FULL PAPER



A three-dimensional (3D) manganese (II) coordination polymer: Synthesis, structure and catalytic activities

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A new Mn (II)-containing coordination polymer, $[Mn_6(Ipa)_6(ad)\cdot 6H_2O]$ (1; Ipa = isophthalate ligand; ad = adenine), was synthesized by reacting hydrated manganese nitrate with isophthalic acid and adenine under solvothermal reaction conditions. Polymer 1 was characterized using single-crystal X-ray diffraction analysis and other techniques such as Fourier transform infrared spectroscopy, elemental analyses and powder X-ray diffraction. The solid-state structure of 1 confirmed the formation of a three-dimensional framework structure based on Mn₆ secondary building units. Phase purity of bulk 1 and its thermal stability were investigated. Polymer 1 was evaluated for its performance as a heterogeneous catalyst for the Henry (nitroaldol) reaction of nitromethane with several aldehydes. The recyclability of 1 and heterogeneity of the reaction were also explored. A plausible mechanism for such reaction is proposed. To the best of our knowledge, polymer 1 represents the first example of a Mn (II)- and adenine-containing coordination polymer as well as the first example of a Mn (II)-containing coordination polymer that has been employed for the Henry reaction.

KEYWORDS

adenine, coordination polymer, Henry reaction, heterogeneous catalyst, single-crystal X-ray diffraction

1 | INTRODUCTION

Presently, metal–organic frameworks (MOFs)/coordination polymers (CPs) are of immense interest among chemists, physicists and material scientists. These highly demanding compounds are synthesized by connecting inorganic metal nodes with organic linkers. Owing to their stable and tunable porous structures, they have emerged as promising functional materials in catalysis,^[1] chemical separations,^[2] gas storage,^[2c,3] molecular sensing,^[4] contaminant removal,^[5] ion exchange^[3b,6] and drug delivery.^[7] A large number of interesting and diverse polydentate ligands have been synthesized and employed in the formulation of MOFs/CPs. Nowadays, biomolecules such as nucleobases, amino acids and peptides are preferred over synthetic ligands in the preparation of such compounds.^[8] These biomolecules are inexpensive, nontoxic and capable of forming hydrogen bonds, inducing chirality as well as providing multiple donor sites.^[9] Interestingly, nucleobases are of prime interests among biomolecules for the construction of CPs. They can offer a rigid and porous framework. In contrast, other biomolecules (peptides, proteins and amino acids) would result in flexible, interpenetrated and nonporous frameworks which limit their applications. Among nucleobases, adenine is a more attractive building unit because of its rigid, planar and π -conjugated structure.^[10] Moreover, it offers five potential donor sites including heterocyclic and imidazole nitrogen atoms (Scheme 1) which can coordinate many metal ions or



SCHEME 1 Five potential donor sites of adenine ligand

form hydrogen bonds and thus leading to new polymeric structures.^[9-11]

Its rich coordination ability and hydrogen bonding capabilities result in the formation of diverse framework structures with applications mainly in gas adsorption and drug encapsulation/delivery.^[12] For instance, bio-MOF-1 exhibits exceptional gas adsorption properties and is suited for loading and controlled release of the cationic drug procainamide HCl.^[13] The anticancer drug methotrexate was successfully loaded into two bio-MOFs (ZJU-64 and ZJU-64-CH₃) and delivered in specific cancer cells to kill the cells with low side effects.^[14] In addition, these adenine-based CPs are also useful for adsorption and/or separation of hydrocarbons, gases and organic dyes.^[15] Sensing abilities of such compounds have recently been investigated against explosives (nitro aromatic compounds), volatile organic amines and toxic metal (Hg).^[16] Many CPs have already been proven to be effective heterogeneous catalysts for organic conversion. Despite the existence of Lewis acid sites (metal ions) and Lewis base sites (nitrogen atoms on adenine), catalytic abilities of such CPs towards organic transformations under heterogeneous reaction condition are scarcely investigated. One can cite a single report where a Zn (II)-containing complex was tested for its catalytic activities only in Knoevenagel condensation reaction.^[17]

