Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

Highly water-soluble dimeric and trimeric lanthanide carbonates with ethylenediaminetetraacetates as precursors of catalysts for oxidative coupling reaction of methane

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Figures and Table Options

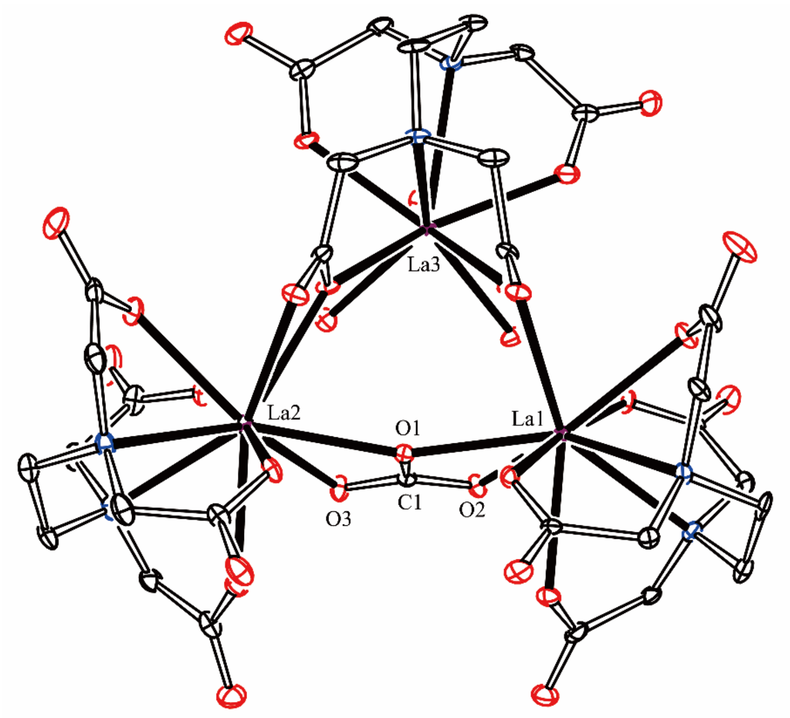

Fig. S1. Anion structure of trimeric complex $(NH_4)_5[La_3(CO_3)(EDTA)_3(H_2O)_3]\cdot 12H_2O$ (**1**) in 30% thermal ellipsoids.

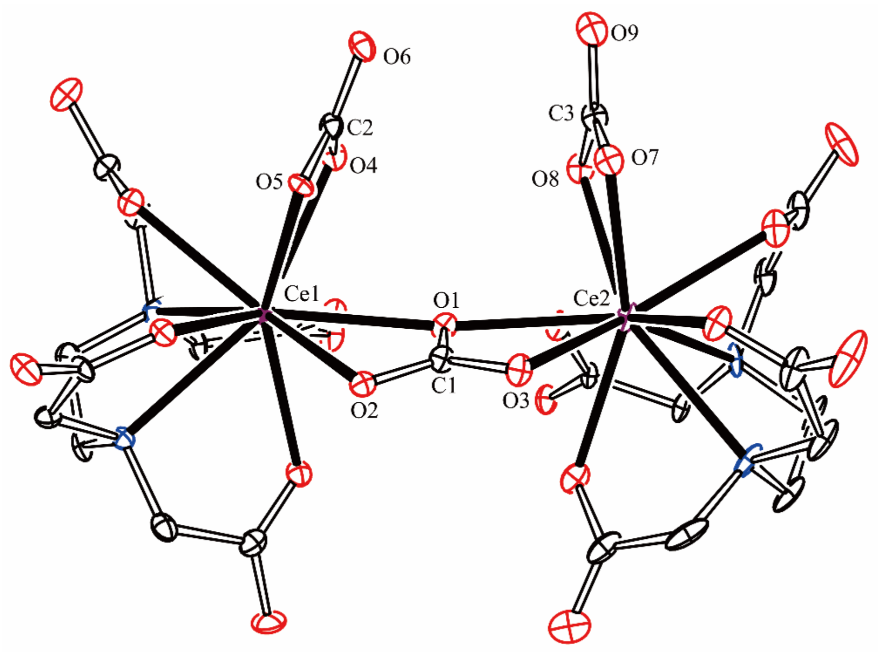

Fig. S2. Anion structure of dimeric complex $Na_8[Ce_2(CO_3)_3(EDTA)_2]\cdot 17.5H2O$ (**3**) in 30% thermal ellipsoids.

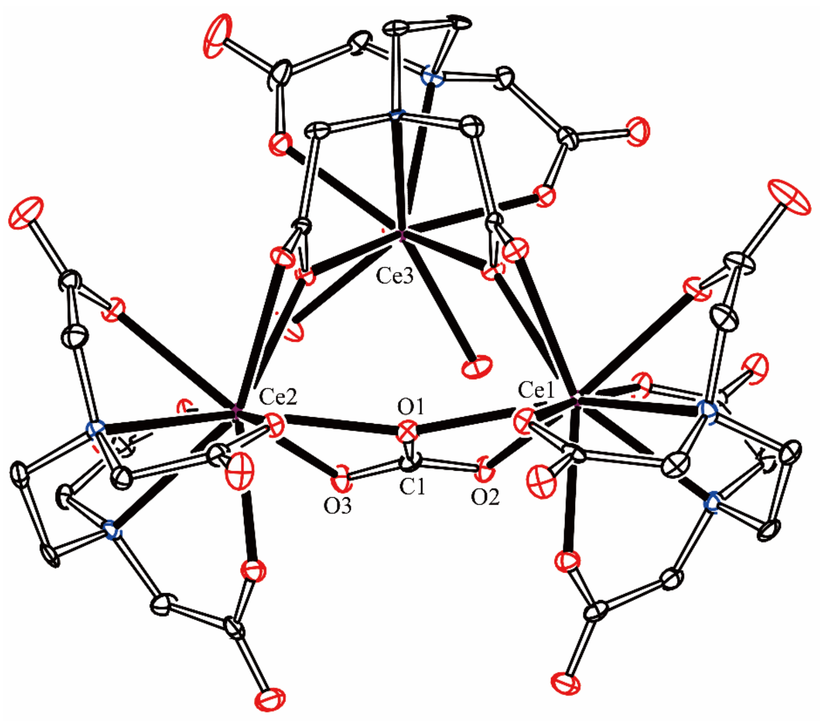

Fig. S3. Anion structure of trimeric complex $K_5[Ce_3(CO_3)(EDTA)_3(H_2O)_3]\cdot 13.5H_2O$ (**5**) in 30% thermal ellipsoids.

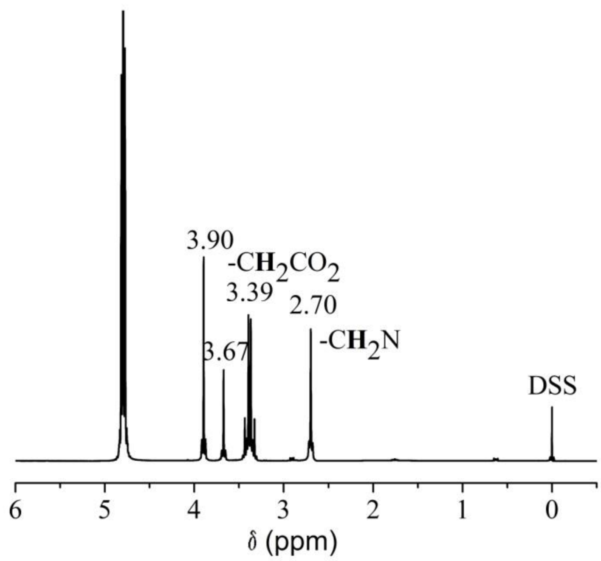

Fig. S4. ^{1}H NMR spectrum of $(NH_4)_5[La_3(CO_3)(EDTA)_3(H_2O)_3]\cdot 12H_2O$ (**1**).

