

Supporting information for

Role of 4,4'-bipyridine versus longer spacers 4,4'-azobipyridine, 1,4-bis(4-pyridyl)ethylene, and 1,2-bis(pyridin-3-ylmethylene)hydrazine in the formation of thermally labile metallophosphate coordination polymers†

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Table S1. Hydrogen bonding in **1-5**.

Compound	D-H	D...A	H...A	D-H...A
1	O5-H1WB: 0.925(2)	O5...N3: 2.979(3) ^a	H1WB...N3:2.067(3) ^a	O5-H1WB...N3:168.48(14) ^a
	O5-H1WB: 0.925(2)	O5...N2: 2.981(3) ^b	H1WB...N2:2.620(2) ^b	O5-H1WB...N2:103.94(13) ^b
	O5-H1WA: 0.800(2)	O5...N2: 2.981(3) ^b	H1WA...N2:2.668(3) ^b	O5-H1WA...N2:105.33(15) ^b
2	O5-H1WA: 0.831(4)	O5...N3: 2.975(7) ^c	H1WA...N3:2.200(5) ^c	O5-H1WA...N3:155.27(30) ^c
	O5-H1WA: 0.831(4)	O5...N2: 3.175(6) ^d	H1WA...N2:2.719(4) ^d	O5-H1WA...N2:116.23(26) ^d
	O5-H1WB: 0.813(4)	O5...N2: 3.175(6) ^d	H1WB...N2:2.843(4) ^d	O5-H1WB...N2:116.81(27) ^d
3	O5-H1WB: 0.818(2)	O5...N3: 2.966(4) ^e	H1WB...N3:2.244(3) ^e	O5-H1WB...N3:147.51(20) ^e
	O5-H1WB: 0.818(2)	O5...N2: 3.166(4) ^d	H1WB...N2:2.644(3) ^d	O5-H1WB...N2:123.13(18) ^d
	O5-H1WA: 0.814(3)	O5...N2: 3.166(4) ^d	H1WA...N2:2.872(3) ^d	O5-H1WA...N2:103.74(18) ^d
4	O5-H5A: 0.893(1)	O5...N3: 2.885(2) ^f	H5A...N3:2.008(3) ^f	O5-H5A...N3:166.83(8) ^f
	O5-H5A: 0.893(1)	O5...N2: 2.956(2) ^g	H5A...N2:2.636(2) ^g	O5-H5A...N2:102.13(11) ^g
	O5-H5B: 0.846(2)	O5...N2: 2.956(2) ^g	H5B...N2:2.496(2) ^g	O5-H5B...N2:115.09(11) ^g
5	O9-H1WA: 0.835(7)	O9...N3: 2.757(12) ^h	H1WA...N3:1.944(9) ^h	O9-H1WA...N3:164.08(57) ^h
	O10-H2WA: 0.864(6)	O10...N4: 2.791(11) ⁱ	H2WA...N4:1.929(9) ⁱ	O10-H2WA...N4:175.12(49) ⁱ

Equivalent positions: (a) x,y,z; (b) x,-y+1,+z-1/2; (c) -x+1/2,-y+1/2+1,-z+1; (d) -x+1/2,+y+1/2,-z+1/2+1; (e) -x+1/2,-y+1/2+1,-z+2; (f) -x,-y+1,-z+1; (g) x,+y+1,+z; (h) x,-y+1/2,+z-1/2; (i) x+1,+y,+z.

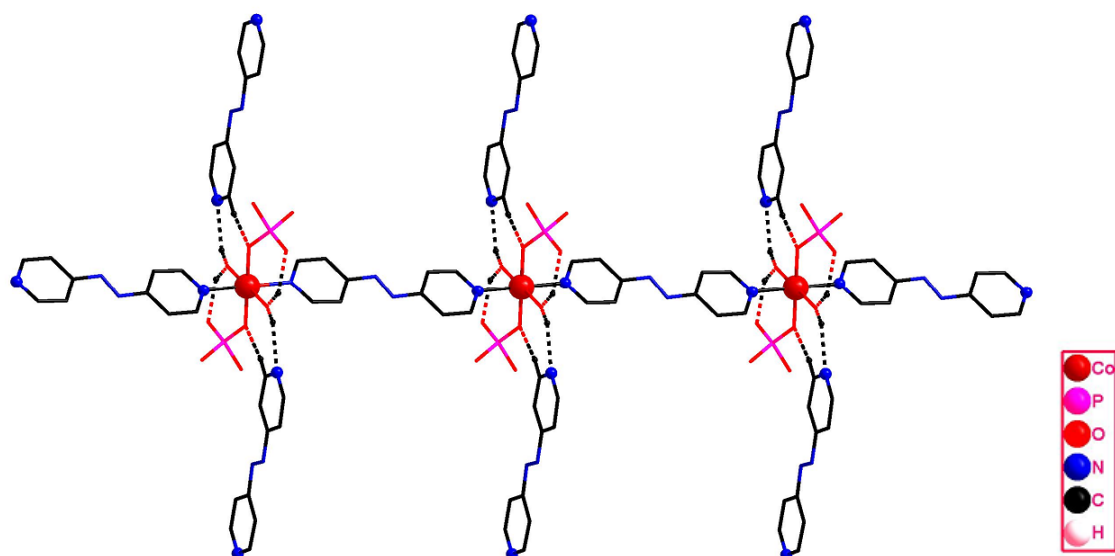


Figure S1. 1-D coordination polymer **2**.

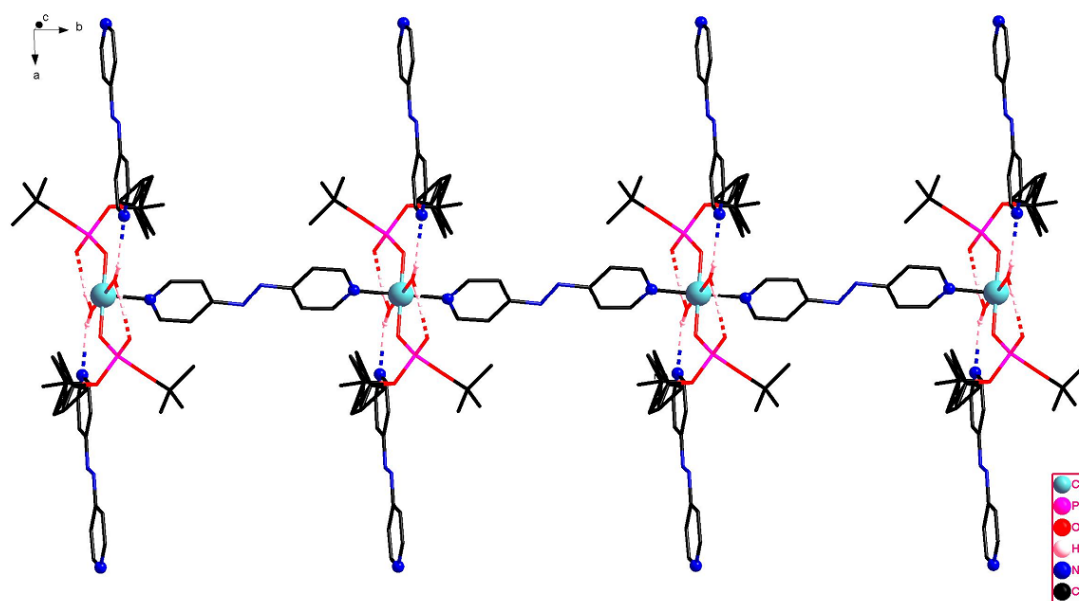


Figure S2. 1-D coordination polymer **3**.

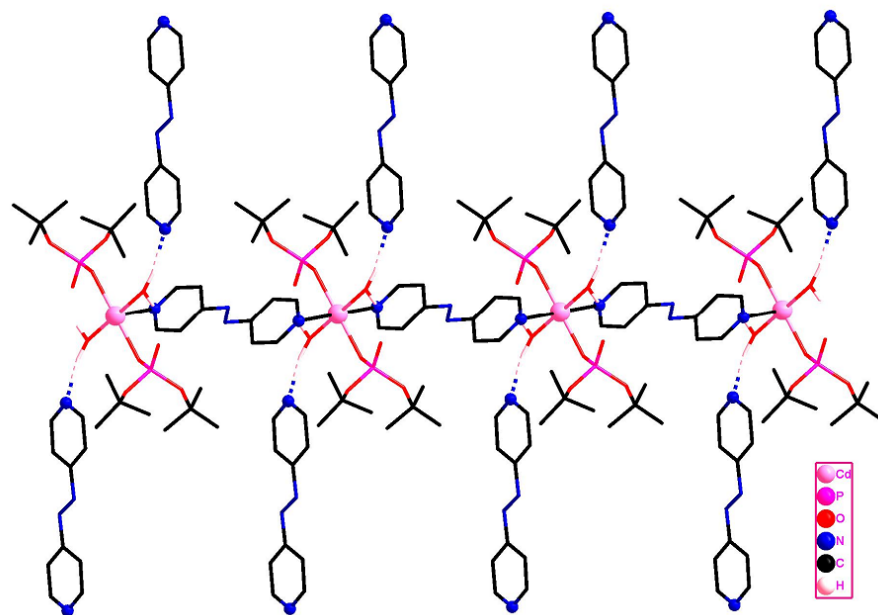


Figure S3. 1-D coordination polymer **4**.

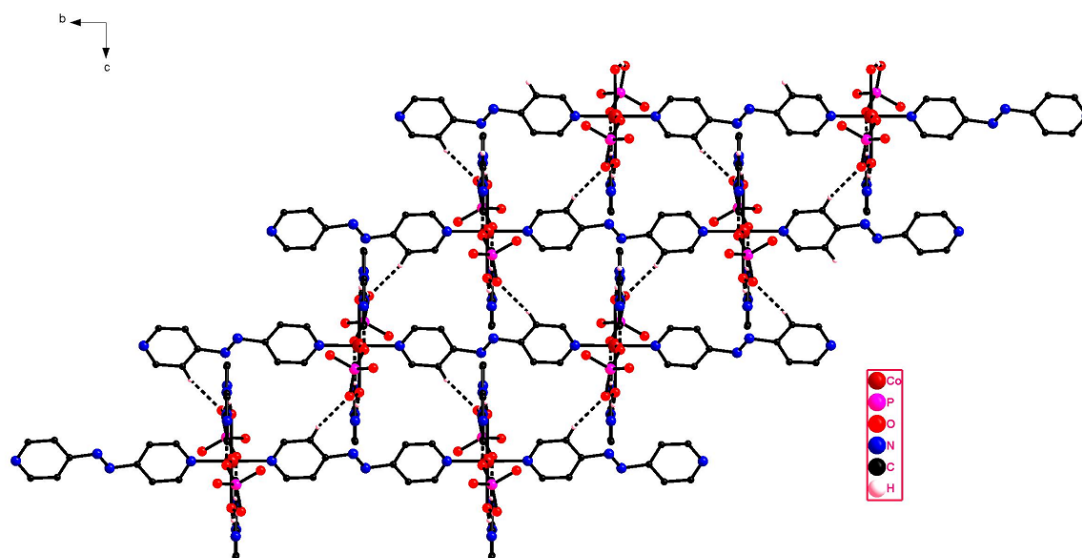


Figure S4. 2-D sheet formation of **2** through intermolecular hydrogen bonding.

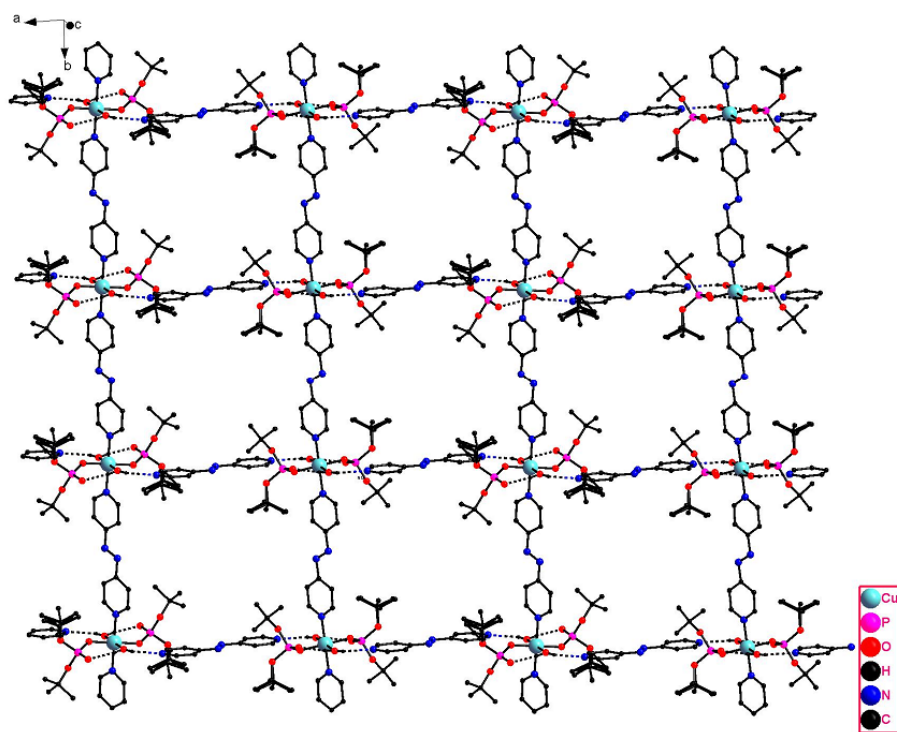


Figure S5. 2-D sheet formation of **3** through intermolecular hydrogen bonding.

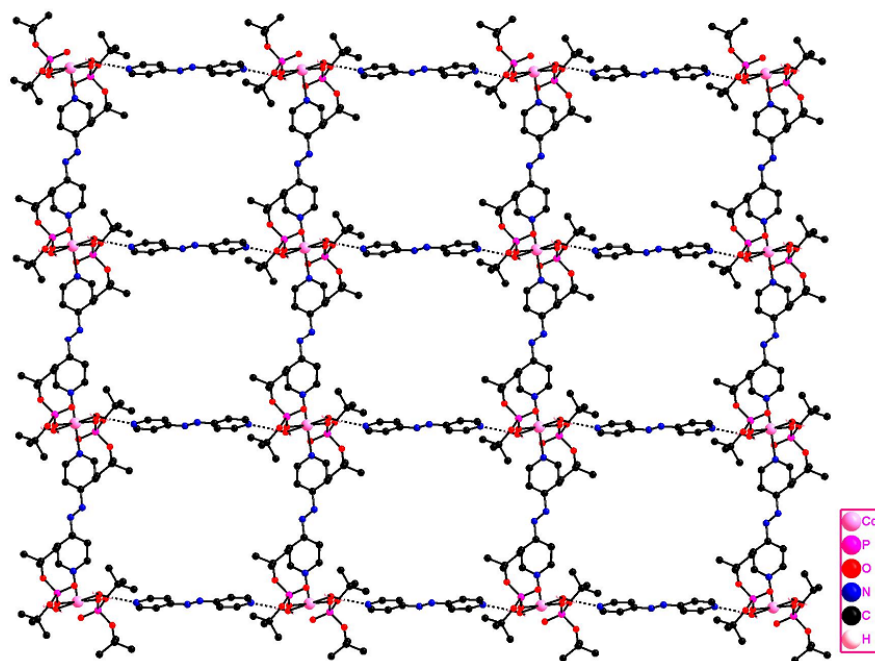


Figure S6. 2-D sheet formation of **4** through intermolecular hydrogen bonding.

