Supporting Information

Heterobimetallic Rare Earth Metal-Zinc Catalysts for Reactions of Epoxides and CO_2 under Ambient Conditions

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Contents

1. Crystallographic figures of complexes 1-3 and 5-10.

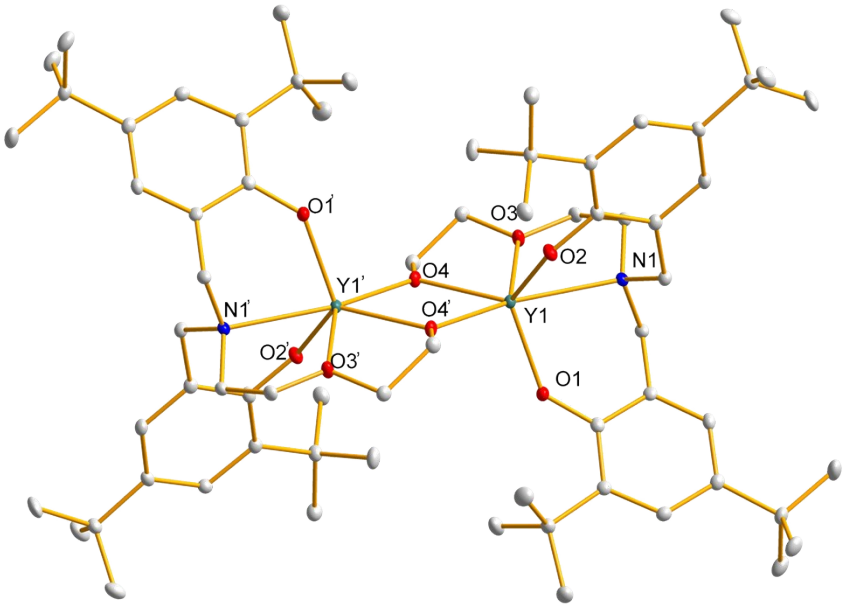


Figure S1. Solid state structure of complex **1**·3tol. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

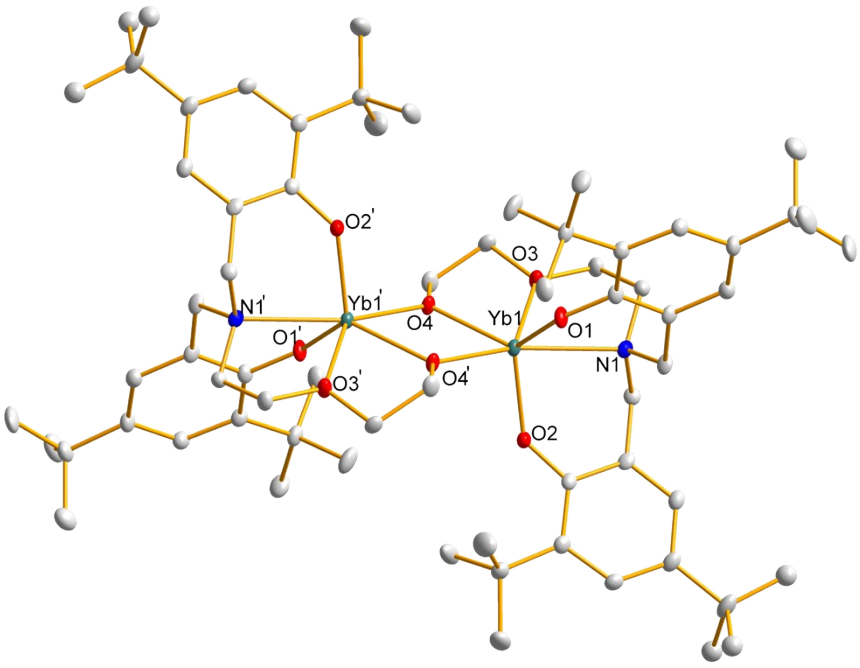


Figure S2. Solid state structure of complex **2**·3tol. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

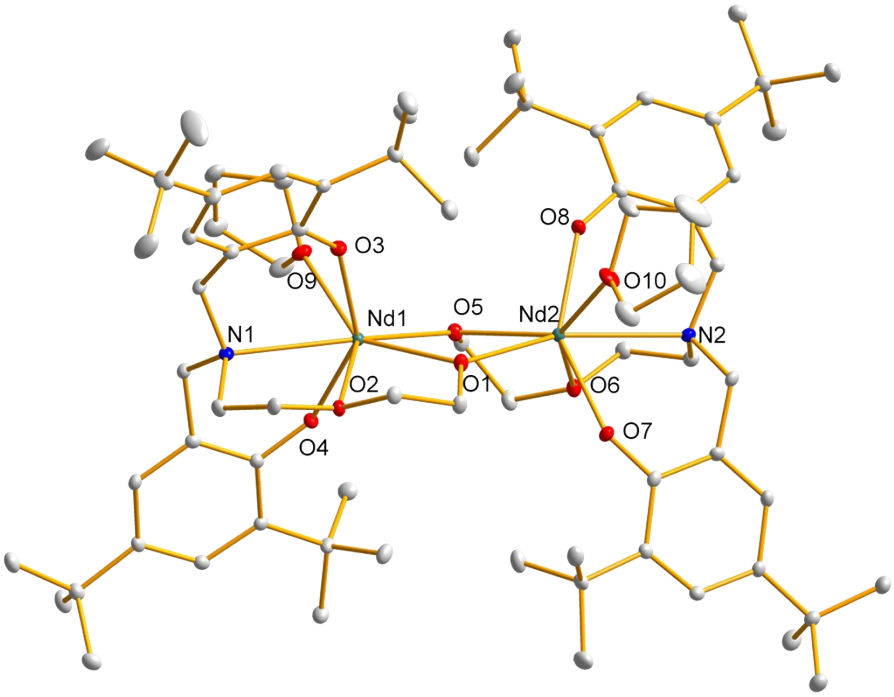


Figure S3. Solid state structure of complex **3**·tol·THF. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

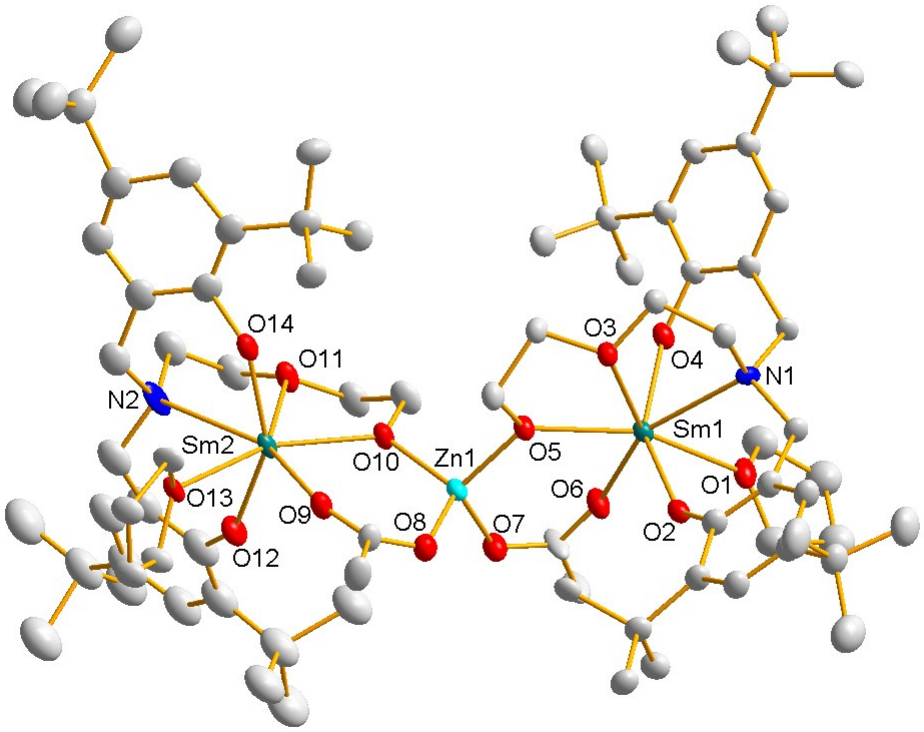


Figure S4. Solid state structure of complex **5**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

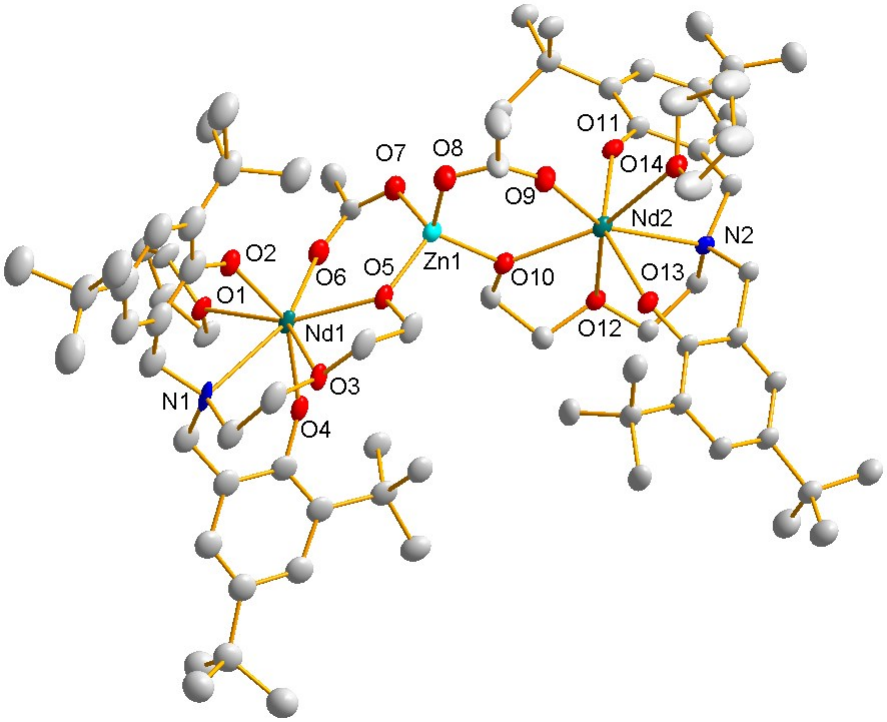


Figure S5. Solid state structure of complex **6**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

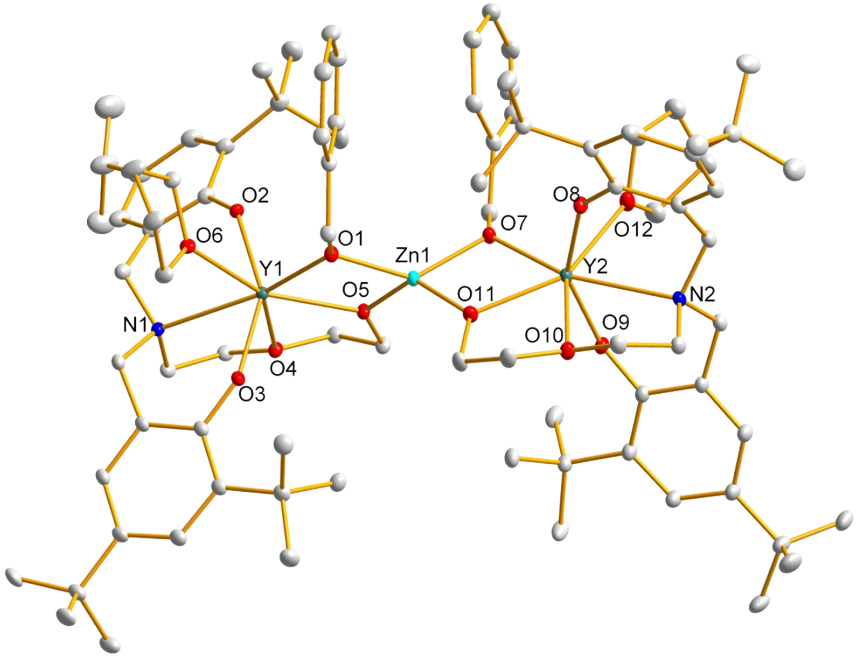


Figure S6. Solid state structure of complex **7**·4THF. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

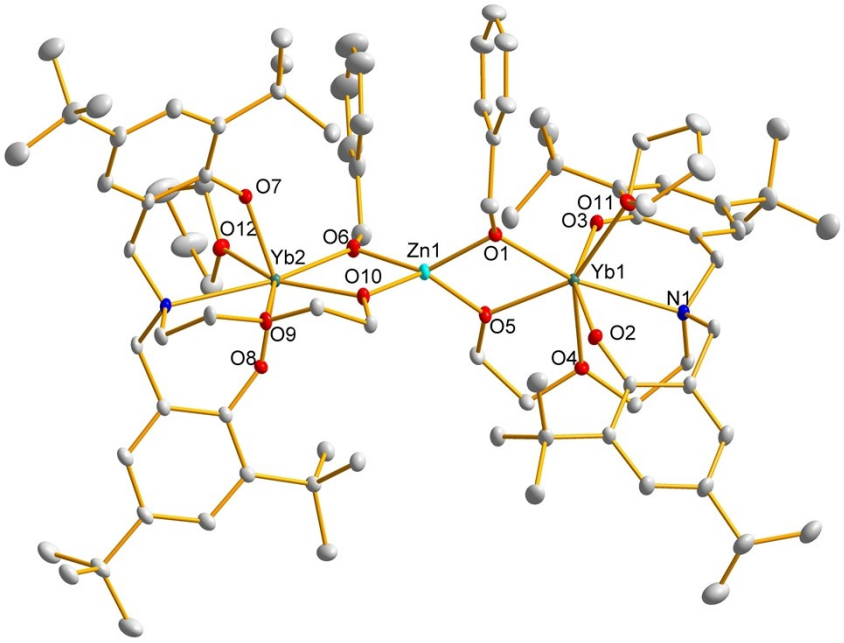


Figure S7. Solid state structure of complex **8**·2THF·hex. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

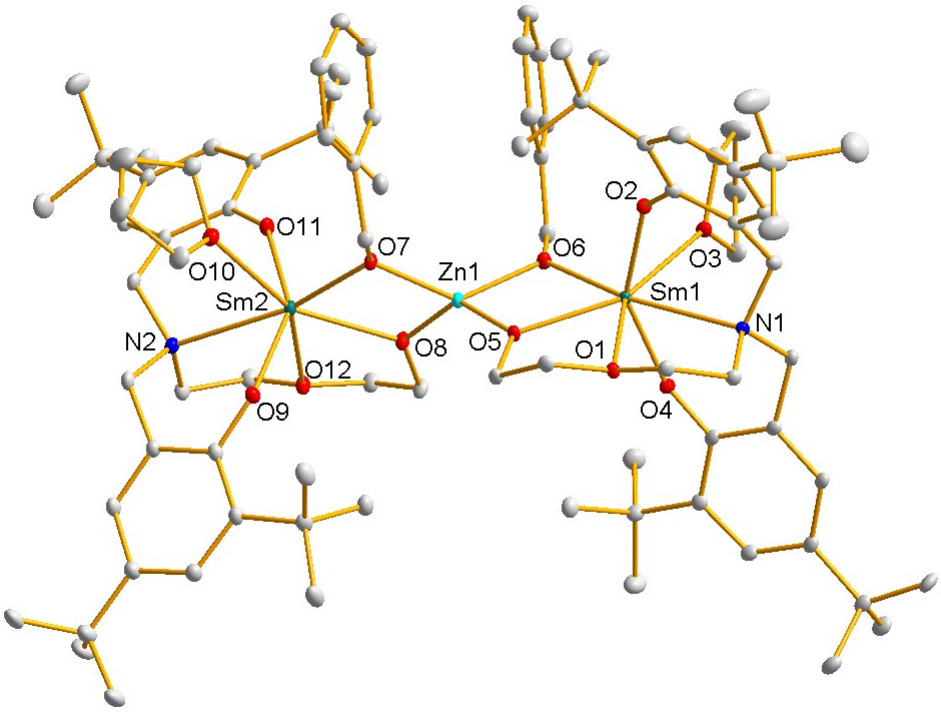


Figure S8. Solid state structure of complex **9**·4THF. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

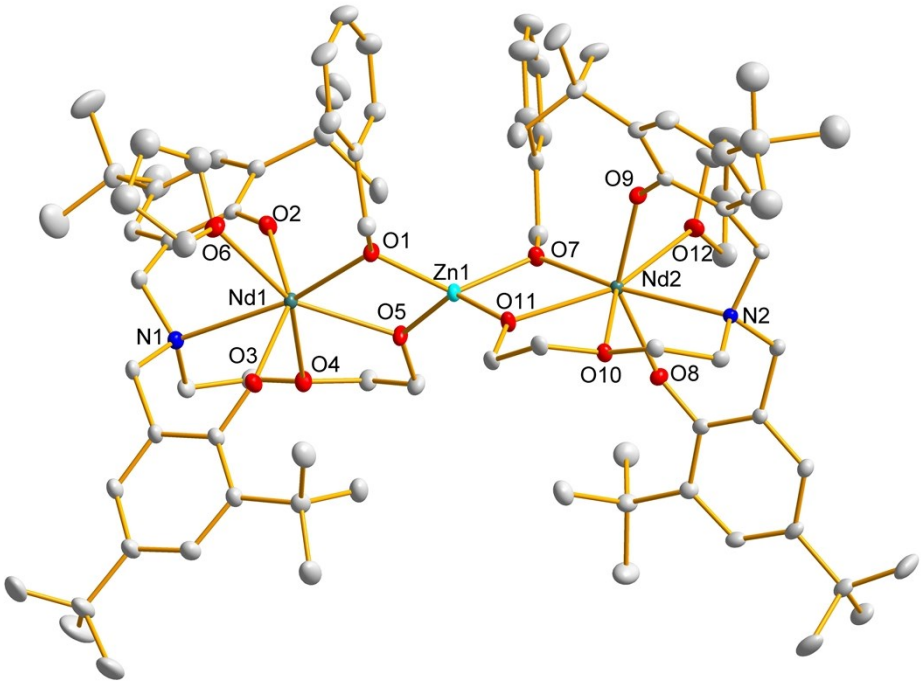


Figure S9. Solid state structure of complex **10**·4THF. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

