

Chiral and Achiral Bis(2-oxazolinyphenolato)nickel(II) Complexes—Synthesis, Crystal Structure, and Catalytic Properties

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A series of chiral and achiral bis(2-oxazolinyphenolato)nickel(II) complexes **2** were synthesized by reactions of various 2-(4,5-dihydro-2-oxazolyl)phenol derivatives with nickel chloride hexahydrate. The molecular structure of complex **2a** was determined by X-ray single crystal diffraction. The crystal of complex **2a** was monoclinic, space group $P2_1$ with cell dimension of $a=1.1121(4)$ nm, $b=0.9472(3)$ nm, $c=1.4113(5)$ nm, $\alpha=\gamma=90^\circ$, $\beta=91.450(6)^\circ$, $V=1.4861(8)$ nm³, $Z=2$, and $\mu=0.693$ mm⁻¹. In the solid state, the nickel(II) ion was in a square-planar coordination geometry. The catalytic activities of complexes **2** in Baeyer-Villiger reaction with molecular oxygen were investigated.

Keywords nickel complexes, oxazoline, crystal structure, Baeyer-Villiger oxidation

Introduction

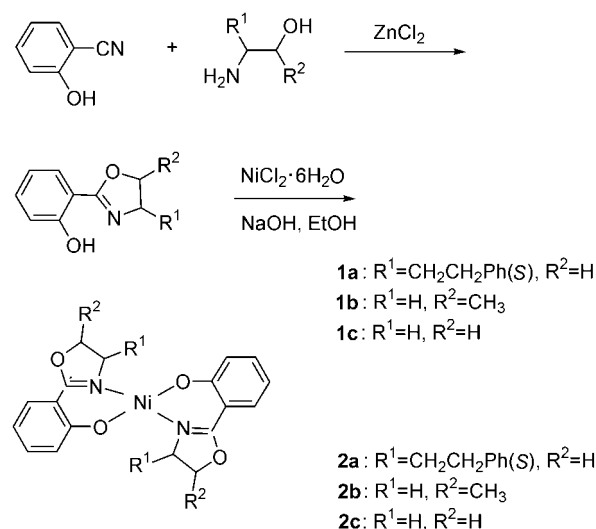
Oxidation was a very important reaction both in synthetic pathways and in industrial processes. Metal-catalyzed oxidation provided excellent alternatives in synthetic processes. However, molecular oxygen has been applied only in a limited number of metal-catalyzed oxidations, because it was very difficult to activate molecular oxygen and most of transition metal complexes were sensitive to oxygen. It was noted that metal-catalyzed Baeyer-Villiger oxidation was a convenient method for activating molecular oxygen, although highly oxidized reagents, for example, peroxide and peracid compounds, were also used as the source of oxygen in the reaction.

Recently, oxazoline compounds received considerable attention in scientific and industrial fields, because they could be used in many aspects, such as in coordination chemistry as important ligands, in asymmetric synthesis as valuable chiral auxiliary reagents, and in synthetic organic chemistry as protecting groups for carboxylic acid.^{1,2} Some transition metal catalysts, containing substituent 2-(4,5-dihydro-2-oxazolyl)phenol ligands and having the strong chelating ability,³⁻⁵ showed good properties especially in the catalytic oxidation reactions.⁶⁻¹⁰ It was significant that Bolm^{11,12} reported that Ni(oxa)₂ and Cu(oxa)₂ complexes catalyzed the Baeyer-Villiger oxidation of ketones using molecular oxygen to afford lactones in high yields, and his group also explored many catalytic oxidation systems, for example, magnesium, aluminum, zirconium, nickel, and copper metal catalysts.¹³⁻¹⁶ Feng *et al.*¹⁷ described

the asymmetric Baeyer-Villiger oxidation catalyzed by Cu(II) complexes bearing chiral salen or oxazoline ligands substituted by two phenyl on the oxazoline ring in 59% yields and with 26% *e.e.*. Uchida *et al.*¹⁸ attempted the enantioselective Baeyer-Villiger oxidation of 3-arylcyclobutanones using H₂O₂ in the presence of cationic Co(III)(salen) complexes.

In this paper, we report the synthesis and characterization of some chiral and achiral bis(2-oxazolinyphenolato)nickel(II) complexes **2** (Scheme 1), and their catalytic behavior in Baeyer-Villiger oxidation with molecular oxygen.

