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Research Paper

The Ability of NCP@POCl_{2-x} Core-Shell Magnetic Nano-Catalyst for Simultaneous Conversion of Epoxides into Cyanohydrin and α,β -Unsaturated Carboxylic Acid

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Abstract:

This paper presents a new environmental, and remarkably efficient heterogeneous magnetic nanocomposite, NCP@POCl_{2-x} (Fe₃O₄@SiO₂@CS@POCl_{2-x}), designed for the regioselective production of cyanide compounds from epoxides using NaCN, subsequently facilitating the synthesis of α,β -unsaturated carboxylic acids. The reactions were conducted under mild conditions, demonstrating the catalyst's remarkable performance with high yields. The presence of POCl_{2-x} and the influence of water and heat facilitated the transformation of epoxides into cyanohydrin and α,β -unsaturated carboxylic acids. Remarkably, the reactions demonstrate excellent regioselectivity, producing clean and quantitative products. NCP@POCl_{2-x} is a heterogeneous magnetic nanocatalyst with a strong magnetic core of Fe₃O₄ surrounded by chitosan as a green layer and functionalized by the POCl_{2-x} group. This catalyst can be easily separated using external magnetic force. The combination of heterogeneity, magnetic properties, easy recovery, and exceptional performance establishes NCP@POCl_{2-x} as a valuable tool for efficient and selective transformations of epoxides.

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1. INTRODUCTION

Cyanide-mediated epoxide cleavage is a crucial process in organic synthesis. This reaction selectively opens the epoxide ring and introduces a cyanide group, leading to the formation of important functional groups. These groups are vital for producing a wide array of natural and bioactive compounds, making this process particularly significant within the pharmaceutical sector. [1, 2]. It generates important intermediates for producing a variety of compounds, including carboxylic acids [3], amides [4], β -amino alcohols [5, 6] and ring-expanded products [7].

Epoxides can react with a variety of reagents such as HCN [8], NaCN [9, 10], KCN [11], LiCN [12], Amberlyst A-21 (a cyanide exchange resin) [13], TBAF/TMSCN [14, 15], or cyanide derived from the treatment of acetone cyanohydrin [16] with different bases. The preference for cyanide attack in these substrates is heavily influenced by their steric structure, with attacks predominantly occurring at the less hindered methylene group.

Cyanohydrin plays a crucial intermediate role in the synthesis of bioactive compounds. Its versatility as a starting material, emphasizes its significance in the intricate pathways leading to a range of compounds with noteworthy pharmacological activities [17-20]. Serving as a precursor for various molecules, including α,β -unsaturated aldehydes [21], α,β -unsaturated amides, α -hydroxy carboxylic acid and α,β -unsaturated carboxylic acids [22], β -amino alcohols [23] and α,β -unsaturated nitrile [24], it plays a crucial role in biological and pharmaceutical applications.

However, the synthesis of compounds using cyanide salts presents several challenges. Conventional methods that utilize cyanide salts often require long reaction times, leading to an undesirable delay in the overall synthesis process. While the selective attack of cyanide in chemical reactions offers advantages, the occurrence of side reactions such as isomerization, polymerization, and ring-opening is disadvantageous [25]. Furthermore, these methods typically involve protic solvents, which, despite their widespread use, can introduce complications due to solubility issues and the necessity for precise reaction conditions. Overcoming these limitations is crucial for advancing streamlined and efficient strategies in the synthesis of cyanohydrins through epoxide ring-opening.

The NCP@POCl₂-x catalyst has shown versatility by facilitating the conversion of alcohols into alkyl halides [26] and amines [27, 28], as well as epoxides into β -amino alcohols [29, 30]. Expanding on our previous

achievements, we revealed that the catalyst NCP@POCl_{2-x} forms a complex with epoxides, effectively activating them for subsequent reactions with cyanide as the nucleophile. The emphasis is on the conversion of epoxide to α,β -unsaturated carboxylic acid, conducted under reflux conditions with water as the solvent. The present study endeavors to overcome limitations observed in alternative methods by introducing NCP@POCl_{2-x} as a highly efficient and environmentally friendly magnetic nanoparticle catalyst for regioselective conversions.

