Dalton Transactions

Supplementary Information

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A cobalt(II) coordination polymer-derived catalyst engineered *via* temperature-induced semi-reversible single-crystal-to-single-crystal (SCSC) dehydration for efficient liquid-phase epoxidation of olefins

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Table S1 Selected bond lengths [Å] and angles [°] for compound **1**.

Bond Length					
Residue: 1					
Co1–O1	2.107(3)	Co1–O10W^{i}	2.085(3)	O3–C5	1.251(5)
Co1–O1^{i}	2.107(3)	Co2–O11W	2.029(3)	O4–C5	1.264(4)
Co2–O4^{ii}	2.104(3)	Co2–O11W^{ii}	2.029(3)	C1–C2	1.499(6)
Co2–O4^{ii}	2.104(3)	Co2–O12W	2.128(3)	C2–C3	1.391(5)
Co1–O9W	2.066(4)	Co2–O12W^{ii}	2.128(3)	C2–C4^{v}	1.401(5)
Co1–O9W^{ii}	2.066(4)	O1–C1	1.272(4)	C3–C4	1.387(6)
Co1–O10W	2.085(3)	O2–C1	1.253(5)	C4–C5	1.512(5)
Residue: 2					
Co3–O5	2.123(3)	Co3–O14W^{iii}	2.096(3)	O7–C10	1.246(6)
Co3–O5^{iii}	2.123(3)	Co4–O15W	2.100(3)	O8–C10	1.278(4)
Co4–O8	2.085(3)	Co4–O15W^{iv}	2.100(3)	C6–C7	1.509(5)
Co4–O8^{iv}	2.085(3)	Co4–O16W	2.080(4)	C7–C8	1.379(6)
Co3–O13W	2.055(4)	Co4–O16W^{iv}	2.080(4)	C7–C9^{vi}	1.401(4)
Co3–O13W^{iii}	2.055(4)	O5–C6	1.265(4)	C8–C9	1.390(5)
Co3–O14W	2.096(3)	O6–C6	1.250(5)	C9–C10	1.505(6)
Bond Angle					
Residue: 1					
O1–Co1–O9W	89.22(13)	O4–Co2–O4^{ii}	180.00	O2–C1–C2	118.5(3)
O1–Co1–O10W	86.11(12)	O4–Co2–O11W^{ii}	92.23(12)	C1–C2–C3	118.3(3)
O1–Co1–O1^{i}	180.00	O4–Co2–O12W^{ii}	87.17(12)	C1–C2–C4^{v}	122.7(3)
O1–Co1–O9W^{i}	90.78(13)	O11W–Co2–O12W	86.80(14)	C3–C2–C4^{v}	118.8(4)
O1–Co1–O10W^{i}	93.89(12)	O11W–Co2–O4^{ii}	92.23(12)	C2–C3–C4	121.9(3)
O9W–Co1–O10W	93.53(14)	O11W–Co2–O11W^{ii}	180.00	C3–C4–C5	117.8(3)
O9W–Co1–O1^{i}	90.78(13)	O11W–Co2–O12W^{ii}	93.20(14)	C3–C4–C2^{v}	119.4(3)
O9W–Co1–O9W^{i}	180.00	O12W–Co2–O4^{ii}	87.17(12)	C5–C4–C2^{v}	122.8(4)
O9W–Co1–O10W^{i}	86.48(14)	O12W–Co2–O11W^{ii}	93.20(14)	O3–C5–O4	125.1(3)
O10W–Co1–O1^{i}	93.89(12)	O12W–Co2–O12W^{ii}	180.00	O3–C5–C4	117.5(3)
O10W–Co1–O9W^{i}	86.48(14)	O4^{ii}–Co2–O11W^{ii}	87.78(12)	O4–C5–C4	117.4(3)
O10W–Co1–O10W^{i}	180.00	O4^{ii}–Co2–O12W^{ii}	92.83(12)	Co1–O9W–H9WA	104(5)
O1^{i}–Co1–O9W^{i}	89.22(13)	O11W^{ii}–Co2–O12W^{ii}	86.80(14)	Co1–O9W–H9WB	136(3)
O1^{i}–Co1–O10W^{i}	86.11(12)	Co1–O1–C1	130.4(3)	Co1–O10W–H10WA	118(3)
O9W^{i}–Co1–O10W^{i}	93.53(14)	Co2–O4–C5	126.8(3)	Co1–O10W–H10WB	121(4)
O4–Co2–O11W	87.78(12)	O1–C1–O2	124.6(4)	Co2–O11W–H11WA	107(4)
O4–Co2–O12W	92.83(12)	O1–C1–C2	116.8(4)	Co2–O11W–H11WB	127(5)

Table S1 Continued...

Bond Angle					
Residue: 1					
Co2–O12W–H12WA	104(5)	Co2–O12W–H12WB	122(3)	C2–C3–H3	120(3)
C4–C3–H3	118(3)	H9WA–O9–H9WB	108(6)	H10WA–O10W–H10WB	107(6)
H11WA–O11W–H11WB	103(6)	H12WA–O12W–H12WB	111(5)		
Residue: 2					
O5–Co3–O13W	87.31(13)	O15W–Co4–O16W	87.05(14)	C8–C9–C7^{vi}	118.3(4)
O5–Co3–O14W	90.69(12)	O15W–Co4–O8W^{iv}	91.50(12)	C10–C9–C7^{vi}	123.7(3)
O5–Co3–O5^{iii}	180.00	O15W–Co4–O15W^{iv}	180.00	O7–C10–O8	124.2(4)
O5–Co3–O13W^{iii}	92.69(13)	O15W–Co4–O16W^{iv}	92.95(14)	O7–C10–C9	119.6(3)
O5–Co3–O14W^{iii}	89.31(12)	O16W–Co4–O8^{iv}	89.95(13)	O8–C10–C9	116.1(4)
O13W–Co3–O14W	92.68(14)	O16W–Co4–O15W^{iv}	92.95(14)	Co3–O13W–H13WA	133(3)
O13W–Co3–O5^{iii}	92.69(13)	O16W–Co4–O16W^{iv}	180.00	Co3–O13W–H13WB	117(5)
O13W–Co3–O13W^{iii}	180.00	O8^{iv}–Co4–O15W^{iv}	88.50(12)	Co3–O14W–H14WA	119(4)
O13W–Co3–O14W^{iii}	87.32(14)	O8^{iv}–Co4–O16W^{iv}	90.05(13)	Co3–O14W–H14WB	103(4)
O14W–Co3–O5^{iii}	89.31(12)	O15W^{iv}–Co4–O16W^{iv}	87.05(14)	Co4–O15W–H15WA	116(3)
O14W–Co3–O13W^{iii}	87.32(14)	Co3–O5–C6	122.6(3)	Co4–O15W–H15WB	112(3)
O14W–Co3–O14W^{iii}	180.00	Co4–O8–C10	131.3(3)	Co4–O16W–H16WA	101(5)
O5^{iii}–Co3–O13W^{iii}	87.31(13)	O5–C6–O6	125.2(3)	Co4–O16W–H16WB	130(3)
O5^{iii}–Co3–O14W^{iii}	90.69(12)	O5–C6–C7	117.9(4)	C7–C8–H8	121(4)
O13W^{iii}–Co3–O14W^{iii}	92.68(14)	O6–C6–C7	116.9(3)	C9–C8–H8	116(4)
O8–Co4–O15W	88.50(12)	C6–C7–C8	117.3(3)	H13WA–O13W–H13BW	106(6)
O8–Co4–O16W	90.05(13)	C6–C7–C9^{vi}	123.3(3)	H14WA–O14W–H14WB	99(6)
O8–Co4–O8^{iv}	180.00	C8–C7–C9^{vi}	119.4(3)	H15WA–O15W–H15WB	109(5)
O8–Co4–O15W^{iv}	91.50(12)	C7–C8–C9	122.3(3)	H16WA–O16W–H16WB	106(6)
O8–Co4–O16W^{iv}	89.95(13)	C8–C9–C10	118.0(3)		

Symmetry codes: (i) 1–x, 2–y, 1–z; (ii) 2–x, 1–y, 2–z; (iii) 1–x, 1–y, 2–z; (iv) –x, 2–y, 1–z); (v) 2–x, 1–y, 1–z; (vi) 1–x, 1–y, 1–z.

Table S2 Selected bond lengths [Å] and angles [°] for compound **1'**.

Bond Length					
Co1–O1	2.024(3)	Co1–O2^{iv}	2.079(3)	C1–C2	1.509(5)
Co1–O2^{ii}	2.194(3)	Co1–O2^{v}	2.079(3)	C2–C3	1.388(5)
Co1–O2^{iii}	2.194(3)	O1–C1	1.244(5)	C2–C2^{vii}	1.389(7)
Co1–O1^{i}	2.024(3)	O2–C1	1.278(5)	C3–H3	0.95
Bond Angle					
O1–Co1–O2^{ii}	87.61(12)	O2^{iii}–Co1–O1^{i}	87.61(12)	Co1^{vi}–O2–Co1^{iv}	103.59(12)
O1–Co1–O2^{iii}	86.33(12)	O2^{iii}–Co1–O2^{iv}	110.89(12)	O1–C1–O2	123.3(4)

Table S2 Continued…

O1–Co1–O1^{i}	98.09(12)	O2^{iii}–Co1–O2^{v}	76.42(12)	O1–C1–C2	116.2(3)
O1–Co1–O2^{iv}	93.11(12)	O1^{i}–Co1–O2^{iv}	159.00(12)	O2–C1–C2	120.4(4)
O1–Co1–O2^{v}	159.00(12)	O1^{i}–Co1–O2^{v}	93.11(12)	C1–C2–C3	115.7(4)
O2^{ii}–Co1–O2^{iii}	170.74(11)	O2^{iv}–Co1–O2^{v}	82.21(12)	C1–C2–C2^{vii}	125.7(3)
O2^{ii}–Co1–O1^{i}	86.33(12)	Co1–O1–C1	127.9(3)	C3–C2–C2^{vii}	118.6(4)
O2^{ii}–Co1–O2^{iv}	76.42(12)	C1–O2–Co1^{vi}	124.5(3)	C2–C3–C2^{viii}	122.9(5)
O2^{ii}–Co1–O2^{v}	110.89(12)	C1–O2–Co1^{iv}	129.2(3)	C2–C3–H3	119.0

Symmetry codes: (i) 1–x, y, 2–z; (ii) x, y, 1+z; (iii) 1–x, y, 1–z; (iv) 1/2–x, 3/2–y, 1–z; (v) 1/2+x, 3/2–y, 1+z; (vi) x, y, –1+z); (vii) –x, y, –z; (viii) x, 1–y, z.

