

Selective Oxidation of Sulfides to Sulfoxides by Hydrogen Peroxide in the Presence of Mn_2ZnO_4 Spinel Nanoparticle Catalyst

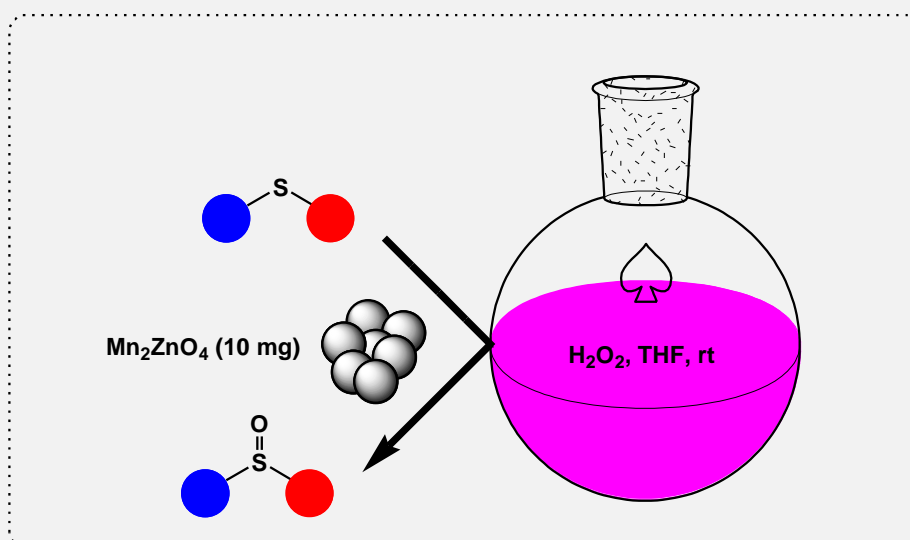
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ABSTRACT: In this research work, considering the importance and application of sulfoxides in various fields, especially in medicinal chemistry and pesticides, a new method for the selective oxidation of sulfides to sulfoxides has been invented. In order to investigate the range of reaction efficiency and the possibility of applying this method to other raw materials, a number of substituted aliphatic and aromatic sulfides were used in this reaction. As a result, the sol-gel method using oxalic acid as a chelating agent followed by deposition at low temperature was used for the synthesis of Mn_2ZnO_4 spinel, and the particle size was recorded by a 15 nm TEM electron microscope. The nature of the produced spinel nanoparticles was determined by TEM, FTIR and BET measurements. Mn_2ZnO_4 spinel nanoparticles with a size of 15 nm were used as a heterogeneous catalyst in the presence of hydrogen peroxide and in ethanol solvent at room temperature for the selective oxidation of sulfides to their respective sulfoxides. All the synthesized aromatic and aliphatic sulfides were easily and with high yield converted to sulfoxide by the above method. This reaction was performed by a fast, cheap, green, clean, environmentally friendly and high yield method. To prove the sulfoxides, we used the methods of thin layer chromatography (TLC) during the experiment and FT-IR to identify the functional groups. The structures of the new concentrated compounds were confirmed by FT-IR and NMR spectra.



KEYWORDS: Sulfoxide, Mn_2ZnO_4 Spinel, Heterogeneous Catalyst, Environmentally Friendly.

■ Introduction

Oxidation of sulfides to sulfoxides is important in organic chemistry, from the laboratory and industrial point of view [1]. The synthesis of sulfoxides was first reported by Marker in 1865, and after that many methods were developed to convert sulfide to sulfoxide [2]. Comprehensive articles on the oxidation of sulfide to sulfoxide have been published in the past, and a large number of these methods have been collected especially in the last 20 years [3]. There are various reagents for this key conversion, unfortunately most of these reagents are not satisfactory [4]. They are often harmful and expensive, and a simple method is not readily available due to further oxidation of sulfoxide to sulfone. Despite careful control of reaction temperature, reaction time and relative amount of oxidants, complete avoidance of further oxidation is difficult [5]. Since sulfoxides are important for C-C bond formation and functional group transformations, researches are always ongoing for newer methods of selective oxidation of sulfides to sulfoxides [6]. Oxidation of sulfides to sulfoxides has always been of interest due to the fact that they are important intermediates in the center of active chemical, biological and medicinal molecules. Most of them are used as anti-bacterial, anti-fungal, anti-arteriosclerosis and proton transfer inhibitors [7]. Sulfuric acid functional groups are among the most important pharmacophore groups in medicinal chemistry. There are many examples of this group of agents in various drugs and poisons. For example, one of the best-selling drugs in the world is omeprazole, which has a sulfoxide functional group as the main drug group [8]. This drug is a substituted derivative of benzimidazole in racemic form and acts as a proton transfer inhibitor. Another example of the use of sulfoxide functional group is fipronil poison, which belongs to the class of pyrazoles and is used as a pesticide (**Figure 1**) [9].

