Crystal structure of an unsymmetrical Schiff base, immobilization of its cobalt and manganese complexes on a silica support, and catalytic studies

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Abstract An unsymmetrical tetradentate Schiff base (H_2L) was synthesized by the reaction of 3-methoxysalicylaldehyde, *o*-phenylenediamine, and salicylaldehyde in EtOH. H_2L was characterized by single-crystallographic X-ray analysis. Its Co(II) and Mn(III) complexes ([CoL] and [MnLC1]) were prepared and immobilized on 3-aminopropyltriethoxysilane functionalized silica gel. The immobilized materials were found to be efficient catalysts for epoxidation of styrene in the presence of *tert*-BuOOH in acetonitrile at 40 °C. The catalysts can be reused several times without significant loss of performance.

Introduction

In recent years, there has been a resurgence of interest in the synthesis and characterization of unsymmetrical Schiff bases and their use as ligands [1, 2]. It is well known that the electronic properties of unsymmetrical Schiff bases can

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Department of Chemistry, Faculty of Science, Anadolu University, 26470 Eskisehir, Turkey be tuned by introducing different electron donating and/or withdrawing groups at the two imine units. In addition, unsymmetrical Schiff bases have been reported to give improved enantioselective activities in various organic transformations compared to their symmetrical derivatives [3].

New catalysts derived from unsymmetrical tetradentate Schiff base complexes seem to be more and more attractive in catalysis [4].

Schiff bases derived from substituted salicylaldehydes and various aromatic amines are common ligands in coordination chemistry because of their ease of preparation [5]. The complexes of Schiff bases containing O and N donor atoms have proved to be of particular interest [6]. Therefore, Schiff base complexes have been amongst the most widely studied coordination compounds and are becoming increasingly important as analytical, biochemical, and antimicrobial reagents [7]. These compounds also find catalytic applications, ranging from unsymmetrical epoxidation [8] to polymerization [9].

Transition metal complexes of Schiff bases have proved to be useful catalysts in the oxidation/epoxidation of organic compounds by various oxidants such as H_2O_2 , tertbutylhydroperoxide (TBHP) and PhIO [10]. Catalytic oxidation/epoxidation of olefins is important for the synthesis of fine chemicals. Schiff base complexes have been used as homogeneous catalysts in epoxidation of olefins, oxidation of alkanes, alcohols and thiols, and amine oxidation [11, 12].

Heterogenization of homogeneous catalysts onto solid supports brings advantages such as easy separation, thermal stability, high selectivity, and recyclability [13]. A general strategy for converting a homogeneous process into a heterogeneous one is to anchor the catalyst onto a large surface area inorganic support [14]. In addition, silane-coupling reagents serve as a linker keeping the catalyst center away from the support material so that it behaves like a homogeneous catalyst.

Various materials (e.g., alumina, mesoporous silica, polymers, carbon materials, zeolites) can be used as supports for immobilized Mn(salen) catalysts [15, 16]. In particular, mesoporous silica materials, particularly SBA-15 and MCM-41 materials, have received much attention because of their large surface areas, uniform hexagonally ordered two-dimensional mesoporous channels, high hydro-thermal stability, and tunable pore dimensions and channel structure, allowing ready diffusion of reactants to the active sites located in the nanopores. More importantly, the nanopores of these mesoporous supports can influence the mechanism of the epoxidation reaction [17], resulting in a different product distribution than seen in homogeneous reactions.

In this article, the preparation and characterization of Co(II) and Mn(III) complexes of an unsymmetrical Schiff base supported on organoamine derivatized silica is reported. Characterization of the compounds was performed by analytical, spectroscopic, and chromatographic methods. The catalytic activities of the compounds were investigated for the epoxidation of styrene.

Experimental

Materials and instrumentation

Silica gel 60 (0.015–0.040 mm), *o*-phenylenediamine, and salicylaldehyde derivatives were purchased from Merck. 3-aminopropyltriethoxysilane (APTS) and *tert*-Butyl hydroperoxide (TBHP) solutions (70 % in H₂O) were purchased from Sigma–Aldrich. Mn(AcO)₂·4H₂O and Co(AcO)₂·4H₂O were supplied by Fluka and were used as received. Solvents and all other reagents were technical grade and were purified and dried by distillation from appropriate desiccants when necessary.

