Electronic Supplementary Information

Phenoxazinone synthase-like catalytic activity of novel mono- and tetranuclear copper(II) complexes with 2-benzylaminoethanol

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Figure S1. IR spectrum of 1.



Figure S2. IR spectrum of 2.



Figure S3. IR spectrum of 3.

1	2
2.3956(15)	2.411(4)
2.0021(12)	1.987(4)
2.0275(13)	2.021(4)
180	180
92.51(6)	86.37(14)
87.49(6)	93.63(14)
92.51(6)	86.37(14)
79.68(5)	79.18(15)
100.32(5)	100.82(15)
87.49(6)	93.63(14)
180	180
86.86(6)	92.57(17)
93.14(6)	87.43(17)
100.32(5)	100.82(15)
93.14(6)	87.43(17)
180	180
79.68(5)	79.18(15)
86.86(6)	92.57(17)
	$ \begin{array}{c} 1\\ 2.3956(15)\\ 2.0021(12)\\ 2.0275(13)\\\\180\\ 92.51(6)\\ 87.49(6)\\ 92.51(6)\\ 79.68(5)\\ 100.32(5)\\ 87.49(6)\\ 180\\ 86.86(6)\\ 93.14(6)\\ 100.32(5)\\ 93.14(6)\\ 180\\ 79.68(5)\\ 86.86(6)\\\\\end{array} $

Table S1. Selected geometrical parameters (distances/Å and angles/°) for 1 and 2.

Symmetry code: *a* 1–x, 1–y, 1–z.

Table S2. Selected geo	metrical parameters	(separations and	distances/Å.	, and angles/°) for 3
• /		· ·			

