Supporting Information

For

Ligand effects on Ni^{II}-catalysed alkane-hydroxylation with *m*-CPBA

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Table S1. Summary of X-ray crystallographic data of the Ni^{II}-complexes

Compound	1b	2a
empirical formula	$C_{84}H_{76}N_{10}O_6Ni_2B_2$	$C_{47}H_{47}N_4O_2NiB$
formula weight	1460.61	769.42
crystal system	monoclinic	triclinic
space group	$C2/c$ (#15)	P-1 (#2)
a, Å	19.523(13)	11.663(8)
b, Å	15.659(9)	13.381(9)
c, Å	24.697(14)	13.386(9)
α, deg	90	96.83(2)
β, deg	105.81(2)	93.04(2)
γ, deg	90	107.82(3)
V, Å^3	7264.5(76)	1965.9(22)
Z	4	2
$F(000)$	3056.00	812.00
D_{calcd}, g/cm^3	1.335	1.300
T, ˚C	−100	−100
crystal size, mm	0.48 x 0.27 x 0.27	0.55 x 0.45 x 0.35
μ (MoKα), cm^{-1}	5.814	5.382
$2\theta_{max}$, deg	54.9	54.9
no. of reflns meads	33599	18122
no. of reflns obsd	5840 [$I > 1.00\sigma(I)$]	6839 [$I > 2.00\sigma(I)$]
no. of variables	507	543
R^a; Rw^b	0.028; 0.035	0.051; 0.067
GOF	0.998	1.001

[a]$R = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$ [b]$R_W = [\, \Sigma \, w \, (|F_o| - |F_c|)^2 \, / \, \Sigma \, w \, F_o^2]^{1/2}$

Table S1. Summary of X-ray crystallographic data of the Ni^{II}-complexes (continued)

Compound	2b	3a•3MeOH
empirical formula	$C_{45}H_{44}N_5O_3NiB$	$C_{57}H_{74}N_3O_7NiB$
formula weight	772.38	982.74
crystal system	orthorhombic	monoclinic
space group	$P2_12_12_1$ (#19)	$P2_1/c$ (#14)
a, Å	7.6143(17)	12.679(6)
b, Å	15.539(5)	21.180(14)
c, Å	31.036(10)	20.233(12)
α, deg	90	90
β, deg	90	97.10(3)
γ, deg	90	90
V, Å^3	3672.1(19)	5391.5(56)
Z	4	4
$F(000)$	1624.00	2104.00
D_{calcd}, g/cm^3	1.397	1.211
T, ˚C	−102	−102
crystal size, mm	0.50 x 0.40 x 0.36	0.25 x 0.20 x 0.20
μ (MoKα), cm^{-1}	5.793	4.128
$2\theta_{max}$, deg	55.0	54.9
no. of reflns meads	34423	49485
no. of reflns obsd	7620 [$I > 2.00\sigma(I)$]	8067 [$I > 0.50\sigma(I)$]
no. of variables	541	693
R^a; Rw^b	0.026; 0.033	0.038; 0.055
GOF	0.997	1.000

[a] $R = \Sigma \; ||F_o| - |F_c|| \; / \; \Sigma \; |F_o|$ [b] $R_W = [\; \Sigma \; w \; (|F_o| - |F_c|)^2 \; / \; \Sigma \; w \; F_o^2]^{1/2}$

Table S1. Summary of X-ray crystallographic data of the Ni^{II}-complexes (continued)

Compound	**3b**	**4a**
empirical formula	$C_{29}H_{38}N_6O_7Ni$	$C_{31}H_{41}N_3O_3Ni$
formula weight	641.36	562.38
crystal system	triclinic	monoclinic
space group	P-1 (#2)	$P2_1/a$ (#14)
a, Å	11.123(5)	11.556(3)
b, Å	12.914(7)	21.132(8)
c, Å	22.138(13)	24.131(11)
α, deg	96.61(2)	90
β, deg	92.99(2)	92.054(17)
γ, deg	89.191(20)	90
V, Å^3	3154.5(29)	5888.9(37)
Z	4	8
$F(000)$	1352.00	2400.00
D_{calcd}, g/cm^3	1.350	1.269
T, ˚C	−102	−102
crystal size, mm	0.23 x 0.22 x 0.15	0.60 x 0.36 x 0.18
μ (MoKα), cm^{-1}	6.686	6.941
$2\theta_{max}$, deg	55.0	55.0
no. of reflns meads	30130	56961
no. of reflns obsd	8700 [$I > 1.00\sigma(I)$]	8218 [$I > 2.00\sigma(I)$]
no. of variables	851	767
R^a; Rw^b	0.040; 0.054	0.032; 0.040
GOF	1.000	1.000