Table S3 Selected bond lengths [Å] and angles [°] for compound **2**.

Bond Length					
Co1–O1^{i}	1.991(6)	Co2–O5W	2.087(8)	O3–C5	1.221(9)
Co1–O4^{ii}	2.082(6)	Co2–O2^{vi}	2.088(5)	O4–C5	1.304(11)
Co1–O4^{iii}	2.172(6)	Co2–O2^{vii}	2.088(5)	C1–C2	1.512(11)
Co1–O4^{iv}	2.172(6)	Co2–O2^{viii}	2.184(5)	C2–C3	1.393(13)
Co1–O1	1.991(6)	Co2–O5W^{viii}	2.087(8)	C2–C4^{v}	1.409(11)
Co1–O4^{v}	2.082(6)	O1–C1	1.248(10)	C3–C4	1.388(12)
Co2–O2	2.184(5)	O2–C1	1.280(9)	C4–C5	1.504(12)
Bond Angle					
O1–Co1–O4^{ii}	93.5(2)	O2–Co2–O2^{viii}	180.00	Co1^{x}–O4–Co1^{xii}	104.2(3)
O1–Co1–O4^{iii}	87.1(2)	O2–Co2–O5W^{viii}	91.3(3)	O1–C1–O2	121.8(7)
O1–Co1–O4^{iv}	92.9(2)	O5W–Co2–O2^{vi}	92.4(3)	O1–C1–C2	122.0(7)
O1–Co1–O1^{i}	180.00	O5W–Co2–O2^{vii}	87.6(3)	O2–C1–C2	115.8(7)
O1–Co1–O4^{v}	86.5(2)	O5W–Co2–O2^{viii}	91.3(3)	C1–C2–C3	114.6(7)
O4^{ii}–Co1–O4^{v}	104.2(2)	O5W–Co2–O5W^{viii}	180.00	C1–C2–C4^{v}	126.8(8)
O4^{ii}–Co1–O4^{iv}	75.8(2)	O2^{vi}–Co2–O2^{vii}	180.0(3)	C3–C2–C4^{v}	118.6(8)
O4^{ii}–Co1–O1^{i}	86.5(2)	O2^{vi}–Co2–O2^{viii}	76.4(2)	C2–C3–C4	123.6(8)
O4^{ii}–Co1–O4^{v}	180.0(3	O2^{vi}–Co2–O5W^{viii}	87.6(3)	C3–C4–C5	114.6(7)
O4^{iii}–Co1–O4^{iv}	180.0(3)	O2^{vii}–Co2–O2^{viii}	103.6(2)	C3–C4–C2^{v}	117.8(8)
O4^{iii}–Co1–O1^{i}	92.9(2)	O2^{vii}–Co2–O5W^{viii}	92.4(3)	C5–C4–C2^{v}	127.6(7)
O4^{iii}–Co1–O4^{v}	75.8(2)	O2^{viii}–Co2–O5W^{viii}	88.7(3)	O3–C5–O4	122.7(8)
O4^{iv}–Co1–O1^{i}	87.1(2)	Co1–O1–C1	144.0(5)	O3–C5–C4	119.2(8)
O4^{iv}–Co1–O4^{v}	104.2(2)	Co2–O2–C1	131.5(5)	O4–C5–C4	118.1(7)
O1^{i}–Co1–O4^{v}	93.5(2)	Co2–O2–Co2^{ix}	103.6(2)	Co2–O5W–H5WA	99(8)
O2–Co2–O5W	88.7(3)	C1–O2–Co2^{ix}	120.1(5)	Co2–O5W–H5WB	129(8)
O2–Co2–O2^{vi}	103.6(2)	C5–O4–Co1^{x}	134.4(5)	C2–C3–H3	119(5)
O2–Co2–O2^{vii}	76.4(2)	C5–O4–Co1^{xii}	113.0(5)	C4–C3–H3	117(5)

Symmetry codes: (i) –x, 2–y, 1–z; (ii) –1+x, 1+y, z; (iii) x, 1+y, z; (iv) –x, 1–y, 1–z; (v) 1–x, 1–y, 1–z); (vi) 1+x, y, z; (vii) –x, 1–y, –z; (viii) 1–x, 1–y, –z; (ix) –1+x, y, z; (x) x, –1+y, z; (xi) 1+x, –1+y, z.

Table S4 List of hydrogen bond interactions for compounds **1**, **1'** and **2**.

CP	D–H···A	*d*(D–H) /Å	*d*(H···A) /Å	*d*(D–A) /Å	∠(D–H···A) /°	Symmetry
1	O1W–H1WB···O2W	0.97(7)	1.79(7)	2.749(7)	170(4)	x, y, z
	O1W–H1WA···O2W	0.70(4)	2.07(4)	2.773(5)	178(8)	1–x, 2–y, 2–z
	O2W–H2WB···O15W	0.72(5)	2.20(6)	2.903(5)	163(7)	x, y, z
	O2W–H2WA···O14W	0.79(7)	2.05(7)	2.800(6)	160(6)	–x, 2–y, 2–z
	O4W–H4WB···O12W	0.78(8)	2.04(7)	2.776(5)	159(8)	x, y, z
	O3W–H3WA···O4W	0.71(5)	2.13(5)	2.773(5)	152(5)	–1+x, y, z
	O3W–H3WB···O10W	0.85(9)	2.11(9)	2.935(7)	164(6)	–1+x, y, z
	O3W–H3WB···O9W	0.85(9)	2.58(6)	2.987(5)	111(6)	–x, 2–y, 1–z
	O4W–H4WA···O3W	0.74(11)	2.01(10)	2.747(5)	179(19)	–x, 2–y, 2–z
	O9W–H9WA···O1	0.85(7)	2.59(9)	2.931(6)	105(6)	
	O9W–H9WA···O2	0.85(7)	1.82(7)	2.645(4)	163(8)	
	O9W–H9WB···O8	0.88(7)	1.85(7)	2.718(6)	170(4)	x, y, z
	O10W–H10WA···O6	0.80(5)	1.93(5)	2.689(4)	160(4)	x, y, z
	O10W–H10WB···O1W	0.84(7)	1.85(7)	2.688(5)	174(5)	x, y, z
	O11W–H11WA···O3	0.82(5)	1.88(5)	2.644(4)	155(5)	2–x, 1–y, 2–z
	O11W–H11WB···O1W	0.68(5)	2.09(5)	2.750(4)	163(8)	1+x, –1+y, z
	O12W–H12WA···O2	0.76(6)	1.95(5)	2.697(4)	173(7)	x, y, 1+z
	O12W–H12WB···O5	0.89(6)	1.91(6)	2.793(5)	171(5)	1–x, 1–y, 2–z
	O13W–H13WA···O4	0.82(6)	1.95(6)	2.772(5)	175(4)	x, y, z
	O13W–H13WB···O7	0.74(5)	2.01(5)	2.732(4)	166(7)	1–x, 1–y, 1–z
	O14W–H14WA···O4W	0.83(8)	1.87(8)	2.696(7)	173(4)	x, y, z
	O14W–H14WB···O6	0.79(5)	1.85(6)	2.595(4)	157(6)	
	O15W–H15WA···O3W	0.84(6)	1.90(6)	2.710(7)	161(4)	x, y, z
	O15W–H15WB···O3	0.79(5)	1.94(5)	2.702(4)	164(4)	–1+x, y, z
	O16W–H16WA···O7	0.84(5)	1.84(6)	2.663(4)	166(7)	–x, 2–y, 1–z
	O16W–H16WA···O8	0.84(5)	2.57(7)	2.944(6)	108(5)	–x, 2–y, 1–z
	O16W–H16WB···O1	0.86(7)	1.90(7)	2.744(6)	170(3)	1–x, 2–y, 1–z
	C8–H8···O8	0.94(5)	2.46(6)	2.795(5)	101(4)	
1'	**No classical hydrogen bonds**					
2	O5W–H5WA···O1	1.05(13)	2.27(13)	3.026(9)	128(9)	1+x, y, z
	O5W–H5WB···O3	0.78(11)	2.21(11)	2.942(10)	151(10)	1–x, 1–y, –z
	O5W–H5WA···O4	1.05(13)	2.51(13)	3.463(9)	151(10)	x, 1+y, z
	C3–H3···O2	0.89(7)	2.32(8)	2.671(11)	103(6)	

