



### Journal of Sulfur Chemistry

ISSN: 1741-5993 (Print) 1741-6000 (Online) Journal homepage: http://www.tandfonline.com/loi/gsrp20

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To cite this article: Ronak Eisavi, Seiran Ghadernejad, Behzad Zeynizadeh & Farkhondeh Mohammad Aminzadeh (2016): Magnetically separable nano CuFe<sub>2</sub>O<sub>4</sub>: an efficient and reusable heterogeneous catalyst for the green synthesis of thiiranes from epoxides with thiourea, Journal of Sulfur Chemistry, DOI: 10.1080/17415993.2016.1196691

To link to this article: http://dx.doi.org/10.1080/17415993.2016.1196691



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Published online: 16 Jun 2016.

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# Magnetically separable nano CuFe<sub>2</sub>O<sub>4</sub>: an efficient and reusable heterogeneous catalyst for the green synthesis of thiiranes from epoxides with thiourea

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#### ABSTRACT

The magnetically separable nano CuFe<sub>2</sub>O<sub>4</sub> was prepared and used as an efficient heterogeneous catalyst for conversion of various epoxides to the corresponding thiiranes with thiourea in refluxing ethanol. The reactions were completed within 34–45 min to give thiiranes in 80–95% yields. The utilized nano CuFe<sub>2</sub>O<sub>4</sub> can be reused for several times without losing its activity.



#### ARTICLE HISTORY

Received 4 March 2016 Accepted 29 May 2016

#### KEYWORDS

Epoxide; CuFe<sub>2</sub>O<sub>4</sub>; nano; thiirane; thiourea

#### 1. Introduction

Thiiranes are valuable synthetic building blocks for the preparation of polymers, pharmaceuticals, pesticides, and herbicides.[1–3] In addition, thiirane is a fundamental heterocyclic core of various biologically active compounds.[4–7] Transformation of epoxides to thiiranes by an oxygen–sulfur exchange reaction is an efficient method and has been achieved with different procedures using sulfur transferring agents.[8–22] However, some of these methods suffer from disadvantages such as long reaction times, the use of unrecoverable catalyst, low yield of the products, difficult workup procedures, use of highly acidic catalysts, rapid increase of pH during the reaction, and the formation of polymeric by-products.

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Supplemental data for this article can be accessed here. http://dx.doi.org/10.1080/17415993.2016.1196691

$$\begin{array}{c} R \\ \swarrow \\ O \end{array} \xrightarrow{R'} \\ R, R': aryl, alkyl, allyl, H \end{array} \xrightarrow{R'} \\ R, R': aryl, alkyl, allyl, H \end{array}$$

Scheme 1. Conversion of epoxides to thiiranes with thiourea/nano CuFe<sub>2</sub>O<sub>4</sub> system.

The development and introduction of convenient catalytic procedures, facile recovery of the catalyst from the reaction medium and recyclability of the catalyst are very significant tasks in new synthetic chemistry. In recent years, the magnetic nanoparticles based catalysts have been extensively used as heterogeneous catalysts for achieving useful chemical transformations. [23–33] Among these heterogeneous catalysts, copper/iron oxide-based catalysts have gained importance in scientific research due to their wide applications in organic reactions. [34,35] These catalysts are environmentally compatible, air and moisture insensitive, and because of their magnetic properties, separation and complete recovery of the catalyst from reaction mixture are very simple and highly possible by magnetization with a permanent magnetic field. [36–42] To the best of our knowledge, the reaction of epoxides with thiourea has not been reported using iron-based nanoparticles/catalysts. As a part of our research program on the synthesis of thiiranes, [8–11] herein, we report the magnetic nano CuFe<sub>2</sub>O<sub>4</sub> as efficient and eco-friendly heterogeneous catalysts for the conversion of structurally different epoxides to thiiranes using thiourea in refluxing EtOH (Scheme 1).

