

Research Article

Synthesis of Ruthenium Complex Based on 2,6-Bis(1-(phenyl)-1H-benzo[d]imidazol-2-yl)pyridine and 2-(1-Phenyl-1H-benzo[d]imidazol-2-yl)benzoate and Catalytical Oxidation Property of 1-(1H-Benzo[d]imidazol-2-yl)ethanol to 1-(1H-Benzo[d]imidazol-2-yl)ethanone with H₂O₂

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A new ruthenium complex, Ru(bpbp)(pbb)Cl, based on 2,6-bis(1-(phenyl)-1H-benzo[d]imidazol-2-yl)pyridine (bpbp) and 2-(1-phenyl-1H-benzo[d]imidazol-2-yl)benzoate (pbb) was synthesized. The complex Ru(bpbp)(pbb)Cl could catalytically oxidize 1-(1H-benzo[d]imidazol-2-yl)ethanol to 1-(1H-benzo[d]imidazol-2-yl)ethanone with H_2O_2 as oxidant. Influence of temperature and catalyst amount on the oxidation reaction was evaluated. The reaction optimal conditions are as follows: molar ratio of catalyst to substrate to H_2O_2 is 1:1000:3000, the proper reaction temperature is 50°C and reaction time lasts 5 h, and the isolated yield of 1-(1H-benzo[d]imidazol-2-yl)ethanone under the optimal reaction conditions is 57%.

1. Introduction

Benzimidazole is one of the oldest known nitrogen heterocycles and was first synthesized by Hoebrecker. The properties of benzimidazole and its derivatives have been studied over more than one hundred years. Benzimidazole derivatives are useful intermediates/subunits for the development of molecules of pharmaceutical or biological interest [1–8]; acetyl group contains carbonyl group and α -H group, which can take part in many reactions; thus 1-(1H-benzo[d]imidazol-2-yl)ethanone is a key intermediate for preparation of complicate benzimidazole-based compounds. Oxidation of 1-(1H-benzo[d]imidazol-2-yl)ethanol to 1-(1H-benzo[d]imidazol-2-yl)ethanone is of great importance for precursors of a variety of valuable fine chemicals. Traditionally, 1-(1H-benzo[d]imidazol-2-yl)ethanone is produced by solid phase oxidation of (1H-benzo[d]imidazol-2-yl)methanol with KMnO4/Al2O3 or oxidized by dichromates salt [9-12]. In these traditional oxidation processes, large amounts of toxic, volatile organic solvents and metal

oxidants were extensively used and it is difficult to magnify the quantity of product. Hence, developing green selective oxidation process of (1H-benzo[d]imidazol-2-yl)ethanol is still a challenging task in catalysis. Hydrogen peroxide is an environmentally benign oxidant, which theoretically generates only water as a by-product. The discovery of new catalyst employing H₂O₂ as oxidant is gathering much attention [13-16]. Ruthenium complex constitutes a versatile class of catalysts for important synthetic transformations in organic chemistry [17]. Benzimidazole is more easily synthesized than imidazole; we continued to focus on the synthesis and applications of complexes based on benzimidazole compound [18-21]. In recent years, we turned our attention to catalytic oxidation properties of ruthenium complex based on benzimidazole group ligand [22, 23]. Herein, we synthesized a new benzimidazole-based ligand and its ruthenium complex to investigate its catalytic oxidation properties of (1Hbenzo[d]imidazol-2-yl)ethanol to 1-(1H-benzo[d]imidazol-2-yl)ethanone with H₂O₂ as oxidant. Our results suggested that ruthenium complex based on 2,6-bis(1-(phenyl)-1H-benzo[d]imidazol-2-yl)pyridine (bpbp) and 2-(1-phenyl-1H-benzo[d]imidazol-2-yl)benzoic acid (pbba) could catalytically oxidize 1-(1H-benzo{d}imidazol-2-yl)ethanol toward 1-(1H-benzo[d]imidazol-2-yl)ethanone with H_2O_2 as oxidant.

