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Selective oxidation of sulfides to sulfoxides by a vanadium-based catalyst using 30% hydrogen peroxide

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ABSTRACT: The vanadium-based catalyst, acts as a homogeneous catalyst for the selective oxidation of various kinds of sulfides with 30% aqueous H_2O_2. Vanadium-based catalyst was successfully used as the oxygen source for the oxidation of sulfides to sulfoxides for the first time. The sulfoxides were obtained in a good way to high yields without any detectable over-oxidation to sulfones under normal conditions. Different functional groups including C–C double bond, ester, ketone, acetal, alcohol, and oxime groups are tolerated under this reaction condition. The prepared catalyst was used to achieve a high-efficiency, low cost, ecofriendly and easy to handle protocol for synthesizing substituted sulfoxide derivatives from sulfides. The catalyst could be recycled for up to four runs without significant loss in catalytic activity. A green, efficient and selective approach for the oxidation of sulfides to sulfoxides and with stoichiometric amount of 30% aq. H_2O_2 is reported.

Keywords: *Heterogeneous, Hydrogen peroxide, Sulfoxidation, Selective oxidation, Vanadium.*

INTRODUCTION

There is a motivation on investigations on new methods of sulfoxide synthesis because of increasing interest and applications of sulfoxides. The oxidation of sulfides is the most straightforward method for the synthesis of sulfoxides (Golchoubian, *et al.*, 2007). The development of the highly efficient catalytic systems for the oxidation of sulfides to sulfoxides has received much attention because they are important as intermediates of biologically significant molecules, ligands in asymmetric catalysis, and oxo-transfer reagents (Chebolu, *et al.*, 2015). Due to the great interest of these compounds, different synthetic methods have been developed for oxidation of sulfides (Gregori, *et al.*, 2008). Unfortunately, most of these reagents are not satisfactory for medium- to large-scale synthesis because of the low content of effective oxygen, the formation of environmentally unfavorable co-products, and high cost (Sato, *et al.*, 2001) Organic sulfoxides are useful synthetic intermediates for the construction of various chemically and biologically active molecules (Haddadi, *et al.*, 2015) that often play an important role as therapeutic agents such as anti-ulcer (proton pump inhibitor), antibacterial, antifungal, anti-atherosclerotic, anthelmintic, antihypertensive, and cardiotonic agents, as well as psycotonics and vasodilators (Kaczorowska, *et al.*, 2005). These often play an important role as therapeutic agents such as antiulcer (proton pump inhibi-

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(*),(**) Corresponding Author - e-mail: Mohammadjavadtaghizaeh31@yahoo.com tor), antibacterial, antifungal, antiatherosclerotic, anthelmintic, antihypertensive, and cardiotonic agents, as well as psycotonics, and vasodilators. Moreover, over-oxidation of the sulfoxides to sulfones is a common problem during the oxidation of sulfides (Selvam, *et al.*, 2008). Despite thousands of oxidants that convert sulfides to the corresponding sulfoxides, most reagents require careful control of the reaction conditions, including the quantity of oxidants, to minimize the formation of sulfones as side products. (Shukla, *et al.*, 2003) To determine functional group compatibility and chemoselectivity of the reaction, variety of substrates were subjected to the developed and optimized method. Various functional groups were compatible and the sulfoxides were obtained in almost quantitative yields. In several cases, reaction was complete in 30 min to 2 h. However, in case of sterically hindered and less nucleophilic sulfides such as diphenyl sulfide and benzyl phenyl sulfide unduly long reaction times were required (Kamata, *et al.*, 2010). In this study, it clearly shows that the double bond also remains unaffected. This method offers the advantage of shorter reaction times, excellent yields, large scale synthesis, high chemoselectivity and easy work-up (Khodaei, *et al.*, 2010). Therefore, our method can be considered the most outstanding methodology of sulfoxidation. In this study, after synthesize Fe_3O_4 as a nanoparticle and coating by SiO_2 shell and functionalizing surface of SiO_2/Fe_3O_4 by aminopropyl groups followed by acidification of amino groups using triflicacid and ion exchange of triflate ion by vanadate (Taghizadeh, *et al.*, 2015). Vanadate catalyst was immobilized onto functionalized aminopropyl SiO_2/Fe_3O_4 (Hashemi, *et al.*, 2014).