Melting points were measured in sealed tubes using a Gallenkamp digital melting point apparatus. IR samples were prepared as KBr pellets, and spectra were recorded on a Perkin–Elmer RX-1 FTIR spectrometer within the range of 4000–400 cm⁻¹. UV–vis spectra were measured using a Perkin–Elmer Lambda 25 UV–vis spectrometer. Room temperature diffuse reflectance spectra in the ultra-violet and visible region (DR–UV–vis) were recorded on a Varian Cary 100 model UV–vis spectrophotometer. C, H, and N elemental microanalyses were performed with a LECO-CHNS-932 elemental analyzer. Metal analysis was carried out with an AAS Perkin–Elmer 3100 instrument in solutions prepared by decomposing the complex in aqua regia and then subsequently digesting in concentrated HCl. Thermogravimetry (TG) and differential thermal analyses

(DTA) of the samples were performed with a Perkin–Elmer Pyrris Thermal Analyzer in nitrogen medium, from 40 to 700 °C at a heating rate of 10 °C min⁻¹. Molar conductances were determined in DMSO ($\sim 10^{-3}$ M) at room temperature using a Jenway Model 4070 conductivity meter. Magnetic measurements were carried out with a Sherwood magnetic susceptibility balance (Model MK1) with CuSO₄.5H₂O as the calibrant.

X-ray structural analysis

Diffraction data for H₂L were collected with a Bruker SMART APEX CCD diffractometer equipped with a rotation anode at 296(2) K using graphite monochrometed Mo K α radiation (λ 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SAINT [18] program package. For further crystal and data collection details see Table 1. Structure solution was carried out with the SHELXS-97 [19] package using direct methods and refined with SHELXL-97 [20] against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure model on calculated positions. Geometric calculations were performed with Platon [21].

Preparation of H₂L

H₂L was prepared according to the modified method described in the literature [1]. To a stirred, cooled solution of 3-methoxysalicylaldehyde (4.56 g, 30 mmol) in EtOH (100 cm³), a cold solution of *o*-phenylenediamine (3.24 g, 30 mmol) in EtOH (100 cm³) was added dropwise followed by addition of a cold solution of salicylaldehyde (3.66 g, 30 mmol) in EtOH ((20 cm³)) over a period of 10 min (Scheme 1). The mixture was then stirred and refluxed for 12 h. After cooling, the ligand was obtained as orange microcrystals. These were filtered off, washed with cold absolute ethanol, and recrystallized several times from ethanol–chloroform (1:1, v/v).

[H_2L]: Color: orange, m. p. 140–142 °C, yield 65 %, UV–vis; 245, 270 and 340 nm.

Preparation of [CoL]

A solution of Co(II) acetate (0.99 g, mmol) in methanol (20 cm³) was added dropwise to a stirred warm solution of H_2L (1.38 g, 4 mmol) in methanol (20 cm³) under N₂, and the resulting solution was stirred for 2 h. The precipitate was filtered off and washed with water, methanol, and diethyl ether and finally dried in vacuum.

Table 1	Crystal	data	and	structure	refinement	for	H ₂	I
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Empirical formula	C21 H18 N2 O3			
Formula weight	346.37			
Temperature	110(2) K			
Wavelength	0.71073 A			
Crystal system, space group	Orthorhombic, P bca			
Unit cell dimensions (Å, °)	a = 36.9886 (19) alpha = 90			
	b = 14.1290 (8) beta = 90			
	c = 6.2938 (3) gamma = 90			
Volume	3298.2(3) A ³			
Z, Calculated density	8, 1.399 Mg/m ³			
Absorption coefficient	0.094 mm^{-1}			
<i>F</i> (000)	1456			
Crystal size	0.43 \times 0.30 \times 0.29 mm			
Theta range for data collection	1.10–22.79 deg.			
Limiting indices	-48<=h <=49, -18<=k <=17, -8<= l<=8			
Reflections collected/ unique	$4042/3411 \ [R(int) = 0.042]$			
Max. and min. transmission	0.973 and 0.966			
Refinement method	Full-matrix least-squares on F^2			
Data/restraints/parameters	1704/0/238			
Goodness-of-fit on F^2	0.97			
Final R indices [$I > 2$ sigma(I)]	R1 = 0.0474, wR2 = 0.1434			



Scheme 1 Synthesis pathway of H₂L

Yield (55 %), color: brown, m.p. >250 °C, μ_{eff} : 4.31 BM, Λ : 0.5 Ω^{-1} cm² mol⁻¹, Anal. Calcd. for C₂₁H₁₆CoN₂ O₃ (%): C, 62.5; H, 4.0; N, 7.0; Co, 14.6. Found: C, 62.6; H, 4.1; N, 6.9; Co, 14.5.