Scheme 1 Synthetic routes of complexes **2**



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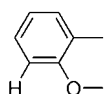
Results and discussion

Synthesis and structure characterization

Bis(2-oxazolinyphenolato)nickel(II) complexes **2** are successfully synthesized by the addition of the sodium hydroxide in ethanol to an alcoholic solution of ligands **1** and the nickel chloride hexahydrate in high yields. The synthetic routes are shown in Scheme 1. Complexes **2** are obtained as dark green needle crystals, and they are soluble and stable in some organic solvents (*e.g.* CH₂Cl₂, CHCl₃, CH₃CN, and THF), allowing for full characterization by ¹H NMR, IR, MS, and EA.

The ¹H NMR spectra of **2** in CDCl₃ show that the signals of phenoxo proton C₆H₄O of **2** are shifted upfield about 0.2–0.4 ppm in comparison with those of ligands **1**. Furthermore, the signals of the aromatic

H-atom adjacent to O-atom in the



2a are drastically shifted upfield (6.35 ppm for **2a** and 7.02 ppm for **1a**). These indicate that the formation of the Ni—O bond leads to the decrease of electron density of the phenyl ring.

In addition, it is noted that the signals of CH₂CH₂ protons of **2a** are different from those of **1a** and (*S*)-NH₂CH(CH₂CH₂Ph)CH₂OH, since the latter both show the distinct AA'BB' system in the ¹H NMR spectra, as shown in Scheme 2.

The signals of CH₂CH₂Ph methylene protons of **2a** form one multiplet at 2.75–2.82 ppm, but the signals of CH₂CH₂Ph methylene protons are two separated multiplets, one of which is shifted downfield about 0.5 ppm in comparison with those of **1a**. The coordination of the nitrogen atom to the central nickel(II) probably constraints the geometry of CH₂CH₂Ph group, which makes the two CH₂CH₂Ph protons lie in different geometric environment and become two magnetic inequivalent

protons. At the same time, in one molecule, the effects of the phenoxy C₆H₄O in the second ligand on the chemical shift of the CH₂CH₂Ph protons in the first ligand are not be neglected since they are adjacent in geometry.

The IR spectra of the free ligands **1** show a very strong absorption band at 1642 cm⁻¹, which is attributed to ν_{C=N} of the oxazoline ring, while the ν_{C=N} of complexes **2** is at 1621–1626 cm⁻¹. The shift of the C=N stretching vibration of oxazoline ring to a lower frequency indicates the decrease of the C=N stretching vibration force constant as a consequence of coordination with the nitrogen atom, which is consistent with the results of X-ray diffraction. The weak absorption bands of **2** at 585–590 cm⁻¹ and 470–479 cm⁻¹ may be attributed to ν_{Ni-N} and ν_{Ni-O}, respectively.¹⁹ So, from the above discussions, we can explain the structure of complexes **2** shown in Scheme 1 very well.

Crystal structure of complex **2a**

The molecular structure of complex **2a** is determined by X-ray diffraction. Data are collected on a Bruker SMART 1000 CCD area-detector diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.071073 nm) at 293 K. Crystal data and structure refinement for complex **2a** are listed in Table 1. Selected geometrical parameters for complex **2a** are given in Table 2. The molecular structure and crystal cell structure are shown in Figure 1 and Figure 2, respectively.

In the solid state of complex **2a**, the nickel(II) atom is a distorted square planar for the four-coordination. The Ni atom is bonded to two oxygen and two nitrogen atoms; both pairs are in *trans* position (O-Ni-N angles: 87.1°–92.5°). However, a comparison of angles around the Ni atom shows a slight deviation from the ideal square-planar arrangement towards the tetrahedral configuration; the angles of O(1)-Ni-O(3) and

