Facile microwave synthesis, structural diversity and herbicidal activity of six novel alkaline-earth metal complexes (AECs) based on skeletal isomerization chlorophenoxyacetic acids

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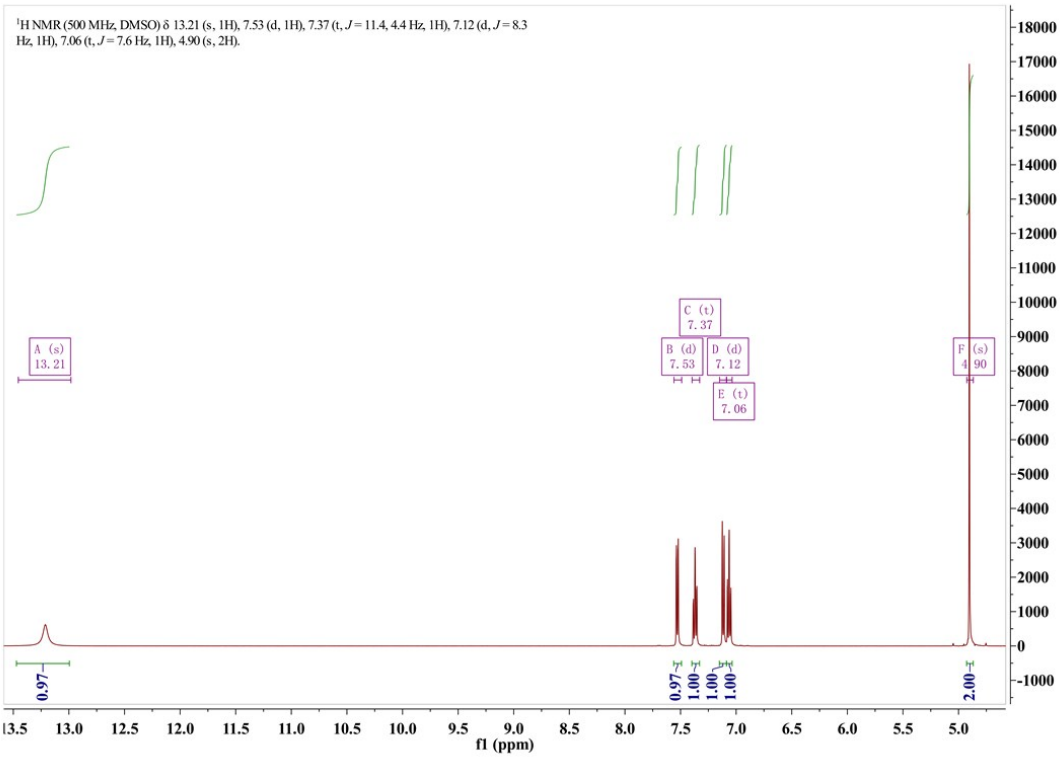

Fig. S1 ^{1}HNMR spectra of ***o*-HCPA**

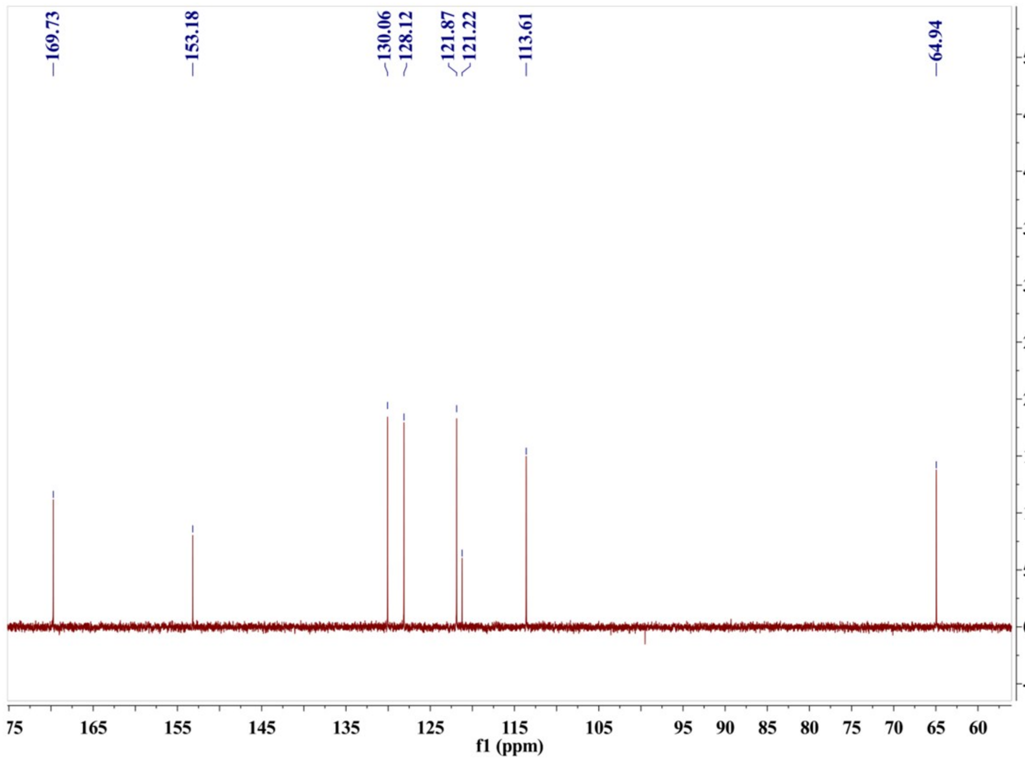

Fig. S2 ^{1}HNMR spectra of ***o*-HCPA**

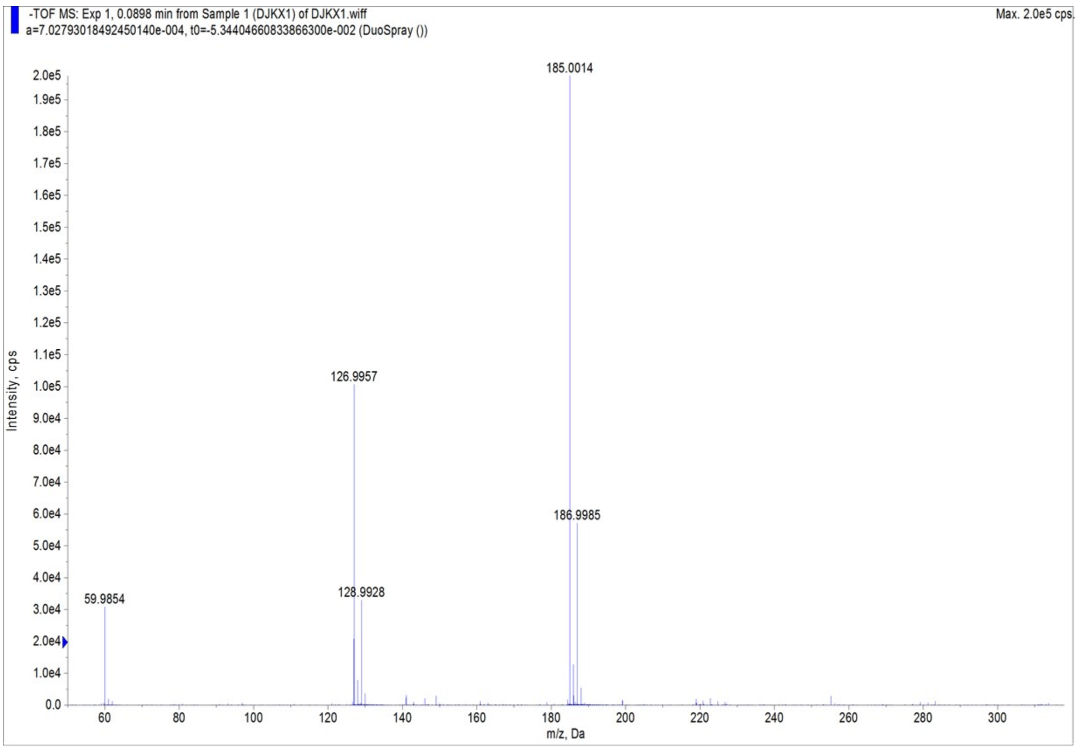

Fig. S3 HRMS spectra of compounds ***o*-HCPA**.