Cu1…Cu2			
eur euz	2 8897(10)	Cu5…Cu6	2 9050(11)
Cu1···Cu4	3 3793(11)	Cu5····Cu8	33133(10)
Cu1···Cu3	3 4323(11)		3 4616(10)
Cu2···Cu4	3 3713(11)		3 3516(11)
Cu2···Cu3	3 3787(11)	Cu6····Cu8	34474(11)
Cu3···Cu4	2 8971(11)	Cu7···Cu8	28804(11)
	,		2.000 ((11)
Cu1–O1	1.963(3)	Cu5-O13	1.950(3)
Cu1–O2	1.928(4)	Cu5–O14	1.919(3)
Cu1–O4	1.976(3)	Cu5–O16	1.997(3)
Cu1–O10	2.455(3)	Cu5–O19	2.402(3)
Cu1–N1	2.030(4)	Cu5–N5	2.032(4)
Cu2–O1	1.952(3)	Cu6–O13	1.970(3)
Cu2–O4	1.980(3)	Cu6–O16	1.960(3)
Cu2–O5	1.928(4)	Cu6–O17	1.943(3)
Cu2–O7	2.420(3)	Cu6–O22	2.417(3)
Cu2–N2	2.018(4)	Cu6–N6	2.014(4)
Cu3–O1	2.445(3)	Cu7–O16	2.461(3)
Cu3–O7	1.970(3)	Cu7–O19	1.978(3)
Cu3–O8	1.927(4)	Cu7–O20	1.926(3)
Cu3–O10	1.975(3)	Cu7–O22	1.961(3)
Cu3–N3	2.024(4)	Cu7–N7	2.010(4)
Cu4–O4	2.419(3)	Cu8–O13	2.453(3)
Cu4–O7	1.985(3)	Cu8–O19	1.953(3)
Cu4–O10	1.964(3)	Cu8–O22	1.971(3)
Cu4011	1.925(4)	Cu8–O23	1.941(3)
Cu4–N4	2.024(4)	Cu8–N8	2.001(4)
$01 C_{2} 1 02$	177 11(16)	012 Cy5 014	$177 \ 97(15)$
01-Cu1-O2	177.11(16)	013–Cu5–O14	177.87(15)
O1–Cu1–O2 O1–Cu1–O4	177.11(16) 83.15(12) 70.56(11)	013-Cu5-014 013-Cu5-016 012 Cu5 010	177.87(15) 82.73(12) 82.05(11)
O1–Cu1–O2 O1–Cu1–O4 O1–Cu1–O10	177.11(16) 83.15(12) 79.56(11) 84.72(15)	013-Cu5-O14 013-Cu5-O16 013-Cu5-O19 012 Cu5 N5	177.87(15) 82.73(12) 82.05(11)
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4	177.11(16) 83.15(12) 79.56(11) 84.72(15) 04.47(15)	O13-Cu5-O14 O13-Cu5-O16 O13-Cu5-O19 O13-Cu5-N5 O14 Cu5 O16	177.87(15) 82.73(12) 82.05(11) 83.90(14) 95.27(14)
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O4	$177.11(16) \\83.15(12) \\79.56(11) \\84.72(15) \\94.47(15) \\102.82(13)$	013-Cu5-O14 013-Cu5-O16 013-Cu5-O19 013-Cu5-N5 014-Cu5-O16 014 Cu5-O10	177.87(15) 82.73(12) 82.05(11) 83.90(14) 95.27(14) 08.28(12)
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O10 O2-Cu1-N1	177.11(16) 83.15(12) 79.56(11) 84.72(15) 94.47(15) 102.82(13) 07.28(16)	013-Cu5-O14 013-Cu5-O16 013-Cu5-O19 013-Cu5-N5 014-Cu5-O16 014-Cu5-O19 014 Cu5 N5	177.87(15) 82.73(12) 82.05(11) 83.90(14) 95.27(14) 98.28(12) 97.92(16)
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O10 O2-Cu1-N1 O4 Cu1-O10	$177.11(16) \\83.15(12) \\79.56(11) \\84.72(15) \\94.47(15) \\102.82(13) \\97.38(16) \\70.56(11) \\$	013-Cu5-O14 013-Cu5-O16 013-Cu5-O19 013-Cu5-N5 014-Cu5-O16 014-Cu5-O19 014-Cu5-N5 016 Cu5 O10	177.87(15) 82.73(12) 82.05(11) 83.90(14) 95.27(14) 98.28(12) 97.93(16) 77.85(11)
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O10 O2-Cu1-N1 O4-Cu1-O10 O4-Cu1-N1	177.11(16) $83.15(12)$ $79.56(11)$ $84.72(15)$ $94.47(15)$ $102.82(13)$ $97.38(16)$ $79.56(11)$ $165 23(15)$	O13-Cu5-O14 O13-Cu5-O16 O13-Cu5-O19 O13-Cu5-N5 O14-Cu5-O16 O14-Cu5-O19 O14-Cu5-N5 O16-Cu5-O19 O16-Cu5-N5	177.87(15) 82.73(12) 82.05(11) 83.90(14) 95.27(14) 98.28(12) 97.93(16) 77.85(11) 162.74(14)
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O10 O2-Cu1-N1 O4-Cu1-O10 O4-Cu1-N1	177.11(16) $83.15(12)$ $79.56(11)$ $84.72(15)$ $94.47(15)$ $102.82(13)$ $97.38(16)$ $79.56(11)$ $165.23(15)$ $106.20(13)$	O13-Cu5-O14 O13-Cu5-O16 O13-Cu5-O19 O13-Cu5-N5 O14-Cu5-O16 O14-Cu5-O19 O14-Cu5-N5 O16-Cu5-O19 O16-Cu5-N5 O19 Cu5 N5	177.87(15) 82.73(12) 82.05(11) 83.90(14) 95.27(14) 98.28(12) 97.93(16) 77.85(11) 162.74(14) 111.01(13)
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O10 O2-Cu1-N1 O4-Cu1-O10 O4-Cu1-N1 O10-Cu1-N1	177.11(16) $83.15(12)$ $79.56(11)$ $84.72(15)$ $94.47(15)$ $102.82(13)$ $97.38(16)$ $79.56(11)$ $165.23(15)$ $106.20(13)$ $83.32(12)$	013-Cu5-O14 013-Cu5-O16 013-Cu5-O19 013-Cu5-N5 014-Cu5-O16 014-Cu5-O19 014-Cu5-N5 016-Cu5-O19 016-Cu5-N5 019-Cu5-N5	177.87(15) 82.73(12) 82.05(11) 83.90(14) 95.27(14) 98.28(12) 97.93(16) 77.85(11) 162.74(14) 111.01(13) 83.19(12)
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O10 O2-Cu1-N1 O4-Cu1-O10 O4-Cu1-N1 O10-Cu1-N1 O1-Cu2-O4 O1-Cu2-O4	177.11(16) $83.15(12)$ $79.56(11)$ $84.72(15)$ $94.47(15)$ $102.82(13)$ $97.38(16)$ $79.56(11)$ $165.23(15)$ $106.20(13)$ $83.32(12)$ $94.66(16)$	013-Cu5-O14 013-Cu5-O16 013-Cu5-O19 013-Cu5-N5 014-Cu5-O16 014-Cu5-O19 014-Cu5-N5 016-Cu5-N5 016-Cu5-N5 019-Cu5-N5 013-Cu6-O16 013 Cu6 O17	177.87(15) $82.73(12)$ $82.05(11)$ $83.90(14)$ $95.27(14)$ $98.28(12)$ $97.93(16)$ $77.85(11)$ $162.74(14)$ $111.01(13)$ $83.19(12)$ $94.11(14)$
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O10 O2-Cu1-N1 O4-Cu1-N1 O10-Cu1-N1 O1-Cu2-O4 O1-Cu2-O5 O1-Cu2-O7	177.11(16) $83.15(12)$ $79.56(11)$ $84.72(15)$ $94.47(15)$ $102.82(13)$ $97.38(16)$ $79.56(11)$ $165.23(15)$ $106.20(13)$ $83.32(12)$ $94.66(16)$ $80.18(11)$	O13-Cu5-O14 O13-Cu5-O16 O13-Cu5-O19 O13-Cu5-N5 O14-Cu5-O16 O14-Cu5-O19 O14-Cu5-O19 O16-Cu5-N5 O16-Cu5-N5 O19-Cu5-N5 O13-Cu6-O16 O13-Cu6-O17 O13-Cu6-O22	177.87(15) 82.73(12) 82.05(11) 83.90(14) 95.27(14) 98.28(12) 97.93(16) 77.85(11) 162.74(14) 111.01(13) 83.19(12) 94.11(14) 77.98(11)