Preparation of [MnLCl]

This complex was prepared by a procedure adapted from the literature. A mixture of H₂L (0.69 g, 2.0 mmol) and Mn(OAc)₂·4H₂O (1.24 g, 5.0 mmol) in ethanol (30 cm³) was refluxed for 1 h [11]. Then, LiCl (0.6 g, 15 mmol) was then added, and the mixture was refluxed for an additional 1 h under exposure to the air. The mixture was concentrated under vacuum and then filtered. The residue was washed with deionized water (3 × 25 cm³), then ethanol, and dried as a dark brown solid.

Yield (53 %), color: brown, m.p. >250 °C, μ_{eff} : 4.46 BM, A: 0.8 Ω^{-1} cm² mol⁻¹, Anal. Calcd. for C₂₁H₁₆ClMn N₂O₃ (%): C, 58.0; H, 3.7; N, 6.4; Mn, 12.7. Found: C, 58.0; H, 3.8; N, 6.4; Co, 12.6.

Modification of silica surface (SiO₂-APTS)

Silica gel was activated by the following procedure. Silica gel 60 (40 g) was treated with and was activated by refluxing it with 6 M HCl for 24 h. It was then filtered off, washed with deionized water until the filtrate was neutral, and dried at 120 °C for 12 h [22].

The activated silica gel (30 g) was suspended in 100 cm^3 of a solution of 3-aminopropyltriethoxysilane (APTS) in dry toluene (10 % v/v). The mixture was refluxed with stirring for 48 h under nitrogen. The slurry was filtered, and the resulting solid SiO₂-APTS was washed successively with copious amounts of toluene, ethanol, and diethyl ether, then dried in a vacuum oven for 10 h.

White color powder, elemental analysis: C 9.0, H 2.3, N 3.4 %. FTIR (cm⁻¹): 3454 (br, Si–OH); 2941 (w, R–H); 1096 (br, Si–O).

Preparation of [CoL]@SiO₂-APTS

The route for preparing the heterogeneous Co(II) catalyst by coordination of the [CoL] catalyst to the amino groups on the support surface is outlined in Scheme 2. [CoL] (0.81 g, 2 mmol) was dissolved in acetonitrile (50 cm³). The solution was added to a suspension of SiO₂–APTS (2.0 g) in dichloromethane (50 cm³). The resulting mixture was stirred at room temperature for 48 h. After filtration, the solid was washed with dichloromethane and acetonitrile until the eluate became colorless.





Scheme 3 Immobilization of [MnLCl] onto SiO2-APTS

Scheme 2 Immobilization of [CoL] onto SiO2-APTS

Preparation of [MnL]@SiO2-APTS

[MnLCl] (0.87 g, 2 mmol) was dissolved in acetonitrile (50 cm³), and 0.62 g (3 mmol) of AgClO₄ was added to remove the chloride from the coordination sphere by precipitation. The suspension was stirred at room temperature for 24 h and then filtered through a filter crucible. The filtrate was then added to a suspension of SiO₂–APTS (2.0 g) in dichloromethane (50 cm³). The resulting suspension was stirred at room temperature for 48 h (Scheme 3). After filtration, the solid was washed with dichloromethane and acetonitrile until the eluate became colorless.

Catalysis studies and product identification

The immobilized [CoL] and [MnLCl] complexes were investigated as catalysts for the epoxidation of styrene with *tert*-butyl hydroperoxide (TBHP) as an oxidant. The typical reaction mixture was composed of styrene (5.0 mmol), TBHP (5.0 mmol), catalyst (0.05 mmol of active centers; 0.098 g [CoL] and 0.11 g [MnLCl]), and dichloromethane or acetonitrile (10 cm^3) as the solvent. The products of the reactions were collected at different time intervals ranging from 8 to 24 h. For repeated catalytic experiments, the catalyst was separated using centrifugation followed by decantation, twice washed with acetonitrile and dichloromethane, dried in air, and then used in a new run.