2. NMR spectra of complexes

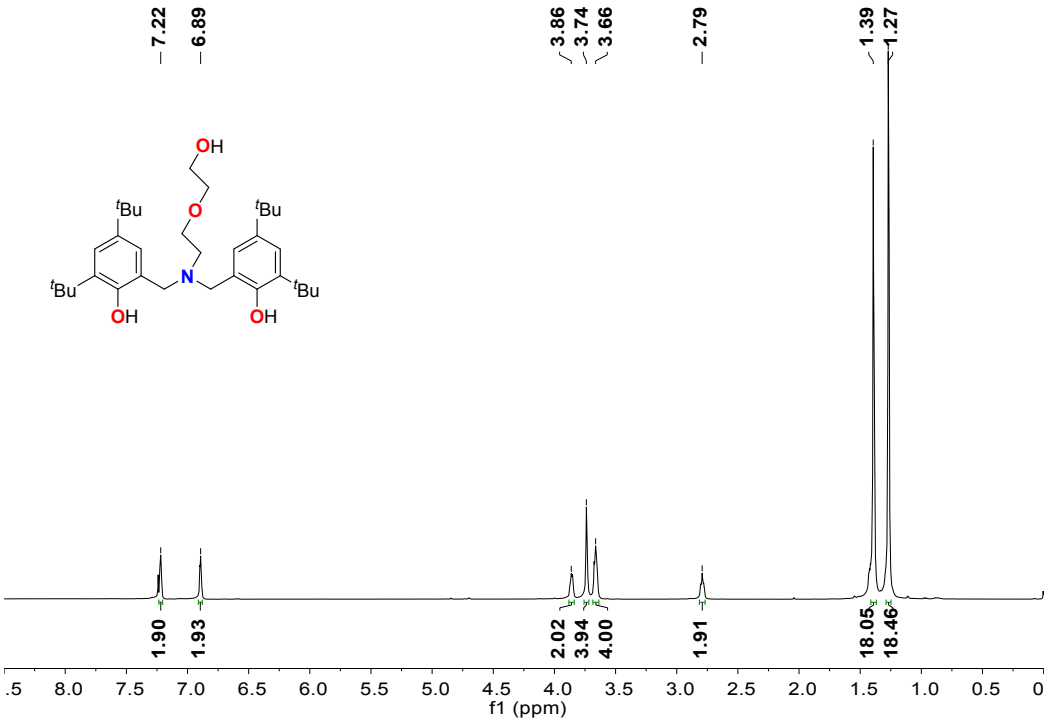


Figure S10. ^{1}H NMR spectrum of LH_3 in $CDCl_3$

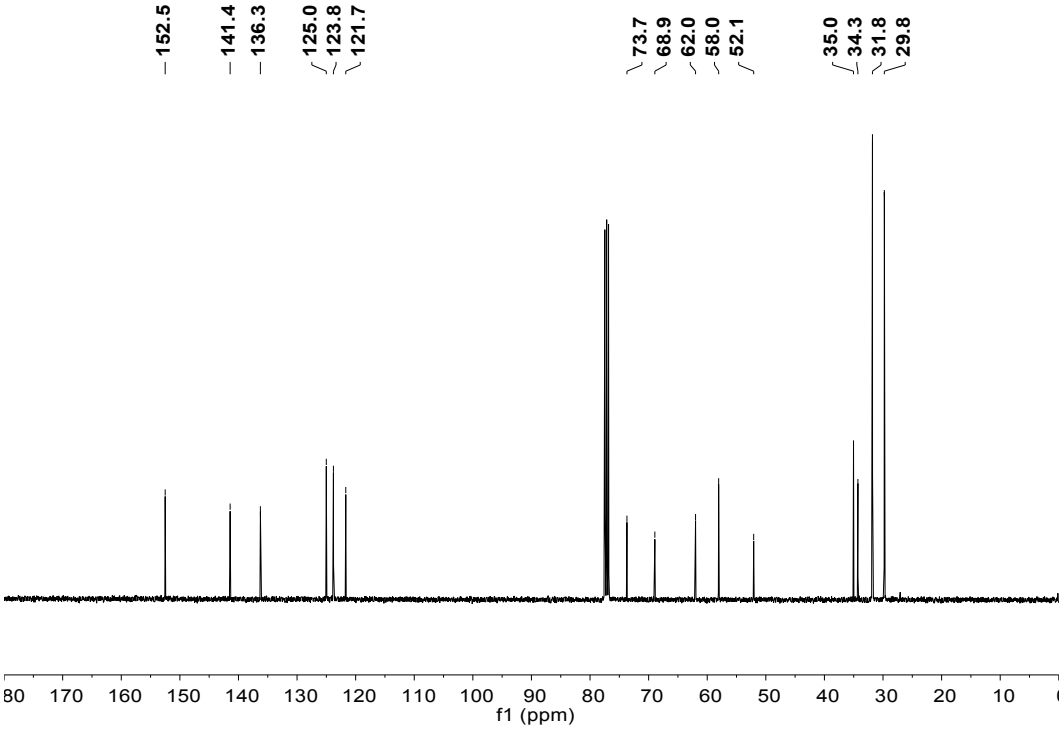


Figure S11. ^{13}C NMR spectrum of LH_3 in $CDCl_3$

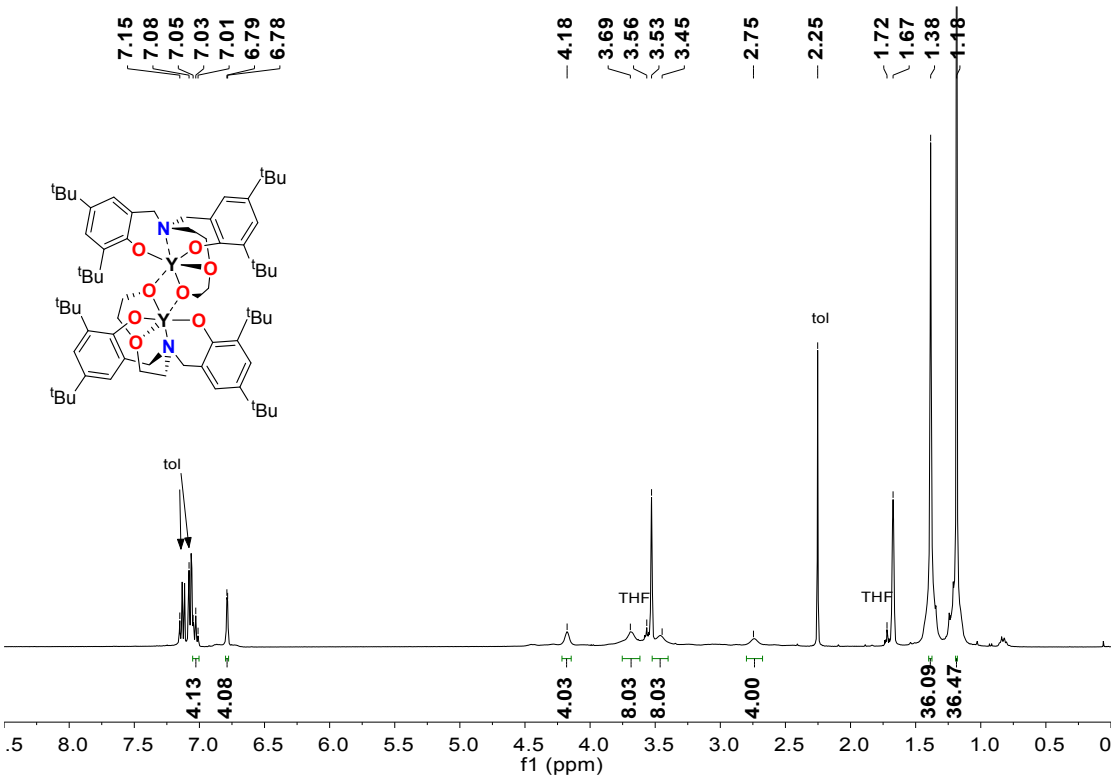


Figure S12. ^{1}H NMR spectrum of complex **1** in THF-*d8*

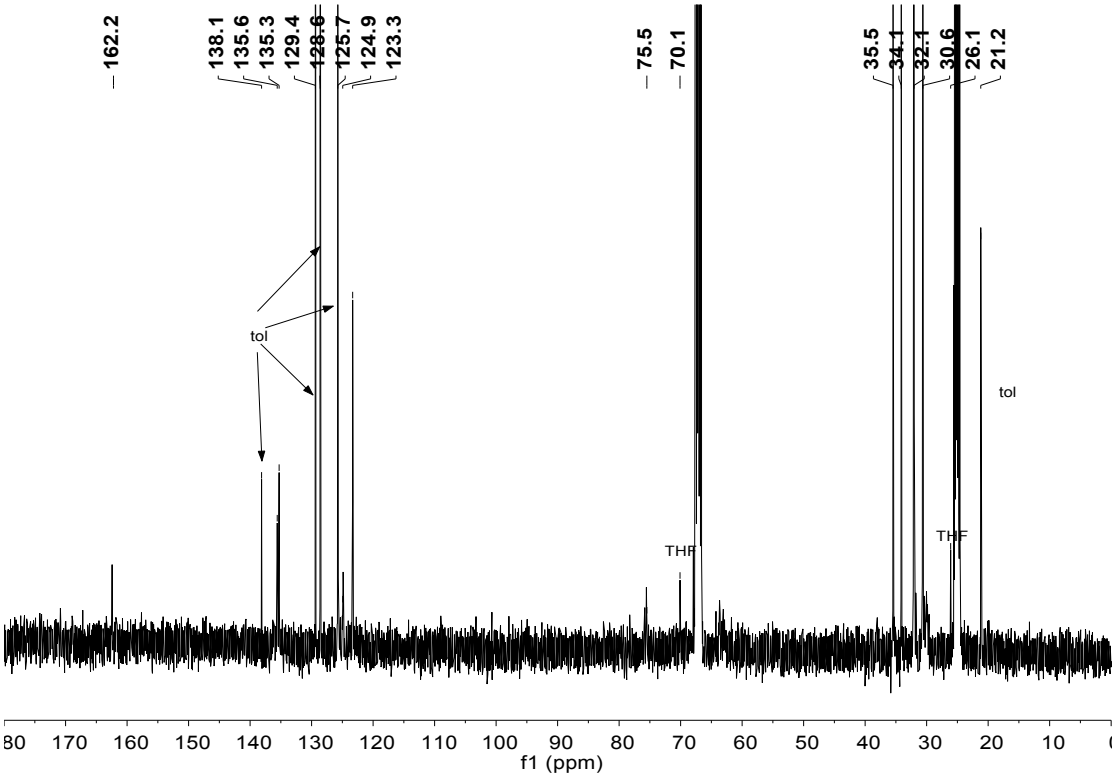


Figure S13. ^{13}C NMR spectrum of complex **1** in THF-*d8* (poor resolution due to low solubility)