Scheme 2 The comparison of ¹H NMR spectra of —CH₂CH₂—

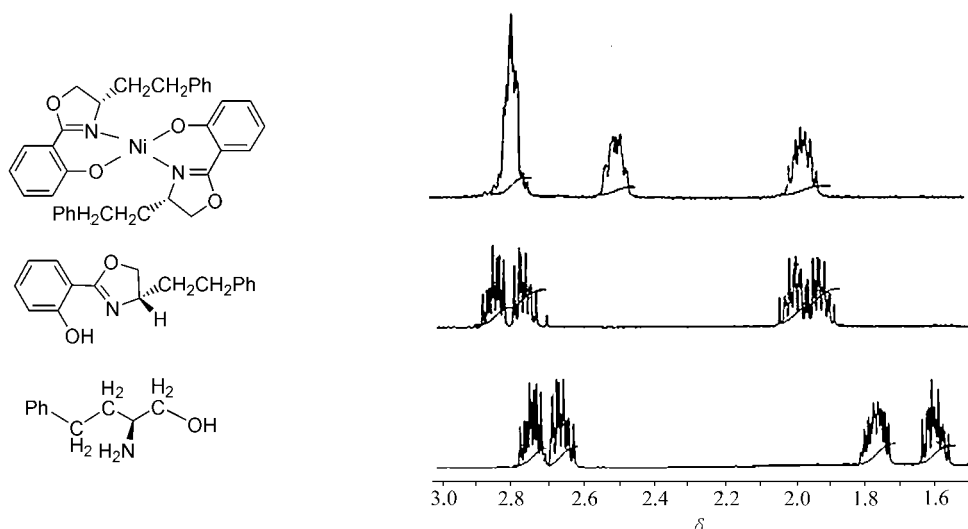


Table 1 Crystal data and structure refinement for complex **2a**

Empirical formula	C ₃₄ H ₃₂ N ₂ O ₄ Ni
<i>M_r</i> /(g·mol ⁻¹)	591.33
Crystal system	Monoclinic
Space group	<i>P</i> 2(1)
<i>a</i> /nm	1.1121(4)
<i>b</i> /nm	0.9472(3)
<i>c</i> /nm	1.4113(5)
<i>α</i> (°)	90
<i>β</i> (°)	91.450(6)
<i>γ</i> (°)	90
Volume/nm ³	1.4861(8)
<i>Z</i>	2
<i>D_c</i> /(Mg·m ⁻³)	1.321
<i>μ</i> (Mo <i>Kα</i>)/mm ⁻¹	0.693
<i>F</i> (000)	620
Crystal size/mm ³	0.233×0.129×0.097
<i>θ</i> range/(°)	1.83< <i>θ</i> <25.50
Ranges of <i>h, k, l</i>	-13≤ <i>h</i> ≤13, -9≤ <i>k</i> ≤11, -14≤ <i>l</i> ≤17
Reflections collected/unique	7746/4585 (<i>R</i> _{int} =0.0967)
Completeness to <i>θ</i> =25.50°	99.9%
Absorption correction	SADABS
Max. and min. transmission	1.00000 and 0.67834
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4585/15/361
GOF on <i>F</i> ²	0.915
Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> ₁ =0.0929, <i>wR</i> ₂ =0.2364
<i>R</i> indices (all data)	<i>R</i> ₁ =0.1719, <i>wR</i> ₂ =0.3206
Extinction coefficient	-0.12(6)
Largest residual peaks/(e·nm ⁻³)	850 and -935

N(1)-Ni-N(2) are 174.8(5)° and 175.8(5)°, respectively, which are smaller than the ideal angle of 180°. It is noted that the Ni—N bond lengths are slightly shorter than the values reported for the *i*-Pr substituent bis(2-oxazolinyphenolato)nickel(II) complex; whereas the Ni—O bond lengths are slightly longer than those of *i*-Pr substituent oxazoline-nickel complex.⁴

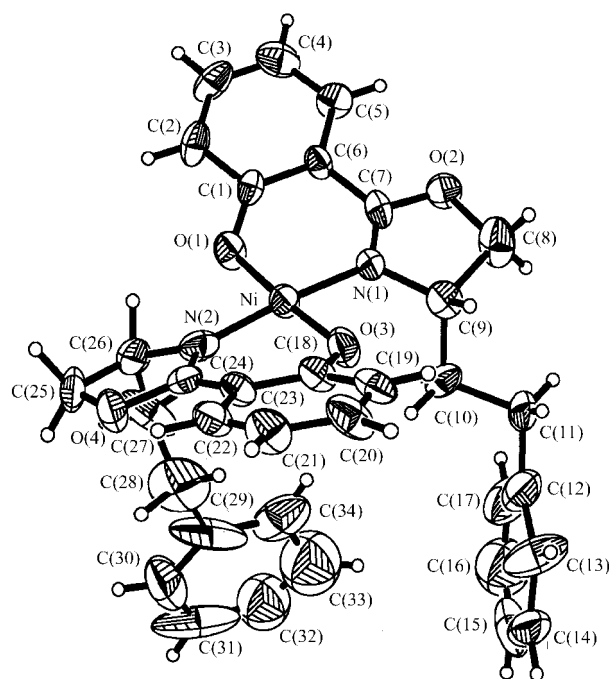
Catalytic Baeyer-Villiger oxidation of cyclohexanone by complexes **2**