Gas chromatography was used for the identification and quantification of the reaction products, using a Finnigan-Trace GC-MS equipped with an auto sampler. Chromatographic separations were accomplished with a Zebron ZB-35 column (30 m 0.2 mm i.d.; 0,25 μ m film thickness), with injections in the split mode with 50:1 split ratio. Analyses were carried out using helium as the carrier gas, flow rate $1.0 \text{ cm}^3 \text{ min}^{-1}$. Conditions used; 40 °C (10 min), 10 °C min⁻¹ to 240 °C (10 min), injector temperature 250 °C, detector temperature 250 °C. The ionization voltage was 70 eV, mass range m/z 41–400 a.m.u. The separated components were identified tentatively by matching with GC-MS results of reference samples. Chlorobenzene was used as an internal standard. Quantitative determinations were carried out based on peak area integration.

Results and discussion

Structural description of H₂L

An ORTEP view of the unsymmetrical Schiff base molecule, which crystallized in orthorhombic P bca space group, is shown in Fig. 1. The crystal data and selected bond lengths and angles are listed in Tables 1 and S1, respectively. The packing diagram is also shown in Fig. S1. The aromatic ring systems are in almost planar conformation, with endocyclic torsion angles of 1.9 $(3)^{\circ}$, -0.9 $(2)^{\circ}$, and -0.6 $(2)^{\circ}$. The mean plane between the rings (C9-C10-C11-C16-C17 and C2-C3-C4-C14-C15) is 55.19°. All the bond lengths are comparable to those observed in similar compounds [1-4]. The bond lengths of C8=N2 [1.285(2) Å] and C5=N1 [1.284 (2) Å] conform to the values for double bonds and are comparable to those in other Schiff bases [23, 24]. In addition, the bond lengths (C6-N1) = 1.410(2) Å and (C7-N2) = 1.408(2) Å are typical for the single bonds. Three torsion angles, C8-N2-C7-C18 [43.4 (2)°], C21-N1-C6-C5 [-10.3 (2)°], N2-C7 -C6-N1 [6.7 (2)°], are responsible for mutual orientation of both aromatic ring systems. In the crystal structure, the $N \cdots N$ distance is equal to 2.732 (2) Å.

The hydrogens attached to O2 and O3 form asymmetric weak intramolecular hydrogen bonds to N2 and N1, respectively: O2–H2…N2 1.875(1), O2…N2 2.608(2) Å, 145.1(8)°; O3–H3…N1 1.871(1), O3…N1 2.610(1) Å, 146.0(7)°. There are columns of molecules arranged in a 2D network connected by intermolecular hydrogen bonds along the crystallographic *c* direction (Fig. S2): C8–H8... O3, 2.716 (2) Å, 142.3° (3), *x*, +*y*, +*z*+1; C12–H12…O1, 2.405 (1) Å, 161.3° (1), -x+/2, -y+1, +z-1/2). These are reinforced by C–H… π interactions formed between rings. Moreover, there is a weak face-to-face stacking interaction [3.632 (2) Å] between the rings C2–C3–C4–C13–C14–C15 and C6–C7–C18–C19–C20–C21.

Characterization of the complexes

The results of elemental analysis are in good agreement with the suggested compositions of the metal complexes.

The effective room temperature magnetic moments of [CoL] and [MnLCl] were calculated as 4.31 BM and 4.46 BM, respectively, indicating distorted tetrahedral [25] and square pyramidal [26] geometries, respectively.

The solution conductivities of [CoL] and [MnLCl] in DMSO were measured as 0.5 and 0.8 Ω^{-1} cm² mol⁻¹, respectively, showing that the complexes are non-electrolyte as expected [27].

The electronic spectra of H_2L , [CoL] and [MnLCl] were measured in chloroform. The UV–vis spectra of H_2L and [CoL] are given in Fig. S3. In the spectra of the complexes, the three bands from the azomethine ligand (π – π *), charge transfer (MLCT), and *d*–*d* transitions are observed at 373 and 378, 419 and 425 and 500 and 520 nm, for [CoL] and [MnLC1], respectively.

