Tetrahedron Letters 60 (2019) 151259

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Highly efficient CuO_x/OMS-2 catalyst for synthesis of phenoxathiin derivatives via intramolecular arylations of phenols with aryl halides

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ARTICLE INFO

Article history:
Received 14 August 2019
Revised 1 October 2019
Accepted 9 October 2019
Available online 11 October 2019

Keywords:
Phenoxathiin
Heterogeneous
Phenols
Aryl halides

ABSTRACT

Phenoxathiin and its derivatives have attracted a great deal of interest due to their unique chemical and physical properties and their applications in fluorescent materials, antifungal activities and selective inhibitors. In the presence of copper supported on manganese oxide-based octahedral molecular sieves OMS-2 (CuO_x/OMS-2), the heterogeneously catalytic synthesis of phenoxathiinan derivatives via intramolecular arylations of phenols with aryl bromide or aryl chloride has been achieved. TEM and XRD have confirmed the CuO_x/OMS-2 catalyst has been successfully reused 8 times without a significant decrease in the yield, with simple filtration and washing as a means of separation.

Introduction

Sulfur-containing heterocycles and their derivatives have stimulated more than a century of research aimed at exploring economical, selective and efficient methodologies for achieving these compounds due to their wide applications in a wide range of interesting biological activities, organic functional materials, sensors, valuable synthetic intermediates and drug industry [1]. Among them, phenoxathiin and its derivatives have attracted a great deal of interest due to their unique chemical and physical properties and their applications in fluorescent materials, antifungal activities and selective inhibitors. For instances, 3-formylphenoxathiin and 3-acetylphenoxathiin exhibited an enhancement of the emission and a hypsochromic shift of the maxima in the presence of β-cyclodextrin by the fluorescence spectra [2]. Hillebrand's group also investigated solvatochromicity, natural lifetimes and fluorescence quantum yields of several 3-substituted phenoxathiin derivatives by the fluorescence spectroscopy. They found that the emission properties of 3-acetylphenoxathiin are dependently impacted by its substituent group [3]. Supuran's group found that 2-aminophenoxathiin's sulfonylamido derivatives exhibited excellent antifungal activities [4]. Moreover, phenoxathiin derivatives have also been used as selective inhibitors of monoamine oxidase [8]. In addition, they have attracted wide attention because of high stability of phenoxathiin's cation radicals [5].

The exploration of highly efficient synthetic methodologies for phenoxathiin and its derivatives is particularly appealing [6,7]. For example, Eastmond's group reported the synthesis of phenoxathiin derivatives by the cyano-activated fluoro replacement reactions between 2,3- and 3,4-difluorobenzonitriles and the nucleophiles (including 2-aminophenol, catechol, benzene-1,2-dithiol either and 2-aminobenzenethiol) in DMF at 130 °C or in DMSO at rt, in the presence of K_2CO_3 [8]. In 2013, Feng and Ma's group also described the regioselective synthesis of phenoxathiin derivatives from the reaction of 1-halo-2-nitroarenes or 1,2-dihaloarenes and 2-sulfanylphenol [9]. In fact, our group has long term interest in the synthesis of heterogeneous catalysts and their applications in cyclization reactions [10]. In 2015, we have developed the aerobic synthesis of 3-iodoimidazo[1,2-a]pyridines by tandem cyclization/iodination of 2-aminopyridines, I_2 and acetophenones by using the heterogeneous and recyclable CuO_x/OMS-2 catalyst [11]. Here, in this work, we first report the highly efficient the copper modified manganese oxide-based octahedral molecular sieves (CuO_x/OMS-2) catalyst for synthesis of phenoxathiin derivatives via intramolecular arylations of phenols with aryl halides. In our study, CuO_x/OMS-2 catalyst was made by wet-impregnation of OMS-2 in copper nitrate solution followed by filtration, washing, drying and calcination. The TEM image

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https://doi.org/10.1016/j.tetlet.2019.151259
0040-4039/

Fig. 1. The TEM image of CuO_x/OMS-2.

showed that CuO_x/OMS-2 are short nanorods (Fig.1). In addition, the CuO_x/OMS-2 catalyst has been reused 8 times without a significant decrease in the yield of **2a** (83–89%), with simple filtration.