#### 2. Results and discussion

The optimization experiments showed that the reaction of styrene oxide (1 mmol) with thiourea (1 mmol) in the presence of nano CuFe<sub>2</sub>O<sub>4</sub> (0.05 mmol, 0.012 g, 5 mol%) was carried out effectively in refluxing EtOH. The epoxide was converted to the corresponding thiirane in 92% yield within 40 min. The effects of other solvents such as CH<sub>3</sub>CN, THF, and MeOH were also investigated for the typical experiment. The results showed that polar and protic solvents are more effective, and in comparison with EtOH, the reaction times were longer and the yields of thiiranes were considerably lower in all other solvents. Alcoholic solvents with hydrogen bonding capability facilitate the ring opening of epoxides by nucleophilic reagents. On the other hand, between ethanol and methanol, ethanol was preferred, because of the lower toxicity. The other important parameter for improving the reaction condition was the amount of CuFe<sub>2</sub>O<sub>4</sub> nanoparticles as catalyst. An increase in the quantity of CuFe<sub>2</sub>O<sub>4</sub> nanoparticles from 0.03 to 0.05 mmol not only accelerated the rate of reaction but also increased the product yield. This showed that the quantity of the catalyst plays a consequential role in the optimization of the product yield. Thus, using 0.05 mmol of nano CuFe<sub>2</sub>O<sub>4</sub> is a sufficient and appropriate choice to push the reaction forward. More amounts of nano CuFe<sub>2</sub>O<sub>4</sub> did not improve the yields of products. It is considerable that in the absence of CuFe<sub>2</sub>O<sub>4</sub> nanoparticles, no conversion of epoxides to thiiranes takes place. Furthermore, the effect of temperature on the conversion of styrene oxide to styrene episulfide was also studied. The results showed that no reaction occurred at room temperature after 1 h. In addition, performing the reaction in an oil bath (70-80°C) exhibited more efficiency than room temperature condition (Table 1).

Entry	Nano CuFe <sub>2</sub> O <sub>4</sub> (mmol)	Condition	Time (min)	Conversion (%) <sup>b</sup>
1	_	EtOH/reflux	20	0
2	0.03 (3 mol%)	EtOH/reflux	80	100
3	0.05 (5 mol%)	EtOH/reflux	40	100
4	0.1 (10 mol%)	EtOH/reflux	30	100
5	0.2 (20 mol%)	EtOH/reflux	20	100
6	0.05 (5 mol%)	CH <sub>3</sub> CN/reflux	50	80
7	0.05 (5 mol%)	THF/reflux	60	50
8	0.05 (5 mol%)	MeOH/reflux	45	90
9	0.05 (5 mol%)	EtOH/r.t.	60	0
10	0.05 (5 mol%)	Solvent-free/oil bath (70–80°C)	55	60

**Table 1.** Optimization experiments for conversion of styrene oxide to styrene episulfide with thiourea in the presence of nano  $CuFe_2O_4^a$ .

<sup>a</sup>All reactions were carried out with 1 mmol of styrene oxide in the presence of thiourea (1 mmol). <sup>b</sup>Conversion less than 100% was determined on basis of the recovered epoxide.

The ability of this synthetic procedure was further investigated by the reaction of various epoxides possessing either electron-donating or -withdrawing substituents, and cyclic epoxides with thiourea in the presence of nano  $CuFe_2O_4$  under the optimized conditions. The results are summarized in Table 2. As it is seen, all reactions were carried out successfully within 34–45 min to give thiiranes in 80–95% yields.

Table 2. Conversion of epoxides to thiiranes with thiourea catalyzed by nano CuFe<sub>2</sub>O<sub>4</sub><sup>a</sup>.

Entry	Epoxide (a)	Thiirane (b)	Time (min)	Yield (%) <sup>b</sup>
1	Ph O	Ph S	40	92
2			42	85
3	MeO	MeO	35	90
4			37	95
5			39	92
6		NC O S	37	90

#### Table 2. Continued.

Entry	Epoxide (a)	Thiirane (b)	Time (min)	Yield (%) <sup>b</sup>
7	MeO O	MeO O S	35	95
8			34	85
9		≫∽o∽ <sub>S</sub>	37	92
10			35	90
11	Cl	Cl S	35	82
12			36	90
13	$\sim \sim $	$\sim \sim $	36	90
14		↓ S	34	85
15	O	S	35	80
16	ο	s	45	85

<sup>a</sup>All reactions were carried out with 1 mmol of epoxide in the presence of thiourea (1 mmol) and CuFe<sub>2</sub>O<sub>4</sub> (0.05 mmol, 0.012 g) in refluxing EtOH.