2. MATERIALS AND METHODS

A. Chemicals and instruments

Chemical reagents were sourced from either Merck or Fluka. The progress of the reactions was followed through Thin Layer Chromatography (TLC) employing SILG-UV 254 silica gel plates. Product identification was confirmed by comparing their physical and spectral properties with data reported in literature. Nuclear Magnetic Resonance (NMR) spectra were obtained using a Bruker Avance DPX 250MHz spectrometer, while Fourier Transform Infrared (FTIR) spectra were acquired using a Shimadzu DR-8001 spectrometer. The GC instrument used was the Agilent model 6990N. Field Emission Scanning Electron Microscopy (FESEM) analyses were performed using the TESCAN MIRA II model, which was manufactured in the Czech Republic.

1) Synthesis of cyanohydrin from epoxides using NCP@POCl_{2-x} catalyst: a general synthetic procedure

The procedure began with preparing a solution of oxirane (1 mmol) in 10 ml of acetonitrile (CH_3CN). The CH_3CN solvent had been dried in the presence of K_2CO_3 for one day before use [31, 32]. According to the optimization showed in Table I, NCP@POCl_{2-x} (0.3 mmol, 0.9 g) was added to the solution, and the mixture was stirred for 1hour under reflux conditions. After this period, the mixture was allowed to cool to room temperature. Sodium cyanide (2 mmol, 0.1g) was then added, and stirring continued for the specified duration at room temperature. The reaction progress was monitored using thin-layer chromatography (TLC) using a mixture of ethyl acetate and dichloromethane in a ratio of 3:7 (v/v). Upon completion of the reaction, the catalyst was separated from the mixture using magnetic filtration. Dichloromethane (CH_2Cl_2 , 20 ml) was added to the residue and the resulting organic phase was washed first with

brine (10 ml) and then with water (2 × 10 ml). The combined filtrate was dried over anhydrous sodium sulfate (Na₂SO₄). The solvent was then removed using a rotary evaporator, resulting in the isolation of the pure product. The identity of the product was confirmed by comparing its boiling or melting point, FTIR, ¹H-NMR, and ¹³CNMR spectra with the corresponding data from known authentic samples. The relevant information for the product in Table II is presented below:

3-Hydroxy-4-phenoxybutanenitrile (Table II, entry 1) [33, 34], CAS number: 137618-52-1, light brown powder, m. p. 90-92°C, FTIR (neat), ν_{\max} (cm⁻¹): 3410, 3000, 2962, 2951, 2399, 1679, 1604, 1502, 1431, 1220, 1065, 952, 679. ¹H-NMR (CDCl₃), δ (ppm): 7.22-6.81 (m, 5H, aromatic), 5.38(s, 1H, OH), 3.95-4.21 (m, 3H), 2.41-2.71(d, 2H). ¹³C-NMR (CDCl₃), δ (ppm): 159.2, 128.0, 123.1, 114.6, 70.1, 67.7, 22.7.

3-Cyano-2-hydroxypropyl methacrylate (Table II, entry 3) [25], yellow to brown powder, m. p. 47-49°C, ¹H-NMR (CDCl₃) δ (ppm): 6.52 (d, 1H), 6.41(d, 1H), 5.39 (s, 1H), 4.15 (m, 3H), 2.67- 2.44 (m, 2H), 2.13 (s, 3H). ¹³C-NMR (CDCl₃), δ (ppm): 171.2, 136.5, 128.0, 124.6, 116.8, 70.1, 66.5, 22.1, 18.1.

3-Hydroxy-4-isopropoxybutanenitrile (Table II, entry 4) [35]: yellow liquid, b. p. 280-283°C, ¹H-NMR (CDCl₃), δ (ppm): 5.41 (s, OH, 1H), 3.82 (m, 1H), 3.64-3.38 (m, 3H), 2.65- 2.47 (d, 2H), 1.15 (6H, d). ¹³C-NMR (CDCl₃), δ (ppm): 118.1, 77.8, 75.3, 69.4, 22.4, 21.6.

2-Hydroxycyclooctane-1-carbonitrile (Table II, entry 5) [25], ¹³C-NMR (CDCl₃), δ (ppm): 120, 70, 32.5, 32, 27.8-22.9.