$\begin{array}{c} 01-Cu1-O2\\ 01-Cu1-O4\\ 01-Cu1-O10\\ 01-Cu1-N1\\ 02-Cu1-O4\\ 02-Cu1-O10\\ 02-Cu1-N1\\ 04-Cu1-O10\\ 04-Cu1-N1\\ 010-Cu1-N1\\ 010-Cu1-N1\\ 01-Cu2-O4\\ 01-Cu2-O5\\ 01-Cu2-O7\\ 01-Cu2-N2\\ \end{array}$	177.11(16) $83.15(12)$ $79.56(11)$ $84.72(15)$ $94.47(15)$ $102.82(13)$ $97.38(16)$ $79.56(11)$ $165.23(15)$ $106.20(13)$ $83.32(12)$ $94.66(16)$ $80.18(11)$ $165.34(16)$	O13-Cu5-O14 O13-Cu5-O16 O13-Cu5-O19 O13-Cu5-N5 O14-Cu5-O16 O14-Cu5-O19 O14-Cu5-N5 O16-Cu5-N5 O16-Cu5-N5 O19-Cu5-N5 O13-Cu6-O16 O13-Cu6-O17 O13-Cu6-O22 O13-Cu6-N6	177.87(15) $82.73(12)$ $82.05(11)$ $83.90(14)$ $95.27(14)$ $98.28(12)$ $97.93(16)$ $77.85(11)$ $162.74(14)$ $111.01(13)$ $83.19(12)$ $94.11(14)$ $77.98(11)$ $164.82(15)$
$\begin{array}{c} O1-Cu1-O2\\ O1-Cu1-O4\\ O1-Cu1-O10\\ O1-Cu1-N1\\ O2-Cu1-O4\\ O2-Cu1-O10\\ O2-Cu1-N1\\ O4-Cu1-O10\\ O4-Cu1-N1\\ O10-Cu1-N1\\ O1-Cu2-O4\\ O1-Cu2-O5\\ O1-Cu2-O7\\ O1-Cu2-N2\\ O4-Cu2-O5\\ $	177.11(16) $83.15(12)$ $79.56(11)$ $84.72(15)$ $94.47(15)$ $102.82(13)$ $97.38(16)$ $79.56(11)$ $165.23(15)$ $106.20(13)$ $83.32(12)$ $94.66(16)$ $80.18(11)$ $165.34(16)$ $176.40(16)$	O13-Cu5-O14 O13-Cu5-O16 O13-Cu5-O19 O13-Cu5-N5 O14-Cu5-O16 O14-Cu5-O19 O14-Cu5-N5 O16-Cu5-O19 O16-Cu5-N5 O19-Cu5-N5 O13-Cu6-O16 O13-Cu6-O17 O13-Cu6-O22 O13-Cu6-N6 O16-Cu6-O17	$\begin{array}{c} 177.87(15)\\ 82.73(12)\\ 82.05(11)\\ 83.90(14)\\ 95.27(14)\\ 98.28(12)\\ 97.93(16)\\ 77.85(11)\\ 162.74(14)\\ 111.01(13)\\ 83.19(12)\\ 94.11(14)\\ 77.98(11)\\ 164.82(15)\\ 176.59(15)\\ \end{array}$
$\begin{array}{c} 01-Cu1-O2\\ 01-Cu1-O4\\ 01-Cu1-O10\\ 01-Cu1-N1\\ 02-Cu1-O4\\ 02-Cu1-O10\\ 02-Cu1-N1\\ 04-Cu1-O10\\ 04-Cu1-N1\\ 010-Cu1-N1\\ 01-Cu2-O4\\ 01-Cu2-O5\\ 01-Cu2-O7\\ 01-Cu2-N2\\ 04-Cu2-O5\\ $	177.11(16) $83.15(12)$ $79.56(11)$ $84.72(15)$ $94.47(15)$ $102.82(13)$ $97.38(16)$ $79.56(11)$ $165.23(15)$ $106.20(13)$ $83.32(12)$ $94.66(16)$ $80.18(11)$ $165.34(16)$ $176.40(16)$ $80.42(11)$	013-Cu5-O14 013-Cu5-O16 013-Cu5-O19 013-Cu5-N5 014-Cu5-O19 014-Cu5-O19 014-Cu5-N5 016-Cu5-N5 019-Cu5-N5 013-Cu6-O17 013-Cu6-O17 013-Cu6-N6 016-Cu6-O17 016-Cu6-O17 016-Cu6-O17 016-Cu6-O17 016-Cu6-O17	$\begin{array}{c} 177.87(15)\\ 82.73(12)\\ 82.05(11)\\ 83.90(14)\\ 95.27(14)\\ 98.28(12)\\ 97.93(16)\\ 77.85(11)\\ 162.74(14)\\ 111.01(13)\\ 83.19(12)\\ 94.11(14)\\ 77.98(11)\\ 164.82(15)\\ 176.59(15)\\ 81.14(11)\\ \end{array}$
$\begin{array}{c} 01-Cu1-O2\\ 01-Cu1-O4\\ 01-Cu1-O10\\ 01-Cu1-N1\\ 02-Cu1-O4\\ 02-Cu1-O10\\ 02-Cu1-N1\\ 04-Cu1-O10\\ 04-Cu1-N1\\ 010-Cu1-N1\\ 010-Cu1-N1\\ 01-Cu2-O4\\ 01-Cu2-O5\\ 01-Cu2-O7\\ 01-Cu2-N2\\ 04-Cu2-O5\\ 04-Cu2-O5\\ 04-Cu2-N2\\ 04-Cu2-N2\\$	177.11(16) $83.15(12)$ $79.56(11)$ $84.72(15)$ $94.47(15)$ $102.82(13)$ $97.38(16)$ $79.56(11)$ $165.23(15)$ $106.20(13)$ $83.32(12)$ $94.66(16)$ $80.18(11)$ $165.34(16)$ $176.40(16)$ $80.42(11)$ $84.90(15)$	O13-Cu5-O14 O13-Cu5-O16 O13-Cu5-O19 O13-Cu5-N5 O14-Cu5-O16 O14-Cu5-O19 O14-Cu5-O19 O16-Cu5-O19 O16-Cu5-N5 O19-Cu5-N5 O13-Cu6-O16 O13-Cu6-O17 O13-Cu6-O22 O13-Cu6-O17 O16-Cu6-O17 O16-Cu6-O17 O16-Cu6-O22 O16-Cu6	$\begin{array}{c} 177.87(15)\\ 82.73(12)\\ 82.05(11)\\ 83.90(14)\\ 95.27(14)\\ 98.28(12)\\ 97.93(16)\\ 77.85(11)\\ 162.74(14)\\ 111.01(13)\\ 83.19(12)\\ 94.11(14)\\ 77.98(11)\\ 164.82(15)\\ 176.59(15)\\ 81.14(11)\\ 84.74(16)\end{array}$
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O10 O2-Cu1-N1 O4-Cu1-O10 O4-Cu1-N1 O10-Cu1-N1 O1-Cu2-O4 O1-Cu2-O5 O1-Cu2-O5 O1-Cu2-O5 O4-Cu2-O5 O4-Cu2-O5 O4-Cu2-O5 O4-Cu2-O7 O4-Cu2-O7 O4-Cu2-O7 O4-Cu2-N2 O5-Cu2-O7	177.11(16) $83.15(12)$ $79.56(11)$ $84.72(15)$ $94.47(15)$ $102.82(13)$ $97.38(16)$ $79.56(11)$ $165.23(15)$ $106.20(13)$ $83.32(12)$ $94.66(16)$ $80.18(11)$ $165.34(16)$ $176.40(16)$ $80.42(11)$ $84.90(15)$ $102.22(13)$	$\begin{array}{c} 013-Cu5-O14\\ 013-Cu5-O16\\ 013-Cu5-O19\\ 013-Cu5-O19\\ 013-Cu5-N5\\ 014-Cu5-O16\\ 014-Cu5-O19\\ 014-Cu5-N5\\ 016-Cu5-N5\\ 019-Cu5-N5\\ 013-Cu6-O16\\ 013-Cu6-O17\\ 013-Cu6-O22\\ 013-Cu6-N6\\ 016-Cu6-O17\\ 016-Cu6-O22\\ 016-Cu6-N6\\ 017-Cu6-N6\\ 017-Cu6-O22\\ 017-C$	$\begin{array}{c} 177.87(15)\\ 82.73(12)\\ 82.05(11)\\ 83.90(14)\\ 95.27(14)\\ 98.28(12)\\ 97.93(16)\\ 77.85(11)\\ 162.74(14)\\ 111.01(13)\\ 83.19(12)\\ 94.11(14)\\ 77.98(11)\\ 164.82(15)\\ 176.59(15)\\ 81.14(11)\\ 84.74(16)\\ 100.38(13)\\ \end{array}$