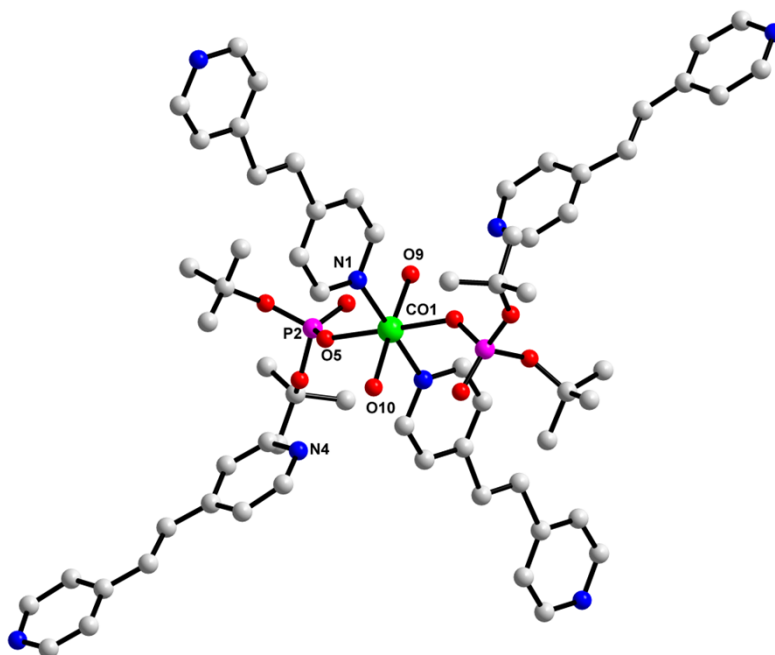


Figure S7. Molecular structure of $[\text{Co}(\text{dtbp})_2(\text{bpe})(\text{H}_2\text{O})_2](\text{bpe})$ (**6**).

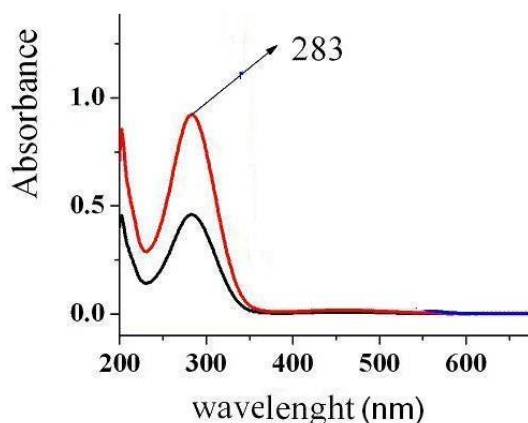
Table S2. TGA data for compounds **1-8**.

Complex	Weight loss °C (%)	Loss of molecules	Complex	Weight loss °C (%)	Loss of molecules
1	85-130 (9.5)	2H ₂ O	5	80-130 (5)	2H ₂ O
	131-230 (68)	4 b and 2 azopy		131-248 (70)	4a and 2 bpe
				248-850 (5)	2 bpe
2	197 (11)	2H ₂ O	6	75-138 (5)	2H ₂ O
	227 (42)	4 b		138-232 (47)	4a
	227-900 (25)	2 azopy		232-500 (18)	2 bpe
3	135 (4)	2H ₂ O	7	55-118 (11)	2H ₂ O
	204 (53)	4 b		118-205 (40)	4a
	204-884 (22)	2 azopy		205-400 (15)	2 bpe
4	190 (4)	2H ₂ O	8	55-118 (11)	2H ₂ O
	190-451 (54)	4 b		118-205 (40)	4a
	451-802 (34)	2 azopy		205-400 (15)	2 bpe

b = (CH₃)₂C=CH₂; azopy = 4,4'-azobipyridine and bpe = 1,2-bis(4-pyridyl)ethylene.

EPR studies. Compound **1** where Mn(II) ($I=5/2$) is in octahedral geometry displays a broad EPR signal ($g=2.04$) and the spectrum is unresolved in this case. Compound **2** however exhibits only six lines. In powder form both parallel and perpendicular geometry of spectra contain hyperfine peaks due to interaction between the electronic spin of magnetic electron and nuclear spin of Co(II) ion. There are unresolved hyperfine peaks because of overlapping and line-broadening effects in the spectrum. In this case $g_{av} = 2.1$, $A_{av} = 360G$. The compound **3** shows four $g_{\parallel}$ signals with a values of 2.5, 2.4, 2.3 and 2.1 due to hyperfine splitting arising from the interaction of nuclear spin $I=3/2$ with electronic spin of magnetic electron, while the g signals merged and appear as broad signal. The hyperfine coupling constant calculated for this spectrum is 200G. The ESR spectrum of **6** shows a broad peak at $g=2.04$ instead of sextet for Mn(II) ($I=5/2$) may due to increased loading of the solid sample, resulting in the loss of resolution. The ESR spectrum of **8** shows one broad $g_{\parallel}$ signal and one $g_{\perp}$ broad signal. For **5** and **7**, no valuable EPR data was obtained. EPR spectra for **1-3**, **5** and **7** are listed in Fig. S31 and S32.

UV-visible studies. The UV-vis spectrum of compound **1** has been recorded in methanol at two different concentrations. It exhibits a strong absorption at 283 nm, which can be assigned to π^* and $n-\pi^*$ transitions of azopy.



The UV-vis spectrum for the complex **2** was recorded in methanol at two different concentrations. It exhibits a strong absorption at 282nm, which can be assigned to $\pi-\pi^*$ and $n-\pi^*$ transitions of 4,4'-azobipyridine same as observed in the case of **2**. The UV-vis spectra for the complexes **3** and **4** were recorded in methanol at two different concentrations. It exhibits a strong absorption at 280 nm, which can be assigned to $\pi-\pi^*$ and $n-\pi^*$ transitions of azopy.

Table S3. Selected structural parameters observed in [Mn(dtbp)₂(azopy)(H₂O)₂](azopy) (**1**).

Bond lengths (Å)			
Mn(1)-O(1)	2.1136(18)	P(1)-O(2)	1.482(2)
Mn(1)-O(1)#1	2.1136(18)	P(1)-O(1)	1.499(2)
Mn(1)-O(5)#1	2.1882(19)	P(1)-O(4)	1.5875(19)
Mn(1)-O(5)	2.1882(19)	P(1)-O(3)	1.5883(19)
Mn(1)-N(1)	2.313(2)	O(3)-C(1)	1.456(3)
N(1)-C(9)	1.339(3)	O(4)-C(5)	1.463(3)
N(1)-C(13)	1.344(3)	N(3)-C(14)	1.341(4)
N(2)-N(2)#2	1.233(4)	N(3)-C(18)	1.349(4)
N(2)-C(11)	1.446(3)	N(4)-N(4)#3	1.230(5)
Bond angles (°)			
O(1)-Mn(1)-O(1)#1	180.00(4)	O(5)#1-Mn(1)-N(1)	90.29(7)
O(1)-Mn(1)-O(5)#1	90.29(7)	O(5)-Mn(1)-N(1)	89.71(7)
O(1)#1-Mn(1)-O(5)#1	89.71(7)	O(1)-Mn(1)-N(1)#1	93.05(7)
O(1)-Mn(1)-O(5)	89.71(7)	O(1)#1-Mn(1)-N(1)#1	86.95(7)
O(1)#1-Mn(1)-O(5)	90.29(7)	O(5)#1-Mn(1)-N(1)#1	89.71(7)
O(5)#1-Mn(1)-O(5)	180.0	O(5)-Mn(1)-N(1)#1	90.29(7)
O(1)-Mn(1)-N(1)	86.95(7)	N(1)-Mn(1)-N(1)#1	180.000(1)
O(1)#1-Mn(1)-N(1)	93.05(7)	O(2)-P(1)-O(1)	116.75(11)
O(1)-Mn(1)-O(1)#1	180.00(4)	O(2)-P(1)-O(4)	111.25(11)

Symmetry equivalents: #1 -x+3/2,-y+3/2,-z+1 #2 -x+3/2,-y+1/2,-z+1 #3 -x+2,y,-z+1/2.

Table S4. Selected structural parameters observed in [Co(dtpb)₂(azopy)(H₂O)₂](azopy) (**2**).

Bond lengths (Å)			
Co-O(1)	1.938(3)	P(1)-O(3)	1.575(4)
Co-O(1)#1	1.938(3)	O(3)-C(1)	1.451(6)
Co-N(1)#1	2.078(4)	O(4)-C(5)	1.45(5)
Co-N(1)	2.078(4)	O(4)-C(5A)	1.451(15)
Co-O(5)	2.406(4)	N(1)-C(13)	1.333(6)
Co-O(5)#1	2.406(4)	N(1)-C(9)	1.338(6)
P(1)-O(2)	1.476(4)	N(2)-N(2)#2	1.221(8)
P(1)-O(1)	1.507(4)	N(2)-C(11)	1.433(6)
P(1)-O(4)	1.576(4)	N(3)-C(14)	1.326(8)
Bond angles (°)			
O(1)-Co-O(1)#1	180.0	N(1)-Co-O(5)	89.22(13)
O(1)-Co-N(1)#1	92.21(14)	O(1)-Co-O(5)#1	91.85(14)
O(1)#1-Co-N(1)#1	87.79(14)	O(1)#1-Co-O(5)#1	88.15(14)
O(1)-Co-N(1)	87.79(14)	N(1)#1-Co-O(5)#1	89.22(13)
O(1)#1-Co-N(1)	92.21(14)	N(1)-Co-O(5)#1	90.78(13)
N(1)#1-Co-N(1)	180.0	O(5)-Co-O(5)#1	180.0
O(1)-Co-O(5)	88.15(14)	O(2)-P(1)-O(1)	116.7(2)
O(1)#1-Co-O(5)	91.85(14)	O(2)-P(1)-O(4)	112.8(2)
N(1)#1-Co-O(5)	90.78(13)	O(1)-P(1)-O(4)	108.5(2)
Symmetry equivalents: #1 -x+1/2,-y+3/2,-z+1 #2 -x+1/2,-y+1/2,-z+1 #3 -x+1,y,-z+1/2.			

Table S5. Selected structural parameters observed in [Cu(dtbp)₂(azopy)(H₂O)₂](azopy) (**3**).

Bond lengths (Å)			
Cu-O(1)	1.931(2)	P(1)-O(4)	1.587(2)
Cu-O(1)#1	1.931(2)	O(3)-C(1)	1.456(4)
Cu-N(1)	2.090(2)	O(4)-C(5A)	1.433(7)
Cu-N(1)#1	2.090(2)	O(4)-C(5)	1.487(19)
Cu-O(5)#1	2.406(2)	N(1)-C(9)	1.336(4)
Cu-O(5)	2.406(2)	N(1)-C(13)	1.336(4)
P(1)-O(2)	1.483(2)	N(2)-N(2)#2	1.233(5)
P(1)-O(1)	1.509(2)	N(2)-C(11)	1.447(4)
P(1)-O(3)	1.584(2)	N(3)-C(18)	1.327(5)
Bond angles (°)			
O(1)-Cu-O(1)#1	180.0	N(1)#1-Cu-O(5)#1	89.19(9)
O(1)-Cu-N(1)	87.70(9)	O(1)-Cu-O(5)	88.14(9)
O(1)#1-Cu-N(1)	92.30(9)	O(1)#1-Cu-O(5)	91.86(9)
O(1)-Cu-N(1)#1	92.30(9)	N(1)-Cu-O(5)	89.19(9)
O(1)#1-Cu-N(1)#1	87.70(9)	N(1)#1-Cu-O(5)	90.81(9)
N(1)-Cu-N(1)#1	180.0	O(5)#1-Cu-O(5)	180.0
O(1)-Cu-O(5)#1	91.86(9)	O(2)-P(1)-O(1)	116.84(13)
O(1)#1-Cu-O(5)#1	88.14(9)	O(2)-P(1)-O(3)	113.94(14)
N(1)-Cu-O(5)#1	90.81(9)	O(1)-P(1)-O(3)	104.11(12)

Symmetry equivalents: #1 -x+1/2,-y+3/2,-z+1 #2 -x+1/2,-y+1/2,-z+1, #3 -x+1,y,-z+5/2.

Table S6. Selected structural parameters observed in [Cd(dtbp)₂(azopy)(H₂O)₂](azopy) (**4**).

Bond lengths (Å)			
Cd(1)-O(1)	2.2504(15)	P(1)-O(3)	1.5990(17)
Cd(1)-O(1)#1	2.2504(15)	O(3)-C(5)	1.461(3)
Cd(1)-O(5)#1	2.2931(15)	O(4)-C(1)	1.460(3)
Cd(1)-O(5)	2.2931(15)	N(1)-C(9)	1.332(3)
Cd(1)-N(1)	2.3617(18)	N(1)-C(13)	1.342(3)
Cd(1)-N(1)#1	2.3617(18)	N(2)-N(2)#2	1.248(4)
P(1)-O(2)	1.4844(17)	N(2)-C(11)	1.436(3)
P(1)-O(1)	1.4951(17)	N(3)-C(18)	1.336(3)
P(1)-O(4)	1.5912(16)	N(3)-C(14)	1.339(3)
Bond angles (°)			
O(1)-Cd(1)-O(1)#1	180.00(8)	O(5)-Cd(1)-N(1)	88.67(6)
O(1)-Cd(1)-O(5)#1	91.69(6)	O(1)-Cd(1)-N(1)#1	94.57(6)
O(1)#1-Cd(1)-O(5)#1	88.31(6)	O(1)#1-Cd(1)-N(1)#1	85.43(6)
O(1)-Cd(1)-O(5)	88.31(6)	O(5)#1-Cd(1)-N(1)#1	88.67(6)
O(1)#1-Cd(1)-O(5)	91.69(6)	O(5)-Cd(1)-N(1)#1	91.33(6)
O(5)#1-Cd(1)-O(5)	180.0	N(1)-Cd(1)-N(1)#1	180.00(9)
O(1)-Cd(1)-N(1)	85.43(6)	O(2)-P(1)-O(1)	118.66(9)
O(1)#1-Cd(1)-N(1)	94.57(6)	O(2)-P(1)-O(4)	105.27(9)
O(5)#1-Cd(1)-N(1)	91.33(6)	O(1)-P(1)-O(4)	110.79(9)

Symmetry equivalents: #1 -x,-y+1,-z #2 -x+1,-y,-z #3 -x-1,-y,-z+1

Table S7. Selected structural parameters observed in [Cd(dtpb)₂(bpe)(H₂O)₂](bpe) (**5**).

Bond lengths (Å)			
Mn(1)-O(5)	2.136(8)	P(1)-O(3)	1.611(7)
Mn(1)-O(1)	2.143(6)	P(2)-O(5)	1.389(8)
Mn(1)-O(10)	2.167(6)	P(2)-O(6)	1.405(11)
Mn(1)-O(9)	2.186(7)	P(2)-O(8)	1.469(13)
Mn(1)-N(2)#1	2.239(12)	P(2)-O(7)	1.646(12)
Mn(1)-N(1)	2.297(11)	O(2)-C(5)	1.409(12)
P(1)-O(4)	1.481(7)	O(3)-C(1)	1.376(12)
P(1)-O(1)	1.525(6)	O(7)-C(9)	1.423(16)
P(1)-O(2)	1.543(6)	O(8)-C(13)	1.61(2)
Bond angles (°)			
O(5)-Mn(1)-O(1)	178.6(4)	O(9)-Mn(1)-N(2)#1	91.9(4)
O(5)-Mn(1)-O(10)	89.2(3)	O(5)-Mn(1)-N(1)	88.8(4)
O(1)-Mn(1)-O(10)	90.5(2)	O(1)-Mn(1)-N(1)	92.5(3)
O(5)-Mn(1)-O(9)	92.8(3)	O(10)-Mn(1)-N(1)	90.5(3)
O(1)-Mn(1)-O(9)	87.6(3)	O(9)-Mn(1)-N(1)	87.3(4)
O(10)-Mn(1)-O(9)	177.0(3)	N(2)#1-Mn(1)-N(1)	179.2(4)
O(5)-Mn(1)-N(2)#1	91.0(4)	O(4)-P(1)-O(1)	118.2(4)
O(1)-Mn(1)-N(2)#1	87.7(3)	O(4)-P(1)-O(2)	113.5(4)
O(10)-Mn(1)-N(2)#1	90.3(4)	O(1)-P(1)-O(2)	107.0(4)

Symmetry equivalents: #1 x,y-1,z #2 x,y+1,z .