In the FTIR spectrum of the free ligand H_2L , a broad band at 3428 cm⁻¹ might be attributed to O–H vibration (Fig. S4a). On the other hand, in the FTIR spectra of [CoL] and [MnLCl], the bands due to the O–H modes are no longer observed, suggesting that the hydroxyl protons are displaced by the metal atoms leading to M–O bonding (Fig. S4b, S4c). In addition, the band due to the CH=N groups of H₂L was shifted from 1613 to 1606 and 1605 cm⁻¹ for [CoL] and [MnLCl], respectively, consistent with involvement of the azomethine nitrogen atoms in the coordination [28].

The bands assigned to the intramolecular H-bonding vibration (O–H…N) (2650–2700 cm⁻¹) of H₂L are absent from the spectra of complexes, as a result of deprotonation and coordination of the oxygen atoms [29]. The bonding of the Co(II) and Mn(III) atoms to the ligand through the nitrogen and oxygen atoms is further supported by the presence of new bands at 520 (Co) and 541 (Mn) cm⁻¹ and 450 (Co) and 445 (Mn) cm⁻¹ assigned to the M–O and M–N stretching, respectively [30].

Immobilization of [CoL] and [MnLCl] onto SiO₂-APTS

Modification of the silica support through surface functionalization with APTS and immobilization of [CoL] and [MnLCl] onto the modified silica was carried out by using the procedure shown in Schemes 2 and 3. On the basis of nitrogen elemental analysis, the amount of APTS anchored to the silica was determined as 2.42 mmol g^{-1} . The amounts of [CoL] and [MnLCl] immobilized onto SiO₂– APTS were 0.51 and 0.46 mmol g^{-1} , respectively, determined from metal analyses by AAS.

The DR–UV–vis spectra of SiO₂–APTS, CoL@SiO₂– APTS, and MnL@SiO₂–APTS are given in Fig. S5. There are important differences between the spectrum of SiO₂– APTS and the spectra of CoL@SiO₂–APTS and MnL@ SiO₂–APTS. In the spectrum of SiO₂–APTS, no peaks are observed in the range from 300 to 500 nm. In contrast, there are two intense peaks in this range at the spectra of both CoL@SiO₂–APTS and MnL@SiO₂–APTS, consistent with the presence of the metal complexes on the surface of SiO₂–APTS.

The FTIR spectra of SiO₂, APTS functionalized silica (SiO₂–APTS), CoL@SiO₂–APTS, and MnL@SiO₂–APTS are shown in Fig. S6. The spectrum of SiO₂ shows a broad band in the range 3430–3080 cm⁻¹, attributed to the silanol (–OH) groups, and a broad absorption at 1089 cm⁻¹ assigned to the Si–O–Si bonds. After functionalization of

Fig. 1 A view of H₂L, showing 50 % probability displacement ellipsoids and the atomnumbering scheme. *Dashed lines* are intramolecular hydrogen bonding in the structure



silica with APTS, the intensity of the 3400 cm⁻¹ band is decreased, indicating successful grafting of the organosilane onto the silica surface via Si–O–Si bond formation. In addition, SiO₂-APTS also shows the characteristic bands for C–H and N–H stretching from 2800 to 3200 cm⁻¹. Upon immobilization of the metal complexes onto SiO₂– APTS, there are no significant changes in the FTIR spectra, as the quantities of the complexes were so low that their absorption bands were obscured by the strong background peaks of SiO₂–APTS [31].

The only difference noticed between the spectra of SiO₂– APTS and CoL@SiO₂–APTS, and MnL@SiO₂–APTS is the appearance of low-intensity bands at the range of 1350– 1650 cm⁻¹ and especially at 1600 cm⁻¹, assigned to C=N groups of the complexes.

The vibrational bands of the counter ion (ClO4⁻) of MnL@SiO₂-APTS, expected at 1100 cm^{-1} , might be overlapped by the broad Si–O–Si band of the support.

Schematic representations of the proposed structures of $CoL@SiO_2$ -APTS and $MnL@SiO_2$ -APTS [32] are given in Schemes 2 and 3.