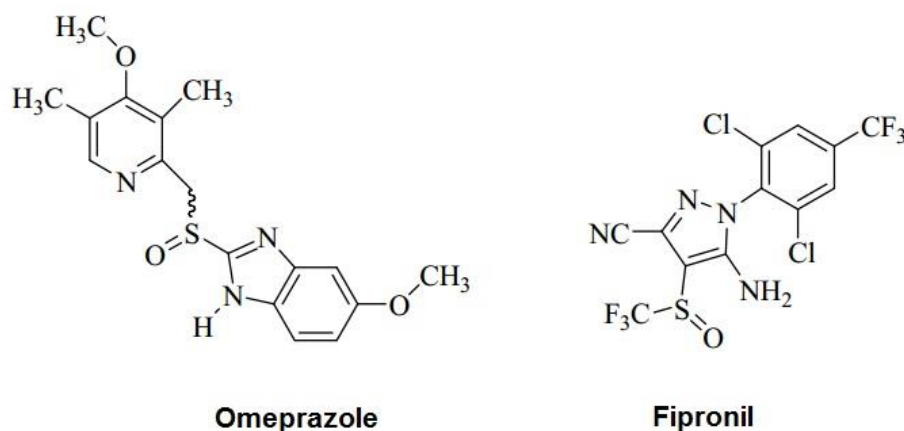


Figure 1. The structure of omeprazole and fipronil compounds.

The most important methods of preparing sulfoxides: The oldest and most common method of preparing sulfoxides is the oxidation of sulfides [10]. This reaction was first reported by the center in 1865. The simplest method of oxidizing sulfides is to use hydrogen peroxide alone or in the presence of various catalysts [11]. Hydrogen peroxide is more efficient than other oxidants such as nitric acid and sodium hypochlorite. When hydrogen peroxide is used correctly, it is stable and safe, and on the other hand, it shows the advantage of being soluble in water and many organic solvents [12]. It is also a green oxidizer because it only produces water as a byproduct, which is safe [13]. The biggest drawback of this reagent is

its ability to re-oxidize sulfoxide to sulfone. Since 1908, when Gazar and Smales reported the oxidation of sulfides to sulfoxides by hydrogen peroxide without the presence of a catalyst in acetone solvent, this solvent has been widely chosen as the reaction medium [14]. The only drawback of this reaction is the long reaction time. This limitation was partially overcome by using methanol as a solvent [15]. The use of methanol made the oxidation process relatively simple [16]. Because the separation and purification of the reaction product only involved adding water to the medium and extracting with chloroform [17]. Since oxidation with hydrogen peroxide was a mild process, it has been successfully used to prepare sulfoxides sensitive to acidic environments, such as allyl sulfoxide or vinyl sulfoxides with silyl substitution [18]. Spinel compounds have the general formula AB_2O_4 , where A is a divalent metal and B is a trivalent metal [19]. Spinel containing intermediary metal ions such as Co, Zn, Mn and Cr have been used as effective catalysts in a number of chemical reactions, including the oxidation of carbon monoxide, the catalytic combustion of hydrocarbons, and the reduction of some organic molecules [20]. The most common method for the preparation of spinels is the solid state reaction of primary metal oxides which are mechanically mixed [21]. In order to complete the reaction, a temperature of about 1027 or higher is applied for several days [22]. In addition, AB_2O_4 has been produced by methods such as precipitation of mixtures of hydroxide and carbonate precursors at high temperature, special co-precipitation and thermal synthesis [23]. The size of AB_2O_4 particles obtained by these methods is usually in the range of 0.1-1 μm . As a result, the sol-gel method using oxalic acid as a chelating agent followed by deposition at low temperature was used for the synthesis of AB_2O_4 spinel [24].