2) A general protocol for the synthesis of α,β -unsaturated carboxylic acids from epoxides using NCP@POCl_{2-x} catalyst

A solution containing oxirane (1 mmol) in CH₃CN (9 ml) was prepared, and NCP@POCl_{2-x} (0.3 mmol, 0.9g) was subsequently added. The reaction was then carried out for 1 hour under reflux conditions. Subsequently, sodium cyanide (2 mmol, 0.1g) dissolved in H₂O (1ml) were introduced into the reaction mixture. The reaction continued for 24 hours under reflux. Upon completion, the catalyst was separated using magnetic filtration. CH₂Cl₂ was added, and the organic phase was washed sequentially with brine (10 mL) and water (2 × 10 mL). The filtrate was dried over anhydrous Na₂SO₄. After solvent removal via rotary evaporation, the product was obtained in a purified state. Validation of the product's identity involved comparing its boiling or melting point, FTIR, ¹H-NMR, and ¹³CNMR spectra with data from established authentic samples. Here is the pertinent information for the products in Table III:

4-Phenoxybut-2-enoic acid (Table III, entry 1), m.p =121-122°C, isolated yield=89%, $^1\text{H-NMR}$ (CDCl_3), δ (ppm):11.00 (s, 1H), 7.50-7.51 (m, 5H), 6.28 (d, 1H), 5.20 (d, 2H), 3.96 (d,1H), 2.48-2.64 (m, 2H). $^{13}\text{C-NMR}$ (CDCl_3), δ (ppm): 171.2, 152.6, 145.0, 129.3, 122.4, 114.6, 53.7.

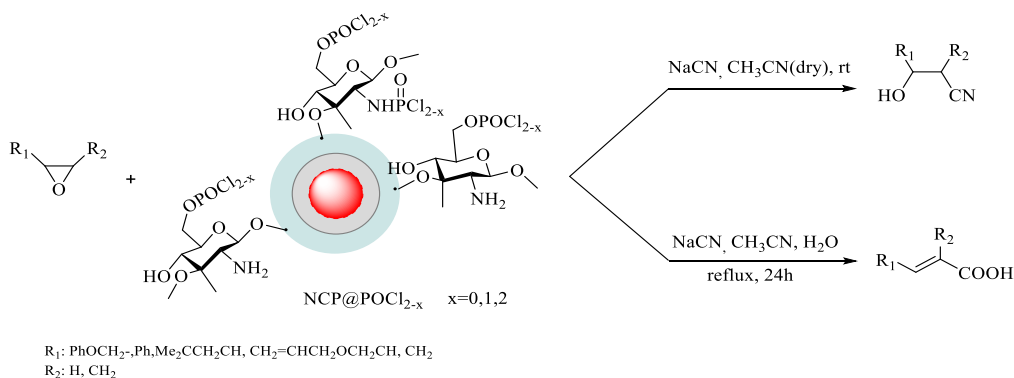
4-(Methacryloyloxy) but-2-enoic acid, (Table III, entry 2), brown solid, m.p. 88-92°C, isolated yield=93%, $^{13}\text{C-NMR}$ (CDCl_3), δ (ppm): 172, 169, 144, 138, 122, 117, 64.5, 18.1.

4-Isopropoxybut-2-enoic acid (Table III, entry 3), yellow powder, m.p. 65-68°C, isolated yield=92%, $^{13}\text{C-NMR}$ (CDCl_3), δ (ppm): 175.6, 141, 123, 77, 66, 22.6.

Cyclooct-1-ene-1-carboxylic acid (Table III, entry 4), light yellow crystal, m.p:88-89°C, $^{13}\text{C-NMR}$ (CDCl_3), δ (ppm): 175.6,159, 130, 35, 29.

3.RESULT AND DISCUSSION

In this research, we used NCP@POCl_{2-x} along with sodium cyanide and an epoxide to produce cyanohydrin. Adding water to the solution, accompanied by a carefully controlled heating period, led to the formation of α,β -unsaturated carboxylic acid, as depicted in Scheme 1.



Scheme 1. schematic for the synthesis of cyanohydrins and α,β -unsaturated carboxylic acids

This chemical transformation not only illustrates an effective and strategic approach but also highlights the versatile nature of NCP@POCl_{2-x} as a catalyst in the controlled synthesis of valuable organic compounds. Particularly notable is the strong activity of NCP@POCl_{2-x} in facilitating the transformation of

oxirans into α,β -unsaturated carboxylic acids, emphasizing its importance in diverse synthetic applications.

While the characterization of NCP@POCl_{2-x} has been previously documented [22], our study provides additional insights. The field emission scanning electron microscopy (FESEM) image of NCP@POCl_{2-x} reveals a varied particle size distribution, ranging an approximately from 2 μm , and showcasing an average particle size of 160 nm, as represented in Figure 1. The core-shell layer of NCP@POCl_{2-x} plays a crucial role in providing stability to the functional group, enhancing its activity, and positioning close to the epoxide for nucleophilic attack.