Based on the previous discussion, we were interested in developing a new biomolecule-derived CP and investigating its catalytic activity towards an organic reaction (Henry reaction). The Henry or nitroaldol reaction is an important C—C bond formation technique in progressive organic chemistry. Generally, the reaction is performed using various basic catalysts, such as alkoxides, alkali metal hydroxides, amines, etc.^[18] Many transition metal complexes have also been used as homogeneous catalysts for such conversion.^[19] Occasionally, a heterogeneous catalyst has been used for such transformation. Recently, a few transition metal- and lanthanide-containing CPs were introduced as heterogeneous catalysts for the nitroaldol reaction. $^{\left[19b,20\right] }$

As adenine-containing CPs contain multiple Lewis acid and Lewis base sites, we presumed that these CPs could exhibit significant catalytic activity towards the Henry (nitroaldol) reaction. Therefore, we report herein the synthesis and characterization of a new adeninebased Mn (II) coordination polymer of formula [Mn₆ $(Ipa)_6(ad) \cdot 6H_2O$ (1; Ipa = isophthalate; ad = adenine).Detailed experimental processes and characterizations of 1 are discussed. Solid-state structures of 1 were determined using single-crystal X-ray diffraction (XRD) analysis. In addition, we explored its catalytic activity towards the Henry reaction of nitromethane with various aldehydes. The stability, recyclability and heterogeneity of 1 were established. To the best of our knowledge, this is the first report of any biomolecule-derived coordination polymer investigated for its catalytic activity towards the Henry reaction.

2 | RESULTS AND DISCUSSION

2.1 | Synthesis and Structure

The formation of 1 was achieved by solvothermal reaction of isophthalic acid (H₂Ipa) and adenine (ad) with Mn (OAc)₂·4H₂O in a mixture of ethanol and water. Polymer 1 appeared as a white crystalline solid. The Fourier transform infrared (FT-IR) spectrum of 1 shows a strong absorption band at 1667 cm⁻¹ assigned to asymmetric stretching vibration of coordinated carboxylate group (Figure S1 in the supporting information). A broad band at approximately 3400 cm^{-1} is assigned to O-H stretching vibrations and thus it confirms the presence of water molecules (coordinated) in **1**. The phase purity and reproducibility of bulk samples of 1 were established using powder XRD (Figure S2 in the supporting information). The composition of the as-synthesized 1 was determined using single-crystal XRD analysis, elemental analysis and thermogravimetric analysis (TGA). Detailed experimental procedures and data are given in Section 4. The result of single-crystal X-ray structural analysis reveals that 1 crystallizes in orthorhombic centrosymmetric space group Pmn2₁. Detailed single-crystal data and refinement parameters are provided in Table 1. Polymer 1 reveals a three dimensional framework structure based on Mn₆ secondary building units. Each Mn₆ secondary building unit is formed from two Mn₃ units assembled with an adenine molecule (Figure 1). Polymer 1 consists of six Mn (II) ions, six isophthalate ligands, one bridging adenine molecule and six coordinated water molecules. There are three crystallographically independent Mn (II) ions in an asymmetric unit of 1. The coordination

TABLE 1Single-crystal data and structure refinement parameters for 1

Formula	$C_{53}H_{40}Mn_6N_5O_{30}$
Formula weight	1556.54
Temperature (K)	100(2)
Crystal system	Orthorhombic
Space group	P mn 2_1
a (Å)	22.0677 (11)
b (Å)	7.7758(4)
<i>c</i> (Å)	17.6217 (10)
β (°)	90
Ζ	2
$d_{\rm calc} ({\rm g} {\rm cm}^{-3})$	1.710
$\mu(\text{mm}^{-1})$	1.311
F(000)	1566
Total reflections	19521
Unique reflections	5579
Observed data $[I > 2\sigma(I)]$	4930
No. of parameters	413
R (int)	0.0474
$R_1 \left[I > 2\sigma(I) \right]$	0.0546
wR2 (all data)	0.1610
Goodness-of-fit (all data)	1.118
Max. peak/hole	1.682/-0.527