2. Experimental

2.1. Reagents and Methods. Chemicals were of analytical grade and purchased from J&K Company without further purification unless indicated. 2-(Chlorocarbonyl)benzoic acid was synthesized according to literature [24]. Mass spectra were obtained on a Shimadzu LCMS-2010A. Elemental analyses were carried out with an Elementar vario EL elemental analyzer. ¹HNMR was recorded on a Bruker AVANCE 400 spectrometer (400 MHz). Chemical shifts are given in ppm and refer to the residual solvent as the internal standard. IR spectra were recorded on a Bruker 550 FT-IR spectrometer.

2.2. Synthesis of 2-((2-(Phenylamino)phenyl)carbamoyl)benzoic Acid. N¹-phenylbenzene-1, 2-diamine (7.36 g, 40 mmol), and triethylamine (10 mL) in 100 mL of CH₂Cl₂ were added to the solution of 2-(Chlorocarbonyl)benzoic acid (7.38 g, 40 mmol) in 100 mL of CH₂Cl₂. The mixture was further stirred for 2 h at ambient temperature. The light yellow solid was collected by filtration, washed with water, and dried in vacuo (yield: 8.10 g, 61.0%). Analysis calculated for $C_{20}H_{16}N_2O_3$ (%), C, 72.28%, H, 4.85%, N, 8.43%, Found: C, 72.32%, H, 4.74%, N, 8.40%. IR (KBr)/cm⁻¹, 3390, 3052, 1781, 1706, 1597, 1508, 1419, 1385, 1290, 1247, 1178, 1109, 1079, 884, 748, 717, 694, 629, 530. ¹HNMR (400 MHz, d⁶-DMSO δ ppm): 6.83–6.87 (t, 1H), 6.91–6.96 (m, 1H), 7.01–7.03 (d, 2H), 7.19–7.23 (t, 2H), 7.27–7.32 (q, 3H), 7.87–7.94 (m, 4H).

2.3. Synthesis of 2-(1-Phenyl-1H-benzo[d]imidazol-2-yl)benzoic Acid (pbba). 2-(1-Phenyl-1H-benzo[d]imidazol-2-yl)benzoic acid was synthesized according to the reference method [25]. 2-((2-(Phenylamino)phenyl)carbamoyl)benzoic acid (6.65 g, 20 mmol) was heated at 250°C for 3 h under nitrogen. After cooling, water (50 mL) was added to the mixture and extracted with CH_2Cl_2 (50 × 3 mL). The combined organic layers were washed with water. Solvent of the filtrate was removed in vacuo to obtain a crude solid. White 2-(1-phenyl-1H-benzo[d]imidazol-2-yl)benzoic acid was purified by recrystallization from ethanol (2.83 g, 45%). Analysis calculated for C₂₀H₁₄N₂O₂ (%), C, 76.42%, H, 4.49%, N, 8.91%. Found: C, 76.32%, H, 4.44%, N, 8.84%. IR (KBr)/cm⁻¹, 3436, 3064, 2922, 2439, 1689, 1593, 1498, 1449, 1140, 1246, 1140, 1075, 1002, 913, 763, 695. ¹HNMR (400 MHz, d^{6} -DMSO, δ ppm): 7.21–7.60 (m, 11H), 7.74–7.77 (d, 1H), 7.81–7.83 (d, 1H).

2.4. Synthesis of N^2 , N^6 -bis(2-(phenylamino)phenyl)pyridine-2,6-dicarboxamide. Pyridine-2, 6-dicarboxylic acid (3.34 g, 20 mmol) was refluxed in thionyl chloride 20 mL for 8 h. Excess thionyl chloride was removed under vacuum. After cooling to room temperature, N^1 -phenylbenzene-1,2-diamine (7.36 g, 40 mmol) and triethylamine (10 mL) in 60 mL of CH₂Cl₂, were added to the solution of the residue in CH₂Cl₂ (30 mL). The mixture was further stirred for 2 h at ambient temperature. The yellow solid was collected by filtration, washed with water, and dried in vacuo (yield: 5.31 g, 53.00%). Analysis calculated for C₃₁H₂₅N₅O₂ (%), C, 74.53%, H, 5.04%, N, 14.02%. Found: C, 74.52%, H, 5.14%, N, 14.20%. IR (KBr)/cm⁻¹, 3353, 3046, 1676, 1641, 1595, 1516, 1456, 1425, 1310, 1260, 1176, 1150, 1076, 999, 882, 745, 676, 493. ¹HNMR (400 MHz, *d*⁶-DMSO, *δ*): 6.74–6.77 (t, 2H), 6.89–6.91 (d, 4H), 7.02–7.09 (t, 2H), 7.10–7.13 (t, 4H), 7.20–7.24 (t, 2H), 7.34– 7.36 (d, 2H), 7.50–7.57 (t, 4H) 8.25–8.28 (q, 1H), 8.33–8.35 (d, 2H).

