Supporting Information

Reactivity of Mixed Methyl-Aminobenzyl Guanidinate Lutetium Complex towards ^{i}PrN=C=N^{i}Pr, CS_2 and Ph_2PH

Wen Jiang,[†] *Lijun Zhang*,*[‡] *and Lixin Zhang*,*[†]

†. Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Jiangwan Campus, Fudan University Shanghai 200438, China.

‡. Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, People's Republic of China.

* E-mail: zljun@mail.ahnu.edu.cn and lixinzh@fudan.edu.cn

Tables of Contents

1. NMR spectra of complexes 1-6 and 8-10

The solid samples were dissolved in C_6D_6, and then transferred into a J-Young NMR tube in the glove-box. The ^1H NMR, $^{13}C\{^1H\}$ NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL ECA-400 NMR spectrometer (FT, 400 MHz for ^1H; 100 MHz for ^{13}C; 161.88 MHz for ^{31}P) in C_6D_6 at room temperature (except for Fig. S8).

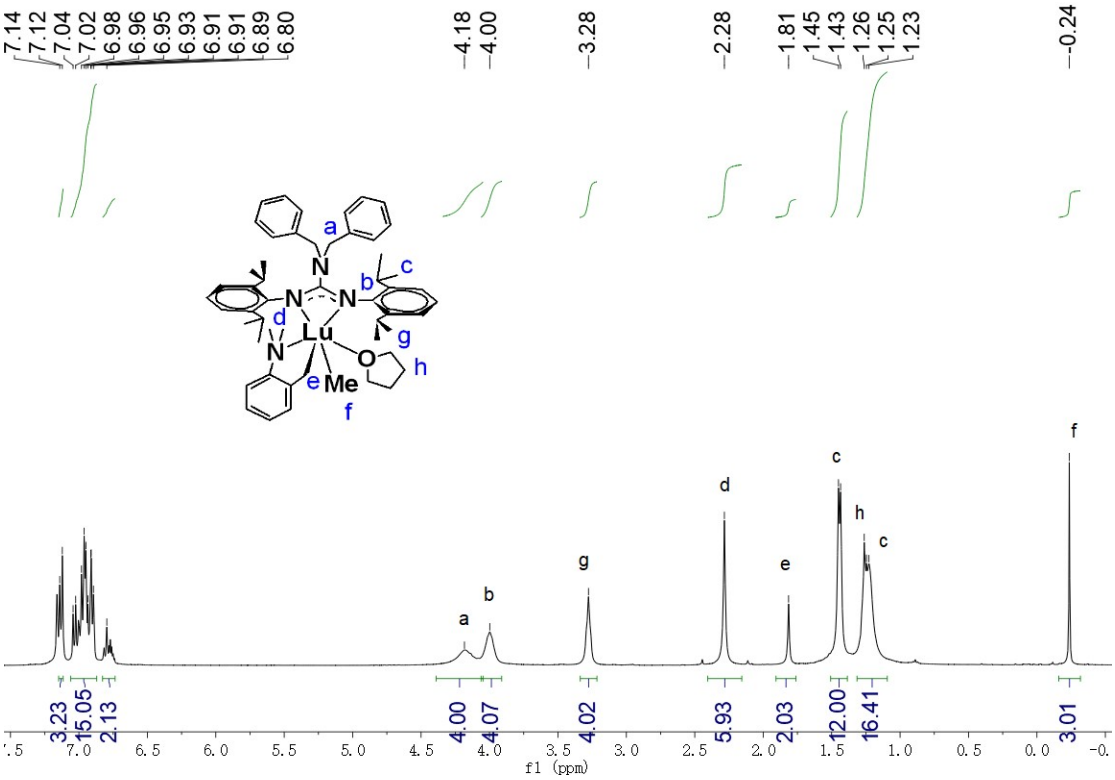

Fig. S1 ^1H NMR spectrum of **1** obtained in C_6D_6 at room temperature.

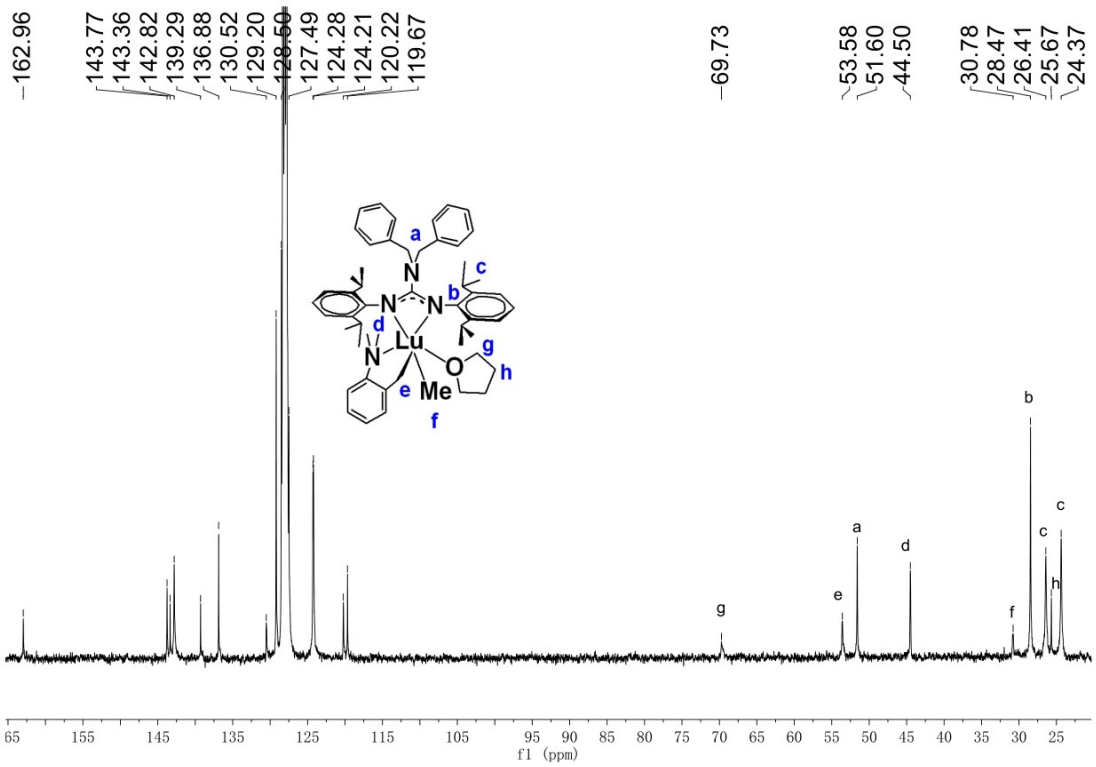

Fig. S2 ^{13}C NMR spectrum of **1** obtained in C_6D_6 at room temperature.

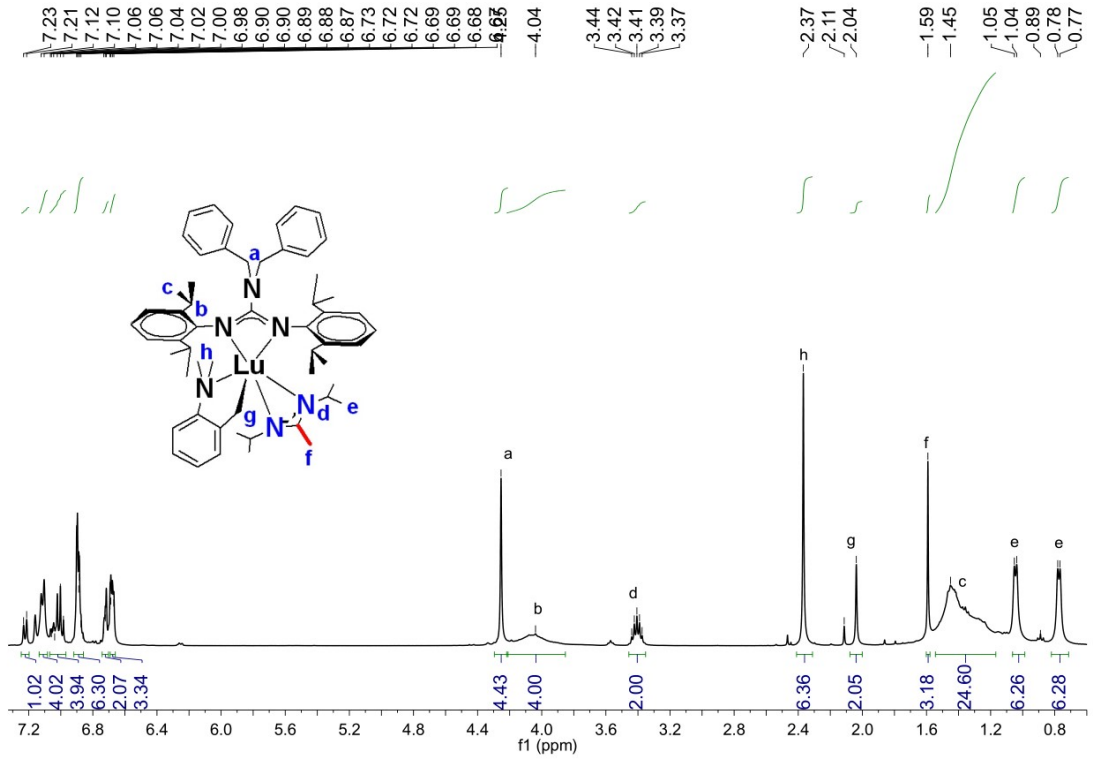

Fig. S3 ^{1}H NMR spectrum of **2** obtained in C_6D_6 at room temperature.

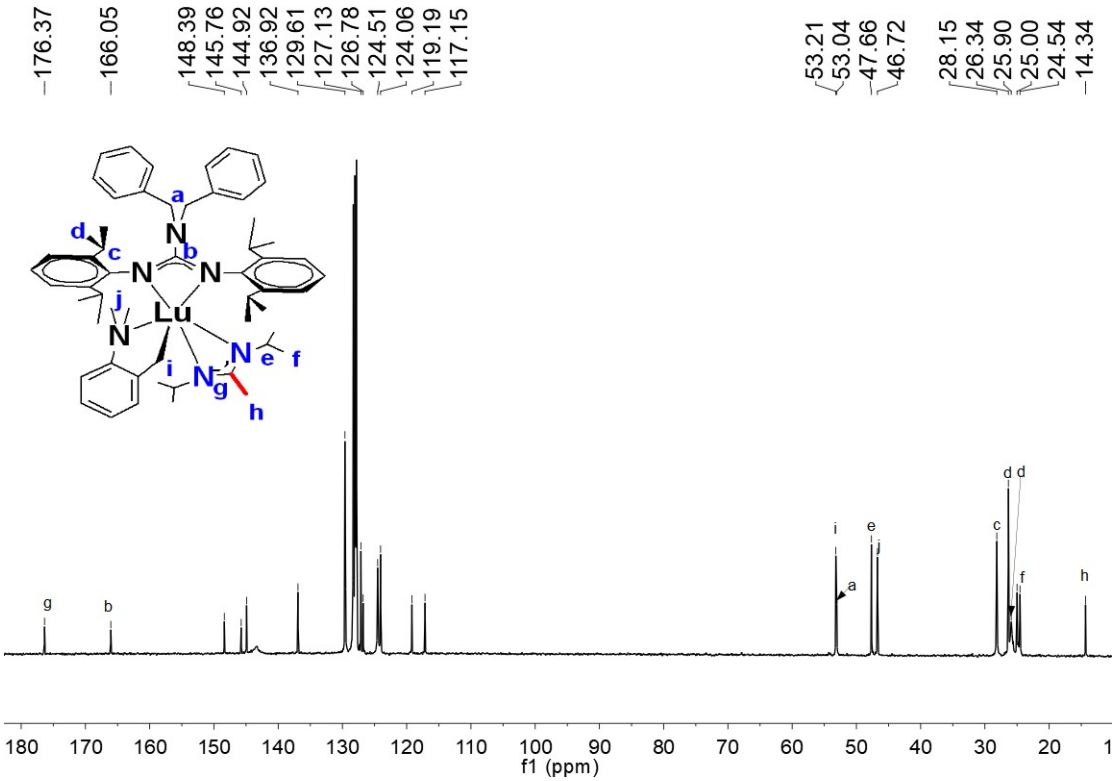

Fig. S4 ^{13}C NMR spectrum of **2** obtained in C_6D_6 at room temperature.