Table S8. Selected structural parameters observed in [Cd(dtpb)₂(bpe)(H₂O)₂](bpe) (**6**).

Bond lengths (Å)			
Co(1)-N(2)#1	2.058(11)	P(1)-O(2)	1.605(14)
Co(1)-O(1)	2.074(17)	P(2)-O(5)	1.402(15)
Co(1)-N(1)	2.090(13)	P(2)-O(6)	1.486(13)
Co(1)-O(5)	2.111(17)	P(2)-O(7)	1.50(2)
Co(1)-O(9)	2.156(10)	P(2)-O(8)	1.618(14)
Co(1)-O(10)	2.167(11)	O(2)-C(1)	1.40(2)
P(1)-O(4)	1.440(11)	O(3)-C(5)	1.42(2)
P(1)-O(1)	1.492(15)	O(7)-C(9)	1.48(2)
P(1)-O(3)	1.538(18)	O(8)-C(13)	1.49(2)
Bond angles (°)			
N(2)#1-Co(1)-O(1)	90(3)	O(5)-Co(1)-O(9)	89.6(5)
N(2)#1-Co(1)-N(1)	178(3)	N(2)#1-Co(1)-O(10)	88(3)
O(1)-Co(1)-N(1)	89.6(5)	O(1)-Co(1)-O(10)	89.0(6)
N(2)#1-Co(1)-O(5)	91(3)	N(1)-Co(1)-O(10)	90.9(5)
O(1)-Co(1)-O(5)	179.1(6)	O(5)-Co(1)-O(10)	91.5(5)
N(1)-Co(1)-O(5)	89.6(5)	O(9)-Co(1)-O(10)	176.9(5)
N(2)#1-Co(1)-O(9)	90(3)	O(4)-P(1)-O(1)	112.9(9)
O(1)-Co(1)-O(9)	89.9(5)	O(4)-P(1)-O(3)	122.8(11)
N(1)-Co(1)-O(9)	92.0(5)	O(1)-P(1)-O(3)	106.4(11)

Symmetry equivalents: #1 x,y+1,z #2 x,y-1,z.

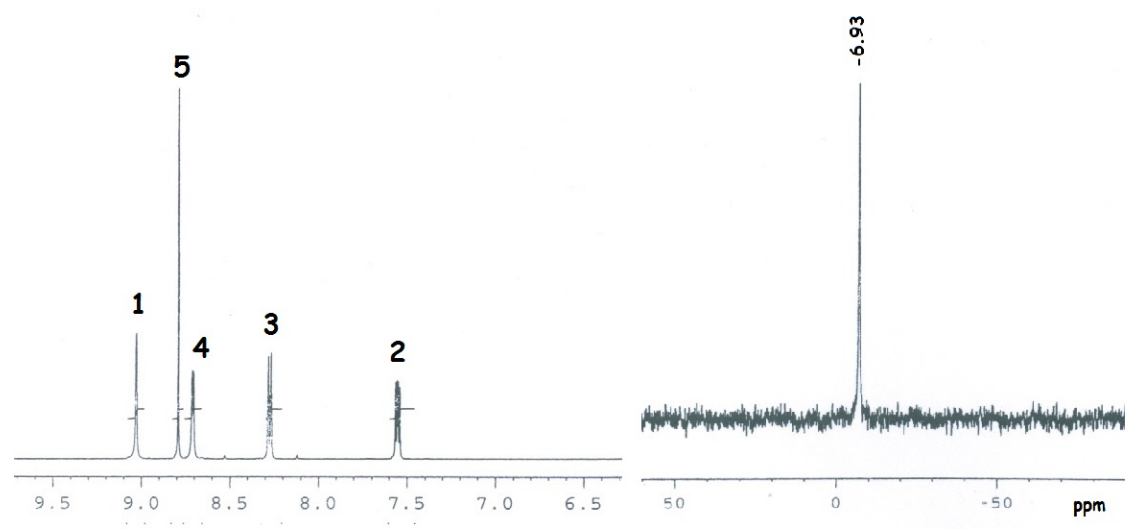


Fig. S8 ¹H NMR (left) and ³¹P NMR (right) spectra of **11** in DMSO-*d*₆.

Table S9. Selected structural parameters observed in [$\{\text{Ni}(\text{L}^1)(\text{H}_2\text{O})_4\} \{(\text{dtbp})_2\}$] (**9**).

Bond lengths (Å)			
Ni(1)-O(7)	2.0609(18)	O(1)-C(11)	1.479(3)
Ni(1)-O(6)	2.070(2)	O(4)-C(8)	1.454(3)
Ni(1)-N(1)	2.095(2)	O(6)-H(6A)	0.79(4)
P(1)-O(2)	1.487(2)	O(6)-H(6B)	0.81(4)
P(1)-O(5)	1.5030(19)	O(7)-H(7E)	0.840(2)
P(1)-O(4)	1.5825(19)	O(7)-H(7D)	0.783(18)
P(1)-O(1)	1.6009(17)	N(1)-C(1)	1.337(3)
Bond angles (°)			
O(7)#1-Ni(1)-O(6)#1	91.63(7)	O(7)#1-Ni(1)-N(1)	88.34(7)
O(7)-Ni(1)-O(6)#1	88.37(7)	O(2)-P(1)-O(5)	117.50(10)
O(7)#1-Ni(1)-O(6)	88.37(7)	O(2)-P(1)-O(4)	106.08(11)
O(7)-Ni(1)-O(6)	91.63(7)	O(5)-P(1)-O(4)	111.34(11)
O(6)#1-Ni(1)-O(6)	180.000(1)	O(2)-P(1)-O(1)	111.09(11)
O(7)#1-Ni(1)-N(1)#1	91.66(7)	O(5)-P(1)-O(1)	103.50(9)
O(7)-Ni(1)-N(1)#1	88.34(7)	O(4)-P(1)-O(1)	106.95(10)
O(6)#1-Ni(1)-N(1)#1	91.86(7)	C(11)-O(1)-P(1)	126.60(15)
O(6)-Ni(1)-N(1)#1	88.14(7)	C(8)-O(4)-P(1)	128.50(17)

Table S10. Selected structural parameters observed in [$\{\text{Co}(\text{L}^1)(\text{H}_2\text{O})_4\} \{(\text{dtbp})_2\}$] (**10**).

Bond lengths (Å)			
Co(1)-O(5)	2.149(8)	O(1)-C(7)	1.512(7)
Co(1)-O(6)	2.153(8)	O(2)-C(11)	1.492(7)
Co(1)-N(1)	2.197(8)	N(1)-C(5)	1.363(7)
P(1)-O(4)	1.515(6)	N(1)-C(1)	1.375(8)
P(1)-O(3)	1.529(5)	N(2)-C(6)	1.306(8)
P(1)-O(2)	1.603(5)	P(1)-O(1)	1.637(5)
Bond angles (°)			
O(5)-Co(1)-O(5)#1	180.0(3)	O(4)-P(1)-O(3)	117.5(2)
O(5)-Co(1)-O(6)#1	91.27(14)	O(4)-P(1)-O(2)	105.7(2)
O(5)#1-Co(1)-O(6)#1	88.73(14)	O(3)-P(1)-O(2)	111.4(3)
O(5)-Co(1)-O(6)	88.73(14)	O(4)-P(1)-O(1)	111.7(3)
O(5)#1-Co(1)-O(6)	91.27(14)	O(3)-P(1)-O(1)	103.3(2)
O(6)#1-Co(1)-O(6)	180.00(18)	O(2)-P(1)-O(1)	106.8(3)
O(5)-Co(1)-N(1)#1	88.63(18)	C(7)-O(1)-P(1)	126.4(3)

Table S11. Selected structural parameters observed in $[\text{Cd}(\text{L}^1)_3(\text{dtbp})_2]_n$ (**11**).

Bond lengths (Å)			
Cd(1)-O(5)	2.242(4)	P(1)-O(1)	1.487(5)
Cd(1)-O(1)	2.252(5)	P(1)-O(4)	1.579(7)
Cd(1)-N(12)#1	2.354(5)	P(1)-O(3)	1.585(5)
Cd(1)-N(9)	2.355(5)	P(2)-O(6)	1.483(5)
Cd(1)-N(5)	2.427(5)	P(2)-O(5)	1.499(5)
Cd(1)-N(1)	2.433(5)	P(2)-O(7)	1.594(4)
P(1)-O(2)	1.467(8)	P(2)-O(8)	1.599(4)
Bond angles (°)			
O(5)-Cd(1)-O(1)	168.66(18)	N(9)-Cd(1)-N(1)	90.70(18)
O(5)-Cd(1)-N(12)#1	91.41(18)	N(5)-Cd(1)-N(1)	173.23(17)
O(1)-Cd(1)-N(12)#1	90.4(2)	O(2)-P(1)-O(1)	116.8(4)
O(5)-Cd(1)-N(9)	85.41(18)	O(2)-P(1)-O(4)	110.1(5)
O(1)-Cd(1)-N(9)	93.1(2)	O(1)-P(1)-O(4)	111.3(4)
N(12)#1-Cd(1)-N(9)	176.02(18)	O(2)-P(1)-O(3)	112.1(3)
O(5)-Cd(1)-N(5)	91.64(17)	O(1)-P(1)-O(3)	105.0(3)
O(1)-Cd(1)-N(5)	99.67(18)	O(4)-P(1)-O(3)	100.0(4)
N(12)#1-Cd(1)-N(5)	84.40(17)	O(6)-P(2)-O(5)	117.0(3)

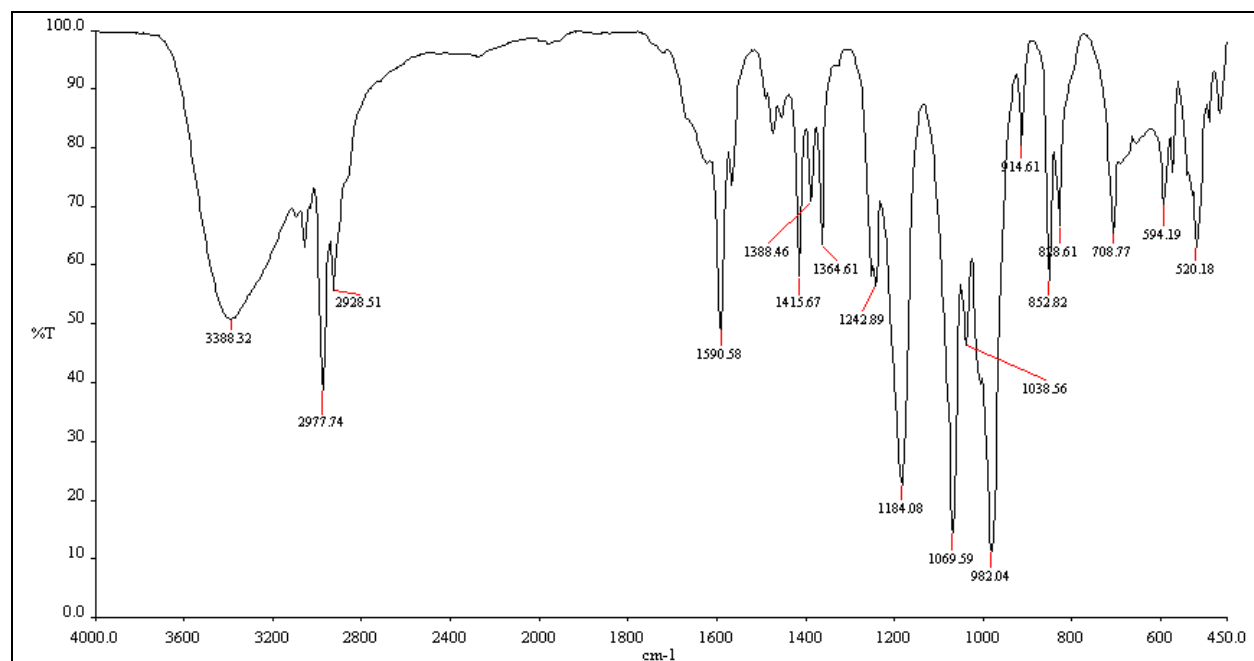


Fig. S9 IR spectrum of compound **1** (KBr disc).

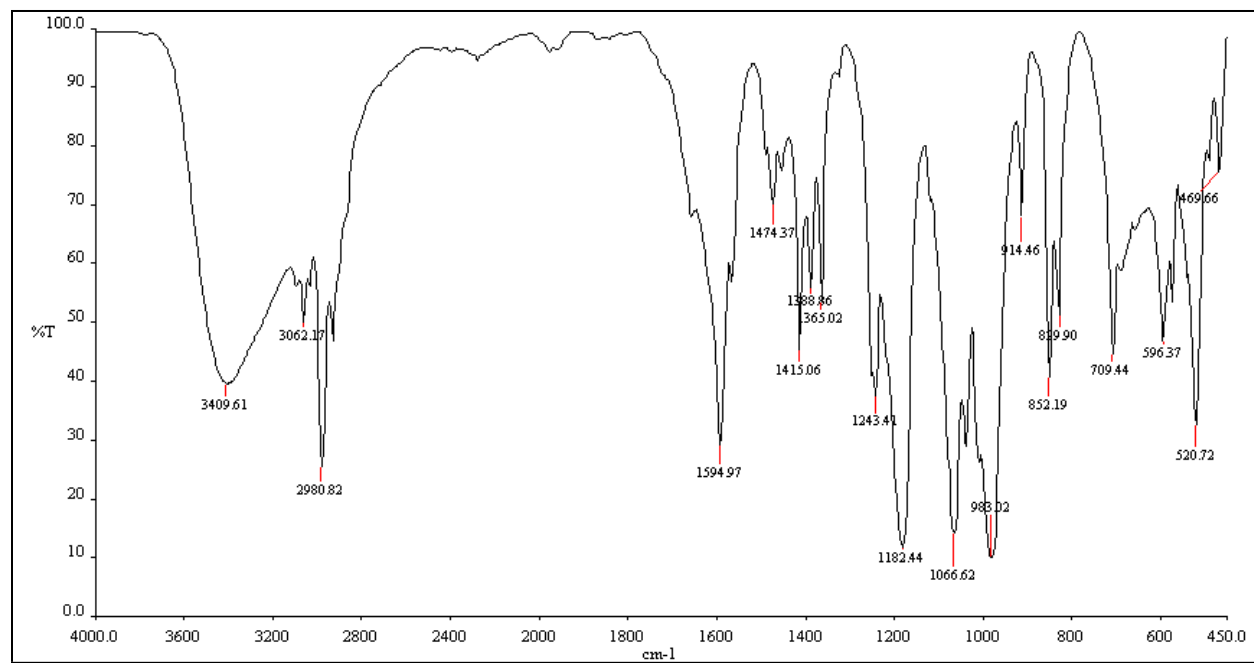


Fig. S10 IR spectrum of compound **2** (KBr disc).

