Synthesis of a ruthenium complex based on 2,6-bis[1-(pyridin-2-yl)-1*H*-benzo[*d*]imidazol-2-yl]pyridine and catalytic oxidation of (1*H*-benzo[*d*]-imidazol-2-yl)methanol to 1H-benzo[*d*]imidazole-2-carbaldehyde with H_2O_2

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2,6-Bis[1-(pyridin-2-yl)-1H-benzo[*d*]-imidazol-2-yl]pyridine (bpbp), which has been synthesised by intramolecular thermocyclisation of N^2,N^6-bis[2-(pyridin-2-ylamino)phenyl]pyridine-2,6-dicarboxamide, reacts with sodium pyridine-2,6-dicarboxylate (pydic) and $RuCl_3$ to give [Ru(bpbp)(pydic)] which can catalyse the oxidation of (1*H*-benzo[*d*]imidazol-2-yl)methanol to 1*H*-benzo[*d*]imidazole-2-carbaldehyde by H_2O_2. The optimal reaction conditions were: molar ratios of catalyst to substrate to H_2O_2 set at 1 : 1000 : 3000; reaction temperature 50 °C; reaction time 5 h. The yield of (1*H*-benzo[*d*]imidazol-2-yl) methanol was 70%.

Keywords: (1*H*-benzo[*d*]imidazol-2-yl)methanol, 1*H*-benzo[*d*]imidazole-2-carbaldehyde, [Ru(bpbp)(pydic)], hydrogen peroxide, oxidation catalysis, X-ray structure

Benzimidazoles are a common group of heterocyclic compounds which are widely used in medical, material, agricultural and industrial fields.[1–8] Aldehyde is a widely used functional group in many reactions. 1*H*-benzo[*d*]imidazole-2-carbaldehyde is a key intermediate for the preparation of complicated benzimidazole-based compounds. Oxidation of (1*H*-benzo[*d*]imidazol-2-yl) methanol to 1*H*-benzo[*d*]imidazole-2-carbaldehyde is of great importance in the synthesis of precursors of a variety of valuable fine chemicals. Traditionally, 1*H*-benzo[*d*]imidazole-2-carbaldehyde is produced by oxidation of (1*H*-benzo[*d*] imidazol-2-yl)methanol by $KMnO_4/Al_2O_3$ in the solid phase or by activated MnO_2 or SeO_2 or dichromate salts.[9–12] In these traditional oxidation processes, large amounts of toxic and volatile organic solvents and metal oxidants are used extensively, and it is difficult to increase the yield of product. Hence, developing 'green' processes for the selective oxidation of (1*H*-benzo[*d*]imidazol-2-yl)methanol 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 catalysts employing H_2O_2 as oxidant is gaining considerable attention.[13–16] Ruthenium complexes constitute a versatile class of catalysts for important synthetic transformations in organic chemistry.[17] We have focused on the synthesis and applications of complexes based on the benzimidazole group[18–21] and have recently turned our attention to the catalytic oxidation properties of ruthenium complexes based on benzimidazole group ligands.[22–23] In this paper, we describe the synthesis of a new benzimidazole-based ligand, 2,6-bis[1-(pyridin-2-yl)-1*H*-benzo[*d*]-imidazol-2-yl]pyridine (bpbp), and its ruthenium complex [Ru(bpbp) (pydic)] as well as an investigation of the catalytic properties of this complex in the oxidation of (1*H*-benzo[*d*]imidazol-2-yl) methanol to 1*H*-benzo[*d*]imidazole-2-carbaldehyde with H_2O_2 as oxidant.