2.5. Synthesis of 2, 6-Bis(1-(phenyl)-1H-benzo[d]imidazol-2yl)pyridine (bpbp). N^2 , N^6 -bis(2-(phenylamino)phenyl)pyridine-2,6-dicarboxamide (5.00 g, 10 mmol) was heated at 250°C for 3 h under nitrogen. After cooling, water (50 mL) was added to the mixture and extracted with CH₂Cl₂ (50 × 3 mL). The combined organic layers were washed with water. Solvent of the filtrate was removed in vacuo to obtain a crude solid. White 2, 6-bis(1-(phenyl)-1H-benzo[d]imidazol-2-yl)pyridine was purified by recrystallization from ethanol. (yield: 2.25 g, 48.59%) Analysis calculated for C₃₁H₂₁N₅ (%), C, 80.32%, H, 4.57%, N, 15.11%. Found: C, 80.42%, H, 4.44%, N, 15.20%. IR (KBr)/cm⁻¹, 3435, 3059, 1525, 1500, 1405, 1330, 1258, 1198, 1158, 1138, 1076, 1004, 823, 745, 695, 639. ¹HNMR (400 MHz, d^6 -DMSO, δ ppm): 7.01–7.07 (m, 4H), 7.17–7.43 (m, 12H), 7.68–7.97 (m, 3H), 8.31–8.38 (m, 2H).

2.6. Synthesis of Ruthenium Complex $Ru(bpbp)Cl_3$. bpbp (1.389 g, 0.3 mmol) and $RuCl_3 \cdot nH_2O$ (1.04 g, 0.31 mmol) were dissolved in ethanol (100 mL); the reaction mixture was refluxed for 4 h at 80°C to form a red brown deposition and then was filtered after cooling to room temperature. The brown red solid was obtained after washing by water (yield: 1.42 g, 71.0%) Analysis calculated for $C_{31}H_{21}N_5Cl_3Ru$ (%), C, 75.49%, H, 3.15%, N, 15.85%. Found: C, 75.51%, H, 3.14%, N, 15.72%. IR (KBr)/cm⁻¹, 3456, 3060, 1592, 1506, 1406, 1337, 1270, 1190, 1148, 1007, 1004, 892, 832, 757, 698, 650, 611. ¹HNMR (400 MHz, d^6 -DMSO, δ ppm): 6.97–7.44 (m, 12H), 7.67–7.83 (m, 4H), 7.89–7.97 (m, 3H), 8.32–8.38 (m, 2H).

2.7. Synthesis of Ruthenium Complex Ru(bpbp)(pbb)Cl. NaOH (0.04 g, 1 mmol), 2-(1-phenyl-1H-benzo[d]imidazol-2-yl)benzoic acid (0.314 g, 1 mmol) was dissolved in ethanol (50 mL) and water (10 mL) was added to Ru(bpbp)Cl₃ (0.667 g, 1 mmol). The whole reaction mixture was again refluxed at 80°C for 4 h to result in violet solution. The solvent was reduced to 10 mL after reaction for 3 h. After filtering, the dark violet precipitate was collected (0.515 g, yield: 56.40%). Calc. for C₅₁H₃₄N₇O₂ClRu: C, 67.06%; H, 3.75%; N, 10.73%. Found: C, 67.41%; H, 3.79%; N, 10.35%; IR (KBr)/cm⁻¹, 3417, 3058, 1592, 1450, 1380, 1332, 1249, 1151, 1078, 1013, 821, 748, 698, 646, 507. ¹HNMR (400 MHz, *d*⁶-DMSO, δ ppm): 6.96–7.43 (m, 28H), 7.60–7.84 (m, 3H), 7.84–8.32 (m, 3H).