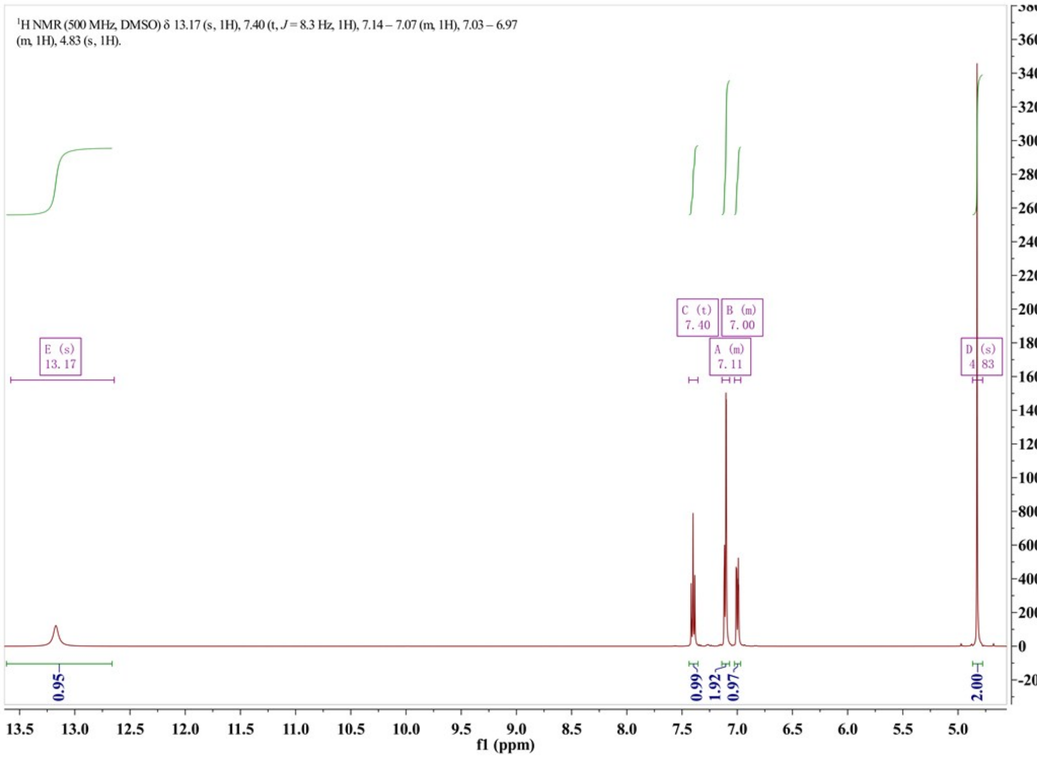

Fig. S4 [1]HNMR spectra of ***m*-HCPA**

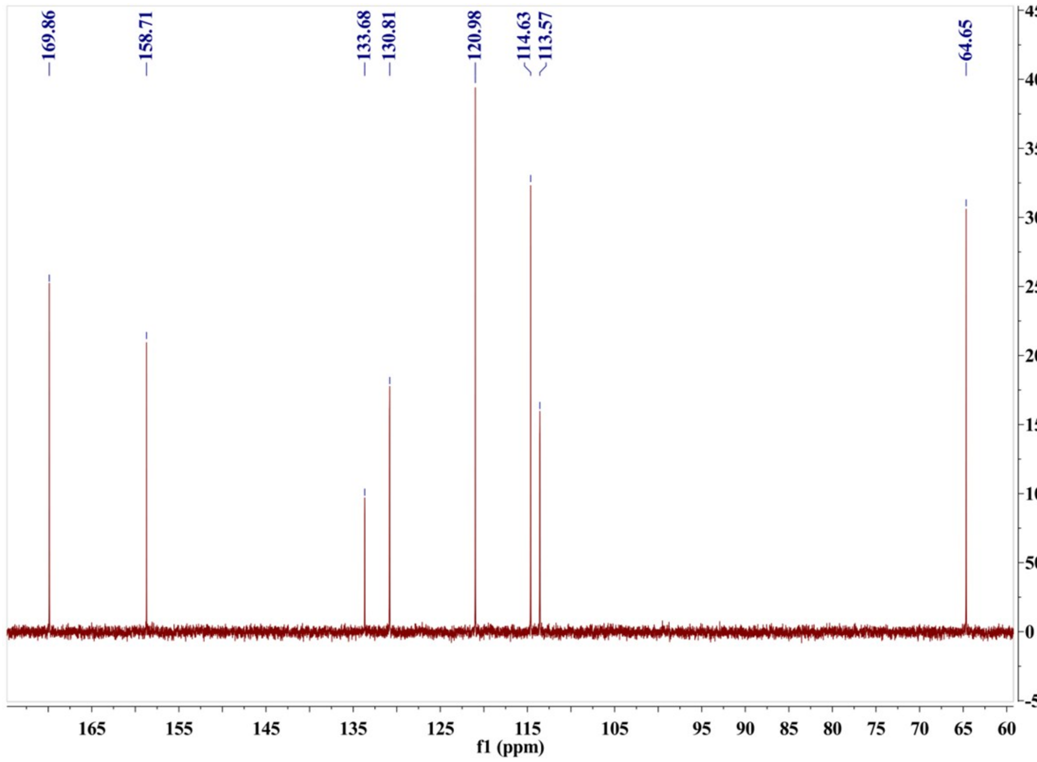

Fig. S5 [13]CNMR spectra of ***m*-HCPA**

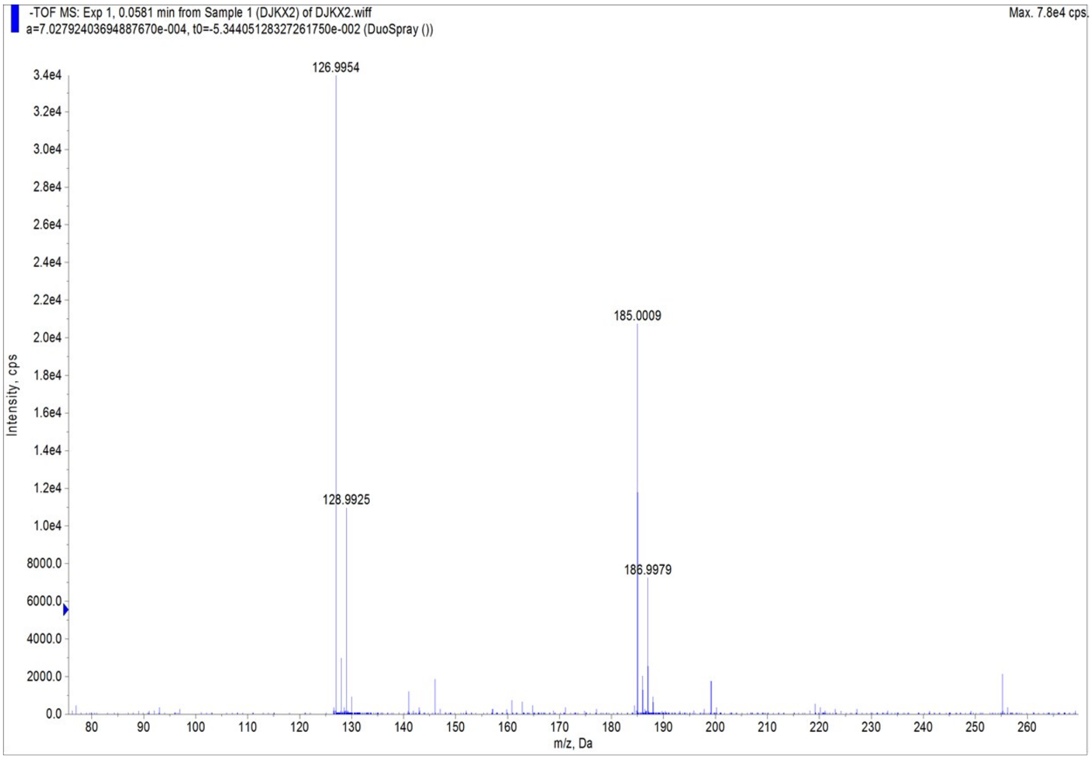

Fig. S6 HRMS spectra of compounds ***m*-HCPA**.