These materials were also investigated by thermogravimetric analysis. The TGA weight loss of the silica gel shows only one peak with a corresponding weight loss of about 4–5 % in the region of 50–150 °C, attributed to the loss of surface adsorbed water [31]. In addition to the loss of adsorbed water in the range 50–150 °C, SiO₂–APTS also displays other significant weight losses (7–8 %) without distinct steps in the region 220–580 °C, attributable to the loss of organic moieties attached to the APTS unit. The TG–DTA thermogram of MnL@SiO₂–APTS is given in Fig. S7. Upon immobilization of the complexes onto the organofunctionalized silica gel, the decomposition of the organic parts of the complexes starts at ca. 300 °C and continues up to ca. 700 °C, with weight loss of about 20 %.

Catalytic studies

Styrene was used as substrate to investigate the behavior of the immobilized complexes as heterogeneous catalysts for olefin epoxidation, using TBHP as an oxidant in dichloromethane or acetonitrile as solvent. The results are summarized in Table 2.

The MnL@SiO₂-APTS complex gave higher conversion and selectivity compared to SiO₂-APTS and CoL@ SiO₂-APTS. Analysis of the products with a Finnigan-Trace GC-MS instrument found that benzaldehyde was the main by-product. The proposed mechanism of the catalytic reaction is given Scheme S1.

The influence of reaction time (8, 16 or 24 h) in the epoxidation of styrene catalyzed by CoL@SiO₂–APTS and

 Table 2
 Epoxidation of styrene with TBHP catalyzed by a variety of catalysts based on immobilized Schiff base-metal complexes

Catalyst	Styrene conversion (%)	Selectivity (%)		
		SE	BA	Other
SiO ₂ –APTS	12	58	34	8
CoL@SiO2-APTS	52	61	30	9
MnL@SiO ₂ -APTS	73	70	24	6
MnL@SiO ₂ -APTS	70 (after 5 recycling)	71	22	7

Reaction conditions: amount of catalyst: 0.05 mmol active center; reaction temperature: 40 $^{\circ}$ C; Styrene (5 mmol); acetonitrile (10 ml) as a solvent; reaction time 24 h

SE Styrene oxide, BA Benzaldehyde

MnL@SiO₂-APTS was investigated. The highest conversion of substrate was achieved for 24-h reaction times. Next, the epoxidation of styrene was studied by varying the reaction temperature from 25 to 40 °C in various solvents. These experiments showed that 40 °C was the best temperature in both solvents.

The influence of solvents (dichloromethane and acetonitrile) on these catalytic epoxidations was explored for both CoL@SiO₂-APTS and MnL@SiO₂-APTS. In both cases, the highest conversion of substrate was achieved in acetonitrile.

Using the optimum conditions, epoxide yields of 52 and 73 % were achieved for CoL@SiO₂-APTS and MnL@SiO₂-APTS, respectively.

Catalyst reusability

The reusability of immobilized catalyst is one of the most important benefits of heterogeneous catalysis. To investigate the stability and the reusability of these catalysts, the catalyst was separated from the reaction mixture after each experiment, washed thoroughly with dichloromethane followed by acetonitrile, and dried before being used in the following experiment. In this way, the catalysts were reused five times without a significant loss of activity. The filtrates were used for determination of the catalyst leaching by atomic absorption spectroscopy. The results showed that in the first run, some catalyst was leached from the organosilica support (about 0.9 %), but in the subsequent runs no leaching was observed. The reusability studies are showed that the styrene conversion drops by 3 % during the consecutive five recycling, experiments in total.

Conclusions

An unsymmetrical Schiff base was synthesized, and its crystal structure was determined by X-ray analysis. The Co(II) and Mn(III) complexes of the Schiff base were

immobilized onto silica through coordination of the amine from APTS which was covalently bound to the silica support. The immobilized Co(II) and Mn(III) complexes are moderately efficient catalysts for epoxidation of styrene with *tert*-BuOOH. The MnL@SiO₂-APTS complex showed higher conversion and selectivity compared to SiO₂-APTS and CoL@SiO₂-APTS. The catalysts could be easily separated from the reaction system and reused. They have potential for further improvement as well as use heterogeneous catalysts, for other reactions.

Supplementary data

Crystallographic data can be obtained from the Cambridge Crystallographic Data Center, by quoting the reference number CCDC-863564. The data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif.

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