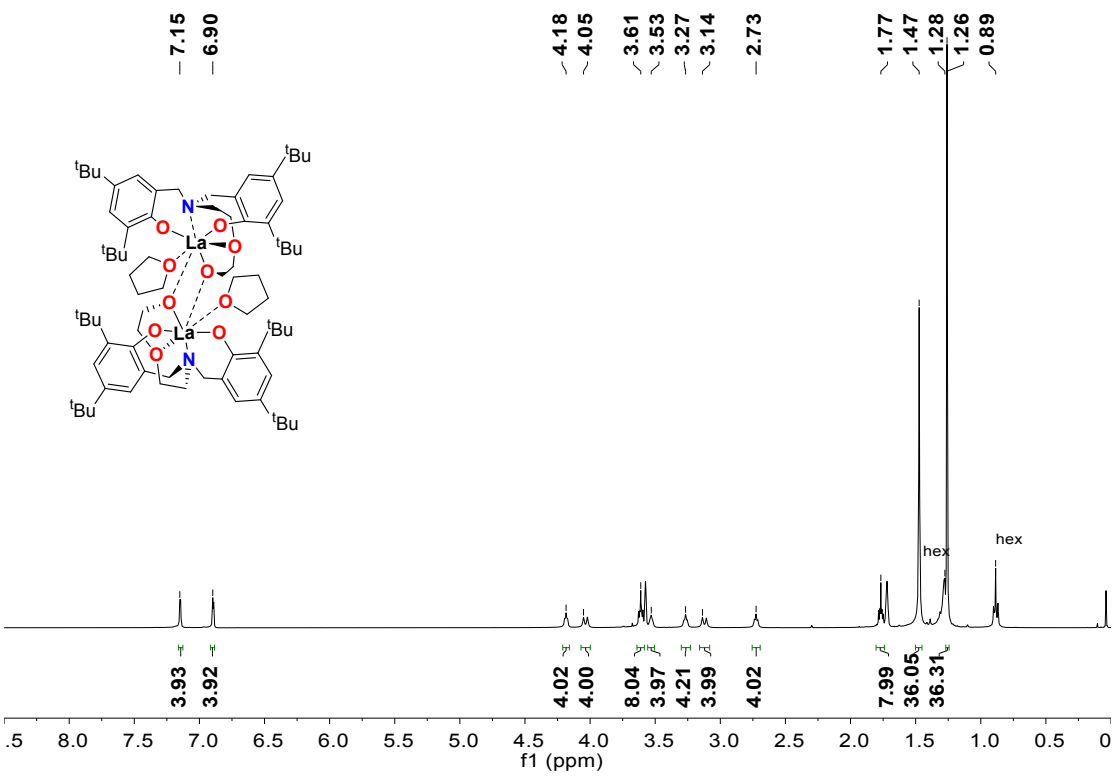


Figure S14. ^{1}H NMR spectrum of complex **4** in THF-*d8*

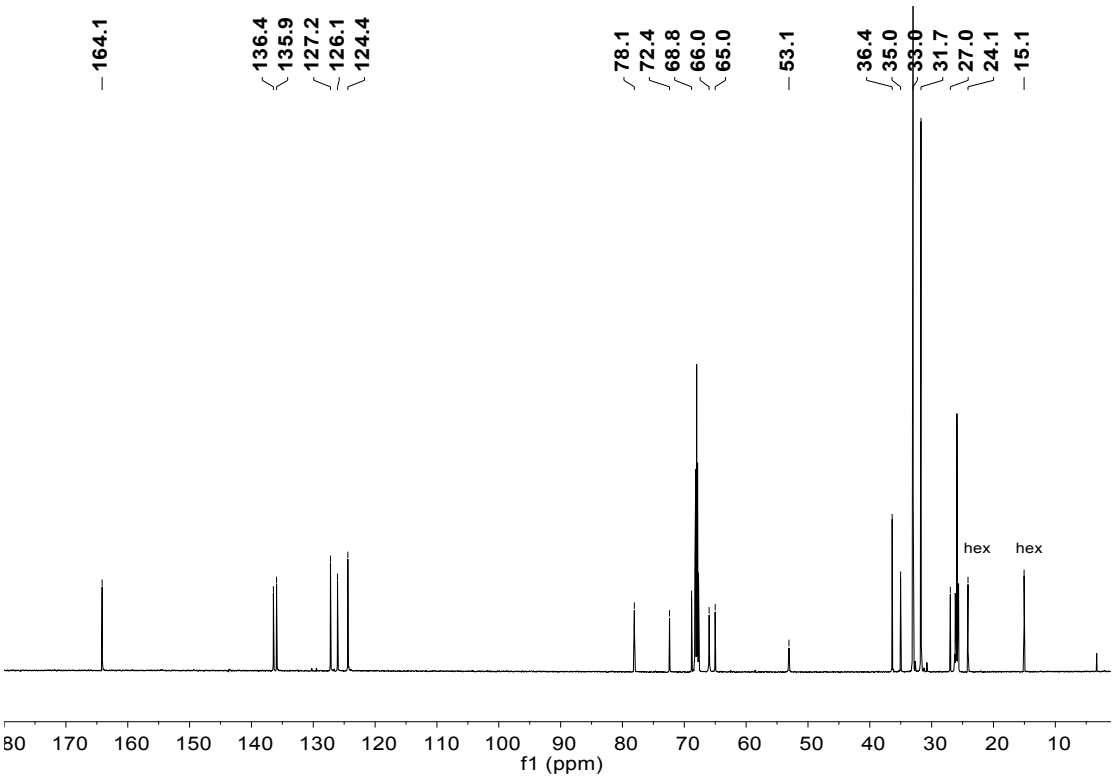


Figure S15. ^{13}C NMR spectrum of complex **4** in THF-*d8*

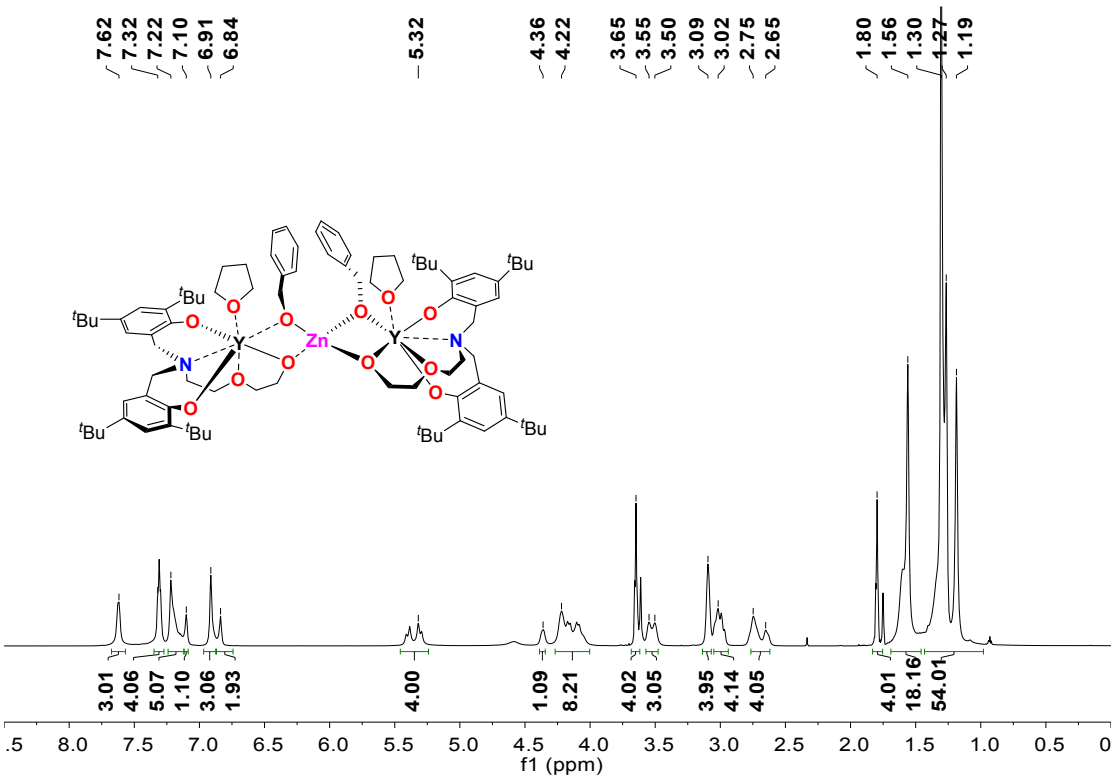


Figure S16. ^{1}H NMR spectrum of complex **7** in THF-*d8*

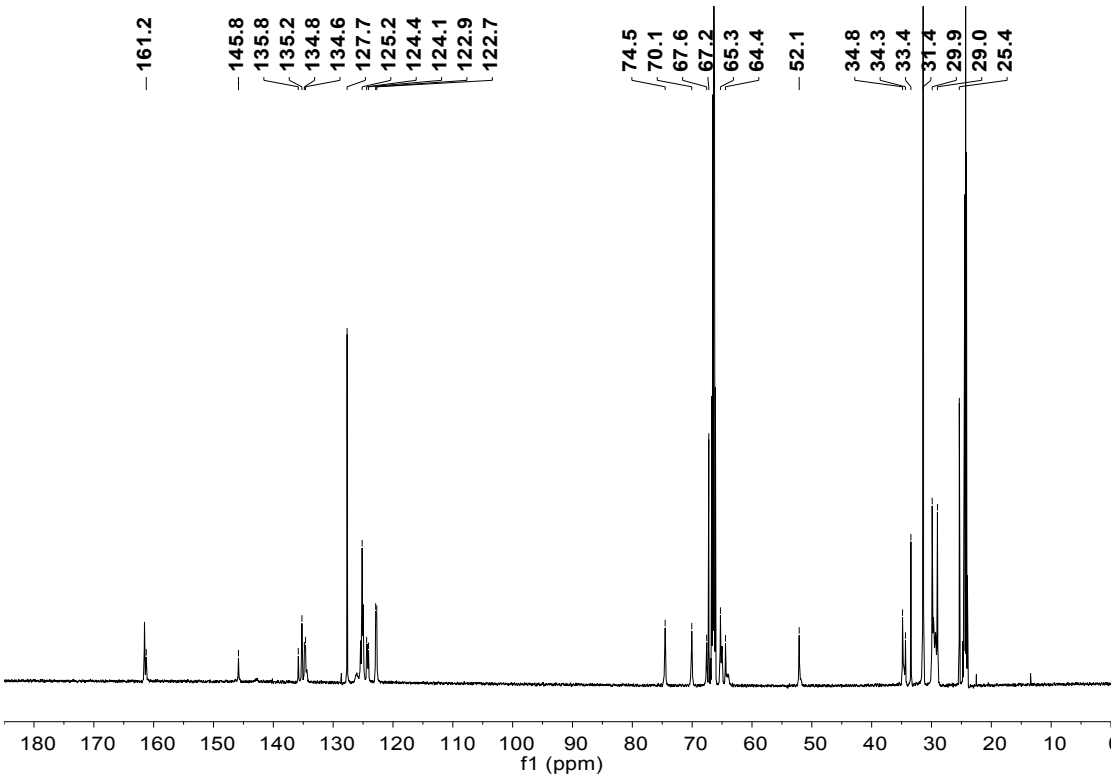


Figure S17. ^{13}C NMR spectrum of complex **7** in THF-*d8*

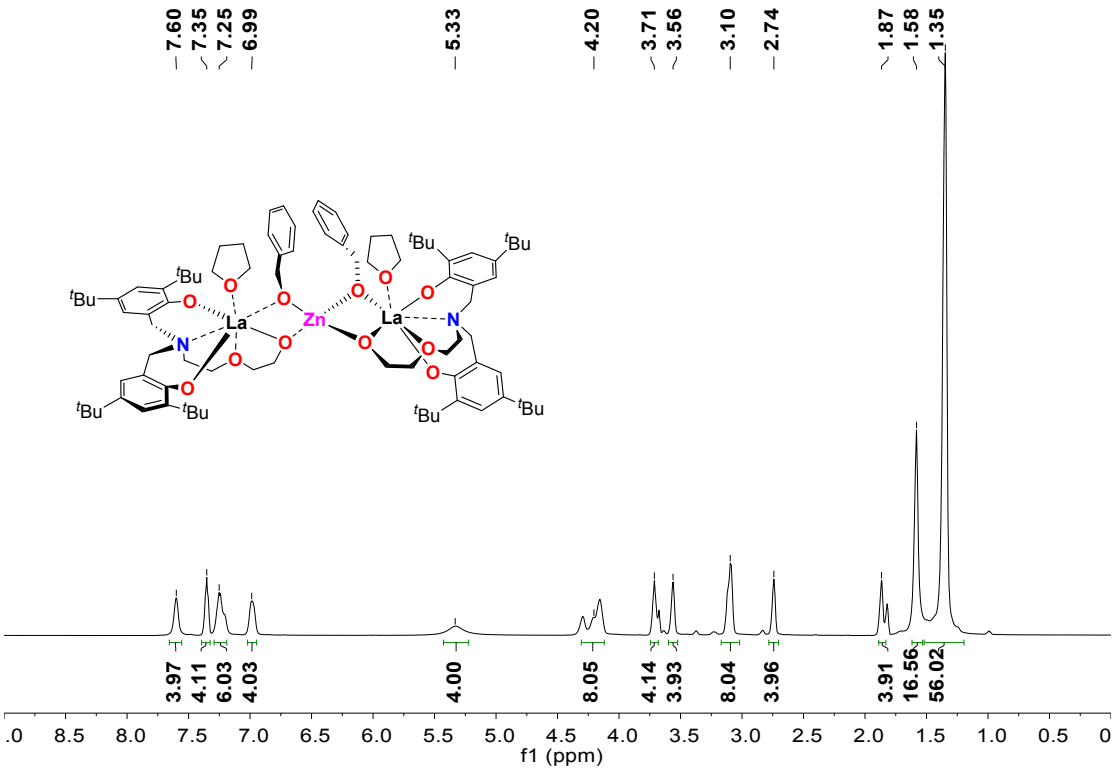


Figure S18. ^{1}H NMR spectrum of complex **11** in THF-*d8*

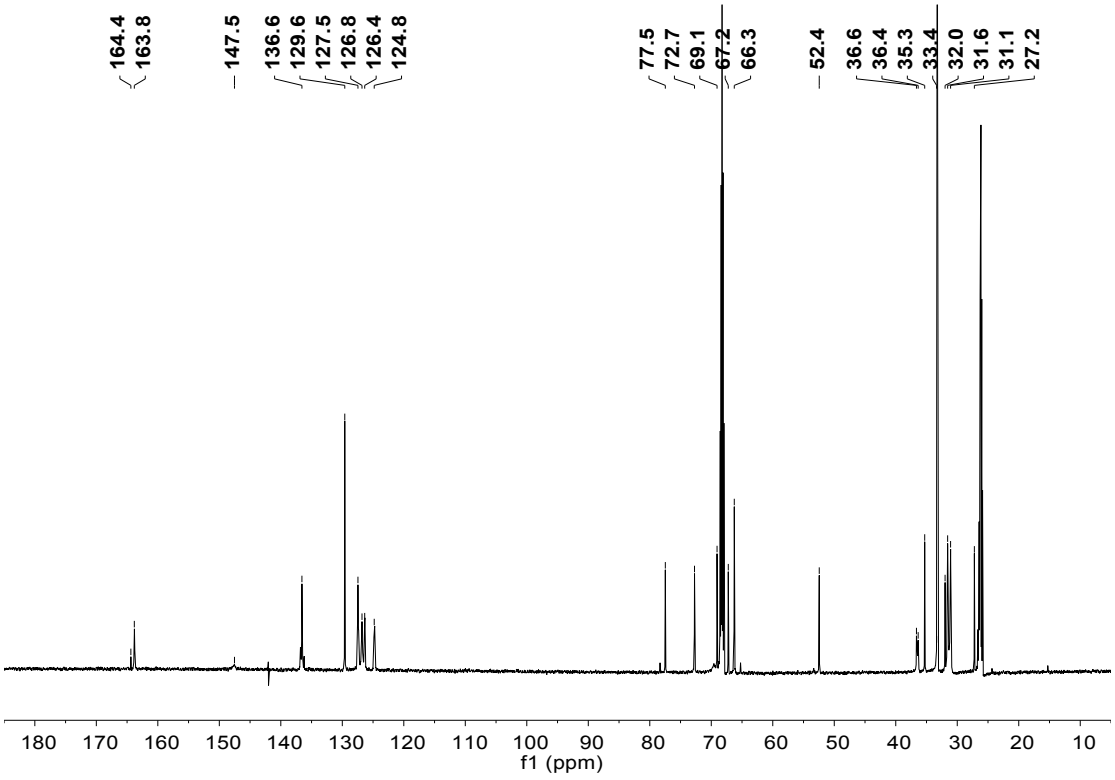


Figure S19. ^{13}C NMR spectrum of complex **11** in THF-*d8*

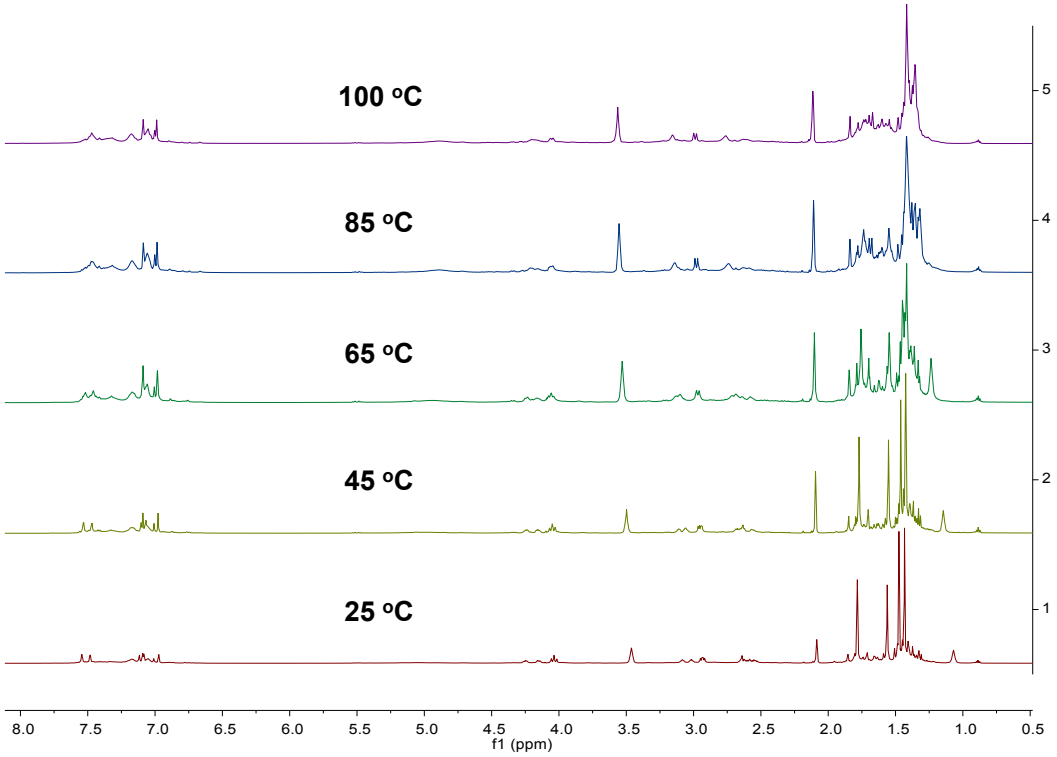
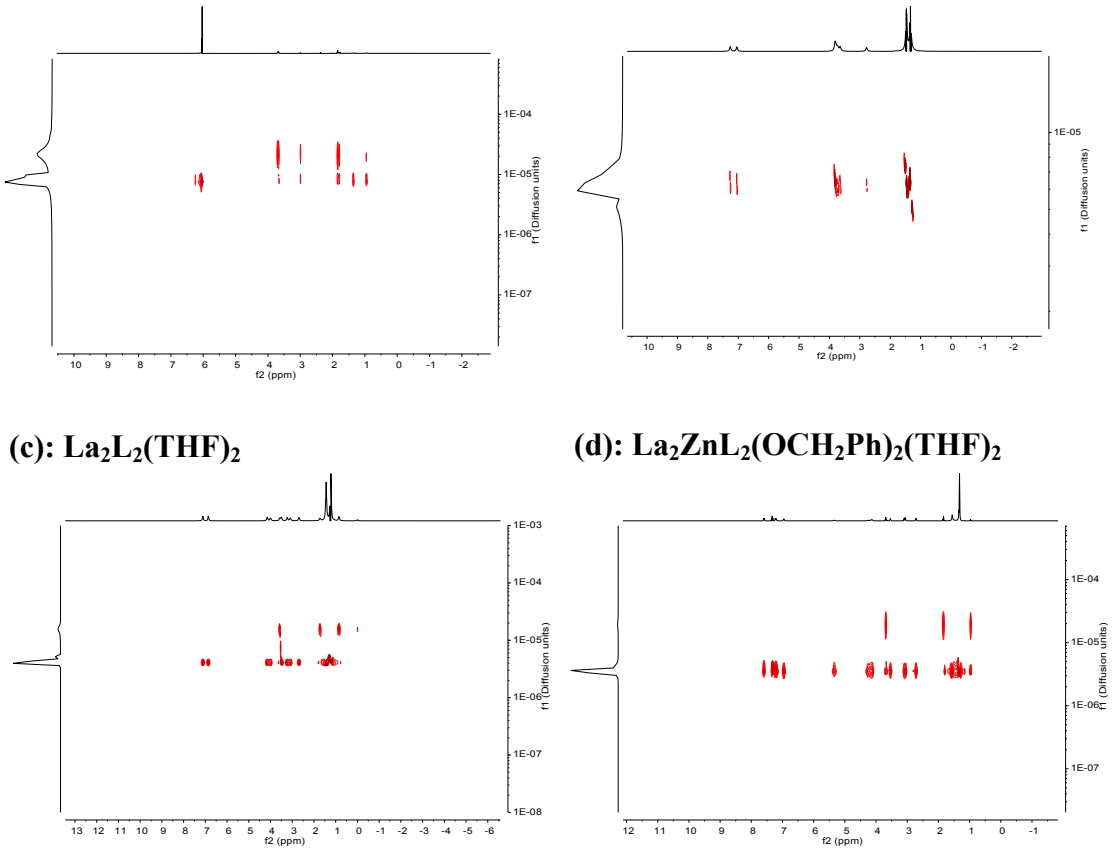


Figure S20. Variable temperature ^{1}H NMR spectra of complex **11** (600 MHz, Tol-*d8*)

3. DOSY analysis of complexes 4 and 11

(a): $LaCp_3(THF)$ **(b): LH_3**



(c): $La_2L_2(THF)_2$ **(d): $La_2ZnL_2(OCH_2Ph)_2(THF)_2$**

Figure S21. ^{1}H DOSY spectrum of $LaCp_3(THF)$, H_3L, complexes **4** and **11.** Conditions: all samples were dissolved in THF-*d8* with the same concentration of 0.056 M, 25 °C. The values of the translational diffusion coefficient (*D*) were calculated by the Bruker Topspin 3.2 program.

Table S1 D-Mw Correlation Result of DOSY Data

Compound	theoretical M_w (g/mol)	log M_w	$\times 10^6$ D (cm^2/s)	log D	calculated M_w (g/mol)	% error
$LaCp_3(THF)$	406	2.61	7.58	-5.12	406	0.00
H_3L	542	2.73	6.55	-5.18	545	0.55
4	1498	3.18	4.02	-5.40	1461	2.47
11	1776	3.25	3.61	-5.44	1815	2.20

4. Crystallographic radius analysis of complexes 4 and 11

Table S2 Comparison of the dimensions of complexes **4** and **11** in the solid state as determined by X-ray crystallography and the dimensions in solution as determined by DOSY NMR experiments.

Complex	Hydrodynamic radius R_h (Å)	Crystalline radius		
		R_{max} (Å)	R_{min} (Å)	$R_{average}$ (Å)
4	11.6 ± 0.5	12.1 ± 0.5	9.0 ± 0.5	10.6 ± 0.5
11	12.9 ± 0.5	13.1 ± 0.5	10.8 ± 0.5	12.0 ± 0.5

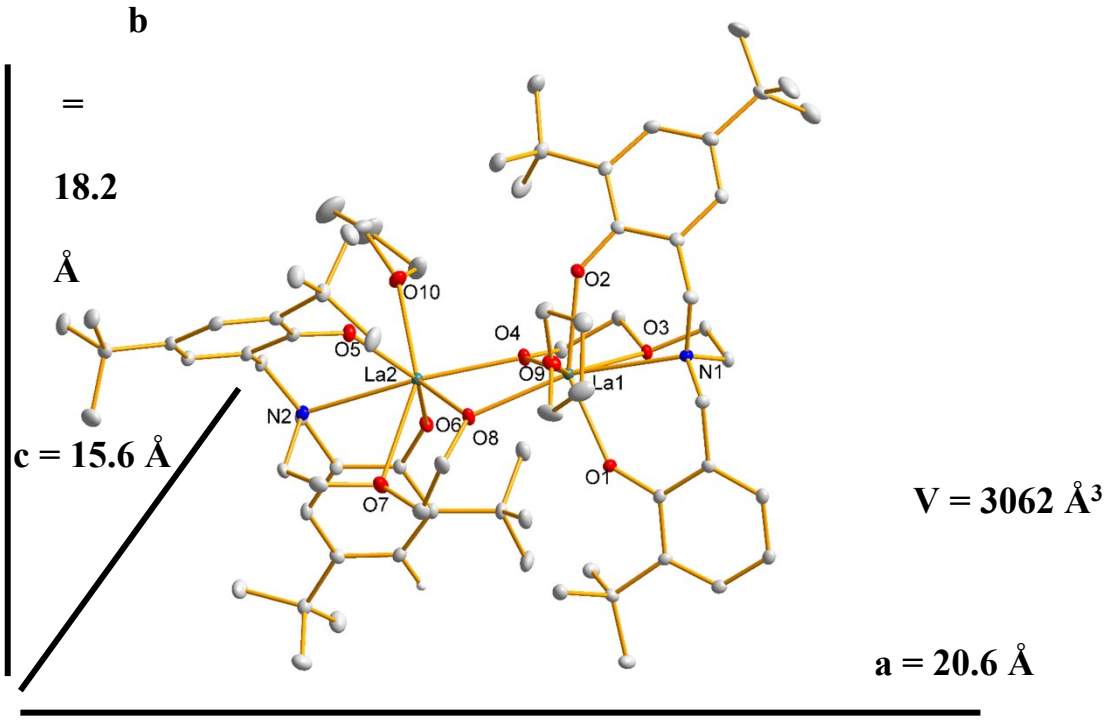


Figure S22. Geometrical parameters (a = 20.6, b = 18.2, c = 15.6 Å) used for the volume estimation of complex **4** based on its solid-state structure. Following an ellipsoidal model [V = 4/3 π (a/2 x b/2 x c/2)] was used for volume estimation of 3062 Å^3.