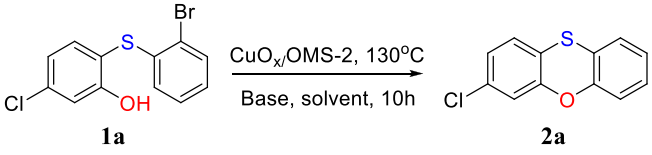
Results and discussion

First, the reaction conditions were optimized using 2-((2-bromophenyl)thio)-5-chlorophenol (**1a**) as model substrates. As shown in Table 1, the reaction was conducted with 2-((2-bromophenyl)thio)-5-chlorophenol (**1a**) (0.5 mmol) in the presence of 1 mmol of NaOH in DMSO (2 mL) at 130 °C under air for 10 h. The desired product 3-chlorophenoxathiine (**2a**) was obtained from intramolecular arylations of phenols with aryl halides in only 68% yield (Table 1, entry 1). When the intramolecular arylations of phenols reactions were carried out in the presence of different bases including KOH, Na_2CO_3, K_2CO_3 and Cs_2CO_3 (Entries 2–5), we found the yield of **2a** increased to 89% by using Cs_2CO_3. Then, we investigated different loadings of Cs_2CO_3, in the amount of 1 eq and 3 eq, and obtained 66% and 89% yields, respectively (Entries 6 and 7). Next, the reactions were conducted in different solvent, such as DMF and Toluene, and the reactions did not afford more higher yields (Entries 8 and 9). We also investigated the reaction at different temperatures (Entries 10 and 11), the yield of **2a** was also influenced by the reaction temperature. Next, the dosages of CuO_x/OMS-2 were examined, we found 8 mg of CuO_x/OMS-2 gave the highest yield, while 4 and 12 mg only provided 48% and 85% yield, respectively (Entries 12 and 13). As a comparative experiment, OMS-2 (instead of CuO_x/OMS-2) was tested under the same condition. The result shows OMS-2 itself only gave 26% yield (Entry 14). In addition, commercial CuO and Cu_2O were also investigated, we found both CuO and Cu_2O gave the excellent yield (85%) as that of CuO_x/OMS-2 (Entries 15 and 16). It is clear that the significant catalytic activity of CuO_x/OMS-2 catalyst is taken into account to its superficial highly active copper species. Finally, the reaction was also conducted without catalyst, and only gave 26% yield (Entry 17). Based on the above-studied results, 2 eq of Cs_2CO_3, 8 mg of CuO_x/OMS-2 130 °C and DMSO are the optimal conditions for this reaction.

Under the optimized reaction conditions, we extended the study with 2-((2-bromophenyl)thio)phenol with different substituting groups for the synthesis of various phenoxathiine derivatives. The results have been shown in Table 2. Various 2-((2-bromophenyl)thio)phenols have afforded the desired phenoxathiine derivatives in moderate to good yields. It is obvious that the nature of the substituent on the aromatic rings showed few influence on the yields of the desired phenoxathiine derivatives (Table 2, entries 1–12). The aromatic ring with whether electron-withdrawing groups (fluoro and chloro group) or electron-donating groups (methyl and methoxy group) gave more than 82% yields (Table 3, entry 1–5).

The recyclability of the CuO_x/OMS-2 catalyst has also been examined in Scheme 1. 2-((2-bromophenyl)thio)-5-chlorophenol (**1a**) was chosen as the model substrates, and the reaction was conducted under the previously optimized conditions: DMSO (2 mL) at 130 °C under air for 10 h in the presence of CuO_x/OMS-2 (8 mg) and Cs_2CO_3 (2 equiv.). As shown in Scheme 1, the CuO_x/OMS-2 cat-

Table 1
Optimization of the reaction condition.[a]

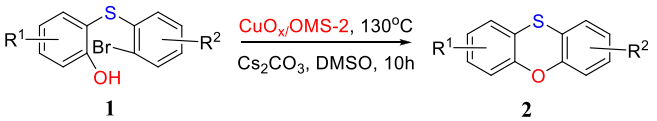


1a **2a**

Entry	Catalyst	Base	Solvent	Yield [%][b]
1	CuO_x/OMS-2 (8 mg)	NaOH (2 eq)	DMSO	68
2	CuO_x/OMS-2 (8 mg)	KOH (2 eq)	DMSO	5
3	CuO_x/OMS-2 (8 mg)	Na_2CO_3 (2 eq)	DMSO	70
4	CuO_x/OMS-2 (8 mg)	K_2CO_3 (2 eq)	DMSO	64
5	CuO_x/OMS-2 (8 mg)	Cs_2CO_3 (2 eq)	DMSO	89
6	CuO_x/OMS-2 (8 mg)	Cs_2CO_3 (1 eq)	DMSO	66
7	CuO_x/OMS-2 (8 mg)	Cs_2CO_3 (3 eq)	DMSO	89
8	CuO_x/OMS-2 (8 mg)	Cs_2CO_3 (2 eq)	DMF	55
9	CuO_x/OMS-2 (8 mg)	Cs_2CO_3 (2 eq)	Toluene	0
10[c]	CuO_x/OMS-2 (8 mg)	Cs_2CO_3 (2 eq)	DMSO	42
11[d]	CuO_x/OMS-2 (8 mg)	Cs_2CO_3 (2 eq)	DMSO	91
12	CuO_x/OMS-2 (4 mg)	Cs_2CO_3 (2 eq)	DMSO	48
13	CuO_x/OMS-2 (12 mg)	Cs_2CO_3 (2 eq)	DMSO	85
14	OMS-2 (8 mg)	Cs_2CO_3 (2 eq)	DMSO	26
15	CuO (2 mg)	Cs_2CO_3 (2 eq)	DMSO	85
16	Cu_2O (1.8 mg)	Cs_2CO_3 (2 eq)	DMSO	85
17	none	Cs_2CO_3 (2 eq)	DMSO	26