<sup>b</sup>Yields refer to isolated pure products.

#### 2.1. Characterization of the catalyst

CuFe<sub>2</sub>O<sub>4</sub> nanoparticles were synthesized according to the procedure reported by Sun et al. [38] X-ray diffraction (XRD), scanning electron micrograph (SEM), transmission electron micrograph (TEM), and FT-IR analyses confirmed the formation of nano CuFe<sub>2</sub>O<sub>4</sub>. The position and relative intensities of all peaks confirm well with standard XRD pattern of CuFe<sub>2</sub>O<sub>4</sub> (JCPDS card No. 34-0425) indicating characteristic of the tetragonal structure. The calcinated copper ferrite at 900°C represents a particle size of 110 nm, calculated using the Scherrer equation (Figure S1). The SEM image shows that there are irregular particles of various sizes (75–150 nm) in the sample calcinated at 900°C. The large particles are composed of small crystallites (Figure S2). The TEM image of the sample is given in Figure S3 and as can be noticed the particles are of nano sizes. The FT-IR spectrum of CuFe<sub>2</sub>O<sub>4</sub> is shown in Figure S4. A strong peak appeared at 586 cm<sup>-1</sup>, corresponding to the vibration

modes of all spinel compounds, which is attributed to the M–O stretching bands in tetrahedral complexes.[43–46] The absorption broad band at 3433 cm<sup>-1</sup> represents the stretching mode of H<sub>2</sub>O molecules and OH groups. The band around 1627 cm<sup>-1</sup> corresponds to the bending mode of H<sub>2</sub>O molecules [47] (Figs. S1–S4 in Supporting information).

The green aspect of this method was investigated by recovery of nano  $CuFe_2O_4$  from the reaction mixture and then reusing it for the conversion of styrene oxide to styrene episulfide. It is notable that the catalyst could be magnetically recovered by an external magnetic field and washed with ethanol sequentially, then with water and finally dried at 80°C for 2 h. After being dried, it was used for repeating the titled reaction at the optimum conditions. The results showed that the catalyst could be cycled four times without a significant loss of activity (Table 3).

In addition, the efficiency of our synthetic method was highlighted by comparing some of our results with the previously reported methods [16–21] (Table 4). A case study

Run	Yield (%) <sup>a</sup>	Recovery of nano CuFe <sub>2</sub> O <sub>4</sub> (%)
1	92	98
2	91	94
3	91	92
4	90	90
5	86	88

**Table 3.** Reusability of recovered nano  $CuFe_2O_4$  in the conversion of styrene oxide to styrene episulfide by use of thiourea.

<sup>a</sup>lsolated yield.

**Table 4.** Comparison of the conversion of styrene oxide to styrene episulfide with thiourea/CuFe<sub>2</sub>O<sub>4</sub> system and other reported methods.

Entry	Catalyst	Condition	Time (min)	Yield (%) <sup>a</sup>	Ref.
1	Nano CuFe₂O₄	EtOH/reflux	40	92	_
2	Ps-AICI3	CH <sub>3</sub> CN/reflux	90	85	16
3	$Mg(HSO_4)_2$	CH <sub>3</sub> CN/reflux	150	80	17
4	Sn <sup>IV</sup> (tpp)(OTf) <sub>2</sub>	CH <sub>3</sub> CN/reflux	60	98	18
5	$Sn^{IV}(tpp)(BF_4)_2$	CH <sub>3</sub> CN/reflux	50	98	21
б	SiO <sub>2</sub> -AICI <sub>3</sub>	CH <sub>3</sub> CN/45°C	84	85	19
7	-	Solvent-free/120 °C	15	65	20

<sup>a</sup> Isolated yields.