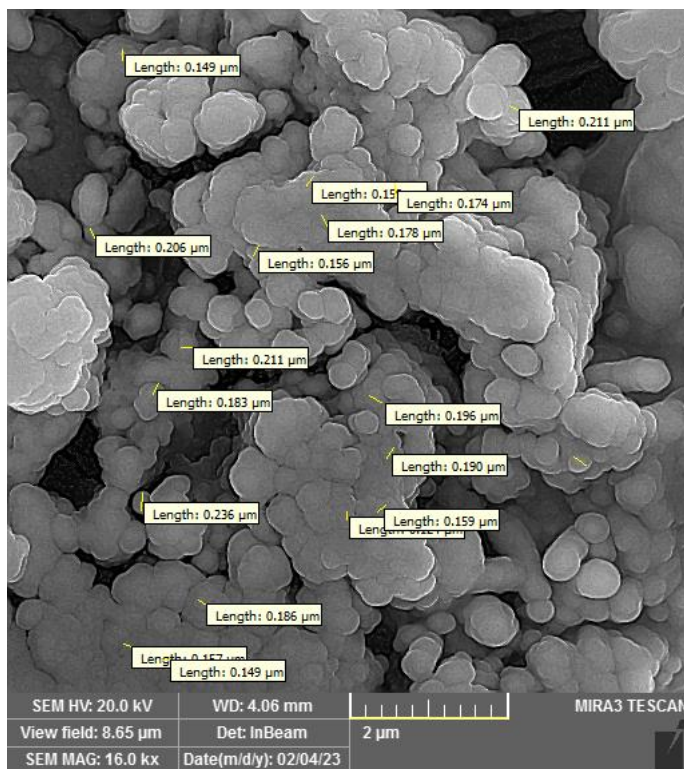


Fig 1. The FESEM image of NCP@POCl_{2-x} reveals an average particle size of 160 nm.

Table I presents the optimized reaction conditions for the production of phenyl glycidyl ether, facilitating the controlled transformation into cyanohydrin and

α,β -unsaturated carboxylic acid. The key parameters, including catalyst quantity, solvent type, reaction time and temperature, were systematically varied to establish favorable conditions. Nonpolar solvents, including *n*-hexane, chloroform, or dichloromethane, demonstrate suboptimal performance and fail to support the successful formation of the expected product, even in the presence of an excess amount of NCP@POCl_{2-x} (Table I, entry 1-4). Elevated temperatures were observed to positively influence the yield of the final product. Employing a catalytic quantity of the catalyst (0.3 mmol) per substrate demonstrated efficient catalysis, resulting in an acceptable product yield. The preferred solvent was identified as CH₃CN. Notably, the introduction of water in a 90:10 ratio with CH₃CN led to the formation of a novel product after 24 h, identified as α,β -unsaturated carboxylic acid. The absence of NCP@POCl_{2-x} in the epoxide reaction, conducted in the presence of aqueous acetonitrile under reflux conditions, resulted in a low-yield product (30%) and emphasized the critical importance of the catalyst's presence (Table I, entry 12).

TABLE I
OPTIMIZATION OF CYANOLYSIS FOR 1 MMOL OF PHENYLGLYCIDYL ETHER USING 2
MMOL SODIUM CYANIDE UNDER VARIOUS SOLVENTS, TEMPERATURES, AND
CATALYTIC AMOUNT

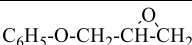
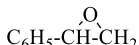
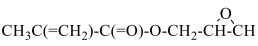
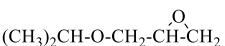
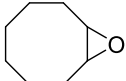
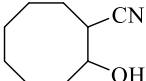
Entry	Solvent	Amount of catalyst (mmol)	Reaction temperature	Time (h)	Conversion of product (%) ^a
1	<i>n</i> -hexane	3	reflux	24	Less than 10
2	CHCl ₃	3	reflux	24	Less than 10
3	CH ₂ Cl ₂	3	reflux	24	21
4	THF	3	reflux	5	43
5	EtOAc	3	rt	24	61
6	CH ₃ CN(dry)	3	rt	immediately	100
7	CH ₃ CN(dry)	1	rt	20 min	100
8	CH ₃ CN(dry)	0.5	rt	30 min	100
9	CH ₃ CN(dry)	0.3	rt	30 min	100
10	H ₂ O	0.3	reflux	24	78 ^b
11	CH ₃ CN-H ₂ O	0.3	reflux	24	95 ^b
12	CH ₃ CN-H ₂ O	0	reflux	24	30

a. GC yield

b. α,β -unsaturated carboxylic acid

The findings elucidate the ring-opening of different substituted epoxides, including phenyl glycidyl ether, styrene oxide, glycidyl methacrylate, 2,3-epoxypropyl isopropyl ether, and 1,2-epoxycyclooctane in the presence of NCP@POCl_{2-x}, are systematically detailed in Tables II.