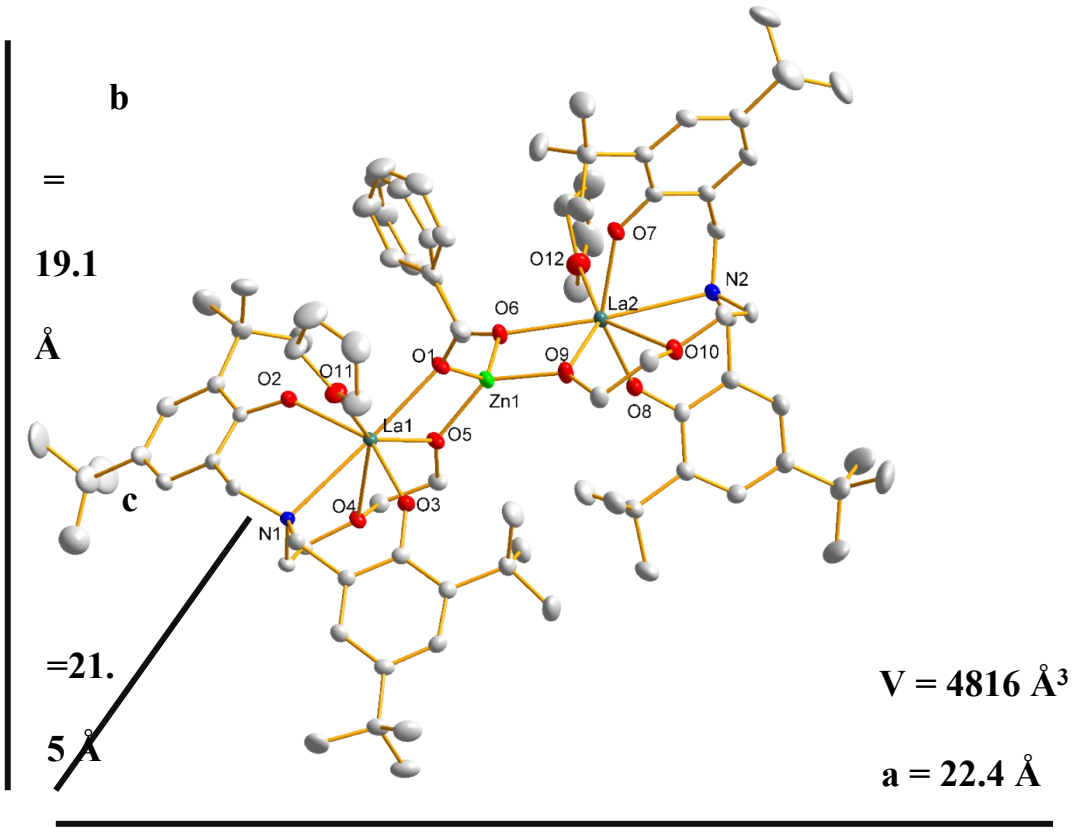
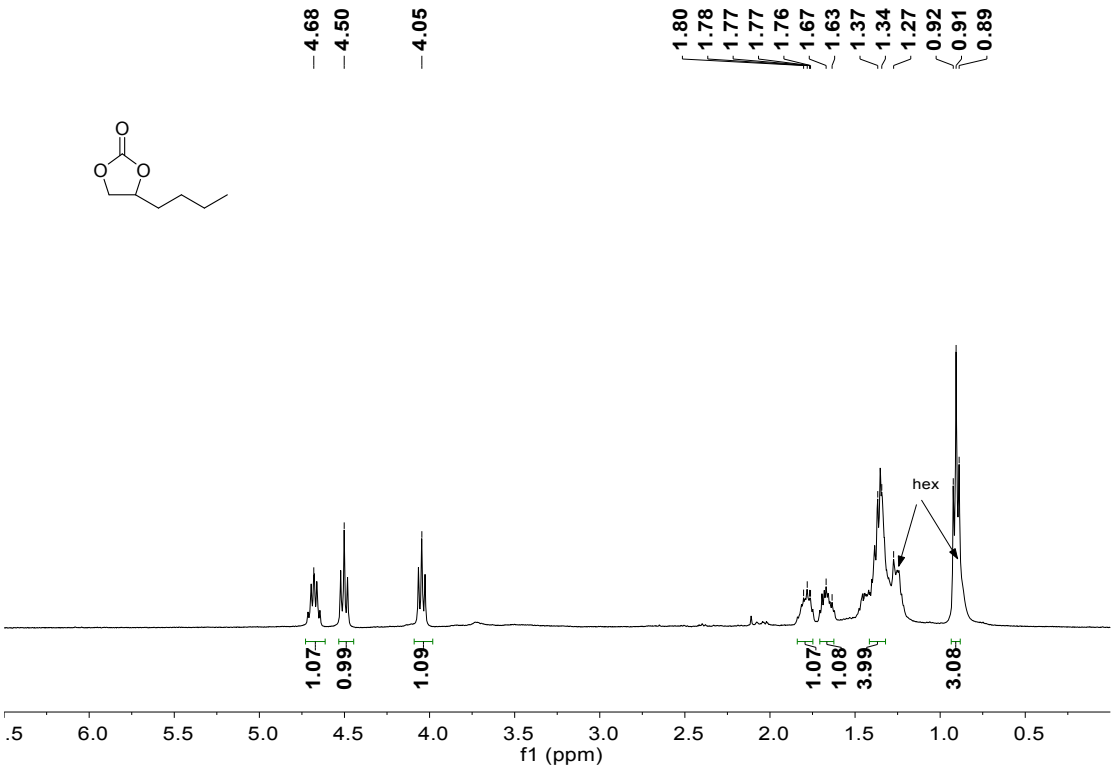


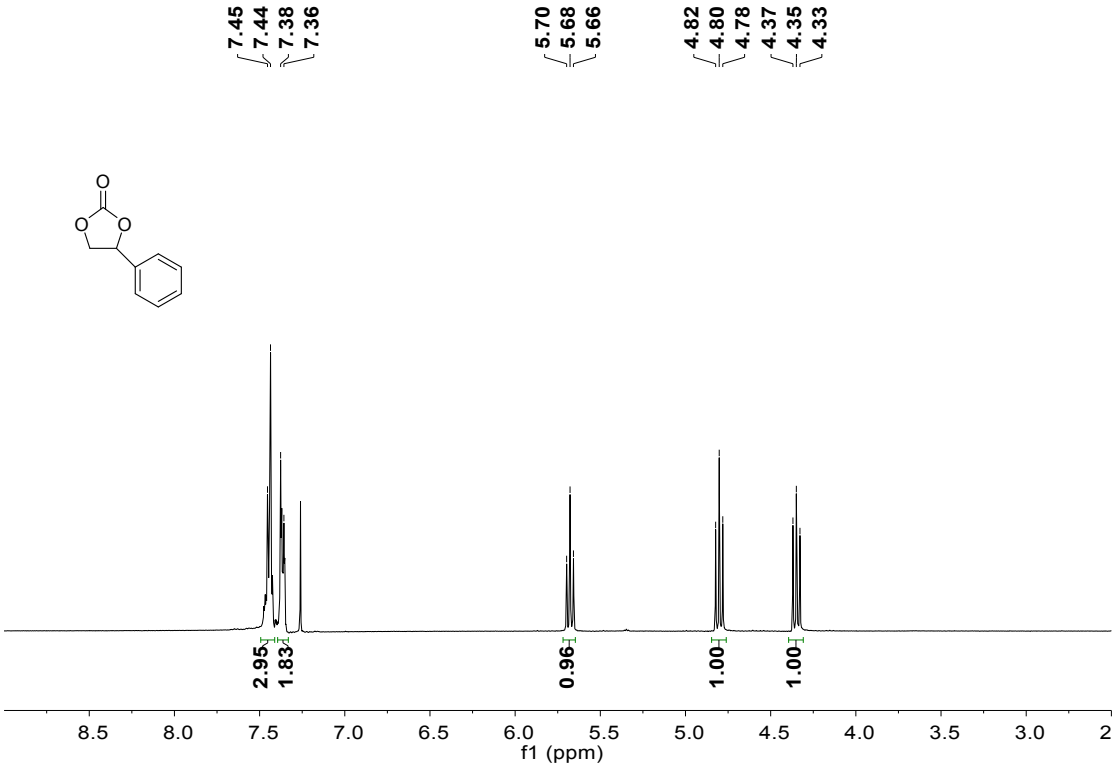
Figure S23. Geometrical parameters (a = 22.4, b = 19.1, c = 21.5 Å) used for the volume estimation of complex **11** based on its solid-state structure. Following an ellipsoidal model [V = 4/3 π (a/2 x b/2 x c/2)] was used for volume estimation of 4816 Å^3.

5. NMR spectra of cyclic carbonates

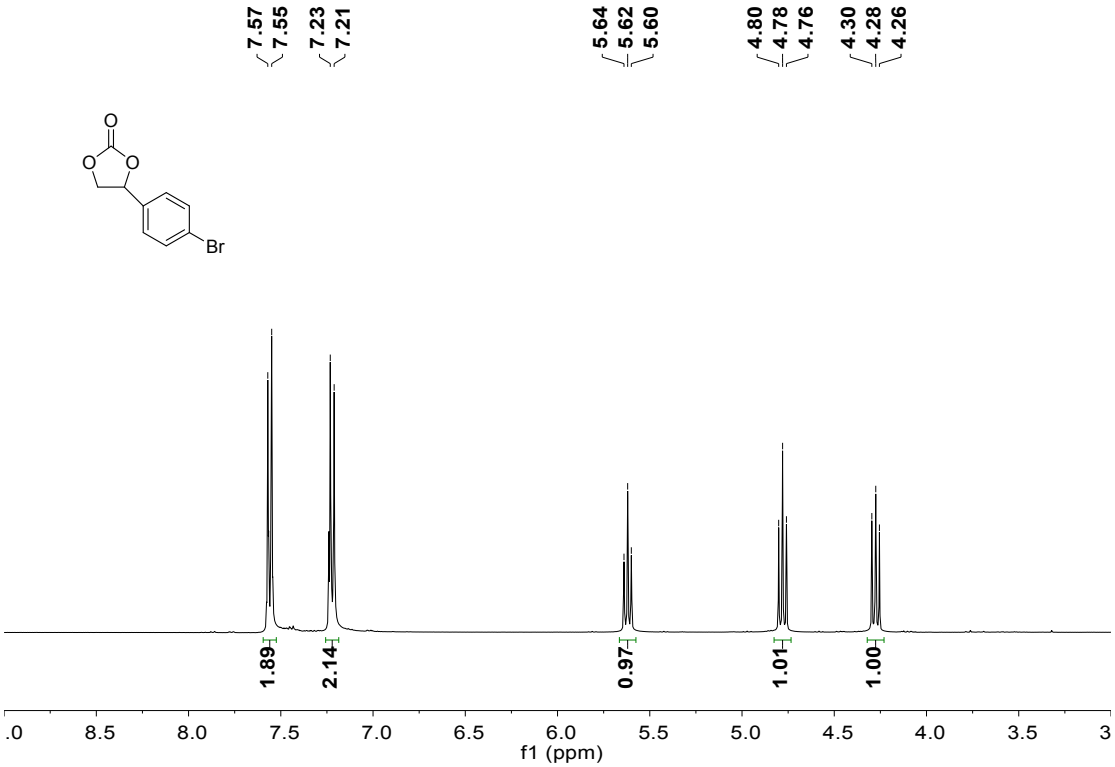
^{1}H NMR spectrum of **4-butyl-1,3-dioxolan-2-one** in $CDCl_3$



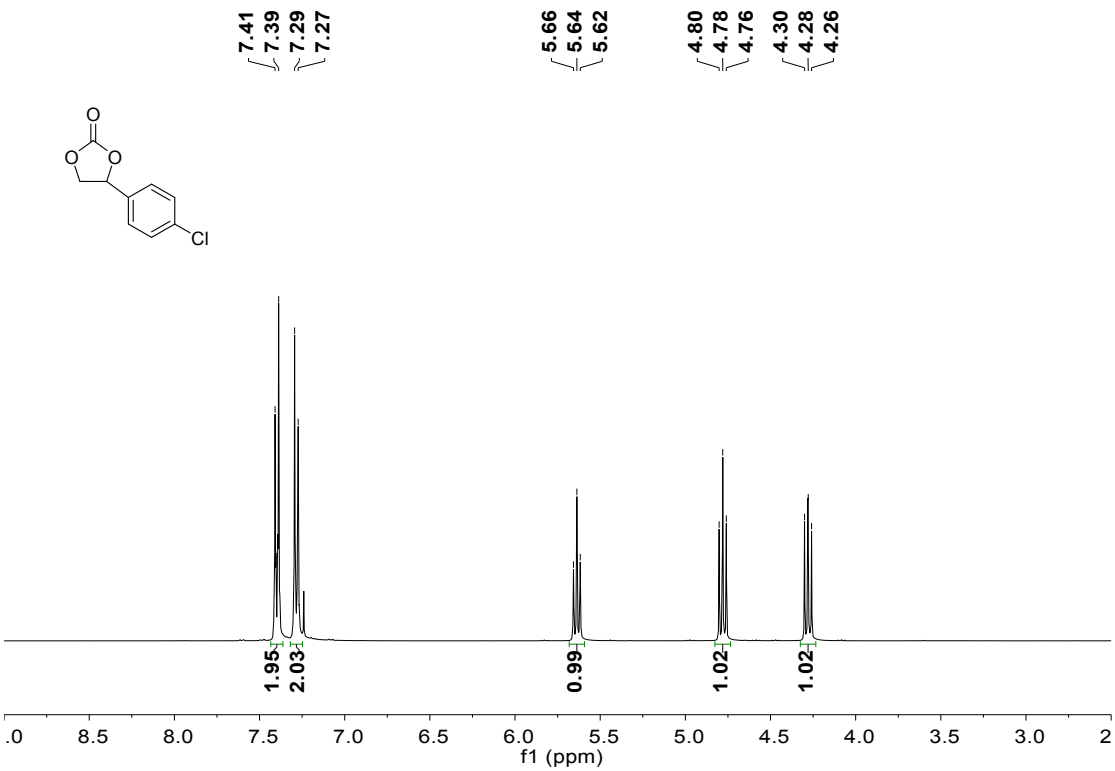
^{1}H NMR spectrum of **12b** in $CDCl_3$



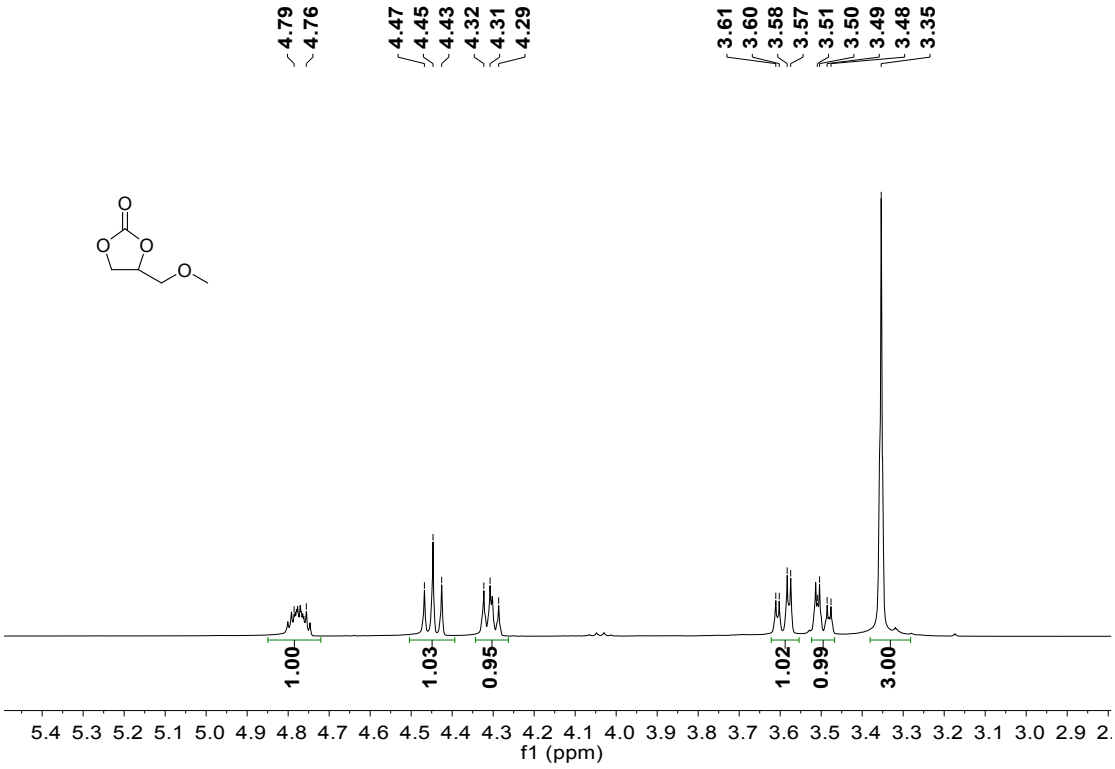
^{1}H NMR spectrum of **12c** in $CDCl_3$



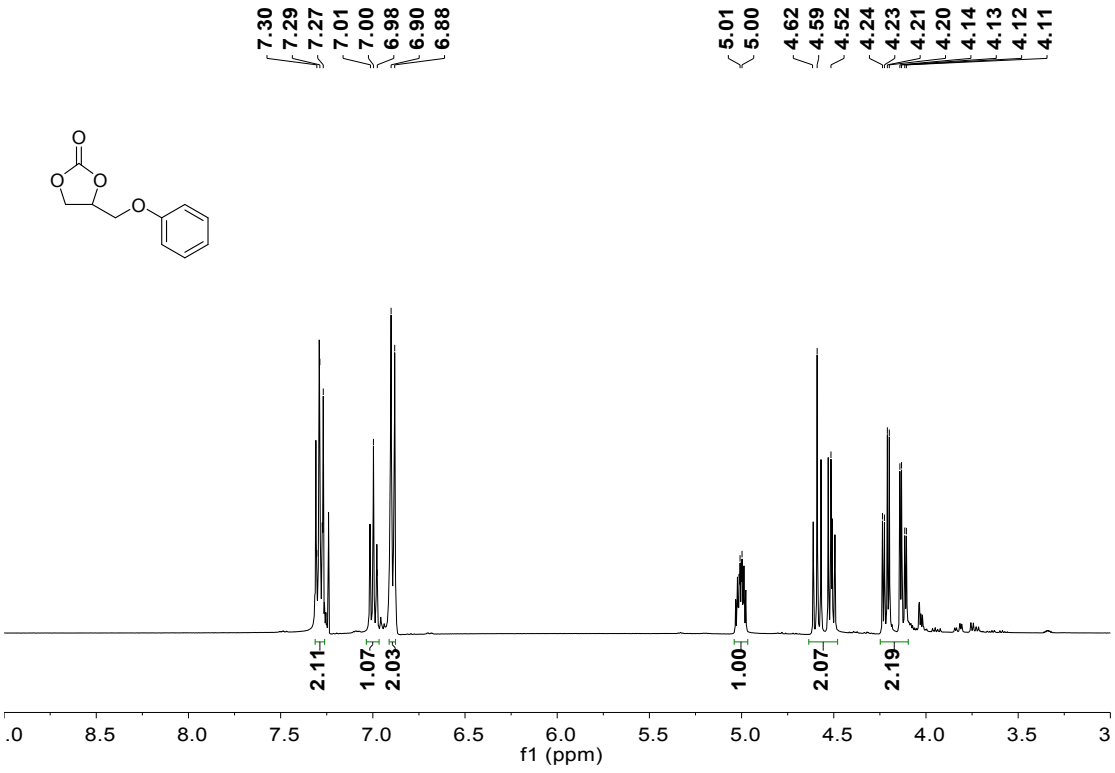
^{1}H NMR spectrum of **12d** in $CDCl_3$



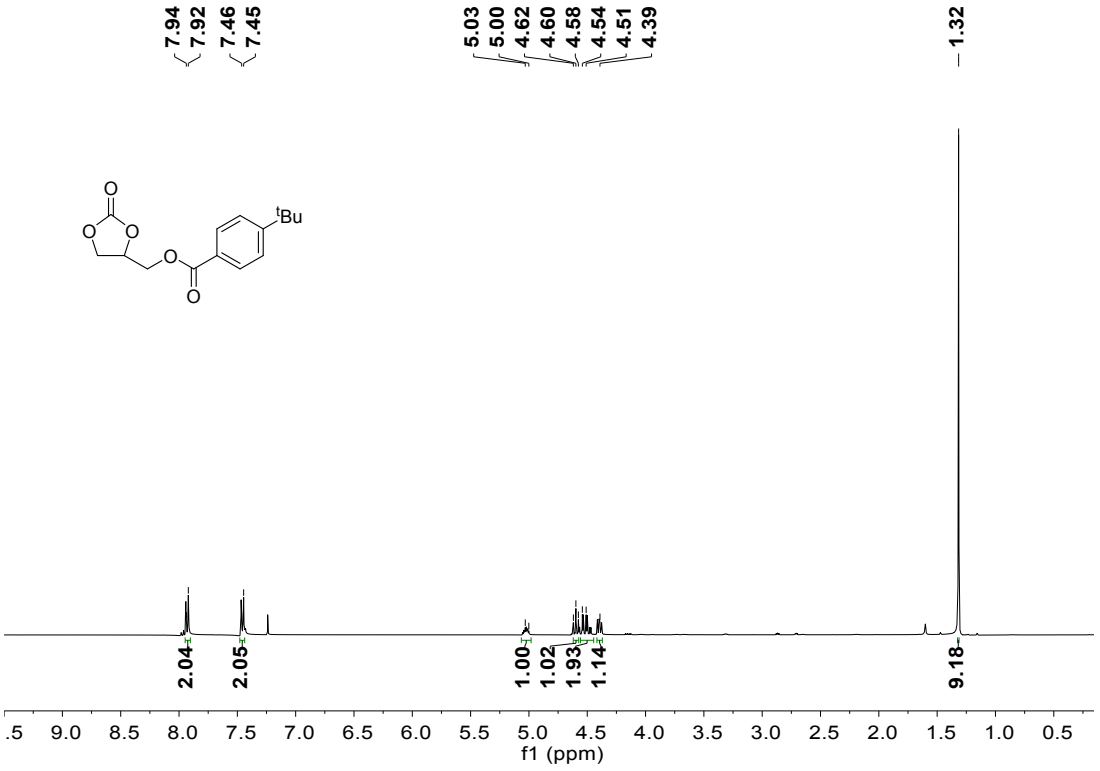
^{1}H NMR spectrum of **12e** in $CDCl_3$