The Baeyer-Villiger oxidations of cyclohexanone and 2-benzylcyclohexanone with molecular oxygen were carried out in 1,2-dichloroethane solution at room temperature with the presence of complexes **2** (0.5 mol%) and the benzaldehyde used as the oxygen acceptor. The corresponding lactones were obtained, as shown in Scheme 3 and Table 3.

Complexes **2** show high activities in the catalytic

Table 2 Selected bond lengths (nm) and angles (°) for complex **2a**

Ni—O(1)	0.1840(10)	N(1)—C(7)	0.1258(18)
Ni—O(3)	0.1877(11)	N(1)—C(9)	0.1523(19)
Ni—N(1)	0.1859(11)	C(6)—C(7)	0.151(3)
Ni—N(2)	0.1844(13)	C(8)—C(9)	0.159(2)
O(1)—C(1)	0.1364(17)	C(9)—C(10)	0.152(2)
O(2)—C(7)	0.1367(17)	C(10)—C(11)	0.156(2)
O(2)—C(8)	0.150(2)	C(11)—C(12)	0.151(3)
O(1)-Ni-N(1)	92.5(5)	C(7)-N(1)-C(9)	106.8(13)
O(1)-Ni-N(2)	88.8(5)	C(7)-N(1)-Ni	129.0(12)
O(3)-Ni-N(1)	87.1(5)	C(9)-N(1)-Ni	124.2(9)
O(3)-Ni-N(2)	91.9(5)	O(1)-C(1)-C(6)	125.9(12)
N(1)-Ni-N(2)	175.8(5)	C(1)-C(6)-C(7)	117.9(11)
O(1)-Ni-O(3)	174.8(5)	N(1)-C(7)-O(2)	119.8(19)
C(1)-O(1)-Ni	124.8(8)	N(1)-C(7)-C(6)	123.9(13)
C(7)-O(2)-C(8)	106.9(13)	O(2)-C(8)-C(9)	101.7(12)
C(18)-O(3)-Ni	123.6(10)	N(1)-C(9)-C(8)	104.1(12)

**Figure 1** The molecular structure of complex **2a**.

Baeyer-Villiger oxidation of cyclohexanones. Under the same conditions, the catalytic activities increase in the order of **2c**>**2b**>**2a**. The highest yield of lactones (86%) is obtained by catalysis of complex **2c**, which has no substituent on its oxazoline ring (Entry 3). Bolm *et al.*¹¹ reported that, when bis[2-(4,4-dimethyl-4,5-dihydro-2-oxazolyl)-6-*t*-butyl-phenolato-*N*²,*O*¹]nickel(II) complex was employed as the catalyst, the cyclohexanone was converted to lactone in 83% yield, which was slightly lower than using complex **2c** as the catalyst. So,

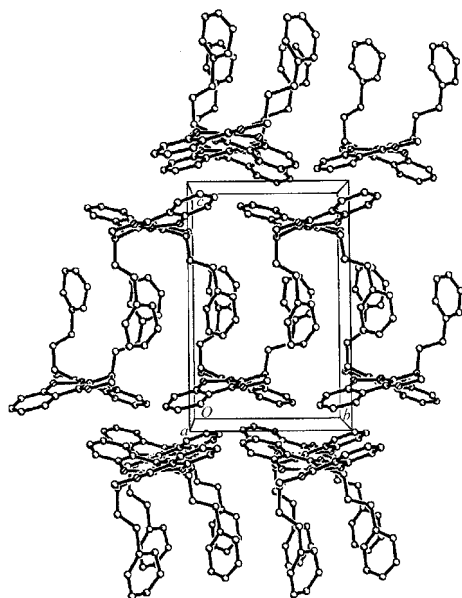


Figure 2 Crystal cell structure of complex 2a.