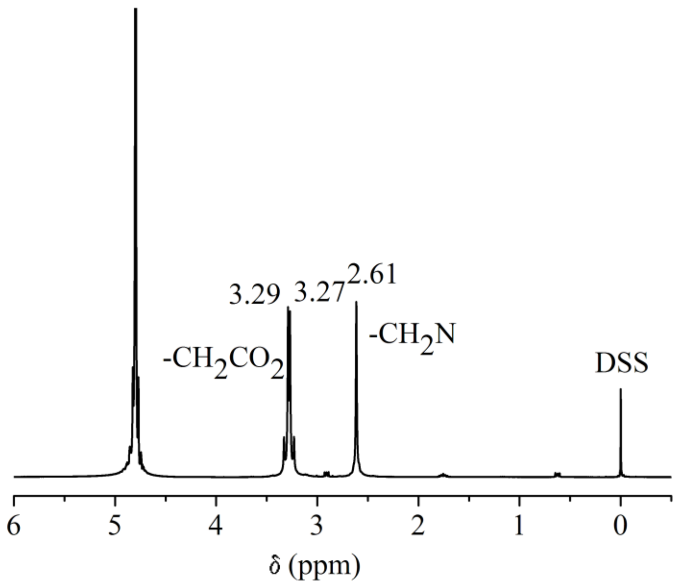

Fig. S5. [1]H NMR spectrum of $Na_8[La_2(CO_3)_3(EDTA)_2]\cdot 17.5H_2O$ (**2**).

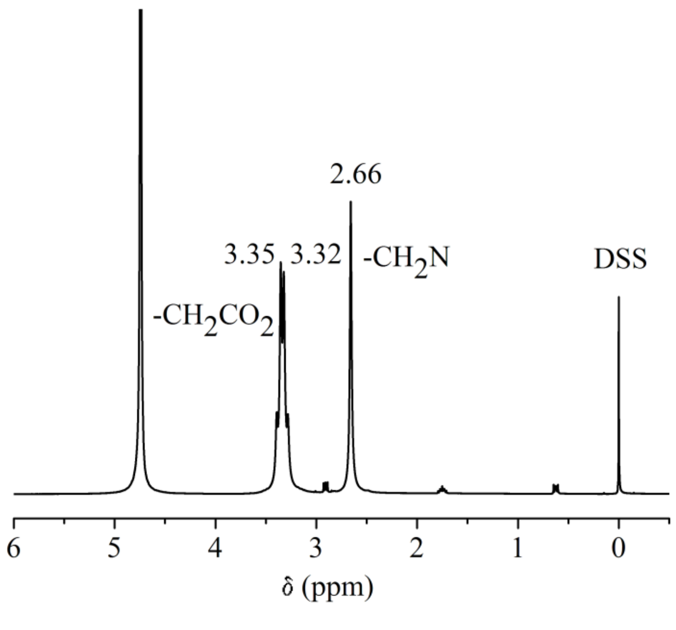

Fig. S6. [1]H NMR spectrum of $K_5[La_3(CO_3)(EDTA)_3(H_2O)_3]\cdot 13.5H_2O$ (**4**).

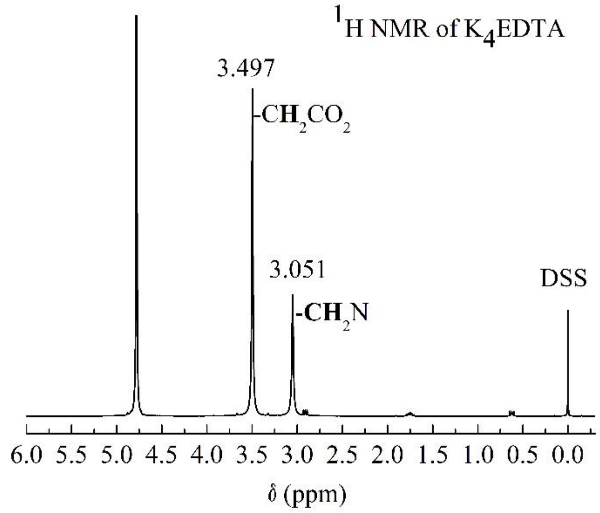

Fig. S7. ¹H NMR spectrum of K_4EDTA.

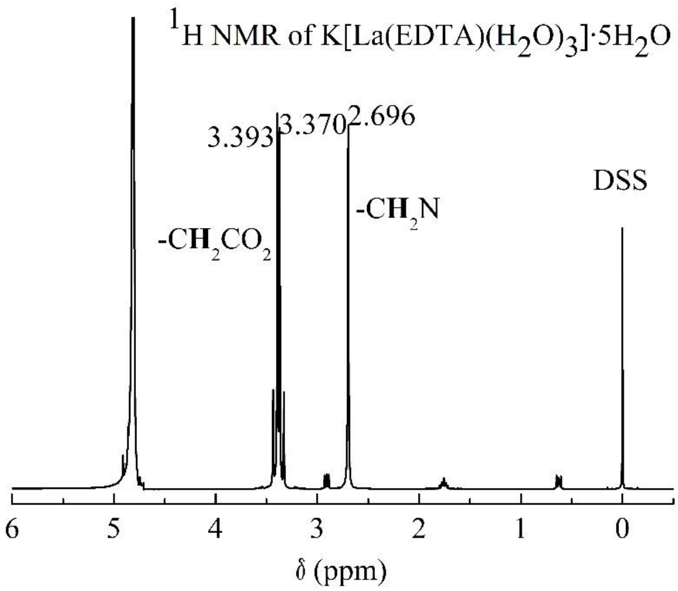

Fig. S8. ¹H NMR spectrum of $K[La(EDTA)(H_2O)_3]\cdot 5H_2O$.

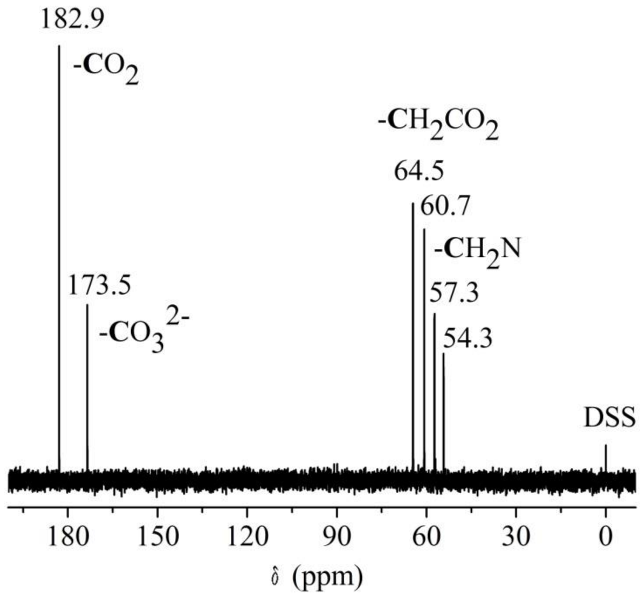

Fig. S9. Solution ^{13}C NMR spectrum of $(NH_4)_5[La_3(CO_3)(EDTA)_3(H_2O)_3]\cdot 12H_2O$ (**1**).