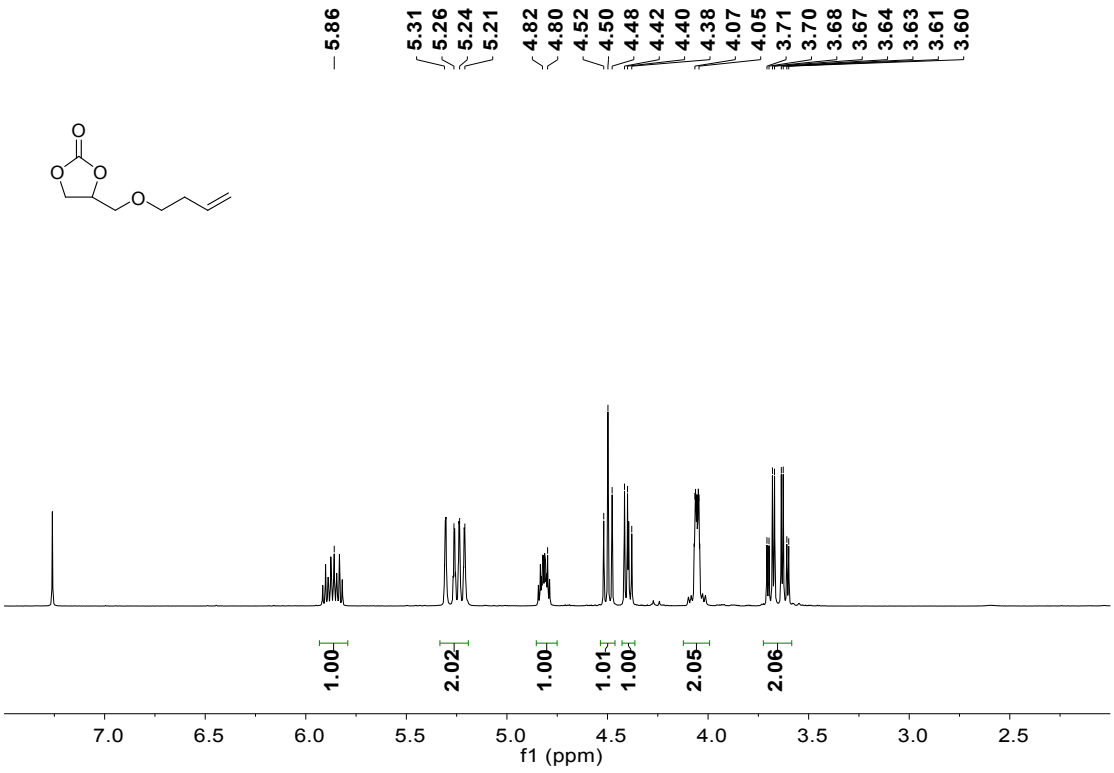
^{1}H NMR spectrum of **12f** in $CDCl_3$



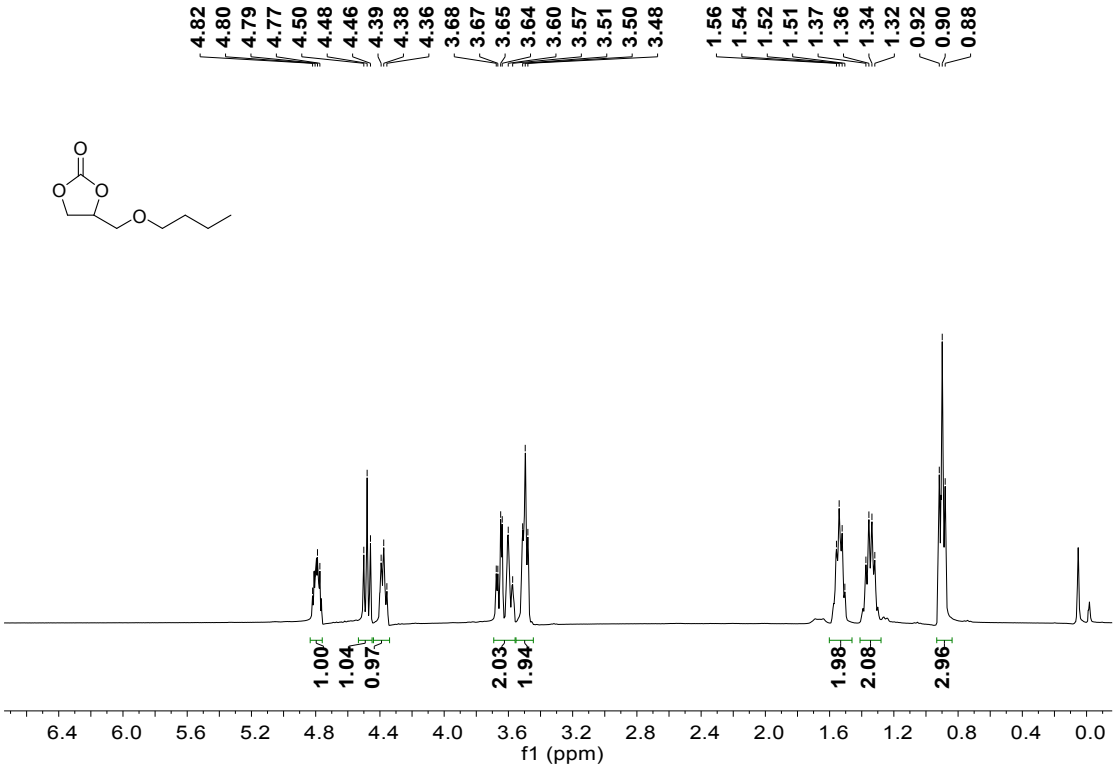
^{1}H NMR spectrum of **12g** in $CDCl_3$



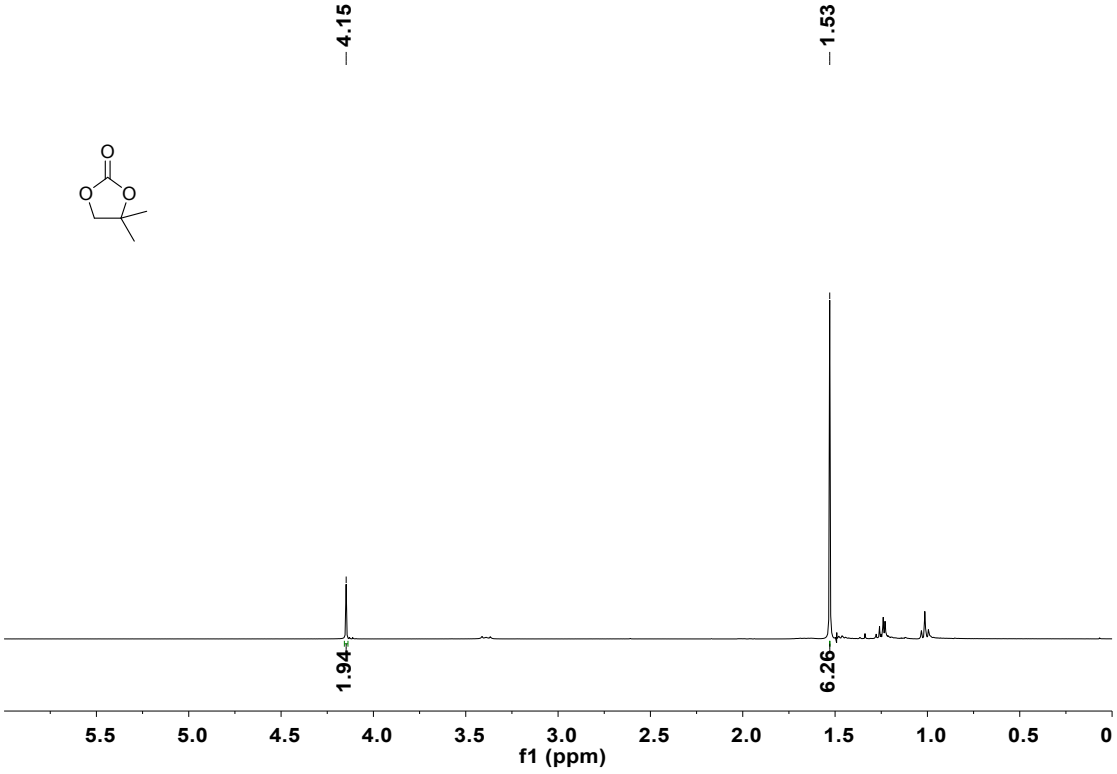
^{1}H NMR spectrum of **12h** in $CDCl_3$



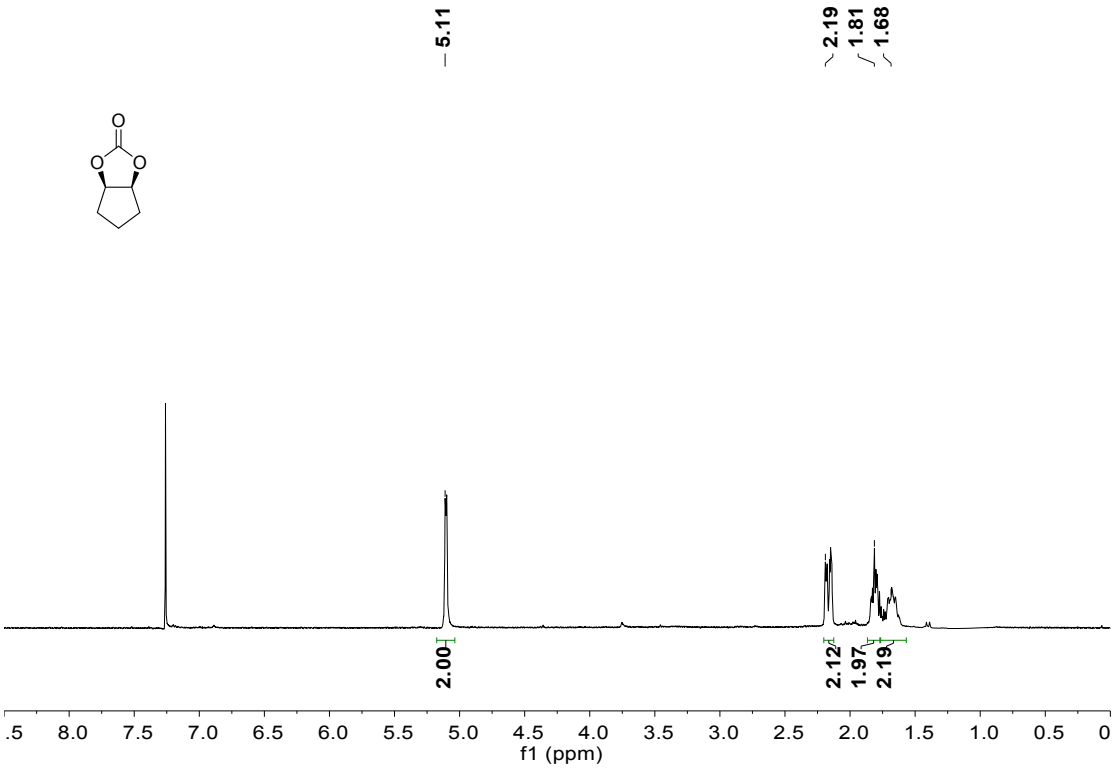
^{1}H NMR spectrum of **12i** in $CDCl_3$



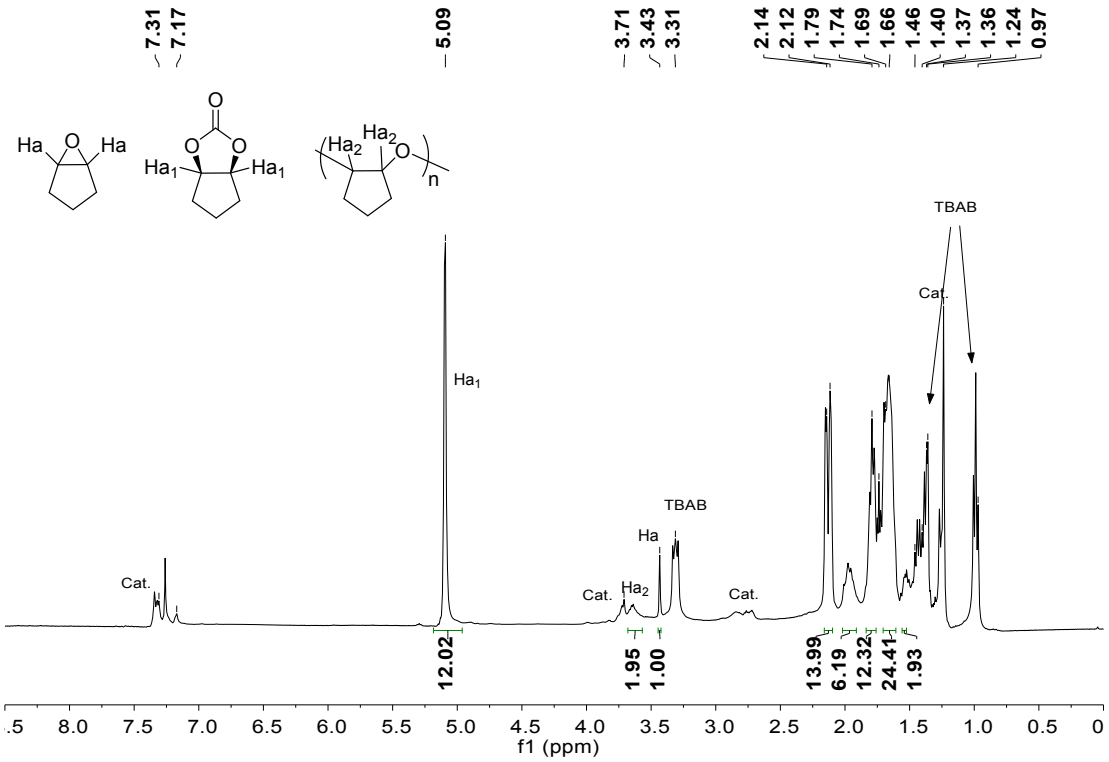
^{1}H NMR spectrum of **12j** in $CDCl_3$



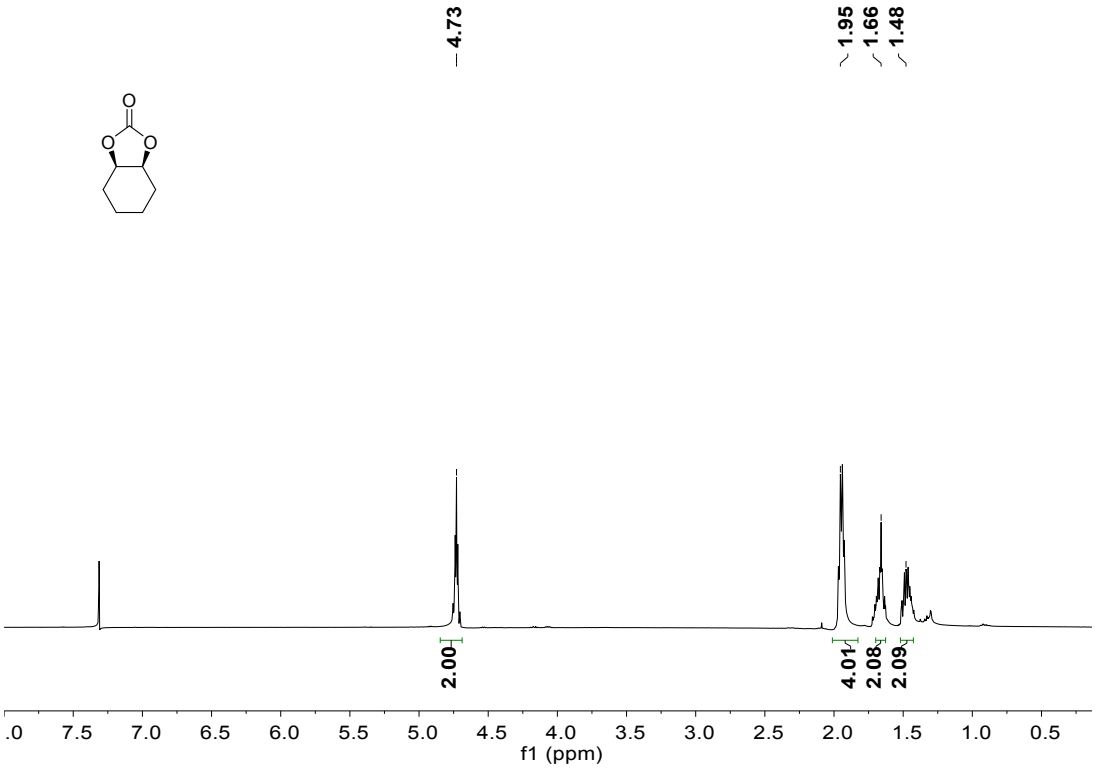
^{1}H NMR spectrum of **12k** (purified) in $CDCl_3$