EXPERIMENTAL

MATERIAL AND METHODS

All chemicals were used without further purification either as received from different commercial sources (Merck, Aldrich, Fluka) or prepared in our laboratories by known methods. All NMR spectra (^{1}HNMR and ^{13}CNMR) were recorded on 500 MHz. Contents of the catalyst samples were determined by X-ray fluorescence (XRF ARL8410). X-ray diffraction (XRD) patterns of prepared catalyst were recorded with a APD 2000, using Cu Kα radiation (50 kV, 40 mA) in the range $2\theta= 10\text{-}120°$. The SEM analysis was done with a KYKY-EM3200 with maximum acceleration voltage of the primary electron between 20 and 25 kV. FT-IR spectra were recorded with Shimadzu FTIR-8400S spectrophotometer using a KBr pellet for sample preparation. Magnetic properties of the samples were determined by a vibrating sample magnetometer (VSM, Lakeshore). An HPLC system (Agalent, knawer, shimadzu) was used to identify the products.

Preparation of Fe_3O_4 nanoparticles

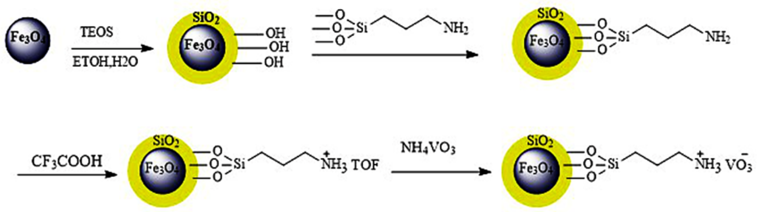
The reagents of analytic grade ($FeCl_3•6H_2O$, $FeCl_2•4H_2O$, NaOH and C_2H_6O) were used as raw materials. Chemical grade sodiumcitrate ($Na_3C_6H_5O_7.2H_2O$) and oleic acid ($C_{17}H_{33}COOH$) were used as modifiers. Firstly, $FeCl_3•6H_2O$ and $FeCl_2•4H_2O$ with molar proportion of 1:2 were dissolved in ethanol or deionized water maintained at different temperatures, and then NaOH solution (3 mol•L^{-1}) was added into the above solution using a peristaltic pump under constant magnetic stirring for 30 min, and the final pH was 10. Afterwards, the sodiumcitrate and oleic acid were respectively added into the suspensions to modify the obtained Fe_3O_4 for 12h. The substance obtained were aged and digested at maintained temperature for 30 min and cooled at room temperature. The resulted particles were magnetically separated and washed repeatedly with deionized water and ethanol until pH was 7. The products were then dried at 60 °C in vacuum for 6 h for further characterizations.

Preparation of SiO_2/Fe_3O_4 nanoparticles

Fe_3O_4/SiO_2 nanoparticles were prepared by the stober method. The magnetic nanoparticals Fe_3O_4 (0.01 g) was dissolved in mixed solution of water (10 mL) and ethanol (50 mL). Ammonia solution (1.2 mL) and TEOS (1.8 mL) were added to the mixed solution with stirring and reactant for 1.5 h. The nanoparticles were isolated by centrifugation and washed with ethanol.