FIGURE 1 Solid state structure of **1**. Color code: Pink Manganese, grey carbon, red oxygen and blue nitrogen atoms. Hydrogen atoms and other isophthalate ligands are not shown for clarity.



FIGURE 2 Coordination environment of Mn (II) ions in 1

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environment of Mn (II) ions in **1** is shown in Figure 2. The Mn1 atom is hexa-coordinated and bonded to four oxygen atoms (O1, O2, O3 and O9) of isophthalate ligands, one nitrogen atom (N3) of a neutral adenine molecule and one oxygen atom O(13) of an aqua ligand.

The central Mn (II) ion (Mn2) occupies the centre of a distorted octahedron and is coordinated by six oxygen atoms (O1, O4, O9, O5, O7 and O12) of the carboxylate groups of isophthalate anions. The terminal Mn (II) ion Mn3 also adopts a distorted octahedral coordination geometry environment. The coordination number of Mn3 is satisfied by four oxygen atoms (O6, O12, O8 and O11) of bridging isophthalate ligands and two oxygen atoms (O14 and O15) of two coordinated water molecules. The Mn-O and Mn-N bond lengths are 2.090(7)-2.334(7) and 2.231 (10) Å, respectively. The Mn…Mn non-bonded distances are 3.511 (Mn1…Mn2) and 3.561 (Mn2···Mn3) Å, respectively. Similar observations for Mn₃ system were previously reported.^[21] Selected bond lengths are given in Table S1 in the supporting information. Three different binding modes of isophthalate anions are observed, in which the carboxylate moieties exhibit bidentate and tridentate coordination fashion to assemble Mn (II) ions as displayed in Figure 3.

Interestingly, adenine adopts bidentate coordination modes (Figure 1) and is bonded to two Mn (II) ions despite its various coordination modes discussed elsewhere.^[9] Similar binding mode was previously observed in a Cd (II) complex derived from adenine and isophthalate ligands.^[22] A fragment of the framework of **1** is depicted in Figure 4.

2.2 | Thermogravimetric Analysis

The thermal stability of **1** was investigated using TGA. The TGA curve shows no weight loss up to 125 °C. Polymer **1** shows a weight loss of *ca* 6.77% (calculated 6.93%) between 125 and 245 °C (Figure 5). This is due to the loss of six water molecules coordinated to Mn (II) ions in **1**. The dehydrated framework of **1** is stable up to 300 °C and slowly decomposes on further temperature increase.



FIGURE 3 Binding modes of isophthalate anion in 1



FIGURE 4 A fragment of framework of **1** viewed along crystallographic b axis. Color code: pink manganese, red oxygen, grey carbon and blue nitrogen atoms.



FIGURE 5 TGA curve of 1

2.3 | Catalytic Activity and Henry Reaction

To explore the use of **1** as a heterogeneous catalyst for the Henry (nitroaldol) reaction, nitromethane was reacted with various aldehydes. Initial reaction was carried out using 4-nitrobenzaldehyde and nitromethane in the presence of 1 mol% of polymer (catalyst) **1** at 70 °C for 18 h (Scheme 2). It was observed that the reaction could offer 80% conversion of 4-nitrobenzaldehyde under these reaction conditions. With this initial result, we screened several reaction parameters such as catalyst loading, solvent, temperature and reaction time (Table 2).