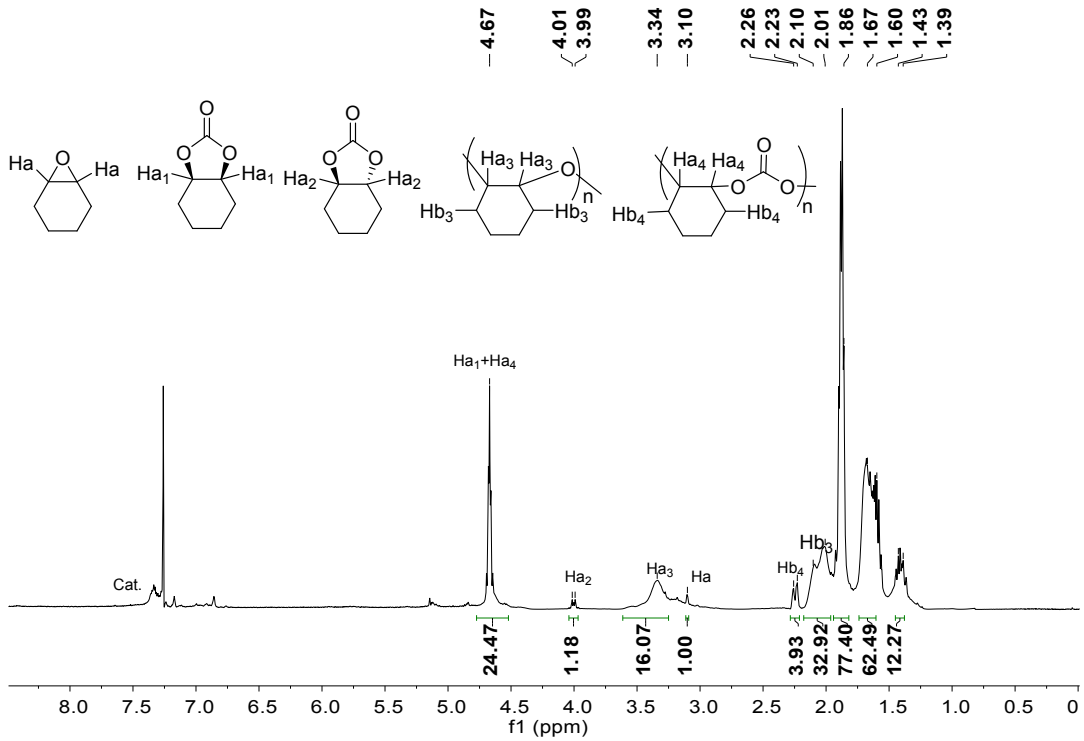
^{1}H NMR spectrum of **12k** (mixture) in $CDCl_3$



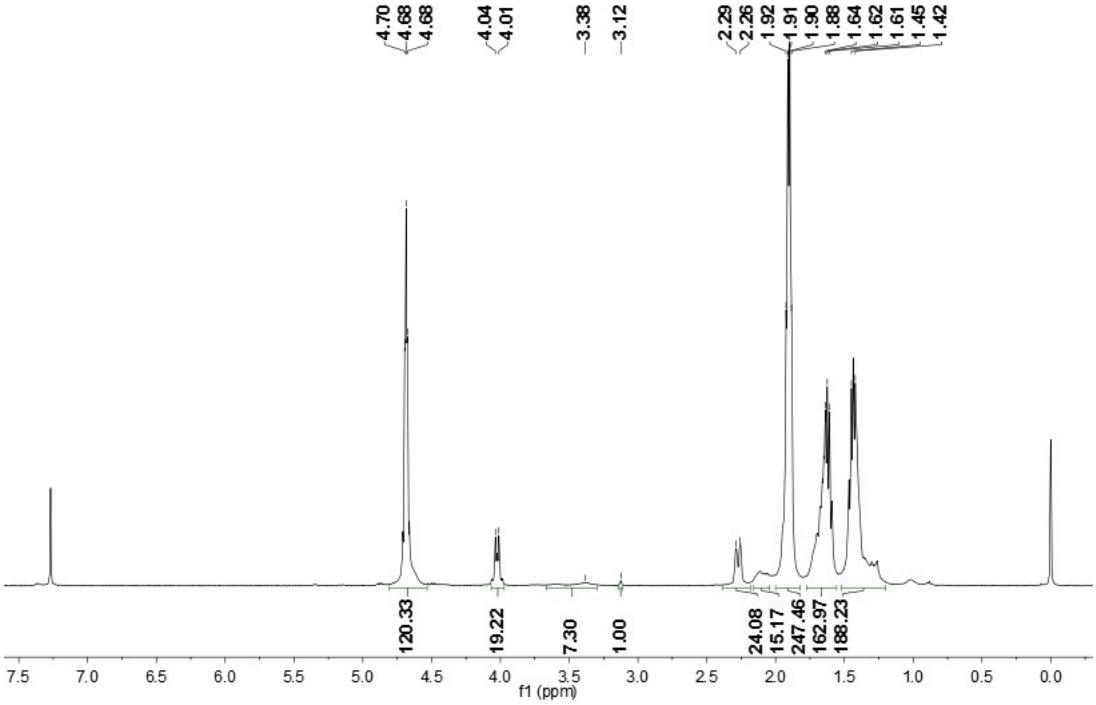
^{1}H NMR spectrum of **12l** (purified) in $CDCl_3$



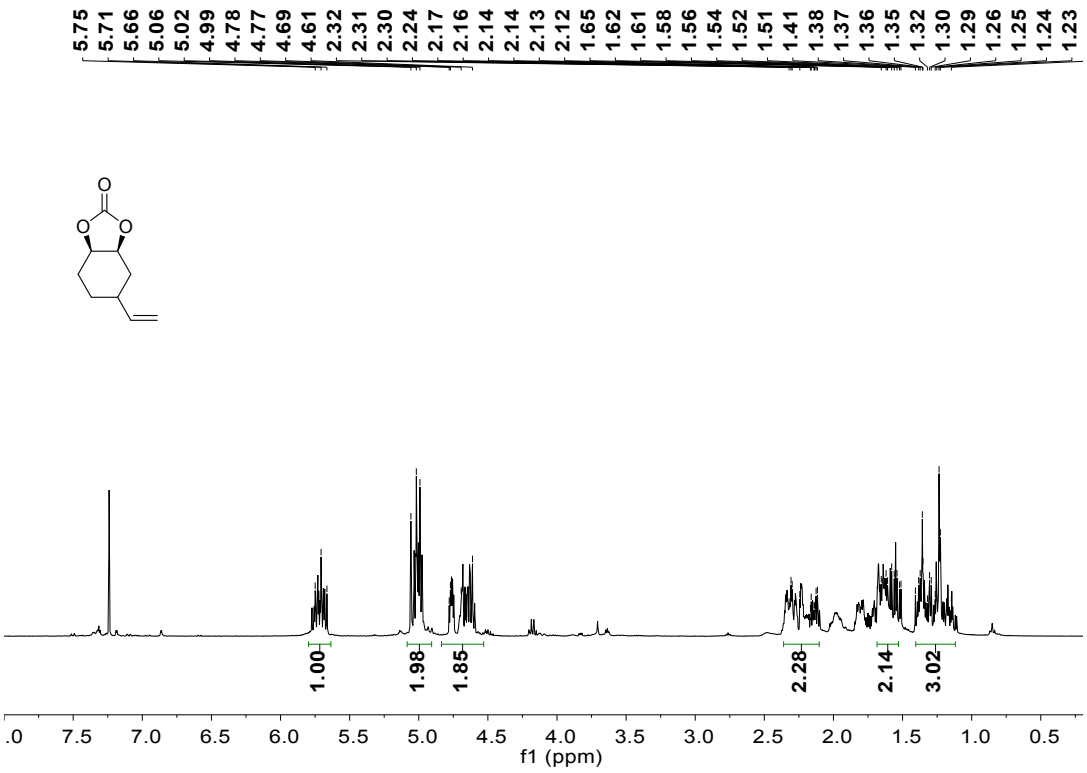
^{1}H NMR spectrum of **12l** (mixture) in $CDCl_3$



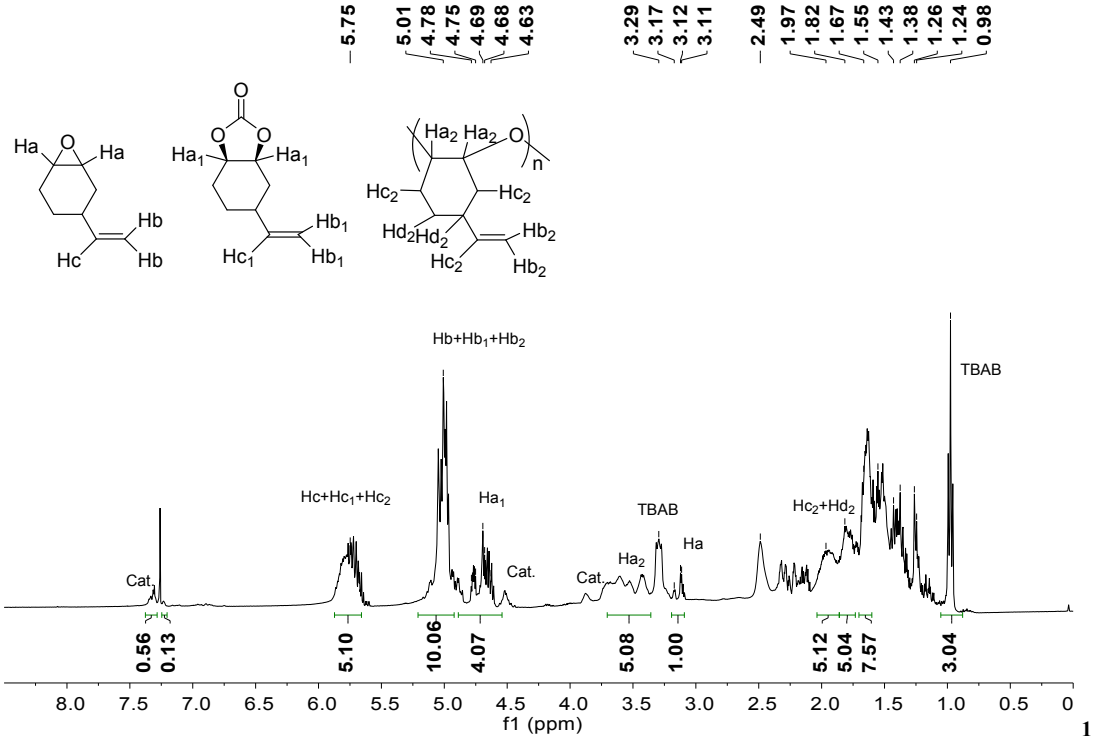
^{1}H NMR spectrum of **12l** (mixture) in $CDCl_3$ (30 atm CO_2)



^{1}H NMR spectrum of **12m** (purified) in $CDCl_3$



^{1}H NMR spectrum of **12m** (mixture) in $CDCl_3$



6. Crystallographic data of complexes 1-11

Table S3 Crystallographic data of complexes **1-2**

complexes	**1**·3tol	**2**·3tol
Empirical formula	$C_{89}H_{128}N_2O_8Y_2$	$C_{89}H_{128}N_2O_8Yb_2$
Formula weight	1531.75	1700.01
Temperature/K	99.99	120.01
Crystal system	Triclinic	triclinic
Space group	P-1	P-1
a/Å	9.8400(16)	9.824(2)
b/Å	15.103(3)	15.246(4)
c/Å	15.585(3)	16.151(4)
α/°	65.375(5)	62.587(6)
β/°	80.978(5)	81.046(7)
γ/°	77.304(5)	78.095(7)
Volume/Å^3	2048.4(6)	2096.2(9)
Z	1	1
ρ_{calc} g/cm^3	1.242	1.347
μ/mm^{-1}	1.465	2.271
F(000)	818.0	880.0
2θ range for data collection/°	4.732 to 52.742	4.7 to 52.744
Reflections collected	61436	103495
Independent reflections	8384, [R_{int} = 0.1021]	8576, [R_{int} = 0.1070]
Data/restraints/parameters	8384/7/7448	8570/20/402
Goodness-of-fit on F^2	1.041	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0501, wR_2 = 0.1231	R_1 = 0.0496, wR_2 = 0.1146
Final R indexes [all data]	R_1 = 0.0665, wR_2 = 0.1306	R_1 = 0.0639, wR_2 = 0.1261
Largest diff. peak/hole / e Å^{-3}	1.26/-1.46	4.05/-1.62

Table S4 Selected bond lengths [Å] and bond angles [deg] for complex 1

Bond lengths			
Y(1)-N(1)	2.562(3)	Y(1)-O(1)	2.115(4)
Y(1)-O(2)	2.137(2)	Y(1)-O(3)	2.385(2)
Y(1)-O(4')	2.250(2),	Y(1)-O(4)	2.282(2)
O4-(Y1')	2.250(2);		
Bond Angles			
O(1)-Y(1)-N (1)	78.42(2)	O(1)-Y(1)-O(3)	108.71(9)
O(1)-Y(1)-O(4)	113.42(8)	O(1)-Y(1)-O(4')	98.09(8)
O(2)-Y(1)-N(1)	76.08(8)	O(2)-Y(1)-O(1)	119.01(9)
O(2)-Y(1)-O(3)	108.94(8)	O(2)-Y(1)-O(4)	124.67(8)
O(2)-Y(1)-O(4')	87.66(8)	O(3)-Y(1)-N(1)	65.28(8)
O(4)-Y(1)-N(1)	132.57(8)	O(4')-Y(1)-N(1)	158.61(8)
O(4)-Y(1)-O(3)	67.50(7),	O(4')-Y(1)-O(3)	134.54(7),
O(4')-Y(1)-O(4)	68.33(9)	Y(1)-O(4)-Y(1')	111.67(9)

Table S5 Selected bond lengths [Å] and bond angles [deg] for complex 2

Bond lengths			
Yb(1)-N(1)	2.524(5)	Yb(1)-O(1)	2.115(4)
Yb(1)-O(2)	2.118(4)	Yb(1)-O(3)	2.366(4)
Yb(1)-O(4')	2.217(4)	Yb(1)-O(4)	2.251(4)
O4-(Yb1')	2.217(4)		
Bond Angles			
O(1)-Yb(1)-N(1)	76.98(15)	O(1)-Yb(1)-O(3)	108.60(16)
O(1)-Yb(1)-O(4)	125.68(15)	O(1)-Yb(1)-O(4')	87.36(15)
O(2)-Yb(1)-N(1)	78.65(15)	O(2)-Yb(1)-O(3)	110.01(16)
O(2)-Yb(1)-O(1)	119.70(16)	O(2)-Yb(1)-O(4)	124.67(8)
O(2)-Yb(1)-O(4')	96.94(15)	O(3)-Yb(1)-N(1)	65.01(15)
O(4)-Yb(1)-N(1)	133.51(15)	O(4')-Yb(1)-N(1)	158.47(15)
O(4)-Yb(1)-O(3)	68.10(14),	O(4')-Yb(1)-O(3)	134.18(14),
O(4')-Yb(1)-O(4)	67.86(16)	Yb(1)-O(4)-Yb(1')	112.14(16)

Table S6 Crystallographic data of complexes **3-4**

complexes	**3**·tol·THF	**4**·2tol
Empirical formula	$C_{87}H_{136}N_2O_{11}Nd_2$	$C_{90}H_{136}N_2O_{10}La_2$
Formula weight	1673.45	1683.83
Temperature/K	120.01	120.01
Crystal system	Orthorhombic	orthorhombic
Space group	Pbca	Pbca
a/Å	28.8956(15)	28.9251(15)
b/Å	19.3068(8)	19.4673(10)
c/Å	30.5515(15)	30.6233(16)
α/°	90.00	90.00
β/°	90.00	90.00
γ/°	90.00	90.00
Volume/Å^3	17044.1(14)	17243.8(15)
Z	8	8
ρ_{calc} g/cm^3	1.305	1.297
μ/mm^{-1}	1.262	1.034
F(000)	7040.0	7072.0
2θ range for data collection/°	4.4 to 55.00	4.184 to 52.744
Reflections collected	148607	221409
Independent reflections	19509 [R_{int} = 0.0647]	17626 [R_{int} = 0.0633]
Data/restraints/parameters	19509/299/990	17626/12/921
Goodness-of-fit on F^2	1.116	1.109
Final R indexes [I>=2σ (I)]	R_1 = 0.0371, wR_2 = 0.769	R_1 = 0.0375, wR_2 = 0.0830
Final R indexes [all data]	R_1 = 0.0617 wR_2 = 0.0926	R_1 = 0.0465 wR_2 = 0.0867
Largest diff. peak/hole / e Å^{-3}	1.11/-1.10	1.69/-0.89

Table S7 Selected bond lengths [Å] and bond angles [deg] for complex 3

Bond lengths			
Nd(1)-O(1)	2.377(2)	Nd(1)-O(2)	2.582(2)
Nd(1)-O(3)	2.262(2)	Nd(1)-O(4)	2.262(2)
Nd(1)-O(5)	2.375(2)	Nd(1)-O(9)	2.511(2)
Nd(1)-N(1)	2.702(3)	Nd(2)-O(1)	2.380(2)
Nd(2)-O(5)	2.388(2)	Nd(2)-O(6)	2.527(2)
Nd(2)-O(7)	2.274(2)	Nd(2)-O(8)	2.284(2)
Nd(2)-O(10)	2.534(3)	Nd(2)-N(2)	2.718(3)
Bond angles			
O(1)-Nd(1)-O(2)	66.82(7)	O(1)-Nd(1)-O(9)	142.85(8)
O(1)-Nd(1)-N(1)	130.22(8)	O(2)-Nd(1)-N(1)	64.29(7)
O(3)-Nd(1)-O(1)	90.00(8)	O(3)-Nd(1)-O(2)	83.09(8)
O(3)-Nd(1)-O(5)	116.72(8)	O(3)-Nd(1)-O(9)	77.36(8)
O(3)-Nd(1)-N(1)	75.61(8)	O(4)-Nd(1)-O(1)	119.60(8)
O(4)-Nd(1)-O(2)	93.65(8)	O(4)-Nd(1)-O(3)	146.29(8)
O(4)-Nd(1)-O(5)	90.89(8)	O(4)-Nd(1)-O(9)	86.03(8)
O(4)-Nd(1)-N(1)	72.84(8)	O(5)-Nd(1)-O(1)	68.13(8)
O(5)-Nd(1)-O(2)	130.34(7)	O(5)-Nd(1)-O(9)	86.47(8)
O(5)-Nd(1)-N(1)	159.79(8)	O(9)-Nd(1)-O(2)	143.16(7)
O(9)-Nd(1)-N(1)	80.64(8)	O(1)-Nd(2)-O(5)	67.86(8)
O(1)-Nd(2)-O(6)	120.31(8)	O(1)-Nd(2)-O(10)	88.14(8)
O(1)-Nd(2)-N(2)	160.85(8)	O(5)-Nd(2)-O(6)	68.28(8)
O(5)-Nd(2)-O(10)	138.79(8)	O(5)-Nd(2)-N(2)	127.10(8)
O(6)-Nd(2)-O(10)	149.64(8)	O(6)-Nd(2)-N(2)	64.36(8)
O(7)-Nd(2)-O(1)	87.45(8)	O(7)-Nd(2)-O(5)	123.06(8)
O(7)-Nd(2)-O(6)	84.30(8)	O(7)-Nd(2)-O(8)	145.54(8)
O(7)-Nd(2)-O(10)	86.84(9)	O(7)-Nd(2)-N(2)	74.25(8)
O(8)-Nd(2)-O(1)	123.01(8)	O(8)-Nd(2)-O(5)	86.37(8)
O(8)-Nd(2)-O(6)	91.97(8)	O(8)-Nd(2)-O(10)	79.25(9)
O(8)-Nd(2)-N(2)	73.71(8)	O(10)-Nd(2)-N(2)	85.29(9)
Nd(1)-O(1)-Nd(2)	111.13(9)	Nd(1)-O(5)-Nd(2)	110.95(9)