**Scheme 2.** A proposed mechanism for conversion of epoxides to thiiranes with thiourea/nano CuFe<sub>2</sub>O<sub>4</sub> system.

shows that the present procedure is more efficient than the reported methods. The exact mechanism of this synthesis is not known. A possible mechanism is presented in Scheme 2.

#### 3. Conclusions

In summary, we have shown that structurally different epoxides are easily and efficiently converted to their corresponding thiiranes with thiourea in the presence of nano  $CuFe_2O_4$  in refluxing EtOH. So, we think that the simple synthesis, reusability, recoverability, non-toxicity, and cheapness of nano  $CuFe_2O_4$ , short reaction times, and high yields of the products make this method a useful addition to the present methodologies.

#### 4. Experimental

#### 4.1. General

All reagents and substrates were purchased from commercial sources with the best quality and they were used without further purification. FT-IR and <sup>1</sup>H, <sup>13</sup>C NMR spectra were recorded on Thermo Nicolet Nexus 670 and Bruker Avance (300 MHz) spectrometers, respectively. The products were characterized by their spectra data and comparison with the reported data in the literature. TLC was applied for the purity determination of substrates, products, and reaction monitoring over silica gel 60F<sub>254</sub> aluminum sheet. The synthesized nano CuFe<sub>2</sub>O<sub>4</sub> was characterized by XRD on a Bruker D8-Advanced diffractometer with graphite-monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54056$ Å) at room temperature. SEM images were determined on a LEO 1430 VP scanning electron microscopy. TEM images were recorded with a Philips CM30 at electron energy of 300 keV.

#### 4.2. Preparation of CuFe<sub>2</sub>O<sub>4</sub> nanoparticles

In a typical synthesis,  $Cu(CH_3COO)_2 \cdot H_2O$ ,  $Fe(NO_3)_3 \cdot 9H_2O$ , NaOH, and NaCl were mixed in a molar ratio (1:2:8:2) and ground together in an agate mortar for 50 min. The reaction started easily during the mixing process and was accompanied by releasing of heat. As the reaction proceeded, the mixture became pasty and its color gradually changed from blue to finally brown. This mixture was washed with distilled water for several times. After washing, the powders were dried at 80°C for 2 h. Then the powders were calcined at 300°C, 500°C, 700°C, 900°C for 2 h to obtain final powders.[38]

## **4.3.** Conversion of epoxides to thiiranes using thiourea in the presence of nano CuFe<sub>2</sub>O<sub>4</sub>: a general procedure

In a round-bottomed flask (25 mL) equipped with a magnetic stirrer and condenser, a solution of the epoxide (1 mmol) and thiourea (0.076 g, 1 mmol) in EtOH (3 mL) was prepared. Nano CuFe<sub>2</sub>O<sub>4</sub> (0.05 mmol) was then added to the resulting solution and the reaction mixture was stirred magnetically under reflux condition for 34–45 min. The progress of the reaction was monitored by TLC. After completion of the reaction, EtOH was evaporated and EtOAc (2 × 5 mL) was added to the reaction mixture followed by stirring for 5 min. In order to separate the catalyst, a magnet was externally appended to the flask, and the magnetic nano CuFe<sub>2</sub>O<sub>4</sub> was accumulated at the walls of the flask. Then, the mixture was

filtered and the organic layer was washed with water (20 mL) and dried over anhydrous  $Na_2SO_4$ . The organic solvent was evaporated to give crude thiirane for further purification by a short-column chromatography over silica gel (80–95% yield) (Table 2). The collected nano  $CuFe_2O_4$  was washed with ethanol, then with water and finally dried and preserved for the next run. All products are known compounds and were identified by comparison of their properties (FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR) with those of authentic samples [10,12,13,22]; these data were given in the Supporting information.

#### Acknowledgements

We thank Research Council of Payame Noor University for the financial support of this investigation.

#### **Disclosure statement**

No potential conflict of interest was reported by the authors.