SCHEME 2 Henry (nitroaldol) reaction between nitromethane and 4-nitrobenzaldehyde

The effect of catalyst loading on reaction conversion was investigated in the Henry reaction in methanol at 70 °C. It was observed that the conversion was enhanced from 80 to 94% with increasing catalyst loading 1.0 to 5.0 mol% (Table 2, entries 4–6). However, further rise in catalyst loading decreases the reaction conversion. The reaction was carried out in various solvents to establish the solvent effects. It was found that 1 exhibit highest activity in methanol (Table 2, entry 4). Aprotic and less polar solvents such as acetonitrile, tetrahydrofuran, dichloromethane and toluene were found to be not suitable media and the reaction did not proceed in those solvents (Table 2, entries 9-12). These results indicate the plausible role of polar and protic solvents in the proton transfer phenomena of the Henry reaction.^[20c] The conversion of 4-nitrobenzaldehyde increased from 0 to 94% with increase in temperature from 25 to 70 °C (Table 2, entries 4 and 13). However, the yield decreased with increasing temperature beyond 70 °C. To explore the optimum reaction time for the highest yield, the yield of the reaction was monitored with respect to time. Initially, the rate of conversion of 4-nitrobenzaldehyde was

Entry	Catalyst	Time (h)	Catalyst amount (mol%)	Temp. (°C)	Solvent	Yield (%)
1	1	6	5	70	МеОН	63
2	1	9	5	70	МеОН	70
3	1	12	5	70	МеОН	78
4	1	18	5	70	МеОН	94
5	1	24	5	70	МеОН	94
6	1	18	1	70	МеОН	80
7	1	18	3	70	МеОН	82
8	1	18	7	70	МеОН	85
9	1	18	5	70	CH ₃ CN	_
10	1	18	5	70	THF	_
11	1	18	5	70	Toluene	—
12	1	18	5	70	DCM	—
13	1	18	5	25	МеОН	—
14	1	18	5	40	MeOH	45
15	1	18	5	55	МеОН	84
16	Blank	18	_	70	МеОН	—
17	Adenine	18	5	70	МеОН	5
18	Mn (OAc) ₂ ·4H ₂ O	18	5	70	МеОН	92

^aReaction conditions: 4-nitrobenzaldehyde (1.0 mmol), nitromethane (4.0 mmol); yield calculated by ¹H NMR spectroscopy.

very high and it resulted 63% conversion in the first 6 h. Prolonging the time of the reaction, the yield increased slowly and reached 94% in 18 h (Table 2, entry 4). No improvement in yield was observed when the reaction was performed for 24 h (Table 2, entry 5; and Figure S3 in the supporting information). A blank experiment was also performed using 4-nitrobenzaldehyde and nitromethane as the substrates in the absence of 1 at 70 °C in methanol. No detectable product was obtained in the blank run even after a reaction time of 18 h (Table 2, entry 16). Only 5% conversion occurred when the reaction was performed in the presence of adenine (Table 2, entry 17). However, 92% conversion was achieved when manganese acetate tetrahydrate was used as a catalyst in a homogenous reaction condition (Table 2, entry 18). Therefore, the Henry reaction of nitromethane with various aldehydes was performed under the optimum reaction condition: nitromethane (4.0 mmol), aldehyde (1.0 mmol) and polymer 1 (5 mol%) in MeOH at 70 °C for 18 h.

The catalyst was separated from the solution by filtration. The filtrate was evaporated to obtain the crude product, which was analysed using ¹H NMR spectroscopy (Figures S4–S10 in the supporting information). It proved that polymer **1** is highly active towards several mono-substituted aromatic aldehydes and gives different β -nitroalkanols (Table 3). It is observed that the conversion is highly influenced by the presence of electron-withdrawing and electron-donating groups attached to aromatic aldehydes. When an electron-withdrawing group is attached to aromatic aldehyde, it enhances the electrophilicity of carbonyl group and thus favours the reaction compared with aromatic benzaldehydes with an attached electron-donating group.^[20c,e] It can also be noted that electronic effects are more prominent for *para*-substituted benzaldehydes. For example, *p*-nitro- and *p*-methylbenzaldehydes exhibit highest and lowest conversion, respectively, among all substituted benzaldehydes (Table 3, entries 2 and 6). Therefore, the nature of the substrates plays crucial role in determining the yield of the reaction.