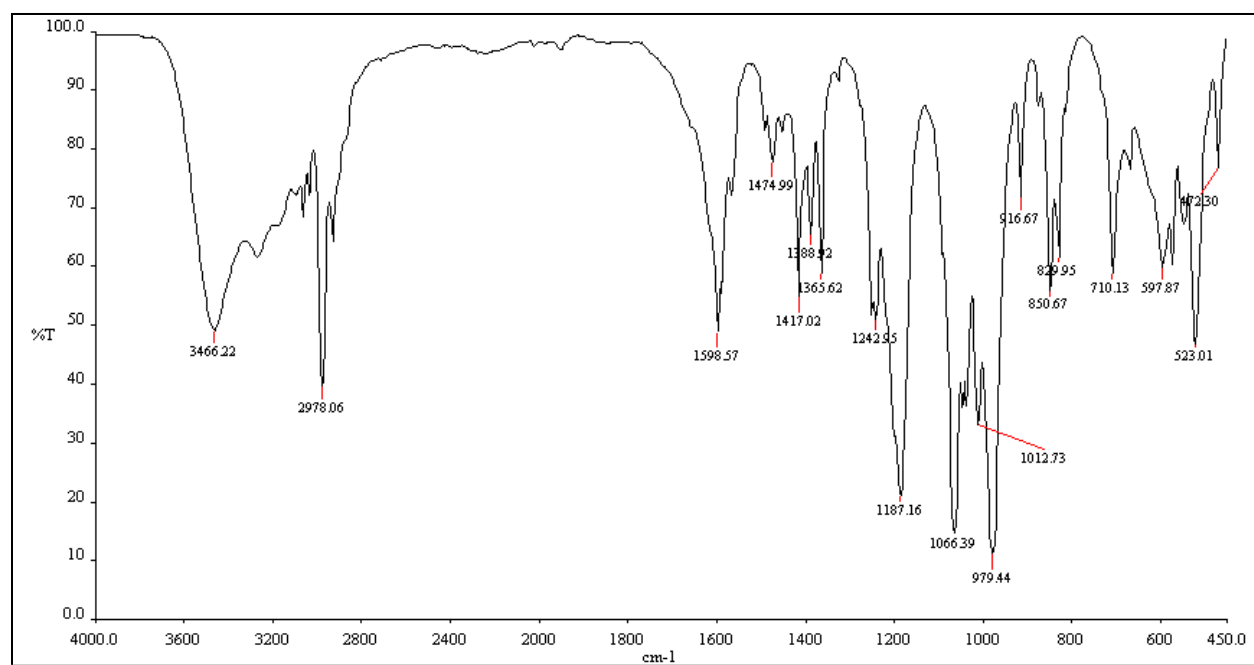


Fig. S11 IR spectrum of compound **3** (KBr disc).

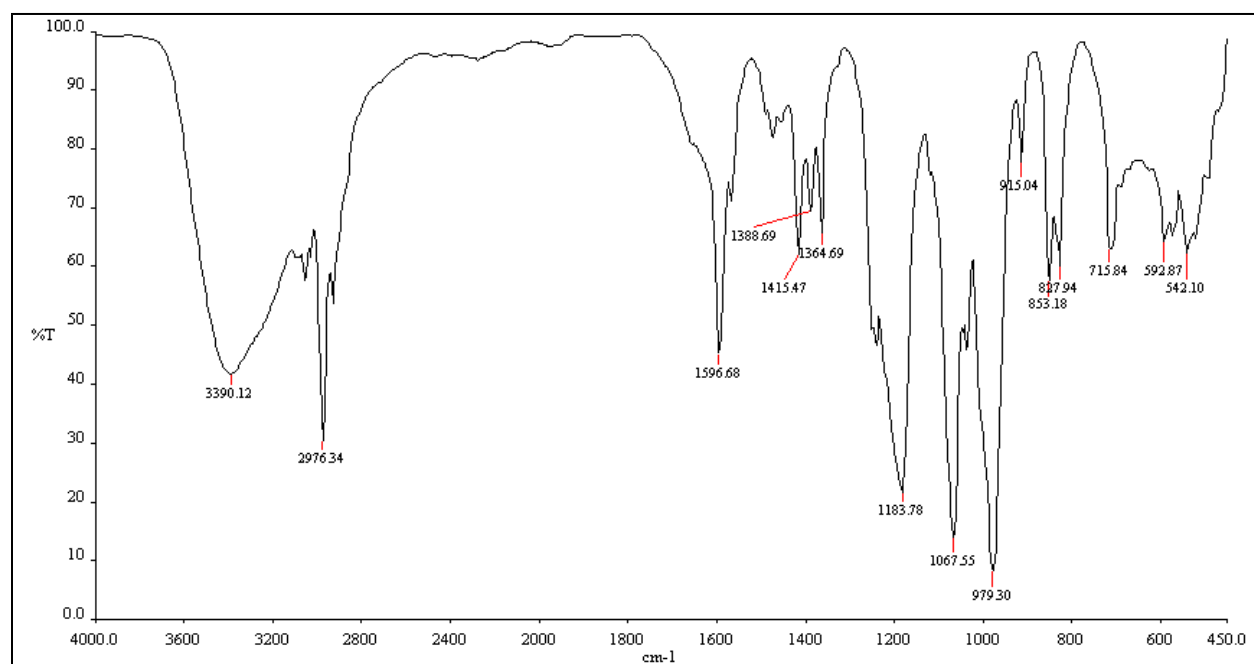


Fig. S12 IR spectrum of compound **4** (KBr disc).

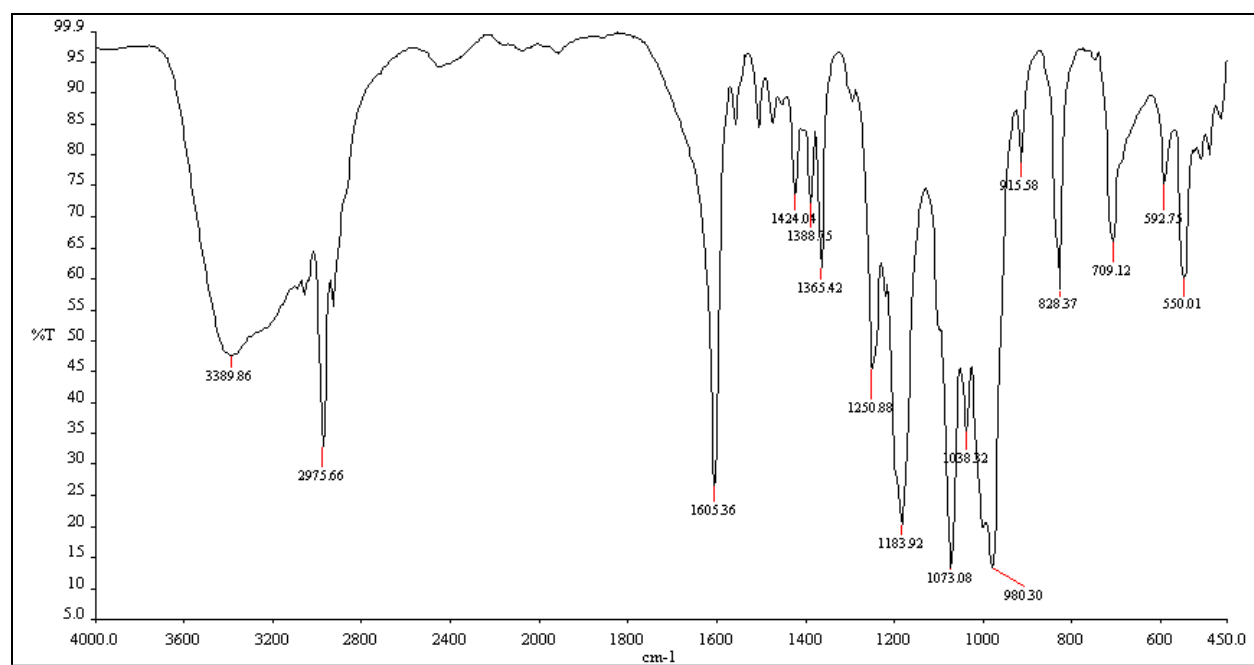


Fig. S13 IR spectrum of compound **5** (KBr disc).

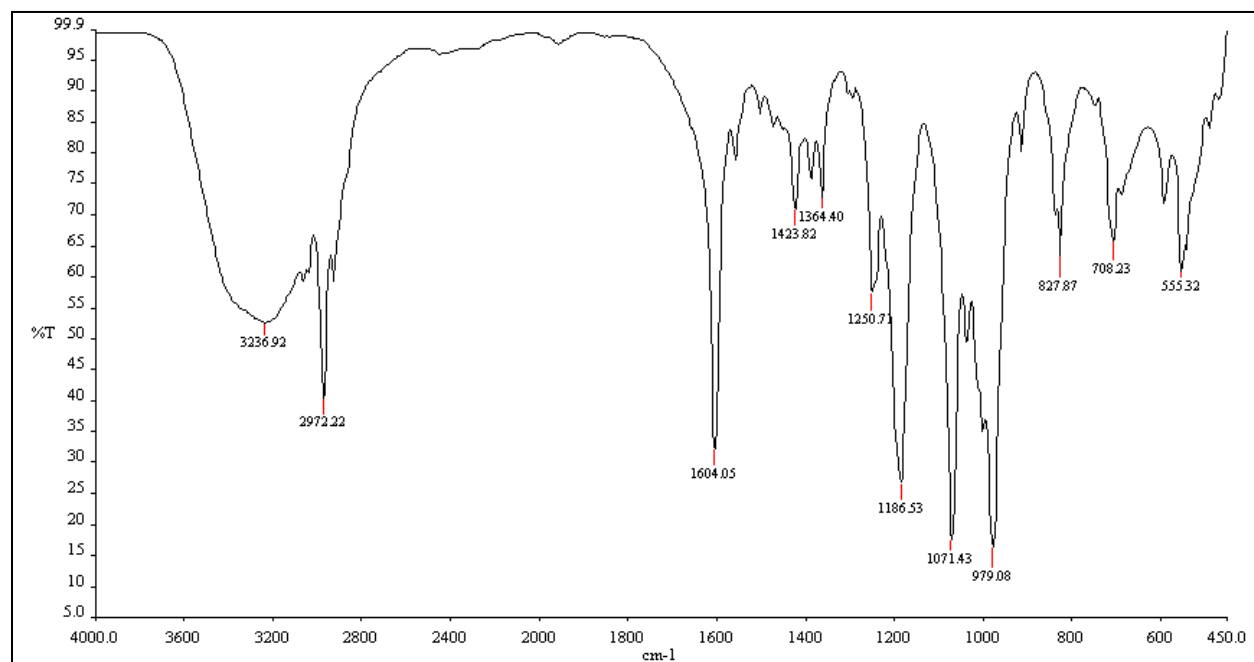


Fig. S14 IR spectrum of compound **6** (KBr disc).

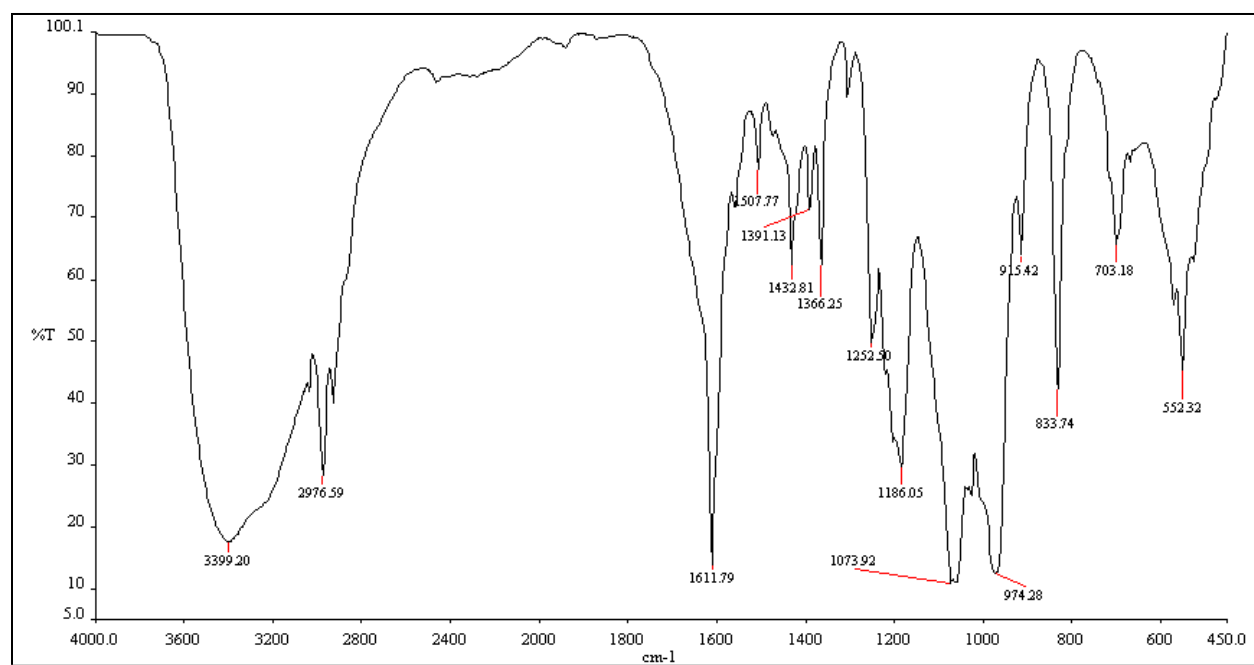


Fig. S15 IR spectrum of compound **7** (KBr disc).

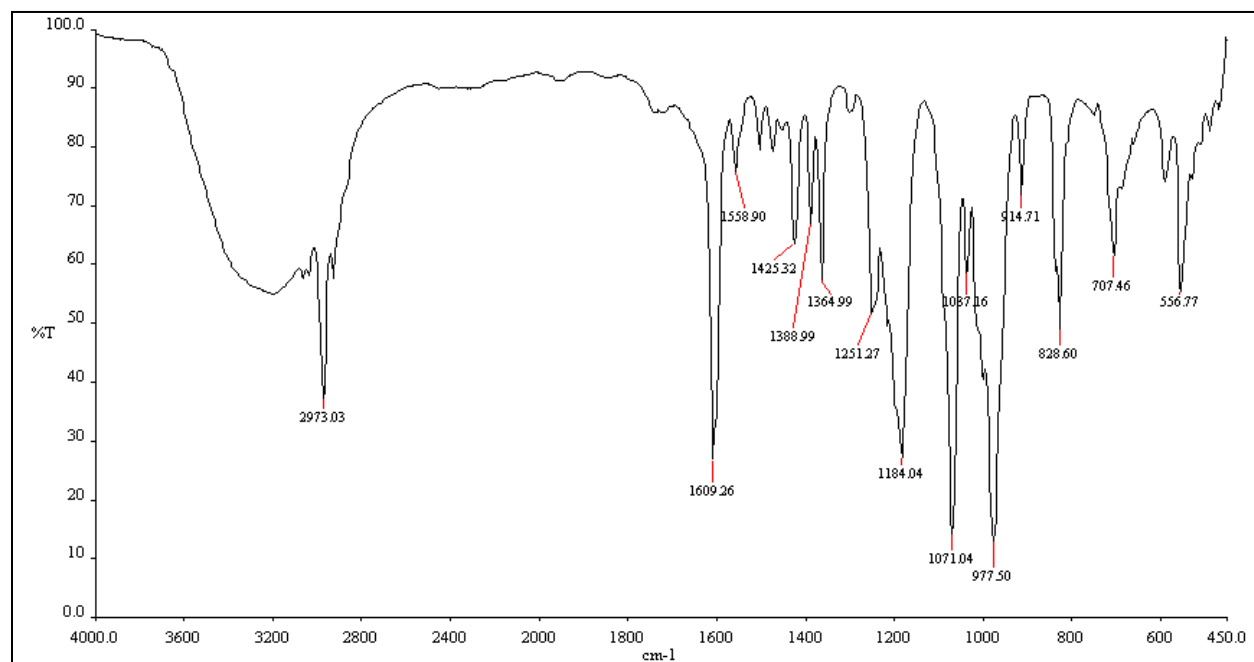


Fig. S16 IR spectrum of compound **8** (KBr disc).