TABLE 1: Crystal data and structure refinement for 2-(1-phenyl-1Hbenzo[d]imidazol-2-yl)benzoic acid.

Formula	$C_{20}H_{14}N_2O_2$		
Formula weight	314.33		
Crystal system	monoclinic		
Space group	P1211		
a/Å	8.6939(10)		
b/Å	9.5718(11)		
c/Å	10.0841(12)		
$\beta/^{\circ}$	109.609		
$V/\text{\AA}^3$	790.49(16)		
μ/mm^{-1}	0.089		
Z	2		
$D_c/g\cdot cm^{-3}$	1.321		
Crystal size	$0.18\times0.16\times0.12$		
Theta range for data collection/°	2.14 to 26.34		
Index ranges	$-10 \le h \le 10, -11 \le k \le 11, -12 \le l \le 12$		
<i>F</i> (000)	328		
GOF on F^2	1.098		
Reflections collected/unique	6094/3151 [R(int) = 0.0160]		
Data/restraints/parameters	3151/1/218		
R indices (all data)	R1 = 0.0452, wR2 = 0.1030		
Final R indices [$I > 2$ sigma(I)]	R1 = 0.0351, wR2 = 0.0882		
Max. and min. transmission	0.9897 and 0.9846		
Largest diff. peak and hole $(e \cdot A^{-3})$	0.185 and -0.222		

2.8. X-Ray Crystallography. Single crystal structure determination was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source, and graphite monochromated Mo-K_{α} radiation (λ = 0.71073 Å) at 173 K. The structure was solved by direct method and refined by program SHELXTL and absorption was adopted by semiempirical method. All nonhydrogen atoms in both structures were refined anisotropic displacement parameters. All hydrogen atoms were theoretically added. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC number 1509858. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (https://www.ccdc.cam.ac.uk). The crystal data are summarized in Table 1.

2.9. Catalytic Oxidation of (1H-Benzo[d]imidazol-2-yl)ethanol. The catalytic oxidation of (1H-benzo[d]imidazol-2yl)ethanol was carried out in a magnetically stirred glass reaction tube fitted with a reflux condenser. A typical procedure was as follows: (1H-benzo[d]imidazol-2-yl)ethanol aqueous solution (0.1 mol/L), ruthenium complex catalyst $(1 \times 10^{-4} \text{ mmol}, 0.01 \text{ mol}\%$ based substrate), and 0.2 mmol (inert internal standard) were added into a reaction tube. The reactor containing this mixture was heated to proper temperature in an oil bath under vigorous stirring, and then the aqueous hydroperoxide (30% H₂O₂, 10 mol/L) was slowly dropped in. The product samples were drawn at regular time intervals and analyzed by GC and GC-MS. GC analyses were performed on a Shimadzu GC-2010 plus chromatography equipped with Rtx-5 capillary column (30 m × 0.25 mm × 0.25 μ m). GC-MS analyses were recorded on a Shimadzu GCMS-QP2010 equipped with Rxi-5 ms capillary column (30 m × 0.25 mm × 0.25 μ m).

3. Results and Discussion

3.1. Synthesis of 2-(1-Phenyl-1H-benzo[d]imidazol-2-yl)benzoic Acid, 2,6-Bis(1-phenyl-1H-benzo[d]imidazol-2-yl)pyridine, and the Ruthenium Complex. The synthetic route of 2-(1phenyl-1H-benzo[d]imidazol-2-yl)benzoic acid (pbba), 2,6bis(1-phenyl-1H-benzo[d]imidazol-2-yl)pyridine (bpbp), and ruthenium complex (Ru (bpbp)(pbb)Cl was shown in Figure 1. 2-(1-Phenyl-1H-benzo[d]imidazol-2-yl)benzoic acid (pbba) and 2,6-bis(1-phenyl-1H-benzo[d]imidazol-2-yl) pyridine (bpbp) ligand are, respectively, prepared by intramolecular thermocyclization condensation of 2-((2-(phenylamino)phenyl)carbamoyl)benzoic acid or N²,N⁶-bis (2-(phenylamino)phenyl)pyridine-2,6-dicarboxamide. The crystals of 2-(1-phenyl-1H-benzo[d]imidazol-2-yl)benzoic acid (pbba) and 2,6-bis(1-phenyl-1H-benzo[d]imidazol-2-yl) pyridine (bpbp) are all obtained by recrystallization from ethanol. The preparation of the ruthenium complex was through two steps. First, the bpbp ligand reacts with RuCl₃ to result in red brown deposition Ru(bpbp)Cl₃; then sodium 2-(1-phenyl-1H-benzo[d]imidazol-2-yl)benzoate substitutes the two Cl ions to form violet Ru(bpbp)(pbb)Cl solution; crude violet solid ruthenium complex could be obtained after evaporation of alcohol. Pure ruthenium complex was obtained from recrystallization from alcohol.