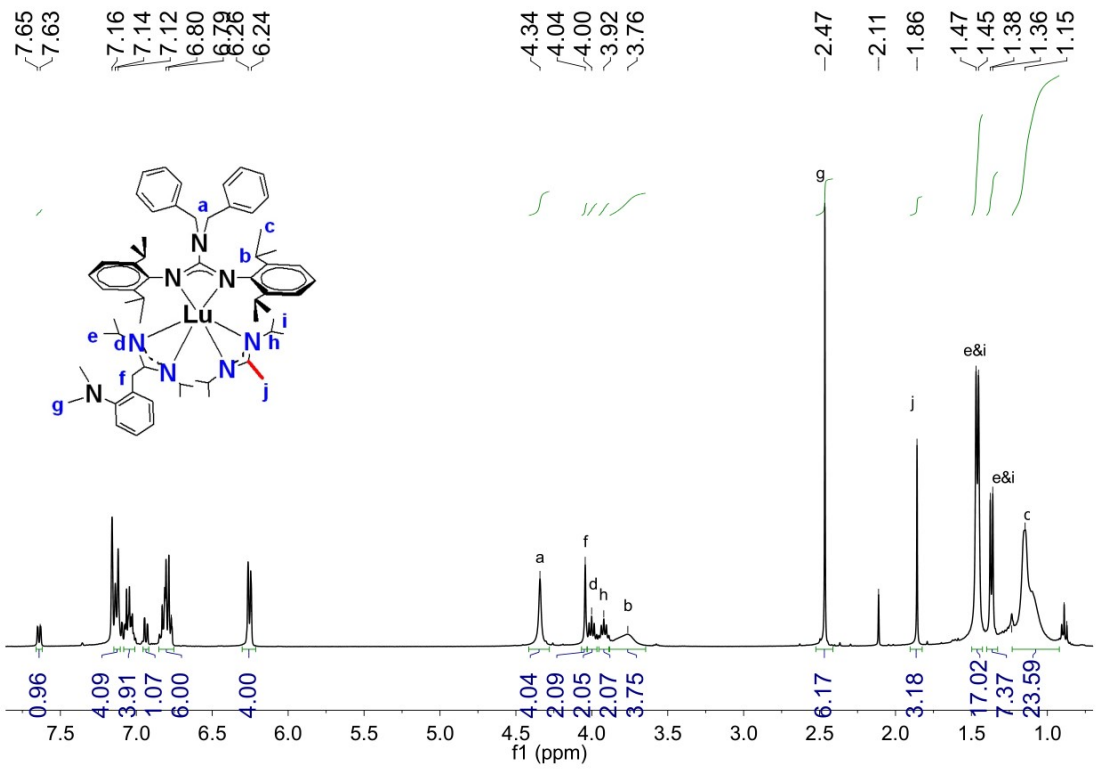

Fig. S5 ^{1}H NMR spectrum of **3** obtained in C_6D_6 at room temperature.

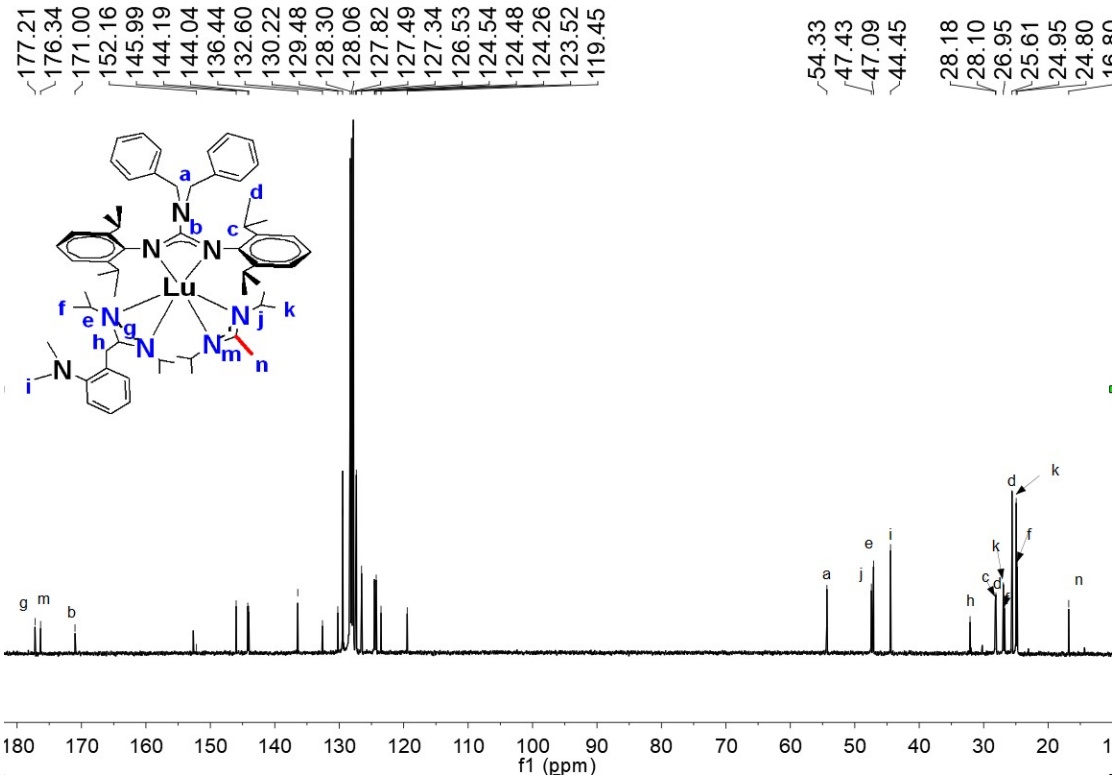

Fig. S6 ^{13}C NMR spectrum of **3** obtained in C_6D_6 at room temperature.

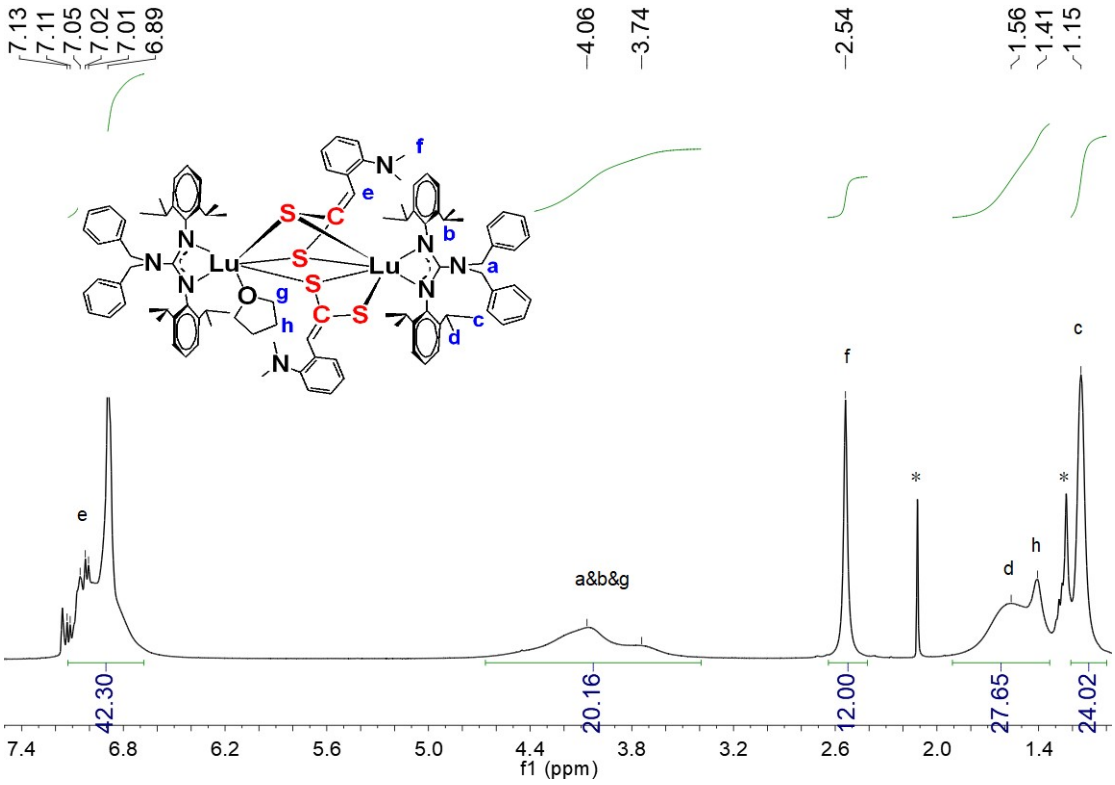

Fig. S7 ^{1}H NMR spectrum of **4** obtained in C_6D_6 at room temperature.

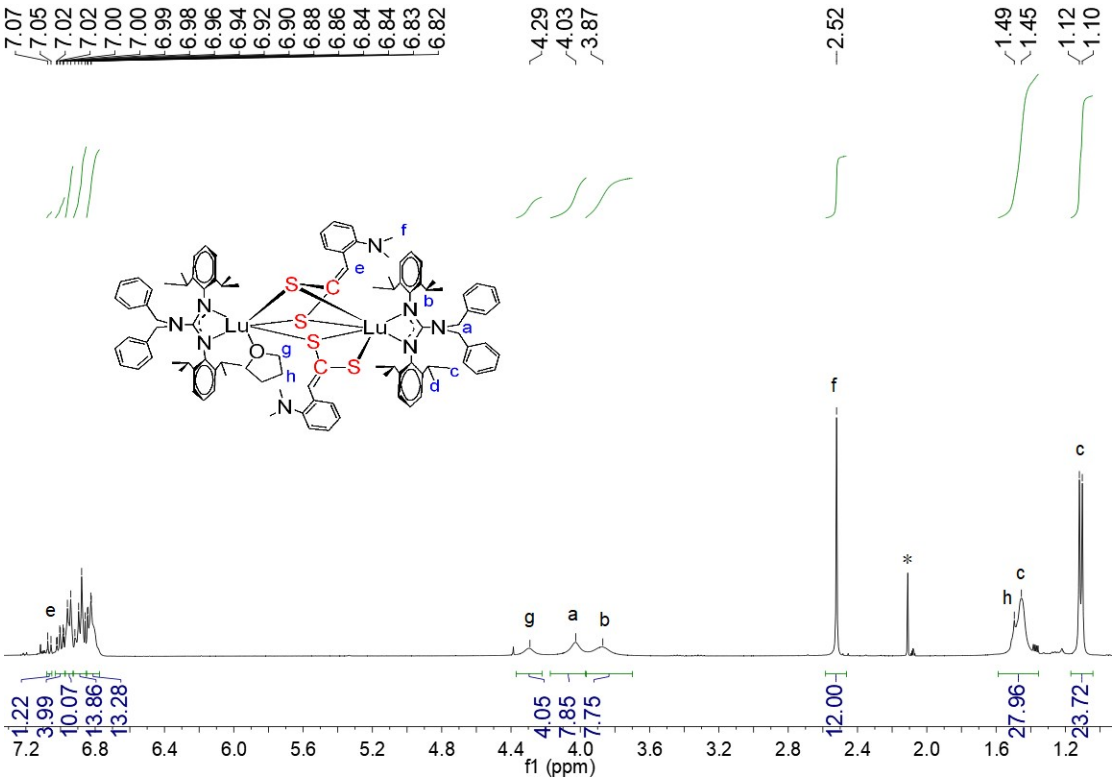

Fig. S8 ^{1}H NMR spectrum of **4** obtained in tol-d_8 at 50 °C.