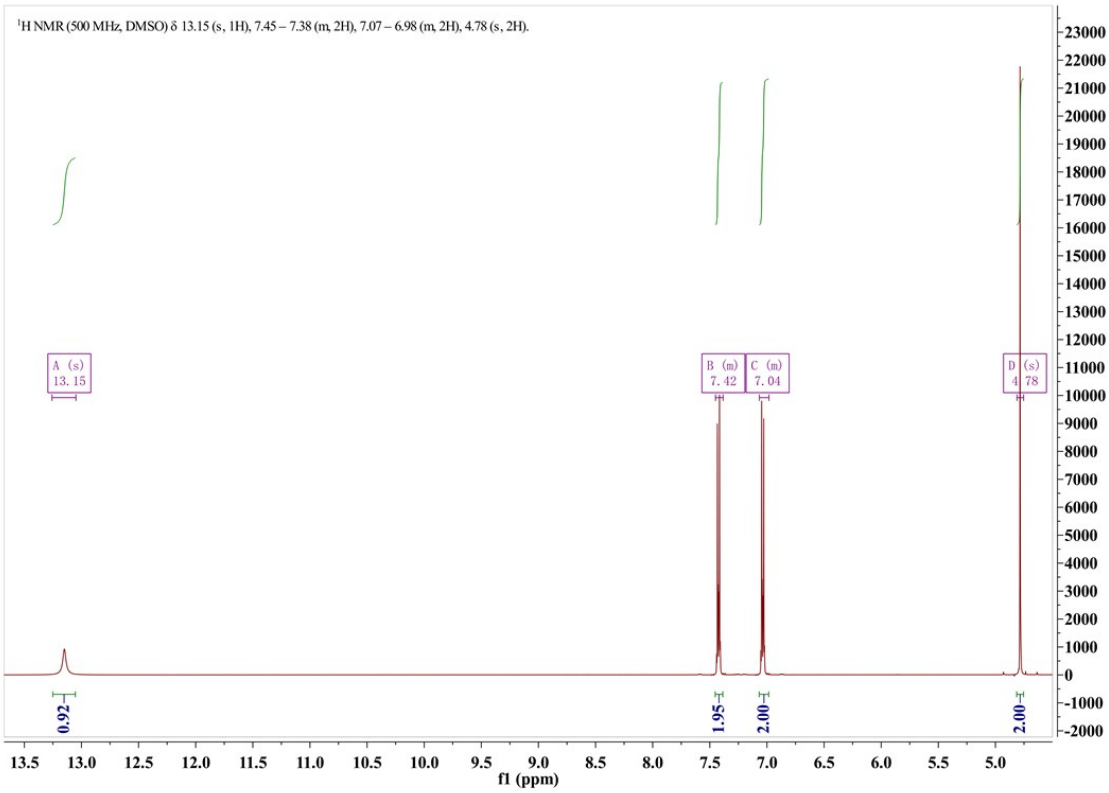

Fig. S7 [1]HNMR spectra of ***p*-HCPA**

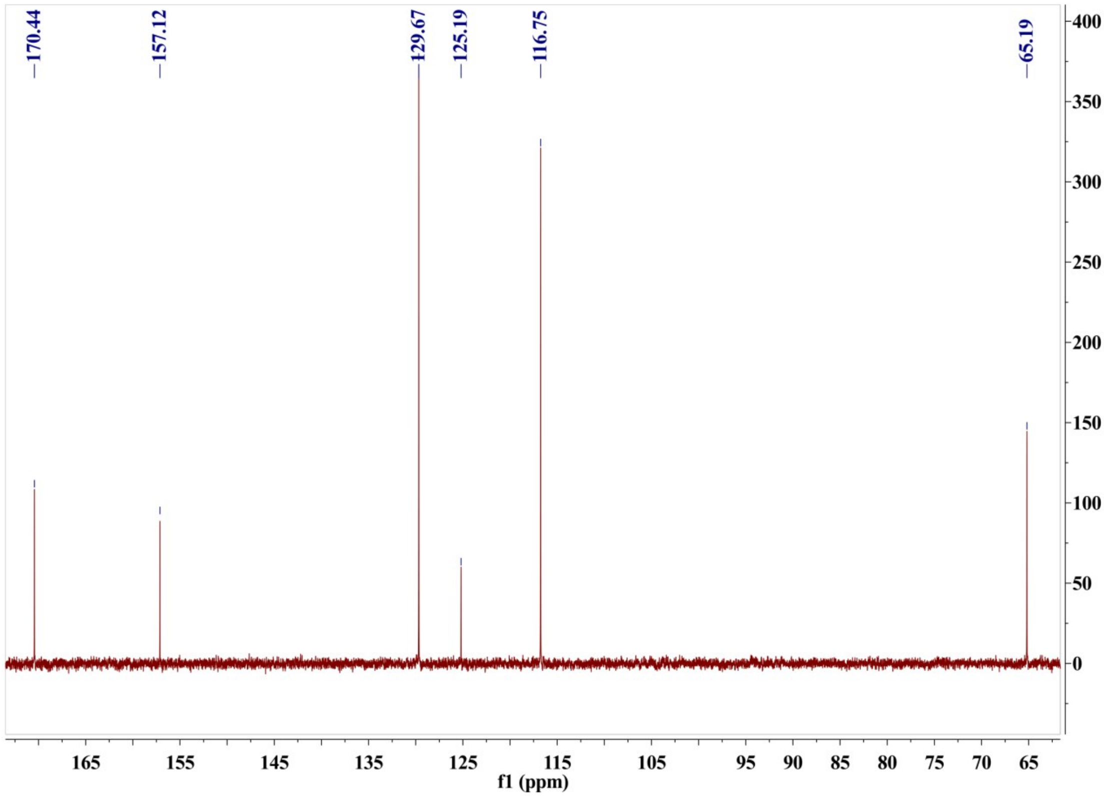

Fig. S8 ^{13}CNMR spectra of ***p*-HCPA**

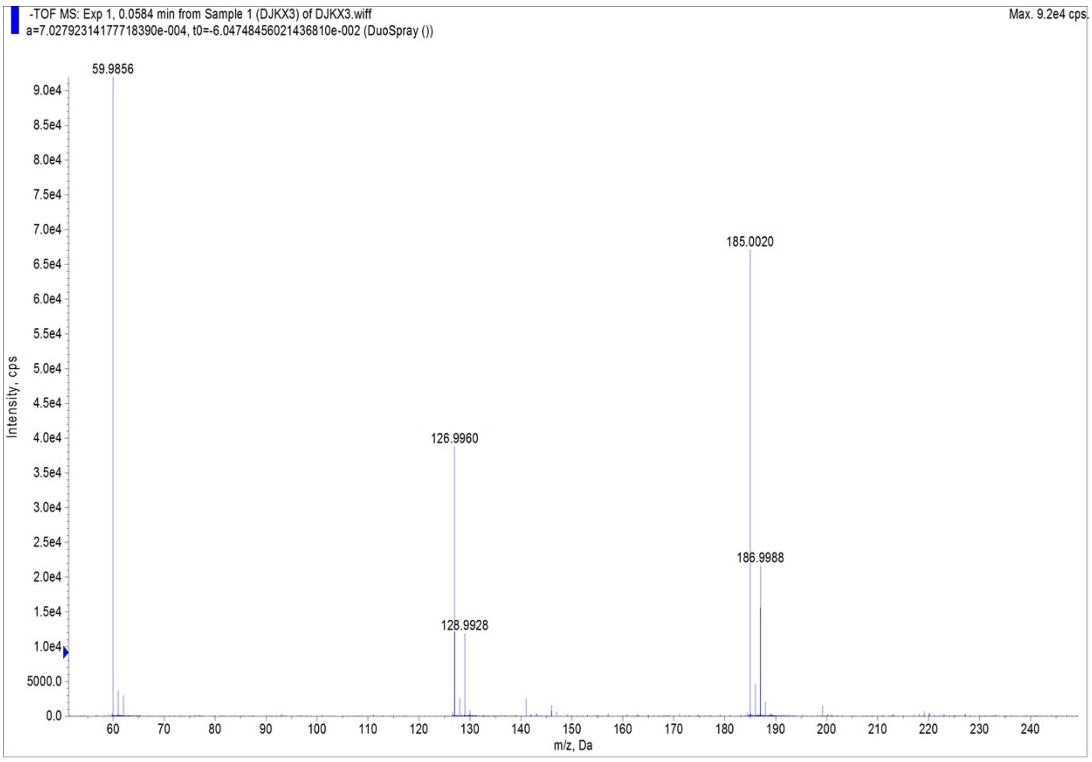