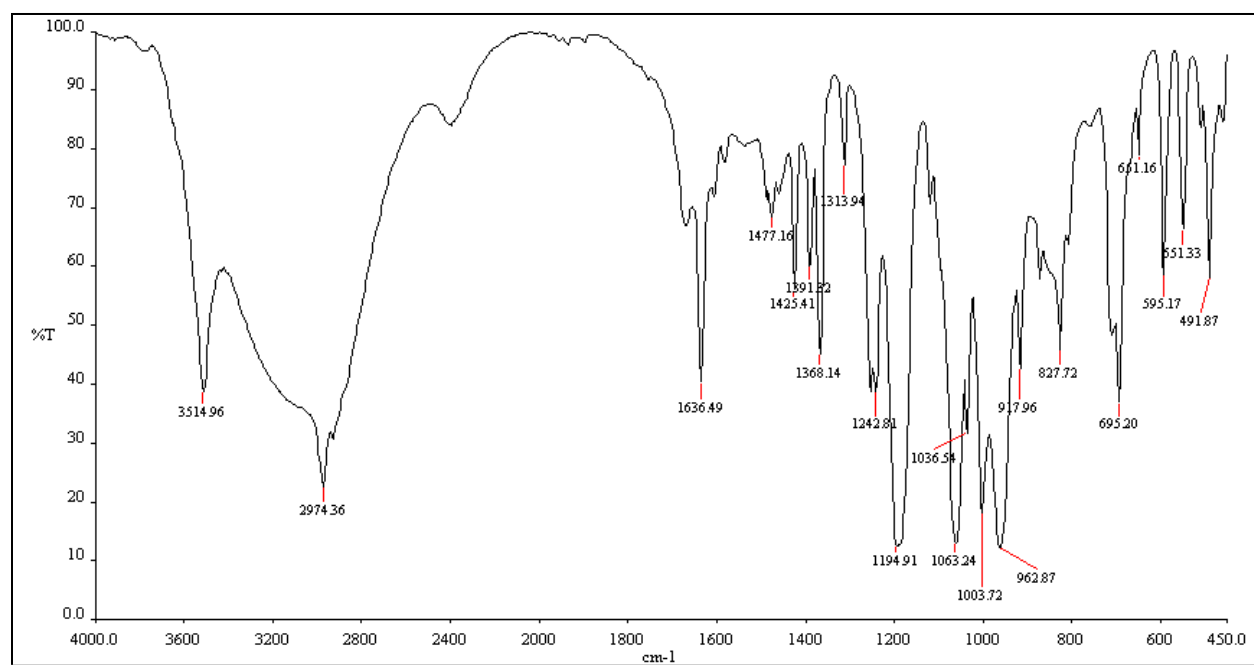


Fig. S17 IR spectrum of compound **9** (KBr disc).

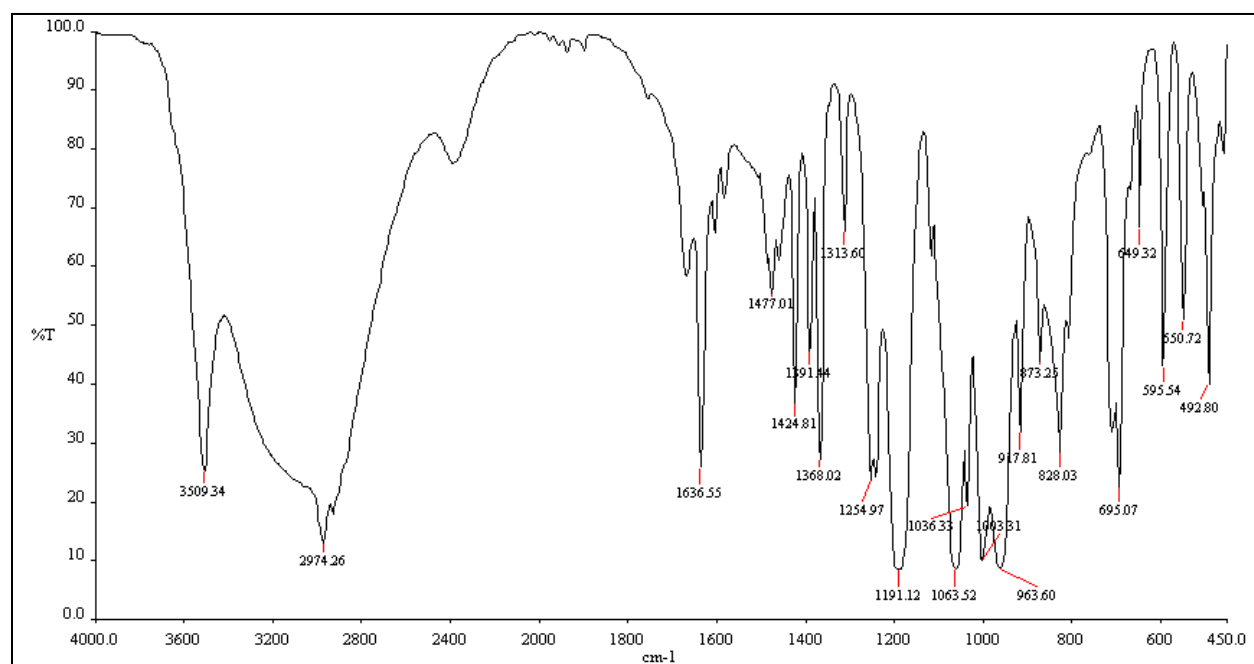


Fig. S18 IR spectrum of compound **10** (KBr disc).

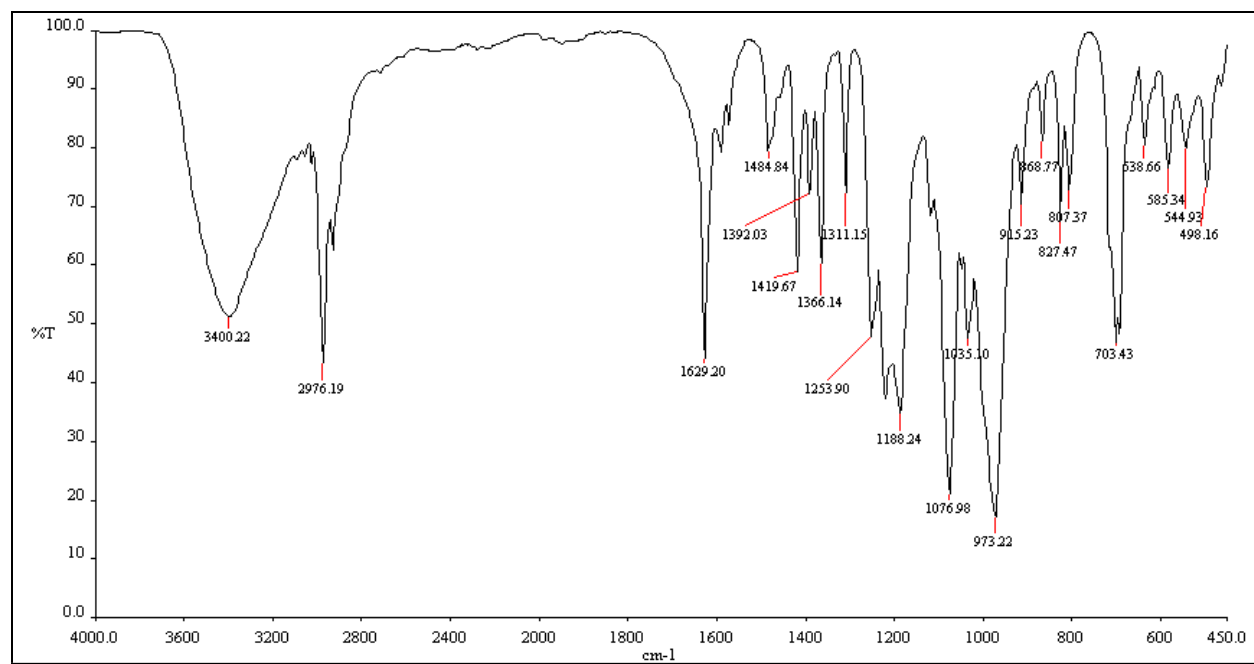


Fig. S19 IR spectrum of compound **11** (KBr disc).

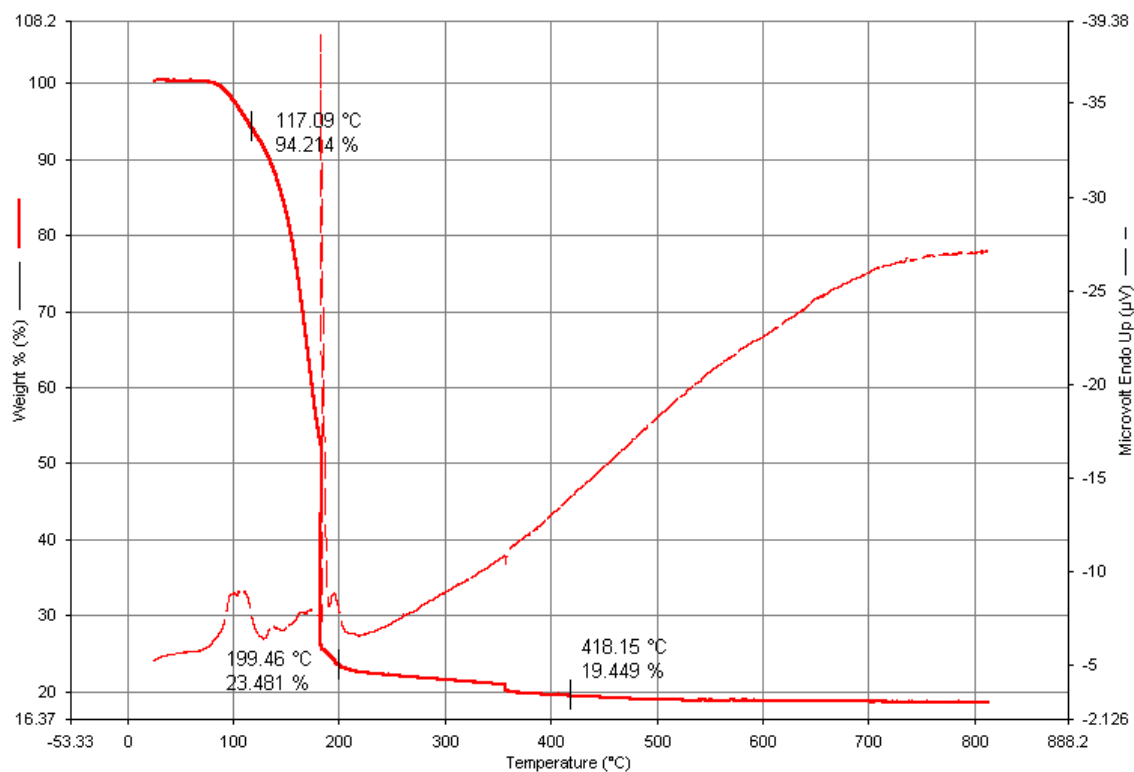


Fig. S20 TG-DTA data for compound **1** (N₂, 10°C/min).

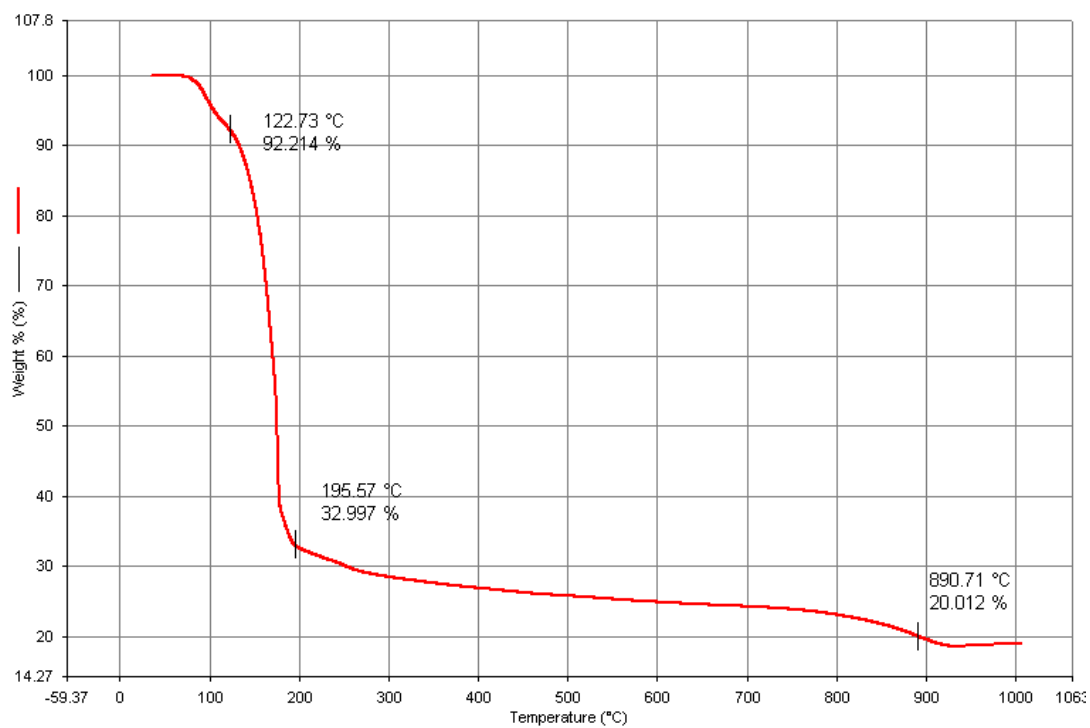


Fig. S21 TGA data for compound **2** (N₂, 10°C/min).

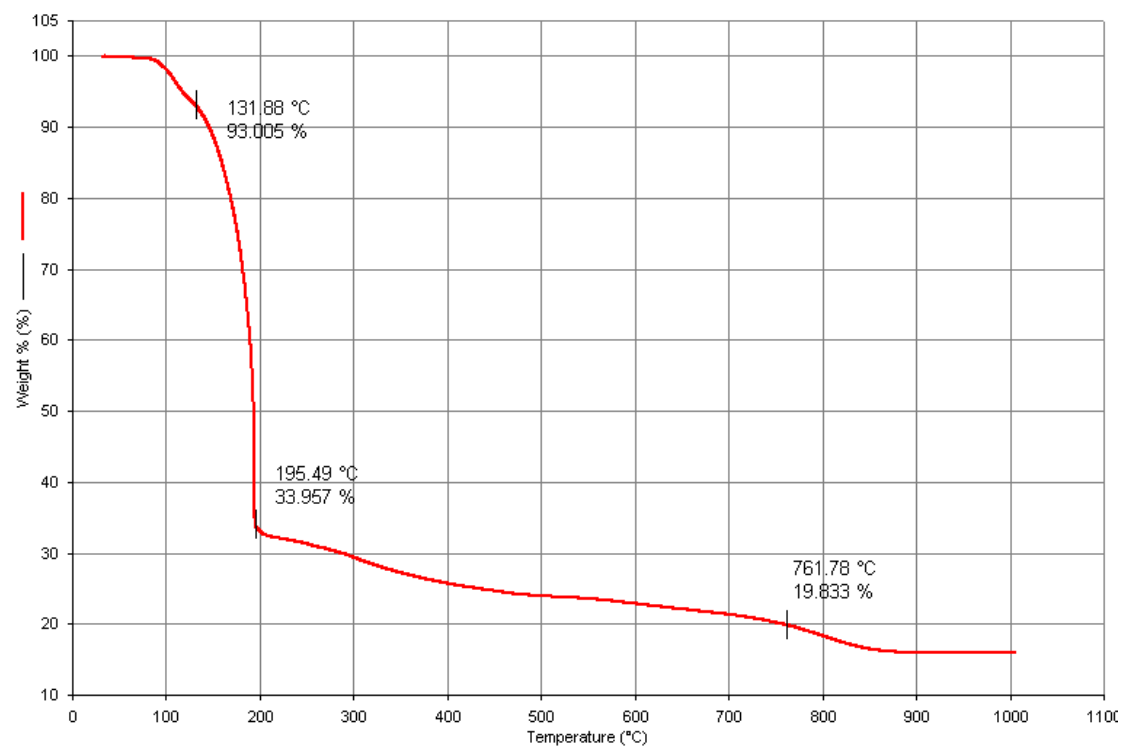


Fig. S22 TGA data for compound **3** (N₂, 10°C/min).