Preparation of APTS modified SiO_2/Fe_3O_4 nanoparticles ($NH3^+$-SiO_2/Fe_3O_4)

By refluxing the SiO_2/Fe_3O_4 (2g) with 3-aminoprop-



Scheme 1. Synthetic route for the preparation of $VO_3^-/NH_3^+-SiO_2/Fe_3O_4$.

yltrimethoxysilane (0.28 mmol) in 10 mL of dry toluene for 18h, the surface of SiO_2/Fe_3O_4 nanoparticles modified with NH_3^+ was prepared. By adding 1ml CF_3COOH dropwise to the sample that dispersed in dichloromethane and stirred at room temperature overnight, NH_2 groups turn to $NH_4^+.NH_3^+-SiO_2/Fe_3O_4$ nanoparticles as final products was filtered and washed with water, ethanol and chloroform several times and then was dried at 60°C for 24h.

Preparation of $VO_3^-/NH_3^+-SiO_2/Fe_3O_4$ nanoparticles catalysts

Mixture of $NH_3^+-SiO_2/Fe_3O_4$ nanoparticles (2g) and an aqueous solution of three fold excess NH_4VO_3 in 35 mL deionized water was stirred at room temperature for 24 h to produce the catalyst. Then it was filtered off, washed with about 500 mL deionized water, ethanol and ether and dried in an oven at 60 ºC overnight. Typical procedure of sulfoxidation (for synthesis of intended sulfoxides)

1 mmol of each substrate was solved at 2 mL of acetonitrile. Then 5 mol% of catalyst and 1.5 mL 30% H_2O_2 were added. The mixture was stirred at room temperature for 45min. The formation of the sulfoxide was monitored by TLC (nhexanes: EtOAc, 1:1). After completion of the reaction, the solvent evaporated and the crude product was purified by recrystallization method (using EtOAC/n-hexane) to give the desired sulfoxide. After reaction completion, the nanoparticles were separated magnetically, then washed several times with EtOAC and MeOH and dried at 60ºC for 8h. The recycled catalyst was applied for further reactions.

RESULTS AND DISCUTION

Scheme 1 depicturing the synthesis of Fe_3O_4@APTS. The silane coating surface of the magnetic Fe_3O_4 cores derived from the hydrolysis of APTS functioned as a coupling agent and provided amino group ($–NH_2$) for binding the VO_3^- ion. The characterization of nanoparticles was carried out by FTIR, XRD, SEM and VSM methods. Fig. 1 shows the Fourier transforms infrared (FTIR) spectra of (a) Fe_3O_4, (b) SiO_2/Fe_3O_4, (c) $NH_3^+-SiO_2/Fe_3O_4$ and (d) $VO_3^-/NH_3^+-SiO_2/Fe_3O_4$. In Fig.1 (a), the band in the range 400-650 cm^{-1} is due to the stretching vibrations of Fe-O band in Fe_3O_4. The absorption bands at about 1100, 970 and 800 cm^{-1} is attributed to Si-O asymmetrical stretching bond, the Si-OH bending and in-plane bending of germinal silanol of silica, respectively. Additionally, the absorption bands at the curves (a) and (b) at 3420 cm^{-1} and 1640 cm^{-1} appear due to the vibration of remainder H_2O in the sample (the O-H stretching of adsorbed water and the hydrogenbondedsilanol groups and the O-H bending of adsorbed water, respectively). In curve (c) two absorption peaks at 2846 and 2918 cm^{-1} are related to stretching vibration of C–H. The vibration of V-O is below 1000 cm^{-1} but this peak was not observed at (d) duo to presence of strong peaks corresponded to SiO_2 and Fe_3O_4.