Fig. S9 HRMS spectra of compounds ***p*-HCPA**.

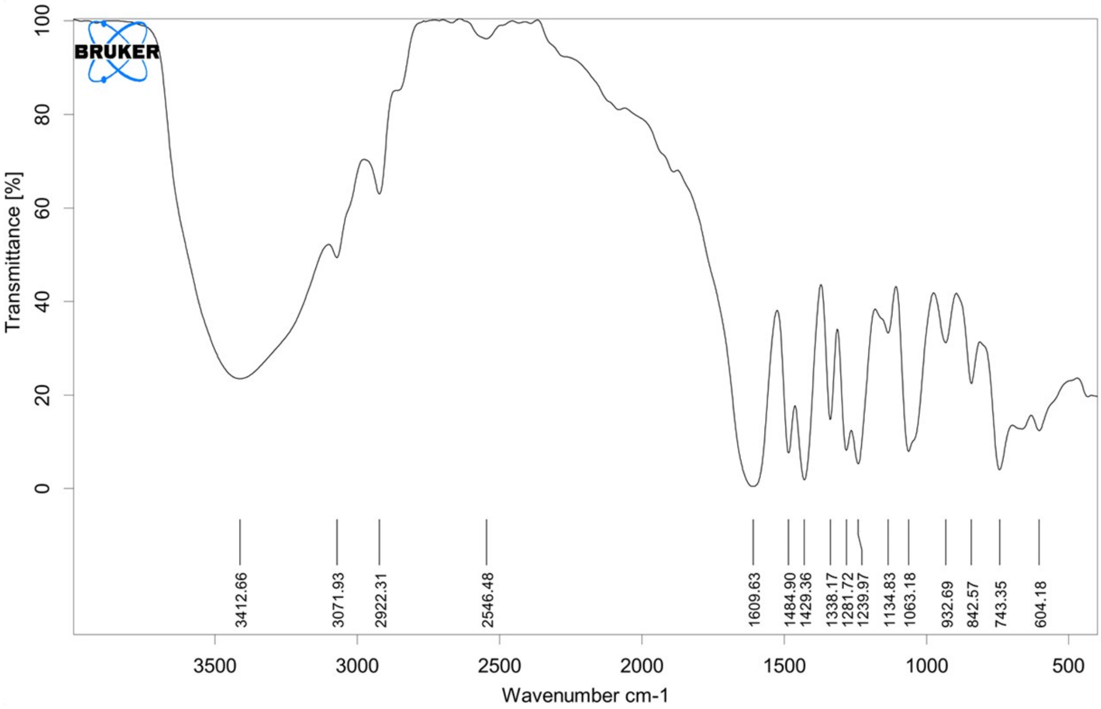

Fig. S10 IR spectra of complex **1**.

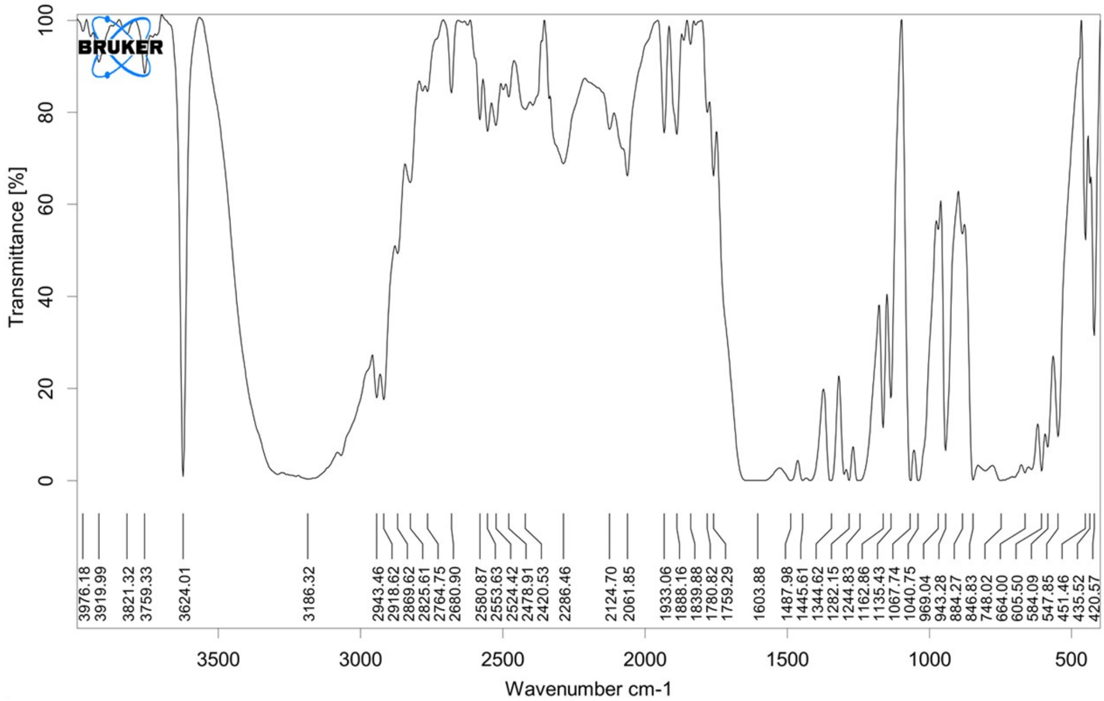

Fig. S11 IR spectra of complex **2**.