Table S8 Selected bond lengths [Å] and bond angles [deg] for complex 4

Bond lengths			
La(1)-N(1)	2.766(3)	La(1)-O(1)	2.300(2)
La(1)-O(2)	2.318(2)	La(1)-O(3)	2.644(2)
La(1)-O(4)	2.424(2)	La(1)-O(8)	2.422(2)
La(1)-O(9)	2.611(2)	La(2)-N(2)	2.779(3)
La(2)-O(4)	2.435(2)	La(2)-O(5)	2.337(2)
La(2)-O(6)	2.314(2)	La(2)-O(7)	2.592(2)
La(2)-O(8)	2.438(2)	La(2)-O(10)	2.595(3)
Bond angles			
O(1)-La(1)-N(1)	71.91(8)	O(1)-La(1)-O(2)	144.23(8)
O(1)-La(1)-O(3)	92.83(8)	O(1)-La(1)-O(4)	119.27(8)
O(1)-La(1)-O(8)	91.56(8)	O(1)-La(1)-O(9)	85.96(8)
O(2)-La(1)-N(1)	74.47(8)	O(2)-La(1)-O(3)	82.47(8)
O(2)-La(1)-O(4)	91.02(8)	O(2)-La(1)-O(8)	118.60(8)
O(2)-La(1)-O(9)	77.22(8)	O(3)-La(1)-N(1)	62.92(7)
O(4)-La(1)-N(1)	127.67(8)	O(4)-La(1)-O(3)	64.58(7)
O(4)-La(1)-O(9)	144.83(8)	O(8)-La(1)-N(1)	160.63(8)
O(8)-La(1)-O(3)	129.82(7)	O(8)-La(1)-O(4)	68.97(7)
O(8)-La(1)-O(9)	87.60(8)	O(9)-La(1)-N(1)	81.37(8)
O(9)-La(1)-O(3)	142.57(7)	O(4)-La(2)-N(2)	161.25(8)
O(4)-La(2)-O(7)	119.97(8)	O(4)-La(2)-O(8)	68.51(7)
O(4)-La(2)-O(10)	88.57(8)	O(5)-La(2)-N(2)	72.43(8)
O(5)-La(2)-O(4)	124.28(8)	O(5)-La(2)-O(7)	91.29(8)
O(5)-La(2)-O(8)	87.23(8)	O(5)-La(2)-O(10)	79.03(9)
O(6)-La(2)-N(2)	73.17(8)	O(6)-La(2)-O(4)	88.51(8)
O(6)-La(2)-O(5)	143.44(8)	O(6)-La(2)-O(7)	83.98(8)
O(6)-La(2)-O(8)	123.06(8)	O(6)-La(2)-O(10)	87.00(9)
O(7)-La(2)-N(2)	63.11(8)	O(7)-La(2)-O(10)	149.68(8)
O(8)-La(2)-N(2)	124.86(8)	O(8)-La(2)-O(7)	66.90(8)
O(8)-La(2)-O(10)	139.91(9)	O(10)-La(2)-N(2)	86.57(9)
La(1)-O(4)-La(2)	109.83(8)	La(1)-O(8)-La(2)	109.81(8)

Table S9 Crystallographic data of complexes **5-6**

complexes	**5**	**6**
Empirical formula	$C_{80}H_{126}N_2O_{14}Sm_2Zn$	$C_{80}H_{126}N_2O_{14}Nd_2Zn$
Formula weight	1705.89	1693.67
Temperature/K	296(2)	293 (2)
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a/Å	17.005(3)	17.271(8)
b/Å	17.245(3)	17.417(8)
c/Å	17.816(3)	17.976(8)
α/°	108.783(4)	108.994(12)
β/°	93.579(4)	93.290(14)
γ/°	90.473(4)	90.941(14)
Volume/Å^3	4934.5(15)	5101(4)
Z	2	2
ρ_{calc} g/cm^3	1.148	1.103
μ/mm^{-1}	1.465	1.284
F(000)	1772.0	1764.0
2θ range for data collection/°	4.538 to 51.362	4.492 to 51.362
Reflections collected	67549	105338
Independent reflections	18455 [R_{int} = 0.2291]	19329 [R_{int} = 0.1287]
Data/restraints/parameters	18455/1926/906	19329/1778/906
Goodness-of-fit on F^2	1.023	1.030
Final R indexes [I>=2 σ (I)]	R_1 = 0.1063, wR_2 = 0.2735	R_1 = 0.1306, wR_2 = 0.3237
Final R indexes [all data]	R_1 = 0.2220 wR_2 = 0.3316	R_1 = 0.2021 wR_2 = 0.3946
Largest diff. peak/hole / e Å^{-3}	1.43/-1.72	4.62/-1.89

Table S10 Selected bond lengths [Å] and bond angles [deg] for complex **5**

Bond lengths			
Sm(1)-O(1)	2.541(11)	Sm(2)-O(11)	2.529(10)
Sm(1)-O(2)	2.175(11)	Sm(2)-O(12)	2.180(11)
Sm(1)-O(3)	2.559(10)	Sm(2)-O(13)	2.535(9)
Sm(1)-O(4)	2.185(10)	Sm(2)-O(14)	2.163(11)
Sm(1)-O(5)	2.339(9)	Sm(2)-N(2)	2.605(14)
Sm(1)-O(6)	2.348(11)	Zn(1)-O(5)	1.933(9)
Sm(1)-N(1)	2.673(11)	Zn(1)-O(7)	1.945(11)
Sm(2)-O(9)	2.358(11)	Zn(1)-O(8)	1.924(12)
Sm(2)-O(10)	2.335(9)	Zn(1)-O(10)	1.940(10)
Bond angles			
O(1)-Sm(1)-O(3)	141.3(3)	O(10)-Sm(2)-O(11)	66.5(4)
O(1)-Sm(1)-O(1)	79.2 (3)	O(10)-Sm(2)-O(13)	150.5(4)
O(2)-Sm(1)-O(1)	82.4(4)	O(10)-Sm(2)-N(2)	131.1(4)
O(2)-Sm(1)-O(3)	91.1(3)	O(11)-Sm(2)-O(13)	143.0(3)
O(2)-Sm(1)-O(4)	149.0(4)	O(11)-Sm(2)-N(2)	64.6(4)
O(2)-Sm(1)-O(5)	103.1(3)	O(12)-Sm(2)-O(9)	101.1(4)
O(2)-Sm(1)-O(6)	98.3(4)	O(12)-Sm(2)-O(10)	101.5(4)
O(2)-Sm(1)-N(1)	72.4(3)	O(12)-Sm(2)-O(11)	87.5(4)
O(3)-Sm(1)-N(1)	65.1(3)	O(12)-Sm(2)-O(13)	83.6(4)
O(4)-Sm(1)-O(1)	81.9(4)	O(12)-Sm(2)-N(2)	76.2(5)
O(4)-Sm(1)-O(3)	86.2(3)	O(13)-Sm(2)-N(2)	78.4(4)
O(4)-Sm(1)-O(5)	103.8(4)	O(14)-Sm(2)-O(9)	100.6(4)
O(4)-Sm(1)-O(6)	102.4(4)	O(14)-Sm(2)-O(10)	102.3(4)
O(4)-Sm(1)-N(1)	76.7(3)	O(14)-Sm(2)-O(11)	86.1(4)
O(5)-Sm(1)-O(1)	150.3(3)	O(14)-Sm(2)-O(12)	150.5(4)
O(5)-Sm(1)-O(3)	65.6(3)	O(14)-Sm(2)-O(13)	84.3(3)
O(5)-Sm(1)-O(6)	77.1(3)	O(14)-Sm(2)-N(2)	75.1(4)

O(5)-Sm(1)-N(1)	130.5(3)	O(5)-Zn(1)-O(7)	113.0(4)
O(6)-Sm(1)-O(1)	73.2(4)	O(5)-Zn(1)-O(10)	109.2(4)
O(6)-Sm(1)-O(3)	142.7(3)	O(8)-Zn(1)-O(5)	106.1(5)
O(6)-Sm(1)-N(1)	152.2(4)	O(8)-Zn(1)-O(7)	109.4(5)
O(9)-Sm(2)-O(11)	144.8(4)	O(8)-Zn(1)-O(10)	113.1(4)
O(9)-Sm(2)-O(13)	72.2(3)	O(10)-Zn(1)-O(7)	106.2(5)
O(9)-Sm(2)-N(2)	150.6(4)	Zn(1)-O(5)-Sm(1)	125.2(5)
O(10)-Sm(2)-O(9)	78.4(3)	Zn(1)-O(10)-Sm(2)	123.9(5)

Table S11 Selected bond lengths [Å] and bond angles [deg] for complex **6**

Bond lengths			
Nd(1)-O(1)	2.569(10)	Nd(2)-O(11)	2.222(11)
Nd(1)-O(2)	2.236(12)	Nd(2)-O(12)	2.609(11)
Nd(1)-O(3)	2.570(10)	Nd(2)-O(13)	2.251(11)
Nd(1)-O(4)	2.213(13)	Nd(2)-O(14)	2.591(13)
Nd(1)-O(5)	2.348(11)	Nd(2)-N(2)	2.715(12)
Nd(1)-O(6)	2.414(13)	Zn(1)-O(5)	1.945(13)
Nd(1)-N(1)	2.683(14)	Zn(1)-O(7)	1.940(13)
Nd(2)-O(9)	2.407(13)	Zn(1)-O(8)	1.988(14)
Nd(2)-O(10)	2.399(12)	Zn(1)-O(10)	1.931(11)
Bond angles			
O(1)-Nd(1)-O(3)	144.0(4)	O(10)-Nd(2)-O(12)	65.1(4)
O(1)-Nd(1)-O(1)	79.7 (4)	O(10)-Nd(2)-O(14)	151.4(4)
O(2)-Nd(1)-O(1)	83.5(4)	O(10)-Nd(2)-N(2)	128.4(4)
O(2)-Nd(1)-O(3)	87.7(4)	O(11)-Nd(2)-O(9)	98.7(5)
O(2)-Nd(1)-O(5)	102.2(4)	O(11)-Nd(2)-O(10)	104.0(4)
O(2)-Nd(1)-O(6)	101.2(5)	O(11)-Nd(2)-O(12)	91.3(4)
O(2)-Nd(1)-N(1)	75.8(5)	O(11)-Nd(2)-O(13)	146.7(4)
O(3)-Nd(1)-N(1)	64.3(4)	O(11)-Nd(2)-O(14)	73.5(4)

O(4)-Nd(1)-O(1)	83.8(4)	O(11)-Nd(2)-N(2)	83.13(4)
O(4)-Nd(1)-O(2)	148.7(5)	O(12)-Nd(2)-N(2)	63.5(4)
O(4)-Nd(1)-O(3)	86.0(4)	O(13)-Nd(2)-O(9)	103.4(4)
O(4)-Nd(1)-O(5)	103.3(4)	O(13)-Nd(2)-O(10)	104.6(4)
O(4)-Nd(1)-O(6)	101.6(4)	O(13)-Nd(2)-O(12)	85.5(4)
O(4)-Nd(1)-N(1)	73.9(5)	O(13)-Nd(2)-O(14)	80.6(4)
O(5)-Nd(1)-O(1)	149.4(4)	O(13)-Nd(2)-N(2)	75.4(4)
O(5)-Nd(1)-O(3)	66.6(4)	O(14)-Nd(2)-O(12)	143.3(4)
O(5)-Nd(1)-O(6)	78.0(4)	O(14)-Nd(2)-N(2)	80.1(4)
O(5)-Nd(1)-N(1)	130.9(4)	O(5)-Zn(1)-O(8)	104.5(6)
O(6)-Nd(1)-O(1)	71.4(4)	O(7)-Zn(1)-O(5)	114.1(5)
O(6)-Nd(1)-O(3)	144.6(4)	O(7)-Zn(1)-O(8)	110.2(6)
O(6)-Nd(1)-N(1)	151.1(4)	O(10)-Zn(1)-O(5)	109.9(5)
O(9)-Nd(2)-O(12)	143.8(4)	O(10)-Zn(1)-O(7)	103.5(5)
O(9)-Nd(2)-O(14)	72.8(4)	O(10)-Zn(1)-N(8)	115.0(5)
O(9)-Nd(2)-N(2)	152.6(4)	Zn(1)-O(5)-Nd(1)	125.5(5)
O(10)-Nd(2)-O(9)	78.7(4)	Zn(1)-O(10)-Nd(2)	124.0(6)

Table S12 Crystallographic data of complexes **7-8**

complexes	**7**·4THF	**8**·2THF·hex
Empirical formula	$C_{106}H_{166}N_2O_{16}Y_2Zn$	$C_{104}H_{164}N_2O_{14}Yb_2Zn$
Formula weight	1967.59	2077.81
Temperature/K	120(2)	296.15(2)
Crystal system	Triclinic	triclinic
Space group	P-1	P-1
a/Å	15.3715(19)	13.7365(7)
b/Å	18.856(2)	18.4813(9)
c/Å	19.968(3)	23.8894(11)

α/°	96.829(4)	111.217(2)
β/°	97.583(4)	97.959(2)
γ/°	111.939(4)	102.216(2)
Volume/Å^3	5231.6(12)	5369.5(5)
Z	2	2
ρ_{calc} g/cm^3	1.249	1.285
μ/mm^{-1}	1.389	2.006
F(000)	2104.0	2168.0
2θ range for data collection/°	4.416 to 52.744	4.512 to 52.744
Reflections collected	184194	293922
Independent reflections	21369 [R_{int} = 0.1265]	21942 [R_{int} = 0.0645]
Data/restraints/parameters	21369/134/1028	21942/2073/1069
Goodness-of-fit on F^2	1.036	1.063
Final R indexes [I>=2 σ (I)]	R_1 = 0.0514, wR_2 = 0.1237	R_1 = 0.0326, wR_2 = 0.0797
Final R indexes [all data]	R_1 = 0.0892 wR_2 = 0.1386	R_1 = 0.0455 wR_2 = 0.0882
Largest diff. peak/hole / e Å^{-3}	0.52/-0.64	1.74/-1.73

Table S13 Selected bond lengths [Å] and bond angles [deg] for complex **7**

Bond lengths			
Y(1)-O(1)	2.132(2)	Zn(1)-O(8)	1.925(2)
Y(1)-O(2)	2.502(2)	Y(2)-O(7)	2.301(2)
Y(1)-O(3)	2.141(2)	Y(2)-O(8)	2.278(2)
Y(1)-O(4)	2.462(2),	Y(2)-O(9)	2.158(2)
Y(1)-O(5)	2.296(2)	Y(2)-O(10)	2.508(2)
Y(1)-O(6)	2.277(2)	Y(2)-O(11)	2.142(2)
Zn(1)-O(5)	1.961(2)	Y(2)-O(12)	2.476(2)
Zn(1)-O(6)	1.929(2)	Y(1)-N(1)	2.644(3)
Zn(1)-O(7)	2.301(2)	Y(2)-N(2)	2.624(3)
Bond angles			

O(1)-Y(1)-O(2)	85.34(9)	O(8)-Y(2)-O(10)	65.31(7)
O(1)-Y(1)-O(3)	150.86(9)	O(8)-Y(2)-O(12)	148.16(8)
O(1)-Y(1)-O(4)	81.99(9)	O(9)-Y(2)-N(2)	78.25(8)
O(1)-Y(1)-O(5)	104.64(8)	O(9)-Y(2)-O(7)	102.16(8)
O(1)-Y(1)-O(6)	102.03(9	O(9)-Y(2)-O(8)	104.09(8)
O(1)-Y(1)-N(1)	75.46(9)	O(9)-Y(2)-O(10)	88.29(8)
O(2)-Y(1)-N(1)	65.46(8)	O(9)-Y(2)-O(12)	80.95(8)
O(3)-Y(1)-N(1)	76.74(8)	O(10)-Y(2)-N(2)	64.75(7)
O(3)-Y(1)-O(2)	91.01(8)	O(11)-Y(2)-N(2)	75.64(8)
O(3)-Y(1)-O(4)	85.34(9)	O(11)-Y(2)-O(7)	98.73(8)
O(3)-Y(1)-O(5)	98.49(8)	O(11)-Y(2)-O(8)	101.99(8)
O(3)-Y(1)-O(6)	102.68(8)	O(11)-Y(2)-O(9)	151.15(8)
O(4)-Y(1)-N(1)	81.23(8)	O(11)-Y(2)-O(10)	91.52(8)
O(4)-Y(1)-O(2)	146.40(8)	O(11)-Y(2)-O(12)	83.43(8)
O(5)-Y(1)-N(1)	159.96(8)	O(12)-Y(2)-N(2)	81.93(8)
O(5)-Y(1)-O(2)	134.50(8)	O(12)-Y(2)-O(10)	146.46(7)
O(5)-Y(1)-O(4)	78.97(8)	O(6)-Zn(1)-O(5)	83.41 (9)
O(6)-Y(1)-N(1)	131.00(8)	O(6)-Zn(1)-O(7)	115.28(9)
O(6)-Y(1)-O(2)	65.56(8)	O(7)-Zn(1)-O(5)	136.68(10)
O(6)-Y(1)-O(4)	147.68(8)	O(8)-Zn(1)-O(5)	112.20(9)
O(6)-Y(1)-O(5)	68.94(8)	O(8)-Zn(1)-O(6)	134.55(10)
O(7)-Y(2)-N(2)	161.39(8)	O(8)-Zn(1)-O(7)	83.05(9)
O(7)-Y(2)-O(10)	133.69(7)	Zn(1)-O(5)-Y(1)	102.91(9)
O(7)-Y(2)-O(12)	79.79(7)	Zn(1)-O(6)-Y(1)	104.63(10)
O(8)-Y(2)-N(2)	129.89(8)	Zn(1)-O(7)-Y(2)	103.29(9)
O(8)-Y(2)-O(7)	68.39(8)	Zn(1)-O(8)-Y(2)	105.18(16)

Table S14 Selected bond lengths [Å] and bond angles [deg] for complex **8**

Bond lengths			
Zn(1)-O(5)	1.928(3)	Yb(1)-O(4)	2.474(3)
Zn(1)-O(10)	1.931(3)	Yb(1)-N(1)	2.595(3)
Zn(1)-O(1)	1.953(3)	Yb(2)-O(8)	2.110(3)
Zn(1)-O(6)	1.958(3)	Yb(2)-O(7)	2.127(3)
Yb(1)-O(3)	2.112(3)	Yb(2)-O(10)	2.233(3)
Yb(1)-O(2)	2.127(3)	Yb(2)-O(6)	2.277(3)
Yb(1)-O(5)	2.233(3)	Yb(2)-O(12)	2.454(3)
Yb(1)-O(1)	2.269(3)	Yb(2)-O(9)	2.465(3)
Yb(1)-O(11)	2.466(3)	Yb(2)-N(2)	2.593(3)
Bond angles			
O(5)-Zn(1)-O(10)	133.65(12)	O(4)-Yb(1)-N(1)	65.26(10)
O(5)-Zn(1)-O(1)	81.73(11)	O(8)-Yb(2)-O(7)	153.42(10)
O(1)0-Zn(1)-O(1)	114.57(11)	O(8)-Yb(2)-O(10)	99.51(10)
O(5)-Zn(1)-O6	114.88(12)	O(7)-Yb(2)-O(10)	104.04(11)
O(10)-Zn(1)-O(6)	82.10(11)	O(8)-Yb(2)-O(6)	100.14(10)
O(1)-Zn(1)-O(6)	138.69(12)	O(7)-Yb(2)-O(6)	99.67(10)
O(3)-Yb(1)-O(2)	153.18(10)	O(10)-Yb(2)-O(6)	68.97(9)
O(3)-Yb(1)-O(5)	99.32(11)	O(8)-Yb(2)-O(12)	82.86(10)
O(2)-Yb(1)-O(5)	104.57(11)	O(7)-Yb(2)-O(12)	83.67(11)
O(3)-Yb(1)-O(1)	105.48(10)	O(10)-Yb(2)-O(12)	147.95(10)
O(2)-Yb(1)-O(1)	94.55(10)	O(6)-Yb(2)-O(12)	79.11(10)
O(5)-Yb(1)-O(1)	68.66(9)	O(8)-Yb(2)-O(9)	91.09(10)
O(3)-Yb(1)-O(11)	82.12(11)	O(7)-Yb(2)-O(9)	87.39(10)
O(2)-Yb(1)-O(11)	84.26(11)	O(10)-Yb(2)-O(9)	66.04(9)
O(5)-Yb(1)-O(11)	147.40(10)	O(6)-Yb(2)-O(9)	134.83(9)
O(1)-Yb(1)-O(11)	79.51(10)	O(12)-Yb(2)-O(9)	145.99(9)
O(3)-Yb(1)-O(4)	89.51(11)	O(8)-Yb(2)-N(2)	76.90(10)