#### References

- [1] Ditter DC, Katritzky AR, Rees CW. Thiiranes and thiiranes in comprehensive heterocyclic chemistry. Elmsford (NY): Pergamon Press; 1984.
- [2] Meyers AL, Ford E. Synthesis via oxazolines one carbon homologation of aldehydes and ketones to thiiranes and olefins. Tetrahedron Lett. 1975;16:2861–2864.
- [3] Iranpoor N, Tamami B, Niknam K. Iodine and iodine supported on polyvinylpyrrolidone as catalysts and reagents for alcoholysis, hydrolysis, and acetolysis of epoxides and thiiranes. Can J Chem. 1997;75:1913–1919.
- [4] Testero SA, Lee M, Staran RT, et al. Sulfonate-containing thiiranes as selective gelatinase inhibitors. Med Chem Lett. 2011;2:177–181.
- [5] Sally AH, Stephen PB, Joel L, Peter JS. New potent and selective A<sub>1</sub> adenosine receptor agonists. Bioorg Med Chem. 2004;12:4877–4884.
- [6] Cho HJ, Jung MJ, Kwon Y, Na Y. Oxiranylmethyloxy or thiiranylmethyloxy-azaxanthones and -acridone analogues as potential topoisomerase I inhibitors. Bioorg Med Chem Lett. 2009;19:6766–6769.
- [7] Kellis JT Jr, Childers WE, Robinson CH, Vickery LE. Inhibition of aromatase cytochrome P-450 by 10-oxirane and 10-thiirane substituted androgens. Implications for the structure of the active site. J Biol Chem. 1987;262:4421–4426.
- [8] Eisavi R, Zeynizadeh B, Baradarani MM. Zeolite molecular sieve 4Å: a reusable catalyst for fast and efficient conversion of epoxides to thiiranes with thiourea. Phosphorus Sulfur Silicon. 2011;186:1902–1909.
- [9] Zeynizadeh B, Baradarani MM, Eisavi R. A practical and eco-friendly method for conversion of epoxides to thiiranes with immobilized thiourea on CaCO<sub>3</sub>. Phosphorus Sulfur Silicon. 2011;186:2208–2215.
- [10] Zeynizadeh B, Yeghaneh S. Solvent-free conversion of epoxides to thiiranes by thiourea/NH<sub>4</sub>Cl system. Phosphorus Sulfur Silicon. 2008;183:2280–2286.
- [11] Eisavi R, Zeynizadeh B. A green protocol for rapid and efficient conversion of epoxides to thiiranes using alumina immobilized thiourea at solvent-free conditions. Phosphorus Sulfur Silicon. 2016;191:65–69.
- [12] Yadav JS, Subba Reddy BV, Reddy CS, Rajasekhar K. [Bmim]PF<sub>6</sub>: A novel and recyclable ionic liquid for conversion of oxiranes to thiiranes in aqueous media. J Org Chem. 2003;68:2525-2527.
- [13] Akhlaghinia B, Rahimizadeh M, Eshghi H, Zhaleh S, Rezazadeh S. Green synthesis of thiiranes from oxiranes under solvent- and catalyst-free conditions. J Sulfur Chem. 2012;33:351–361.
- [14] Firouzabadi H, Iranpoor N, Khoshnood A. Aluminum tris (dodecyl sulfate) trihydrate Al(DS)<sub>3</sub>·3H<sub>2</sub>O as an efficient Lewis acid–surfactant-combined catalyst for organic reactions in

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water: Efficient conversion of epoxides to thiiranes and to amino alcohols at room temperature. J Mol Catal A: Chem. 2007;274:109–115.