In this work, Mn_2ZnO_4 catalyst was synthesized by sol-gel method using oxalic acid as a chelating agent followed by deposition at low temperature. In the next step, these spinel nanoparticles were used as a heterogeneous catalyst in the presence of hydrogen peroxide and in the THF solvent at room temperature for the selective oxidation of sulfides to their corresponding sulfoxides.

■ Results and Discussion

In this research, Mn_2ZnO_4 was synthesized as a heterogeneous catalyst by sol-gel method, using oxalic acid as a chelating agent. In this way, the heterogeneous catalyst Mn_2ZnO_4 was prepared, which showed a very significant ability in the selective oxidation reaction of sulfides to the corresponding sulfoxides. The nature of the synthesized nanopowders was identified by IR spectroscopy. The spectrum of these nanopowders is shown in **Figure 2**. This spectrum shows two strong absorption bands at 561 and 650 cm^{-1} . The peak at 650 cm^{-1} is related to the M-O vibrational stretching model for tetrahedrally deionized metal ions and at 561 cm^{-1} is related to octahedrally deionized metal ions.

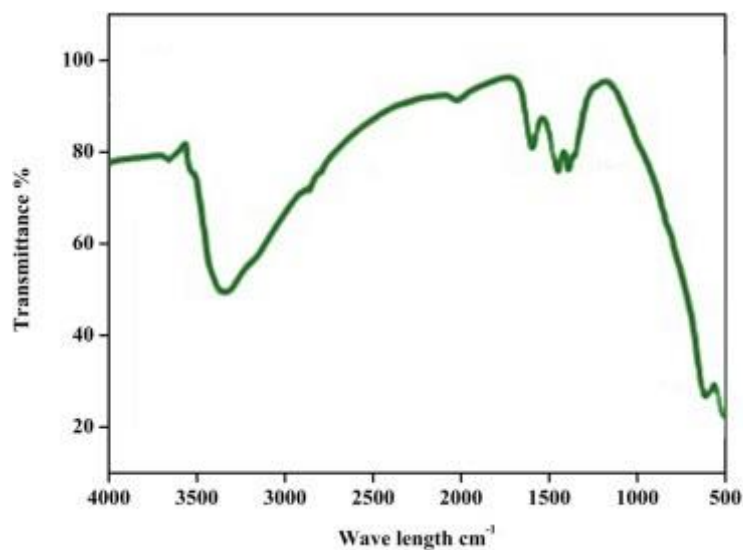


Figure 2. FT-IR spectra for Mn₂ZnO₄ catalyst.

Figure 3 shows TEM images for Mn₂ZnO₄ nanoparticles prepared at 450 temperature. Based on TEM images, it was found that the nanoparticles are uniform spherical crystals with an average size of 15 nm. The results obtained are in accordance with the results of BET.

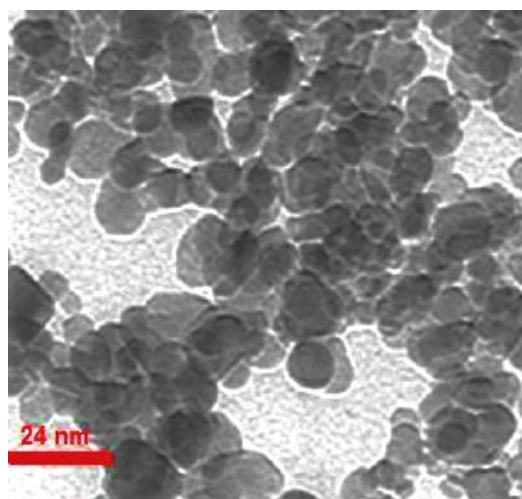


Figure 3. TEM images of Mn₂ZnO₄ spinel nanoparticles obtained at 450 temperature.