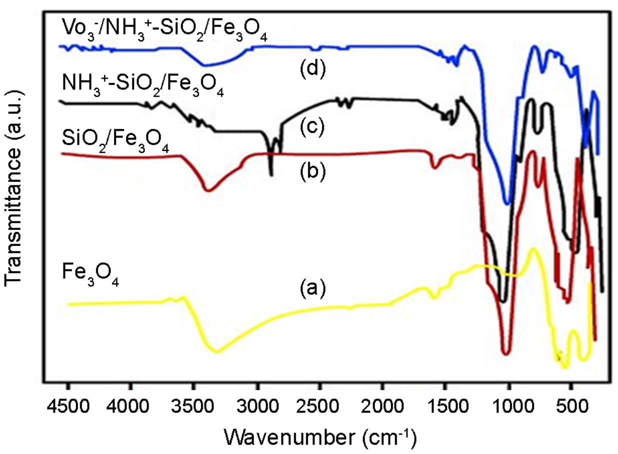


Fig. 1. The FT-IR spectra of Fe_3O_4, SiO_2/Fe_3O_4, $NH_3^+-SiO_2/Fe_3O_4$ and $VO_3^-/NH_3^+-SiO_2/Fe_3O_4$ catalyst.

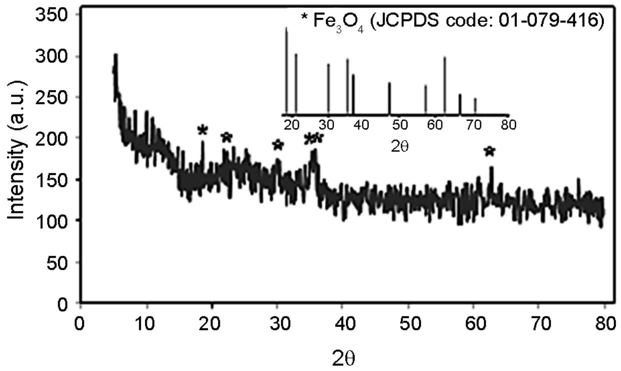


Fig. 2. The XRD pattern of VO_3^-/NH_3^+-SiO_2/Fe_3O_4 catalyst-catalyst.

The X-ray diffraction pattern of VO_3^-/NH_3^+-SiO_2/Fe_3O_4 catalyst is shown in Fig. 2. The amorphous silica template shows light variety of peak in the 10-30°. The diffraction on the crystal structure of Fe_3O_4 due to the sharp peaks.

Scanning electron microscopy (SEM) which was illustrated in Fig. 3, determine the average size and the morphology of VO_3^-/NH_3^+-SiO_2/Fe_3O_4. The SEM image of VO_3^-/NH_3^+-SiO_2/Fe_3O_4 shows that this particle was roughly spherical in shape, and the average size is about smaller than 100 nm.

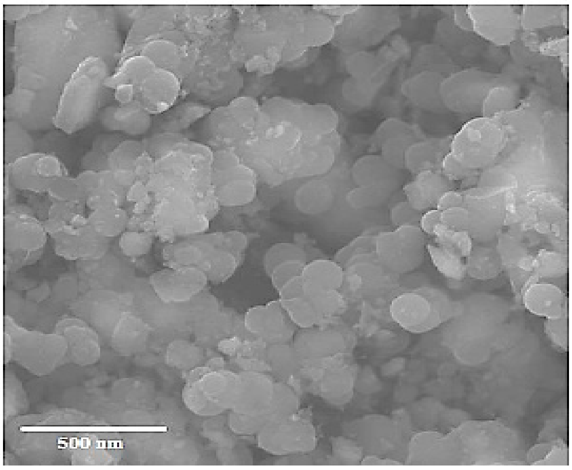


Fig. 3. The SEM image of VO_3^-/NH_3^+- $/NH_3^+$-SiO_2/Fe_3O_4.

VSM was performed to measure the magnetic property of catalyst. Two measurements for Fe_3O_4 nanoparticles and VO_3^-/NH_3^+-SiO_2/Fe_3O_4 were done at 300 K, and their curves are compared in Fig. 4. In Fig. 4 the saturation magnetization (Ms) of Fe_3O_4 and VO_3^-/NH_3^+-SiO_2/Fe_3O_4 is obtained 59 and 24 emu/g respectively, where this reduction in Ms (35 emu/g) corresponds to shell thickness. Even with this situation of falling, with the employ of an external magnetic force, the catalyst can be completely separated from the solution.