[a] Reaction conditions: 1a (0.5 mmol), base (1.0 mmol), CuO_x/OMS-2 (8 mg), solvent (2 mL), 130 °C, 10 h.
[b] Isolated yield.
[c] The reaction was carried out at 110 °C.
[d] The reaction was carried out at 150 °C.

Table 2
Reactions of 2-((2-bromophenyl)thio)phenol with different substituting groups.[a]

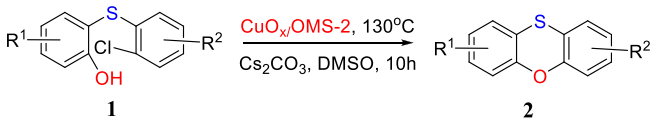


1 **2**

Entry	Product	R^1	R^2	Yield [%][b]
1	**2a**	5-Cl	H	89
2	**2b**	5-F	H	83
3	**2c**	3-Cl	H	92
4	**2d**	5-OCH_3	H	94
5	**2e**	3-CH_3	H	61
6	**2f**	5-F	4-CH_3	84
7	**2g**	5-Cl	4-CH_3	90
8	**2h**	5-CH3	4-CH_3	81
9	**2i**	5-OCH3	4-CH_3	78
10	**2j**	5-Cl	4-Cl	80
11	**2k**	H	H	87
12	**2l**	5-Cl	3-CH_3	82

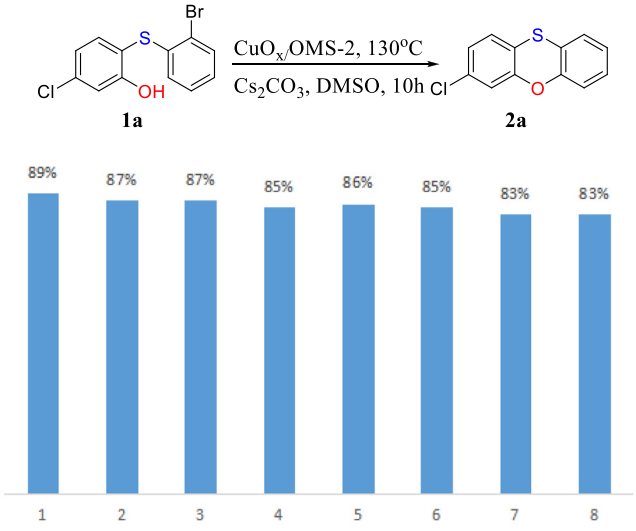
[a] Reaction conditions: **1** (0.5 mmol), Cs_2CO_3 (1.0 mmol), CuO_x/OMS-2 (8 mg), solvent (2 mL), 130 °C, 10 h.
[b] Isolated yield.

Table 3
Reactions of 2-((2-chlorophenyl)thio)phenol with different substituting groups.[a]



Entry	Reactant	R^1	R^2	Yield [%][b]
1	**1m**	5-Cl	H	87
2	**1n**	5-OCH_3	H	95
3	**1o**	5-Cl	4-CH_3	82
4	**1p**	5-OCH_3	4-CH_3	86
5	**1q**	H	H	83

[a] Reaction conditions: **1** (0.5 mmol), Cs_2CO_3 (1.0 mmol), CuO_x/OMS-2 (8 mg), solvent (2 mL), 130 °C, 10 h.
[b] Isolated yield.



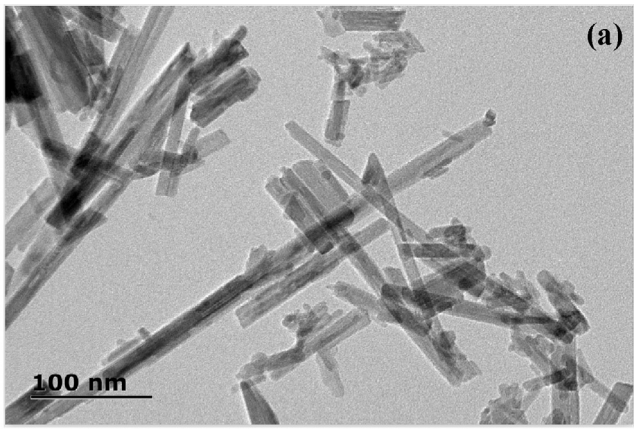
Scheme 1. Recyclability of the CuO_x/OMS-2 catalyst.