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O10 O2-Cu1-N1 O4-Cu1-O10 O4-Cu1-N1 O10-Cu1-N1 O1-Cu2-O4 O1-Cu2-O5 O1-Cu2-O7 O1-Cu2-O5 O4-Cu2-O5 O4-Cu2-O5 O4-Cu2-O5 O4-Cu2-O7 O4-Cu2-N2 O5-Cu2-O7 O5-Cu2-N2	177.11(16) $83.15(12)$ $79.56(11)$ $84.72(15)$ $94.47(15)$ $102.82(13)$ $97.38(16)$ $79.56(11)$ $165.23(15)$ $106.20(13)$ $83.32(12)$ $94.66(16)$ $80.18(11)$ $165.34(16)$ $176.40(16)$ $80.42(11)$ $84.90(15)$ $102.22(13)$ $96.61(18)$	O13-Cu5-O14 O13-Cu5-O16 O13-Cu5-O19 O13-Cu5-O19 O14-Cu5-O16 O14-Cu5-O19 O14-Cu5-O19 O16-Cu5-O19 O16-Cu5-N5 O19-Cu5-N5 O13-Cu6-O16 O13-Cu6-O17 O13-Cu6-O22 O13-Cu6-O17 O16-Cu6-O17 O16-Cu6-O17 O16-Cu6-O17 O16-Cu6-O17 O16-Cu6-O22 O16-Cu6-N6 O17-Cu6-O22 O17-Cu6-O22 O17-Cu6-N6	$\begin{array}{c} 177.87(15)\\ 82.73(12)\\ 82.05(11)\\ 83.90(14)\\ 95.27(14)\\ 98.28(12)\\ 97.93(16)\\ 77.85(11)\\ 162.74(14)\\ 111.01(13)\\ 83.19(12)\\ 94.11(14)\\ 77.98(11)\\ 164.82(15)\\ 176.59(15)\\ 81.14(11)\\ 84.74(16)\\ 100.38(13)\\ 97.58(17)\\ \end{array}$
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O10 O2-Cu1-N1 O4-Cu1-O10 O4-Cu1-N1 O1-Cu2-O4 O1-Cu2-O5 O1-Cu2-O7 O1-Cu2-O5 O4-Cu2-O5 O4-Cu2-O5 O4-Cu2-O5 O4-Cu2-O7 O4-Cu2-N2 O5-Cu2-N2 O5-Cu2-N2 O7-Cu2-N2	177.11(16) $83.15(12)$ $79.56(11)$ $84.72(15)$ $94.47(15)$ $102.82(13)$ $97.38(16)$ $79.56(11)$ $165.23(15)$ $106.20(13)$ $83.32(12)$ $94.66(16)$ $80.18(11)$ $165.34(16)$ $176.40(16)$ $80.42(11)$ $84.90(15)$ $102.22(13)$ $96.61(18)$ $106.41(14)$	O13-Cu5-O14 O13-Cu5-O16 O13-Cu5-O19 O13-Cu5-O19 O14-Cu5-O16 O14-Cu5-O19 O14-Cu5-O19 O16-Cu5-O19 O16-Cu5-N5 O19-Cu5-N5 O13-Cu6-O16 O13-Cu6-O17 O13-Cu6-O22 O13-Cu6-O17 O16-Cu6-O17 O16-Cu6-O17 O16-Cu6-O17 O16-Cu6-O12 O16-Cu6-O22 O16-Cu6-N6 O17-Cu6-O22 O17-Cu6-N6 O22-Cu6-N6	$\begin{array}{c} 177.87(15)\\ 82.73(12)\\ 82.05(11)\\ 83.90(14)\\ 95.27(14)\\ 98.28(12)\\ 97.93(16)\\ 77.85(11)\\ 162.74(14)\\ 111.01(13)\\ 83.19(12)\\ 94.11(14)\\ 77.98(11)\\ 164.82(15)\\ 176.59(15)\\ 81.14(11)\\ 84.74(16)\\ 100.38(13)\\ 97.58(17)\\ 109.19(13)\\ \end{array}$
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O10 O2-Cu1-N1 O4-Cu1-O10 O4-Cu1-N1 O10-Cu1-N1 O1-Cu2-O4 O1-Cu2-O5 O1-Cu2-O7 O1-Cu2-O7 O4-Cu2-O5 O4-Cu2-O7 O4-Cu2-O7 O4-Cu2-N2 O5-Cu2-O7 O5-Cu2-N2 O7-Cu2-N2 O7-Cu2-N2 O1-Cu2-N2 O7-Cu2-N2 O7-Cu2-N2 O1-Cu2-N2 O7-Cu2-N2 O7-Cu2-N2 O1-Cu2-N2 O7-Cu2-N2 O1-Cu2-N2 O7-Cu2-N2 O1-Cu2-N2 O7-Cu2-N2 O1-Cu2-N2 O1-Cu2-N2 O7-Cu2-N2 O1-Cu2-N2 O1-Cu2-N2 O7-Cu2-N2 O1-Cu2-N2 O1-Cu2-N2 O7-Cu2-N2 O1-Cu2-N2 O1-Cu2-N2 O7-Cu2-N2 O1-Cu2-N2 O1-Cu2-N2 O1-Cu2-N2 O7-Cu2-N2 O1-Cu2-N2 O1-Cu2-N2 O7-Cu2-N2 O1-Cu2-N2 O1-Cu2-N2 O7-Cu2-N2 O1-Cu2-N2 O1-Cu2-N2 O1-Cu2-N2 O1-Cu2-N2 O7-Cu2-N2 O1-Cu2-N2 O7-Cu2-N2 O1-Cu2-N2 O1-Cu2-N2 O7-Cu2-N2 O7-Cu2-N2 O1-Cu2-N2 O7-Cu2-N2 O7-Cu2-N2 O7-Cu2-N2	177.11(16) $83.15(12)$ $79.56(11)$ $84.72(15)$ $94.47(15)$ $102.82(13)$ $97.38(16)$ $79.56(11)$ $165.23(15)$ $106.20(13)$ $83.32(12)$ $94.66(16)$ $80.18(11)$ $165.34(16)$ $176.40(16)$ $80.42(11)$ $84.90(15)$ $102.22(13)$ $96.61(18)$ $106.41(14)$ $79.23(11)$	O13-Cu5-O14 O13-Cu5-O16 O13-Cu5-O19 O13-Cu5-N5 O14-Cu5-O16 O14-Cu5-O19 O14-Cu5-O19 O16-Cu5-O19 O16-Cu5-N5 O19-Cu5-N5 O13-Cu6-O16 O13-Cu6-O17 O13-Cu6-O22 O13-Cu6-O17 O16-Cu6-O22 O16-Cu6-O22 O16-Cu6-O22 O16-Cu6-N6 O17-Cu6-O22 O17-Cu6-N6 O22-Cu6-N6 O16-Cu7-O19	$\begin{array}{c} 177.87(15)\\ 82.73(12)\\ 82.05(11)\\ 83.90(14)\\ 95.27(14)\\ 98.28(12)\\ 97.93(16)\\ 77.85(11)\\ 162.74(14)\\ 111.01(13)\\ 83.19(12)\\ 94.11(14)\\ 77.98(11)\\ 164.82(15)\\ 176.59(15)\\ 81.14(11)\\ 84.74(16)\\ 100.38(13)\\ 97.58(17)\\ 109.19(13)\\ 76.74(11)\\ \end{array}$
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O10 O2-Cu1-N1 O4-Cu1-O10 O4-Cu1-N1 O10-Cu1-N1 O1-Cu2-O4 O1-Cu2-O5 O1-Cu2-O7 O1-Cu2-O5 O4-Cu2-O7 O4-Cu2-O5 O4-Cu2-O7 O4-Cu2-O7 O4-Cu2-O7 O4-Cu2-N2 O5-Cu2-O7 O5-Cu2-N2 O7-Cu2-N2 O7-Cu2-N2 O1-Cu3-O7 O1-Cu3-O8	177.11(16) $83.15(12)$ $79.56(11)$ $84.72(15)$ $94.47(15)$ $102.82(13)$ $97.38(16)$ $79.56(11)$ $165.23(15)$ $106.20(13)$ $83.32(12)$ $94.66(16)$ $80.18(11)$ $165.34(16)$ $176.40(16)$ $80.42(11)$ $84.90(15)$ $102.22(13)$ $96.61(18)$ $106.41(14)$ $79.23(11)$ $100.58(13)$	O13-Cu5-O14 O13-Cu5-O16 O13-Cu5-O19 O13-Cu5-N5 O14-Cu5-O16 O14-Cu5-O19 O14-Cu5-O19 O16-Cu5-N5 O19-Cu5-N5 O13-Cu6-O16 O13-Cu6-O17 O13-Cu6-O22 O13-Cu6-O17 O16-Cu6-O22 O16-Cu6-O17 O16-Cu6-O22 O16-Cu6-N6 O17-Cu6-O22 O17-Cu6-N6 O22-Cu6-N6 O16-Cu7-O19 O16-Cu7-O19 O16-Cu7-O20	$\begin{array}{c} 177.87(15)\\ 82.73(12)\\ 82.05(11)\\ 83.90(14)\\ 95.27(14)\\ 98.28(12)\\ 97.93(16)\\ 77.85(11)\\ 162.74(14)\\ 111.01(13)\\ 83.19(12)\\ 94.11(14)\\ 77.98(11)\\ 164.82(15)\\ 176.59(15)\\ 81.14(11)\\ 84.74(16)\\ 100.38(13)\\ 97.58(17)\\ 109.19(13)\\ 76.74(11)\\ 103.44(13)\\ \end{array}$