[a]$R = \Sigma \ ||F_o| - |F_c|| \ / \ \Sigma \ |F_o|$ [b]$R_W = [\ \Sigma \ w \ (|F_o| - |F_c|)^2 \ / \ \Sigma \ w \ F_o^2]^{1/2}$

Table S1. Summary of X-ray crystallographic data of the Ni^{II}-complexes (continued)

Compound	**4b**	**5a**
empirical formula	$C_{29}H_{38}N_4O_4Ni$	$C_{23}H_{27}N_3O_5Ni$
formula weight	565.34	484.18
crystal system	monoclinic	monoclinic
space group	$P2_1/c$ (#14)	$P2_1/n$ (#14)
a, Å	11.887(6)	12.217(7)
b, Å	20.791(10)	12.711(6)
c, Å	11.743(5)	14.359(9)
α, deg	90	90
β, deg	93.758(18)	92.65(2)
γ, deg	90	90
V, Å^3	2896.0(24)	2227.5(21)
Z	4	4
$F(000)$	1200.00	1016.00
D_{calcd}, g/cm^3	1.297	1.444
T, ˚C	−102	−102
crystal size, mm	0.60 x 0.35 x 0.10	0.60 x 0.35 x 0.30
μ (MoKα), cm^{-1}	7.094	9.110
$2\theta_{max}$, deg	54.9	54.8
no. of reflns meads	27773	20740
no. of reflns obsd	4552 [$I > 1.00\sigma(I)$]	3644 [$I > 2.00\sigma(I)$]
no. of variables	381	316
R[a]; Rw[b]	0.023; 0.033	0.029; 0.036
GOF	0.996	1.008

[a]$R = \Sigma \ ||F_o| - |F_c|| \ / \ \Sigma \ |F_o|$ [b]$R_W = [\ \Sigma \ w \ (|F_o| - |F_c|)^2 \ / \ \Sigma \ w \ F_o^2 \ ]^{1/2}$

Table S1. Summary of X-ray crystallographic data of the Ni^{II}-complexes (continued)

Compound	**6a•C$_3$H$_6$O**
empirical formula	C$_{50}$H$_{54}$N$_3$O$_4$NiB
formula weight	830.50
crystal system	triclinic
space group	P-1 (#2)
a, Å	12.478(8)
b, Å	14.135(8)
c, Å	14.821(8)
α, deg	62.383(15)
β, deg	82.53(2)
γ, deg	70.83(2)
V, Å^3	2187.1(22)
Z	2
$F(000)$	880.00
D_{calcd}, g/cm^3	1.261
T, ˚C	−102
crystal size, mm	0.55 x 0.35 x 0.30
μ (MoKα), cm^{-1}	4.915
$2\theta_{max}$, deg	54.9
no. of reflns meads	21606
no. of reflns obsd	6266 [$I > 2.00\sigma(I)$]
no. of variables	586
R^a; Rw^b	0.032; 0.039
GOF	1.028

[a] $R = \Sigma \ ||F_o| - |F_c|| \ / \ \Sigma \ |F_o|$ [b] $R_W = [\ \Sigma \ w \ (|F_o| - |F_c|)^2 \ / \ \Sigma \ w \ F_o^2]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (deg) of the Ni^{II}-complexes

1b

Ni(1)–O(1)	2.0711(12)	Ni(1)–O(2)*	2.1233(15)
Ni(1)–N(1)	2.0851(14)	Ni(1)–N(2)	2.0469(14)
Ni(1)–N(3)	2.0408(16)	Ni(1)–N(4)	2.0547(13)
Ni(1)–Ni(1)*	4.8370(2)		