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We compared the catalytic efficiency of **1** with those of other reported MOFs/CPs utilized for the Henry reaction using 4-nitrobenzaldehyde as a model compound (Table 4). The conversion is comparable with that for other MOFs/CPs and maximum with **1** being the first Mn (II)-containing CP used for such reactions.

2.4 | Heterogeneity Test of Reaction

To further confirm whether the catalytic reaction proceeds via 1 or any possible leached Mn (II) ions from 1in solution, the Henry reaction was performed. We carried out a controlled experiment with 1 until a

TABLE 3 Henry reaction of various aldehydes with nitromethane promoted by catalyst 1 in methanol^a

Entry	Compound	Product	Yield (%)	TON ^b	TOF $(h^{-1})^c$
1	СНО	⟨──── <mark>──</mark> H NO ₂	93	18.6	1.03
2	O ₂ N-CHO	O ₂ N- NO ₂	94	17.6	0.97
3	FСНО	F-COH NO ₂	73	14.6	0.81
4			65	13.0	0.72
5	Br-CHO	Br - OH - NO ₂	49	9.8	0.54
6	H ₃ C-CHO	H ₃ C-	19	3.8	0.21
7	СІСНО		45	9.0	0.50

^aReaction conditions: 5.0 mol% of polymer 1, aldehyde (1.0 mmol), nitromethane (4.0 mmol) and methanol (5 ml).

^bNumber of moles of β -nitroalkanol per mole of catalyst.

^cNumber of moles of β -nitroalkanol per mole of catalyst per hour.

Entry	Catalyst	Solvent/temperature/time	Aldehyde	Yield (%)	Ref.
1	1	MeOH/70 °C/18 h	4-Nitrobenzaldehyde	94	This work
2	$[Cu_4 (HL_{ala})_2(H_2O)_4 (MeO)_4]_n$	MeOH/70 °C/24 h	4-Nitrobenzaldehyde	95	[23]
3	[Cu ₃ (pdtc)(L _a) ₂ (H ₂ O) ₃]·2DMF·10H ₂ O	Solvent free/70 °C/36 h	4-Nitrobenzaldehyde	78	[24]
4	$[Zn_2 (L_b)_2(4,4'-bipyridine)_2(H_2O)(DMF)]_n$	MeOH/70 °C/48 h	4-Nitrobenzaldehyde	98	[20c]
5	[Zn ₃ (TCPB) ₂ ·2H ₂ O]·2H ₂ O·4DMF	Solvent free/70 °C/72 h	4-Nitrobenzaldehyde	15	[24]
6	[Zn (3,3'-TPDC) (DABCO)]·DMF·2H ₂ O	Solvent free/60 °C/120 h	4-Nitrobenzaldehyde	34	[25]
7	$[Zn (L_c)(H_2O)_2]_n$	MeOH/70 °C/48 h	4-Nitrobenzaldehyde	97	[20e]
8	$[{\rm Cu (L1)(DMF)} \cdot {\rm DMF} \cdot {\rm H}_2{\rm O}]_n$	Water/75 °C/40 h	4-Nitrobenzaldehyde	98	[20b]
9	$[Zn (L1)(H_2O)]_n$	Water/75 °C/40 h	4-Nitrobenzaldehyde	94	[20b]
10	[{Cd ₂ (L-glu) ₂ (bpe) ₃ (H ₂ O)}·2H ₂ O]	MeOH/r.t./72 h	4-Nitrobenzaldehyde	100	[20d]
11	$[\text{Sm }(\text{L1})_2]_n \cdot 1n (\text{HCONH}_2)\text{H} \cdot 2n (\text{HCONH}_2)$	Water/70 °C/36 h	4-Nitrobenzaldehyde	96	[20a]