Scheme 3 Baeyer-Villiger oxidation of cyclic ketones

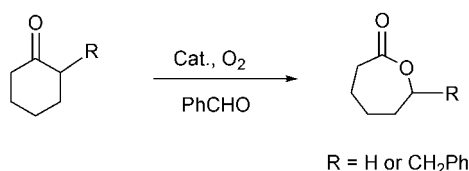


Table 3 Baeyer-Villiger oxidation of cyclic ketones with 2

Entry	Ketone	Cat.	Yield/%
1	cyclohexanone	2a	78
2	cyclohexanone	2b	81
3	cyclohexanone	2c	86
4	2-benzylcyclohexanone	2a	9
5	2-benzylcyclohexanone	2b	14
6	2-benzylcyclohexanone	2c	19

the steric hindrance of the oxazoline ring strongly influences the activity of the catalysts.

To study the effect of substrate on the catalytic activities, we also choose 2-benzylcyclohexanone as the model compound (Entries 4—6 in Table 3). Complexes 2 show lower catalytic activities on 2-benzylcyclohexanone than on cyclohexanone, and only small amounts of the desired lactones are obtained in low yields 9%—19%. Bolm and coworkers¹¹ revealed that, with the catalysis of Ni(oxa)₂ complexes, cyclohexanone and 2-phenylcyclohexanone were converted to the corresponding lactones in 83% and 72% yields, respectively. Although the yield of the latter is lower than that of the former, the difference between them is not very drastic. It is noted that, in the two catalytic systems, the catalytic activities on cyclohexanone are similar, while the catalytic activity on 2-benzylcyclohexanone is lower than on 2-phenylcyclohexanone. It may be because of the

difference in the aromaticity of benzyl group and phenyl group. Furthermore, the steric hindrance of 2-benzylcyclohexanone is larger than that of 2-phenylcyclohexanone.

As a result, it is possible to conclude that bis(2-oxazolinyphenolato)nickel(II) complexes 2 are the excellent catalysts in small molecular activation especially in molecular oxygen. A series of studies on the asymmetric Baeyer-Villiger oxidation of cyclohexanone using complex 2a as the catalyst are now in progress.

Experimental

¹H NMR spectra were acquired on a Bruker Advance 500 spectrometer in CDCl₃, and TMS was used as an internal standard. IR spectra were recorded on a Nicolet Magna-IR 550 spectrophotometer. Elemental (C, H, N) analyses were performed on an EA-1106 instrument. EI-HRMS and EI-MS (*m/z*, 70 eV) were obtained on a Micromass GCT mass spectrometer. Tetrahydrofuran (THF) was freshly distilled from sodium wire and benzophenone ketyl under argon prior to use. Other solvents and chemicals (A.R.) were obtained from commercial suppliers and used without further purification. 2-Hydroxybenzoinitril, and 2-(4,5-dihydro-2-oxazolyl)phenol were prepared according to the literature procedure.^{20,21}

Preparation of (2*S*)-2-amino-4-phenyl-1-butanol

According to the reported method,²² the reaction of LiAlH₄ (3 g, 0.08 mol) with (*S*)-PhCH₂CH₂CH(COOEt)NH₂·HCl (5 g, 0.02 mol) in THF afforded a yellow oil as (*S*)-NH₂CH(CH₂CH₂Ph)CH₂OH in 88% yield. [α]_D²⁵ -8.3 (*c* 0.42, EtOH); ¹H NMR (CDCl₃, 500 MHz) δ : 1.59—1.64 (m, 1H), 1.75—1.83 (m, 1H), 1.90 (s, 3H), 2.63—2.69 (m, 1H), 2.72—2.78 (m, 1H), 2.85—2.89 (m, 1H), 3.32 (dd, *J*=10.6, 7.8 Hz, 1H), 3.62 (dd, *J*=10.6, 3.8 Hz, 1H), 7.19 (d, *J*=8.1 Hz, 3H), 7.28 (t, *J*=7.6 Hz, 2H).