O(1)–Ni(1)–O(2)*	89.15(5)	O(1)–Ni(1)–N(1)	169.62(5)
O(1)–Ni(1)–N(2)	102.65(6)	O(1)–Ni(1)–N(3)	87.22(5)
O(1)–Ni(1)–N(4)	95.01(5)	O(2)*–Ni(1)–N(1)	99.29(6)
O(2)*–Ni(1)–N(2)	96.49(5)	O(2)*–Ni(1)–N(3)	173.82(5)
O(2)*–Ni(1)–N(4)	83.07(5)	N(1)–Ni(1)–N(2)	82.50(5)
N(1)–Ni(1)–N(3)	83.83(6)	N(1)–Ni(1)–N(4)	80.14(5)
N(2)–Ni(1)–N(3)	89.19(6)	N(2)–Ni(1)–N(4)	162.32(6)
N(3)–Ni(1)–N(4)	92.26(6)		

2a

Ni(1)–O(1)	2.0971(17)	Ni(1)–O(2)	2.1653(17)
Ni(1)–N(1)	2.094(2)	Ni(1)–N(2)	2.145(2)
Ni(1)–N(3)	2.081(2)	Ni(1)–N(4)	2.126(2)

O(1)–Ni(1)–O(2)	62.02(7)	O(1)–Ni(1)–N(1)	166.87(8)
O(1)–Ni(1)–N(2)	88.26(8)	O(1)–Ni(1)–N(3)	96.00(7)
O(1)–Ni(1)–N(4)	87.49(8)	O(2)–Ni(1)–N(1)	104.85(7)
O(2)–Ni(1)–N(2)	82.87(7)	O(2)–Ni(1)–N(3)	157.78(8)
O(2)–Ni(1)–N(4)	88.01(8)	N(1)–Ni(1)–N(2)	89.88(9)
N(1)–Ni(1)–N(3)	97.10(8)	N(1)–Ni(1)–N(4)	92.43(9)
N(2)–Ni(1)–N(3)	93.86(9)	N(2)–Ni(1)–N(4)	170.88(8)
N(3)–Ni(1)–N(4)	94.61(9)		

[a]Estimated standard deviations are given in parentheses.

Table S2. Selected bond lengths (Å) and angles (deg) of the Ni[II]-complexes (continued)

2b

Ni(1)–O(1)	2.1576(12)	Ni(1)–O(2)	2.1676(12)
Ni(1)–N(1)	2.1044(13)	Ni(1)–N(2)	2.0988(15)
Ni(1)–N(3)	2.0451(14)	Ni(1)–N(4)	2.1692(15)

O(1)–Ni(1)–O(2)	59.85(4)	O(1)–Ni(1)–N(1)	165.79(4)
O(1)–Ni(1)–N(2)	84.14(5)	O(1)–Ni(1)–N(3)	96.20(5)
O(1)–Ni(1)–N(4)	88.03(5)	O(2)–Ni(1)–N(1)	106.90(4)
O(2)–Ni(1)–N(2)	85.93(5)	O(2)–Ni(1)–N(3)	156.04(5)
O(2)–Ni(1)–N(4)	84.90(5)	N(1)–Ni(1)–N(2)	90.03(5)
N(1)–Ni(1)–N(3)	96.88(5)	N(1)–Ni(1)–N(4)	96.21(5)
N(2)–Ni(1)–N(3)	91.25(5)	N(2)–Ni(1)–N(4)	170.10(5)
N(3)–Ni(1)–N(4)	95.61(5)		

3a

Ni(1)–O(1)	2.0803(19)	Ni(1)–O(2)	2.0986(18)
Ni(1)–O(4)	2.054(2)	Ni(1)–N(1)	2.079(2)
Ni(1)–N(2)	2.063(2)	Ni(1)–N(3)	2.064(2)

O(1)–Ni(1)–O(2)	87.08(7)	O(1)–Ni(1)–O(4)	90.83(8)
O(1)–Ni(1)–N(1)	92.67(8)	O(1)–Ni(1)–N(2)	92.38(8)
O(1)–Ni(1)–N(3)	168.90(8)	O(2)–Ni(1)–O(4)	92.30(8)
O(2)–Ni(1)–N(1)	91.89(8)	O(2)–Ni(1)–N(2)	174.57(9)
O(2)–Ni(1)–N(3)	83.59(8)	O(4)–Ni(1)–N(1)	174.67(8)
O(4)–Ni(1)–N(2)	93.11(8)	O(4)–Ni(1)–N(3)	95.51(9)
N(1)–Ni(1)–N(2)	82.73(9)	N(1)–Ni(1)–N(3)	81.68(9)
N(2)–Ni(1)–N(3)	96.35(8)		

[a]Estimated standard deviations are given in parentheses.