transitional yield (*ca* 70%) was found (9 h) and then removed the catalyst by filtration and kept the solution (without catalyst) under the same reaction conditions for an additional 9 h (total of 18 h). The yield of the product did not further increase significantly after the removal of the catalyst. These results indicate the heterogeneous nature of the catalyst. Additionally the amount of manganese was determined from the solution after the removal of catalyst using inductively coupled plasma atomic emission spectroscopy (ICP-AES). There was no Mn (II) present in the filtrate after the nitroaldol reaction, thus ruling out any notable leaching of the catalyst.

2.5 | Recyclability of 1

In order to investigate possible reusability of **1** in nitroaldol reaction, a recyclability experiment was performed under optimized reaction conditions using 4-nitrobenzaldehyde and nitromethane. After each cycle, the catalyst was collected, washed with methanol, dried in vacuum and used in a subsequent reaction without further modification. It is observed that catalytic activity of **1** gradually decreases upon reuse and conversions of 4-nitrobenzaldehyde in five consecutive reactions are 94, 82, 78, 76 and 68% (Figure 6). There are two possible

reasons for this. Firstly, polymer **1** is not stable in the reaction mixture, which is excluded by the heterogeneity test of the reaction. Secondly, active metal sites of **1** are blocked after each cycle, thus resulting in a perturbation in the structure of **1**. In order to prove that, FT-IR spectra and powder XRD patterns of fresh catalyst and catalyst after five recycles were recorded. Significant changes were found in both FT-IR spectra (Figure S11 in the supporting information) and powder XRD patterns (Figure 7), thus confirming a structural change of **1** during the reaction.

2.6 | Plausible Mechanism

A plausible mechanism for the nitroaldol reaction of nitromethane and benzaldehydes in the presence of **1** is proposed, as depicted in Scheme 3. Similar to other homogeneous or heterogeneous catalytic systems containing transition metal ions (Cu (II), Zn (II) and Cd (II)),^[19b, 26] both aldehyde and nitromethane are activated initially by Mn (II) ions ((b), Scheme 3). This further enhances the electrophilic character of benzaldehyde and acidity of nitromethane. In the next step, reactive nitronate species is generated through deprotonation of activated acidic nitromethane. This process may further be stimulated by the presence of basic adenine molecules, coordinated to Mn (II) ions in 1. Subsequently, formation of C-C bond takes place via nucleophilic attack of nitronate ion to coordinated benzaldehyde ((c), Scheme 3). Finally, another molecule of benzaldehyde ligates to Mn (II) and corresponding β nitroalkanol is released from it, thus completing the catalytic cycle.



FIGURE 6 β -Nitroalkanol yield in five consecutive reaction cycles employing 1 as catalyst



FIGURE 7 Powder XRD patterns of 1.



SCHEME 3 Proposed catalytic cycle for Henry reaction catalysed by **1**

3 | CONCLUSIONS

We have successfully synthesized a Mn(II)-containing three-dimensional CP (1) from affordable chemicals such as isophthalic acid and adenine. The solid-state structure of 1 showed that it possesses a three-dimensional structure with Mn_6 secondary building units. Polymer 1 exhibited significant catalytic activity in the Henry reaction of various aldehydes with nitromethane. Polymer 1 can also be employed in important organic transformations demanding both acidic and basic sites for activation of substrates.