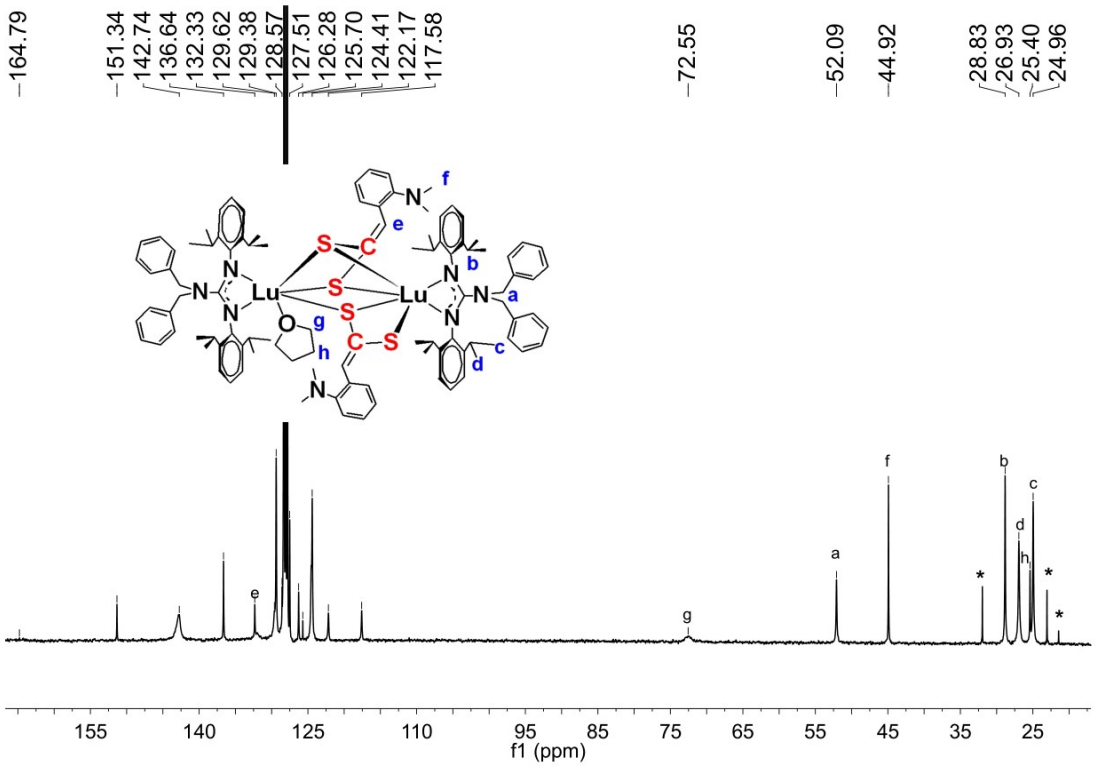

Fig. S9 ^{13}C NMR spectrum of **4** obtained in C_6D_6 at room temperature.

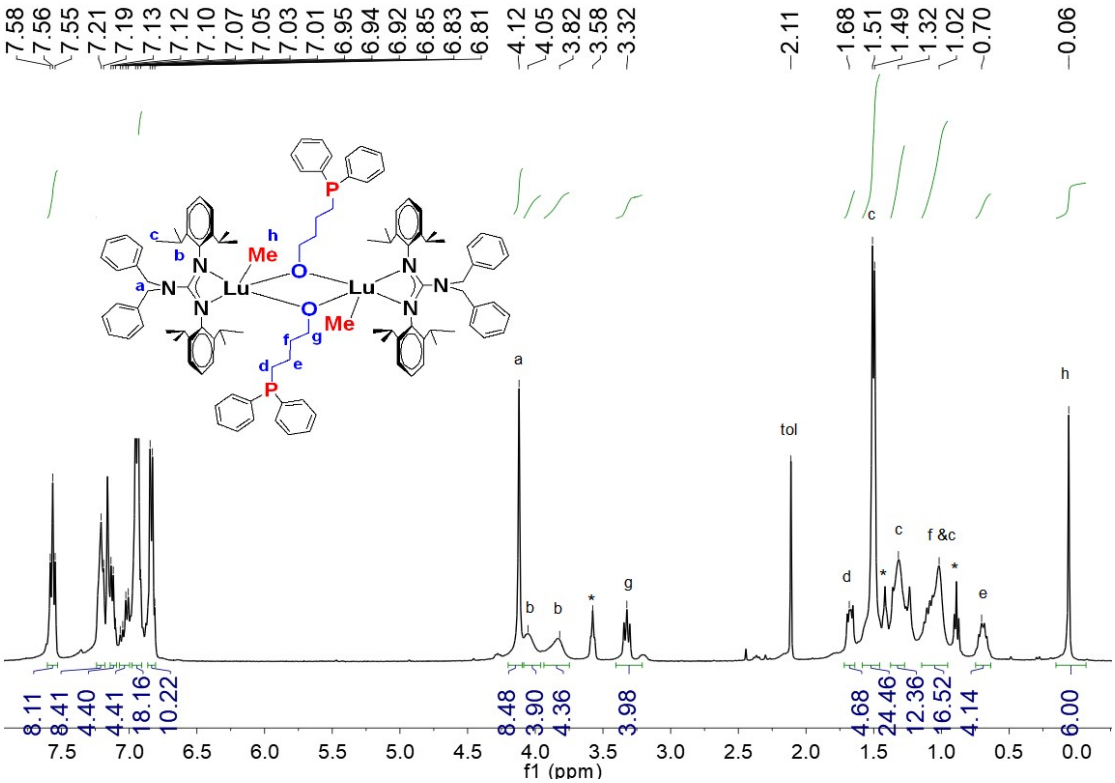

Fig. S10 ^{1}H NMR spectrum of **5** obtained in C_6D_6 at room temperature.

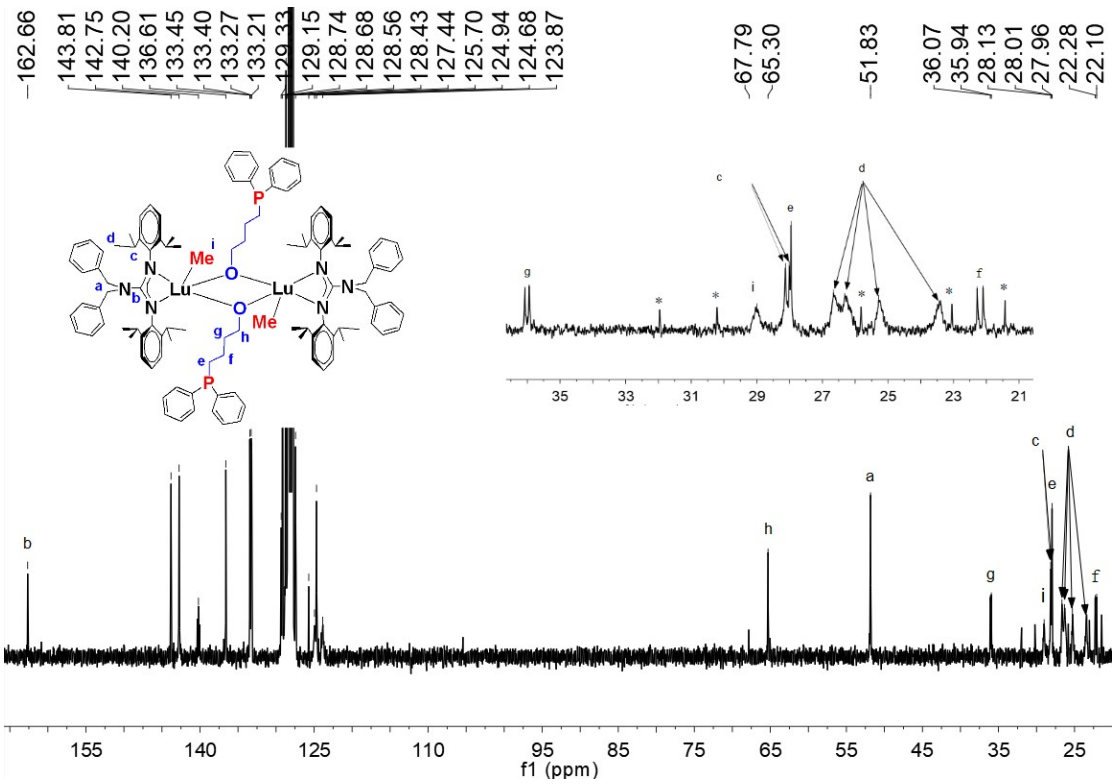

Fig. S11 ^{13}C NMR spectrum of **5** obtained in C_6D_6 at room temperature.

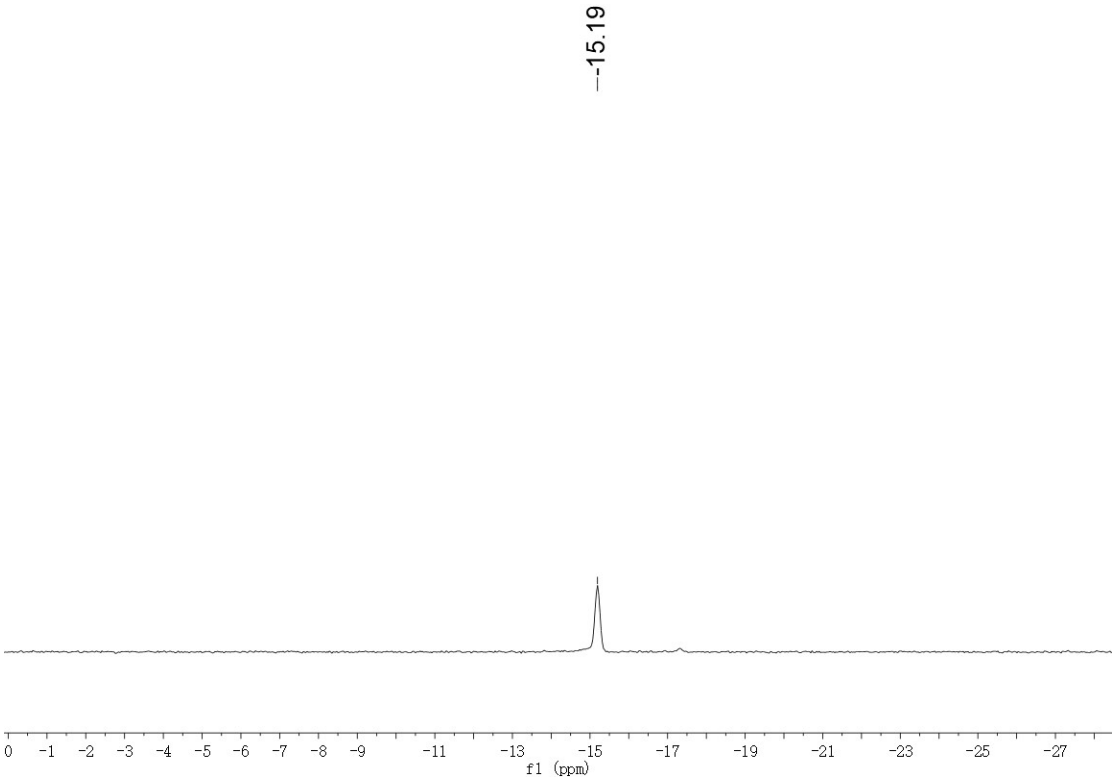

Fig. S12 ^{31}P NMR spectrum of **5** obtained in C_6D_6 at room temperature.