Table S2. Selected bond lengths (Å) and angles (deg) of the Ni^{II}-complexes (continued)

3b (Molecule 1)

Ni(1)–O(1)	2.148(2)	Ni(1)–O(2)	2.089(2)
Ni(1)–N(1)	2.075(2)	Ni(1)–N(2)	2.057(3)
Ni(1)–N(3)	2.081(3)	Ni(1)–N(5)	2.025(3)
O(1)–Ni(1)–O(2)	177.16(9)	O(1)–Ni(1)–N(1)	90.14(9)
O(1)–Ni(1)–N(2)	87.11(10)	O(1)–Ni(1)–N(3)	96.24(10)
O(1)–Ni(1)–N(5)	87.65(10)	O(2)–Ni(1)–N(1)	88.05(10)
O(2)–Ni(1)–N(2)	90.49(11)	O(2)–Ni(1)–N(3)	85.58(11)
O(2)–Ni(1)–N(5)	94.37(10)	N(1)–Ni(1)–N(2)	82.66(11)
N(1)–Ni(1)–N(3)	79.38(11)	N(1)–Ni(1)–N(5)	173.92(12)
N(2)–Ni(1)–N(3)	161.73(11)	N(2)–Ni(1)–N(5)	102.87(12)
N(3)–Ni(1)–N(5)	95.23(12)		

3b (Molecule 2)

Ni(2)–O(5)	2.151(2)	Ni(2)–O(6)	2.091(2)
Ni(2)–N(6)	2.079(2)	Ni(2)–N(7)	2.046(3)
Ni(2)–N(8)	2.075(3)	Ni(2)–N(10)	2.027(3)
O(5)–Ni(2)–O(6)	176.42(10)	O(5)–Ni(2)–N(6)	89.79(9)
O(5)–Ni(2)–N(7)	87.77(10)	O(5)–Ni(2)–N(8)	95.67(10)
O(5)–Ni(2)–N(10)	88.16(10)	O(6)–Ni(2)–N(6)	87.78(10)
O(6)–Ni(2)–N(7)	89.32(11)	O(6)–Ni(2)–N(8)	86.47(10)
O(6)–Ni(2)–N(10)	94.50(10)	N(6)–Ni(2)–N(7)	82.63(11)
N(6)–Ni(2)–N(8)	79.67(11)	N(6)–Ni(2)–N(10)	174.49(12)
N(7)–Ni(2)–N(8)	161.94(11)	N(7)–Ni(2)–N(10)	102.39(12)
N(8)–Ni(2)–N(10)	95.45(12)		

[a]Estimated standard deviations are given in parentheses.

Table S2. Selected bond lengths (Å) and angles (deg) of the Ni^II-complexes (continued)

4a (Molecule 1)

Ni(1)–O(1)	1.9874(16)	Ni(1)–O(2)	2.1086(18)
Ni(1)–O(3)	2.1829(18)	Ni(1)–N(1)	2.134(2)
Ni(1)–N(2)	2.069(2)	Ni(1)–N(3)	2.0749(19)

O(1)–Ni(1)–O(2)	84.63(7)	O(1)–Ni(1)–O(3)	83.56(6)
O(1)–Ni(1)–N(1)	93.73(7)	O(1)–Ni(1)–N(2)	93.20(7)
O(1)–Ni(1)–N(3)	172.23(7)	O(2)–Ni(1)–O(3)	61.39(6)
O(2)–Ni(1)–N(1)	169.70(7)	O(2)–Ni(1)–N(2)	96.30(7)
O(2)–Ni(1)–N(3)	89.50(7)	O(3)–Ni(1)–N(1)	108.34(7)
O(3)–Ni(1)–N(2)	157.63(7)	O(3)–Ni(1)–N(3)	89.17(7)
N(1)–Ni(1)–N(2)	93.93(7)	N(1)–Ni(1)–N(3)	91.14(7)
N(2)–Ni(1)–N(3)	92.50(7)		

4a (Molecule 2)

Ni(2)–O(4)	1.9956(15)	Ni(2)–O(5)	2.1202(18)
Ni(2)–O(6)	2.1619(17)	Ni(2)–N(4)	2.087(2)
Ni(2)–N(5)	2.0747(19)	Ni(2)–N(6)	2.087(2)