3.2. Structure Analytical of 2-(1-Phenyl-1H-benzo[d]imidazol-2-yl)benzoic Acid, 2,6-Bis(1-phenyl-1-benzo[d]imidazol-2-yl) pyridine, and the Ruthenium Complex. The structures of 2-(1-phenyl-1H-benzo[*d*]imidazol-2-yl)benzoic acid (pbba) and 2,6-bis(1-(phenyl)-1H-benzo[d]imidazol-2-yl)pyridine (bpbp) are shown in Figure 2. The crystal structure of 2, 6bis(1-(phenyl)-1H-benzo[d]imidazol-2-yl)pyridine has been reported [21]. Selected bond lengths and angles for 2-(1phenyl-1H-benzo[d]imidazol-2-yl)benzoic acidare listed in Table 2. All the C-N bond and angles of 2-(1-phenyl-1Hbenzo[d]imidazol-2-yl)benzoic acid are within normal range. The two phenyl rings are not coplanar with the benzimidazole ring. The dihedral angle between phenyl ring (C7 to C12) and benzimidazole is 63.3° and between the phenyl ring (C15 to C19) and benzimidazole is 76.7°. The COOH is coplanar with the phenyl ring (C15 to C19). The pack diagram of molecule is shown in Figure 3. The hydrogen bond O_2 -H···N1 (2.707 Å) links the molecules to form 1D chain along with the b axis. The ruthenium complex, Ru(bpbp)(pbb)Cl, was characterized by element analysis and

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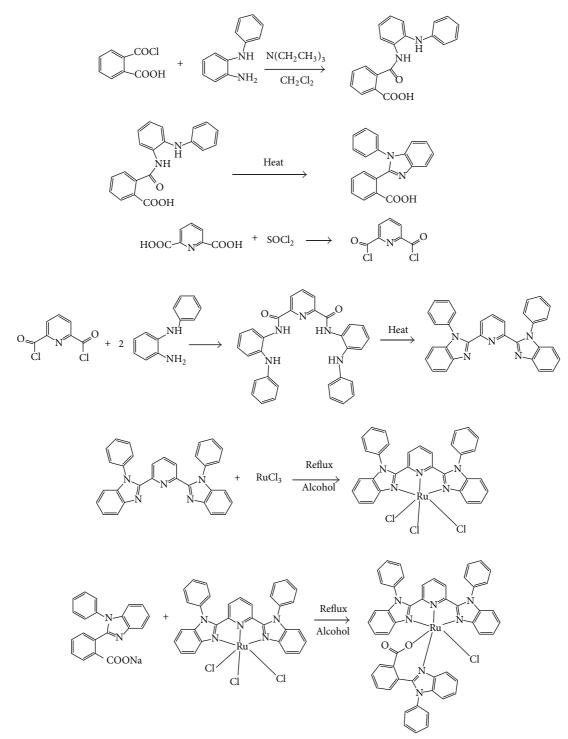


FIGURE 1: Synthetic route of ruthenium complex Ru(bpbp)(pbb)Cl.

IR. The measurements of C, H, and N element analysis are in good agreement with the theory calculated values. The appearance of 1592 and 1450 cm⁻¹ in the ruthenium complex Ru(bpbp)(pbb)Cl shows deprotonation to coordination to Ru²⁺ ion.