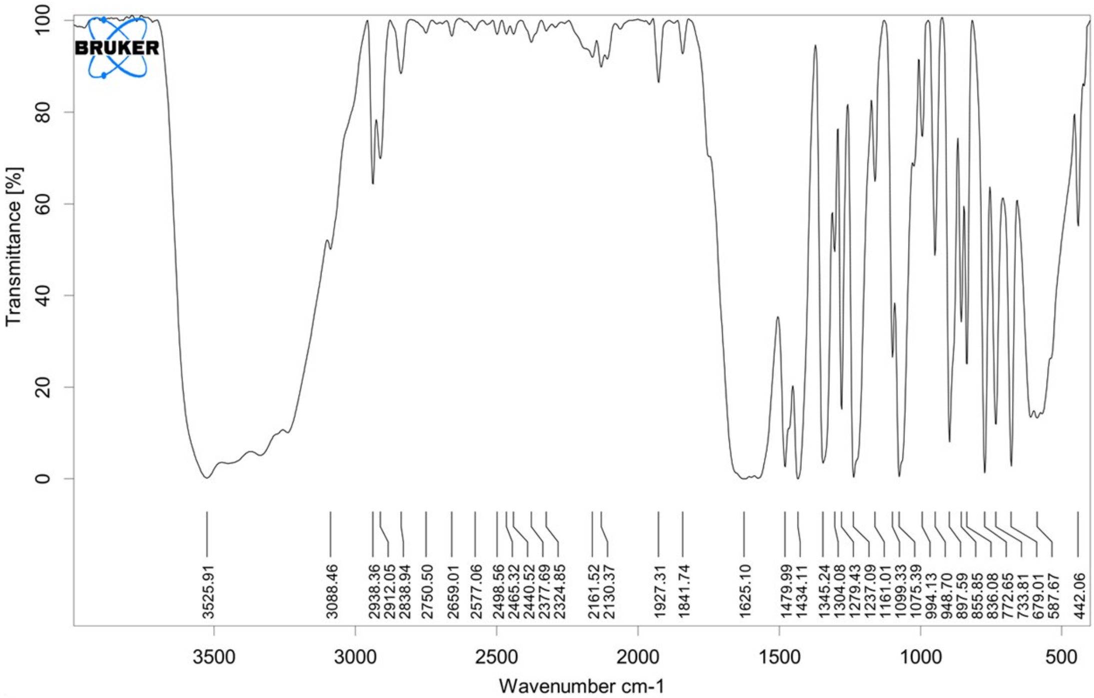

Fig. S12 IR spectra of complex **3**.

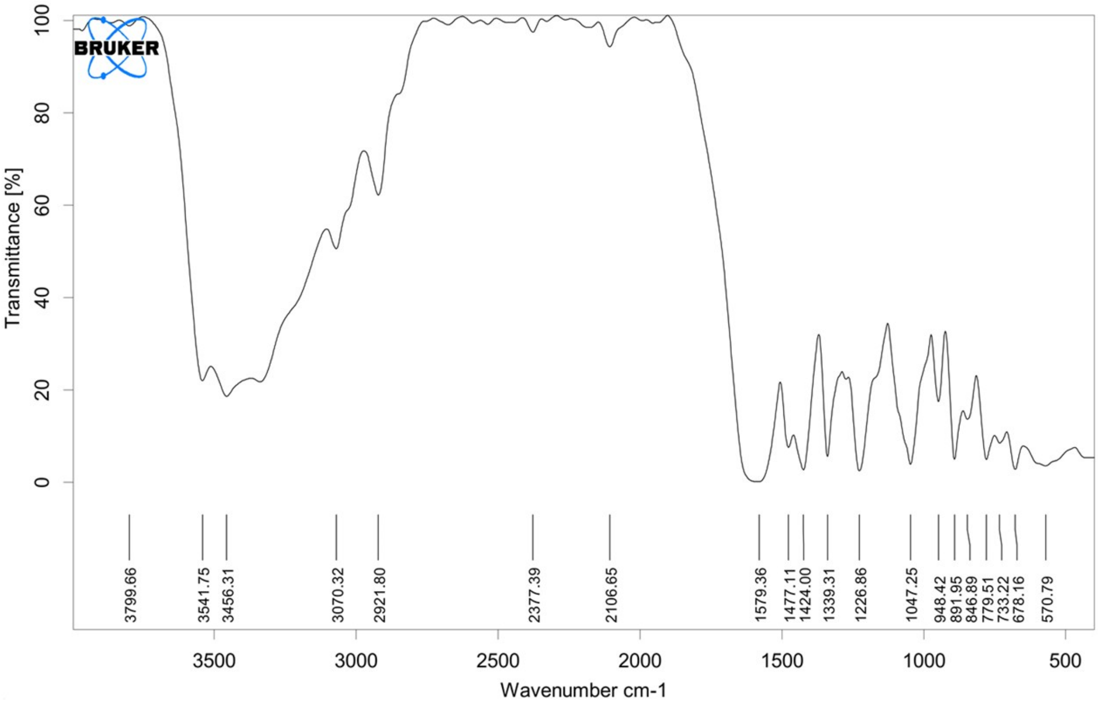

Fig. S13 IR spectra of complex **4**.

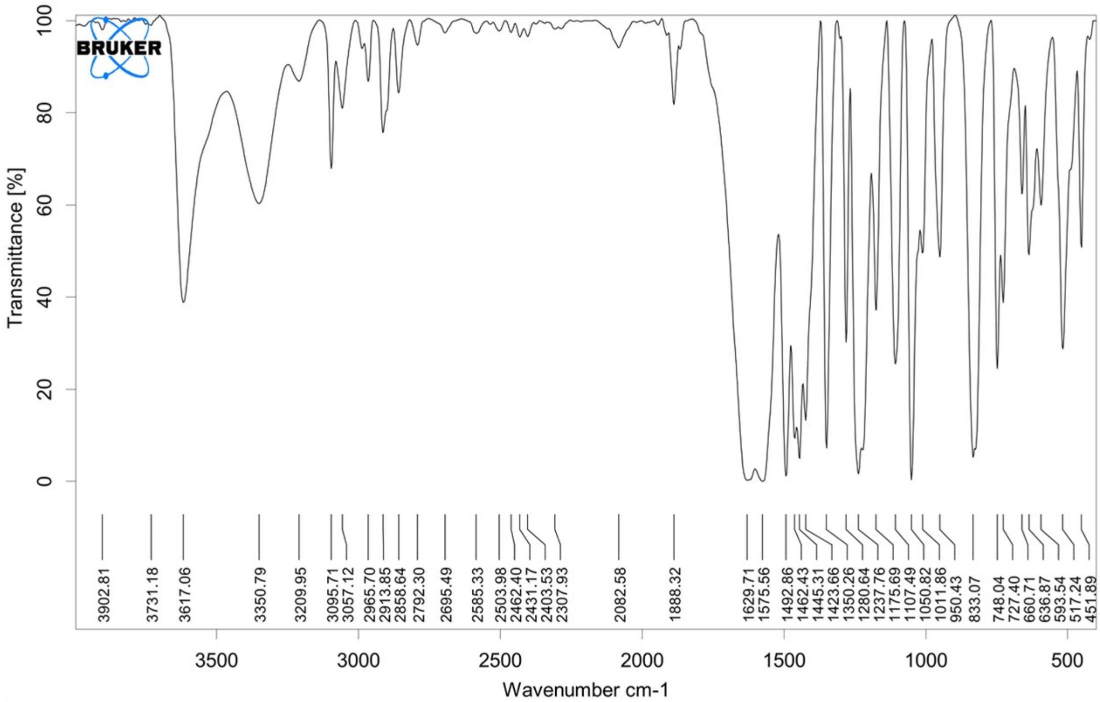

Fig. S14 IR spectra of complex **5**.