O(4)–Ni(2)–O(5)	85.10(6)	O(4)–Ni(2)–O(6)	87.68(6)
O(4)–Ni(2)–N(4)	93.70(7)	O(4)–Ni(2)–N(5)	87.79(7)
O(4)–Ni(2)–N(6)	174.82(7)	O(5)–Ni(2)–O(6)	61.76(6)
O(5)–Ni(2)–N(4)	164.41(7)	O(5)–Ni(2)–N(5)	99.66(7)
O(5)–Ni(2)–N(6)	89.74(7)	O(6)–Ni(2)–N(4)	102.69(7)
O(6)–Ni(2)–N(5)	161.19(7)	O(6)–Ni(2)–N(6)	90.25(7)
N(4)–Ni(2)–N(5)	95.81(8)	N(4)–Ni(2)–N(6)	91.39(7)
N(5)–Ni(2)–N(6)	92.68(8)		

[a]Estimated standard deviations are given in parentheses.

Table S2. Selected bond lengths (Å) and angles (deg) of the Ni^{II}-complexes (continued)

4b

Ni(1)–O(1)	1.9742(10)	Ni(1)–O(2)	2.1624(13)
Ni(1)–O(3)	2.1639(13)	Ni(1)–N(1)	2.0805(14)
Ni(1)–N(2)	2.0516(14)	Ni(1)–N(3)	2.0764(13)

O(1)–Ni(1)–O(2)	82.94(4)	O(1)–Ni(1)–O(3)	85.12(4)
O(1)–Ni(1)–N(1)	95.69(5)	O(1)–Ni(1)–N(2)	93.17(5)
O(1)–Ni(1)–N(3)	170.68(5)	O(2)–Ni(1)–O(3)	59.96(4)
O(2)–Ni(1)–N(1)	164.51(5)	O(2)–Ni(1)–N(2)	99.08(5)
O(2)–Ni(1)–N(3)	88.35(5)	O(3)–Ni(1)–N(1)	104.56(5)
O(3)–Ni(1)–N(2)	159.04(5)	O(3)–Ni(1)–N(3)	87.67(5)
N(1)–Ni(1)–N(2)	96.40(5)	N(1)–Ni(1)–N(3)	91.82(5)
N(2)–Ni(1)–N(3)	91.46(5)		

5a

Ni(1)–O(1)	2.0380(15)	Ni(1)–O(3)	2.0784(15)
Ni(1)–O(5)	2.0890(14)	Ni(1)–N(1)	2.1636(17)
Ni(1)–N(2)	2.0775(18)	Ni(1)–N(3)	2.1020(17)

O(1)–Ni(1)–O(3)	95.45(5)	O(1)–Ni(1)–O(5)	93.75(6)
O(1)–Ni(1)–N(1)	166.53(6)	O(1)–Ni(1)–N(2)	90.01(6)
O(1)–Ni(1)–N(3)	94.39(6)	O(3)–Ni(1)–O(5)	89.58(5)
O(3)–Ni(1)–N(1)	90.54(6)	O(3)–Ni(1)–N(2)	83.65(6)
O(3)–Ni(1)–N(3)	169.81(6)	O(5)–Ni(1)–N(1)	98.36(6)
O(5)–Ni(1)–N(2)	172.55(6)	O(5)–Ni(1)–N(3)	87.16(6)
N(1)–Ni(1)–N(2)	78.65(6)	N(1)–Ni(1)–N(3)	80.40(6)
N(2)–Ni(1)–N(3)	98.98(6)		

[a]Estimated standard deviations are given in parentheses.

Table S2. Selected bond lengths (Å) and angles (deg) of the Ni^{II}-complexes (continued)

6a

Ni(1)–O(1)	2.1779(15)	Ni(1)–O(2)	2.1077(12)
Ni(1)–O(3)	2.1146(14)	Ni(1)–N(1)	2.097(2)
Ni(1)–N(2)	2.0641(17)	Ni(1)–N(3)	2.0891(18)
O(1)–Ni(1)–O(2)	61.62(6)	O(1)–Ni(1)–O(3)	80.71(5)
O(1)–Ni(1)–N(1)	159.74(6)	O(1)–Ni(1)–N(2)	102.96(6)
O(1)–Ni(1)–N(3)	89.53(6)	O(2)–Ni(1)–O(3)	88.00(5)
O(2)–Ni(1)–N(1)	98.98(6)	O(2)–Ni(1)–N(2)	164.44(7)
O(2)–Ni(1)–N(3)	85.81(5)	O(3)–Ni(1)–N(1)	93.54(6)
O(3)–Ni(1)–N(2)	91.61(6)	O(3)–Ni(1)–N(3)	170.09(6)
N(1)–Ni(1)–N(2)	96.57(7)	N(1)–Ni(1)–N(3)	95.06(7)
N(2)–Ni(1)–N(3)	92.28(7)		

[a]Estimated standard deviations are given in parentheses.