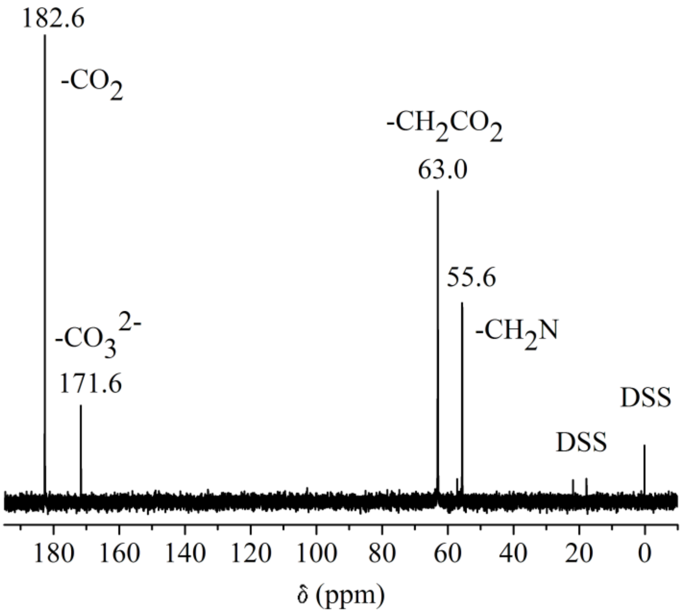

Fig. S10. Solution ^{13}C NMR spectrum of $Na_8[La_2(CO_3)_3(EDTA)_2]\cdot 17.5H_2O$ (**2**).

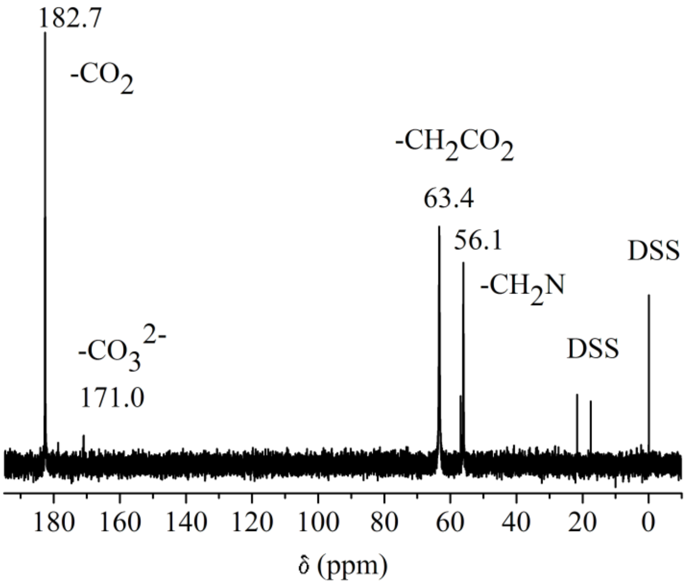

Fig. S11. Solution [13]C NMR spectrum of $K_5[La_3(CO_3)(EDTA)_3(H_2O)_3]\cdot 13.5H_2O$ (**4**).

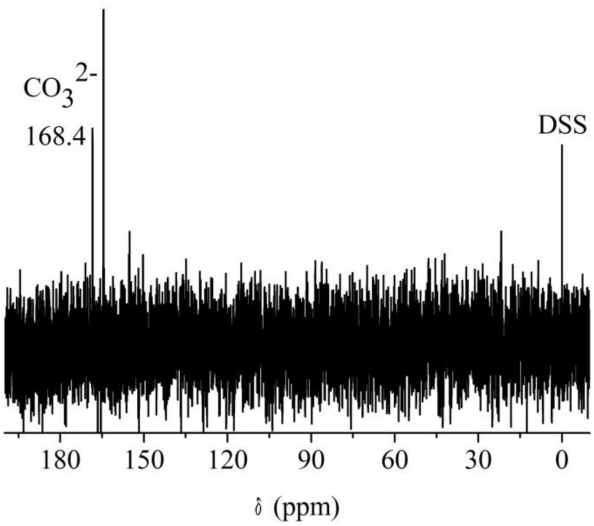

Fig. S12. Solution [13]C NMR spectrum of $(NH_4)_2CO_3$.

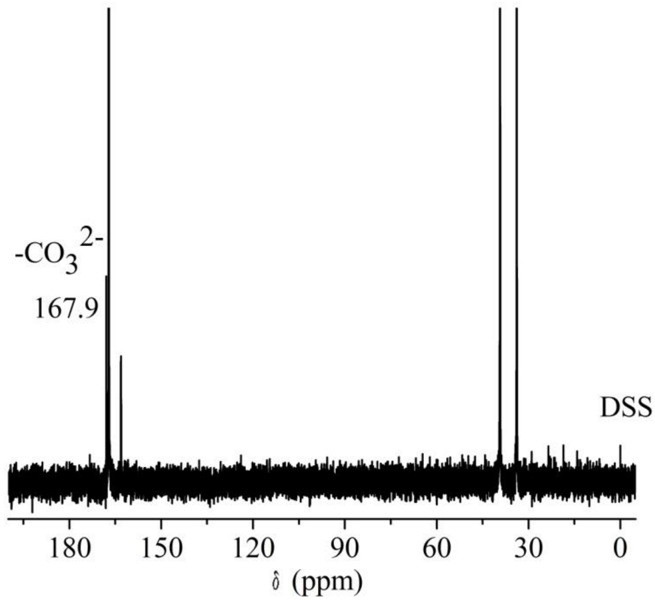

Fig. S13. Solution ^{13}C NMR spectrum of $(NH_4)_2CO_3$ in dimethylformamide-water.

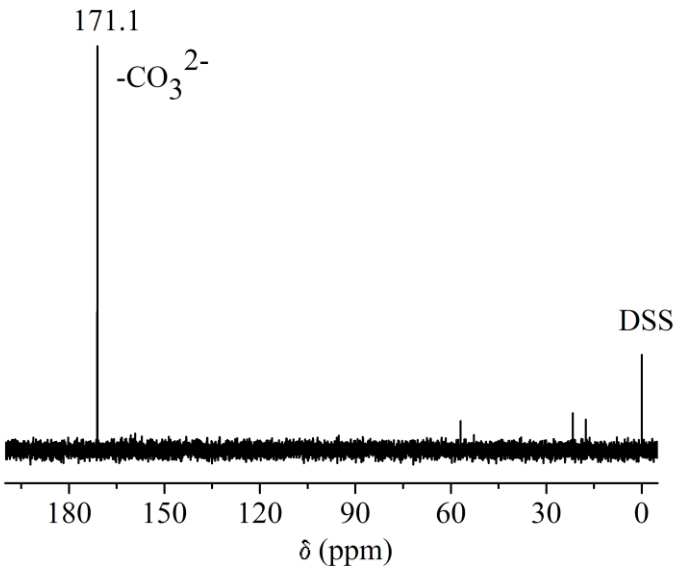

Fig. S14. Solution ^{13}C NMR spectrum of Na_2CO_3.

