25)	111.62(7)
C(29)-Yb(1)-C(25)	107.71(8)
N(3)-Yb(1)-N(2)	68.96(6)
C(29)-Yb(1)-N(2)	103.33(7)
C(25)-Yb(1)-N(2)	145.67(7)
N(3)-Yb(1)-N(1)	130.58(6)
C(29)-Yb(1)-N(1)	98.97(7)
C(25)-Yb(1)-N(1)	94.23(7)
N(2)-Yb(1)-N(1)	66.45(6)
C(4)-S(1)-C(2)	90.15(11)
C(25)-Si(1)-C(27)	111.56(11)
C(25)-Si(1)-C(28)	111.50(11)
C(27)-Si(1)-C(28)	106.26(12)
C(25)-Si(1)-C(26)	114.34(11)
C(27)-Si(1)-C(26)	106.22(11)
C(28)-Si(1)-C(26)	106.44(11)
C(29)-Si(2)-C(31)	110.63(13)
C(29)-Si(2)-C(30)	111.30(14)
C(31)-Si(2)-C(30)	107.86(18)
C(29)-Si(2)-C(32)	115.07(12)
C(31)-Si(2)-C(32)	104.38(13)
C(30)-Si(2)-C(32)	107.15(17)
C(4)-N(1)-C(3)	110.22(18)
C(4)-N(1)-Yb(1)	115.58(14)

C(3)-N(1)-Yb(1)	133.07(14)
C(9)-N(2)-C(5)	120.13(18)
C(9)-N(2)-Yb(1)	117.79(14)
C(5)-N(2)-Yb(1)	121.58(14)
C(13)-N(3)-C(10)	114.56(17)
C(13)-N(3)-Yb(1)	124.75(13)
C(10)-N(3)-Yb(1)	120.68(13)
C(3)-C(2)-C(1)	130.4(2)
C(3)-C(2)-S(1)	108.70(17)
C(1)-C(2)-S(1)	120.89(16)
C(2)-C(3)-N(1)	116.6(2)
N(1)-C(4)-C(5)	121.5(2)
N(1)-C(4)-S(1)	114.28(17)
C(5)-C(4)-S(1)	124.22(16)
N(2)-C(5)-C(6)	121.9(2)
N(2)-C(5)-C(4)	112.95(18)
C(6)-C(5)-C(4)	125.1(2)
C(7)-C(6)-C(5)	118.2(2)
C(6)-C(7)-C(8)	120.2(2)
C(7)-C(8)-C(9)	118.8(2)
N(2)-C(9)-C(8)	120.7(2)
N(2)-C(9)-C(10)	116.51(18)
C(8)-C(9)-C(10)	122.7(2)
N(3)-C(10)-C(9)	107.46(18)
N(3)-C(10)-C(11)	114.35(19)
C(9)-C(10)-C(11)	109.3(2)
N(3)-C(10)-C(12)	111.17(19)
C(9)-C(10)-C(12)	106.02(19)
C(11)-C(10)-C(12)	108.2(2)
C(14)-C(13)-C(18)	118.51(19)

C(14)-C(13)-N(3)	121.59(19)
C(18)-C(13)-N(3)	119.89(19)
C(15)-C(14)-C(13)	119.6(2)
C(15)-C(14)-C(19)	119.0(2)
C(13)-C(14)-C(19)	121.37(19)
C(16)-C(15)-C(14)	121.6(2)
C(17)-C(16)-C(15)	118.8(2)
C(16)-C(17)-C(18)	121.7(2)
C(17)-C(18)-C(13)	119.6(2)
C(17)-C(18)-C(22)	118.5(2)
C(13)-C(18)-C(22)	121.83(19)
C(14)-C(19)-C(21)	110.1(2)
C(14)-C(19)-C(20)	112.1(2)
C(21)-C(19)-C(20)	111.1(2)
C(18)-C(22)-C(23)	113.70(19)
C(18)-C(22)-C(24)	109.93(18)
C(23)-C(22)-C(24)	108.9(2)
Si(1)-C(25)-Yb(1)	126.39(11)
Si(2)-C(29)-Yb(1)	128.68(11)

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters (A^2 x 10^3) for **8**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Yb(1)	13(1)	12(1)	12(1)	0(1)	-1(1)	1(1)
S(1)	14(1)	21(1)	21(1)	1(1)	-2(1)	3(1)
Si(1)	25(1)	14(1)	14(1)	2(1)	-3(1)	-1(1)
Si(2)	22(1)	20(1)	19(1)	6(1)	4(1)	1(1)
N(1)	13(1)	19(1)	13(1)	0(1)	-1(1)	-3(1)
N(2)	16(1)	13(1)	14(1)	0(1)	0(1)	1(1)
N(3)	22(1)	11(1)	13(1)	1(1)	-1(1)	2(1)
C(1)	18(1)	25(1)	32(1)	-2(1)	4(1)	2(1)
C(2)	18(1)	19(1)	23(1)	-2(1)	4(1)	-1(1)
C(3)	16(1)	19(1)	19(1)	-1(1)	1(1)	-2(1)
C(4)	11(1)	17(1)	21(1)	1(1)	2(1)	-3(1)
C(5)	16(1)	19(1)	15(1)	3(1)	0(1)	-4(1)
C(6)	21(1)	21(1)	21(1)	2(1)	-7(1)	0(1)
C(7)	37(1)	18(1)	20(1)	-1(1)	-10(1)	-4(1)
C(8)	41(1)	15(1)	17(1)	-2(1)	-3(1)	4(1)
C(9)	26(1)	14(1)	13(1)	4(1)	1(1)	0(1)
C(10)	31(1)	20(1)	12(1)	-3(1)	-1(1)	7(1)
C(11)	55(2)	27(1)	21(1)	-8(1)	-13(1)	14(1)
C(12)	36(1)	44(2)	17(1)	-2(1)	6(1)	10(1)
C(13)	22(1)	11(1)	11(1)	0(1)	3(1)	3(1)
C(14)	20(1)	18(1)	16(1)	2(1)	6(1)	3(1)
C(15)	16(1)	24(1)	23(1)	2(1)	0(1)	6(1)
C(16)	29(1)	16(1)	21(1)	3(1)	0(1)	9(1)
C(17)	24(1)	14(1)	18(1)	3(1)	2(1)	-2(1)
C(18)	18(1)	13(1)	15(1)	-3(1)	2(1)	-1(1)
C(19)	18(1)	22(1)	26(1)	6(1)	5(1)	0(1)
C(20)	22(1)	39(2)	38(1)	9(1)	15(1)	3(1)

C(21)	38(1)	32(2)	33(1)	5(1)	5(1)	-10(1)
C(22)	16(1)	19(1)	25(1)	0(1)	-2(1)	-1(1)
C(23)	26(1)	26(1)	43(2)	0(1)	-7(1)	-10(1)
C(24)	19(1)	32(1)	37(2)	-4(1)	6(1)	-3(1)
C(25)	25(1)	15(1)	18(1)	0(1)	-4(1)	3(1)
C(26)	29(1)	26(1)	16(1)	0(1)	-2(1)	1(1)
C(27)	32(1)	35(2)	19(1)	2(1)	-2(1)	-11(1)
C(28)	48(2)	17(1)	28(1)	0(1)	-13(1)	4(1)
C(29)	14(1)	23(1)	23(1)	3(1)	0(1)	1(1)
C(30)	132(3)	52(2)	27(1)	3(1)	8(2)	1(2)
C(31)	27(1)	46(2)	90(2)	44(2)	9(2)	11(1)
C(32)	29(1)	41(2)	72(2)	34(2)	1(1)	-1(1)