Fig. S1
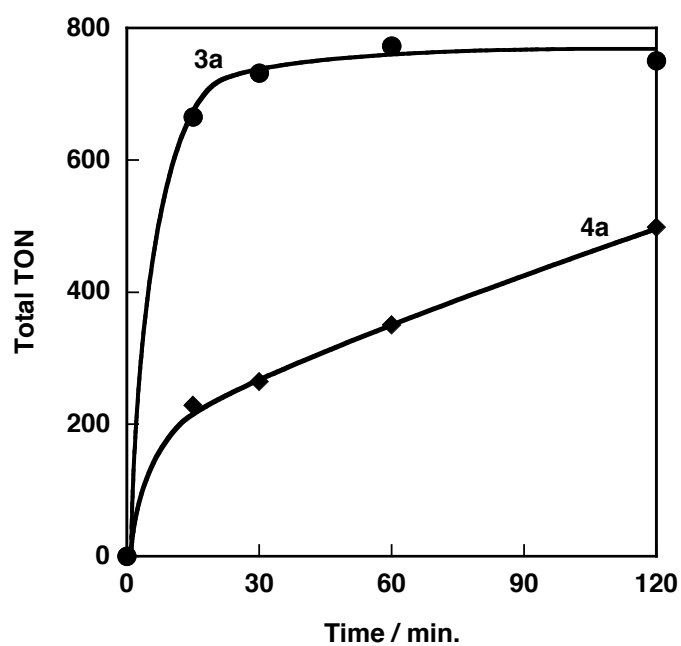
Fig. S1 Time courses for the oxidation of cyclohexane (2.5 M) with *m*-CPBA (0.33 M) catalyzed by (●) [Ni^{II}(^{Dtbp}Pym2H)(OAc)(MeOH)]BPh$_4$ (**3a**) (0.33 mM) and by (◆) [Ni^{II}(^{Dtbp}Pye2)(OAc)] (**4a**) (0.33 mM) in CH$_2$Cl$_2$/CH$_3$CN (v/v = 3/1, totally 6 ml) at room temperature.

Fig. S2
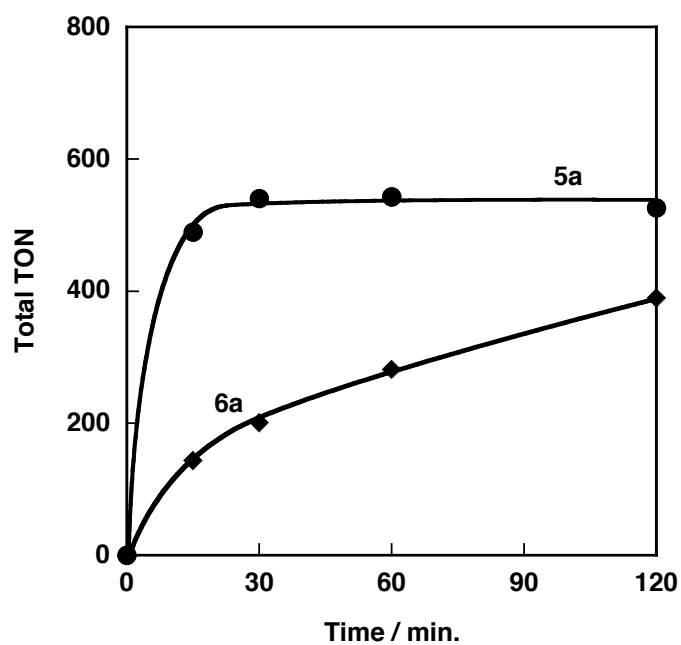
Fig. S2   Time courses for the oxidation of cyclohexane (2.5 M) with *m*-CPBA (0.33 M) catalyzed by (●) [Ni^{II}(^{Bz}Pym2)(OAc)$_2$(H$_2$O)] (**5a**) (0.33 mM) and by (◆) [Ni^{II}(^{Bz}Pye2)(OAc)(H$_2$O)]BPh$_4$ (**6a**) (0.33 mM) in CH$_2$Cl$_2$/CH$_3$CN (v/v = 3/1, totally 6 ml) at room temperature.