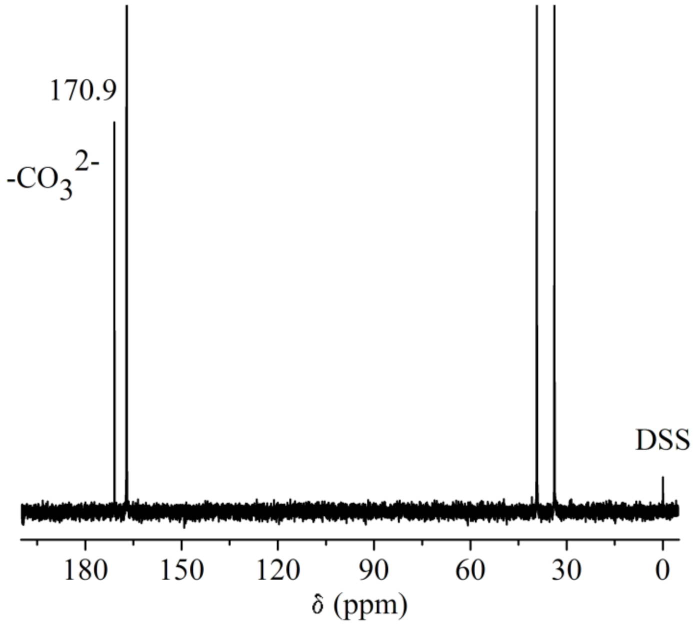

Fig. S15. Solution ^{13}C NMR spectrum of Na_2CO_3 in dimethylformamide-water.

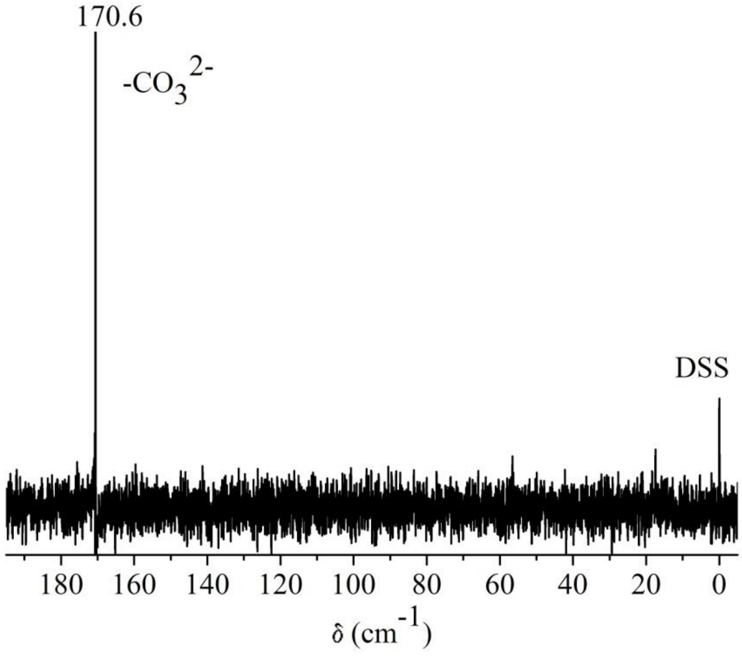

Fig. S16. Solution ^{13}C NMR spectrum of K_2CO_3.

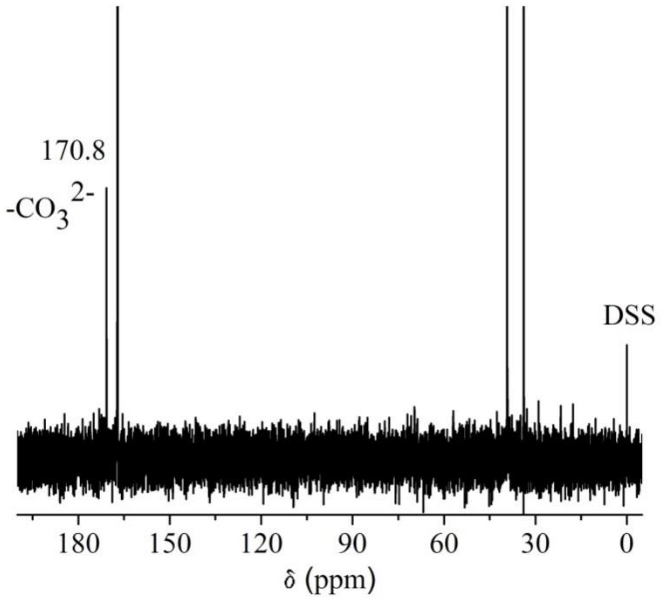

Fig. S17. Solution ^{13}C NMR spectrum of K_2CO_3 in dimethylformamide-water.

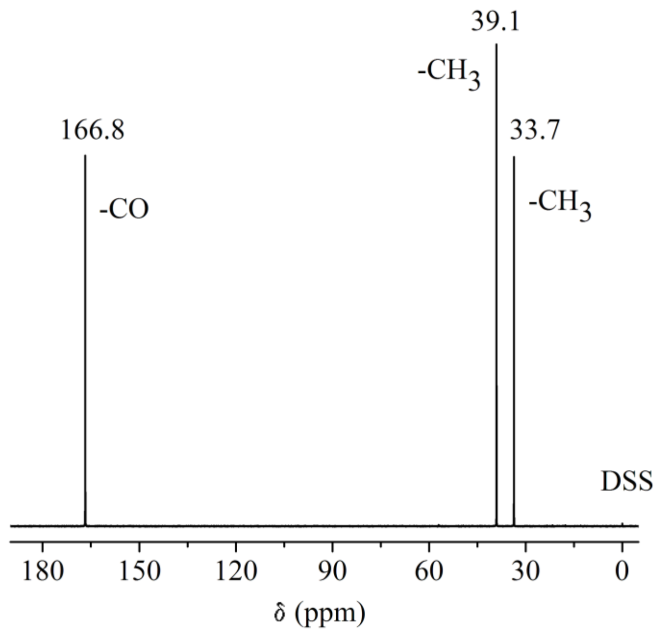

Fig. S18. Solution ^{13}C NMR spectrum of DMF.

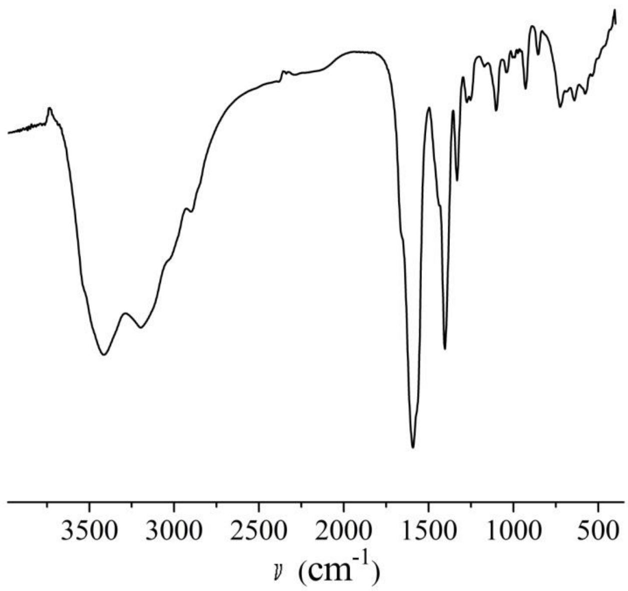

Fig. S19. IR spectrum of $(NH_4)_5[La_3(CO_3)(EDTA)_3(H_2O)_3]\cdot 12H_2O$ (**1**).

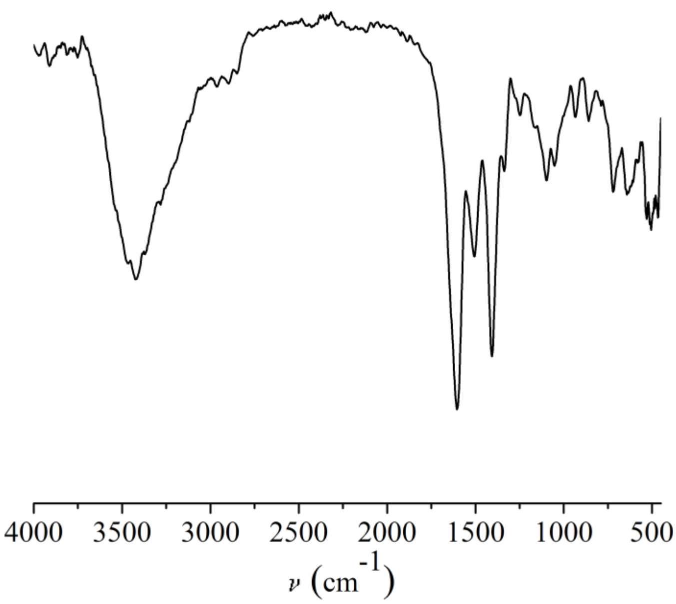

Fig. S20. IR spectrum of $Na_8[La_2(CO_3)_3(EDTA)_2]\cdot 17.5H_2O$ (**2**).