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O10 O2-Cu1-N1 O4-Cu1-N1 O10-Cu1-N1 O1-Cu2-O4 O1-Cu2-O5 O1-Cu2-O7 O1-Cu2-O5 O4-Cu2-O5 O4-Cu2-O5 O4-Cu2-O5 O4-Cu2-O5 O4-Cu2-O7 O4-Cu2-N2 O5-Cu2-N2 O5-Cu2-N2 O7-Cu2-N2 O7-Cu2-N2 O1-Cu3-O7 O1-Cu3-O8 O1-Cu3-O10	$\begin{array}{c} 177.11(16)\\ 83.15(12)\\ 79.56(11)\\ 84.72(15)\\ 94.47(15)\\ 102.82(13)\\ 97.38(16)\\ 79.56(11)\\ 165.23(15)\\ 106.20(13)\\ 83.32(12)\\ 94.66(16)\\ 80.18(11)\\ 165.34(16)\\ 176.40(16)\\ 80.42(11)\\ 84.90(15)\\ 102.22(13)\\ 96.61(18)\\ 106.41(14)\\ 79.23(11)\\ 100.58(13)\\ 78.44(11)\\ \end{array}$	O13-Cu5-O14 O13-Cu5-O16 O13-Cu5-O19 O13-Cu5-O19 O14-Cu5-O16 O14-Cu5-O19 O14-Cu5-O19 O16-Cu5-O19 O16-Cu5-N5 O19-Cu5-N5 O13-Cu6-O16 O13-Cu6-O17 O13-Cu6-O22 O13-Cu6-O17 O16-Cu6-O22 O16-Cu6-O17 O16-Cu6-O22 O16-Cu6-O22 O17-Cu6-N6 O17-Cu6-N6 O22-Cu6-N6 O16-Cu7-O19 O16-Cu7-O20 O16-Cu7-O20 O16-Cu7-O20	$\begin{array}{c} 177.87(15)\\ 82.73(12)\\ 82.05(11)\\ 83.90(14)\\ 95.27(14)\\ 98.28(12)\\ 97.93(16)\\ 77.85(11)\\ 162.74(14)\\ 111.01(13)\\ 83.19(12)\\ 94.11(14)\\ 77.98(11)\\ 164.82(15)\\ 176.59(15)\\ 81.14(11)\\ 84.74(16)\\ 100.38(13)\\ 97.58(17)\\ 109.19(13)\\ 76.74(11)\\ 103.44(13)\\ 79.98(11)\\ \end{array}$
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O10 O2-Cu1-N1 O4-Cu1-O10 O4-Cu1-N1 O1-Cu2-O4 O1-Cu2-O5 O1-Cu2-O7 O1-Cu2-O5 O4-Cu2-O5 O4-Cu2-O5 O4-Cu2-O5 O4-Cu2-O7 O4-Cu2-N2 O5-Cu2-N2 O5-Cu2-N2 O7-Cu2-N2 O7-Cu2-N2 O1-Cu3-O7 O1-Cu3-O8 O1-Cu3-O10 O1-Cu3-N3	177.11(16) $83.15(12)$ $79.56(11)$ $84.72(15)$ $94.47(15)$ $102.82(13)$ $97.38(16)$ $79.56(11)$ $165.23(15)$ $106.20(13)$ $83.32(12)$ $94.66(16)$ $80.18(11)$ $165.34(16)$ $176.40(16)$ $80.42(11)$ $84.90(15)$ $102.22(13)$ $96.61(18)$ $106.41(14)$ $79.23(11)$ $100.58(13)$ $78.44(11)$ $106.76(13)$	O13-Cu5-O14 O13-Cu5-O16 O13-Cu5-O19 O13-Cu5-N5 O14-Cu5-O19 O14-Cu5-O19 O14-Cu5-O19 O16-Cu5-O19 O16-Cu5-N5 O19-Cu5-N5 O13-Cu6-O16 O13-Cu6-O17 O13-Cu6-O22 O13-Cu6-O17 O16-Cu6-O22 O16-Cu6-N6 O17-Cu6-O22 O17-Cu6-N6 O12-Cu6-N6 O12-Cu6-N6 O12-Cu6-N6 O12-Cu6-N6 O12-Cu6-N6 O12-Cu6-N6 O12-Cu6-N6 O12-Cu6-N6 O16-Cu7-O19 O16-Cu7-O20 O16-Cu7-O22 O16-Cu7-O22 O16-Cu7-O22 O16-Cu7-N7	$\begin{array}{c} 177.87(15)\\ 82.73(12)\\ 82.05(11)\\ 83.90(14)\\ 95.27(14)\\ 98.28(12)\\ 97.93(16)\\ 77.85(11)\\ 162.74(14)\\ 111.01(13)\\ 83.19(12)\\ 94.11(14)\\ 77.98(11)\\ 164.82(15)\\ 176.59(15)\\ 81.14(11)\\ 84.74(16)\\ 100.38(13)\\ 97.58(17)\\ 109.19(13)\\ 76.74(11)\\ 103.44(13)\\ 79.98(11)\\ 105.66(13)\\ \end{array}$
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O10 O2-Cu1-N1 O4-Cu1-O10 O4-Cu1-N1 O10-Cu1-N1 O1-Cu2-O4 O1-Cu2-O5 O1-Cu2-O7 O1-Cu2-O7 O4-Cu2-O5 O4-Cu2-O7 O4-Cu2-O7 O4-Cu2-O7 O4-Cu2-N2 O5-Cu2-N2 O5-Cu2-N2 O7-Cu2-N2 O7-Cu2-N2 O1-Cu3-O7 O1-Cu3-O8 O1-Cu3-O8 O1-Cu3-O8 O1-Cu3-O8 O7-Cu3-O8	$\begin{array}{c} 177.11(16)\\ 83.15(12)\\ 79.56(11)\\ 84.72(15)\\ 94.47(15)\\ 102.82(13)\\ 97.38(16)\\ 79.56(11)\\ 165.23(15)\\ 106.20(13)\\ 83.32(12)\\ 94.66(16)\\ 80.18(11)\\ 165.34(16)\\ 176.40(16)\\ 80.42(11)\\ 84.90(15)\\ 102.22(13)\\ 96.61(18)\\ 106.41(14)\\ 79.23(11)\\ 100.58(13)\\ 78.44(11)\\ 106.76(13)\\ 178.25(14) \end{array}$	O13-Cu5-O14 O13-Cu5-O16 O13-Cu5-O19 O13-Cu5-N5 O14-Cu5-O16 O14-Cu5-O19 O14-Cu5-O19 O16-Cu5-N5 O19-Cu5-N5 O13-Cu6-O16 O13-Cu6-O17 O13-Cu6-O22 O13-Cu6-O17 O16-Cu6-O22 O16-Cu6-N6 O17-Cu6-O22 O16-Cu6-N6 O17-Cu6-N6 O122-Cu6-N6 O122-Cu6-N6 O16-Cu7-O19 O16-Cu7-O20 O16-Cu7-O22 O16-Cu7-O22 O16-Cu7-N7 O19-Cu7-O20	$\begin{array}{c} 177.87(15)\\ 82.73(12)\\ 82.05(11)\\ 83.90(14)\\ 95.27(14)\\ 98.28(12)\\ 97.93(16)\\ 77.85(11)\\ 162.74(14)\\ 111.01(13)\\ 83.19(12)\\ 94.11(14)\\ 77.98(11)\\ 164.82(15)\\ 176.59(15)\\ 81.14(11)\\ 84.74(16)\\ 100.38(13)\\ 97.58(17)\\ 109.19(13)\\ 76.74(11)\\ 103.44(13)\\ 79.98(11)\\ 105.66(13)\\ 177.47(15)\\ \end{array}$
O1-Cu1-O2 O1-Cu1-O4 O1-Cu1-O10 O1-Cu1-N1 O2-Cu1-O4 O2-Cu1-O10 O2-Cu1-O10 O4-Cu1-O10 O4-Cu1-N1 O10-Cu1-N1 O1-Cu2-O4 O1-Cu2-O5 O1-Cu2-O7 O1-Cu2-O7 O1-Cu2-O7 O4-Cu2-O5 O4-Cu2-O7 O4-Cu2-O7 O4-Cu2-O7 O4-Cu2-O7 O4-Cu2-N2 O5-Cu2-O7 O5-Cu2-N2 O7-Cu2-N2 O7-Cu2-N2 O1-Cu3-O7 O1-Cu3-O7 O1-Cu3-O8 O7-Cu3-O8 O7-Cu3-O10	177.11(16) $83.15(12)$ $79.56(11)$ $84.72(15)$ $94.47(15)$ $102.82(13)$ $97.38(16)$ $79.56(11)$ $165.23(15)$ $106.20(13)$ $83.32(12)$ $94.66(16)$ $80.18(11)$ $165.34(16)$ $176.40(16)$ $80.42(11)$ $84.90(15)$ $102.22(13)$ $96.61(18)$ $106.41(14)$ $79.23(11)$ $100.58(13)$ $78.44(11)$ $106.76(13)$ $178.25(14)$ $83.46(12)$	O13-Cu5-O14 O13-Cu5-O16 O13-Cu5-O19 O13-Cu5-N5 O14-Cu5-O16 O14-Cu5-O19 O14-Cu5-O19 O16-Cu5-N5 O19-Cu5-N5 O13-Cu6-O16 O13-Cu6-O17 O13-Cu6-O12 O13-Cu6-O22 O13-Cu6-O17 O16-Cu6-O22 O16-Cu6-O22 O16-Cu6-N6 O17-Cu6-O22 O17-Cu6-N6 O12-Cu6-N6 O12-Cu6-N6 O12-Cu6-N6 O12-Cu6-N6 O16-Cu7-O19 O16-Cu7-O19 O16-Cu7-O22 O16-Cu7-O22 O16-Cu7-N7 O19-Cu7-O20 O19-Cu7-O20 O19-Cu7-O20	$\begin{array}{c} 177.87(15)\\ 82.73(12)\\ 82.05(11)\\ 83.90(14)\\ 95.27(14)\\ 98.28(12)\\ 97.93(16)\\ 77.85(11)\\ 162.74(14)\\ 111.01(13)\\ 83.19(12)\\ 94.11(14)\\ 77.98(11)\\ 164.82(15)\\ 176.59(15)\\ 81.14(11)\\ 84.74(16)\\ 100.38(13)\\ 97.58(17)\\ 109.19(13)\\ 76.74(11)\\ 103.44(13)\\ 79.98(11)\\ 105.66(13)\\ 177.47(15)\\ 82.80(12)\\ \end{array}$