- [15] Reddy CS, Nagavani S. LiClO<sub>4</sub> catalyzed mild and efficient method for the synthesis of thiiranes from oxiranes. Heteroatom Chem. 2008;19:97–99.
- [16] Tamami B, Parvanak Borujeny K. Synthesis of thiiranes from oxiranes using cross-linked polystyrene supported aluminium chloride as a catalyst. Synth Commun. 2004;34:65–70.
- [17] Salehi P, Khodaei MM, Zolfigol MA, Keyvan A. Magnesium hydrogensulfate: a cheap and efficient catalyst for the conversion of epoxides into  $\beta$ -alkoxy alcohols, vicinal-diols, and thiiranes. Synth Commun. 2003;33:3041–3048.
- [18] Moghadam M, Tangestaninejad S, Mirkhani V, Shaibani R. Rapid and efficient ring opening of epoxides catalyzed by a new electron deficient tin(IV) porphyrin. Tetrahedron. 2004;60:6105-6111.
- [19] Parvanak Borujeny K. Conversion of oxiranes to thiiranes catalyzed with silica gel-supported aluminium chloride. Synth Commun. 2005;35:2575–2579.
- [20] Kiasat AR, Kazemi F, Fallah Mehrjardi M. Solvent-free conversion of oxiranes to thiiranes with thiourea. Phosphorus Sulfur Silicon. 2004;179:1841–1844.
- [21] Moghadam M, Tangestaninejad S, Mirkhani V, Mohammadpoor-Baltork I, Taghavi SA. Highvalent tin(IV) porphyrin, Sn<sup>IV</sup>(TPP)(BF<sub>4</sub>)<sub>2</sub>, as an efficient catalyst for the ring opening of epoxides. Catal Commun. 2007;8:2087–2095.
- [22] Wu L, Wang Y, Yan F, Yang C. Facile conversion of epoxides to thiiranes with ammonium thiocyanate catalyzed with etidronic acid. Bull Korean Chem Soc. 2010;31:1419–1420.
- [23] Polshettiwar V, Luque R, Fihri A, Zhu H, Bouhrara M, Basset JM. Magnetically recoverable nanocatalysts. Chemical Rev. 2011;111:3036–3075.
- [24] Shylesh S, Schünemann V, Thiel WR. Magnetically separable nanocatalysts: bridges between homogeneous and heterogeneous catalysis. Angew Chem Int Ed. 2010;49:3428–3459.
- [25] Astruc D, Lu F, Aranzaes JR. Nanoparticles as recyclable catalysts: the frontier between homogeneous and heterogeneous catalysis. Angew Chem Int Ed. 2005;44:7852–7872.
- [26] Gawande MB, Branco PS, Varma RS. Nano-magnetite (Fe<sub>3</sub>O<sub>4</sub>) as a support for recyclable catalysts in the development of sustainable methodologies. Chem Soc Rev. 2013;42:3371–3393.
- [27] Baghbanian SM, Farhang M. CuFe<sub>2</sub>O<sub>4</sub> nanoparticles: a magnetically recoverable and reusable catalyst for the synthesis of coumarins via pechmann reaction in water. Syn Commun. 2014;44:697–706.
- [28] Karami B, Hoseini SJ, Nikoseresht S, Khodabakhshi S. Fe<sub>3</sub>O<sub>4</sub> nanoparticles: a powerful and magnetically recoverable catalyst for the synthesis of novel calix[4]resorcinarenes. Chin Chem Lett. 2012;23:173–176.
- [29] Kundu D, Chatterjee T, Ranu BC. Magnetically separable CuFe<sub>2</sub>O<sub>4</sub> nanoparticles catalyzed ligand-free C-S coupling in water: access to (*E*)- and (*Z*)-styrenyl-, heteroaryl and sterically hindered aryl sulfides. Adv Synth Catal. 2013;355:2285–2296.
- [30] Nemati F, Saeedirad R. Nano-Fe<sub>3</sub>O<sub>4</sub> encapsulated-silica particles bearing sulfonic acid groups as a magnetically separable catalyst for green and efficient synthesis of functionalized pyrimido[4,5-b]quinolines and indeno fused pyrido[2,3-d]pyrimidines in water. Chin Chem Lett. 2013;24:370–372.
- [31] Ma FP, Li PH, Li BL, et al. A recyclable magnetic nanoparticles supported antimony catalyst for the synthesis of *N*-substituted pyrroles in water. Appl Catal A: Gen. 2013;457:34–41.
- [32] Li PH, Li BL, An ZM, Mo LP, Cui ZS, Zhang ZH. Magnetic nanoparticles (CoFe<sub>2</sub>O<sub>4</sub>)supported phosphomolybdate as an efficient, green, recyclable catalyst for synthesis of  $\beta$ hydroxy hydroperoxides. Adv Synth Catal. 2013;355:2952–2959.
- [33] Feng C, Zhang HY, Shang NZ, Gao ST, Wang C. Magnetic graphene nanocomposite as an efficient catalyst for hydrogenation of nitroarenes. Chin Chem Lett. 2013;24:539–541.
- [34] Hajipour AR, Karimzadeh M, Azizi G. Highly efficient and magnetically separable nano-CuFe<sub>2</sub>O<sub>4</sub> catalyzed S-arylation of thiourea by aryl/heteroaryl halides. Chin Chem Lett. 2014;25:1382–1386.

- [35] Swapna K, Narayana Murthy S, Jyothi MT, Nageswar YVD. Nano-CuFe<sub>2</sub>O<sub>4</sub> as a magnetically separable and reusable catalyst for the synthesis of diaryl/aryl alkyl sulfides *via* cross-coupling process under ligand-free conditions. Org Biomol Chem. 2011;9:5989–5996.
- [36] Jiao H, Jiao GS, Wang JL. Preparation and magnetic properties of CuFe<sub>2</sub>O<sub>4</sub> nanoparticles. Syn React Inorg Met. 2013;43:131–134.
- [37] Parella R, Naveen Kumar A, Babu SA. Catalytic Friedel-Crafts acylation: magnetic nanopowder CuFe<sub>2</sub>O<sub>4</sub> as an efficient and magnetically separable catalyst. Tetrahedron Lett. 2013;54:1738–1742.
- [38] Sun ZP, Liu L, Jia DZ, Pan WY. Simple synthesis of CuFe<sub>2</sub>O<sub>4</sub> nanoparticles as gas-sensing materials. Sens Actuators B: Chem. 2007;125:144–148.
- [39] Yoon TJ, Lee W, Oh YS, Lee JK. Magnetic nanoparticles as a catalyst vehicle for simple and easy recycling. New J Chem. 2003;27:227–229.
- [40] Stevens PD, Fan J, Gardimalla HMR, Yen M, Gao Y. Superparamagnetic nanoparticlesupported catalysis of Suzuki cross-coupling reactions. Org Lett. 2005;7:2085–2088.
- [41] Stevens PD, Li G, Fan J, Yen M, Gao Y. Recycling of homogeneous Pd catalysts using superparamagnetic nanoparticles as novel soluble supports for Suzuki, Heck, and Sonogashira cross-coupling reactions. Chem Commun. 2005;35:4435–4437.
- [42] Hu A, Yee GT, Lin W. Magnetically recoverable chiral catalysts immobilized on magnetite nanoparticles for asymmetric hydrogenation of aromatic ketones. J Am Chem Soc. 2005;127:12486–12487.
- [43] Selvan RK, Augustin CO, Berchmans LB, Sarawathi R. Combustion synthesis of CuFe<sub>2</sub>O<sub>4</sub>. Mater Res Bull. 2003;38:41–54.
- [44] Wang F, Deng KJ, Lai GY, Cao L, Wen LL, Li DF. Ionothermal syntheses and crystal structures of two 1D inorganic–organic hybrid frameworks. J Inorg Organomet Polym. 2009;19:494–500.
- [45] Ding Y, Fu ZB, Hu XL, Xia CF. Hydrothermal synthesis, crystal structure and electrochemical property of two inorganic-organic hybrid frameworks via hydrogen bonding. J Inorg Organomet Polym. 2010;20:642–648.
- [46] Wen LL, Wang F, Leng XK, et al. Efficient detection of organophosphate pesticide based on a metal-organic framework derived from biphenyltetracarboxylic acid. Cryst Growth Des. 2010;10:2835–2838.
- [47] Huang Z, Zhu Y, Wang S, Yin G. Controlled growth of aligned arrays of Cu–Ferrite nanorods. Cryst Growth Des. 2006;6:1931–1935.