Synthesis of (4*S*)-4-phenylethyl-4,5-dihydro-2-(2'-hydroxyphenyl)oxazole (1a) and 5-methyl-4,5-dihydro-2-(2'-hydroxyphenyl)oxazole (1b)

General procedure According to the literature method,^{7,23} the reactions of 2-hydroxybenzoinitril (1.19 g, 10 mmol) with (*S*)-NH₂CH(CH₂CH₂Ph)CH₂OH (2.48 g, 15 mmol) or NH₂CH₂CH(CH₃)OH (1.13 g, 15 mmol) in the presence of ZnCl₂ (0.07 g, 0.5 mmol) in chlorobenzene afforded a yellow oil.

1a Yield 72%, [α]_D²⁵ -67.7 (*c* 0.63, EtOH); ¹H NMR (CDCl₃, 500 MHz) δ : 1.92—2.02 (m, 2H), 2.71—2.89 (m, 2H), 4.01 (t, *J*=7.9 Hz, 1H), 4.33—4.37 (m, 1H), 4.47 (t, *J*=8.8 Hz, 1H), 6.87 (td, *J*=7.6, 0.9 Hz, 1H), 7.02 (dd, *J*=8.2, 0.7 Hz, 1H), 7.21 (dd, *J*=8.0, 2.3 Hz, 3H), 7.30 (td, *J*=6.9, 1.3 Hz, 2H), 7.38 (td, *J*=7.8, 1.7 Hz, 1H), 7.64 (dd, *J*=7.8, 1.7 Hz, 1H), 12.2 (br, 1H); IR (KBr) ν : 3026 (m), 2926 (s), 2858 (m), 1642 (vs), 1618 (s), 1582 (m), 1492 (vs), 1454 (m), 1367 (vs), 1311 (s), 1260 (vs), 1067 (s), 962 (m), 831 (w), 755 (m)

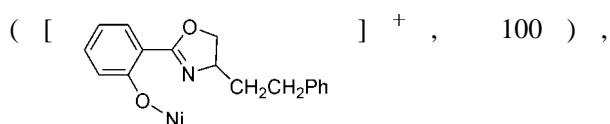
cm⁻¹.

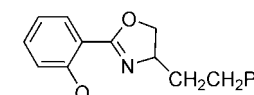
1b Yield 71%; ¹H NMR (CDCl₃, 500 MHz) δ: 1.45 (d, *J*=6.2 Hz, 3H), 3.65 (dd, *J*=14.1, 7.4 Hz, 1H), 4.18 (dd, *J*=14.1, 9.3 Hz, 1H), 4.79—4.91 (m, 1H), 6.87 (td, *J*=7.8, 1.0 Hz, 1H), 7.01 (dd, *J*=8.3, 0.6 Hz, 1H), 7.37 (td, *J*=7.9, 1.7 Hz, 1H), 7.66 (dd, *J*=7.8, 1.7 Hz, 1H), 12.1 (br, 1H).

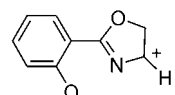
Synthesis of bis(2-oxazolinyphenolato)nickel(II) complexes 2a—2c

General procedure To a solution of ligands **1** (2.4 mmol) and nickel(II) chloride hexahydrate (1.3 mmol) in ethanol (20 mL) was dropwise added an aqueous ethanolic solution (20 mL of ethanol and 0.5 mL of water) of sodium hydroxide (2.5 mmol) at room temperature. After stirring for 20 h, the precipitate was collected through filtration and purified by crystallization from dichloromethane/ethanol. The dark green needle crystals as **2** were obtained.

2a Yield 81%, m.p. 204—205 °C, [α]_D²⁵ +1548 (*c* 0.14, CHCl₃); ¹H NMR (CDCl₃, 500 MHz) δ: 1.92—2.00 (m, 2H), 2.46—2.53 (m, 2H), 2.75—2.82 (m, 4H), 4.07—4.11 (m, 2H), 4.28 (dd, *J*=8.6, 3.5 Hz, 2H), 4.36 (t, *J*=8.7 Hz, 2H), 6.35 (d, *J*=8.4 Hz, 2H), 6.44 (t, *J*=7.4 Hz, 2H), 7.04 (td, *J*=8.4, 1.4 Hz, 2H), 7.17—7.30 (m, 10H), 7.42 (dd, *J*=7.9, 1.2 Hz, 2H); IR (KBr) ν : 3023 (m), 2972 (m), 2909 (m), 2860 (w), 1626 (vs), 1546 (s), 1479 (s), 1405 (s), 1340 (s), 1267 (s), 1232 (m), 1154 (m), 1074 (m), 762 (s), 688 (m), 588 (w), 470 (w) cm⁻¹; MS (70 eV) *m/z* (%): 590 (M⁺, 34), 323