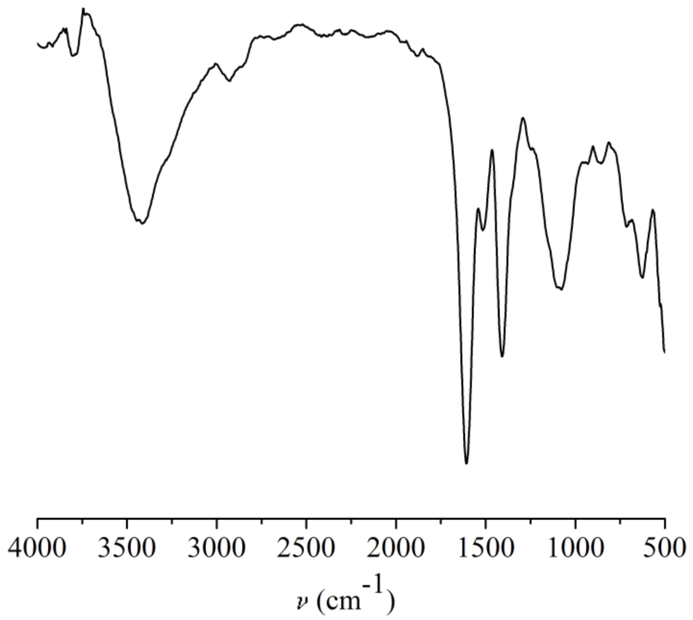

Fig. S21. IR spectrum of $Na_8[Ce_2(CO_3)_3(EDTA)_2]\cdot 17.5H_2O$ (**3**).

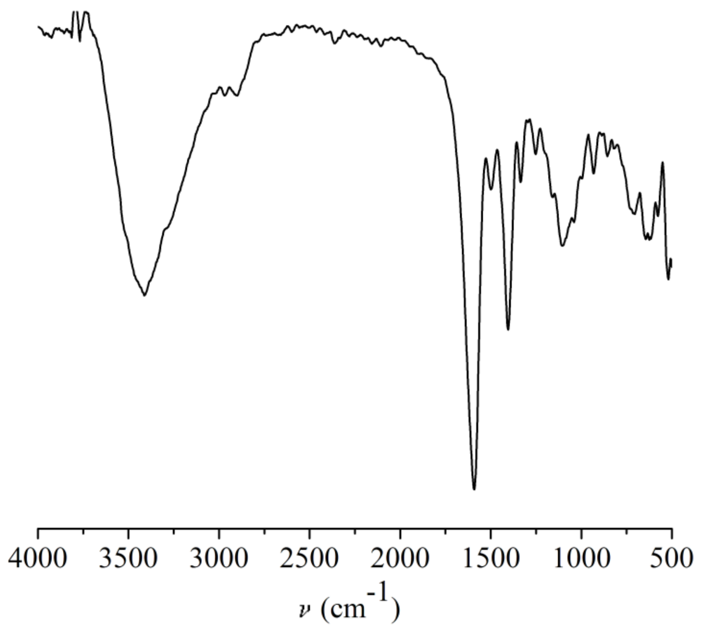

Fig. S22. IR spectrum of $K_5[La_3(CO_3)(EDTA)_3(H_2O)_3]\cdot 13.5H_2O$ (**4**).

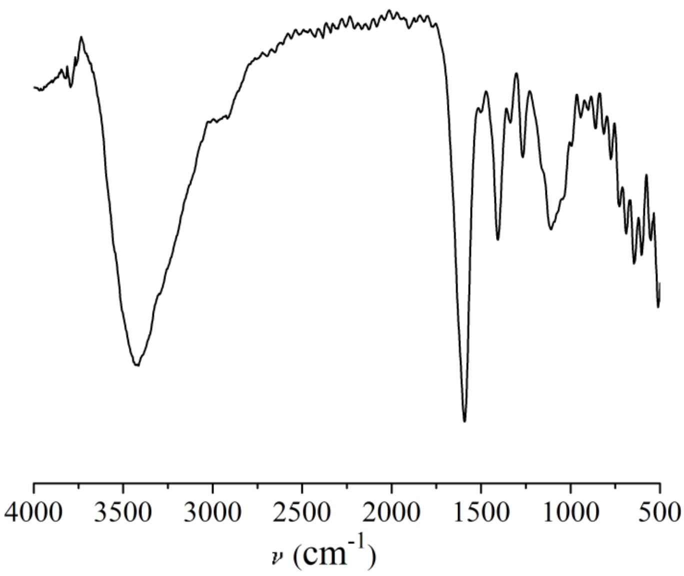

Fig. S23. IR spectrum of $K_5[Ce_3(CO_3)(EDTA)_3(H_2O)_3] \cdot 13.5H_2O$ (**5**).

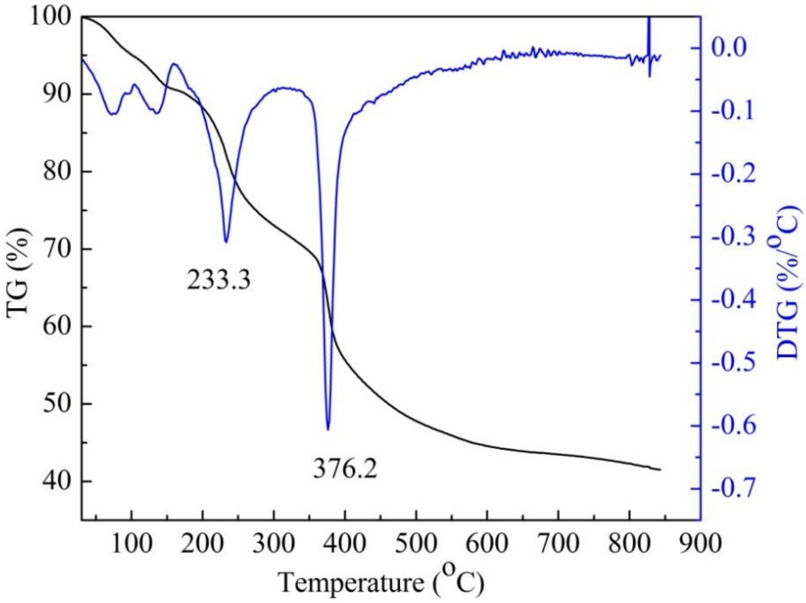

Fig. S24. TG-DTG curve of $(NH_4)_5[La_3(CO_3)(EDTA)_3(H_2O)_3] \cdot 12H_2O$ (**1**).