4 | EXPERIMENTAL

Isopthalic acid (Loba chemie, India), adenine (SRL, India), Mn $(OAc)_2 \cdot 4H_2O$ (Merck, India), benzaldehyde, 2nitrobenzaldehyde, 4-chlorobenzaldehyde (Sigma Aldrich, 8 of 9 WILEY Organometallic Chemistry

India), 4-bromobenzaldehyde, 4-fluorobenzaldehyde, 4nitrobenzaldehyde and 4-methylbenzaldehyde (Alfa Aesar, India) were received and used without further purification unless otherwise noted. All solvents were distilled prior to use. The NMR solvents CDCl₃ and DMSO were purchased from SRL, India. ¹H NMR spectra were recorded with a Bruker AVANCE II-400 spectrometer and a Varian (Mercury Plus) 400 NMR spectrometer. A Cary 600 series FT-IR spectrometer (Agilent Technology) was used for FT-IR measurements. Powder XRD patterns were recorded using a $Cu_{K\alpha}$ radiation source with a Bruker D2 Phaser X-ray diffractometer. TGA was performed with an SDT Q600 (TA Instrument) at a scan rate of 10 °C min ⁻¹ under N₂ flow at a rate of 100 ml min⁻¹. ICP-AES analysis was carried out with an ARCOS simultaneous ICP spectrometer (SPECTRO Analytical Instruments GmbH, Germany).

4.1 | Preparation of 1

A mixture of isophthalic acid (0.033 g, 0.2 mmol), adenine (0.027 g, 0.2 mmol) and Mn (OAc)₂·4H₂O (0.049 g, 0.2 mmol) was dissolved in a mixture of ethanol (7 ml) and water (3 ml) at room temperature. The mixture was sealed in a Teflon-lined autoclave of 30 ml capacity. The autoclave was heated to 80 °C, held for 48 h and cooled to room temperature. Colourless needle-shaped single crystals of **1** were collected, washed with ethanol and dried in vacuum. Yield: 0.217 g, 70% (with respect to Mn (OAc)₂·4H₂O). FT-IR (ATR, cm⁻¹): 3420(w), 3356(w), 3244(w), 2360(m), 1667(w), 1604(s), 1558(s), 1377(s), 737(m), 713(m), 424(w).

4.2 | General Procedure for Henry Reaction Catalysed by 1

A mixture of aldehyde (1.0 mmol), nitromethane (4.0 mmol) and catalyst (5 mol%) in 5 ml methanol contained in a 10 ml round-bottom flask was stirred at 70 °C for 18 h. The solution was filtered to remove the catalyst. The crude product was collected after evaporation of the solvent. The product was identified using ¹H NMR analysis. The yield of the reaction was calculated based on the relative amount of unreacted aldehyde and β -nitroalkanol present in the crude product. Detailed calculation of yield is provided in the supporting information.

4.3 | X-ray Crystallography

Diffraction data for **1** were collected with a XtaLAB SuperNova (Rigaku Oxford Diffraction) diffractometer equipped with an EosS2 CCD detector and graphite-monochromatic Mo $K\alpha(0.71073$ Å) radiation. Initial

structure was obtained by direct methods (SIR92)^[27] and refined on F^2 by full-matrix least-squares methods using SHELXL-2013.^[28] Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $\left[\sum w (F_o^2 - F_c^2)^2\right] (w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]),$ where $P = (Max(F_0^2, 0) + 2F_c^2)/3$ with $\sigma^2(F_0^2)$ from counting statistics. The functions R1 and wR2 were $(\sigma ||F_{o}| - |F_{c}|)/\sigma |F_{o}|$ and $[\sigma w (F_{o}^{2} - F_{c}^{2})^{2}/\sigma (w F_{o}^{4})]^{1/2}$ respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1552157. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +(44) 1223 336 033; e-mail: deposit@ccdc. cam.ac.uk).

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

This includes FT-IR spectrum of **1**, power XRD pattern of **1**, plot of β -nitroalkanol yield versus time for the Henry reaction of 4-nitrobenzaldehyde and nitromethane with **1**, calculation of yield, ¹H NMR spectra of product of Henry reaction between various aromatic aldehydes and nitromethane, FT-IR spectra of **1** in five consecutive reaction cycles, selected bond lengths for **1**.

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