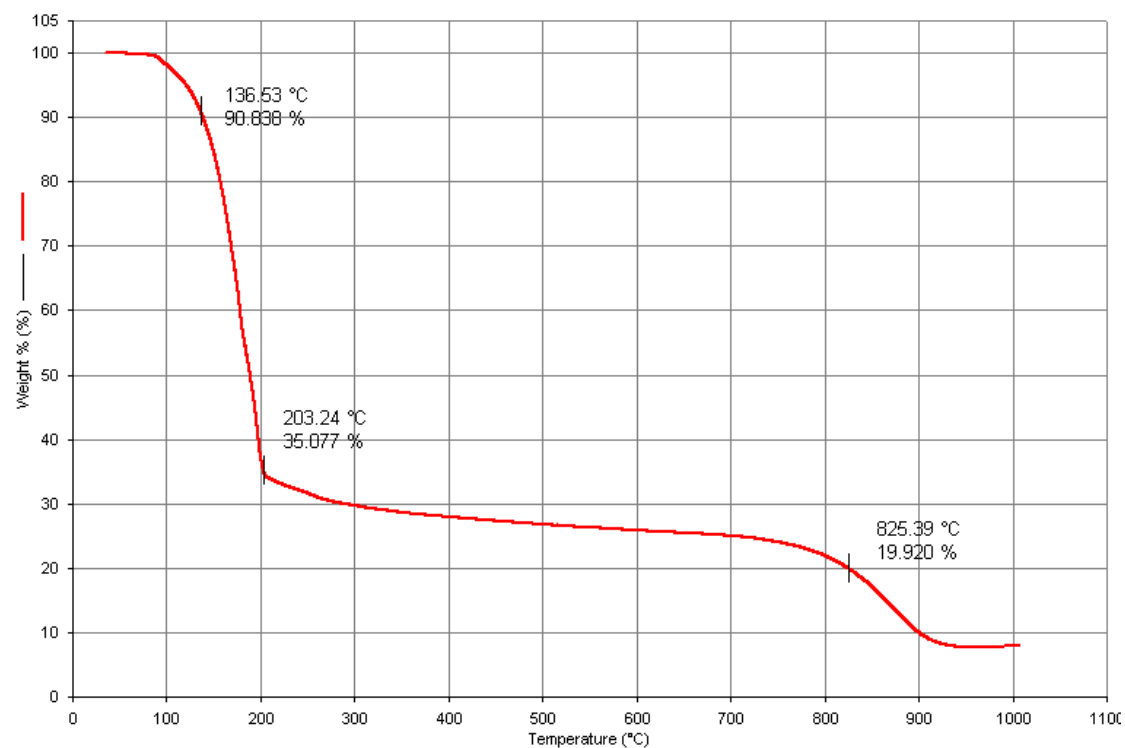


Fig. S23 TGA data for compound **4** (N₂, 10°C/min).

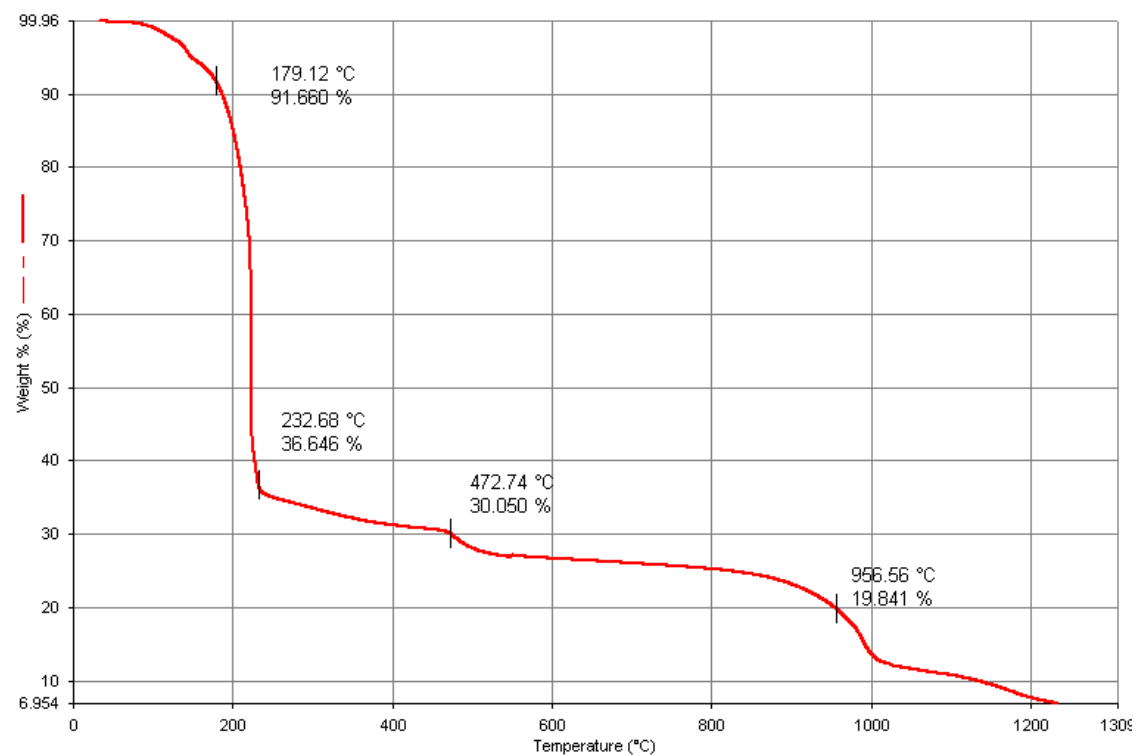


Fig. S24 TGA data for compound **5** (N₂, 10°C/min).

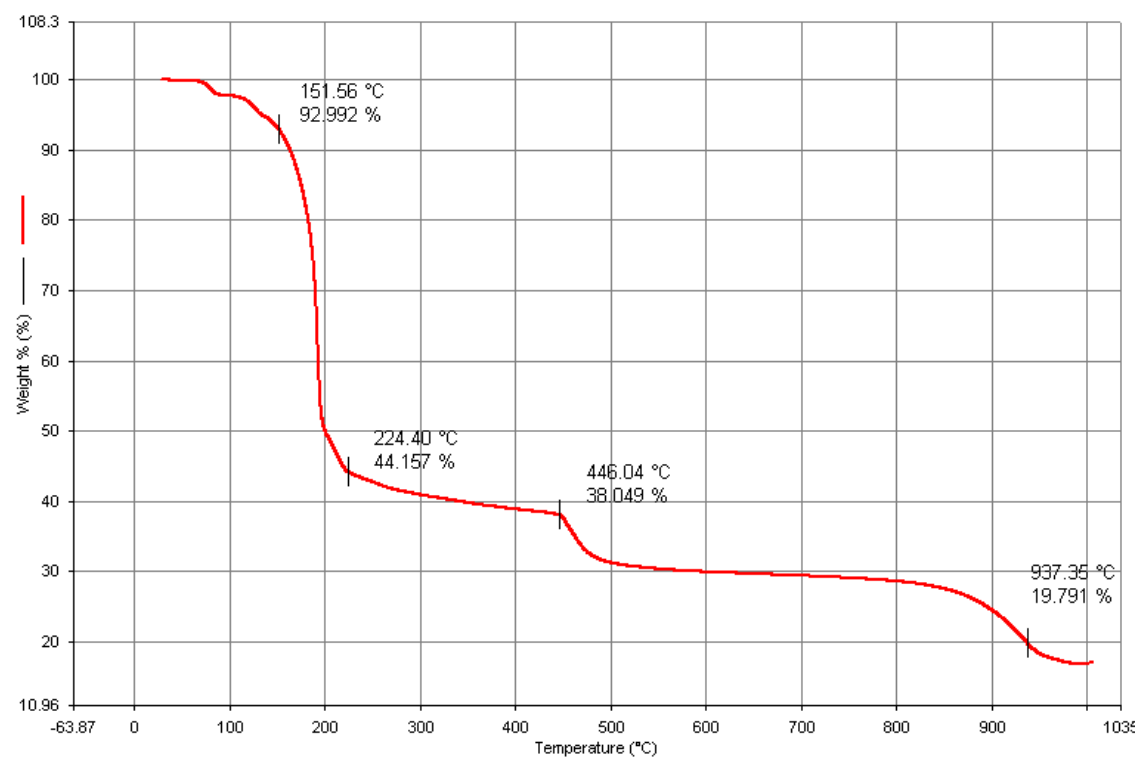


Fig. S25 TGA data for compound **6** (N₂, 10°C/min).

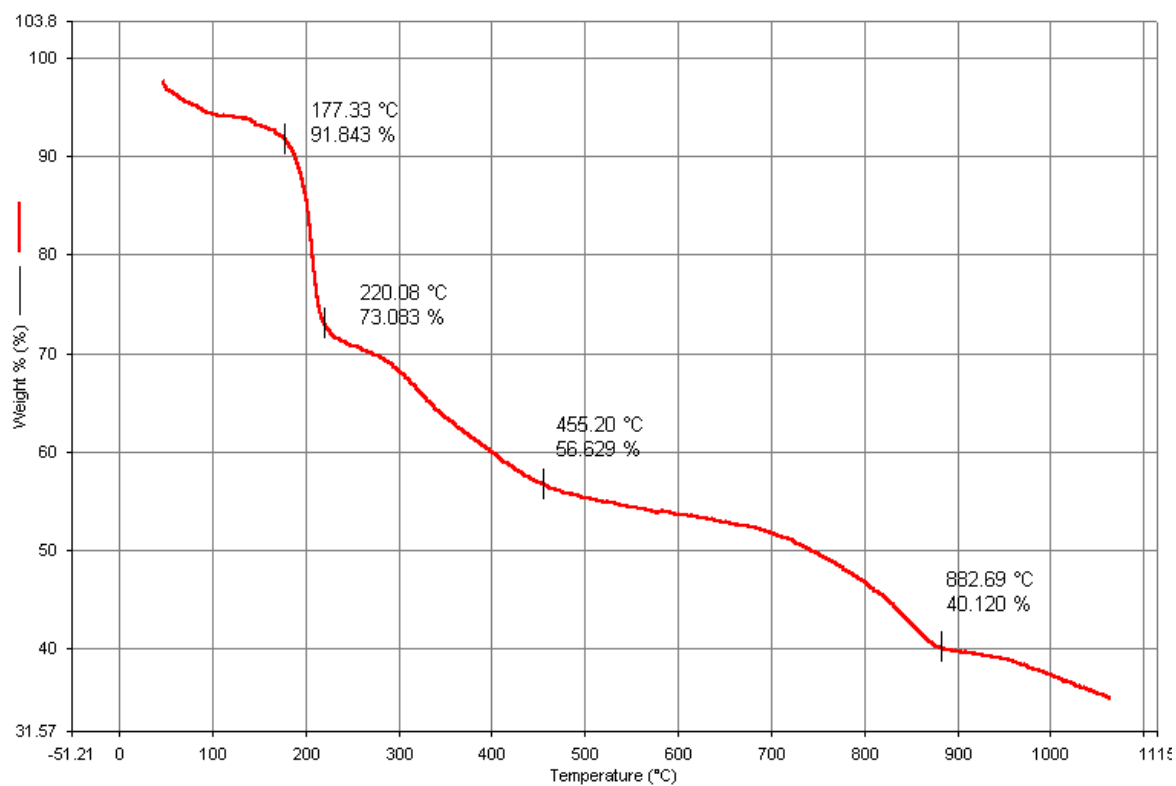


Fig. S26 TGA data for compound **7** (N₂, 10°C/min).

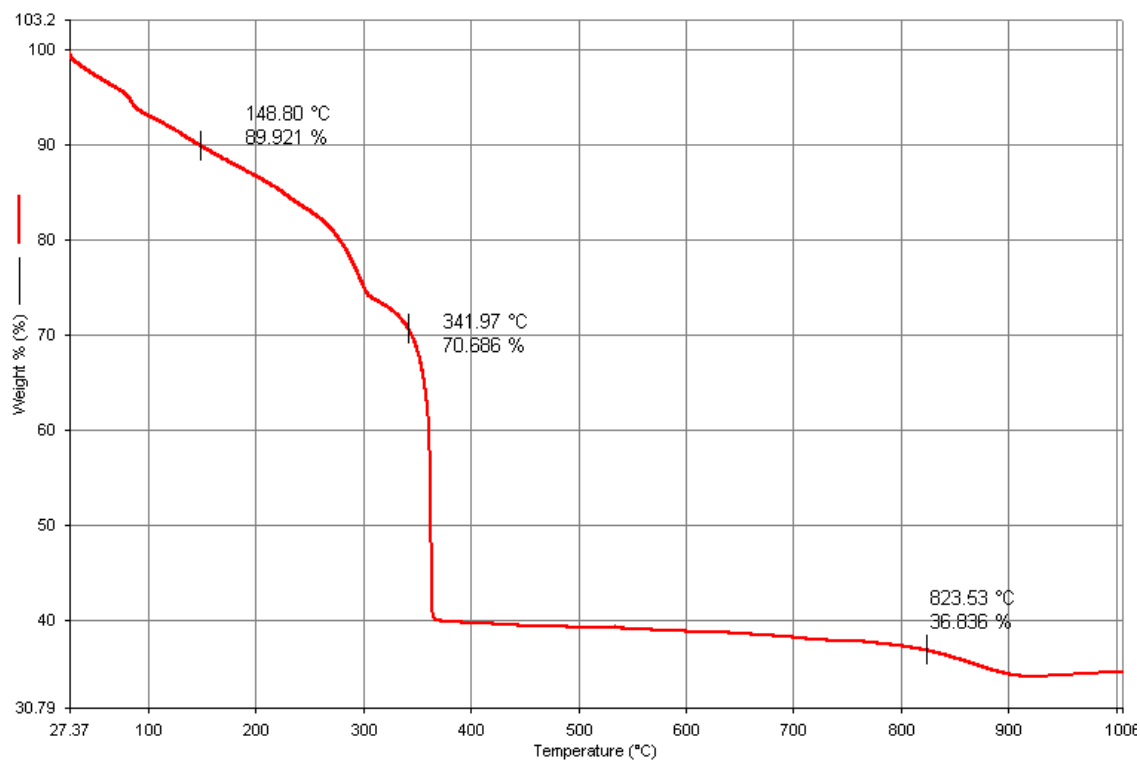


Fig. S27 TGA data for compound **8** (N₂, 10°C/min).

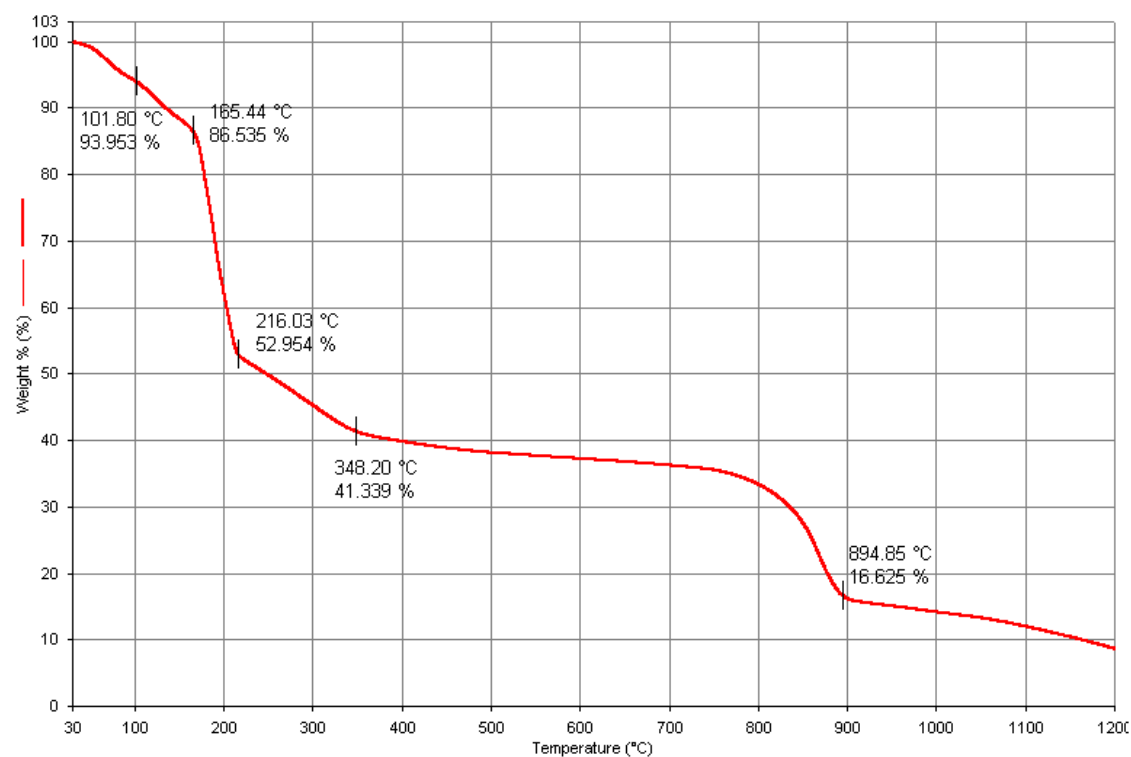


Fig. S28 TGA data for compound **9** (N₂, 10°C/min).