Results and discussion

*Synthesis of 2,6-bis[1-(pyridin-2-yl)-1*H*-benzo[*d*]imidazol-2-yl] pyridine (bpbp) and its ruthenium complex*

The route to synthesising the bpbp ligand and ruthenium complex [Ru(bpbp)(pydic)] is shown in Fig. 1. The bpbp ligand was prepared by intramolecular thermocyclisation condensation of N^2,N^6-bis[2-(pyridin-2-ylamino)phenyl]pyridine-2,6-dicarboxamide which was obtained by reaction of pyridine-2,6-dicarbonyl dichloride and N^1-(pyridin-2-yl)benzene-1,2-diamine in the presence of triethylamine in CH_2Cl_2 at room temperature. Crystals of N^2,N^6-bis[2-(pyridin-2-ylamino)phenyl]pyridine-2,6-dicarboxamide and bpbp were obtained by recrystallisation from ethanol. The ruthenium complex was prepared in two steps from $RuCl_3$. First, the bpbp ligand was treated in ethanol with $RuCl_3$ to give a red-brown deposit of [Ru(bpbp)Cl_3], then sodium pyridine-2,6-dicarboxylate was used to substitute the three Cl^- ions to form a violet solution of [Ru(bpbp)(pydic)] from which the violet, solid ruthenium complex was obtained after evaporation of some of the ethanol. This route is cheaper and more convenient to operate than preparation from [Ru(*p*-cymene)Cl_2]$_2$[24] and the synthesis can be carried under air instead of a nitrogen atmosphere.

Structural analysis of N^2,N^6-bis[2-(pyridin-2-ylamino)phenyl]-pyridine-2,6-dicarboxamide and (bpbp)

The structures of N^2,N^6-bis[2-(pyridin-2-ylamino)phenyl]-pyridine-2,6-dicarboxamide and bpbp are shown in Fig. 2. The two molecules are not co-planar, and both lie across a twofold axis of symmetry through the centre of the pyridine ring. Selected bond lengths and angles for N^2,N^6-bis[2-(pyridin-2-ylamino)phenyl]-pyridine-2,6-dicarboxamide and bpbp are listed in Table 1.

In the N^2,N^6-bis[2-(pyridin-2-ylamino)phenyl]-pyridine-2,6-dicarboxamide molecule the average bond length of N(1)–C(7), N(2)–C(13) is 1.344 Å. Following intramolecular thermocyclisation condensation, N^2,N^6-bis[2-(pyridin-2-ylamino)phenyl]-pyridine-2,6-dicarboxamide is converted to bpbp. The average bond length of N(5)–C(18), N(2)–C(12) is 1.313 Å, which is much shorter than in N^2,N^6-bis[2-(pyridin-2-ylamino)phenyl]pyridine-2,6-dicarboxamide (1.344 Å). The other C–N bond lengths of imidazoles are all shorter than those in the amide molecule. Following intramolecular thermocyclisation condensation the two C–N bonds which link the substituent pyridine to the imidazoles also became shorter than those in the amide molecule, their average bond length being from 1.429 Å to 1.374 Å. The distance in the two crystal molecules suggests that bpbp is more stable than N^2,N^6-bis[2-(pyridin-2-ylamino)phenyl]pyridine-2,6-dicarboxamide.

Characterisation of [Ru(bpbp)(pydic)]

This complex was characterised by elemental analysis and spectroscopy. The ^{1}H NMR spectrum of [Ru(bpbp)(pydic)]