Absorption and desorption analysis is very important to check the porosity and specific surface area of materials. This method is based on the surface absorption method, which is completely non-destructive and cheaper than other methods, and the ability to analyze existing data is very accurate, convenient and effective, and it is based on measuring the volume of nitrogen gas absorbed and desorbed by the surface. The substance is at a constant temperature. The cell containing the sample to be analyzed is placed inside the tank with a constant temperature, and by gradually increasing the pressure of the carrier gas and then

by gradually decreasing the pressure of the carrier gas, the amount of gas absorbed by the substance is calculated. The information obtained from this process is obtained in the form of a graph of the volume of absorbed and desorbed gas, which can be used to calculate the specific surface area of the desired substance, the diameter, volume and size distribution of the pores of the substance. Nitrogen adsorption and desorption isotherm of Mn_2ZnO_4 nanocatalyst is shown in **Figure 4**. Based on the IUPAC classification, the sample shows a type three curve. The BET curve for Mn_2ZnO_4 shows a surface area of $25.6 \text{ m}^2/\text{g}$ and a pore diameter of 15 nm .

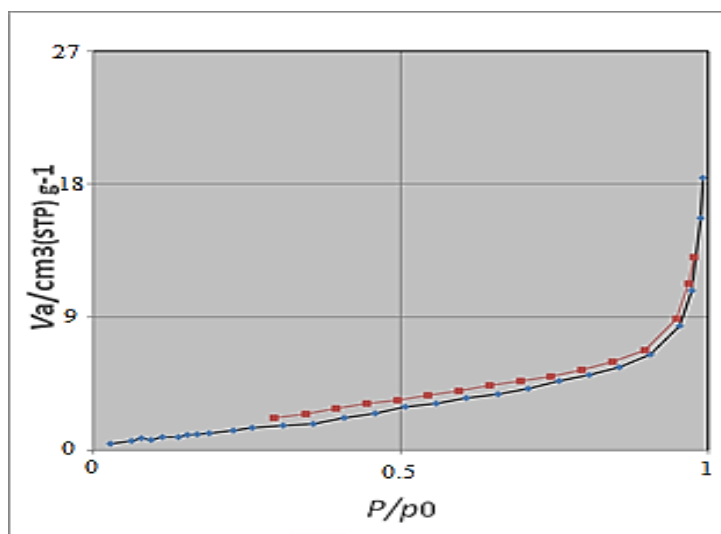


Figure 4. Adsorption and desorption isotherm of Mn_2ZnO_4 .

The general method of oxidation includes adding Mn_2ZnO_4 spinel nanoparticles to the solvent and sulfide, after a certain period of time to reach equilibrium, the process of sulfide absorption on the catalyst and then adding H_2O_2 oxidant. In order to optimize the reaction and find the most suitable conditions, the parameters of the solvent, temperature and amount of the catalyst have been investigated. As we know, different solvents have different effects on the activation energy and the reaction process due to different interactions with reactants. These effects can appear as a change in the yield rate and chemoselectivity of the reaction. In order to investigate the effect of the solvent on the reaction factors and to choose the most suitable solvent in the selective oxidation reaction of sulfides to sulfoxide in the presence of Mn_2ZnO_4 nanospinel catalyst, the oxidation reaction of the methyl phenyl sulfide molecule to the corresponding sulfoxide was carried out in different solvents. The results of this study are shown in **Table 1**. Solvents with less polarity form a heterogeneous solvent system with aqueous OH. In polar solvents, methyl phenyl sulfide is slowly oxidized to the corresponding sulfone. Therefore, the higher the polarity of the solvent, the higher the possibility of sulfone formation. As a result, for the selectivity of the reaction, THF solvent with lower polarity than other solvents is used. In order to investigate the effect of the amount of catalyst in the process of oxidation of methyl phenyl sulfide molecule to sulfoxide by OH oxidant in THF solvent and at room temperature with the presence of different amounts of Mn_2ZnO_4 nanospinel catalyst, the yield of the products was measured. The results of this investigation showed that the best results were reported for 10 mg . Also, the reaction was investigated in the absence of a catalyst and showed a mixture

of sulfone sulfoxide and the starting material in the reaction mixture. In order to investigate the effect of temperature on the process of oxidation of sulfide molecule to sulfoxide, the reaction was carried out at 5 different temperatures of 100, 80, 60, 40 and room temperature and the yield of the products was measured. It increases significantly in the case of sulfides with different functional groups such as hydroxyl or double bonds due to the high kinetic energy of the particles, there is also the possibility of other side reactions. Although the reaction proceeds faster at a higher temperature, the reaction has a good speed and benefit at room temperature. As a result, in order to avoid energy loss and to avoid other side reactions and to check the reaction in mild conditions, all the reactions were investigated using spinel Mn_2ZnO_4 nanoparticles in THF solvent at 25°C.