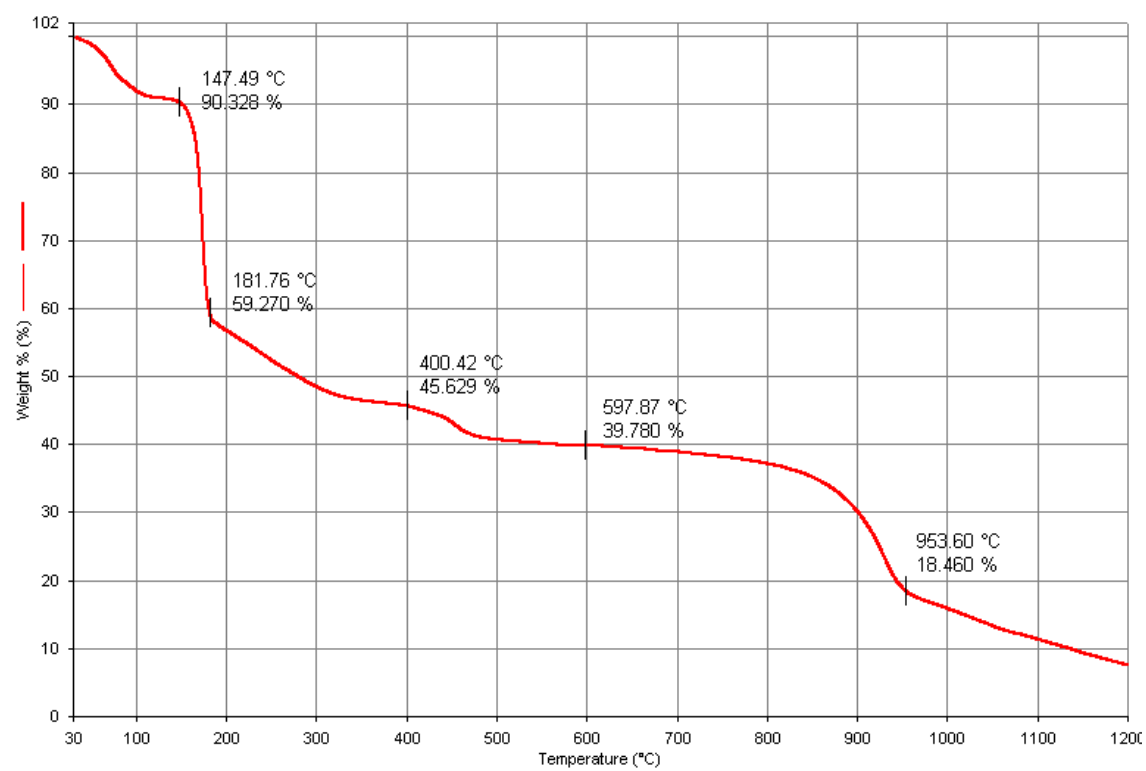


Fig. S29 TGA data for compound **10** (N₂, 10°C/min).

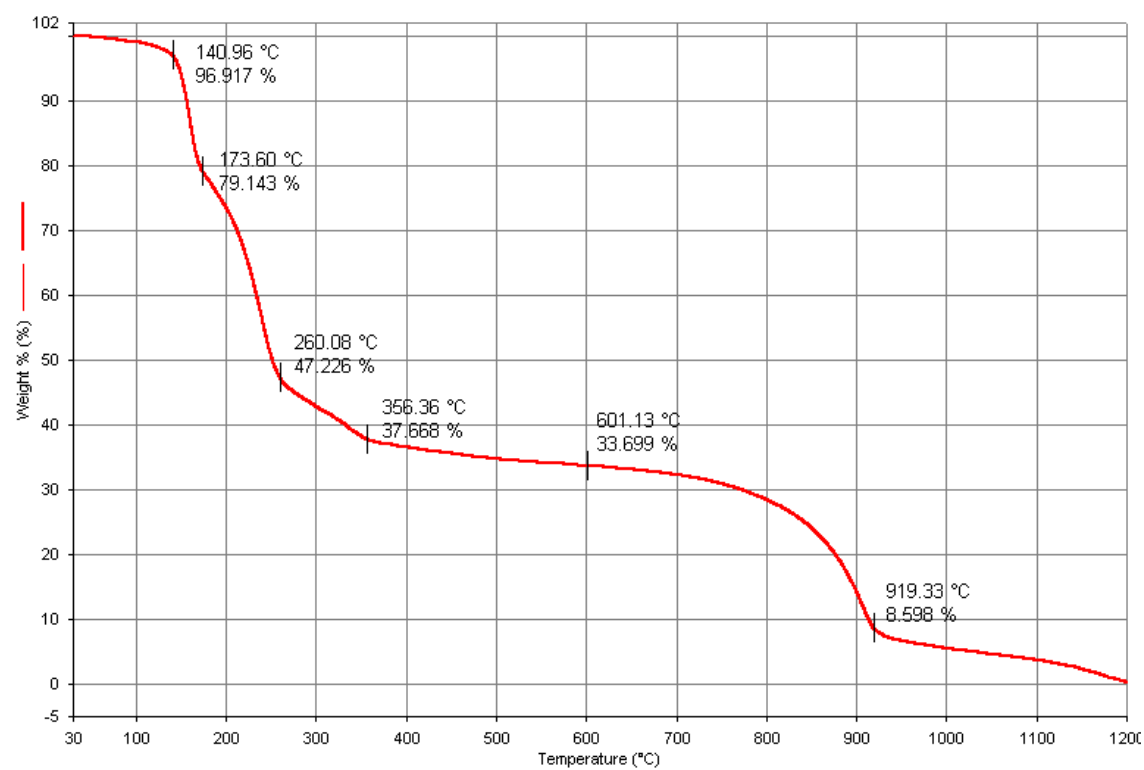


Fig. S30 TGA data for compound **11** (N₂, 10°C/min).



Fig. S31 EPR spectra for compounds **1(a)**, **2(b)** and **3(c)** (Recorded at room temperature).

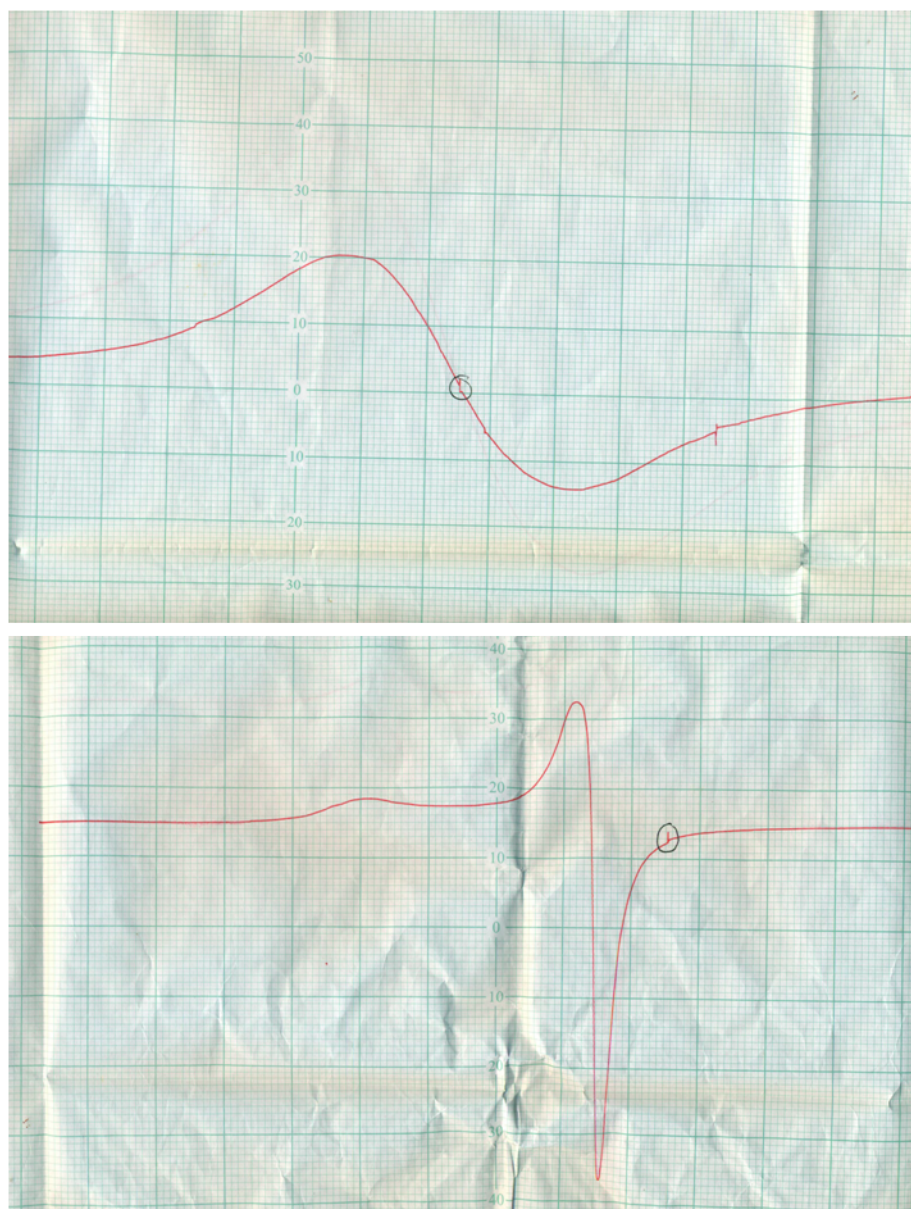


Fig. S32 EPR spectra for compounds **5** (top) and **7** (bottom) (Recorded at room temperature).

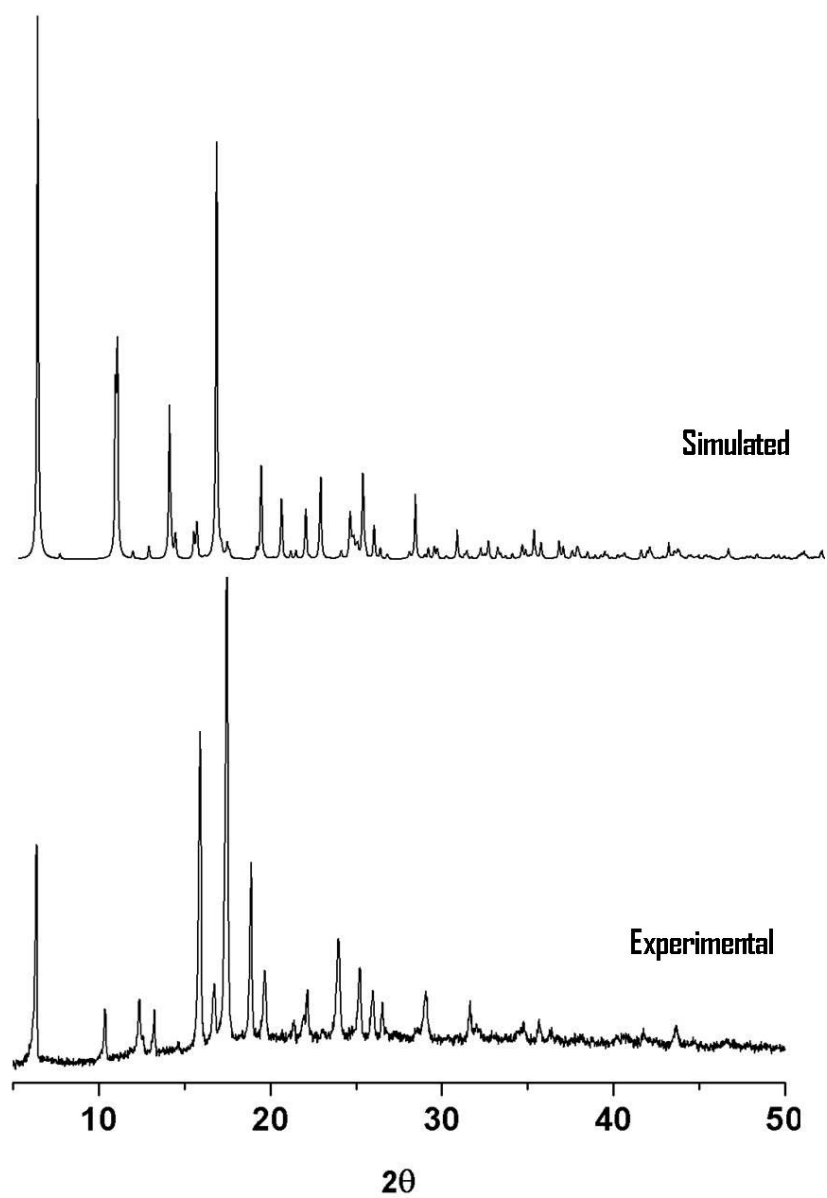


Fig. S33 PXRD pattern of **2**.

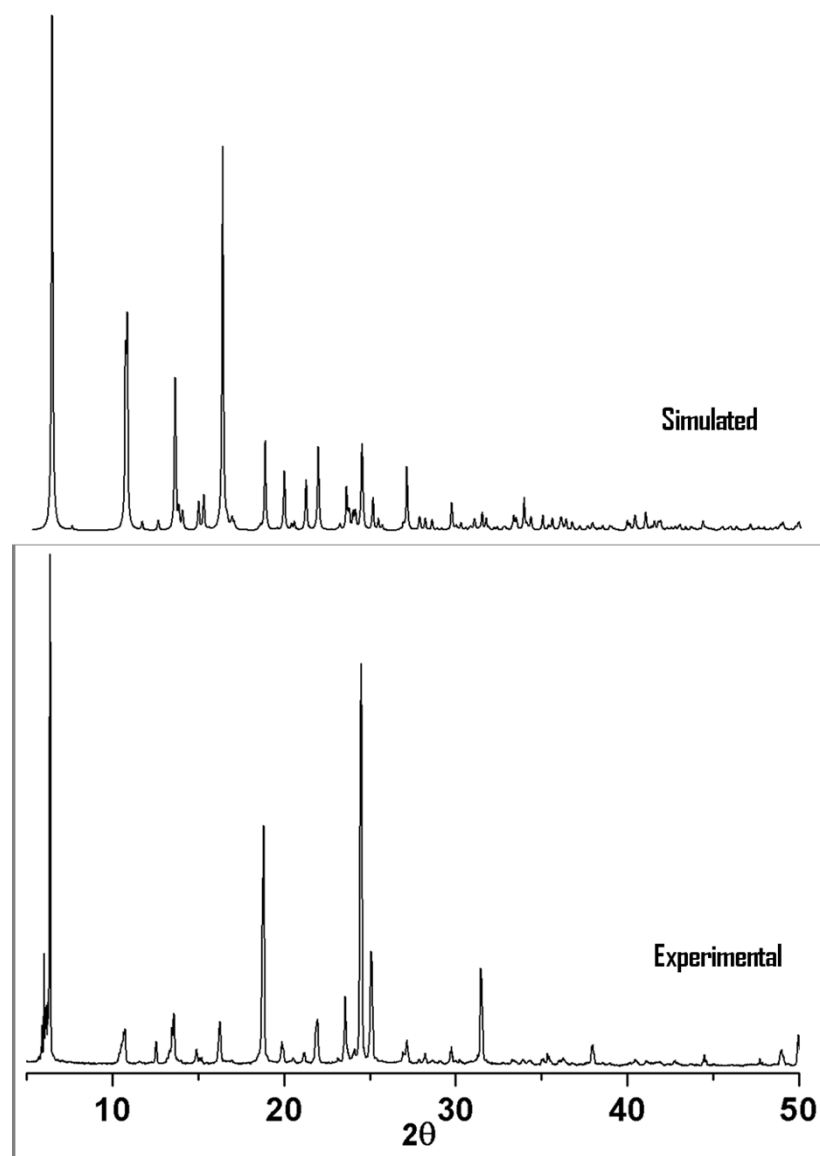


Fig. S34 PXRd pattern of **3**.

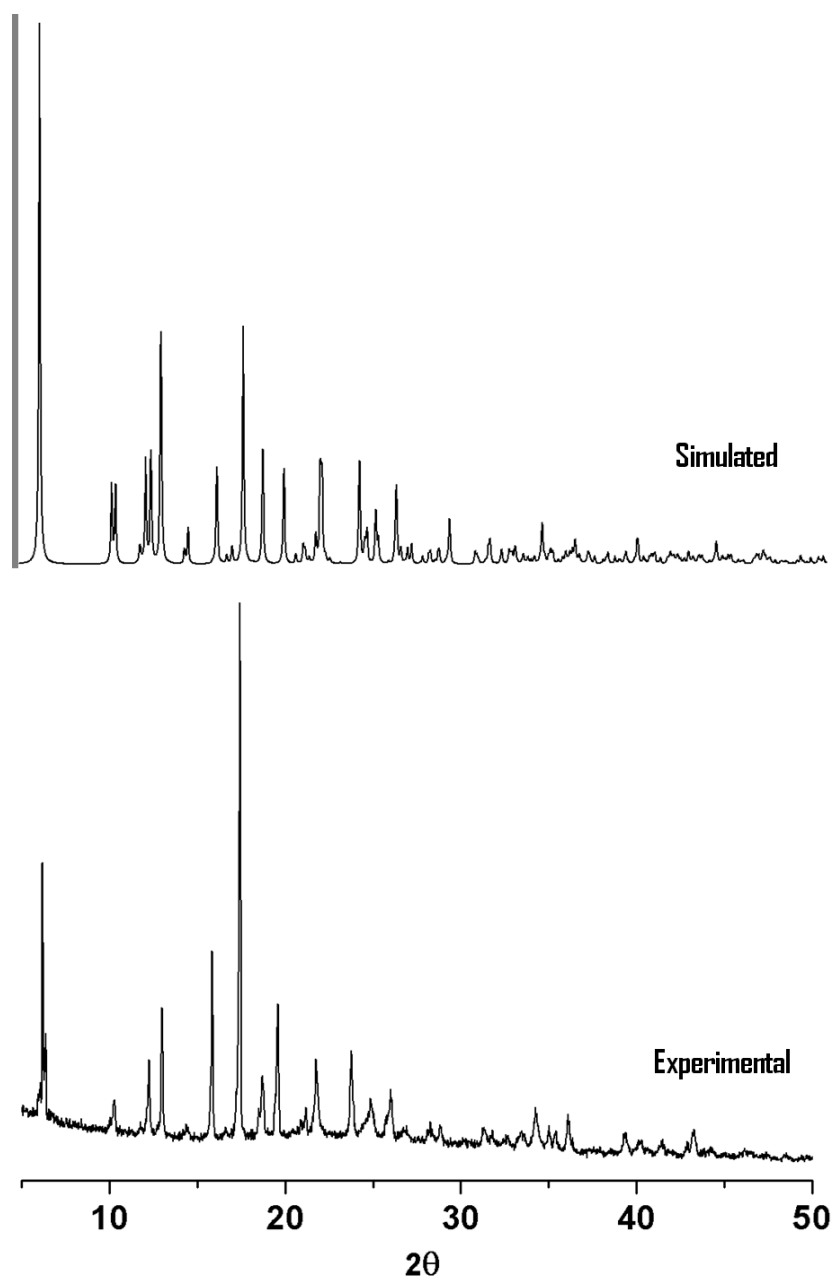


Fig. S35 PXRD pattern of **4**.

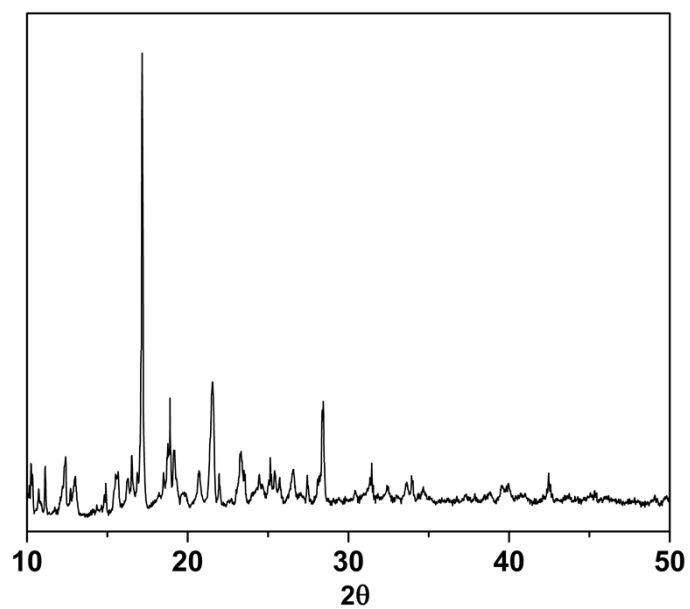


Fig. S36 PXRD pattern of **5**.

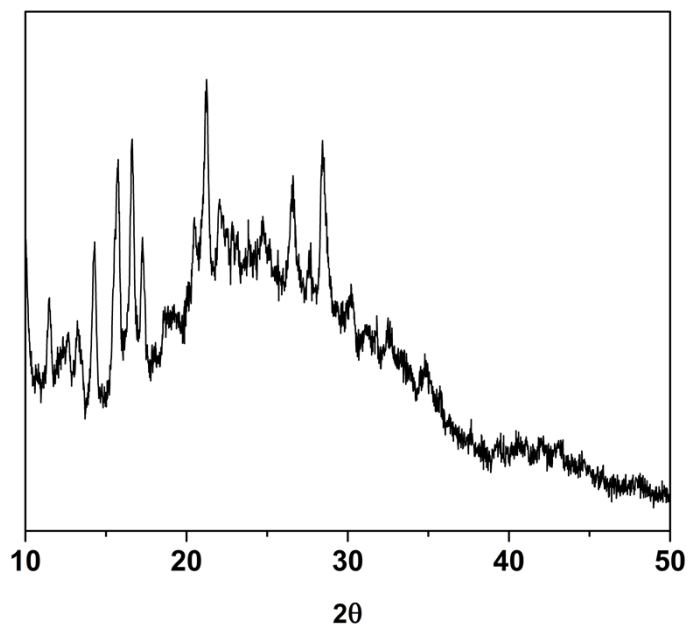


Fig. S37 PXRD pattern of **6**.

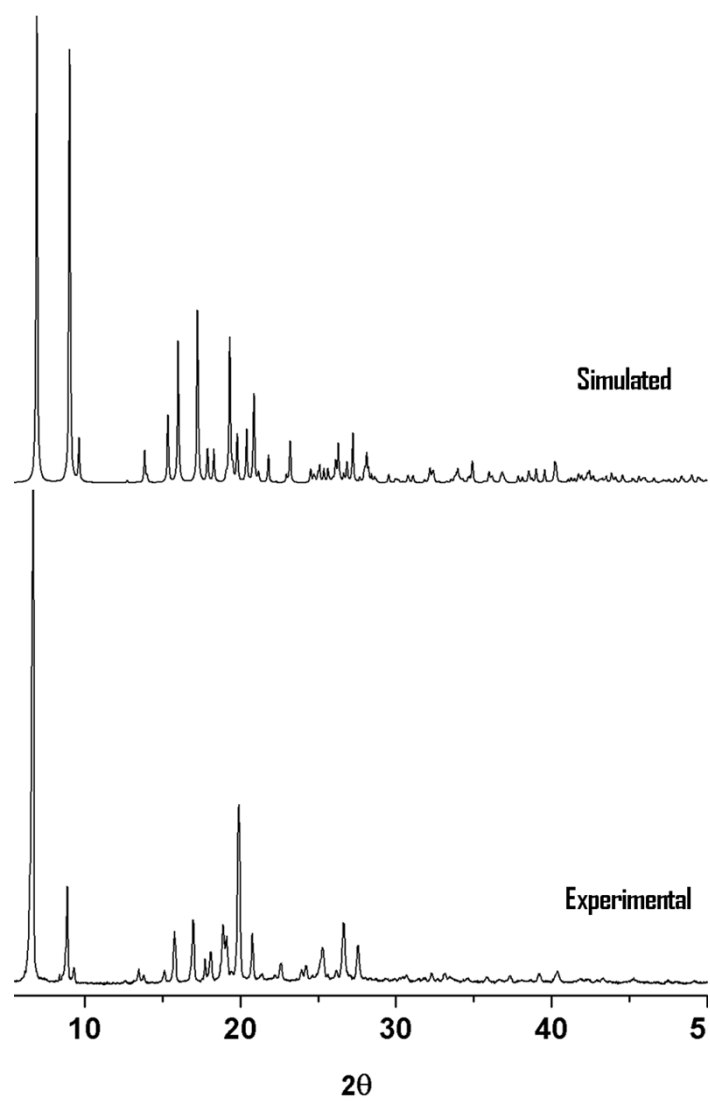


Fig. S38 PXRD pattern of **9**.

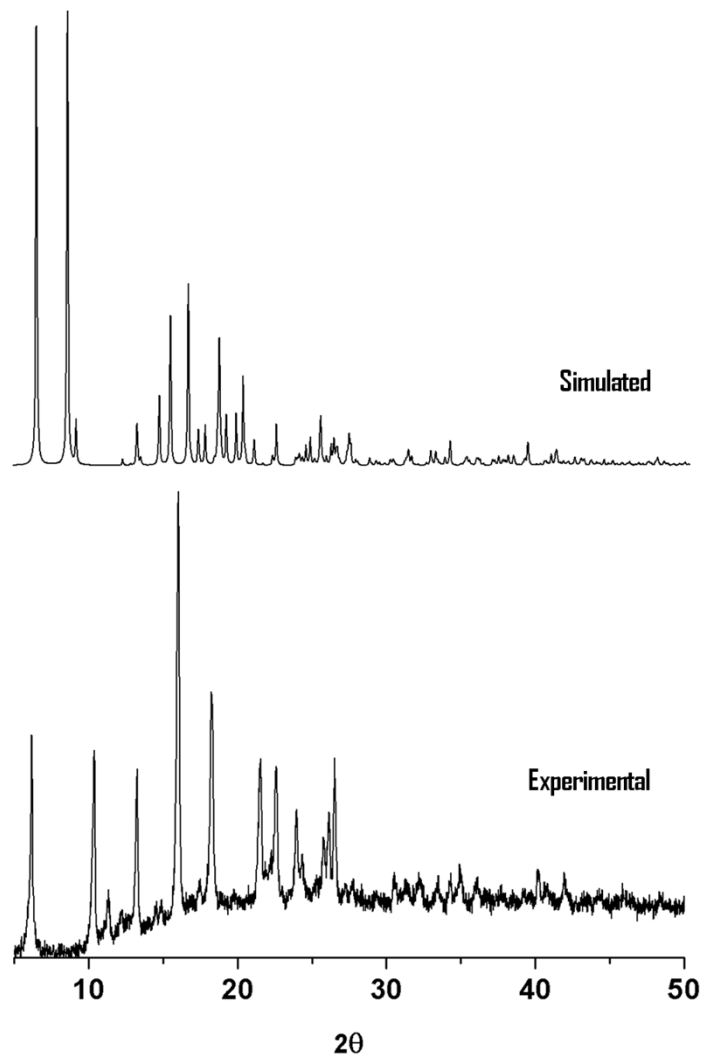


Fig. S39 PXRd pattern of **10**.

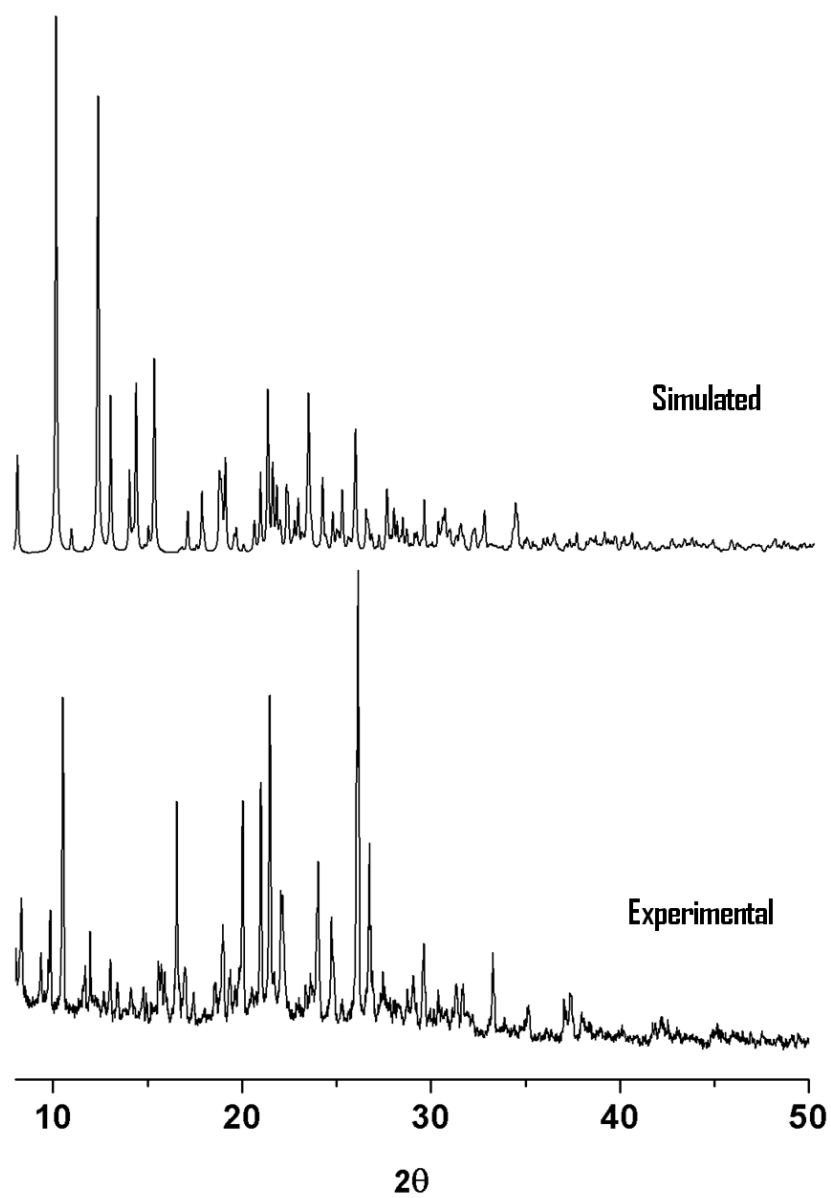


Fig. S40 PXRd pattern of **11**.