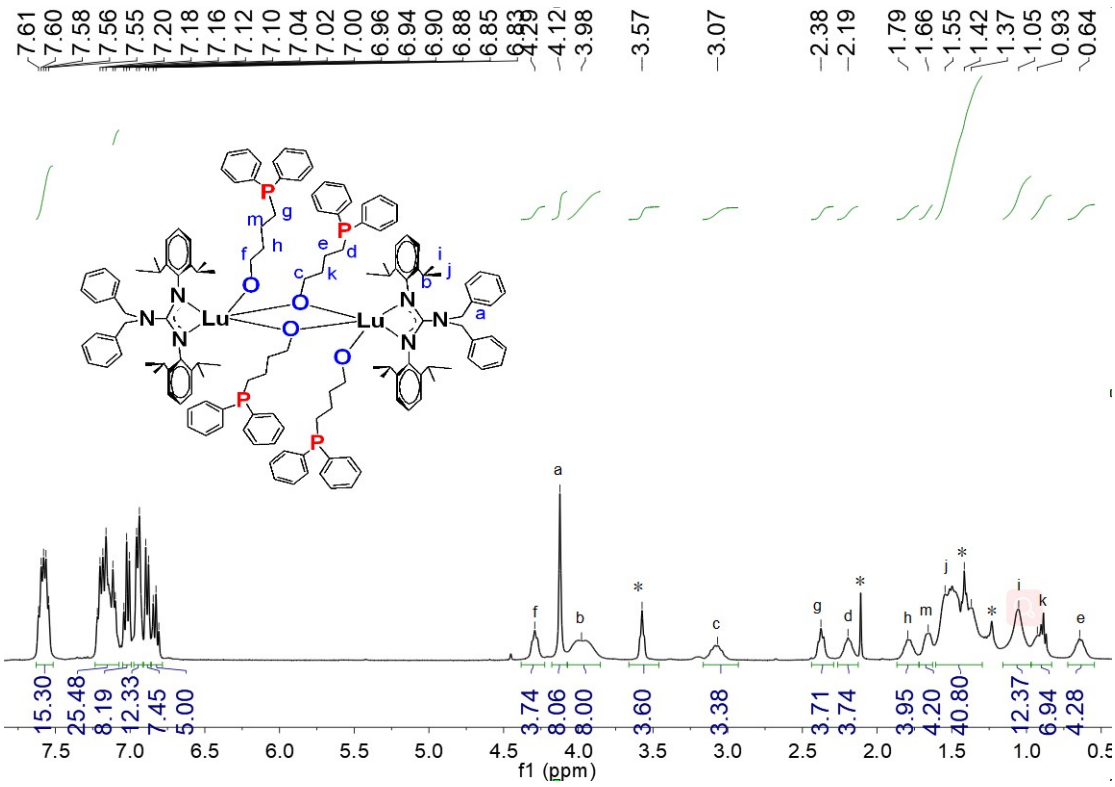

Fig. S13 ^{1}H NMR spectrum of **6** obtained in C_6D_6 at room temperature.

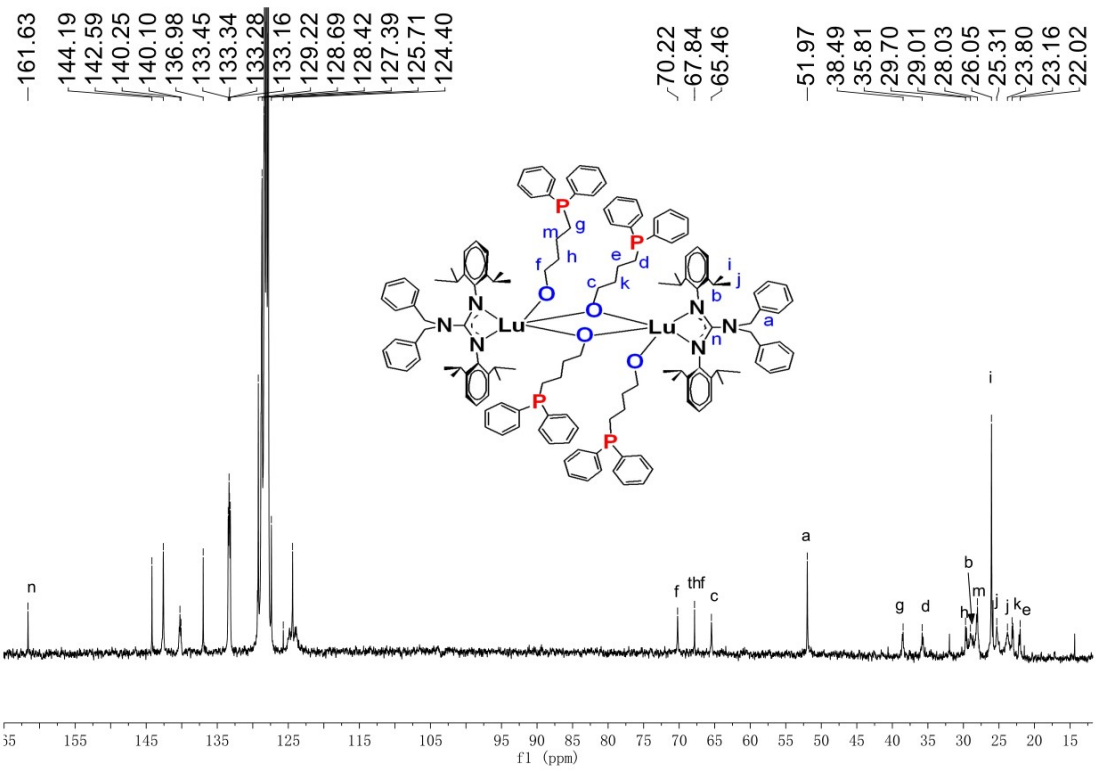

Fig. S14 ^{13}C NMR spectrum of **6** obtained in C_6D_6 at room temperature.

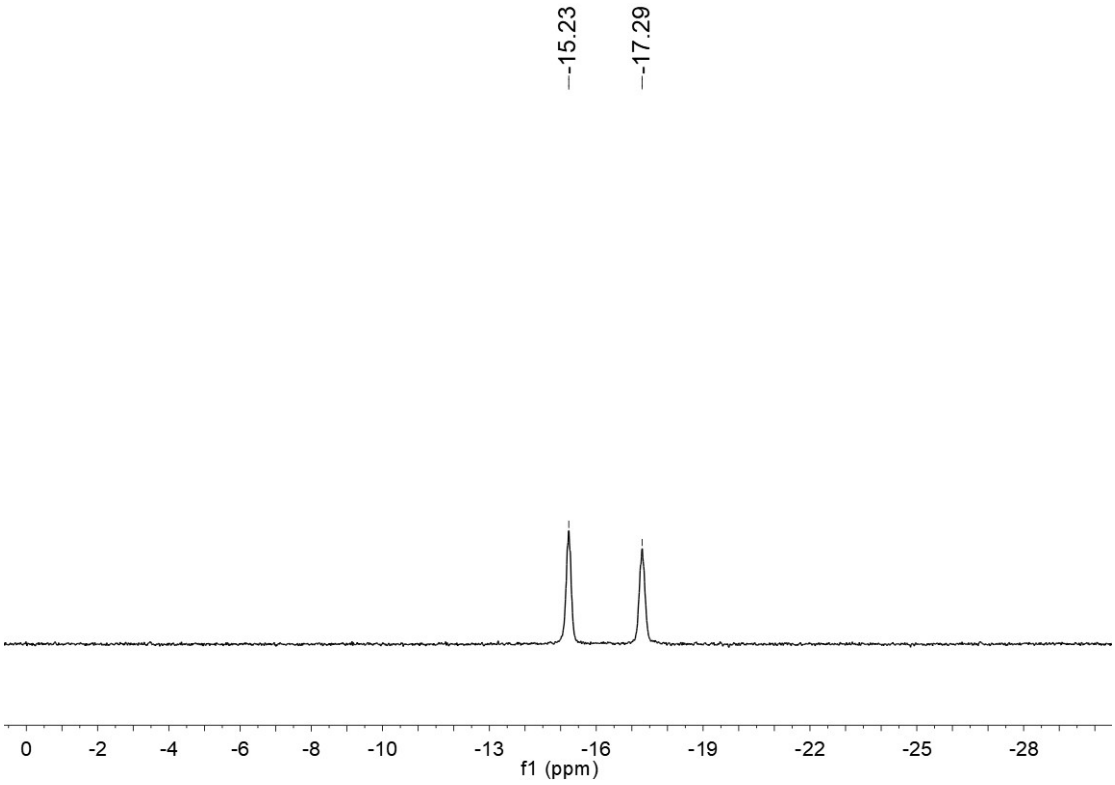

Fig. S15 ^{31}P NMR spectrum of **6** obtained in C_6D_6 at room temperature.

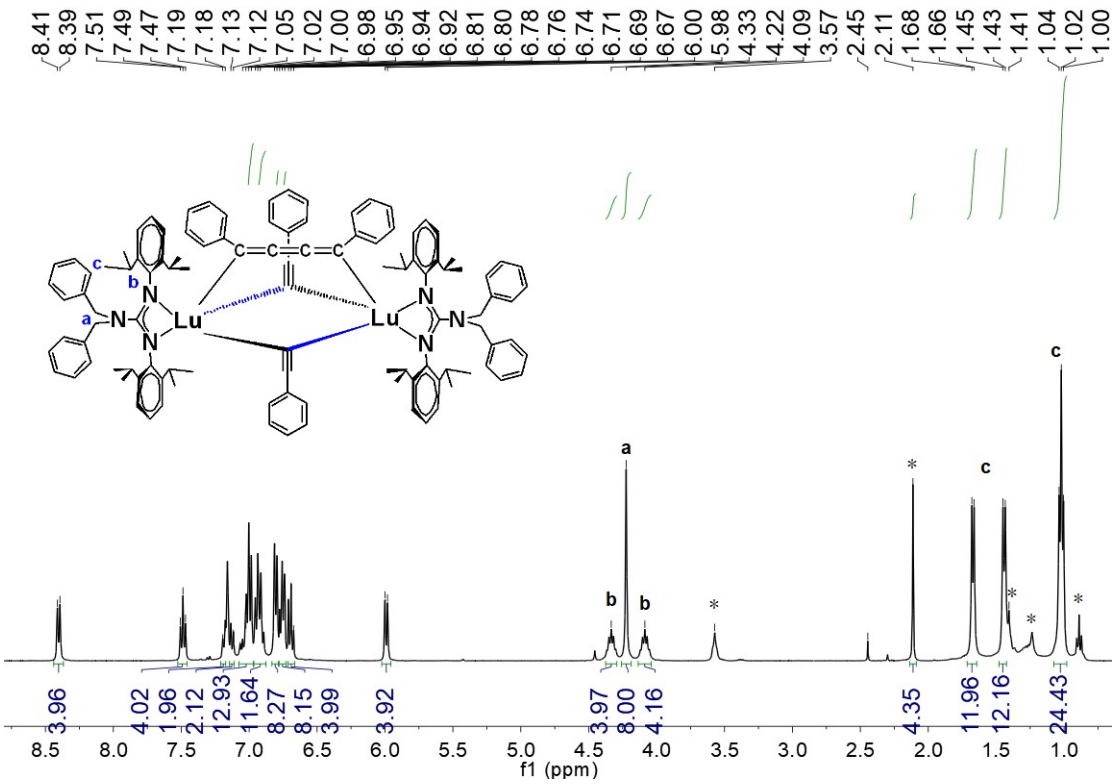

Fig. S16 ^{1}H NMR spectrum of **8** obtained in C_6D_6 at room temperature.