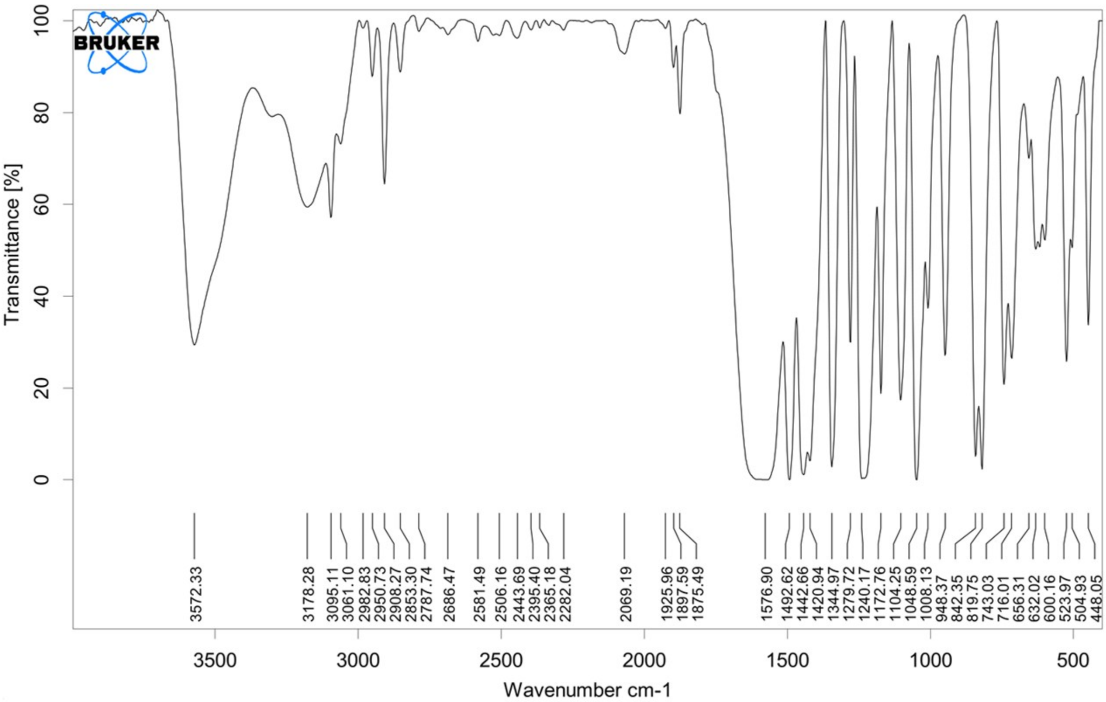

Fig. S15 IR spectra of complex **6**.

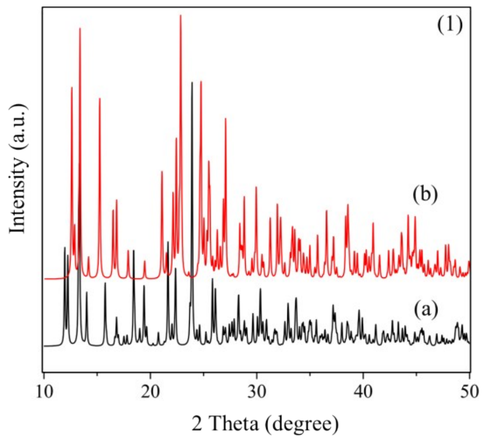

Fig. S16 The PXRD graph for complex **1** ((a) modulated by Mercury; (b) observed.)

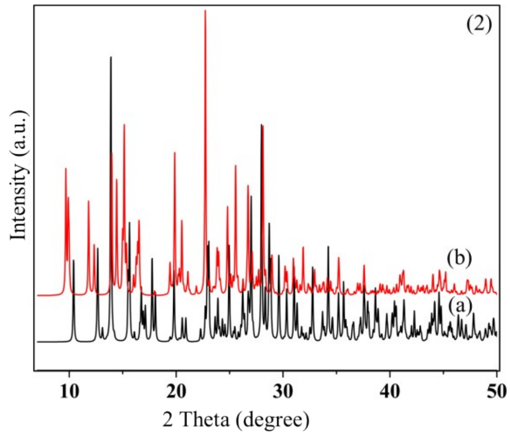

Fig. S17 The PXRD graph for complex **2** ((a) modulated by Mercury; (b) observed.)

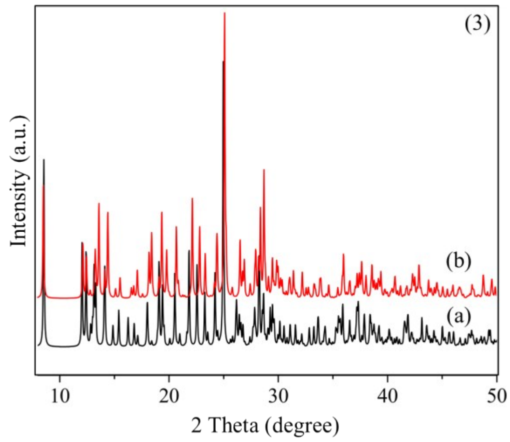

Fig. S18 The PXRD graph for complex **3** ((a) modulated by Mercury; (b) observed.)

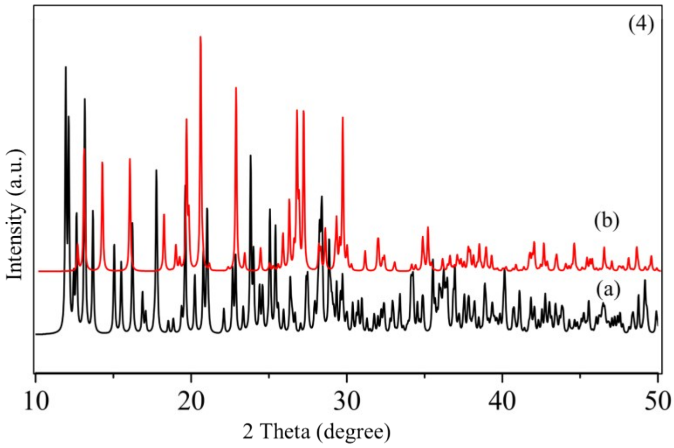

Fig. S19 The PXRD graph for complex **4** ((a) modulated by Mercury; (b) observed.)

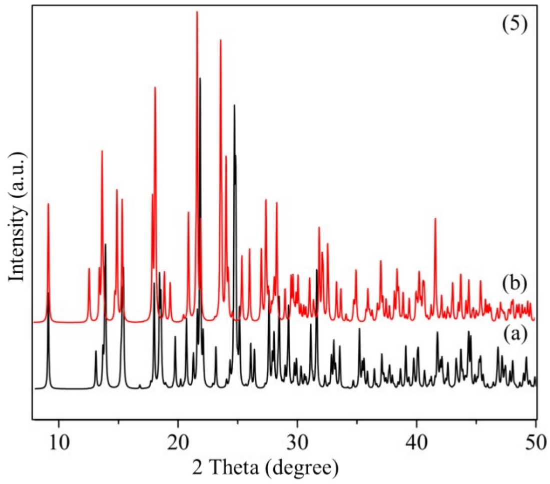

Fig. S20 The PXRD graph for complex **5** ((a) modulated by Mercury; (b) observed.)

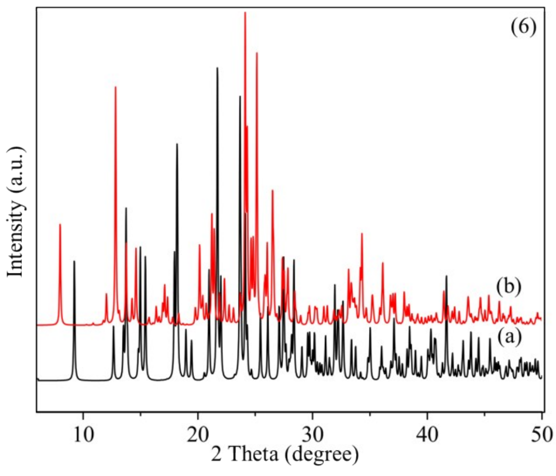

Fig. S21 The PXRD graph for complex **6** ((a) modulated by Mercury; (b) observed.)

Table S1. Selected bond lengths (Å) and angles (°) for **1-6**.