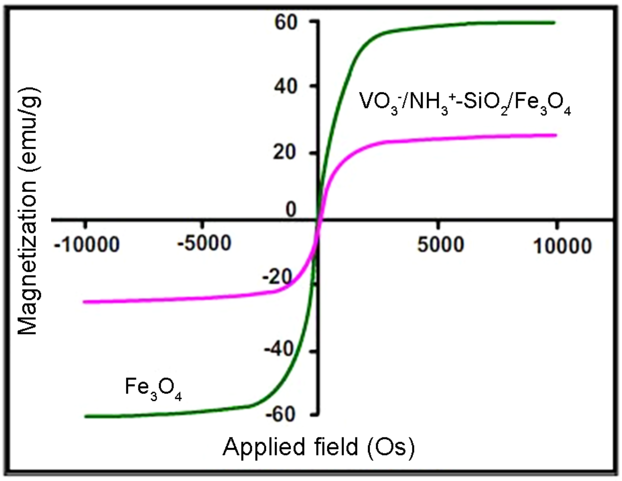
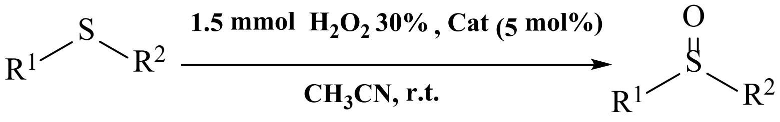


Fig. 4. Magnetization curves of Fe_3O_4 and VO_3^- SiO_2/Fe_3O_4 nanoparticles catalyst.

Catalyst activity

The oxidation of various kinds of sulfides to sulfoxides and H_2O_2 as oxidant reagent was investigated and results are shown in Table 1.

Before that, the time and the amount of catalyst was optimized and determined as shown in Table 2. 50 minutes and 5% mol of the catalyst (Entry 7) is the best option for the most yield of the reaction. After accomplishing the reaction, the superparamagnetic nanocatalyst was separated from the medium, as usual with application of an external magnet, then washed with EtOAC, followed by methanol and dried at 60 OC and used for another reaction run. The nanocatalyst was reused until the results were not satisfactory. In this way, the recyclability of our synthesized nanocatalyst was examined (Fig. 5). The catalyst shows



Scheme 2. Preparation of sulfoxide from sulfide in the presence of VO_3^-/NH_3^+-SiO_2/Fe_3O_4.

Table 1. Sulfoxidation of sulfide compounds with hydrogen peroxide using 5 mol% VO_3^-/NH_3^+-SiO_2/Fe_3O_4 nanoparticles catalyst.

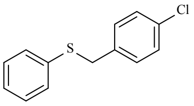
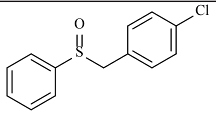
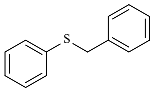
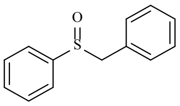
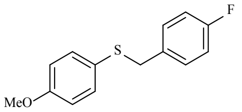
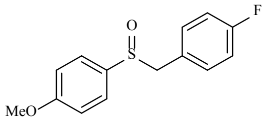
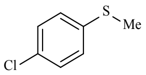
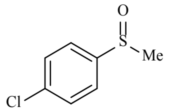
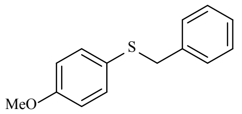
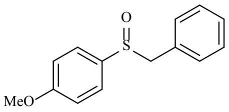
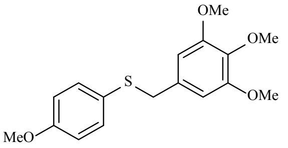
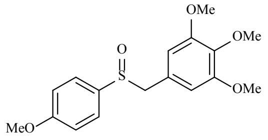
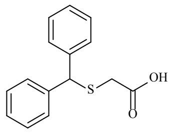
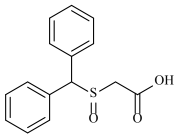
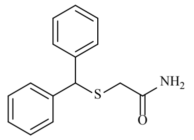
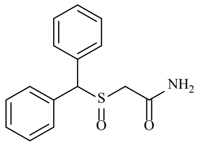
Entry	Sulfide	Product	Time (min)	Yield (%)	m.p. (°C)
1			50	90	49-50
2			45	91	45-56
3			45	93	50-51
4			50	91	44-45
5			45	94	49-50
6			40	92	51-52
7			40	94	149-150 (Chi, *et al.*, 2012)
8			45	93	161-162 (Chi, *et al.*, 2012)

Table 2. Sulfoxidation of sulfides using H_2O_2 as oxidant in the presence of the VO_3^-/NH_3^+-SiO_2/Fe_3O_4 at different conditions.

Entry	Catalyst (mol %)	Time (min)	Yield (%)
1	0	300	24
2	1	240-300	50
3	2	240	78
4	3	180	80
5	4	90	84
6	5	90	88
7	5	45-50	92
8	6	45-50	92
9	7	45	92
10	10	45	93

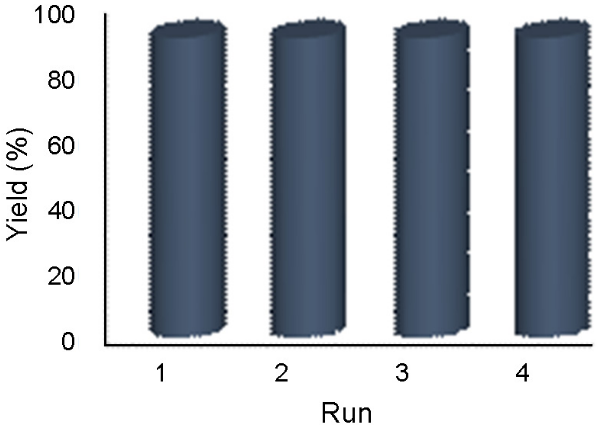


Fig. 5. Reusability of VO_3^-/NH_3^+-SiO_2/Fe_3O_4 nanoparticles catalyst for sulfoxidation (Condition reaction: 1 mmol (diphenylmethanetio) acetohydroxamicacid, 2 mL acetonitrile, 5 mol% catalyst).

excellent result for four repeat cycles, after which we witness deterioration in its catalytic activity

CONCLUSIONS

In summary, this novel represents how we synthesized $VO_3^-/NH_3^+-SiO_2/Fe_3O_4$ superparamagnetic nanoparticles and characterized their various properties with FT-IR spectroscopy, XRD, SEM and VSM techniques and optimized the way of their processing. Then, we used these recyclable nanoparticles to catalyse the oxidation of sulfides to sulfoxids which are useful and important as intermediates for the construction of various chemically and biologically active molecules that act as therapeutic agents, at room temperature, as a benign and environmentally friendly process.

Representative spectral data

1-chloro-4-((phenylsulfinyl)methyl)benzene: ^{1}H NMR (500 MHz; $CDCl_3$, δ, ppm): 7.70-7.71 (d, J= 7 Hz, 2H), 7.63-7-66 (M, 3H), 7.59-7-60 (d, J= 7.5 Hz, 2H), 7-53-7.54 (d, J= 7.5 Hz, 2H), 5.3 (S, 2H).
^{13}C NMR (250 MHz; $CDCl_3$, δ, ppm): 132.07, 130.90, 128.72, 123.02, 122.38, 118.40, 62.40.

(benzylsulfinyl)benzene: ^{1}H NMR (500 MHz; $CDCl_3$, δ, ppm): 7.70-7.71 (d, J= 7 Hz, 2H), 7.63-7.66 (M, 3H), 7.59-7.60 (d, J= 7.5 Hz, 2H), 7.51-7.54 (t, M, 3H), 5.32 (s, 2H). ^{13}C NMR (250 MHz; $CDCl_3$, δ, ppm): 141.59, 134.78, 131.99, 130.85, 128.72, 125.97, 123.06, 122.54, 62.39.

1-fluoro-4-(((4-methoxyphenyl) sulfinyl)methyl) benzene: ^{1}H NMR (500 MHz; $CDCl_3$, δ, ppm): 7.58-7.61 (dd, 3J= 8.5 Hz, 4J= 5 Hz, 2H), 7.33-7-34 (dd, 3J= 3.5 Hz, 4J= 2 Hz, 2H), 7.12-7.16 (t, 3J= 8 Hz, 4J= 7.5 Hz, 2H), 6.91-6.93 (d, J= 4Hz, 2H), 6.63 (s, 2H), 3.7(s, 3H). ^{13}C NMR (250 MHz; $CDCl_3$, δ, ppm): 159.98, 158.06, 157.60, 139.17, 136.13, 128.74, 126.64, 126.58, 114.61, 114.43, 114.24, 62.22, 55.29.

1-chloro-4-(methylsulfinyl)benzene: ^{1}H NMR (500 MHz; CDCl3, δ, ppm): 7.29-7.31 (d, J= 8.5, 2H), 7.21-7.23 (d, J= 8, 2H), 4.56 (s, 3H). 13C NMR (250 MHz; $CDCl_3$, δ, ppm): 122.91, 117.71, 116.97, 114.4, 56.34.

1-(benzylsulfinyl)-4-methoxybenzene: ^{1}H NMR (500 MHz; D2O, δ, ppm): 8.02-8.03(d, J= 7, 2H), 7.50-7.54 (d, J= 17.5, 2H), 7.22-7.43 (M, 3H), 7.08-7.10 (d, J= 7.5, 2H), 4.86 (s, 2H), 2.5 (s, 3H). ^{13}C NMR (250 MHz; D2O, δ, ppm): 122.91, 117.7, 116.97, 114.44, 56.34.

1,2,3-trimethoxy-5-(((4-methoxyphenyl)sulfinyl) methyl)benzene: ^{1}H NMR (500 MHz; D2O, δ, ppm): 7.72-7.74 (d, J= 8.5, 2H), 7.0-7.02 (d, J= 8.5, 2H), 6.42 (s, 2H), 4.73 (s, 2H), 3.82 (s, 3H), 3.03 (M, 6H), 2.5 (s, 3H). ^{13}C NMR (250 MHz; D2O, δ, ppm): 185.32, 157.30, 145.12, 131.86, 128.91, 126.70, 123.92, 115.08, 114.18, 62.73, 55.52, 54.81.

(benzhydrylsulfinyl)methanol: ^{1}H NMR (500 MHz; D2O, δ, ppm): 10.34(s,1H), 7.43-7.45 (d, J= 7.5, 2H), 7.30-7.33 (t, J= 7.25, 2H),7.22-7.25 (t, J= 7 , 2H), 5.11 (s, 1H), 3.49 (s, 2H). ^{13}C NMR (250 MHz; D2O, δ, ppm): 170.63, 136.02, 128.67, 128.45, 128.91, 127.57, 69.30, 61.13.

(benzhydrylsulfinyl)methanamine: ^{1}H NMR (500 MHz; D2O, δ, ppm): 7.39-7.41 (d, J= 7, 4H), 7.30-7.33 (t, J= 7.25, 4H), 7.22-7.25 (t, J= 7.25 ,2H), 5.99-6.50 (Broad ,2H), 5.18 (s, 1H), 3.70 (s, 2H). 13C NMR (250 MHz; D2O, δ, ppm): 171.37, 135.10, 128.72, 128.24, 127.60, 69.01, 61.00.

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