Fig. S3
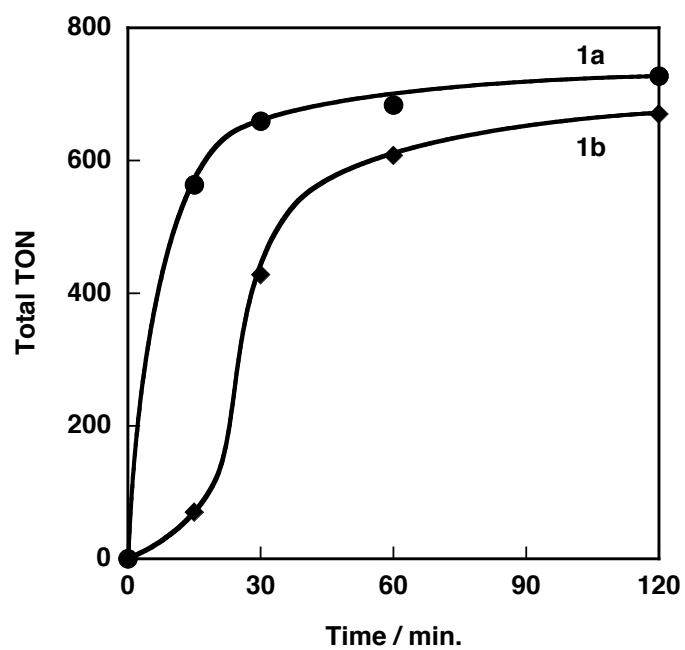
Fig. S3 Time courses for the oxidation of cyclohexane (2.5 M) with *m*-CPBA (0.33 M) catalyzed by (●) [Ni^{II}(TPA)(OAc)(H$_2$O)]BPh$_4$ (**1a**) (0.33 mM) and by (◆) [Ni^{II}$_2$(TPA)$_2$(μ-NO$_3$)$_2$](BPh$_4$)$_2$ (**1b**) (0.17 mM) in CH$_2$Cl$_2$/CH$_3$CN (v/v = 3/1, totally 6 ml) at room temperature.

Fig. S4
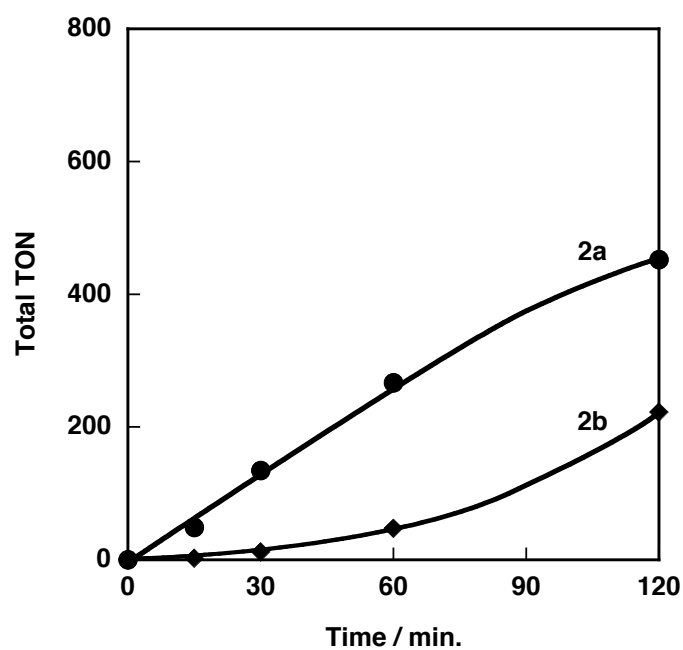
Fig. S4 Time courses for the oxidation of cyclohexane (2.5 M) with *m*-CPBA (0.33 M) catalyzed by (●) [Ni^{II}(TEPA)(OAc)]BPh$_4$ (**2a**) (0.33 mM) and by (◆) [Ni^{II}(TEPA)(NO$_3$)]BPh$_4$ (**2b**) (0.33 mM) in CH$_2$Cl$_2$/CH$_3$CN (v/v = 3/1, totally 6 ml) at room temperature.