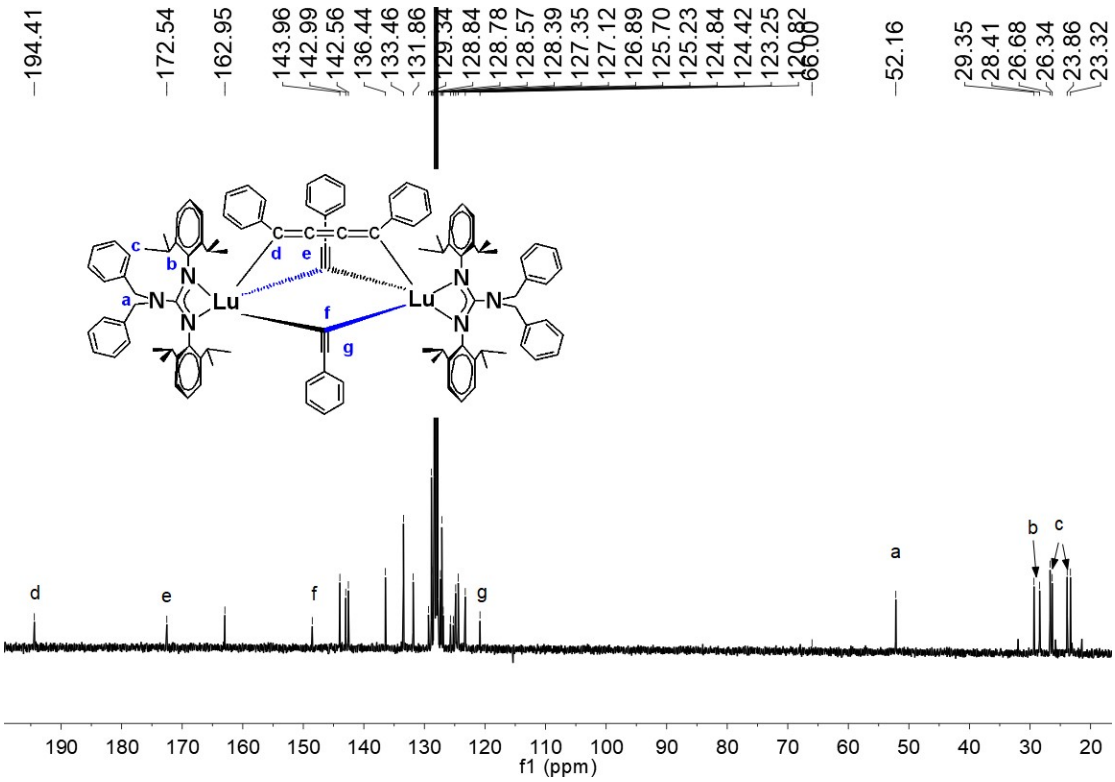

Fig. S17 ^{13}C NMR spectrum of **8** obtained in C_6D_6 at room temperature.

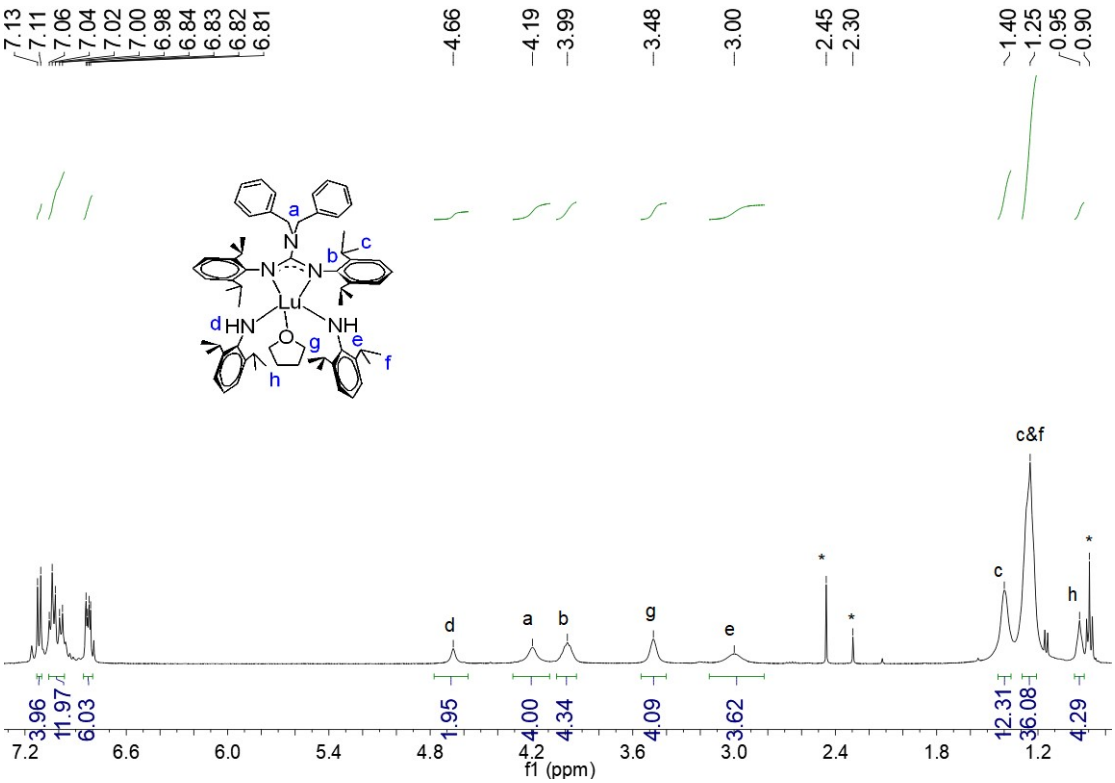

Fig. S18 ^{1}H NMR spectrum of **9** obtained in C_6D_6 at room temperature.

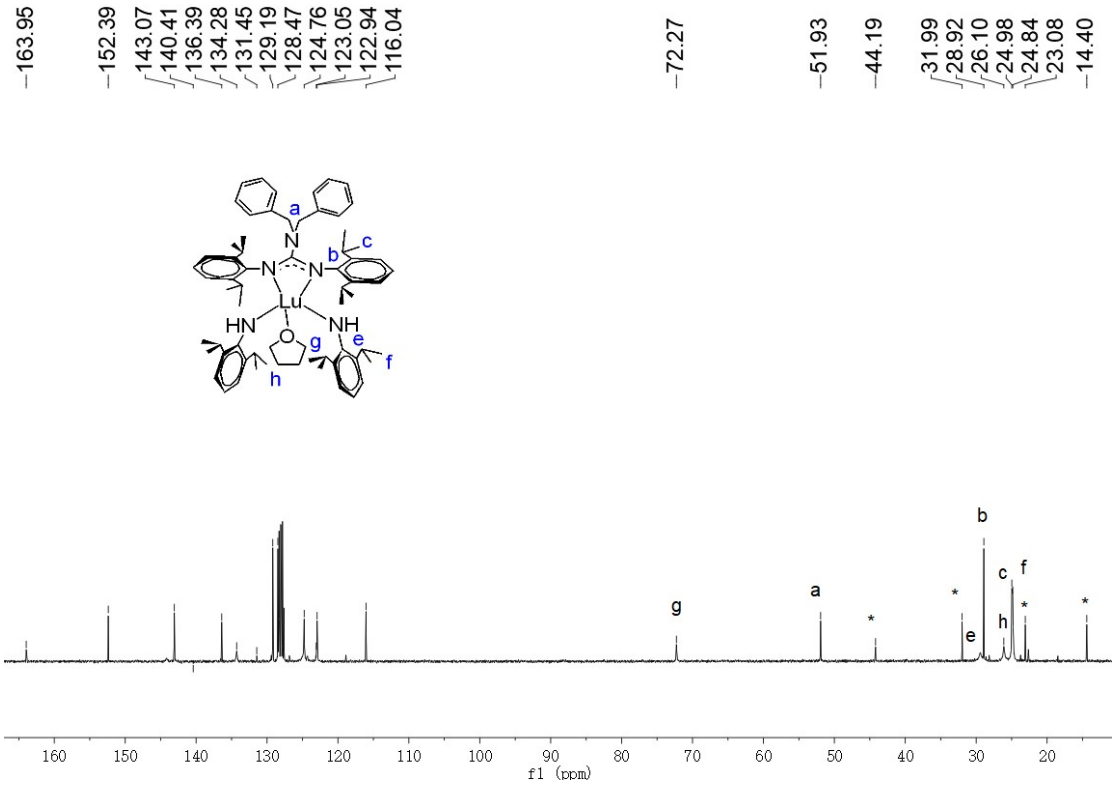

Fig. S19 ^{13}C NMR spectrum of **9** obtained in C_6D_6 at room temperature.