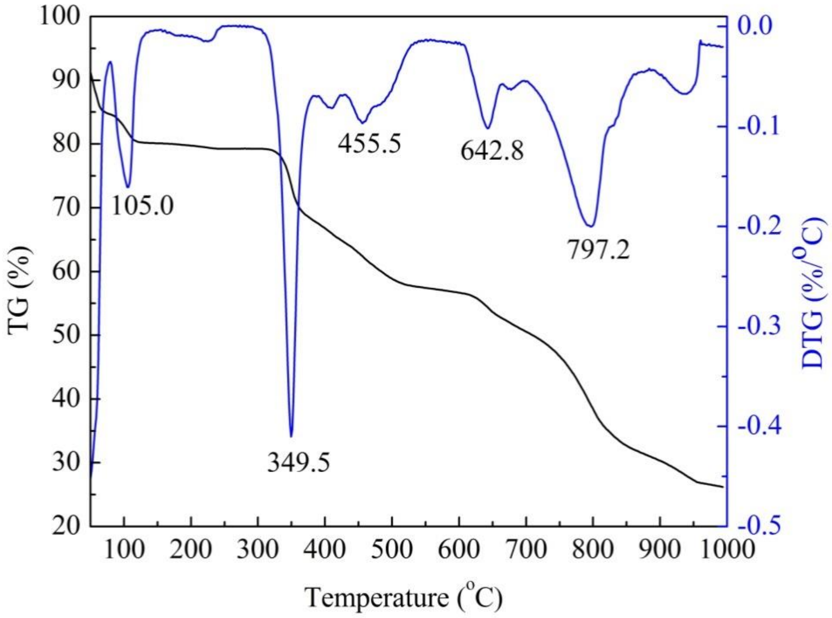

Fig. S25. TG-DTG curve of $Na_8[La_2(CO_3)_3(EDTA)_2]\cdot17.5H_2O$ (**2**).

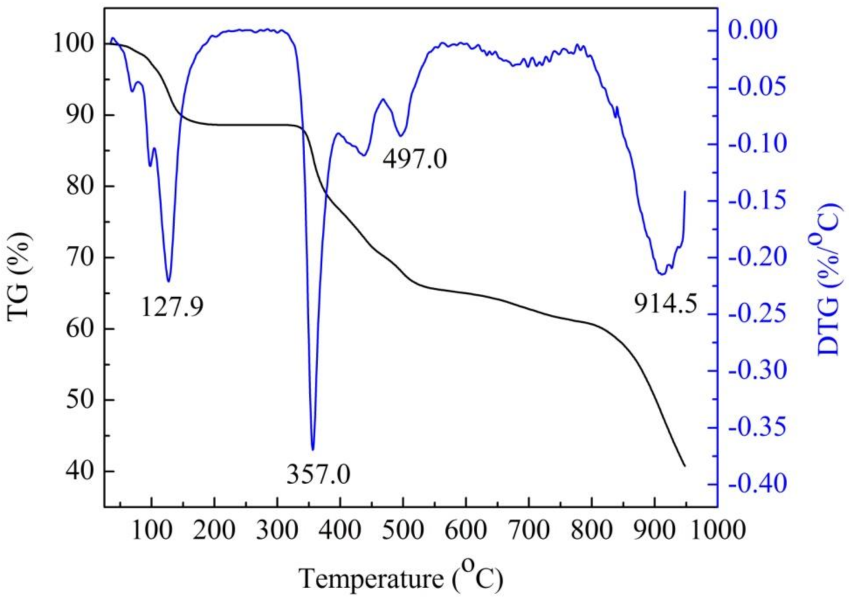

Fig. S26. TG-DTG curve of $Na_8[Ce_2(CO_3)_3(EDTA)_2]\cdot17.5H_2O$ (**3**).

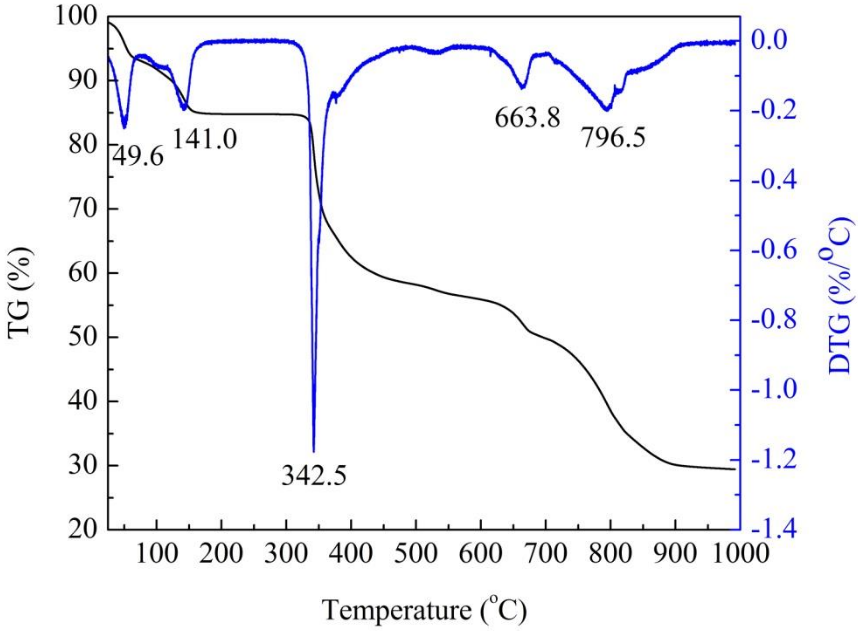

Fig. S27. TG-DTG curve of $K_5[La_3(CO_3)(EDTA)_3(H_2O)_3]\cdot13.5H_2O$ (**4**).

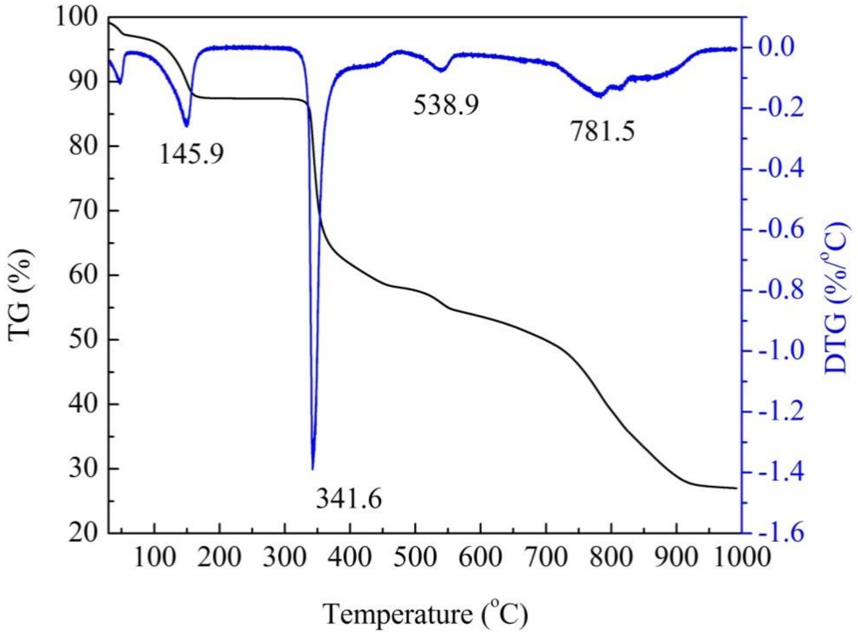

Fig. S28. TG-DTG curve of $K_5[Ce_3(CO_3)(EDTA)_3(H_2O)_3]\cdot13.5H_2O$ (**5**).