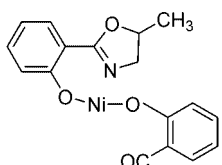


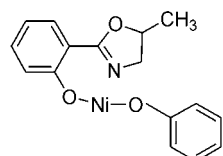
267 ([]⁺, 67), 219

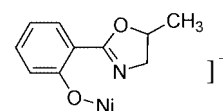
([], 31). Anal. calcd for C₃₄H₃₂N₂NiO₄:

C 69.06, H 5.45, N 4.74; found C 69.16, H 5.47, N 4.57.

2b Yield 86%, m.p. 235—236 °C; ¹H NMR (CDCl₃, 500 MHz) δ: 1.45 (d, *J*=5.2 Hz, 6H), 3.27 (dd, *J*=13.1, 7.7 Hz, 2H), 3.80 (t, *J*=12.4 Hz, 2H), 4.86 (s, 2H), 6.46 (s, 2H), 6.62 (d, *J*=7.9 Hz, 2H), 7.06 (s, 2H), 7.44 (d, *J*=7.1 Hz, 2H); IR (KBr) ν : 3026 (m), 2975 (m), 1621 (vs), 1545 (m), 1477 (s), 1408 (s), 1348 (s), 1249 (s), 1155 (m), 1082 (m), 760 (s), 590 (w), 479 (w) cm⁻¹; MS (70 eV) *m/z* (%): 410 (M⁺, 100),

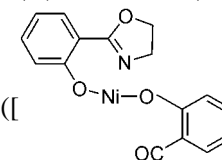
354 ([]⁺, 33),

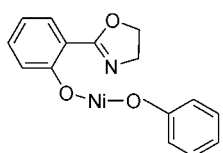
327 ([]⁺, 43),

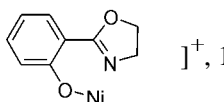
234 ([]⁺, 19). Anal. calcd for

C₂₀H₂₀N₂NiO₄: C 58.44, H 4.90, N 6.81; found C 58.44, H 4.98, N 6.67.

2c²⁴ Yield 88%, m.p. >220 °C; ¹H NMR (CDCl₃, 500 MHz) δ: 3.69 (t, *J*=10 Hz, 4H), 4.41 (t, *J*=10 Hz, 4H), 6.46 (t, *J*=7.3 Hz, 2H), 6.60 (d, *J*=8.5 Hz, 2H), 7.07 (t, *J*=7.3 Hz, 2H), 7.43 (d, *J*=7.8 Hz, 2H); IR (KBr) ν : 3056 (m), 2979 (m), 2957 (m), 2910 (m), 1626 (vs), 1546 (m), 1471 (s), 1441 (s), 1409 (m), 1345 (s), 1248 (s), 1158 (w), 1080 (m), 935 (m), 748 (s), 679 (m), 585 (w), 474 (w) cm⁻¹; MS (70 eV) *m/z* (%):

382 (M⁺, 100), 340 ([]⁺, 39), 313

([]⁺, 13), 220

([]⁺, 10). Anal. calcd for C₁₈H₁₆N₂NiO₄:

C 56.44, H 4.21, N 7.31; found C 56.52, H 4.15, N 7.11 (HRMS calcd for C₁₈H₁₆N₂NiO₄ 382.0464, found 382.0457).

Catalytic oxidation reactions

To a suspension of **2** (5 μmol) and ketone (1 mmol) in 1,2-dichloroethane (2.5 mL) was added benzaldehyde (3 mmol). The reaction mixture was stirred for 20 h under an oxygen atmosphere in dark. After diluted with Et₂O, the mixture was washed with saturated aqueous NaHCO₃. The organic phase was dried over Na₂SO₄ and distilled under vacuum to give oil. The product was purified by column chromatography on silica gel and identified by ¹H NMR spectroscopy.

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