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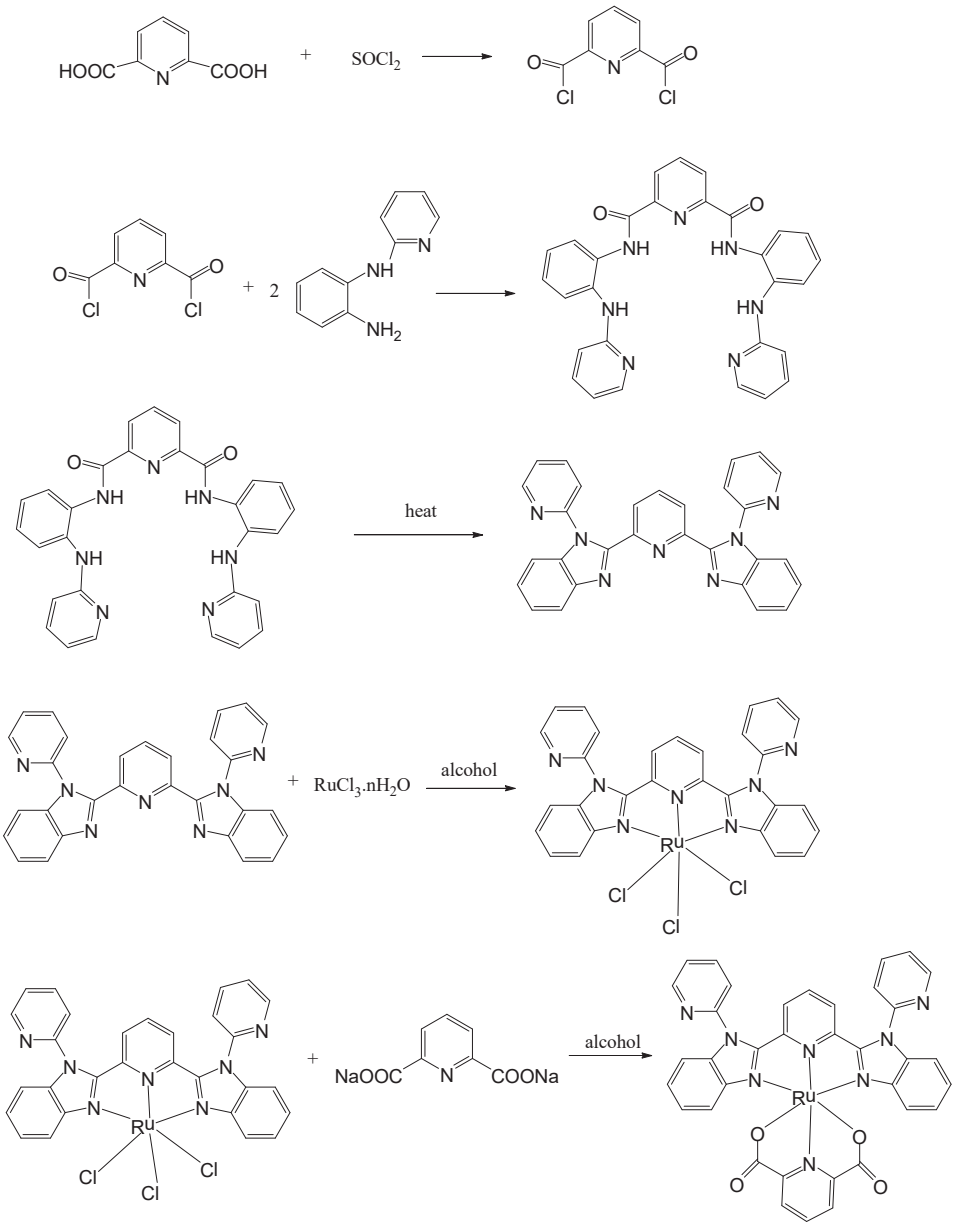

Fig. 1 Synthetic route to ruthenium complex [Ru(bpbp)(pydic)].