Table 1. Optimizing reaction conditions for sulfoxides synthesis in the presence of Mn_2ZnO_4 catalyst^a

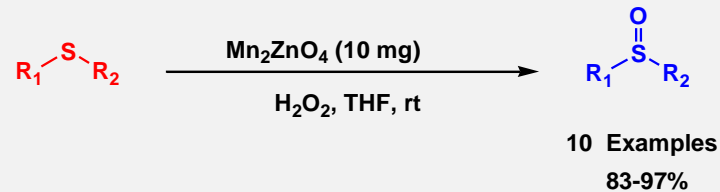
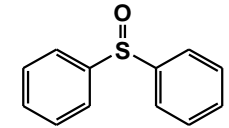
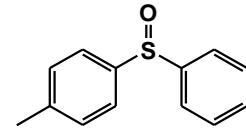
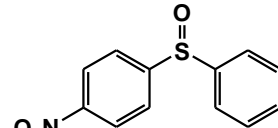
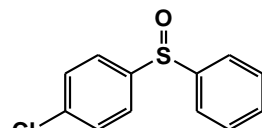
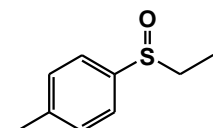
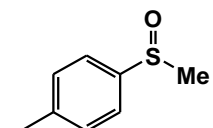
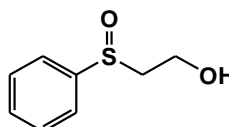
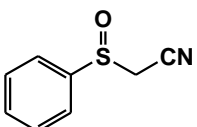
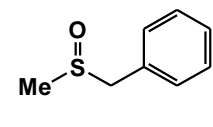
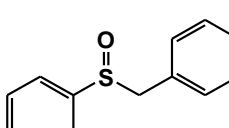
$\text{R}_1\text{-S-R}_2 \xrightarrow[\text{H}_2\text{O}_2, \text{Solvent}]{\text{Mn}_2\text{ZnO}_4 \text{ nanoparticles}} \text{R}_1\text{-S(=O)-R}_2$

10 Examples
83-97%

Entry	Catalyst (mg)	Solvent	Temp (°C)	Yield (%) ^a
1	--	THF	rt	No
2	5	THF	rt	35
3	10	THF	rt	81
4	15	THF	rt	97
5	10	THF	100	75
6	10	THF	80	61
7	10	THF	60	59
8	10	THF	40	41
9	10	DMF	rt	32
10	10	EtOH	rt	35
11	10	CH_3CN	rt	81
12	10	CHCl_3	rt	62
13	10	MeOH	rt	28
14	10	DMSO	rt	41

Sulfoxide preparation reaction was carried out at room temperature and THF solvent with 10 equivalents of H_2O_2 oxidant, 10 mg of Mn_2ZnO_4 , and new derivatives were synthesized in different conditions with high efficiency. The results are shown in **Table 2**.

Table 2. Reaction yield of substituted sulfoxides synthesis in the presence of Mn_2ZnO_4 catalyst derivatives^a

		
 2a (97%)	 2b (89%)	 2c (94%)
 2d (93%)	 2e (84%)	 2f (85%)
 2g (89%)	 2 (87%)	 2i (83%)
 2j (92%)		

After the completion of the reaction, the catalyst is separated by a centrifuge. The separated catalyst is washed with ethyl acetate (10 ml) and then dried at 100 °C for 2 hours. The catalyst is ready for reuse. This catalyst has the ability to be reused 5 times.