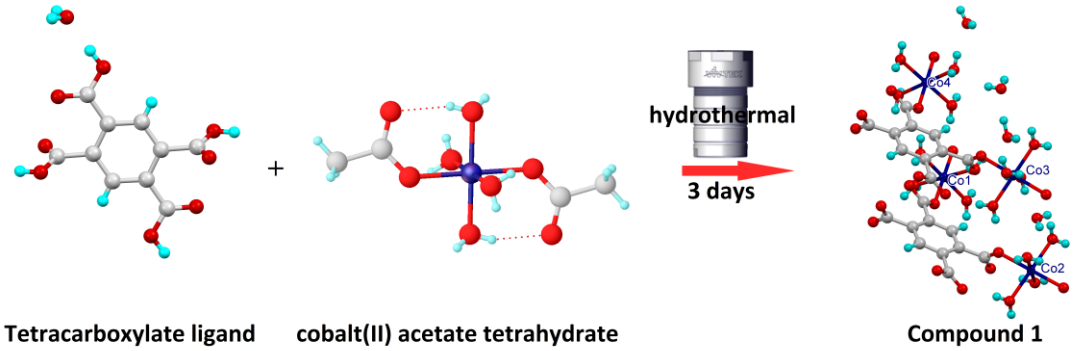
Table S5 Selected geometry parameters for Cg(I)–Cg(J), Y–X···Cg(J) intermolecular interactions along with all the associated angles in compounds **1**, **1′** and **2**.[a]

Cg(I)–Cg(J)	Cg–Cg (Å)	α (°)	β (°)	γ (°)	CgI_Perp (Å)	CgJ_Perp (Å)	Symmetry
compound 1							
Cg(1)···Cg(2)	5.398(3)	4.2(2)	43.7	42.5	3.9784(18)	-3.9030(17)	x, y, z
Cg(1)···Cg(2)	5.399(3)	4.2(2)	43.7	42.5	-3.9785(18)	3.9030(17)	1+x, y, z
Cg(1)···Cg(2)	5.398(3)	4.2(2)	43.7	42.5	-3.9784(18)	-3.9030(17)	1–x, 1–y, 1–z
Cg(1)···Cg(2)	5.399(3)	4.2(2)	43.7	42.5	3.9785(18)	3.9030(17)	2–x, 1–y, 1–z
Cg(2)···Cg(1)	5.399(3)	4.2(2)	42.5	43.7	3.9033(17)	-3.9784(18)	–1+x, y, z
Cg(2)···Cg(1)	5.398(3)	4.2(2)	42.5	43.7	-3.9027(17)	3.9784(18)	x, y, z
Cg(2)···Cg(1)	5.399(3)	4.2(2)	42.5	43.7	-3.9033(17)	-3.9784(18)	1–x, 1–y, 1–z
Cg(2)···Cg(1)	5.398(3)	4.2(2)	42.5	43.7	3.9027(17)	3.9784(18)	2–x, 1–y, 1–z
compound 1′							
Cg(1)···Cg(1)	4.548(3)	0.0(3)	44.8	44.8	-3.228(2)	3.228(2)	x, y, –1+z
Cg(1)···Cg(1)	4.548(3)	0.0(3)	44.8	44.8	3.228(2)	-3.228(2)	x, y, 1+z
Cg(1)···Cg(1)	4.548(3)	0.0(3)	44.8	44.8	3.228(2)	3.228(2)	–x, y, –1–z
Cg(1)···Cg(1)	4.548(3)	0.0(3)	44.8	44.8	-3.228(2)	-3.228(2)	–x, y, 1–z
Cg(1)···Cg(1)	4.548(3)	0.0(3)	44.8	44.8	3.228(2)	3.228(2)	–x, 1–y, –1–z
Cg(1)···Cg(1)	4.548(3)	0.0(3)	44.8	44.8	-3.228(2)	-3.228(2)	–x, 1–y, 1–z
Cg(1)···Cg(1)	4.548(3)	0.0(3)	44.8	44.8	-3.228(2)	3.228(2)	x, 1–y, –1+z
Cg(1)···Cg(1)	4.548(3)	0.0(3)	44.8	44.8	3.228(2)	-3.228(2)	x, 1–y, 1+z
compound 2							
Cg(1)···Cg(3)	4.9849(9)	34.8(3)	18.7	52.6	3.030(2)	-4.721(2)	–1+x, y, z
Cg(1)···Cg(3)	5.6657(10)	34.8(3)	33.6	57.7	-3.030(2)	4.721(2)	–1+x, 1+y, 1+z
Cg(1)···Cg(4)	4.9849(9)	34.8(3)	18.7	52.6	3.030(2)	-4.721(2)	–2+x, y, z
Cg(1)···Cg(4)	5.6657(10)	34.8(3)	33.6	57.7	-3.030(2)	4.721(2)	–2+x, 1+y, 1+z
Cg(1)···Cg(5)	5.799(4)	82.4(3)	54.9	70.6	-1.930(2)	-3.332(4)	x, y, z
Cg(1)···Cg(5)	5.431(4)	82.4(3)	52.2	37.4	-4.314(2)	3.332(4)	x, 1+y, z
Cg(2)···Cg(3)	4.9849(9)	34.8(3)	18.7	52.6	3.030(2)	-4.721(2)	x, y, z
Cg(2)···Cg(3)	5.6657(10)	34.8(3)	33.6	57.7	-3.030(2)	4.721(2)	x, 1+y, 1+z
Cg(2)···Cg(4)	4.9849(9)	34.8(3)	18.7	52.6	3.030(2)	-4.721(2)	–1+x, y, z
Cg(2)···Cg(4)	5.6657(10)	34.8(3)	33.6	57.7	-3.030(2)	4.721(2)	–1+x, 1+y, 1+z
Cg(2)···Cg(5)	5.431(4)	82.4(3)	52.2	37.4	4.314(2)	-3.332(4)	–1+x, 1+y, 1+z
Cg(2)···Cg(5)	5.799(4)	82.4(3)	54.9	70.6	1.930(2)	3.332(4)	–1+x, 1+y, z
Cg(3)···Cg(1)	4.9849(9)	34.8(3)	52.6	18.7	4.721(2)	-3.030(2)	x, –1+y, –1+z
Cg(3)···Cg(1)	5.6657(10)	34.8(3)	57.7	33.6	-4.721(2)	3.030(2)	x, y, z
Cg(3)···Cg(2)	5.6657(10)	34.8(3)	57.7	33.6	-4.721(2)	-3.030(2)	x, –1+y, –1+z
Cg(3)···Cg(2)	4.9849(9)	34.8(3)	52.6	18.7	-4.721(2)	3.030(2)	x, y, z
Cg(4)···Cg(1)	4.9849(9)	34.8(3)	52.6	18.7	4.721(2)	-3.030(2)	1+x, –1+y, –1+z
Cg(4)···Cg(1)	5.6658(10)	34.8(3)	57.7	33.6	-4.721(2)	3.030(2)	1+x, y, z

Table S5 Continued…

Cg(4)···Cg(1)	5.6657(10)	34.8(3)	57.7	33.6	4.721(2)	-3.030(2)	2+x, –1+y, –1+z
Cg(4)···Cg(1)	4.9850(9)	34.8(3)	52.6	18.7	-4.721(2)	3.030(2)	2+x, y, z
Cg(4)···Cg(1)	4.9849(9)	34.8(3)	52.6	18.7	-4.721(2)	-3.030(2)	–x, 1–y, –z
Cg(4)···Cg(1)	5.6658(10)	34.8(3)	57.7	33.6	4.721(2)	3.030(2)	–x, 2–y, 1–z
Cg(4)···Cg(2)	4.9849(9)	34.8(3)	52.6	18.7	4.721(2)	-3.030(2)	x, –1+y, –1+z
Cg(4)···Cg(2)	5.6658(10)	34.8(3)	57.7	33.6	-4.721(2)	3.030(2)	x, y, z
Cg(5)···Cg(1)	5.431(4)	82.4(3)	37.4	52.2	3.332(4)	-4.314(2)	x, –1+y, z
Cg(5)···Cg(1)	5.431(4)	82.4(3)	37.4	52.2	-3.332(4)	4.314(2)	2+x, y, z
Cg(5)···Cg(2)	5.431(4)	82.4(3)	37.4	52.2	3.332(4)	-4.314(2)	–1+x, –1+y, z
Cg(5)···Cg(2)	5.431(4)	82.4(3)	37.4	52.2	-3.332(4)	4.314(2)	1+x, y, z
Cg(5)···Cg(3)	5.309(4)	72.2(3)	46.7	74.4	1.428(4)	-3.638(2)	x, y, 1+z
Cg(5)···Cg(3)	5.309(4)	72.2(3)	46.7	74.4	-1.428(4)	3.638(2)	1+x, y, z
Cg(5)···Cg(4)	5.309(4)	72.2(3)	46.7	74.4	1.428(4)	-3.638(2)	–1+x, y, 1+z
Cg(5)···Cg(4)	5.309(4)	72.2(3)	46.7	74.4	-1.428(4)	3.638(2)	x, y, z
Cg(5)···Cg(5)	3.358(4)	0.0(3)	21.6	21.6	-3.122(3)	-3.122(3)	–x, 1–y, 1–z
Cg(5)···Cg(5)	3.358(4)	0.0(3)	21.6	21.6	3.122(3)	3.122(3)	2–x, 1–y, 1–z
Y–X(I)···Cg(J)	**X···Cg(J)**	**X–Perp**	**γ (°)**	**Y–X···Cg(J)**	**Y···Cg(J)**	**Y–X, Pi**	**Symmetry**
compound 1							
C1–O2···Cg(2)	3.275(3)	3.240	8.36	127.77(19)	4.162(5)	32.04	x, y, z
C1–O2···Cg(2)	3.275(3)	-3.240	8.36	127.77(19)	4.162(5)	32.04	1–x, 1–y, 1–z
C10–O7···Cg(1)	3.310(3)	3.234	12.31	124.2(2)	4.140(5)	25.88	–1+x, y, z
C10–O7···Cg(1)	3.310(3)	-3.234	12.31	124.2(2)	4.140(5)	25.88	1–x, 1–y, 1–z
compound 1'							
No short ring-interactions							
compound 2							
O5W–H5WB···Cg(3)	2.92(12)	2.56	28.75	61(7)	2.625(8)	37	x, y, z
O5W–H5WB···Cg(3)	2.92(12)	-2.56	28.75	61(7)	2.625(8)	37	–x, 1–y, –z
O5W–H5WB···Cg(4)	2.92(12)	2.56	28.75	61(7)	2.625(8)	37	–1+x, y, z
O5W–H5WB···Cg(4)	2.92(12)	-2.56	28.75	61(7)	2.625(8)	37	1–x, 1–y, –z