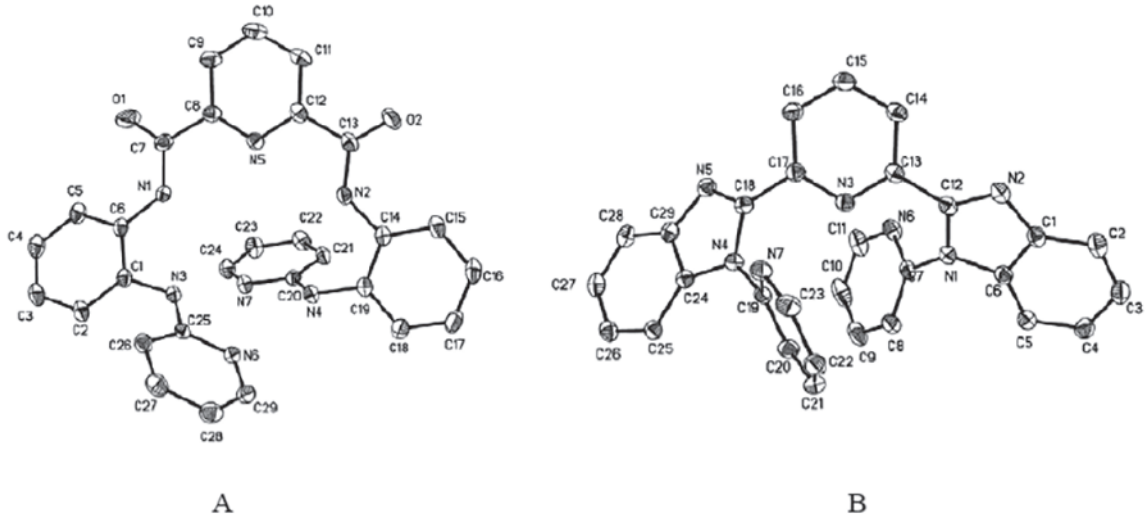

Fig. 2 Molecular structure of N^2,N^6-bis[2-(pyridin-2-ylamino)phenyl]pyridine-2,6-dicarboxamide (A) and bpbp (B) (ORTEP, 30% ellipsoids).

Table 1 Selected bond lengths (Å) and bond angles (°)

N^2,N^6-Bis[2-(pyridin-2-ylamino)phenyl]pyridine-2,6-dicarboxamide					
Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
N(1)–C(7)	1.341(2)	N(1)–C(6)	1.413(2)	N(3)–C(1)	1.417(2)
N(3)–C(25)	1.374(2)	N(2)–C(13)	1.347(2)	N(2)–C(14)	1.409(2)
N(4)–C(19)	1.425(2)	C(20)–N(4)	1.374(2)		
Angle	Degrees (°)	Angle	Degrees (°)	Angle	Degrees (°)
C(25)–N(3)–C(1)	126.07(14)	C(7)–N(1)–C(6)	127.23(15)	C(13)–N(2)–C(14)	129.75(15)
C(20)–N(4)–C(19)	122.46(14)				
2,6-Bis[1-(pyridin-2-yl)-1*H*-benzo[*d*]imidazol-2-yl]pyridine					
Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
N(1)–C(6)	1.3921(19)	N(1)–C(7)	1.4305(18)	N(1)–C(12)	1.3877(19)
N(2)–C(12)	1.3115(19)	N(2)–C(1)	1.394(2)	N(4)–C(18)	1.3832(18)
N(4)–C(24)	1.3928(18)	N(4)–C(19)	1.4280(17)	N(5)–C(18)	1.3143(18)
N(5)–C(29)	1.3942(19)				
Angle	Degrees (°)	Angle	Degrees (°)	Angle	Degrees (°)
C(12)–N(1)–C(6)	105.92(12)	C(12)–N(2)–C(1)	104.90(12)	C(18)–N(4)–C(24)	106.47(11)
C(18)–N(5)–C(29)	105.28(12)				

is very similar to the simulation by the Chembio Ultra soft program. In the IR of the complex the appearance of bands at 1650 and 1400 cm^{-1} shows the coordination of COO^- to the Ru ion.

*Catalytic oxidation of (1*H*-benzo[*d*]imidazol-2-yl)methanol to 1*H*-benzo[*d*]imidazole-2-carbaldehyde*