1

Sr(1)-O(4W)	2.570(6)	Sr(1)-O(1)	2.685(5)
Sr(1)-O(2)A	2.572(5)	Sr(1)-O(2W)C	2.726(5)
Sr(1)-O(1W)	2.590(6)	Sr(1)-O(2W)	2.773(5)
Sr(1)-O(1)B	2.637(5)	Sr(1)-O(3W)B	2.844(5)
Sr(1)-O(3W)	2.673(5)		
O(4W)-Sr(1)-O(2)A	72.42(18)	O(3W)-Sr(1)-O(1)	61.89(16)
O(4W)-Sr(1)-O(1W)	88.4(2)	O(4W)-Sr(1)-O(2W)	139.10(17)
O(2)B-Sr(1)-O(1W)	69.8(2)	O(2)A-Sr(1)-O(2W)	66.70(16)
O(4W)-Sr(1)-O(3W)	137.50(17)	O(1W)-Sr(1)-O(2W)	78.79(19)
O(2)A-Sr(1)-O(3W)	134.48(18)	O(3W)-Sr(1)-O(2W)	77.21(16)
O(1W)-Sr(1)-O(3W)	77.0(2)	O(1)-Sr(1)-O(2W)	136.78(15)
O(1)B-Sr(1)-O(3W)	61.61(16)	O(2W)C-Sr(1)-O(2W)	82.98(15)
O(4W)-Sr(1)-O(1)	76.31(18)	O(3W)-Sr(1)-O(3W)B	93.11(14)
O(2)A-Sr(1)-O(1)	135.78(16)	O(2W)-Sr(1)-O(3W)B	141.68(15)
O(1W)-Sr(1)-O(1)	79.0(2)	O(1)B-Sr(1)-O(1)	88.99(14)

2

Ba(1)-O(3)A	2.724(2)	Ba(1)-O(1W)	2.894(2)
Ba(1)-O(5)B	2.782(3)	Ba(1)-O(3)	2.904(2)
Ba(1)-O(6)C	2.828(2)	Ba(1)-O(2)	2.938(2)
Ba(1)-O(1W)C	2.848(2)	Ba(1)-O(4)	3.054(2)
Ba(1)-O(6)	2.872(2)		
O(3)A-Ba(1)-O(5)B	88.69(7)	O(5)B-Ba(1)-O(2)	85.43(7)
O(5)B-Ba(1)-O(1W)C	74.65(7)	O(6)-Ba(1)-O(2)	126.00(6)
O(5)B-Ba(1)-O(6)	72.62(6)	O(1W)-Ba(1)-O(2)	120.97(7)
O(6)C-Ba(1)-O(6)	123.43(6)	O(3)-Ba(1)-O(2)	44.65(6)
O(5)B-Ba(1)-O(1W)	141.12(7)	O(5)B-Ba(1)-O(4)	69.06(7)
O(1W)C-Ba(1)-O(1W)	135.67(4)	O(6)-Ba(1)-O(4)	52.12(6)
O(6)-Ba(1)-O(1W)	68.73(6)	O(1W)-Ba(1)-O(4)	89.98(7)
O(3)A-Ba(1)-O(3)	132.32(5)	O(3)-Ba(1)-O(4)	109.20(6)
O(5)B-Ba(1)-O(3)	123.22(7)	O(2)-Ba(1)-O(4)	74.08(7)
O(6)-Ba(1)-O(3)	152.62(6)	O(1W)-Ba(1)-O(3)	94.09(7)

3

Sr(1)-O(1W)	2.548(5)	Sr(1)-O(6)B	2.588(5)
Sr(1)-O(4W)	2.553(5)	Sr(1)-O(2W)	2.646(5)
Sr(1)-O(6)	2.562(5)	Sr(1)-O(3W)	2.660(5)
Sr(1)-O(5)A	2.585(4)	Sr(1)-O(3W)C	2.717(5)
O(1W)-Sr(1)-O(4W)	138.99(19)	O(5)A-Sr(1)-O(2W)	67.07(15)
O(1W)-Sr(1)-O(6)	74.60(16)	O(1W)-Sr(1)-O(3W)	75.88(17)
O(4W)-Sr(1)-O(6)	74.40(19)	O(4W)-Sr(1)-O(3W)	143.80(18)
O(1W)-Sr(1)-O(5)A	73.08(15)	O(6)-Sr(1)-O(3W)	119.02(16)
O(4W)-Sr(1)-O(5)A	123.9(2)	O(5)A-Sr(1)-O(3W)	66.50(15)
O(6)-Sr(1)-O(5)A	144.32(15)	O(6)B-Sr(1)-O(3W)	76.50(15)

O(6)-Sr(1)-O(6)B	73.02(17)	O(2W)-Sr(1)-O(3W)	132.65(16)
O(1W)-Sr(1)-O(2W)	82.47(17)	O(3W)-Sr(1)-O(3W)C	86.36(15)
O(4W)-Sr(1)-O(2W)	73.7(2)	O(6)-Sr(1)-O(2W)	94.13(15)

4

Ba(1)-O(5)A	2.700(4)	Ba(1)-O(1W)	2.840(4)
Ba(1)-O(3W)	2.779(6)	Ba(1)-O(1W)B	2.853(4)
Ba(1)-O(4)B	2.808(4)	Ba(1)-O(2W)A	2.862(4)
Ba(1)-O(4)	2.823(4)	Ba(1)-O(2W)	2.871(4)
Ba(1)-O(4W)	2.826(5)		
O(5)A-Ba(1)-O(3W)	72.70(18)	O(4)B-Ba(1)-O(1W)B	59.25(11)
O(5)A-Ba(1)-O(4)	134.41(12)	O(1W)-Ba(1)-O(1W)B	90.61(11)
O(3W)-Ba(1)-O(4)	129.9(2)	O(4)-Ba(1)-O(2W)A	77.38(11)
O(4)B-Ba(1)-O(4)	89.36(10)	O(5)A-Ba(1)-O(2W)	69.37(13)
O(5)A-Ba(1)-O(4W)	73.14(16)	O(3W)-Ba(1)-O(2W)	141.67(15)
O(3W)-Ba(1)-O(4W)	97.4(2)	O(4)-Ba(1)-O(2W)	76.92(11)
O(4)-Ba(1)-O(4W)	127.85(16)	O(4W)-Ba(1)-O(2W)	76.85(15)
O(5)A-Ba(1)-O(1W)	133.38(15)	O(1W)-Ba(1)-O(2W)	133.91(10)
O(3W)-Ba(1)-O(1W)	72.24(18)	O(4)-Ba(1)-O(1W)	59.25(11)

5

Sr(1)-O(2)A	2.473(3)	Sr(1)-O(1W)	2.571(4)
Sr(1)-O(5)B	2.512(3)	Sr(1)-O(4)C	2.591(3)
Sr(1)-O(1)	2.513(3)	Sr(1)-O(5)C	2.821(3)
Sr(1)-O(4)	2.570(3)	Sr(1)-O(3)	2.948(3)
O(2)A-Sr(1)-O(5)B	96.84(11)	O(4)-Sr(1)-O(4)C	69.97(11)
O(2)A-Sr(1)-O(1)	137.87(11)	O(1W)-Sr(1)-O(4)C	77.79(12)
O(5)B-Sr(1)-O(1)	85.08(11)	O(5)B-Sr(1)-O(5)C	75.14(10)
O(2)A-Sr(1)-O(4)	79.66(10)	O(4)-Sr(1)-O(5)C	116.03(9)
O(5)B-Sr(1)-O(4)	163.48(11)	O(1W)-Sr(1)-O(5)C	76.16(11)
O(1)-Sr(1)-O(4)	86.85(11)	O(2)A-Sr(1)-O(3)	80.19(9)
O(2)A-Sr(1)-O(1W)	72.77(11)	O(5)B-Sr(1)-O(3)	91.91(10)
O(5)B-Sr(1)-O(1W)	86.33(13)	O(1)-Sr(1)-O(3)	57.69(10)
O(1)-Sr(1)-O(1W)	148.99(12)	O(4)-Sr(1)-O(3)	71.61(10)
O(4)-Sr(1)-O(1W)	107.70(13)	O(1W)-Sr(1)-O(3)	152.46(10)
O(5)A-Sr(1)-O(4)C	122.90(9)		