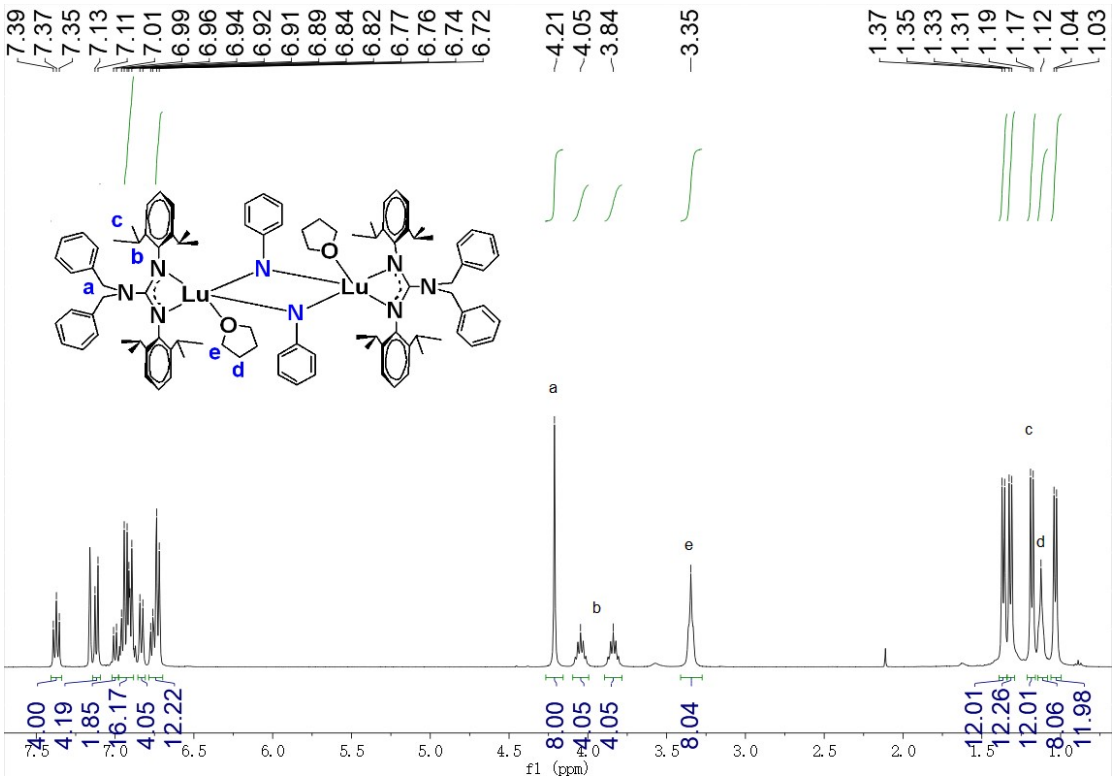

Fig. S20 ^{1}H NMR spectrum of **10** obtained in C_6D_6 at room temperature.

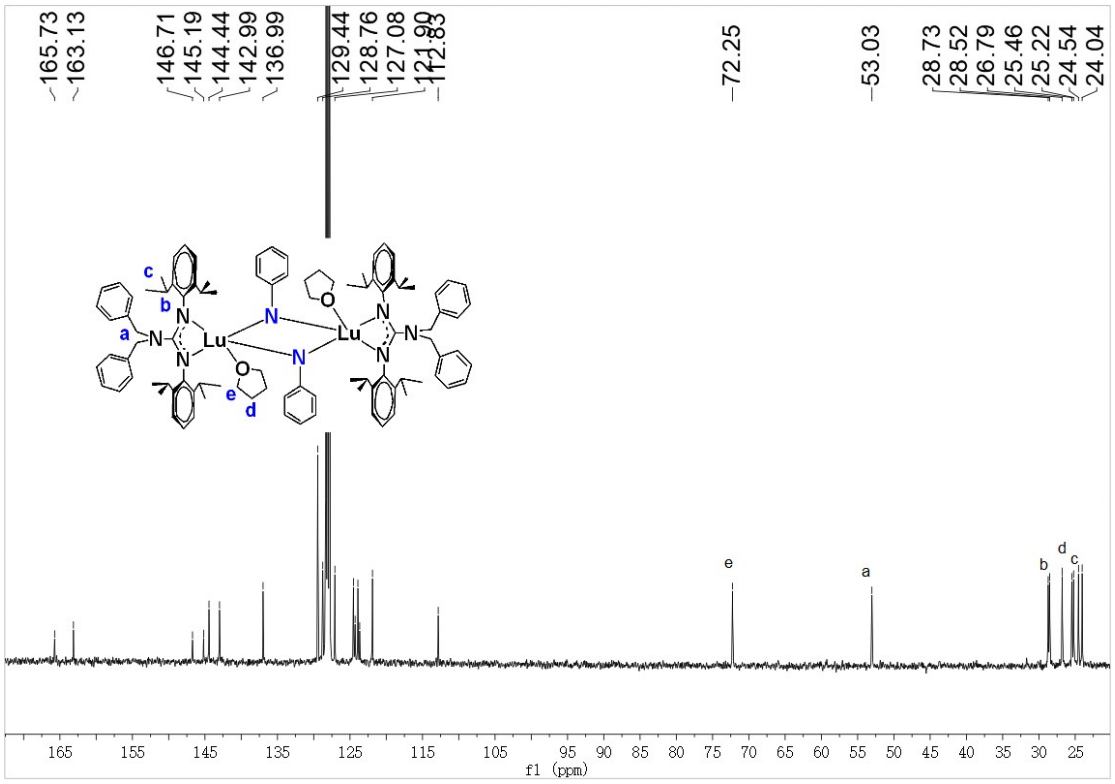

Fig. S21 ^{13}C NMR spectrum of **10** obtained in C_6D_6 at room temperature.

2. X-ray Crystallographic Analysis of Complexes 1-8 and 10

X-ray crystallographic data collections were performed on a Bruker SMART APEX or Bruker SMART APEX II (at 173 K) diffractometer with CCD area detector using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) or Ga-Kα radiation (λ = 1.34138 Å). The structure was solved by using SHELXTL program. Refinement was performed on F^2 anisotropically by the full-matrix least-squares method for all the non-hydrogen atoms. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2133403 (for **1**), 2133397 (for **2**), 2133400 (for **3**), 2133398 (for **4**), 2133395 (for **5**), 2133396 (for **6**), 2133399 (for **7**), 2133402 (for **8**), and 2133401 (for **10**), contain the supplementary crystallographic data for this paper.

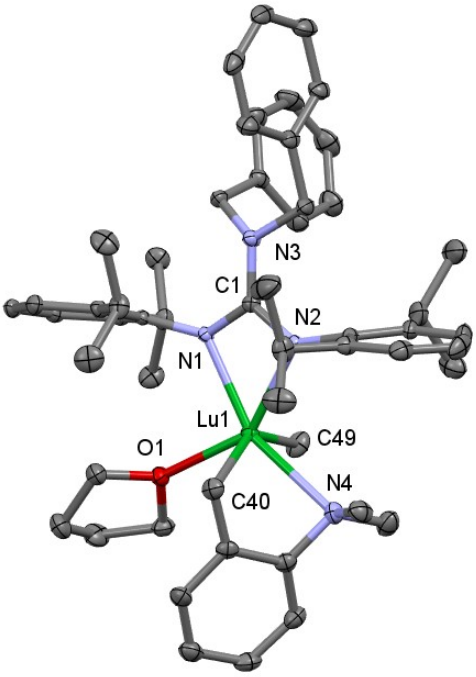

Fig. S20 Molecular structure of complex **1** with thermal ellipsoids at 30% probability. All of the hydrogen atoms are omitted in complex **1**. Selected bond distances(Å) and angles(◦): Lu(1)−N(1) 2.306(3), Lu(1)−N(2) 2.324(3), Lu(1)−O(1) 2.351(5), Lu(1)−C(49) 2.369(4), Lu(1)−C(40) 2.440(4) Lu(1)−N(4) 2.609(3); N(1)−Lu(1)−N(2) 57.19(10), N(1)−Lu(1)−O(1) 89.10(10), N(2)−Lu(1)−O(1) 145.75(10), N(1)−Lu(1)−C(49) 100.37(14).

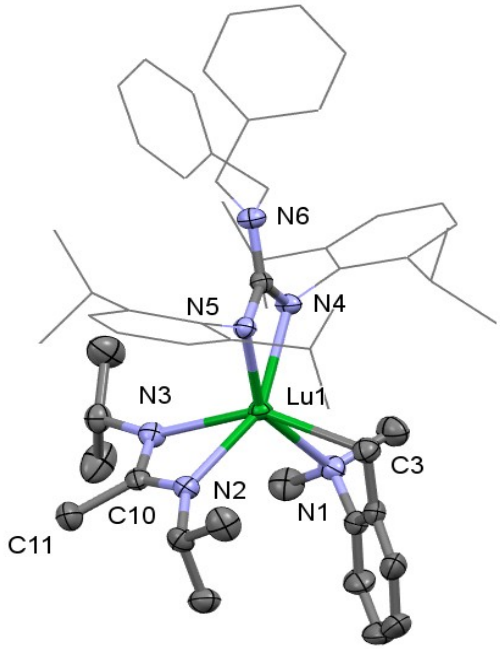

Fig. S21 Molecular structures of **2** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted and selected carbon atoms are depicted as wireframe for clarity. Selected bond lengths (Å) and angles (deg): Lu(1)−N(1) 2.492(19), Lu(1)−N(2) 2.320(2), Lu(1)−N(3) 2.390(2), Lu(1)−N(4) 2.374(17), Lu(1)−N(5) 2.312(16), Lu(1)−C(3) 2.392(17), C(10)−C(11) 1.530(3), C(10)−N(2) 1.310(3), C(10)−N(3) 1.400(3); N(5)−Lu(1)−N(2) 105.7(7), N(5)−Lu(1)−N(3) 110.4(6), N(5)−Lu(1)−C(3) 98.0(6), N(5)−Lu(1)−N(1) 153.4(6), N(4)−Lu(1)−C(3) 103.5(6), N(4)−Lu(1)−N(3) 107.8(7), N(4)−Lu(1)−N(1) 102.8(6), N(2)−Lu(1)−N(4) 153.3(6), N(2)−Lu(1)−N(1) 99.2(7), N(2)−Lu(1)−C(3) 98.4(7), N(3)−Lu(1)−N(1) 91.0(7), C(3)−Lu(1)−N(3) 145.9(6).

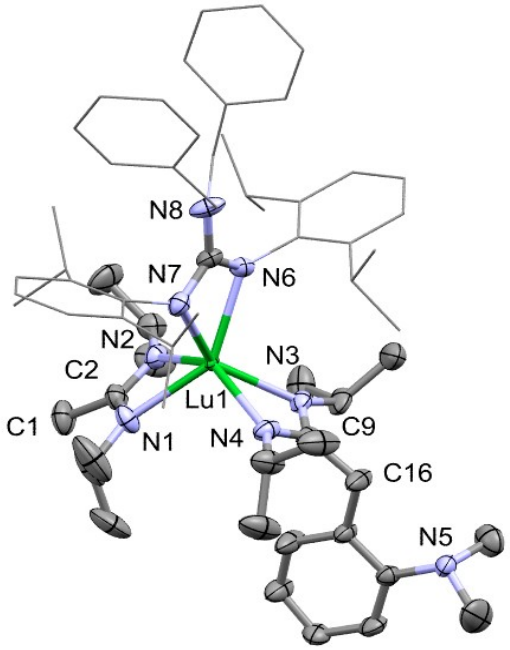

Fig. S22 Molecular structures of **3** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted and selected carbon atoms are depicted as wireframe for clarity. Selected bond lengths (Å) and angles (deg): Lu(1)−N(3) 2.305(5), Lu(1)−N(2) 2.306(6), Lu(1)−N(4) 2.312(6), Lu(1)−N(1) 2.311(5), Lu(1)−N(6) 2.346(5), Lu(1)−N(7) 2.360(5), C(2)−N(1) 1.318(9), C(2)−N(2) 1.328(9), C(9)−N(3) 1.326(10), C(9)−N(4) 1.328(11), C(1)−C(2) 1.529(10), C(9)−C(16) 1.520(9); N(3)−Lu(1)−N(6) 100.6(2), N(2)−Lu(1)−N(6) 101.23(19), N(4)−Lu(1)−N(6) 116.51(19), N(1)−Lu(1)−N(6) 142.2(2), N(3)−Lu(1)−N(7) 139.48(19), N(2)−Lu(1)−N(7) 116.04(18), N(4)−Lu(1)−N(7) 99.9(2), N(1)−Lu(1)−N(7) 102.6(2), N(1)−C(2)−N(2) 113.5(6), N(3)−C(9)−N(4) 115.5(6).