In order to explore the preparation method of 1*H*-benzo[*d*]imidazole-2-carbaldehyde we focused on the oxidation reaction of (1*H*-benzo[*d*]imidazol-2-yl)methanol (Fig. 3) by employing the ruthenium complex [Ru(bpbp)(pydic)] as catalyst and hydrogen peroxide as oxidant. The effect of different reaction parameters was examined in water as solvent, as listed in Table 2. Only a 35% yield of 1*H*-benzo[*d*]imidazole-2-carbaldehyde was obtained when the reaction was conducted at 30 °C, while the selectivity became poor on further increase of temperature to 80 °C (entries 1, 2, 3). Therefore, the optimised temperature was shown to be 50 °C. The yield of 1*H*-benzo[*d*]imidazole-2-carbaldehyde increased with increase in the molar ratio of H_2O_2/(1*H*-benzo[*d*]imidazol-2-yl)methanol (entries 2, 4, 5). A large excess amount of H_2O_2 could promote over-oxidation of (1*H*-benzo[*d*]imidazol-2-yl)methanol, which resulted in a slight decrease in selectivity towards 1*H*-benzo[*d*]imidazole-2-carbaldehyde (entry 6). The reaction almost did not occur in the absence of catalyst (entry 7). Similarly, the yield of 1*H*-benzo[*d*]imidazole-2-carbaldehyde increased with increasing amounts of catalyst, while an excess amount of catalyst caused a decrease in selectivity to 1*H*-benzo[*d*]imidazole-2-carbaldehyde (entries 8, 9).

The procedure for gram scale oxidation of (1*H*-benzo[*d*]imidazol-2-yl)methanol to 1*H*-benzo[*d*]imidazole-2-carbaldehyde was as follows: (1*H*-benzo[*d*]imidazol-2-yl)methanol (0.1 mol, 14.8 g) and [Ru(bpbp)(pydic)] (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% H_2O_2 (30 mL, 0.3 mol) was slowly dropwise over a period of 30 min.

Table 2 Optimisation of reaction conditions[a]

Entry	Substrate : H_2O_2[b]	*T* (°C)	Conv. (%)[c]	Yield (%)[c]
1	1 : 3	30	47	45
2	1 : 3	50	82	78
3	1 : 3	80	>99	80
4	1 : 1	50	58	56
5	1 : 2	50	64	62
6	1 : 4	50	94	83
7[d]	1 : 3	50	4	2
8[e]	1 : 3	50	78	76
9[f]	1 : 3	50	>95	82

[a]Reaction conditions: (1*H*-benzo[*d*]imidazol-2-yl)methanol (2 mmol), catalyst (2×10^{-3} mmol), 60 min.
[b]Molar ratio.
[c]Determined by GC.
[d]In the absence of catalyst.
[e]Catalyst (2×10^{-4} mmol).
[f]Catalyst (2×10^{-2} mmol).

The mixture was stirred for 5 h. After filtering, the solution was evaporation under reduced pressure at 50 °C. Pure 1*H*-benzo[*d*]imidazole-2-carbaldehyde (0.07 mmol, 10.2 g) was obtained with a yield of 70% after recrystallisation from 30% H_2SO_4 solution. The product, 1*H*-benzo[*d*]imidazole-2-carbaldehyde, was identified by its ^1H NMR spectrum.

Conclusions

A new ruthenium complex, [Ru(bpbp)(pydic)], has been used as catalyst for the oxidation of (1*H*-benzo[*d*]imidazol-2-yl)methanol to 1*H*-benzo[*d*]imidazole-2-carbaldehyde with H_2O_2 as oxidant. The reaction optimal conditions were: molar ratios of catalyst to substrate to H_2O_2 of 1 : 1000 : 3000, optimal reaction temperature of 50 °C and reaction time of 5 h. The yield of (1*H*-benzo[*d*]imidazol-2-yl)methanol from 1*H*-benzo[*d*]imidazole-2-carbaldehyde under the optimal reaction conditions was 70%.

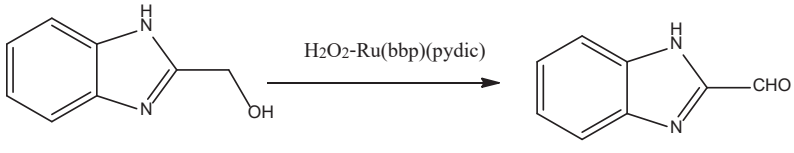

Fig. 3 Reaction scheme of (1*H*-benzo[*d*]imidazol-2-yl)methanol to 1*H*-benzo[*d*]-imidazole-2-carbaldehyde.