6

Ba(1)-O(4)	2.666(3)	Ba(1)-O(1)C	2.813(4)
Ba(1)-O(5)A	2.705(4)	Ba(1)-O(1)	2.742(5)
Ba(1)-O(2)B	2.707(5)	Ba(1)-O(2)C	2.947(5)
Ba(1)-O(1W)	2.708(11)	Ba(1)-O(3)	3.193(3)
O(4)-Ba(1)-O(5)A	129.26(12)	O(1)-Ba(1)-O(1)C	111.79(10)
O(4)-Ba(1)-O(2)B	78.8(2)	O(1W)-Ba(1)-O(1W')	28.1(4)
O(5)A-Ba(1)-O(2)B	109.47(16)	O(2)B-Ba(1)-O(2)C	112.75(12)
O(4)-Ba(1)-O(1W)	152.3(3)	O(1W)-Ba(1)-O(2)C	83.3(3)
O(5)A-Ba(1)-O(1W)	78.4(3)	O(1)-Ba(1)-O(2)C	67.17(12)
O(2)B-Ba(1)-O(1W)	91.0(3)	O(4)-Ba(1)-O(3)	52.66(9)

O(4)-Ba(1)-O(1)	78.46(18)	O(5)A-Ba(1)-O(3)	76.68(10)
O(5)A-Ba(1)-O(1)	81.14(14)	O(2)B-Ba(1)-O(3)	92.84(15)
O(2)B-Ba(1)-O(1)	156.59(14)	O(1W)-Ba(1)-O(3)	154.7(3)
O(1W)-Ba(1)-O(1)	111.8(3)	O(1)-Ba(1)-O(3)	68.77(12)
O(4)-Ba(1)-O(1)C	80.50(14)	O(1W)-Ba(1)-O(1)C	71.8(3)
O(2)B-Ba(1)-O(1)C	69.59(13)		

Symmetry transformations used to generate equivalent atoms in **1**: A x-1, y , z; B -x+1, -y+1, -z; C –x, -y+1, -z; in **2**: A –x, y-1/2, -z+1/2; B –x, -y+1, -z; C –x, y+1/2, -z+1/2; in **3**: A x-1, y, z ; B -x+1, -y+1, -z+1; C –x, -y+1, -z+1; in **4**: A -x+1, -y+1, -z ; B -x+2, -y+1, -z; in **5**: A x-1, y, z; B x, y-1, z ;C -x+2, -y+1, -z ; in **6**: A x+1, y, z; B x, y-1, z ;C –x, y-1/2, -z+1.

Table S2. Bond lengths (Å) and angles (°) of hydrogen-bond for **1-6**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠DHA
		1		
O1W-	0.96	2.16	3.054(10)	155
O2W-	0.97	1.97	2.892(7)	158
O2W-	0.97	1.95	2.867(7)	157
O3W-	0.97	1.87	2.793(8)	158
O3W-	0.97	1.95	2.901(8)	166
O4W-	0.96	2.08	2.947(8)	150
O4W-	0.96	1.99	2.877(8)	153
		2		
O1W-	0.97	1.88	2.751(3)	148
O1W-	0.97	1.89	2.817(3)	160
O2W-	0.85	2.79	3.0474(3)	138
O2W-	0.93	2.15	2.713(3)	118
		3		
O1W-	0.96	1.85	2.753(7)	155
O1W-	0.96	2.53	2.991(7)	109
O1W-	0.96	2.27	3.205(7)	166
O2W-	0.96	2.53	3.152(7)	122
O2W-	0.96	2.04	2.938(7)	155
O3W-	0.97	1.96	2.928(6)	172
O3W-	0.97	2.02	2.776(6)	134
O4W-	0.96	2.02	2.966(9)	168
O4W-HWB···O3	0.96	2.19	2.823(8)	123
		4		
O1W-	0.85	2.04	2.820(6)	152
O1W-	0.85	2.10	2.841(6)	145
O2W-	0.85	1.97	2.780(6)	160
O2W-	0.85	2.03	2.842(6)	160
O3W-	0.96	2.10	2.984(8)	152
O3W-	0.96	2.24	2.92(2)	127
O3W-	0.96	1.73	2.587(17)	146
O4W-	0.85	2.30	2.843(7)	122

		5		
O1W-	0.96	1.98	2.861(5)	151
O1W-	0.96	2.34	3.192(6)	147
		6		
Cl15-H15B···O5	0.97	2.46	3.347(8)	152

Table S3. Themal decomposition data of the complexes **1-6**.

Complex	Stage	Weight loss process	Temperature Range/(°C)	Weight loss rate/%		Final solid products	
				Found	calcd	Found	calcd
1	I	$(H_2O)_4$	25.00~175.73	13.57	13.56	SrO	
	II	collapse	175.73~379.10	66.93	66.92	19.50	19.52
	III	collapse	379.10~648.07				
2	I	(H_2O) H_2O	25.00~177.25	6.59	6.61	BaO	
	II	collapse	177.25~359.14	65.24	65.23	28.17	28.16
	III	collapse	359.14~668.67				
3	I	$(H_2O)_4$	25.00~181.35	13.55	13.56	SrO	
	II	collapse	181.35~375.82	66.94	66.92	19.51	19.52
	III	collapse	375.80~657.44				
4	I	$[(H_2O)_4]_2 \cdot H_2O$	25.00~198.76	15.25	15.27	BaO	
	II	collapse	198.76~340.43	58.70	58.72	26.05	26.01
	III	collapse	340.43~620.51				
5	I	(H_2O)	25.00~148.26	3.77	3.78	SrO	
	II	collapse	148.26~347.45	74.51	74.49	21.72	21.73
	III	collapse	347.45~738.80				
6	I	(H_2O)	25.00~153.87	3.43	3.42	BaO	
	II	collapse	153.87~369.42	67.45	67.46	29.12	29.12
	III	collapse	369.42~672.41				

Table S4. Allelopathic Effects on edible Amaranth (Amaranthus spp.) of ligands and complexes

	Germination rate				Shoot elongation（RI）				Root elongation（RI）			
	50	100	150	200	50	100	150	200	50	100	150	200
***o*-CPA**	0.58	0.92	0.92	1.00	-0.49	-0.30	-0.15	-0.39	-0.56	-0.60	-0.62	-0.85
1	0.92	1.00	1.00	0.75	-0.32	-0.32	-0.43	-0.76	-0.09	-0.24	-0.43	-0.69
2	0.92	1.00	1.00	1.00	-0.84	-0.84	-0.85	-0.83	-0.93	-0.95	-0.95	-0.95
***m*-CPA**	0.92	1.00	1.00	0.92	-0.49	-0.63	-0.78	-0.82	-0.90	-0.94	-0.90	-0.91
3	0.58	0.92	1.00	1.00	-0.74	-0.73	-0.70	-0.76	-0.90	-0.93	-0.93	-0.95
4	0.83	0.75	0.83	1.00	-0.82	-0.89	-0.88	-0.88	-0.94	-0.91	-0.93	-0.92
***p*-CPA**	1.00	1.00	1.00	0.92	-0.61	-0.69	-0.77	-0.78	-0.94	-0.93	-0.95	-0.94
5	1.00	1.00	0.58	1.00	-0.83	-0.84	-0.74	-0.79	-0.68	-0.70	-0.92	-0.93
6	1.00	0.92	1.00	1.00	-0.76	-0.79	-0.83	-0.82	-0.87	-0.83	-0.87	-0.87
gp	1.00	1.00	0.63	0.67	-0.21	-0.35	-0.54	-0.85	-0.66	-0.7549	-0.86	-0.95
ck	0.83	0.92	0.92	1.00								