[a]**Note**: The slippage {= distance between Cg(I) and perpendicular projection of Cg(J) on Ring I (Å)} does not exist for **1** while it is 3.204 and 1.236 for **1'** and **2**, respectively. Cg(I)···Cg(J) = distance between ring centroids (Å); Cg(I) = plane number I (= ring number in () above); α = dihedral angle between planes I and J (°); β = angle Cg(I)–Cg(J) or Cg(I)–Me vector and normal to plane I (°); γ = angle Cg(I)–Cg(J) vector and normal to plane J (°); CgI_Perp = perpendicular distance of Cg(I) on ring J (Å) and CgJ_Perp = perpendicular distance of Cg(J) on ring I (Å); Cg(J) = centre of gravity of ring J (plane number above); X···Cg(J) = distance of X to Cg (Å); X–Perp = perpendicular distance of X to ring plane J (Å); γ = angle between Cg–X vector and ring J normal (°); Y–X···Cg(J) = Y–X–Cg(J) angle (°); Y···Cg(J) = distance of Y to Cg (Å); Y–X, Pi = angle of the Y–X bond with the π-plane (*i.e.*' perpendicular = 90°, parallel = 0°).



Scheme S1 Hydrothermal synthesis of compound **1** with 63% yield.

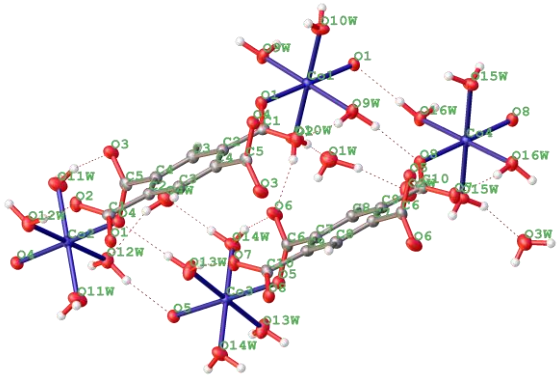


Fig. S1 (a) Ortep view and atom numbering scheme with displacement ellipsoids drawn at 50% probability level for compound **1**.

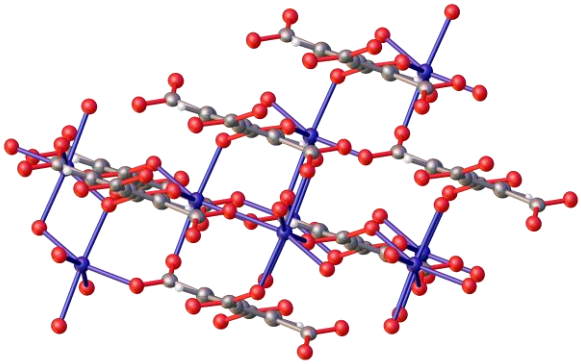


Fig. S1 (b) Repeating structural motifs showing dimers consisting of two edge-sharing symmetry-related cobaltous ions in compound **1'**.

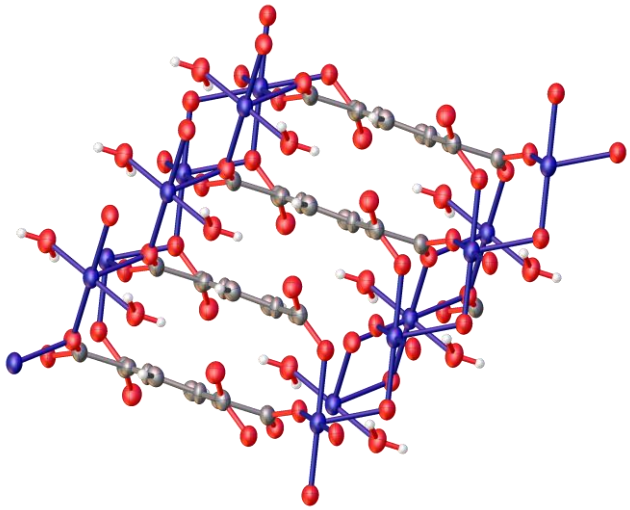


Fig. S1 (c) A depiction illustrating a six-coordinated Co1 octahedron surrounded by carboxylate oxygen atoms and water molecules in compound **2**.

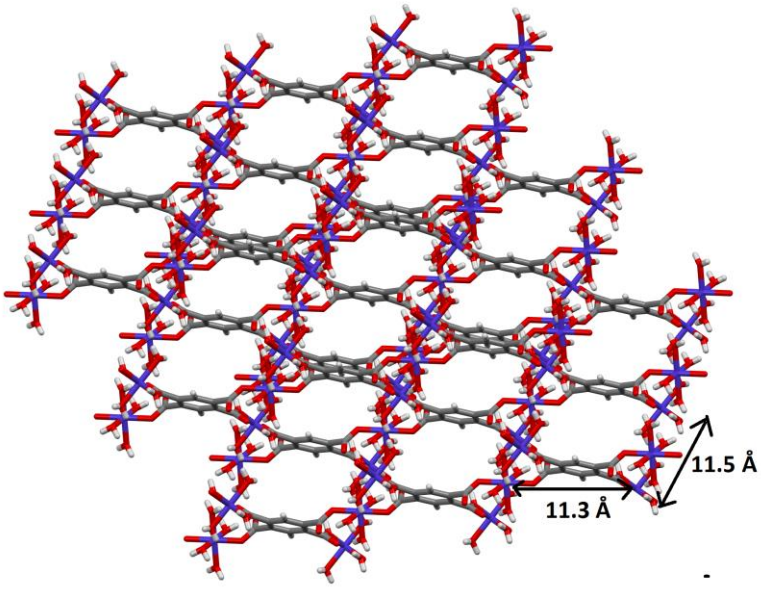


Fig. S2 (a) A 1D intersecting channel system illustrating a narrow open window with approx. 11.5 Å × 11.3 Å dimensions in the polymeric structure of network **1**.

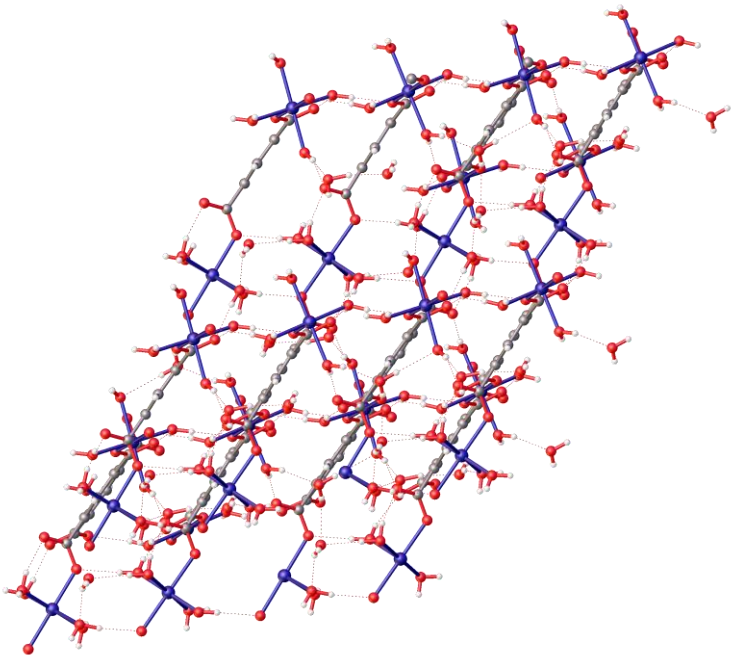


Fig. S2 (b) A 3D supramolecular framework of **1** showing extensive O–H···O hydrogen bond interactions primarily generated by water molecules.

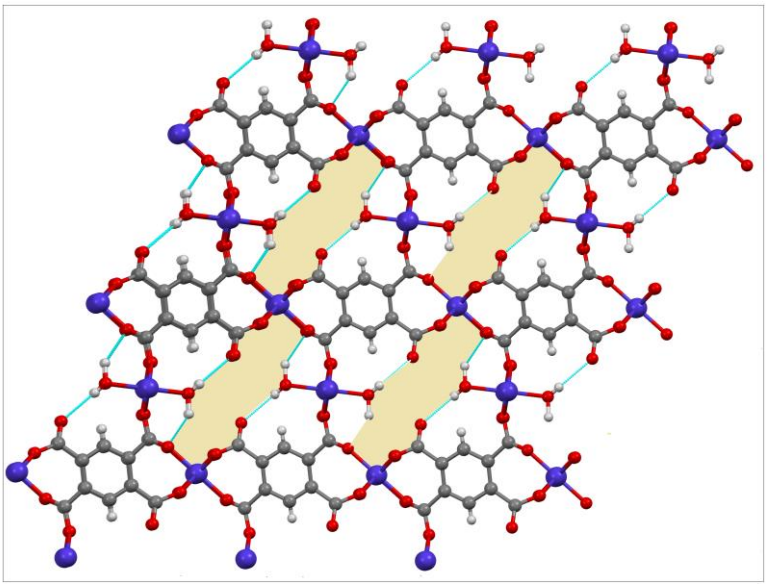


Fig. S2 (c) A 3D supramolecular network of **2** displaying O–H···O hydrogen bond interactions mainly manifested by water molecules.