Experimental

Reagents and methods

All chemicals were of analytical grade and were purchased from J&K Company without further purification. N^1-(pyridin-2-yl)benzene-1,2-diamine was synthesised according to the literature.[25] Mass spectra were obtained on a Shimadzu LCMS-2010A instrument. Elemental analyses were carried out with an Elementar Vario EL Elemental Analyzer. ^{1}H NMR were 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.

Synthesis of N^2,N^6-bis[2-(pyridin-2-ylamino)phenyl]pyridine-2,6-dicarboxamide; general procedure

N^2,N^6-Bis[2-(pyridin-2-ylamino)phenyl]pyridine-2,6-dicarboxamide was synthesised according to a published method.[26]

Pyridine-2,6-dicarboxylic acid (3.34 g, 10 mmol) was refluxed in thionyl chloride (10 mL) for 8 h. Excess thionyl chloride was removed under vacuum. After cooling to room temperature, N^1-(pyridin-2-yl)benzene-1,2-diamine (7.36 g, 20 mmol) and triethylamine (6 mL) in 60 mL of CH_2C1_2 were added to a solution of the residue in CH_2C1_2 (30 mL). The mixture was further stirred for 2 h at ambient temperature. The white solid product was collected by filtration, washed with water and dried in a vacuum (yield: 6.50 g, 64.87%). Anal. calcd for: $C_{29}H_{23}N_7O_2$: C, 69.4; H, 4.6; N, 19.55; found: C, 69.65; H, 4.66; N, 19.51%.

Synthesis of 2,6-bis[1-(pyridin-2-yl)-1H-benzo[d]imidazol-2-yl]pyridine (pdpd); general procedure

2,6-Bis[1-(pyridin-2-yl)-1*H*-benzo[*d*]imidazol-2-yl)]pyridine was synthesised according to a published method.[27]

N^2,N^6-Bis[2-(pyridine-2-ylamino)phenyl]pyridine-2,6-dicarboxamide (5.01 g) was heated at 250 °C for 3 h under a nitrogen atmosphere. After cooling, water (50 mL) was added and the mixture extracted with CH_2Cl_2 (50 × 3 mL). The combined organic layers were washed with water. After filtration the solvent was removed in a vacuum to obtain crude, solid bpbp which was recrystallised from ethanol (2.78 g, 59.78%). IR (KBr)/cm^{-1}: 3425, 3064, 1586, 1438, 1404, 1368, 1329, 1291, 1255, 1200, 1147, 1065, 995, 921, 868, 825, 791, 743, 637, 589, 517, 407; ^{1}H NMR (400 MHz, d_6-DMSO): 7.04–7.23(m, 3H), 7.26–7.44 (m, 8H), 7.73–7.80 (m, 4H), 8.09–8.27 (m, 2H), 8.35–8.42 (m, 2H).

Synthesis of ruthenium complex [Ru(bpbp)(pydic)]; general procedure

$RuCl_3 \cdot nH_2O$ (690 mg, 0.22 mmol) and bpbp (930 mg, 0.2 mmol) were dissolved in ethanol (60 mL). After the reaction mixture was refluxed for 4 h at 80 °C to form a red-brown deposit, it was cooled to room temperature and filtered. The red-brown solid was collected (0.672 g, 0.1 mmol) and sodium pyridine-2,6-dicarboxylate (211 mg, 0.1 mmol), dissolved in ethanol (20 mL) and water (10 mL), were added to it. The whole reaction mixture was again refluxed at 80 °C for 4 h to yield a violet solution. After reaction for a further 3 h the solvent was reduced to 10 mL to give a dark-violet precipitate, which was filtered off and dried in a vacuum (450 mg, 0.61 mmol, yield: 64.01%). Anal. calcd for $C_{36}H_{22}N_8O_4Ru$: C, 59.09; H, 3.03; N, 15.31; found: C, 59.41; H, 3.09; N, 15.35%; IR (KBr)/cm^{-1}: 3445, 1650, 1468, 1444, 1400, 1335, 1261, 1154, 1090, 1020, 911, 747; ^{1}H NMR (400 MHz, d_6-DMSO): δ 8.80–8.98 (d, 2H), 8.30–8.78 (q, 3H), 7.77–8.25 (t, 6H), 7.50–7.73(m, 7H), 7.03–7.47(m, 4H).