alyst has been recycled 8 times without a significant decrease in the yield of 3-chlorophenoxathiine (**2a**) (83–89%), with simple filtration and washing as a means of separation. The separated CuO_x/OMS-2 catalyst after the 8th run of reaction has been further examined by using XRD and TEM. Both TEM and XRD of the 8th recycled CuO_x/OMS-2 do not exhibit any apparent structural changes in comparison with the images of the fresh catalyst (Fig. 2), confirming the high stability and recyclability of CuO_x/OMS-2 catalyst.

Based on the analogous mechanisms discussed in literature [12], a plausible mechanism for the intramolecular arylations of phenols with aryl halides has been proposed as shown in Scheme 2. The catalytic cycle starts with the formation of the intermediate **3** by the attack of [CuO_x] to 2-((2-bromophenyl)thio)phenol **1a**. The intermediate **4** is produced from the **3** via another intramolecular oxidative addition. In the presence of Cs_2CO_3, subsequently, the intermediate **5** is obtained from intermediate **4** after removal of HBr. Finally, concomitant C—O coupling via a concerted process inside the aggregate would then lead to the formation of the intramolecular coupling product **2a**.

Conclusion

In summary, a highly efficient and heterogeneous the copper modified manganese oxide-based octahedral molecular sieves



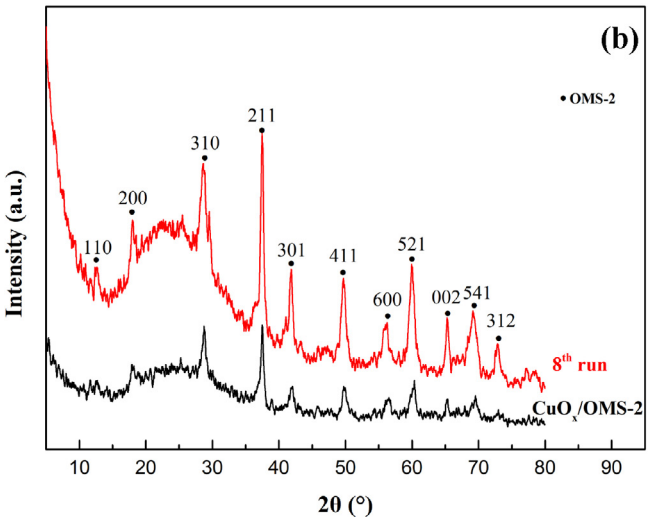
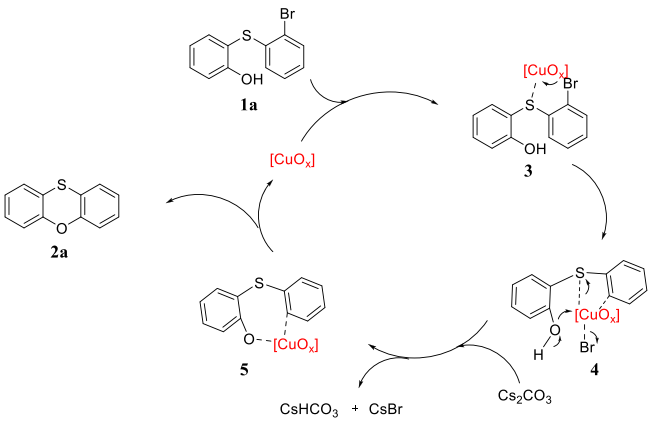


Fig. 2. (a) TEM and (b) XRD of 8th used CuO_x/OMS-2 catalyst.



Scheme 2. Proposed mechanism for synthesis of phenoxathiins.

(CuO_x/OMS-2) nanocomposite for synthesis of phenoxathiinan derivatives *via* intramolecular arylations of phenols with aryl halides has been successfully developed. The intramolecular arylations of phenols reactions with aryl bromide or aryl chloride tolerated a large number of substrates and gave moderate to great yields of phenoxathiinan derivatives that could be applied in fluorescent materials, antifungal activities and selective inhibitors. In addition, the CuO_x/OMS-2 catalyst has been successfully reused 8 times without a significant decrease in the yield, with simple filtration and washing as a means of separation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Financial support from the National Natural Science Foundation of China (Nos. 21602123, 21805166 and 21403256), the 111 Project of Hubei Province (No. 2018-19-1), the Foundation of Hubei Key Laboratory of Natural Products Research and Development (NPRD 2018007), the Youth Innovation Promotion Association CAS (2018456) and China Three Gorges University is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2019.151259.

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