O8–Cu3–O10	94.80(14)	O20–Cu7–O22	94.73(15)	
O8–Cu3–N3	97.28(16)	O20–Cu7–N7	97.25(16)	
O10-Cu3-N3	165.66(15)	O22–Cu7–N7	165.10(15)	
O4–Cu4–O7	80.34(11)	O13–Cu8–O19	80.65(10)	
O4-Cu4-O10	80.70(11)	O13–Cu8–O22	77.08(11)	
O4-Cu4-O11	98.51(13)	O13–Cu8–O23	103.62(13)	
O4-Cu4-N4	107.13(14)	O13–Cu8–N8	104.32(13)	
O7-Cu4-O10	83.34(12)	O19–Cu8–O22	83.17(12)	
O7-Cu4-O11	95.48(15)	O19–Cu8–O23	92.84(14)	
O7–Cu4–N4	164.78(15)	O19–Cu8–N8	166.08(15)	
O10-Cu4-O11	178.68(15)	O22–Cu8–O23	175.81(14)	
O10-Cu4-N4	84.83(15)	O22–Cu8–N8	85.28(14)	
O11-Cu4-N4	96.43(18)	O23–Cu8–N8	98.48(16)	
			. /	

Table S3. Hydrogen bonding distances (Å) and angles (°) for complexes **1–4**.