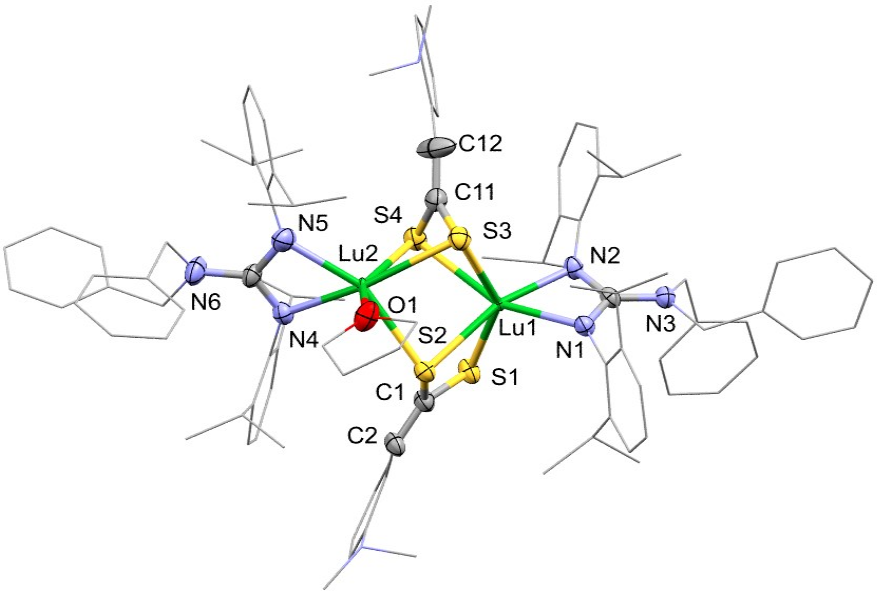

Fig. S23 Molecular structures of **4** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted and selected carbon atoms are depicted as wireframe for clarity. Selected bond lengths (Å) and angles (deg): Lu(1)−S(1) 2.6033(17), Lu(1)−S(2) 2.7128(15), Lu(1)−S(4) 2.7356(18), Lu(1)−S(3) 2.7933(18), Lu(1)−Lu(2) 3.6076(5), Lu(2)−O(1) 2.3180(5), Lu(2)−S(2) 2.6988(17), Lu(2)−S(4) 2.7040(17), Lu(2)−S(3) 2.7607(17), C(1)−S(1) 1.7620(7), C(1)−S(2) 1.7980(7), C(1)−C(2) 1.3430(9), C(11)−C(12) 1.3440(12); S(1)−Lu(1)−S(2) 68.26(5), O(1)−Lu(2)−S(2) 79.14(14), N(2)−Lu(1)−S(1) 101.72(14), N(1)−Lu(1)−S(1) 106.24(14).

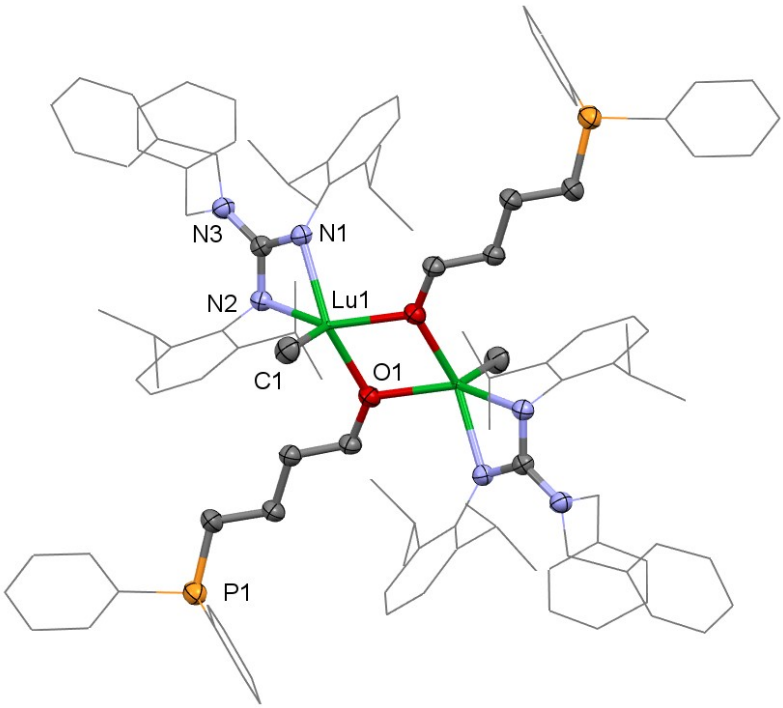

Fig. S24 Molecular structures of **5** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted and selected carbon atoms are depicted as wireframe for clarity. Selected bond lengths (Å) and angles (deg): Lu(1)−O(1) 2.193(5), Lu(1)−N(1) 2.293(6), Lu(1)−C(1) 2.311(9), Lu(1)−N(2) 2.321(6), C(2)−O(1) 1.419(8), C(5)−P(1) 1.825(9); O(1)−Lu(1)−C(1) 109.6(3), N(1)−Lu(1)−C(1) 105.7(3), C(1)−Lu(1)−N(2) 112.0(3),

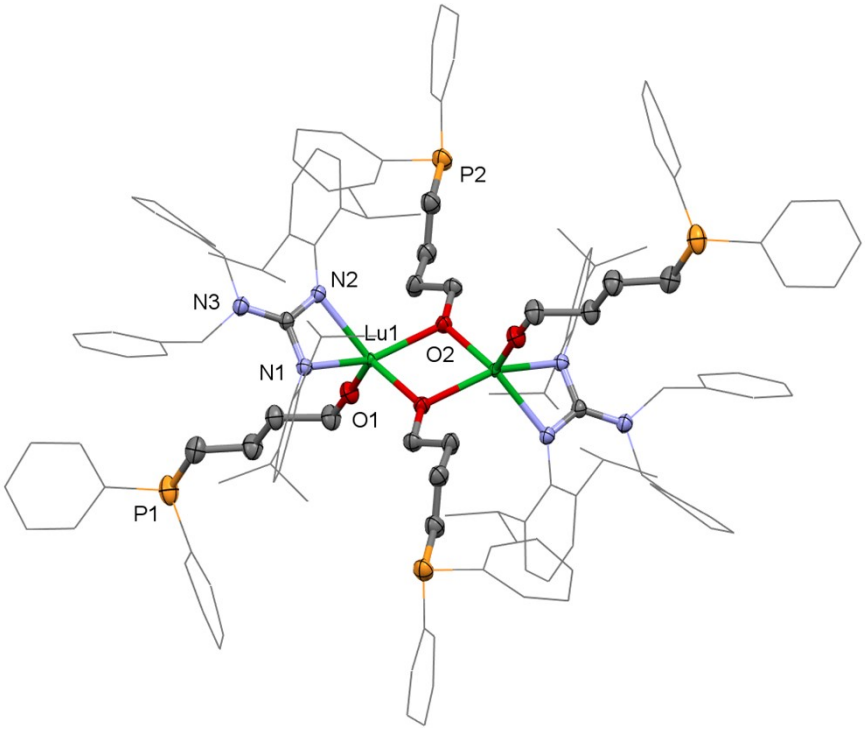

Fig. S25 Molecular structures of **6** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted and selected carbon atoms are depicted as wireframe for clarity. Selected bond lengths (Å) and angles (deg): Lu(1)−O(1) 2.022(6), Lu(1)−O(2) 2.203(4), Lu(1)−N(2) 2.287(6), Lu(1)−N(1) 2.335(6), C(4)−P(1) 1.812(14), C(20)−P(2) 1.884(12); O(1)−Lu(1)−O(2) 112.6(2), O(1)−Lu(1)−N(2) 105.4(2), O(2)−Lu(1)−N(2) 97.08(18), O(1)−Lu(1)−N(1) 110.1(2), O(2)−Lu(1)−N(1) 134.9(2),

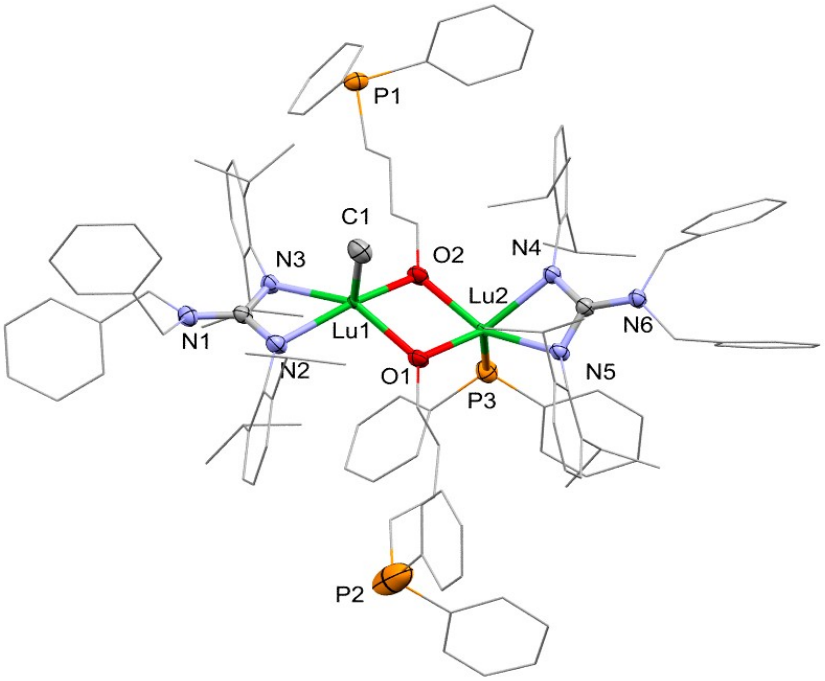

Fig. S26 Molecular structures of **7** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted and selected carbon atoms are depicted as wireframe for clarity. Selected bond lengths (Å) and angles (deg): Lu(1)−O(1) 2.206(5), Lu(1)−O(2) 2.226(5), Lu(2)−O(2) 2.181(5), Lu(2)−O(1) 2.190(4), Lu(1)−Lu(2) 3.532(5), Lu(1)−C(1) 2.325(8), Lu(2)−P(3) 2.755(19), O(1)−Lu(1)−C(1) 111.3(2), O(2)−Lu(1)−C(1) 105.1(2), N(2)−Lu(1)−C(1) 97.7(2), N(3)−Lu(1)−C(1) 104.8(2), C(1)−Lu(1)−Lu(2) 111.2(2), O(2)−Lu(2)−P(3) 104.96(14), O(1)−Lu(2)−P(3) 114.98(13), N(5)−Lu(2)−P(3) 109.20(13), N(4)−Lu(2)−P(3) 112.48(14), P(3)−Lu(2)−Lu(1) 116.88(4).