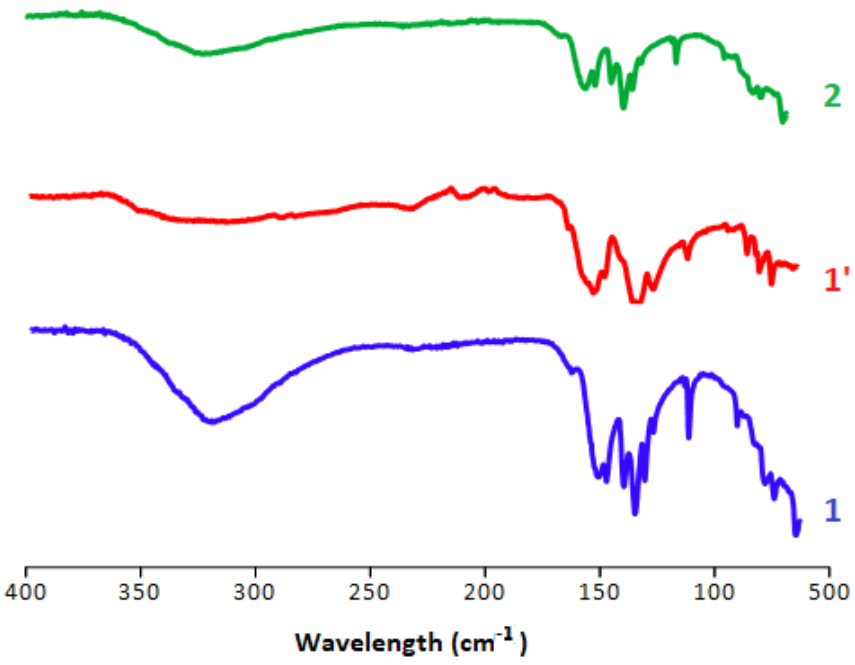


Fig. S3 Infrared (IR) spectra for compounds **1**, **1'** and **2**.

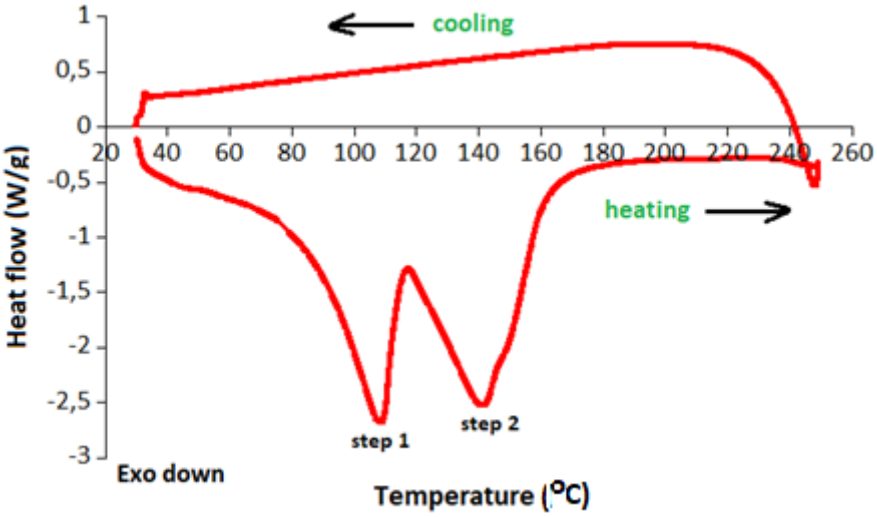


Fig. S4 Single-cycle heat-cool differential scanning calorimetry (DSC) profile for **1** (step 1: onset dehydration is 109.3 ℃ and, step 2: onset phase transition is 142.4 ℃).

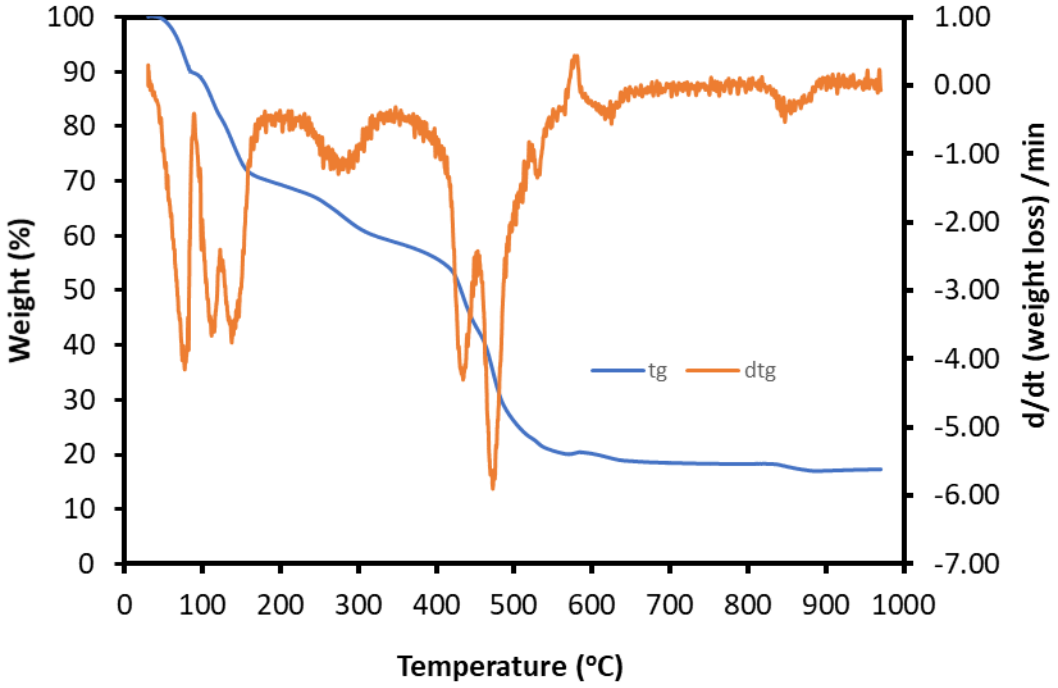


Fig. S5 (a) Thermogravimetric (tg; blue thermogram) plot and its derivative (dtg; red curve) for compound **1**.

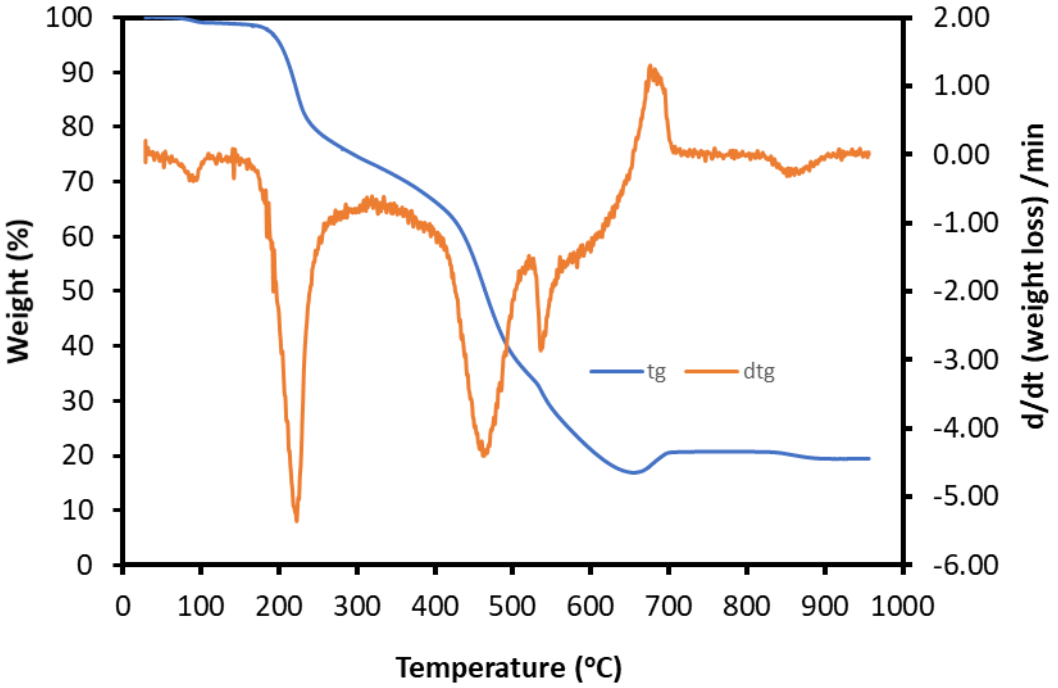


Fig. S5 (b) Thermogravimetric (tg; blue thermogram) plot and its derivative (dtg; red curve) for compound **1'**.

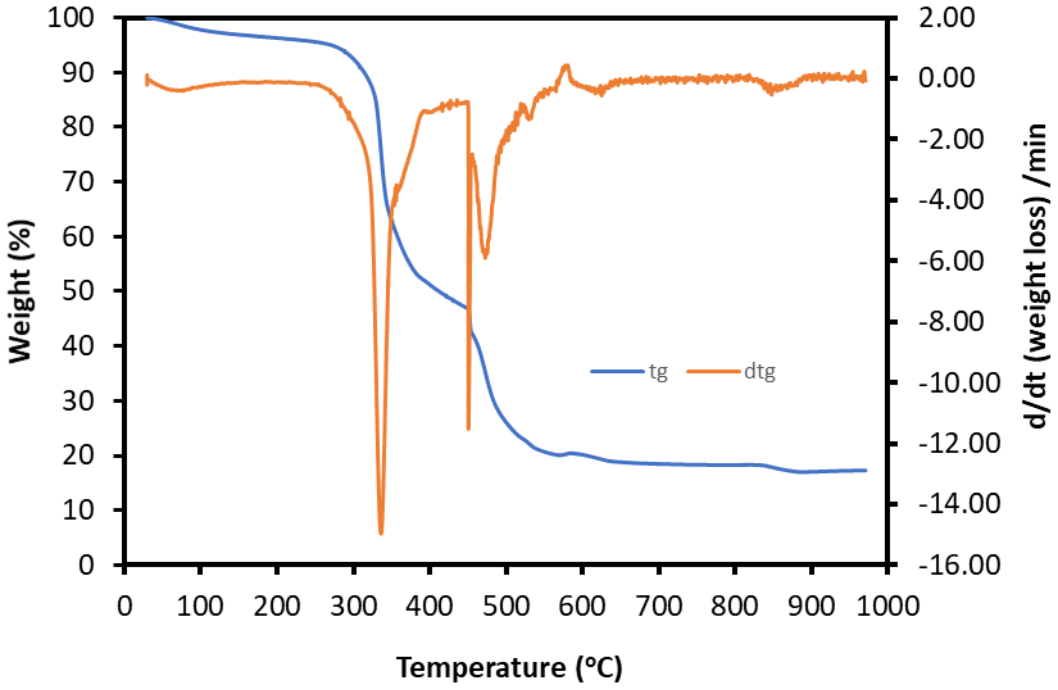


Fig. S5 (c) Thermogravimetric (tg; blue thermogram) plot and its derivative (dtg; red curve) for compound **2**.