X-ray crystallography

Single-crystal structure determinations were performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source and graphite monochromated Mo-K_a radiation (l = 0.71073 Å) at 173 K. The semi-empirical absorption was applied to the intensity data.

The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 program. All non-hydrogen atoms in both structures were refined using anisotropic displacement parameters. All hydrogen atoms were added theoretically. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 1499925 and 1499926. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (http://www.ccdc.cam.ac.uk). The crystal data are summarised in Table 3.

Catalytic oxidation of (1H-benzo[d]imidazol-2-yl)methanol; general procedure

The catalytic oxidation of (1*H*-benzo[*d*]imidazol-2-yl)methanol was carried out in a magnetically stirred glass reaction tube fitted with a reflux condenser. A typical procedure was as follows: (1*H*-benzo[*d*]

Table 3 Crystal data and structure refinement for the compounds

Compound	N^2,N^6-Bis[2-(pyridin-2-ylamino)phen-yl]-pyridine-2,6-dicarboxamide	2,6-Bis[1-(pyridin-2-yl)-1*H*-benzo[*d*]-imidazol-2-yl]pyridine
Formula	$C_{29}H_{23}N_7O_2$	$C_{29}H_{19}N_7$
Formula weight	501.54	465.51
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n
a/Å	9.2468(14)	12.465(2)
b/Å	25.869(4)	14.152(2)
c/Å	11.0007(16)	13.790(2)
β/°	109.256(3)	109.383(2)
V/Å^3	2484.2(6)	2294.9(6)
μ/mm^{-1}	0.089	0.084
Z	4	4
D_c/g cm^{-3}	1.341	1.347
Crystal size	0.39 × 0.29 × 0.13	0.25 × 0.23 × 0.21
Theta range for data collection/°	2.11 to 27.05	1.91 to 25.00
Index ranges	−10≤ *h* ≤11, −28≤ *k* ≤33, −13≤ *l* ≤7	−6≤ *h* ≤14, −13≤ *k* ≤16, −16≤ *l* ≤15
F(000)	1048	968
GOF on F^2	1.048	1.004
Reflections collected/unique	12562/5374 [$R_{(int)}$ = 0.0198]	9891/4031 [$R_{(int)}$ = 0.0201]
Data/restraints/parameters	5374/0/343	4031/0/325
R indices (all data)	R_1 = 0.0650, wR_2 = 0.1441	R_1 = 0.0461, wR_2 = 0.1008
Final *R* indices [*I* > 2 sigma (*I*)]	R_1 = 0.0492, wR_2 = 0.1320	R_1 = 0.0333, wR_2 = 0.0911
Max. and min. transmission	0.988, 0.970	0.9826, 0.9793
Largest diff. peak and hole (e A^{-3})	0.456 and −0.428	0.148 and −0.166

imidazol-2-yl)methanol (aqueous solution, 0.1 mol L^{-1}), ruthenium complex catalyst (1×10^{-4} mmol, 0.01 mol% based substrate) and inert internal standard (0.2 mmol) were added to a reaction tube which was heated to a chosen temperature in an oil bath under vigorous stirring, and then aqueous hydrogen peroxide (30% H_2O_2, 10 mol L^{-1}) was added slowly dropwise. Product samples were drawn at regular time intervals and analysed by GC and GC-MS. GC analyses were performed on a Shimadzu GC-2010 plus chromatograph equipped with an Rtx-5 capillary column (30 m × 0.25 mm × 0.25 μm). GC-MS analyses were recorded on a Shimadzu GCMS-QP2010 instrument equipped with an Rxi-5ms capillary column (30 m × 0.25 mm × 0.25 μm).

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