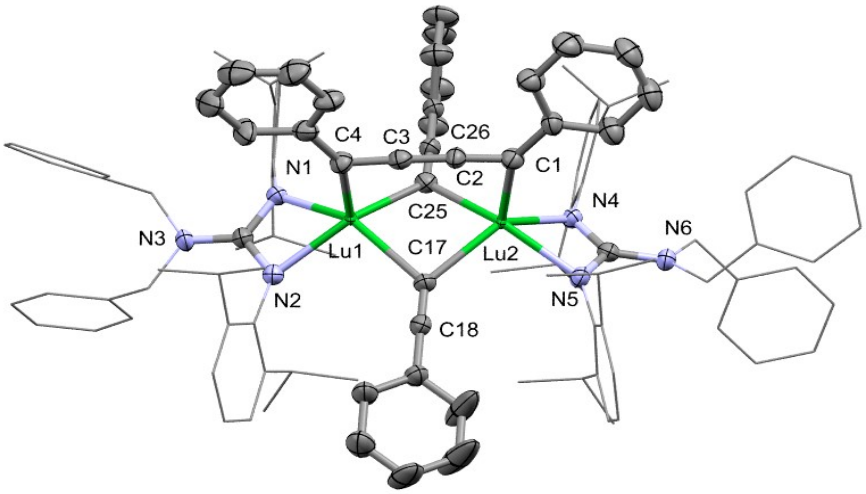

Fig. S27 Molecular structures of **8** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted and selected carbon atoms are depicted as wireframe for clarity. Selected bond lengths (Å) and angles (deg): Lu(1)−Lu(2) 3.4506(5), Lu(1)−C(4) 2.325(6), Lu(2)−C(1) 2.305(6), Lu(2)−C(2) 2.640(6), Lu(1)−C(3) 2.635(7), Lu(1)−C(25) 2.398(7), Lu(1)−C(17) 2.436(6), Lu(2)−C(17) 2.420(7), Lu(2)−C(25) 2.428(7), C(1)−C(2) 1.313(9), C(2)−C(3) 1.282(9), C(3)−C(4) 1.342(9), C(17)−C(18) 1.224(9), C(25)−C(26) 1.242(9); C(4)−Lu(1)−C(25) 107.8(2), C(4)−Lu(1)−C(17) 104.2(2), C(1)−Lu(2)−C(17) 108.4(2), C(1)−Lu(2)−C(25) 102.2(2), N(1)−Lu(1)−C(4) 105.3(2), N(2)−Lu(1)−C(4) 115.6(2), N(5)−Lu(2)−C(1) 108.0(2), N(4)−Lu(2)−C(1) 113.1(2), C(3)−C(2)−C(1) 174.8(7), C(2)−C(3)−C(4) 176.0(7), C(25)−Lu(1)−C(17) 84.7(2), Lu(2)−C(17)−Lu(1) 90.6(2).

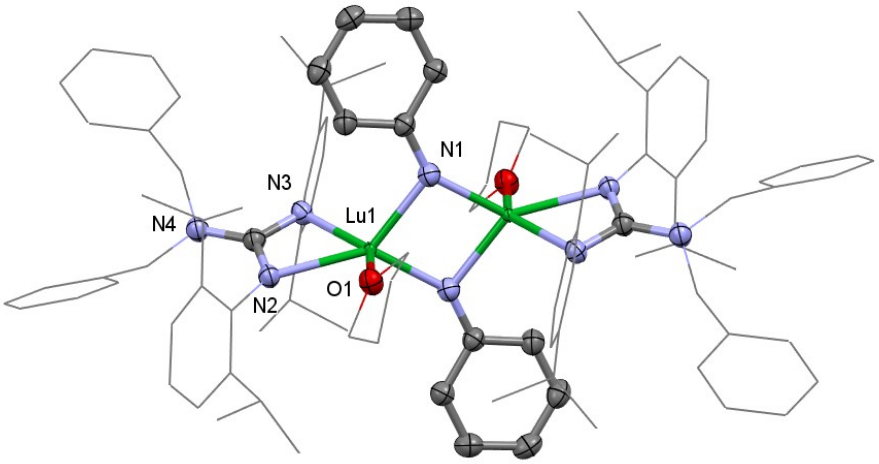

Fig. S28 Molecular structures of **9** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted and selected carbon atoms are depicted as wireframe for clarity. Selected bond lengths (Å) and angles (deg): Lu(1)−N(1) 2.210(3), Lu(1)−N(2) 2.358(2), Lu(1)−N(3) 2.339(2), Lu(1)−O(1) 2.339(1); N(2)−Lu(1)−O(1) 85.97(13), N(1)−Lu(1)−O(1) 84.04(13), N(2)−Lu(1)−N(1) 157.45(16), N(1)−Lu(1)−N(3) 100.71(13), N(1)−Lu(1)−N(4) 99.27(13), N(2)−Lu(1)−N(3) 98.50(13), N(2)−Lu(1)−N(4) 100.99(13).

Table 1. Crystal and Data Collection Parameters of Complexes 1, 2 and 3

	1	2	3
Formula	$C_{53}H_{71}N_4LuO$	$C_{56}H_{77}N_5Lu$	$C_{63}H_{91}N_8Lu$
Formula weight	955.10	995.23	1135.40
Temperature (K)	173(2)	298(2)	203(2)
Wavelength (Å)	0.71073	0.71073	1.34138
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P1	C2/c
a(Å)	10.8584(6)	10.2506(14)	18.5416(9)
b(Å)	11.5196(6)	12.2916(17)	18.5847(9)
c(Å)	21.0813(12)	22.231(3)	36.1653(18)
α (deg)	82.416(2)	80.511(2)	90
β (deg)	84.118(2)	77.101(2)	104.630(2)
γ (deg)	65.697(2)	69.932(2)	90
V (Å ^{3})	2378.9(2)	2552.6(6)	12058.1(10)
Z	2	2	8
Dc (g/m^3)	1.333	1.313	1.251
μ (mm^{-1})	2.116	1.975	2.274
F(000)	992	1052	4768
Crystal size (mm)	0.50 x 0.25 x 0.04	0.420 x 0.400 x 0.200	0.110 x 0.090 x 0.080
θ range (°)	1.952 to 27.000	1.888 to 27.675	2.978 to 56.994
h, k, l range	-13<=h<=13 -14<=k<=14 -26<=l<=26	-9<=h<=13 -15<=k<=16 -29<=l<=28	-23<=h<=23 -23<=k<=22 -45<=l<=45
Reflections collected / unique	107198/10376 [R(int) = 0.1253]	18786/11583 [R(int) = 0.0213]	74964/12333 [R(int) = 0.0638]
Completeness to θ	99.9 %	97.7 %	99.8 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	10376 / 18 / 577	11583 / 0 / 582	12333 / 341 / 821
Goodness-of-fit on F^2	1.030	1.072	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0379 wR2 =0.0790	R1 = 0.0241 wR2 = 0.0614	R1 = 0.0550 wR2 = 0.1629
R indices (all data)	R1 = 0.0549 wR2 = 0.0860	R1 = 0.0285 wR2 = 0.0636	R1 = 0.0673 wR2 = 0.1733
Largest diff. peak and hole (e. Å $^{-3}$)	1.110 and -1.660	0.702 and -0.370	1.181 and -0.424

Table 2. Crystal and Data Collection Parameters of Complexes 4, 5 and 6

	4	5	6
Formula	$C_{102}H_{118}Lu_2N_8S_4O$	$C_{112}H_{138}Lu_2O_2N_6P_2$	$C_{142}H_{168}Lu_2O_4N_6P_4$
Formula weight	1950.31	2012.25	2496.52
Temperature (K)	173(2)	173(2)	173(2)
Wavelength (Å)	1.34138 Å	1.34138	1.34138
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	P-1	P-1
a(Å)	22.8411(6)	11.4744(5)	14.5232(14)
b(Å)	16.4502(4)	15.9967(7) Å	15.3348(15)
c(Å)	30.0192(7)	16.4196(7) Å	15.5621(15)
α (deg)	90	99.226(2)	85.697(4)
β (deg)	95.0260(10)	102.621(2)	70.525(4)
γ (deg)	90	100.950(2)	77.353(4)
V ($Å^3$)	11236.1(5)	2822.7(2)	3188.3(5)
Z	4	1	1
Dc (g/m^3)	1.158	1.269	1.300
μ (mm^{-1})	2.835	2.585	2.534
F(000)	4032	1120	1296
Crystal size (mm)	0.320 x 0.230 x 0.220	0.100 x 0.100 x 0.080	0.090 x 0.070 x 0.040
θ range (°)	2.950 to 57.074	3.859 to 55.029	6.388 to 114.994
h, k, l range	-28<=h<=28 -20<=k<=20 -37<=l<=29	-13<=h<=14 -19<=k<=19 -20<=k<=19	-18<=h<=17 -19<=k<=19 -19<=k<=19
Reflections collected / unique	135456/22991 [R(int) = 0.0476	31302/10365 [R(int) = 0.0718]	48926/13112 [R(int) = 0.0916]
Completeness to θ	99.8 %	96.5 %	99.9 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	22995 / 484 / 1298	10365 / 12 / 568	13112 / 408 / 727
Goodness-of-fit on F^2	1.072	1.070	1.125
Final R indices [I>2sigma(I)]	R1 = 0.0520 wR2 = 0.1564	R1 = 0.0838 wR2 = 0.2340	R1 = 0.1008 wR2 = 0.2775
R indices (all data)	R1 = 0.0599 wR2 = 0.1607	R1 = 0.0927 wR2 = 0.2410	R1 = 0.1190 wR2 = 0.2923
Largest diff. peak and hole (e. $Å^{-3}$)	0.879and -0.718	1.649 and -1.155	2.51 and -1.12

Table 3. Crystal and Data Collection Parameters of Complexes 7, 8 and 9

	7	8	9
Formula	$C_{123}H_{145}Lu_2O_2N_6P_3$	$C_{110}H_{116}N_6Lu_2$	$C_{98}H_{122}Lu_2N_8O_2$
Formula weight	2182.29	1872.02	1793.96
Temperature (K)	173(2)	173(2)	173(2)
Wavelength (Å)	1.34138	1.34138	1.34138
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	$P2_1/c$	P-1
a(Å)	16.9768(7)	34.1224(14)	11.7160(6)
b(Å)	18.2805(7)	12.8198(5)	12.8939(8)
c(Å)	20.4588(8)	23.4595(10)	17.0465(10)
α (deg)	96.866(2)	90	95.663(2)
β (deg)	92.540(2)	108.391(2)	107.984(2)
γ (deg)	117.586(2)	90	113.851(2)
V ($Å^3$)	5551.1(4)	9738.0(7)	2164.9(2)
Z	2	4	4
Dc (g/m^3)	1.306	1.270	1.376
μ (mm^{-1})	2.713	2.729	3.068
F(000)	2256	3815	924
Crystal size (mm)	0.300 x 0.200 x 0.100	0.050 x 0.050 x 0.040	0.160 x 0.110 x 0.080
θ range (°)	3.137 to 54.904	3.279 to 55.254	3.716 to 57.129
h, k, l range	-20<=h<=20 -22<=k<=22 -24<=l<=23	-41<=h<=41 -15<=k<=15 -28<=l<=28	-14<=h<=14 -16<=k<=16 -21<=l<=21
Reflections collected / unique	70607/20964 [R(int) = 0.0473]	114001/18621 [R(int) = 0.1127]	48291/8861 [R(int) = 0.0604]
Completeness to θ	99.5 %	99.8 %	99.9 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	20964 / 400 / 1422	18621 / 572 / 1142	8861 / 12 / 505
Goodness-of-fit on F^2	1.067	1.022	1.120
Final R indices [I>2sigma(I)]	R1 = 0.0552 wR2 = 0.1483	R1 = 0.0506 wR2 = 0.1251	R1 = 0.0372 wR2 = 0.0992
R indices (all data)	R1 = 0.0698 wR2 = 0.1566	R1 = 0.0868 wR2 = 0.1420	R1 = 0.0427 wR2 = 0.1017
Largest diff. peak and hole (e. $Å^{-3}$)	1.243 and -0.838	0.826 and -0.464	0.740 and -0.308