O(2)-Yb(1)-O(4)	89.34(11)	O(7)-Yb(2)-N(2)	78.40(10)
O(5)-Yb(1)-O(4)	65.67(9)	O(10)-Yb(2)-N(2)	131.03(10)
O(1)-Yb(1)-O(4)	133.62(9)	O(6)-Yb(2)-N(2)	159.94(10)
O(11)-Yb(1)-O(4)	146.74(10)	O(12)-Yb(2)-N(2)	80.83(10)
O(3)-Yb(1)-N(1)	77.16(10)	O(9)-Yb(2)-N(2)	65.23(9)
O(2)-Yb(1)-N(1)	78.05(10)	Zn(1)-O(1)-Yb(1)	103.71(11)
O(5)-Yb(1)-N(1)	130.82(10)	Zn(1)-O(5)-Yb(1)	105.90(11)
O(1)-Yb(1)-N(1)	160.22(10)	Zn(1)-O(6)-Yb(2)	103.06(11)
O(11)-Yb(1)-N(1)	81.49(10)	Zn(1)-O(10)-Yb(2)	105.60(11)

Table S15 Crystallographic data of complexes **9-11**

complexes	**9**·4THF	**10**·4THF	**11**·4THF
Empirical formula	$C_{154}H_{262}N_2O_{28}Sm_2Zn$	$C_{94}H_{142}N_2O_{13}Nd_2Zn$	$C_{106}H_{166}N_2O_{16}La_2Zn$
Formula weight	2955.71	1854.79	2067.59
Temperature/K	120(2)	296(2)	296(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
a/Å	15.4179(6)	15.5910(8)	15.652(2)
b/Å	19.0726(8)	19.2543(10)	19.351(3)
c/Å	19.8412(8)	20.0408(10)	20.081(3)
α/°	96.9020(10)	96.615(2)	96.633(4)
β/°	97.1110(10)	97.694(2)	97.800(4)
γ/°	111.8820(10)	111.723(2)	111.422(4)
Volume/Å^3	5284.1(4)	5449.2(5)	5519.1(12)
Z	2	2	2
ρ_{calc} g/cm^3	1.858	1.130	1.244
μ/mm^{-1}	1.421	1.207	1.034
F(000)	3150.0	974.0	2176.0
2θ range for data collection/°	4.206 to 55.038	4.4 to 52.12	4.568 to 55.044

Reflections collected	109255	314402	317522
Independent reflections	24239 [R_{int} = 0.0707]	25095 [R_{int} = 0.0692]	25376 [R_{int} = 0.0786]
Data/restraints/parameters	24239/26/998	25095/66/1032	25376/261/1247
Goodness-of-fit on F^2	1.017	1.094	1.045
Final R indexes [I>=2 σ (I)]	R_1 = 0.0391, wR_2 = 0.0999	R_1 = 0.0565, wR_2 = 0.1900	R_1 = 0.0408, wR_2 = 0.0925
Final R indexes [all data]	R_1 = 0.0574, wR_2 = 0.1136	R_1 = 0.0815 wR_2 = 0.2112	R_1 = 0.0681 wR_2 = 0.1039
Largest diff. peak/hole / e $Å^{-3}$	1.97/-0.85	2.51/-1.67	0.94/-0.79

Table S16 Selected bond lengths [Å] and bond angles [deg] for complex **9**

Bond lengths			
Sm(1)-Zn(1)	3.3888(4)	Sm(2)-O(8)	2.355(2)
Sm(1)-O(1)	2.538(2)	Sm(2)-O(9)	2.563(2)
Sm(1)-O(2)	2.197(2)	Sm(2)-O(10)	2.192(2)
Sm(1)-O(3)	2.563(2)	Sm(2)-O(11)	2.203(2)
Sm(1)-O(4)	2.216(2)	Sm(2)-O(12)	2.536(3)
Sm(1)-O(5)	2.335(2)	Sm(2)-N(2)	2.691(3)
Sm(1)-O(6)	2.353(2)	Zn(1)-O(5)	1.931(2)
Sm(1)-N(1)	2.675(3)	Zn(1)-O(6)	1.950(2)
Sm(2)-Zn(1)	3.3784(4)	Zn(1)-O(7)	1.932(2)
Sm(2)-O(7)	2.334(2)	Zn(1)-O(8)	1.959(2)
Bond angles			
O(2)-Sm(1)-O(3)	90.47(8)	O(8)-Sm(2)-O(10)	147.95(11)
O(2)-Sm(1)-O(4)	148.47(9)	O(8)-Sm(2)-N(11)	128.91(12)
O(2)-Sm(1)-O(5)	102.68(9)	O(9)-Sm(2)-O(7)	99.30(12)
O(2)-Sm(1)-O(6)	98.79(9)	O(9)-Sm(2)-O(8)	103.00(12)
O(3)-Sm(1)-N(1)	64.11(8)	O(10)-Sm(2)-O(7)	104.19(9)
O(4)-Sm(1)-N(1)	76.58(8)	O(10)-Sm(2)-O(8)	106.41(9)

O(4)-Sm(1)-O(1)	80.46(8)	O(10)-Sm(2)-O(9)	84.83(9)
O(4)-Sm(1)-O(3)	88.76(8)	O(10)-Sm(2)-O(11)	147.99(9)
O(4)-Sm(1)-O(5)	105.28(9)	O(10)-Sm(2)-O(12)	81.83(9)
O(4)-Sm(1)-O(6)	105.15(9)	O(11)-Sm(2)-N(2)	75.70(9)
O(5)-Sm(1)-N(1)	128.25(8)	O(11)-Sm(2)-O(7)	102.94(9)
O(5)-Sm(1)-O(1)	148.19(8)	O(11)-Sm(2)-O(8)	99.25(9)
O(5)-Sm(1)-O(3)	64.24(8)	O(11)-Sm(2)-O(9)	91.75(9)
O(5)-Sm(1)-O(6)	67.42(8)	O(11)-Sm(2)-O(12)	84.22(9)
O(6)-Sm(1)-N(1)	163.73(8)	O(12)-Sm(2)-N(2)	83.09(9)
O(6)-Sm(1)-O(1)	80.83(8)	O(12)-Sm(2)-O(9)	147.29(8)
O(6)-Sm(1)-O(3)	131.64(8)	O(5)-Zn(1)-O(6)	84.20(10)
O(7)-Sm(2)-N(2)	129.04(9)	O(5)-Zn(1)-O(7)	111.74(10)
O(7)-Sm(2)-O(8)	68.07(8)	O(5)-Zn(1)-O(8)	136.15(14)
O(7)-Sm(2)-O(9)	64.60(8)	O(6)-Zn(1)-O(8)	134.63(10)
O(7)-Sm(2)-O(12)	147.87(9)	O(7)-Zn(1)-O(6)	113.45(10)
O(8)-Sm(2)-O(9)	132.66(8)	O(7)-Zn(1)-O(8)	84.81(10)
O(8)-Sm(2)-O(12)	79.91(8)	Zn(1)-O(5)-Sm(1)	104.78(10)
O(8)-Sm(2)-N(2)	162.69(9)	Zn(1)-O(6)-Sm(1)	103.54(10)
O(9)-Sm(2)-N(2)	64.54(8)	Zn(1)-O(7)-Sm(2)	104.34(10)
O(10)-Sm(2)-N(2)	74.13(9)	Zn(1)-O(8)-Sm(2)	102.71(10)

Table S17 Selected bond lengths [Å] and bond angles [deg] for complex **10**

Bond lengths

Nd(1)-Zn(1)	3.3995(4)	Nd(2)-O(8)	2.223(2)
Nd(1)-O(1)	2.389(2)	Nd(2)-O(9)	2.240(2)
Nd(1)-O(2)	2.217(2)	Nd(2)-O(10)	2.597(2)
Nd(1)-O(3)	2.221(2)	Nd(2)-O(11)	2.369(2)
Nd(1)-O(4)	2.587(2)	Nd(2)-O(12)	2.573(2)
Nd(1)-O(5)	2.367(2)	Nd(2)-N(2)	2.713(2)

Nd(1)-O(6)	2.566(2)	Zn(1)-O(1)	1.958(2)
Nd(1)-N(1)	2.722(3)	Zn(1)-O(5)	1.932(2)
Nd(2)-Zn(1)	3.4122(4)	Zn(1)-O(7)	1.954(2)
Nd(2)-O(7)	2.384(2)	Zn(1)-O(11)	1.933(2)

Bond angles

O(1)-Nd(1)-O(4)	131.63(7)	O(8)-Nd(2)-O(10)	90.26(8)
O(1)-Nd(1)-O(6)	80.10(8)	O(8)-Nd(2)-O(11)	103.02(8)
O(1)-Nd(1)-N(1)	164.16(8)	O(8)-Nd(2)-O(12)	82.09(8)
O(2)-Nd(1)-O(1)	106.79(8)	O(8)-Nd(2)-N(2)	74.04(8)
O(2)-Nd(1)-O(3)	146.99(9)	O(9)-Nd(2)-O(7)	105.52(8)
O(2)-Nd(1)-O(4)	84.73(9)	O(9)-Nd(2)-O(10)	89.41(8)
O(2)-Nd(1)-O(5)	104.41(9)	O(9)-Nd(2)-O(11)	106.78(8)
O(2)-Nd(1)-O(6)	82.24(9)	O(9)-Nd(2)-O(12)	80.59(8)
O(2)-Nd(1)-N(1)	73.67(8)	O(9)-Nd(2)-N(2)	75.84(8)
O(3)-Nd(1)-O(1)	100.78(8)	O(10)-Nd(2)-N(2)	63.48(7)
O(3)-Nd(1)-O(4)	90.41(8)	O(11)-Nd(2)-O(7)	67.11(7)
O(3)-Nd(1)-O(5)	102.62(9)	O(11)-Nd(2)-O(10)	63.47(7)
O(3)-Nd(1)-O(6)	85.01(9)	O(11)-Nd(2)-O(12)	148.55(8)
O(3)-Nd(1)-N(1)	74.86(8)	O(11)-Nd(2)-N(2)	126.83(7)
O(4)-Nd(1)-N(1)	64.11(8)	O(12)-Nd(2)-O(10)	147.98(7)
O(5)-Nd(1)-O(1)	67.64(8)	O(12)-Nd(2)-N(2)	84.55(8)
O(5)-Nd(1)-O(4)	63.99(7)	O(5)-Zn(1)-O(1)	85.78(9)
O(5)-Nd(1)-O(6)	147.67(8)	O(5)-Zn(1)-O(7)	112.91(10)
O(5)-Nd(1)-N(1)	128.01(8)	O(5)-Zn(1)-O(11)	135.61(10)
O(6)-Nd(1)-O(4)	148.14(8)	O(7)-Zn(1)-O(1)	133.39(10)
O(6)-Nd(1)-N(1)	84.32(9)	O(11)-Zn(1)-O(1)	111.59(10)
O(7)-Nd(2)-O(10)	130.57(7)	O(11)-Zn(1)-O(7)	85.06(9)
O(7)-Nd(2)-O(12)	81.44(8)	Zn(1)-O(1)-Nd(1)	102.42(9)

O(7)-Nd(2)-N(2)	165.46(8)	Zn(1)-O(5)-Nd(1)	104.08(9)
O(8)-Nd(2)-O(7)	100.05(8)	Zn(1)-O(7)-Nd(2)	103.30(9)
O(8)-Nd(2)-O(9)	146.41(8)	Zn(1)-O(11)-Nd(2)	104.50(9)

Table S18 Selected bond lengths [Å] and bond angles [deg] for complex **11**

Bond lengths			
La(1)-O(1)	2.436(2)	La(2)-O(8)	2.270(2)
La(1)-O(2)	2.290(2)	La(2)-O(9)	2.418(2)
La(1)-O(3)	2.272(2)	La(2)-O(10)	2.647(2)
La(1)-O(4)	2.658(2)	La(2)-O(12)	2.615(2)
La(1)-O(5)	2.424(2)	La(2)-N(2)	2.779(3)
La(1)-O(11)	2.622(2)	Zn(1)-O(1)	1.952(2)
La(1)-N(1)	2.768(2)	Zn(1)-O(5)	1.933(2)
La(2)-O(6)	2.443(2)	Zn(1)-O(6)	1.958(2)
La(2)-O(7)	2.270(2)	Zn(1)-O(9)	1.935(2)
Bond angles			
O(1)-La(1)-O(4)	128.98(7)	O(7)-La(2)-O(9)	105.63(9)
O(1)-La(1)-O(11)	82.64(8)	O(7)-La(2)-O(10)	84.47(8)
O(1)-La(1)-N(1)	167.77(7)	O(7)-La(2)-O(12)	82.45(9)
O(2)-La(1)-O(1)	107.36(8)	O(7)-La(2)-N(2)	72.42(8)
O(2)-La(1)-O(4)	89.16(7)	O(8)-La(2)-O(6)	102.76(8)
O(2)-La(1)-O(5)	107.69(8)	O(8)-La(2)-O(9)	102.64(8)
O(2)-La(1)-O(11)	80.57(8)	O(8)-La(2)-O(10)	89.59(8)
O(2)-La(1)-N(1)	74.59(7)	O(8)-La(2)-O(12)	85.11(9)
O(3)-La(1)-O(1)	101.30(8)	O(8)-La(2)-N(2)	73.69(8)
O(3)-La(1)-O(2)	144.08(8)	O(9)-La(2)-O(6)	66.98(7)
O(3)-La(1)-O(4)	89.32(7)	O(9)-La(2)-O(10)	63.07(7)
O(3)-La(1)-O(5)	103.33(8)	O(9)-La(2)-O(12)	147.63(8)
O(3)-La(1)-O(11)	82.15(8)	O(9)-La(2)-N(2)	126.01(8)

O(3)-La(1)-N(1)	72.95(7)	O(10)-La(2)-N(2)	63.05(8)
O(4)-La(1)-N(1)	62.55(7)	O(12)-La(2)-O(10)	149.16(8)
O(5)-La(1)-O(1)	66.38(7)	O(12)-La(2)-N(2)	86.36(9)
O(5)-La(1)-O(4)	62.62(7)	O(1)-Zn(1)-O(6)	131.14(10)
O(5)-La(1)-O(11)	149.02(7)	O(5)-Zn(1)-O(1)	86.43(9)
O(5)-La(1)-N(1)	125.07(7)	O(5)-Zn(1)-O(6)	111.02(10)
O(11)-La(1)-O(4)	148.36(7)	O(5)-Zn(1)-O(9)	135.69(10)
O(11)-La(1)-N(1)	85.84(8)	O(9)-Zn(1)-O(1)	112.19(10)
O(6)-La(2)-O(10)	130.03(7)	O(9)-Zn(1)-O(6)	87.11(9)
O(6)-La(2)-O(12)	80.68(8)	Zn(1)-O(1)-La(1)	103.06(9)
O(6)-La(2)-N(2)	166.84(8)	Zn(1)-O(5)-La(1)	104.11(9)
O(7)-La(2)-O(6)	107.81(8)	Zn(1)-O(6)-La(2)	102.15(9)
O(7)-La(2)-O(8)	144.48(8)	Zn(1)-O(9)-La(2)	103.70(9)

7. Plausible mechanism

Synergism between metal centers is proposed to explain the enhanced activity of the heterobimetallic system (**Figure S24**). The catalytic cycle starts with the coordination of epoxide with one of the rare earth metal centers, followed by attack of the co-catalyst (NBu_4Br) to cause ring-opening process. CO_2 may be activated by the zinc center, which is attacked by the alkoxide group resulting from ring-opening. In addition, Zn center contributes to stabilizing the resulting carbonate, as has been proved computationally. Finally, an intramolecular nucleophilic substitution leads to cyclization along with the release of the bromide anion.

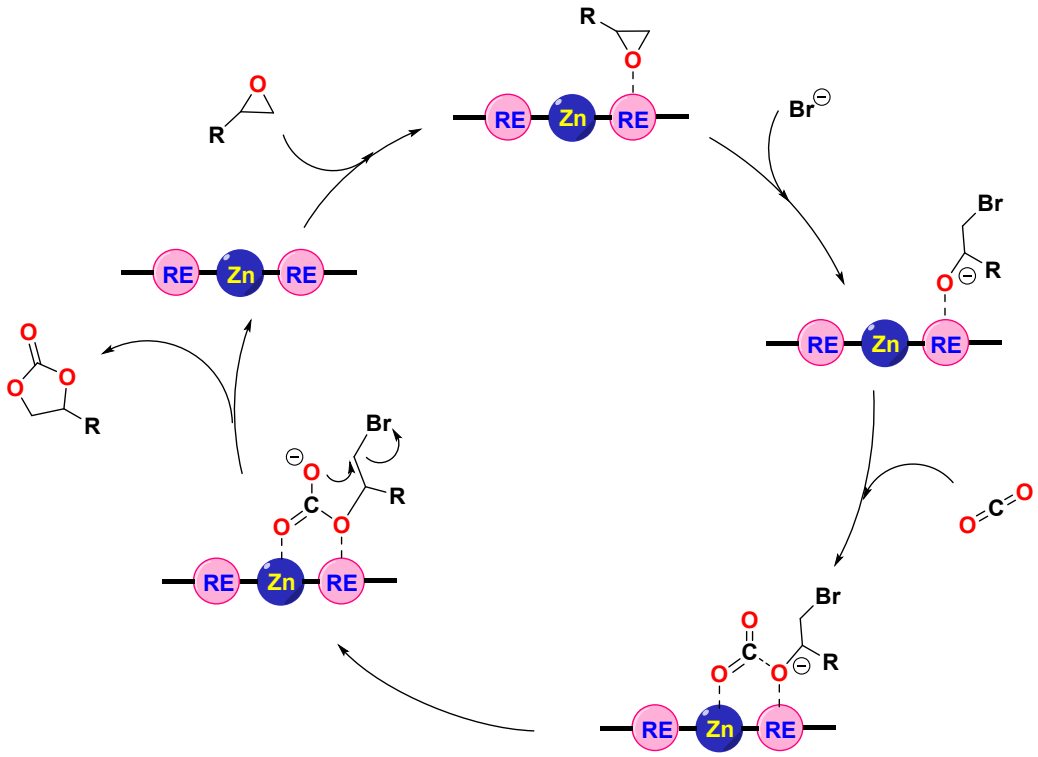


Figure S24. Proposed mechanism for the cycloaddition reaction