Fig. S5
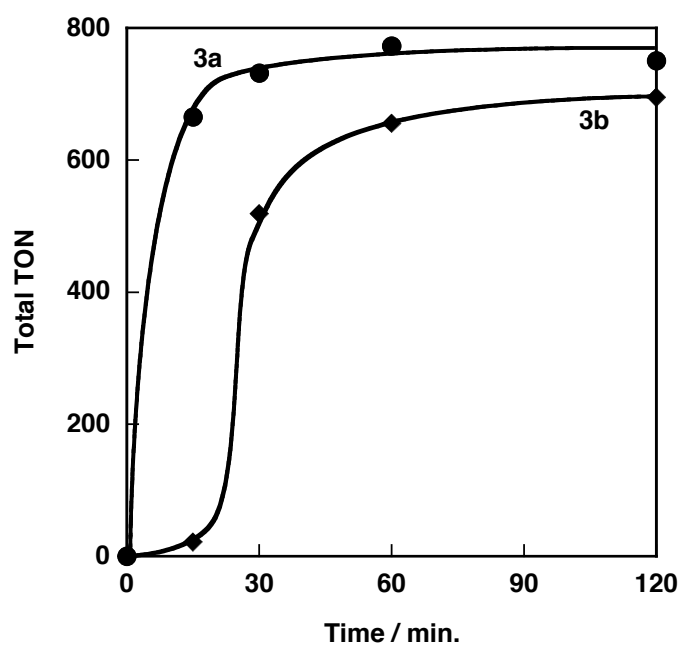
Fig. S5 Time courses for the oxidation of cyclohexane (2.5 M) with *m*-CPBA (0.33 M) catalyzed by (●) [Ni^{II}(^{Dtbp}Pym2H)(OAc)(MeOH)]BPh$_4$ (**3a**) (0.33 mM) and by (◆) [Ni^{II}(^{Dtbp}Pym2H)(NO$_3$)(MeCN)]NO$_3$ (**3b**) (0.33 mM) in CH$_2$Cl$_2$/CH$_3$CN (v/v = 3/1, totally 6 ml) at room temperature.

Fig. S6
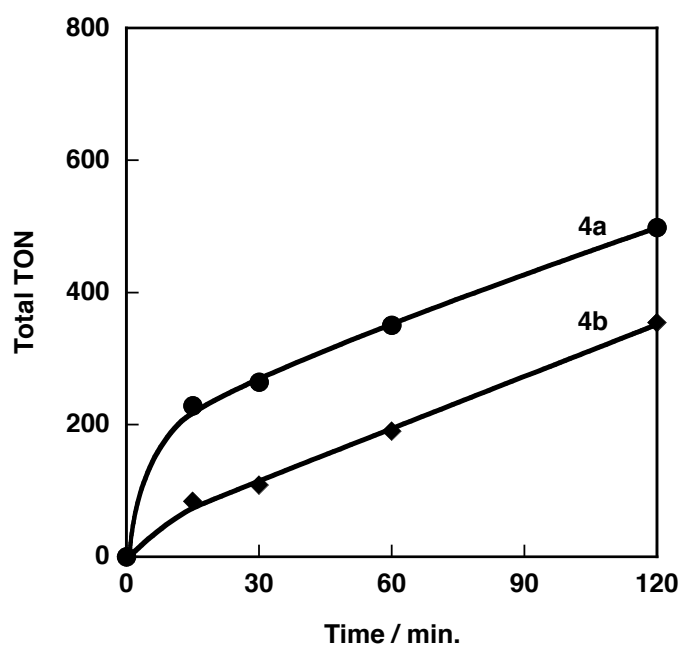
Fig. S6 Time courses for the oxidation of cyclohexane (2.5 M) with *m*-CPBA (0.33 M)

catalyzed by (●) [Ni^{II}(^{Dtbp}Pye2)(OAc)] (**4a**) (0.33 mM) and by (◆)

[Ni^{II}(^{Dtbp}Pye2)(NO$_3$)] (**4b**) (0.33 mM) in CH$_2$Cl$_2$/CH$_3$CN (v/v = 3/1, totally 6 ml) at

room temperature.