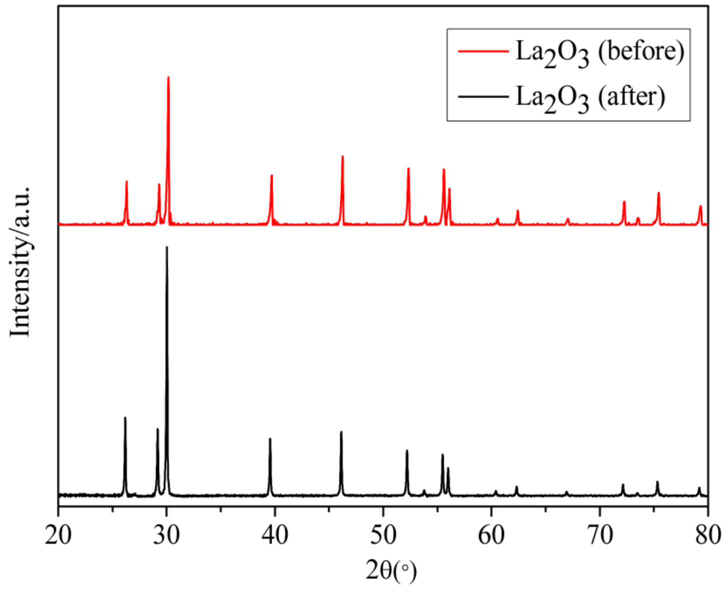

Fig. S29. The X-ray diffraction patterns of the conventional bulk La_2O_3 (before and after catalytic reactions).

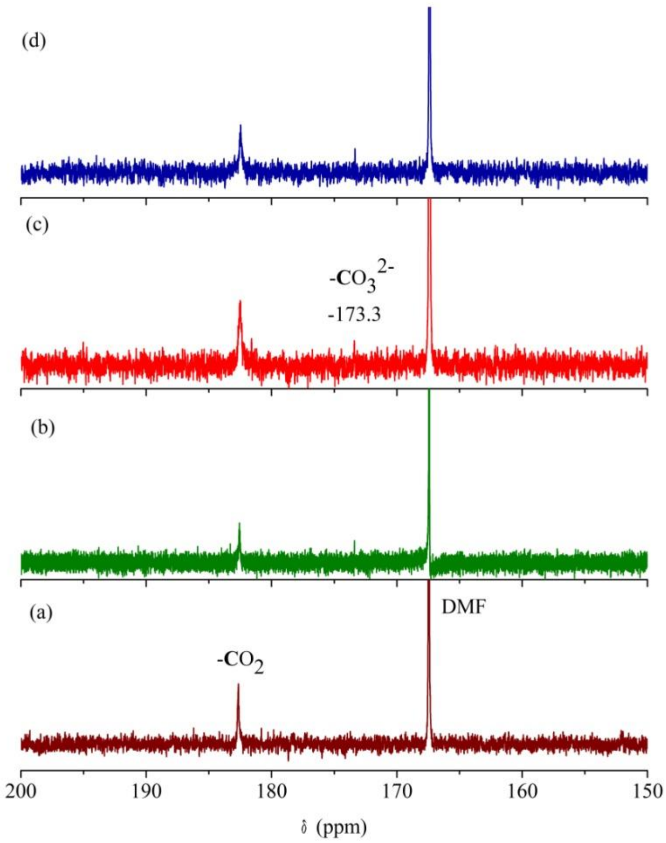

Fig. S30. Reaction of K[La(EDTA)(H_2O)] $5H_2O$ with atmospheric CO_2 monitored by ^{13}C NMR. (a) The spectrum of the sample was recorded after 12 hours. (b) The spectrum of the sample was recorded after 1 day. (c) The spectrum of the sample was recorded after 2 days. (d) The spectrum of the sample was recorded after 4 days.

Table S1. Crystal data and structure refinements for **1** ~ **5**.

Compounds	**1**	**2**	**3**	**4**	**5**
Chemical formula	$C_{31}H_{78.5}La_3N_{11}O_{42}$	$C_{23}H_{38}La_2Na_8N_4O_{42.5}$	$C_{23}H_{41.5}Ce_2N_4Na_8O_{42.5}$	$C_{31}H_{54}K_5La_3N_6O_{43.5}$	$C_{31}H_{60.5}Ce_3K_5N_6O_{43.5}$
Formula weight	1694.27	1512.31	1518.26	1819.03	1829.21
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
a/Å	13.8336(5)	12.4288(8)	12.416(2)	18.3281(1)	18.3813(7)
b/Å	17.2510(5)	14.3340(1)	14.310(2)	15.3082(6)	15.2765(6)
c/Å	27.2896(7)	16.0464(1)	16.017(3)	23.6676(1)	23.6607(9)
α/ °	94.969(2)	73.795(6)	73.825(1)	90	90
β/ °	97.482(2)	85.301(5)	85.236(1)	104.899(5)	104.641(4)
γ/ °	99.709(3)	82.669(5)	82.697(1)	90	90
Unit cell volume/$Å^3$	6325.1(3)	2719.5(3)	2707.5(8)	6417.2(5)	6428.2(4)
Temperature/K			173		
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
No. of formula units per unit cell, *Z*	4	2	2	4	4
No. of reflections measured	65391	24018	25042	35831	36008
No. of independent reflections	29117	12373	13550	14603	14908
R_{int}	0.0573	0.0611	0.1065	0.0695	0.0612
Final R_1 values ($I > 2\sigma(I)$)	0.0501	0.0531	0.0800	0.0665	0.0614
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0978	0.1086	0.1192	0.1290	0.1091
Final R_1 values (all data)	0.0725	0.0737	0.1416	0.0993	0.0831
Final $wR(F^2)$ values (all data)	0.1066	0.1217	0.1477	0.1438	0.1169
Goodness of fit on F^2	1.024	1.020	0.974	1.032	1.111

Table S2. Selected bond lengths for **1** ~ **5** and $K[La(EDTA)(H_2O)_3]\cdot5H_2O$, $\{[La(EDTA)(H_2O)]_2\}_n$, $[La(EDTA)(H_2O)_3]\cdot5H_2O$, $Na[Ce(EDTA)(H_2O)_3]\cdot5H_2O$, $N_2H_5[Ce(edta)(H_2O)_3]\cdot4H_2O$, $[La(CO_3)(OH)]_n$, $La(CO_3)(OH)$, $LaCl(CO_3)\cdot3H_2O$, $Na_{12n}[La(edta)CO_3]_{4n}\cdot8nNaCl\cdot4nH_2O$, $Na_8[(CO_3)_3Ce]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}O_2)_2\cdot12H_2O$.

Compound	Ln-O-carbonate(av)	Ln-Oβ-carboxy(av)	Ln-N(av)
1	2.557(4)	2.579(4)	2.771(4)
2	2.581(3)	2.572(4)	2.785(4)
3	2.566(6)	2.553(6)	2.764(7)
4	2.576(5)	2.573(5)	2.766(6)
5	2.562(5)	2.557(4)	2.750(5)
$K[La(EDTA)(H_2O)_3]\cdot5H_2O$[1]		2.507(6)	2.755(6)
$\{[La(EDTA)(H_2O)]_2\}_n$[2]		2.555(3)	2.848(3)
$[La(EDTA)(H_2O)_3]\cdot5H_2O$[3]		2.507(6)	2.755(6)
$Na[Ce(EDTA)(H_2O)_3]\cdot5H_2O$[4]		2.49(2)	2.71(2)
$N_2H_5[Ce(edta)(H_2O)_3]\cdot4H_2O$[5]		2.471(3)	2.730(3)
$[La(CO_3)(OH)]_n$[6]	2.648(7)		
$La(CO_3)(OH)$[7]	2.680 (5)		
$LaCl(CO_3)\cdot3H_2O$[8]	2.612(2)		
$Na_{12n}[La(edta)CO_3]_{4n}\cdot8nNaCl\cdot4nH_2O$[9]	2.630(7)		2.829(7)
$Na_8[(CO_3)_3Ce]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}O_2)_2\cdot12H_2O$[10]	2.417(2)		

Table S3. Comparisons of C–O bond lengths in complexes **1** ~ **5** and $[La(CO_3)(OH)]_n$, $La(CO_3)(OH)$, $LaCl(CO_3)\cdot 3H_2O$, $Na_{12n}[La(edta)CO_3]_{4n}\cdot 8nNaCl\cdot 4nH_2O$, $Na_8[(CO_3)_3Ce]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}O_2)_2\cdot 12H_2O$, $\{[La_2(HL)_2(H_2O)_2(CO_3)](H_2O)_7\}_\infty$, $\{[Ce_2(CO_3)(ox)_2(H_2O)_2]\cdot 3H_2O\}_n$, K_2CO_3, free CO_2.