D–H···A	D–H	H···A	D···A	D–H…A
1				
$O1-H1\cdots O3^{a}$	0.75(3)	1.95(3)	2.680(2)	164(3)
N1–H2····O3 ^b	0.79(2)	2.13(2)	2.8322(19)	148(2)
2				
$O1-H2\cdots O3^{c}$	0.92(4)	1.75(4)	2.666(5)	170(4)
N1-H1O3	0.85(5)	2.18(5)	2.877(6)	139(4)
3				
N1–H1C···O24 d	0.98	2.25	3.115(6)	146.0
N2–H2C···O21 ^{d}	0.98	2.24	3.097(6)	144.9
N3–H3C····O15	0.98	2.09	2.977(6)	149.6
N4–H4A…O18	0.98	2.10	2.997(6)	150.8
N5−H5B…O9	0.98	2.04	2.951(6)	153.7
N6–H6B…O12	0.98	2.18	3.062(6)	148.6
N7–H7B····O6 e	0.98	2.17	3.076(6)	152.7
N8−H8B…O3 ^e	0.98	2.21	3.083(6)	147.1
4				
$O1-H3\cdots N1^{f}$	0.91(2)	1.87(2)	2.7696(13)	167.7(18)
N1–H2···O1 ^g	0.856(17)	2.259(17)	3.0576(13)	155.5(14)
Symmetry codes: <i>a</i> –x, 1–y, 1–	-z; ^b 1–x, 1–y, 1–z; ^c	x, y, -1+z; d 1+x, y	<i>x</i> , <i>z</i> ; <i>^e</i> −1+ <i>x</i> , <i>y</i> , <i>z</i> ; ^{<i>f</i>} <i>x</i> −	-1/2, -y+1/2, 1-z; ^g
1-x, -y, 1-z.				