3.3. Catalytical Oxidation Property of (1H-Benzo[d]imidazol-2-yl)ethanol to 1-(1H-Benzo[d]imidazol-2-yl)ethanone. In order to explore preparation method of 1-(1H-benzo[d]imidazol-2-yl)ethanone, we focus our attention on the oxidation reaction of (1H-benzo[d]imidazol-2-yl)ethanol (Figure 4), by employing ruthenium complex, Ru(bpbp)(pbb)Cl as catalyst, and hydrogen peroxide as oxidant. The effect of reaction parameters was examined in water solvent, as listed in Table 3. Only 35% yield of 1-(1H-benzo[d]imidazol-2-yl)ethanone was obtained when the reaction was conducted at 30°C,

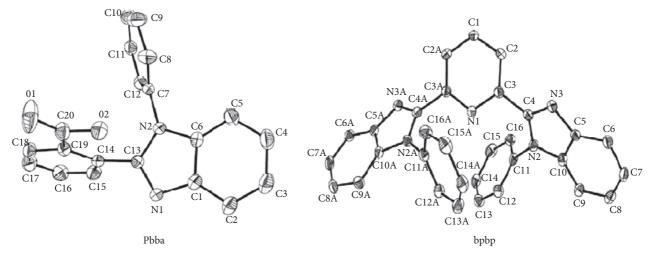
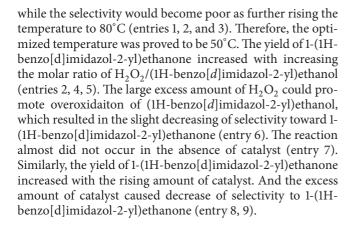


FIGURE 2: Molecular structure of 2-(1-phenyl-1H-benzo[d]imidazol-2-yl)benzoic acid (pbba) and 2,6-bis(1-(phenyl)-1H-benzo[d]imidazol-2-yl)pyridine (bpbp) (ORTEP, 30% ellipsoids).

Bond	Dist. (Å)
N(1)-C(13)	1.312(2)
N(1)-C(1)	1.399(2)
C(20)-O(1)	1.204(3)
N(2)-C(7)	1.436(2)
O(2)-C(20)	1.310(2)
C(13)-C(14)	1.490(2)
N(2)-C(13)	1.364(2)
N(2)-C(6)	1.390(2)
C(19)-C(20)	1.497(3)
Angle	(°)
C(13)-N(2)-C(6)	107.07(14)
N(1)-C(13)-N(2)	112.46(15)
C(13)-N(2)-C(7)	127.15(15)
N(1)-C(13)-C(14)	124.36(15)
C(13)-N(1)-C(1)	105.44(14)
C(2)-C(1)-N(1)	130.57(18)

TABLE 2: Selected bond length (Å) and bond angles (°).



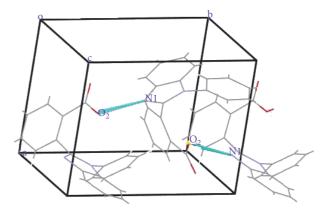


FIGURE 3: Pack diagraph of pbba molecules.

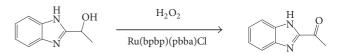


FIGURE 4: Oxidation reaction scheme of 1-(1H-benzo[d]imidazol-2-yl)ethanol to 1-(1H-benzo[d]imidazol-2-yl)ethanone.

The procedure for gram scale oxidation of (1Hbenzo[*d*]imidazol-2-yl)ethanol to 1-(1H-benzo[*d*]imidazol-2-yl)ethanone was performed as follows: (1H-benzo[*d*]imidazol-2-yl)ethanol (0.1 mol, 14.8 g) and Ru(bpbp)(pbb)Cl (0.001 mmol, 7.32×10^{-3} g) were added into a reactor. The reactor containing this mixture was heated to 50°C in an oil bath under vigorous stirring, and then 30% H₂O₂ (30 mL, 0.3 mol) was slowly dropped into the reactor in 30 min. The mixture was stirred for 5 h. After filter, the solution was evaporated under reduced pressure at 50°C. After extraction with CH₂Cl₂, the crude product was chromatographed on silica gel (eluent: CH₂Cl₂). Pure 1-(1H-benzo[d]imidazol-2-yl)ethanone (0.07 mmol, 10.2 g) was obtained with the

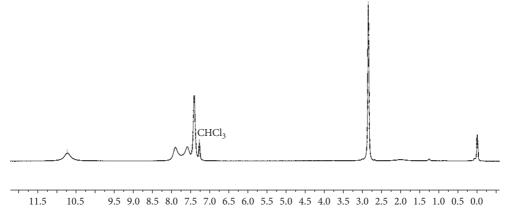


FIGURE 5: ¹HNMR spectrum of 1-(1H-benzo[d]imidazol-2-yl)ethanone (solvent: CDCl₃).