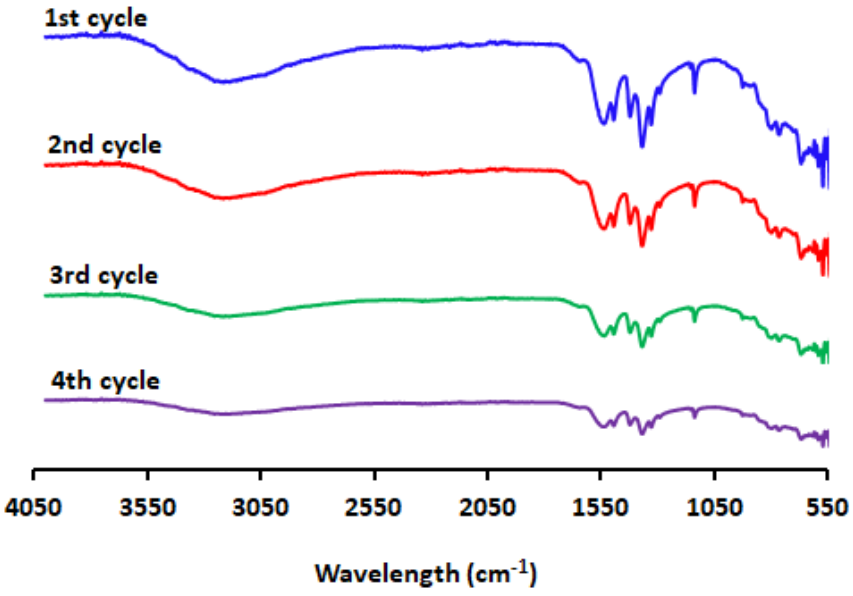


Fig. S6 Infrared spectra of catalyst **2** after the first (blue), second (red), third (green), and fourth (purple) recycled runs.

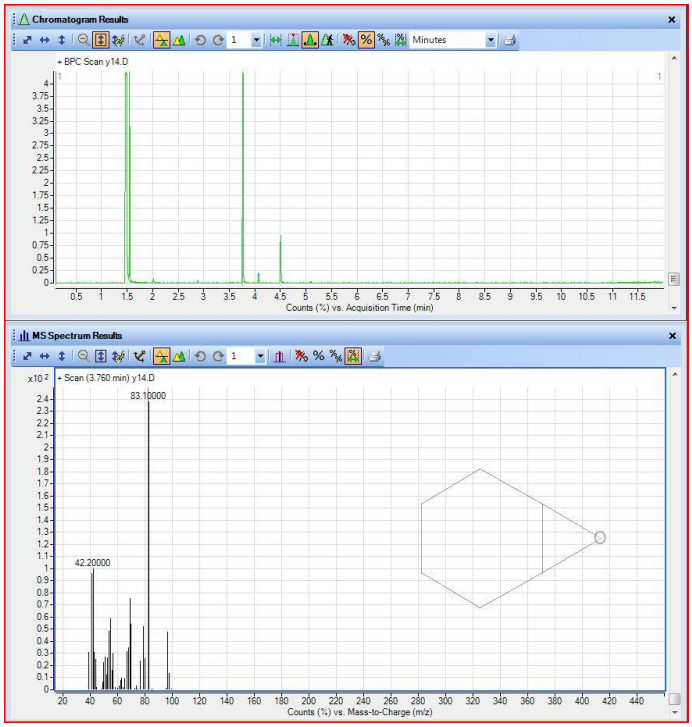


Fig. S7 (a) GC-MS spectrum for the selective oxidation of cyclohexene to cyclohexene epoxide utilizing O_2 over catalyst **2** for 20 h.

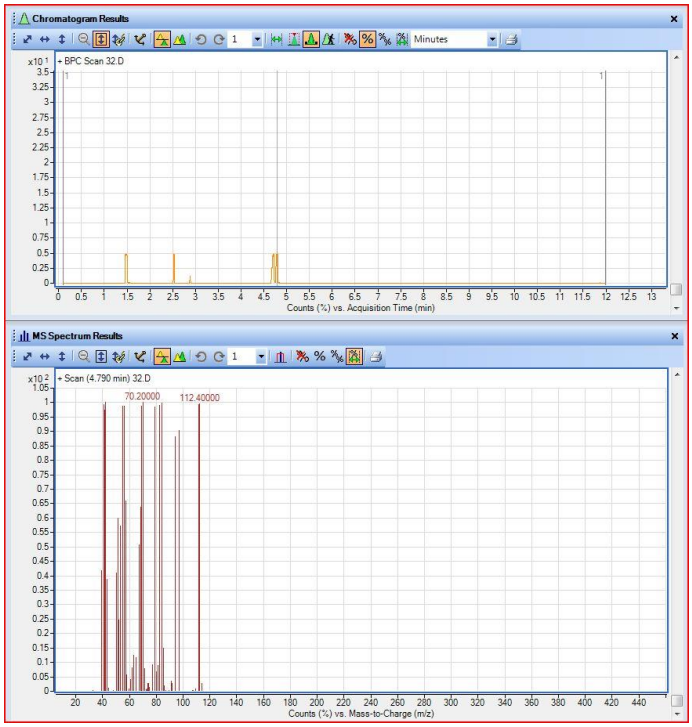


Fig. S7 (b) GC-MS spectrum for the selective oxidation of 3-methylcyclohexene to 3-methylcyclohexene epoxide utilizing O_2 over catalyst **2** for 20 h.

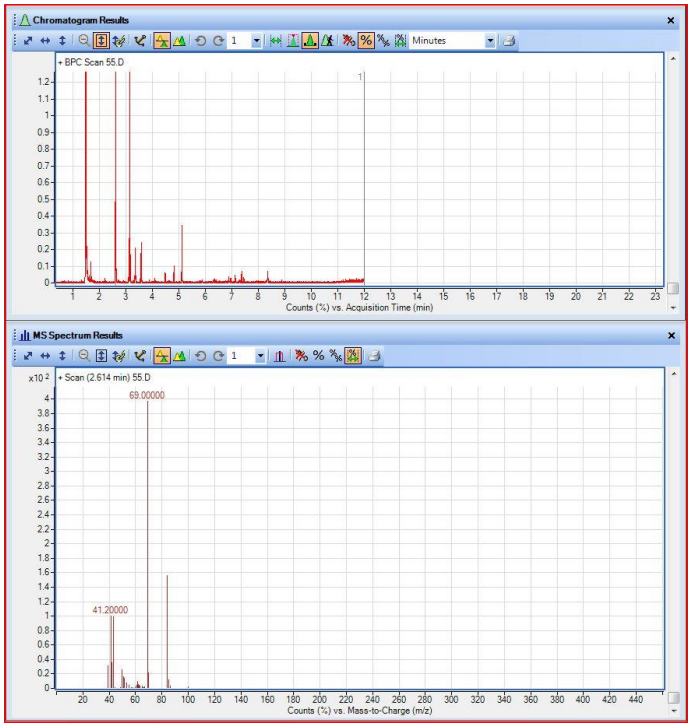


Fig. S7 (c) GC-MS spectrum for the selective oxidation of cyclopentene to cyclopentene epoxide utilizing O_2 over catalyst **2** for 20 h.

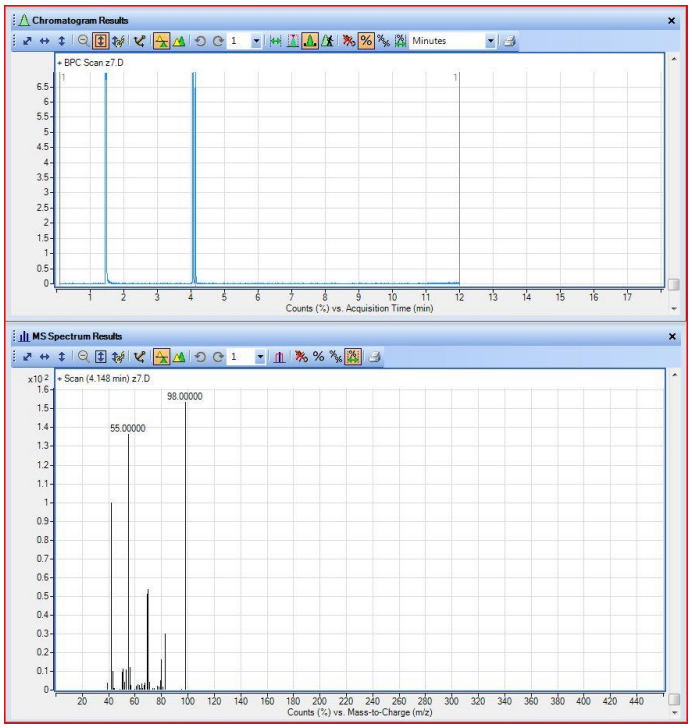


Fig. S7 (d) GC-MS spectrum for the selective oxidation of 3-methylcyclopentene to 3-methylcyclopentene epoxide utilizing O_2 over catalyst **2** for 20 h.