Compound	C–O-bridging	C–O-unbridging	C–O-normal
1	1.315(6), 1.282(6), 1.275(6)		
2	1.309(6), 1.280(6), 1.273(6)	1.297(6), 1.302(6), 1.315(7) 1.272(6), 1.250(7), 1.293(6)	
3	1.293(9), 1.286(1), 1.278(1)	1.293(9), 1.304(9), 1.300(1) 1.278(1), 1.277(1), 1.294(9)	
4	1.303(8), 1.280(9), 1.272(8)		
5	1.301(7), 1.298(8), 1.265(8)		
$[La(CO_3)(OH)]_n$[6]	1.308(2),1.291(1),1.291(1)		
$La(CO_3)(OH)$[7]	1.265(5) – 1.294(3)		
$LaCl(CO_3)\cdot 3H_2O$[8]	1.277(3), 1.278(3), 1.284(4)		
$Na_{12n}[La(edta)CO_3]_{4n}\cdot 8nNaCl\cdot 4nH_2O$[9]	1.270(8),1.270(8),1.310(1)		
$Na_8[(CO_3)_3Ce]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}O_2)_2\cdot 12H_2O$[10]		1.260(3),1.294(3),1.308(3)	
$\{[La_2(HL)_2(H_2O)_2(CO_3)](H_2O)_7\}_\infty$[11]	1.270(8),1.270(8),1.284(1)		
$\{[Ce_2(CO_3)(ox)_2(H_2O)_2]\cdot 3H_2O\}_n$[12]	1.269(9),1.287(9),1.293(9)		
K_2CO_3[13]			1.250
free CO_2[14]			1.160

Table S4. The coordination number and the selected average bond length for **1** ~ **5** and other lanthanide carbonate complexes (O_c are the coordinated O atoms by carbonate).

Compound	Coordination number	Ln-O_c(av)	C–O_c(av)
1	10	2.557(4)	1.290(6)
2	10	2.581(3)	1.287(6)
3	10	2.566(6)	1.286(6)
4	10	2.576(5)	1.285(8)
5	10	2.562(5)	1.288(8)
$LaCl[CO_3]\cdot 3H_2O$[8]	10	2.612(2)	1.280(3)
$Na_{12n}[La(edta)CO_3]_{4n}\cdot 8nNaCl\cdot 4nH_2O$[9]	10	2.630(7)	1.283(6)
$[Eu_2(CO_3)(ox)_2(H_2O)_2]\cdot 4H_2O$[15]	9	2.493(5)	1.280(9)
$[C(NH_2)]_3[Pr(CO_3)_4(H_2O)]\cdot 2H_2O$[16]	9	2.502(30)	1.299(14)
$[C(NH_2)]_3[Lu(CO_3)_4]\cdot 2H_2O$[16]	8	2.311(12)	1.304(12)
$[C(NH_2)_3]_3[Er(EDTA)(CO_3)]\cdot H_2O$[17]	8	2.329(2)	1.299(5)
$[C(NH_2)]_6[Eu_2(L)_2(CO_3)_2]\cdot 8H_2O$[18]	8	2.432(4)	1.290(9)

Table S5. ^{13}**C** NMR spectral data (in ppm) of complexes **1**, **2**, **4**, K_2CO_3, K_3Hcit, K_4EDTA, K_2Hmal, K[La(EDTA)(H_2O)$_3$] 5H_2O.

Compound	CO_3^{2-}	−CH_2N	−NCH_2CO_2	−CO_2
1	173.5(2.9)	54.3(0.6), 57.3(3.6)	60.7(0.6), 64.5(4.4)	182.9(4.4)
2	171.6(1.0)	55.6(1.9)	63.0(2.9)	182.6(4.1)
4	171.0(0.4)	56.1(2.4)	63.4(3.3)	182.7(4.2)
CO_3^{2-}	170.6			
[EDTA]$^{4-}$		53.7	60.1	178.5
[La(EDTA)(H_2O)$_3$]$^-$		57.2(3.5)	64.4(4.3)	183.0(4.5)
Solid				
1		58.8. 52.4	63.6, 61.3	183.0, 180.8, 177.2
2	171.1, 169.8	59.0, 55.5, 52.9, 51.9	63.6, 62.7, 61.9, 60.6	181.3, 180.7, 179.4, 178.5
4	170.2	58.5, 57.4, 55.1, 51.7	68.2, 64.6, 62.9, 60.1	184.5, 182.1, 180.3, 177.7

Table S6. Comparisons of catalytic activity of the thermal decomposition products (T = 650 °C and 750 °C) from **1**, **2**, reported La_2O_3 and $La_2O_2CO_3$ towards the OCM reaction.

Sample	T/ ℃	Conv CH_4/%	Sel C2/%	Yield C2/%	Sample	T/ ℃	Conv CH_4/%	Sel C2/%	Yield C2/%
1(650 °C)	550	17.8	20.6	3.7	La_2O_3[19] (650 °C)	550	23.2	34.6	8.0
	600	26.4	24.6	6.5		600	26.5	42.0	11.1
	650	38.2	29.1	11.1		650	28.1	44.2	12.4
	700	41.5	32.2	13.4		700	27.2	45.7	12.4
	750	43.1	32.5	14.0		750	29.6	45.4	13.4
1(750 °C)	550	28.5	43.7	12.5	$La_2O_2CO_3$[20] (650 °C)	550	0.0	0.0	0.0
	600	29.3	46.1	13.5		600	13.1	28.4	3.7
	650	29.8	49.2	14.6		650	17.4	42.4	7.4
	700	31.6	46.0	14.5		700	23.0	45.8	10.5
	750	31.1	45.7	14.2		750	29.6	46.6	13.8
2(650 °C)	550	0	0	0					
	600	1.7	0	0					
	650	3.1	49.1	1.5					
	700	4.5	57.9	2.6					
	750	8.4	63.6	5.3					

Table S7. Catalytic Performances of **1**, **2** and $La_2O_2CO_3$–H, $La_2O_2CO_3$–P, La_2O_3, $BaCO_3$/LaOBr, $LaAlO_3$_C, $La_2O_2CO_3$, $La_2O_2SO_4$, La_2O_3 for OCM.

Sample	T/ ℃	Conv CH_4/%	Sel C2/%	Yield C2/%
1	750	43.1	32.5	14.0
2	750	8.4	63.6	5.3
$La_2O_2CO_3$–H[21]	500	30.5	48.6	14.8
$La_2O_2CO_3$–P[21]	500	26.8	29.1	7.8
La_2O_3[22]	750	24.1	28.1	6.8
$BaCO_3$/LaOBr[22]	750	29.1	46.8	13.6
$LaAlO_3$_C[23]	750	24	50	
$La_2O_2CO_3$[24]	750	30.1	46.6	
$La_2O_2SO_4$[24]	750	26.5	43.2	
La_2O_3[25]	700	30	47	

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