TABLE 3: Optimization of reaction conditions^a.

Entry	Substrate : $H_2O_2^{b}$	<i>T</i> (°C)	Conv. (%) ^c	Yield (%) ^c
1	1:3	30	38	35
2	1:3	50	74	69
3	1:3	80	93	82
4	1:1	50	58	56
5	1:2	50	66	63
6	1:4	50	87	80
7^{d}	1:3	50	4	2
8 ^e	1:3	50	78	76
$9^{\rm f}$	1:3	50	89	81

^aReaction condition: (1H-benzo[*d*]imidazol-2-yl)ethanol (2 mmol), catalyst (2×10^{-3} mmol), 60 min. ^bMolar ratio. ^cDetermined by GC. ^dIn the absence of catalyst. ^eCatalyst (2×10^{-4} mmol). ^fCatalyst (2×10^{-2} mmol).

isolated yield of 57% by removing the solvent. The product was identified by ¹HNMR spectrum (400 MHz, CDCl₃) (Figure 5) and IR spectrum (Figure 6), which are all in agreement with the assumed structure. IR is also same with the standard Bio-Rad/Sadtler IR Data.

4. Conclusion

In conclusion, a new ruthenium complex, Ru(bpbp)(pbb)Cl, was exploited for the oxidation of (1H-benzo[*d*]imidazol-2-yl)ethanol to 1-(1H-benzo[d]imidazol-2-yl)ethanone with H_2O_2 as oxidant. The reaction optimal conditions are as follows: molar ratio of catalyst to substrate to H_2O_2 is 1:1000:3000, the proper reaction temperature is 50°C and reaction time last 5 h, and the isolated yield of 1-(1H-benzo[d]imidazol-2-yl)ethanol to 1-(1H-benzo[d]imidazol-2-yl)ethanol to 57%.

Competing Interests

The authors declare that they have no competing interests.

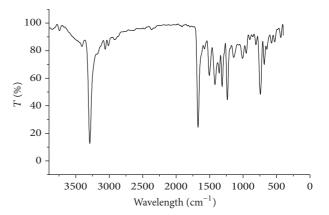


FIGURE 6: IR spectrum of 1-(1H-benzo[d]imidazol-2-yl)ethanone.

Acknowledgments

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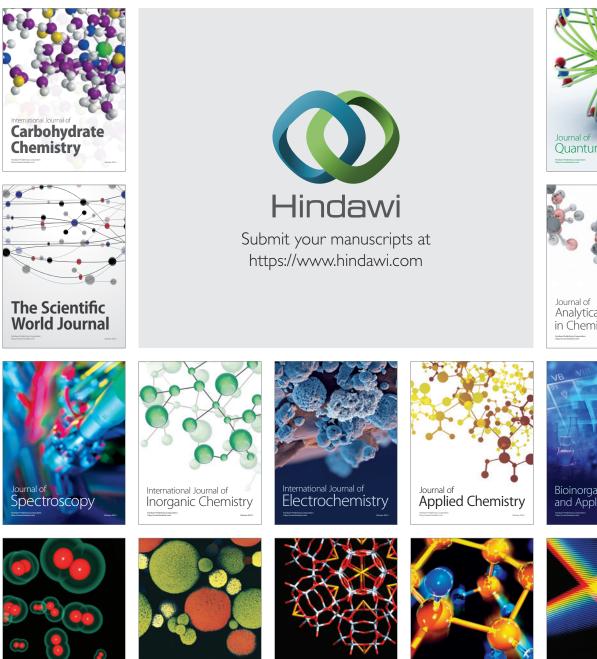




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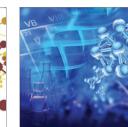
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