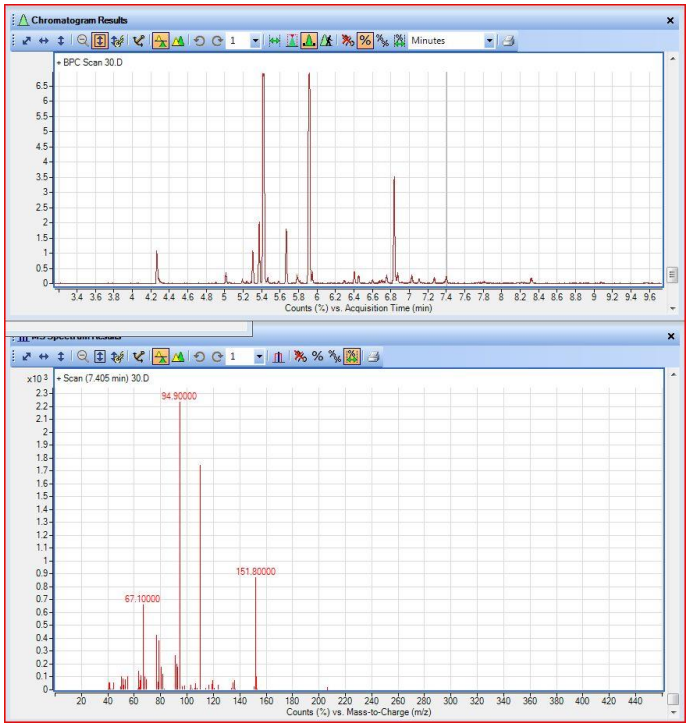


Fig. S7 (e) GC-MS spectrum for the selective oxidation of limonene to limonene-1,2-epoxide utilizing O_2 over catalyst **2** for 20 h.

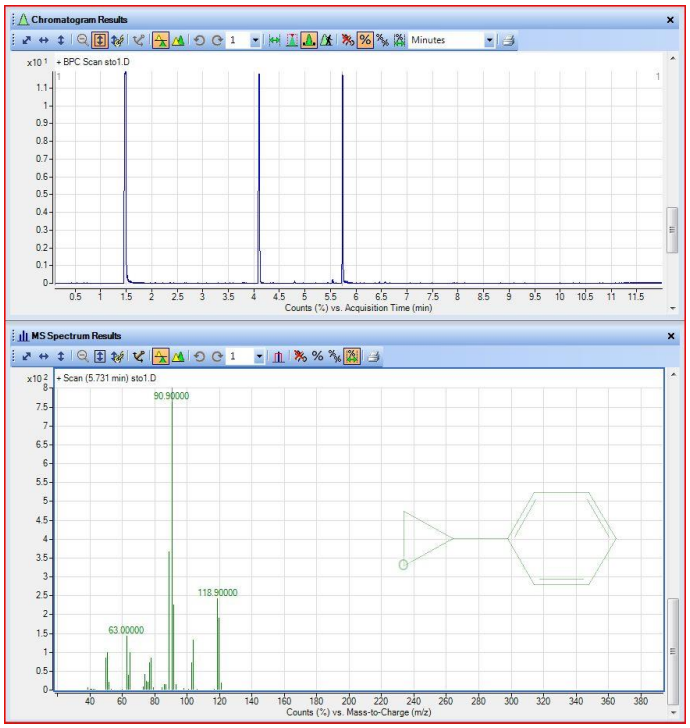


Fig. S7 (f) GC-MS spectrum for the selective oxidation of styrene to styrene epoxide utilizing O_2 over catalyst **2** for 20 h.

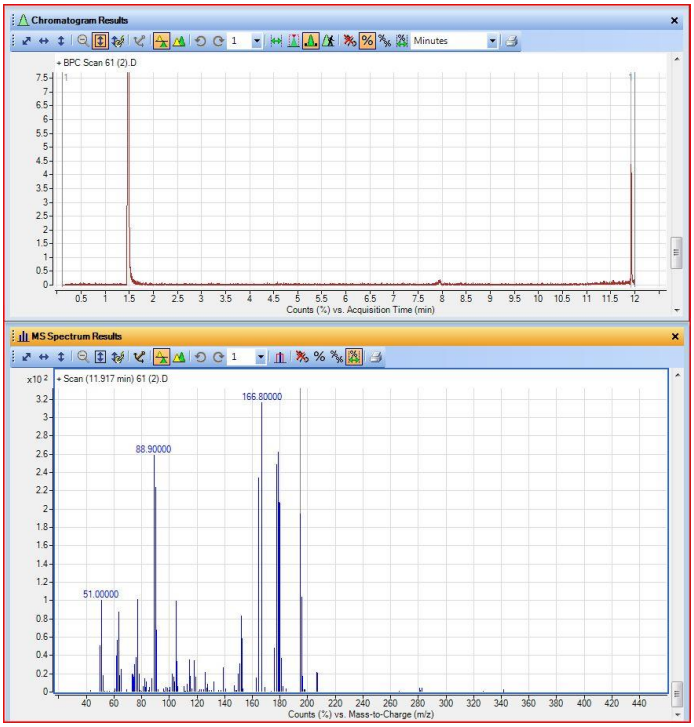


Fig. S7 (g) GC-MS spectrum for the selective oxidation of *trans*-stilbene to *trans*-stilbene epoxide utilizing O_2 over catalyst **2** for 20 h.

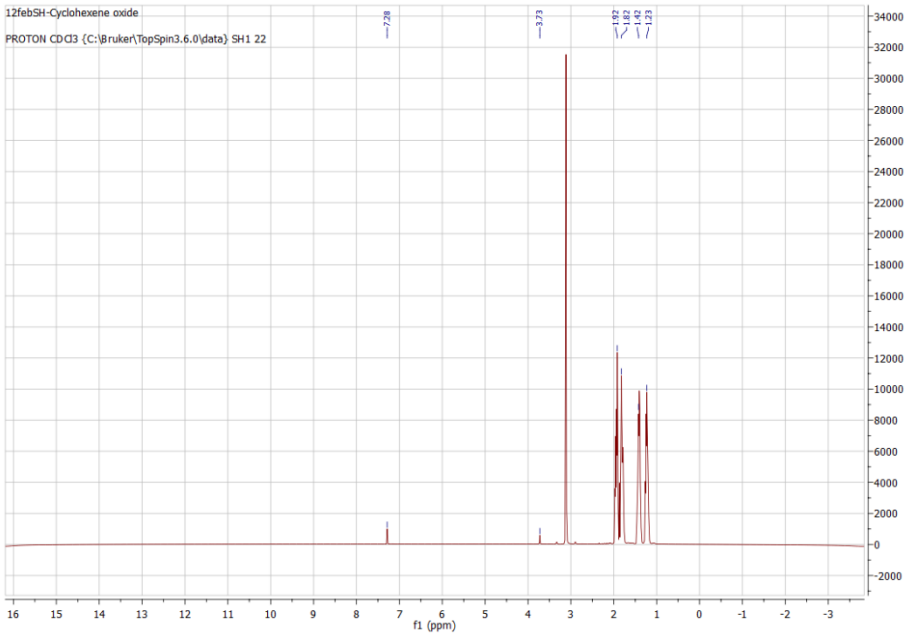


Fig. S8 (a) ^{1}H NMR spectra (in $CDCl_3$) for cyclohexene epoxide.

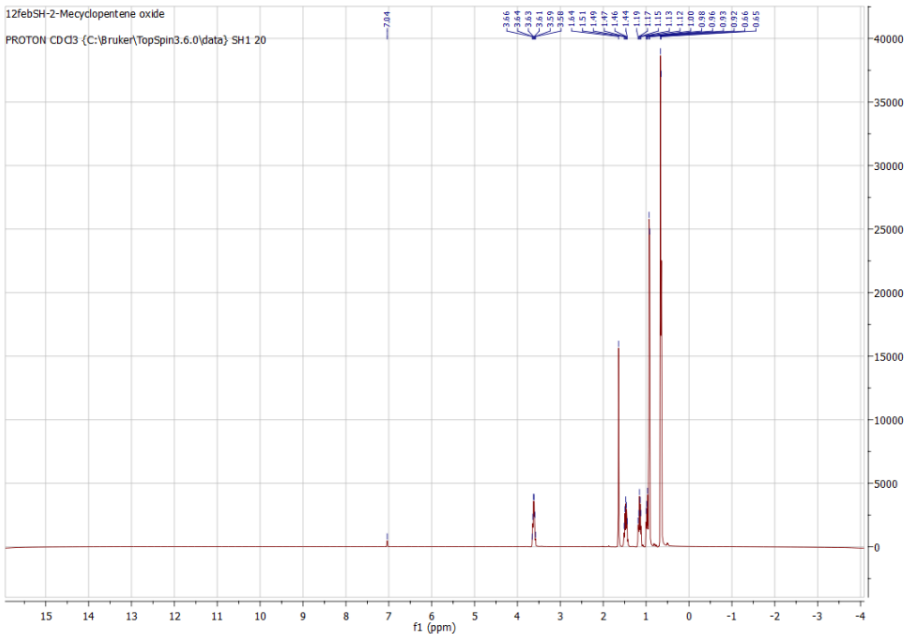


Fig. S8 (b) ^{1}H NMR spectra (in $CDCl_3$) for 3-methylcyclohexene epoxide.