TABLE II
REACTION OF VARIOUS EPOXIDES WITH SODIUM CYANIDE IN CH₃CN (DRY),
CATALYZED BY NCP@POCl_{2-x}

Entry	Substrate	Product	Time	Yield (%) ^a
1	 phenyl glycidyl ether	C ₆ H ₅ -O-CH ₂ -CH(OH)-CH ₂ -CN 3-hydroxy-4-phenoxybutanenitrile	30 min	92
2	 styrene oxide	C ₆ H ₅ -CH(CN)-CH ₂ (OH) C ₆ H ₅ -CH(OH)-CH ₂ (CN)	20 min	90(10)
3	 glycidyl methacrylate	CH ₃ C(=CH ₂)-C(=O)-O-CH ₂ -CH(OH)-CH ₂ -CN 3-cyano-2-hydroxypropyl methacrylate	1h	89
4	 2,3-epoxypropyl isopropyl ether	(CH ₃) ₂ CH-O-CH ₂ -CH(OH)-CH ₂ -CN 3-hydroxy-4-isopropoxybutanenitrile	45 min	95
5	 1,2-epoxycyclooctane	 2-hydroxycyclooctane-1-carbonitrile	100 min	87

a. isolated yield

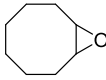
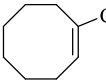
Simple esters, such as those in entry 3 of Table II, maintain stability throughout the reaction. This stability comes from the fact that the reaction progresses smoothly without causing any unwanted transesterification reactions. The same level of stability is observed for the phenyl group (Table II, entry 1), alkene group (Table 2, entry 3), and isopropyl group (Table II, entry 4) throughout the reaction. This highlights the compatibility and resilience of these functional groups in the reaction conditions.

Because of the predominant tendency for cyanide ion to attack the less hindered carbon of the epoxide, all terminal epoxides exhibited a notable tendency to produce highly regioselective cyanohydrins with quantitative yields. In these reactions, it becomes evident that the attack preferentially targets the primary carbon atom of the epoxide ring. This phenomenon is likely influenced by both steric and electronic factors. Particularly, the regioselectivity of the reactions was remarkably high for most epoxides, leading to the exclusive formation of a single isomer. However, in the case of styrene oxide (Table II, entry 2), some additional regioisomers were generated as side products.

A distinguished advantage lies in the catalyst's magnetic properties, allowing for facile separation and regeneration and multiple reuses without a significant decline in its catalytic capacity and efficiency, as exemplified in the data presented in Table II.

Interestingly, by adding water to the reaction mixture, accompanied by sufficient heating and time, the epoxide undergoes an in-situ transformation to α,β -unsaturated carboxylic acid in a one-pot reaction. The product and the corresponding isolated yields are presented in Table III.