а

b

Figure S4. The representation of the packing of supramolecular chains in 1 down the c axis (a) and 2 down the a axis (b). H atoms are omitted for clarity. Colour scheme: Cu, cyan; O, red; N, blue; C, grey.



Figure S5. The representation of the packing of supramolecular chains in 1 down the *a* axis. H atoms are omitted for clarity. Colour scheme: Cu, cyan; O, red; N, blue; C, grey.



Figure S6. The representation of the packing of supramolecular chains in 2 down the *c*. H atoms are omitted for clarity. Colour scheme: Cu, cyan; O, red; N, blue; C, grey.



Figure S7. The diagram showing the shortest intermolecular Cu \cdots Cu separations in the crystal structures of Cu₄O₄ molecular complexes, basing on the CSD data.



Figure S8. Fragment of the ESI-MS spectrum of **2** showing the experimental and theoretical (inset) MS isotopic patterns for $[Cu_4(va)_3(bae)_4 - H]^+$.



Figure S9. ESI-MS spectra of 1 in methanol depending on the full concentration of copper.



Figure S10. ESI-MS spectra of 2 in methanol depending on the full concentration of copper.



Figure S11. ESI-MS spectra of 3 in methanol depending on the full concentration of copper.



Figure S12. Fragments of the chromatogram (bottom) showing the peak of a phenoxazinone chromophore (at 10.9 min) after 24 h oxidation of OAP catalysed by 2 mM of **2**. The inset shows the respective EI mass spectrum. The top chromatogram shows the intensity of 109 m/z signal, corresponding to a substrate (OAP), indicating the complete conversion of OAP.



Figure S13. UV-Vis spectrum of the solution obtained after 24 h stirring of 0.01 mM of OAP and 1.1 mM of **3** in methanol, under inert atmosphere. Due to strong absorbance of phenoxazinone chromophore direct measurement of solution spectrum was not possible. Instead, 0.5 mL of reaction mixture was diluted with 4 mL of methanol, the resulting solution was immediately transferred to UV cuvette. Further measurements performed after 5 and 10 min did not show notable changes of absorbance.

Table S4. Initial reaction rates W_0 of the OAP (0.01 M) oxidation with air dioxygen in methanol, catalysed by copper complexes (1 mM of total copper concentration).

Catalyst	$W_0, M s^{-1}$	Reference
1	1.3×10^{-7}	this work
2	7.0×10^{-8}	this work
3	4.0×10^{-8}	this work
$[Cu_{8}^{II}O(tbdea)_{6}(H_{2}O)_{2}](BF_{4})_{2}\cdot 3CH_{3}OH^{a}$	7.7×10^{-9}	[30]
$[Cu^{II}_{8}O(tbdea)_{5}(Htbdea)Cl_{2}][Cu^{I}Cl_{2}]\cdot 2H_{2}O$	2.2×10^{-8}	[31]
$[Cu^{I}(CH_{3}CN)_{2}](PF_{6})$	8.6×10^{-8}	this work
Cu(OAc) ₂	3.7×10^{-8}	this work
CuCl ₂ ^b	$8.4 imes 10^{-8}$	this work
$Cu(NO_3)_2$	3.5×10^{-7}	this work
Cu(NO ₃) / bipy ^c	4.7×10^{-8}	this work
3 / bipy	1.3×10^{-7}	this work

^a H_2t bdea = *N*-tert-butyldiethanolamine; ^b 0.5 mM of the catalyst was used; ^c bipy = 2,2'-bipyridine (1 mM).



Figure S14. ESI-MS spectra of 1 mM solutions of $CuCl_2 \cdot 2H_2O$ (top) and $Cu(NO_3)_2 \cdot 2H_2O$ (bottom) in methanol.



Figure S15. ESI-MS spectra of 1mM of **3** in methanol (top) and of the catalytic mixture of **3** (1 mM) and OAP (10 mM) in methanol taken one minute after the reaction initiation (bottom).



Figure S16. Increase in the phenoxazine band (435 nm) over time (the spectra were recoded with 2 min intervals) in the oxidation of OAP (2.4 mM) catalysed by **3** ($[Cu]_0 = 0.5 \text{ mM}$) in CH₃OH at room temperature. Green line shows the absorption spectra of pure **3** (1 mM) in CH₃OH taken. Inset shows evolution of 620 nm absorption with time.



Figure S17. Fragment of the chromatogram, showing the peaks of dioxygen (1.77 min) and water (1.83) in the oxidation of OAP (10 mM) with ¹⁸O₂, catalysed by **3** (1.2 mM), in methanol, after 3 h. The inset shows the EI mass-spectrum that discloses the presence of $H_2^{18}O_2$.



Figure S18. Fragment of the chromatogram showing the reaction products, non-reacted substrates and ligands in the oxidation of oxidation of 2-amino-*p*-cresol (APC) and *o*-aminophenol (OAP), 5 mM each, catalysed by 1 (1 mM). The inset shows the EI mass-spectra of the products.



Figure S19. The ball-and-stick representation of the structure of 4.



Figure S20. Fragments of the chromatograms showing the products of the aerobic oxidation of cis-1,2-dimethylcyclohexane, catalysed by 3 (1.5 mM), in the presence or absence of OAP.