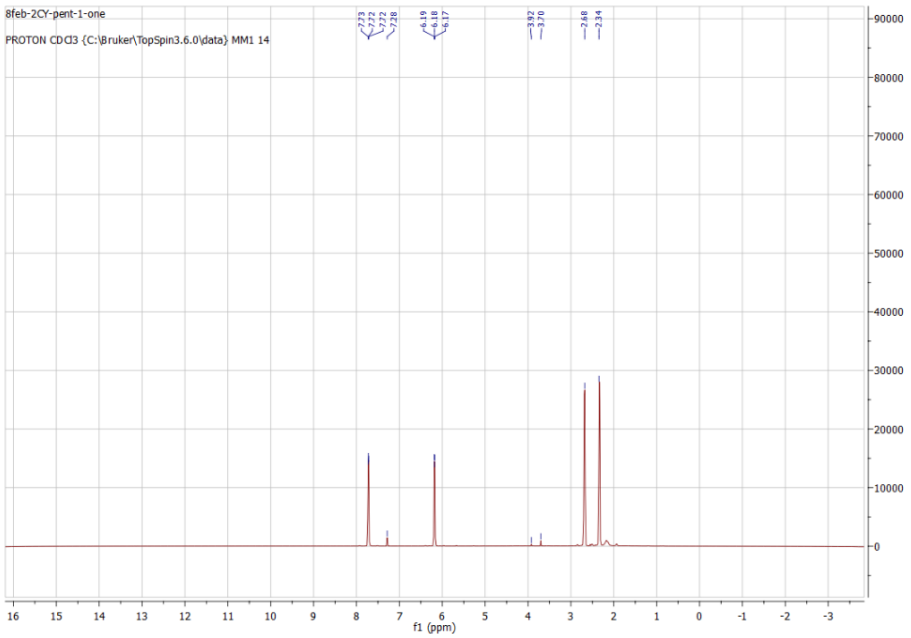


Fig. S8 (c) ^{1}H NMR spectra (in $CDCl_3$) for cyclopentene epoxide.

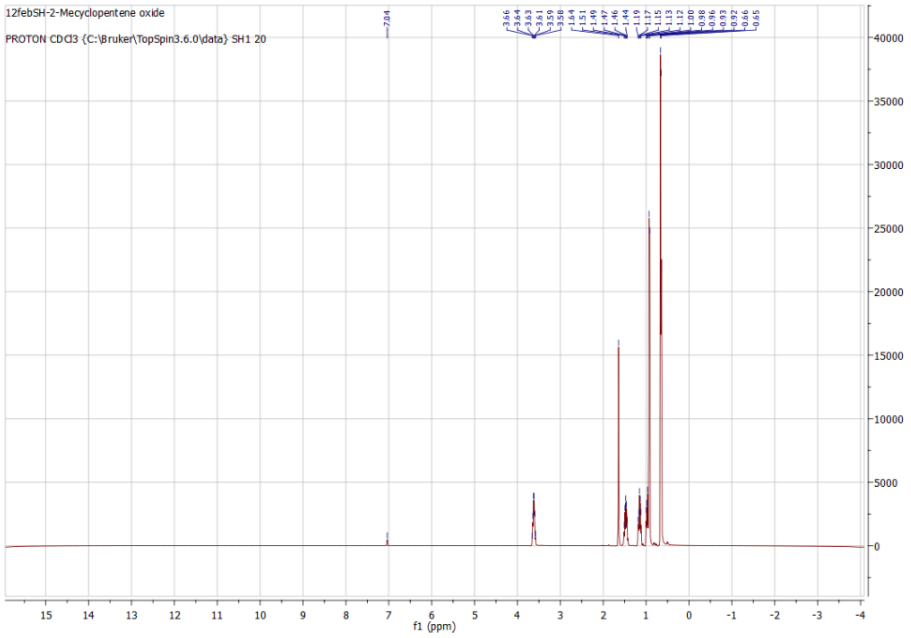


Fig. S8 (d) ^{1}H NMR spectra (in $CDCl_3$) for 3-methylcyclopentene epoxide.

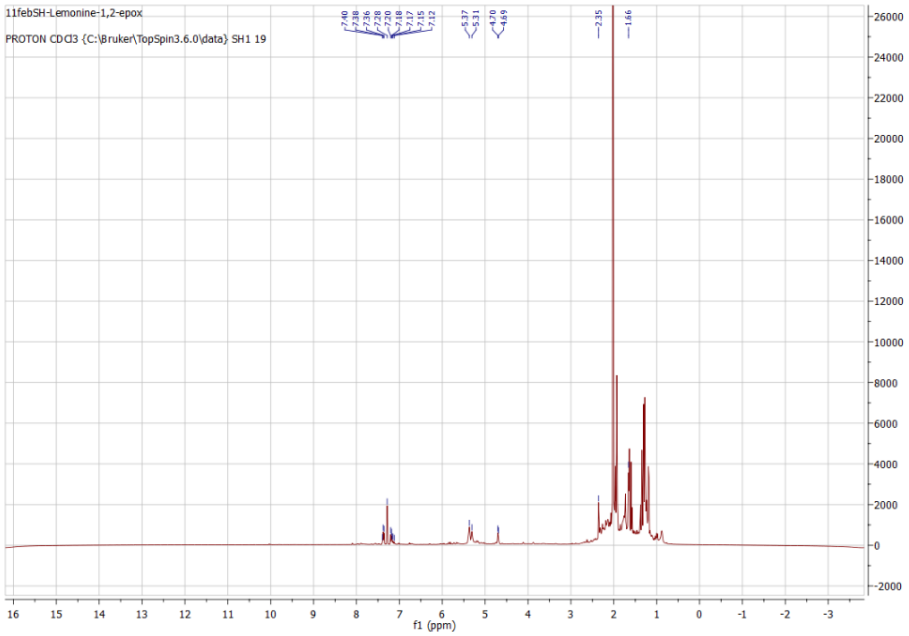


Fig. S8 (e) ^{1}H NMR spectra (in $CDCl_3$) for limonene-1,2-epoxide.

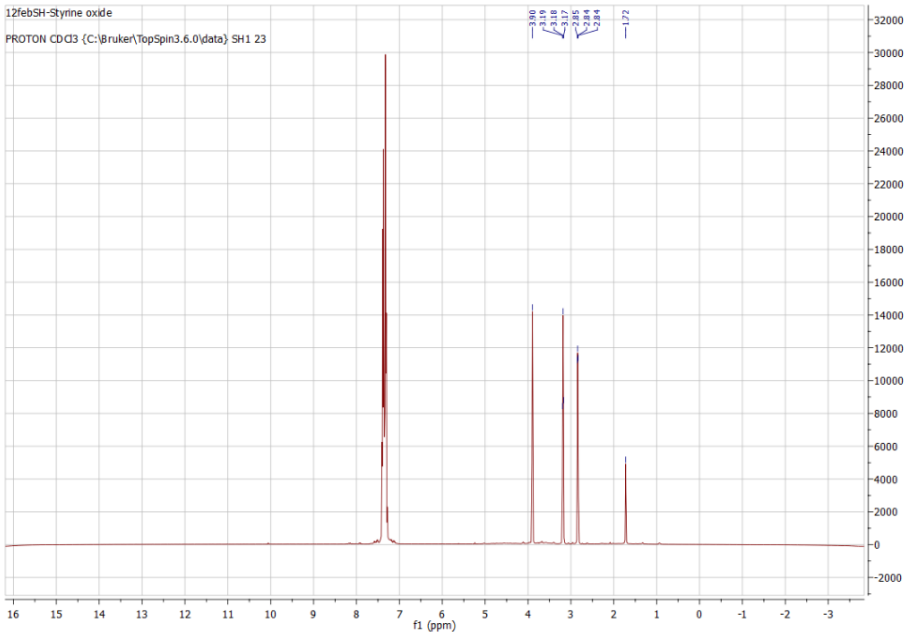


Fig. S8 (f) ^{1}H NMR spectra (in $CDCl_3$) for styrene epoxide.

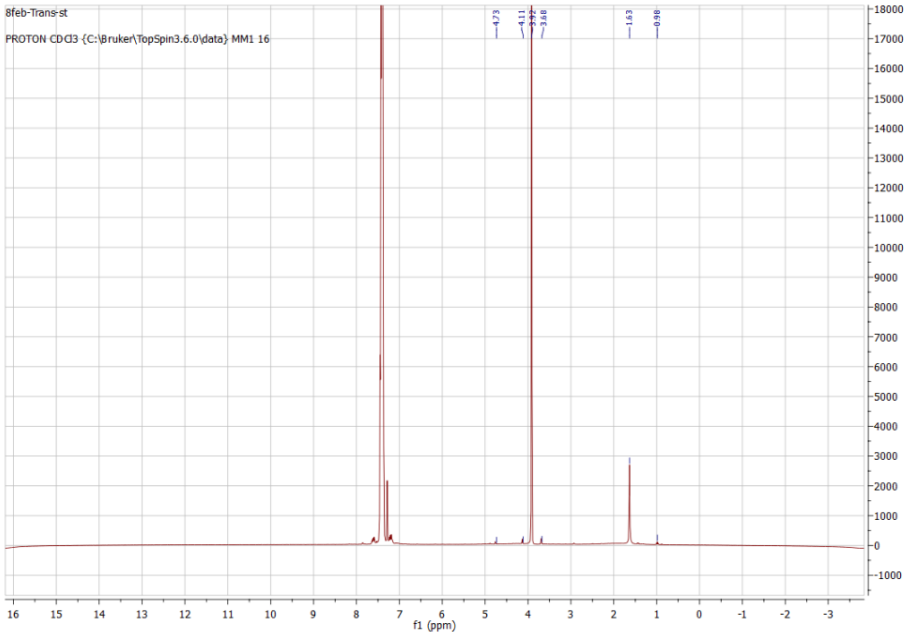


Fig. S8 (g) ^{1}H NMR spectra (in $CDCl_3$) for *trans*-stilbene epoxide.