TABLE III
EPOXIDE REACTION WITH CH₃CN: H₂O (90:10) IN THE PRESENCE OF NCP@POCL_{2-x} OVERNIGHT

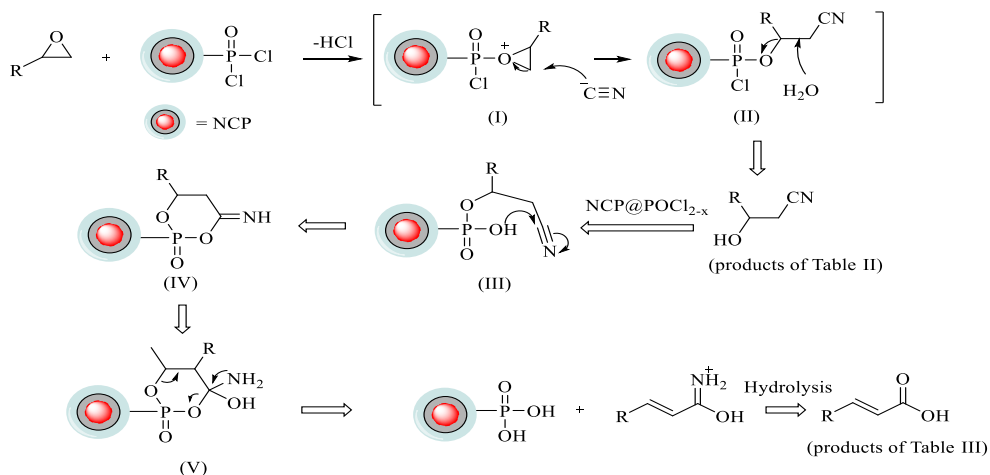
Entry	Substrate	Product	Isolated yield (%)
1	$\text{C}_6\text{H}_5\text{-O-CH}_2\text{-CH}\overset{\text{O}}{\text{---}}\text{-CH}_2$ phenyl glycidyl ether	$\text{C}_6\text{H}_5\text{-O-CH}_2\text{-CH=CH-COOH}$ 4-phenoxybut-2-enoic acid	88
2	$\text{CH}_3\text{C(=CH}_2\text{)-C(=O)-O-CH}_2\text{-CH}\overset{\text{O}}{\text{---}}\text{-CH}$ glycidyl methacrylate	$\text{CH}_3\text{C(=CH}_2\text{)-C(=O)-O-CH}_2\text{-CH=CH-COOH}$ 4-(methacryloyloxy)but-2-enoic acid	93
3	$(\text{CH}_3)_2\text{CH-O-CH}_2\text{-CH}\overset{\text{O}}{\text{---}}\text{-CH}_2$ 2,3-epoxypropyl isopropyl ether	$(\text{CH}_3)_2\text{CH-O-CH}_2\text{-CH=CHCOOH}$ 4-isopropoxybut-2-enoic acid	92
4	 1,2-epoxycyclooctane	 cyclooct-1-ene-1-carboxylic acid	85

Understanding the reaction mechanism holds paramount importance in the

realm of literature. In this context, we elucidate the reaction mechanism in the presence of NCP@POCl_{2-x}, as illustrated in Scheme 2. Upon interaction with an epoxide, oxygen tends to interact with the phosphorous group in NCP@POCl_{2-x}, resulting in the formation of intermediate (I) when mixed with the epoxide. This epoxide intermediate exhibits heightened reactivity, leading to ring opening due to the inherent instability arising from oxygen possessing three bonds, especially in the presence of cyanide as a nucleophile. Notably, nucleophilic attacks from a specific side encounter less hindrance, contributing to the regioselectivity observed in the product. In the presence of water and prolonged heating (overnight), the cyanohydrin product comes into close proximity to NCP@POCl_{2-x}, generating intermediate (III). Owing to the favorable structural constraints, the hydroxyl group inside the catalyst can attack the cyanide group, resulting in the generation of intermediate (IV) with a six-membered ring.

Intermediate (IV) is attacked by water as a nucleophile, generating intermediate (V). Due to the presence of heteroatoms around the carbon, it is not stable and easily decomposed. In the presence of heating, the removal of water occurs in situ. Through an electron transfer mechanism demonstrated in intermediate (V), the synthesis of α,β -unsaturated carboxylic acid is achieved.

This thorough comprehension of the reaction mechanism elucidates the intricate steps involved in the formation of the final product, as illustrated in Scheme 2.



Scheme 2. Proposed mechanism for synthesizing α,β -unsaturated carboxylic acid from an epoxide using NCP@POCl_{2-x}.

4. CONCLUSION

In this study, an innovative and environmentally friendly nanocatalyst, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{CS}@PO\text{Cl}_{2-x}$ (NCP@ $PO\text{Cl}_{2-x}$), was introduced for the regioselective cyanolysis of epoxides and subsequent synthesis of α,β -unsaturated carboxylic acid. The catalyst exhibited exceptional performance under mild conditions, providing high yields and demonstrating versatility in facilitating controlled transformations. The regioselectivity observed was excellent, and the reactions proceeded cleanly and quantitatively. Notably, NCP@ $PO\text{Cl}_{2-x}$'s strong activity in the transformation of oxirans into α,β -unsaturated carboxylic acid was a key highlight, showing its significance in diverse synthetic applications. The combination of heterogeneity, magnetic properties, and facile functionalization of chitosan with $PO\text{Cl}_{2-x}$ as functional groups underscores the development of an environmentally friendly and sustainable synthetic strategy.

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6. ACKNOWLEDGMENT

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