Conclusion

This review is the first example of using Mn_2ZnO_4 spinel nanoparticles as a heterogeneous catalyst in the oxidation reaction of sulfides, which showed that the oxidation of sulfides by this catalyst in the presence of H_2O_2 is very selective in such a way that only sulfoxide is created. The spinel nanocatalyst increases the

reaction speed so that it produces more sulfoxide in a shorter period of time. In carrying out the reaction without the presence of nanocatalyst, the duration of the reaction increases and with the passage of time sulfone is also created. Mn_2ZnO_4 spinel nanoparticles were produced by sol-gel method in the presence of oxalic acid as a chelating agent, and TEM showed that Mn_2ZnO_4 nanoparticles are produced by drying the resulting gel at 450 temperature to produce spinel structure crystals. The size of the Mn_2ZnO_4 spinel nanoparticle obtained is 15 nm, and the structure of the spinel Mn_2ZnO_4 nanoparticle has been confirmed by IR spectroscopy. This method is suitable for the oxidation of a wide range of aliphatic and aromatic sulfides with different functional groups to the respective sulfoxides. Finally, the simplicity of this method, the mild reaction conditions, high yield, high chemoselectivity, short reaction time, ease of separation of the reaction mixture, and especially the ability to recycle the catalyst without losing activity are the reasons for the high efficiency of this method in the selective oxidation reaction of sulfides to corresponding sulfoxides. In addition, the use of H_2O_2 as an oxidant has advantages such as being non-harmful to the environment, producing a safe by-product of water, being cost-effective, and being easy to store and move.

■ Experimental

Solvents used for reaction and separation were obtained from Merck and Fluka. The progress of the reactions was monitored by TLC. TLC thin layer chromatography was performed using C60254 silica gel sheets from Merck Chemical Company, Germany. Spectral data were obtained as solvent and CDCl_3 in ASPECT 3000 Bruker Ac 125 MHz using H-NMR TMS as internal standard and chemical shift is defined as parts per million (ppm) and coupling constants are scaled. Hertz are expressed. IR spectra were taken by 370-FTIR Thermo Nicolet AVATAR spectrophotometer.

General synthesis method of Mn_2ZnO_4 spinel nano catalyst

First, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.005 mol 2 grams) and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2.60 mol 2.9 grams) are dissolved in ethanol (20 ml). Then a solution of oxalic acid (0.15 mol) (1.9 g in ethanol (10 ml) is slowly added to the above mixing solution. After the addition is completed, the resulting mixture is mixed for 5 hours at room temperature. The mixture is stirred for 2 hours at 80 °C is mixed until the solvent evaporates. Then the mixture is heated at a temperature of 120. This gel is a precursor of oxalate and is dried in an oven at a temperature of 450 °C for 8 hours to produce crystallized spinel.

General method of selective oxidation of sulfides to sulfoxides by catalyst

First, in a flask, 1 mmol of the desired sulfide was added to the THF (10 ml) solvent while stirring. Then Mn_2ZnO_4 spinel nanoparticles are added to it and the reaction mixture is vigorously stirred for 30 minutes in order to reach the equilibrium of sulfide surface absorption on the catalyst surface. During the entire duration of the reaction, stirring must be done vigorously so that the solid catalyst is distributed homogeneously in the environment. Then 30%w (10) equivalents of H_2O_2 is added drop by drop to the reaction mixture. The reaction process is monitored by TLC. After the completion of the reaction, the heterogeneous catalyst is separated by a centrifuge, then the solvent is removed under reduced pressure. Before the complete removal of the solvent, CH_2Cl_2 (20 ml) is added to the reaction mixture and then it is

separated with H₂O (10 ml). The separated organic phase is dried by Na₂SO₄ and the solvent is removed under reduced pressure. The product is obtained without the need for purification.

Supporting Information

1-benzenesulfinyl-4-chloro-benzene (2d):

¹H NMR (500 MHz, CDCl₃) δ 7.50 (d, J=8.2 Hz, 2H), 7.33 (d, J=7.6 Hz, 2H), 7.48 (d, J=7.2 Hz, 3H), 7.42-7.46 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 145.5, 144.9, 137.3, 131.7, 129.4, 129.1, 126.4, 124.6.

1-(ethylsulfinyl)-4-methylbenzene (2e):

¹H NMR (500 MHz, CDCl₃) δ 7.63 (t, J=7.2 Hz, 2H), 7.58 (d, J=7.3 Hz, 2H), 2.83-2.90 (m, 1 H), 2.72-2.79 (m, 1H), 2.41 (s, 3H), 1.20 (t, J=7.2 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 141.2, 140.0, 129.9, 124.3, 50.3, 21.4, 6.9.

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Copies of NMR spectra of synthesized compounds:

