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Research Article

Spiropyrans Containing the Reactive Substituents in the 2H-Chromene Moiety

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Some spiropyrans containing functional substituents in the [2*H*]-chromene part of the molecule were synthesized and their photochromic properties in solution and solid state were investigated. The presence of the formyl group in the [2*H*]-chromene fragment enhances the possibility to show photochromic properties in solution.

1. INTRODUCTION

Photochromism is a reversible conversion between differently-colored isomers induced in one or both directions by absorption of electromagnetic radiation [1]. Many classes of organic compounds can reversibly change their colour under irradiation in various spectral regions. Photochromic compounds attract a great attention due to their powerful application potential, for example, high-density optical information storage systems, optoelectronic systems, and so forth [2–4]. Spiropyrans are photosensitive compounds that have been investigated intensively [5, 6]. Photochromic derivatives of spiropyrans are perspective nonsilver light-sensitive material for obtaining new photo-switches, filters with variable density, different multifunctional materials [7], and for solving more complicated scientific problems, for example, creation of molecular computer [8].

The photochromic properties of spiropyrans depend on many structural factors, and one of the key factors is the nature of substituents in the [2*H*]-chromene part.

Both synthesis and investigation of spiropyrans bearing various substituents are very important for the investigation of the correlation between structure and photochromic behaviour of compounds.

This paper is concerned with the introduction of reactive functional groups like formyl into the spiropyran molecule that can open up the ways to synthesize numerous new derivatives with specific photochromic properties for potential practical application.

2. METHODS AND MATERIALS

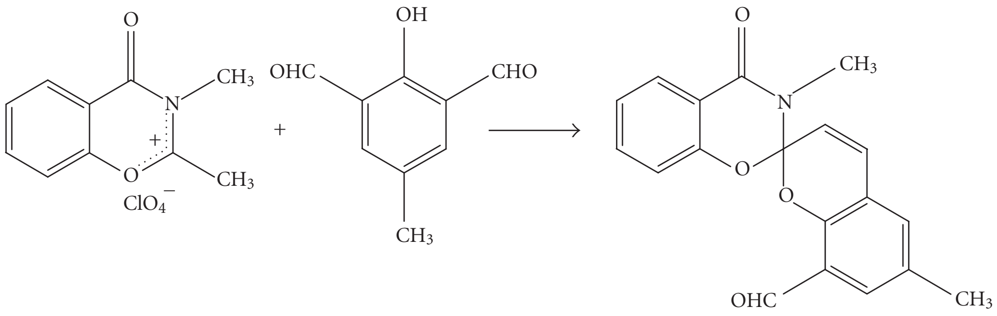
The structures of all synthesized compounds were determined using elemental analyses, IR and ^{1}H NMR spectroscopy as well as X-ray structural analysis. The Raman spectra were recorded with a DFS-52M (LOMO) spectrometer, and an ILA-120 argon laser (Carl Zeiss) was used as an excitation source. The power density of laser radiation was about 10 mW/mm^2. A 250 W high-pressure mercury discharge lamp (DRSh-250) was used for continuous irradiation. The absorption spectra were detected with the spectrophotometer "Specord M 40" (Germany).

3. RESULTS AND DISCUSSION

3.1. *Derivatives of the previously synthesized compounds*

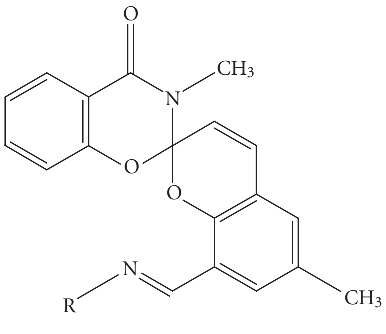
3,6′-dimethyl-8′-formyl-4-oxo-3,4-dihydro-2*H*-1,3-spiro-benzoxazine-2,2′[2*H*]-chromene **I** (see Scheme 1) containing a free formyl group in 8′-position was synthesized earlier [9].

This spiropyran shows photochromic properties both in solution and in the solid state [10]. UV irradiation (365 nm) of the vacuum deposited thin films results in conversion of



I

Scheme 1



II

(a) R = Alk
(b) R = p-Ar-NO$_2$
(c) R = o-Ar-OH
(d) R=ArCONH
(e) R=AlkCONH
(f) R=ArOCH$_2$NH

Scheme 2

the colourless ($\lambda_{\max} = 360$ nm) form into photocoloured one with $\lambda_{\max} = 615$ nm. The decolouration takes place thermally ($t = 70°$C) or photochemically by visible light irradiation in the longwave maximum region. The back dark reaction results in full decolouration within four hours (the half-life of a colored form is ∼1 h). Following UV irradiation (365 nm) regenerates the colored form again.

Chemical reactions of the formyl group can give the possibility to obtain various derivatives like hydrazones and azomethines **II** (a)–(f) (see Scheme 2) [11].

Among all compounds **II** (a)–(f), only azomethine **II** (b) shows photochromic properties in solution.

Spiropyrans possesing photochromic properties both in solution and solid states could be used as chemosensors for the detection of metal ions in the environment. In the view of this fact, the structure of compound **II** (c) in adsorbed state on the silver film was investigated by methods of Raman and giant Raman spectroscopy. The giant Raman spectra of compound **II** (c) adsorbed on silver films are presented in Figure 1.

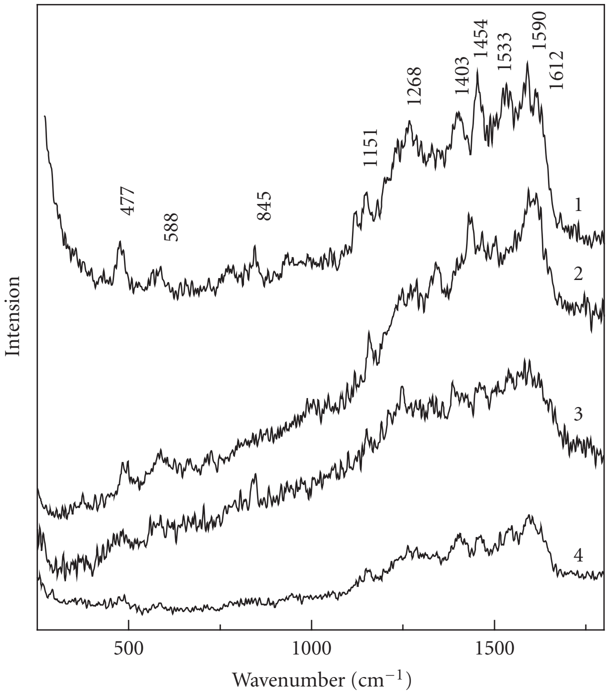
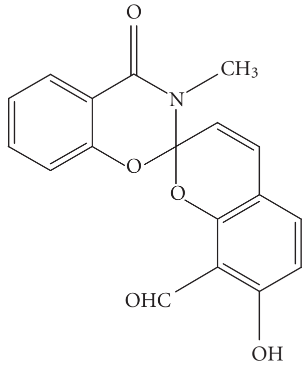


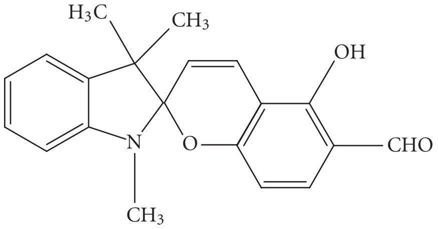
Figure 1: The giant Raman spectra of compound **II** (c) adsorbed on the unannealed (1,2) and annealed (3,4) silver films ($\lambda_{\text{exc}} = 514$ HM (1,3); $\lambda_{\text{exc}} = 488$ HM (2,4)).

The typical band of the vibrational spectra of the spiropyran colourless form in the area of 1640 cm^{-1} is absent in all four spectra independently of the experimental conditions (Figure 1). Consequently, only the coloured opened form of the spiropyran molecules is observed in this experiment. Shift of the equilibrium "closed form ↔ opened form" to the opened one can be associated with the fact that an interaction of the heteroatom O with the surface can result in decreasing the C$_{\text{sp}}$−O bond energy [12]. The general intensity of the giant Raman signal on the annealed silver films is several times smaller. This phenomenon correlates well with previously investigated mechanism of the interactions between metal films and molecules containing heteroatoms



III

Scheme 3



IV

Scheme 4

[13]. Also, one can note that shifting the irradiation maximum from $\lambda = 514$ nm to 488 nm (i.e., increasing the irradiation energy) results in a decrease in the giant Raman signal that can be a result of the photodestruction of the adsorbed molecules and their desorption.

3.2. Spiropyrans based on the 2,4-dihydroxy-benzene-1,3-dicarbaldehyde

2,4-dihydroxy-benzene-1,3-dicarbaldehyde was used as precursor for synthesis of two spiropyrans **III, IV** (see Schemes 3, 4) containing *ortho*-located formyl and hydroxy groups [14].

These spiropyrans show photochromic properties in solution but also in the solid state. The photochromism of these compounds was investigated in toluene solution using monochromatic continuous irradiation with UV light $\lambda_{\max} = 365$ nm. Irradiation results in the appearance of the well-defined longwave absorption bands corresponding to the opened forms (for compound **III** $\lambda_{\max} = 510$ nm, for compound **IV** $\lambda_{\max 1} = 431$ nm and $\lambda_{\max 2} = 566$ nm) (Figure 2).

Compound **III** was used as the unique analogue of salicylic aldehyde for the synthesis of bispiropyran **V** (see Scheme 5) [15].

This compound is promising for practical application due to expected strong longwave shift of the absorption maximum of the form with both opened 2*H*-pyran rings.

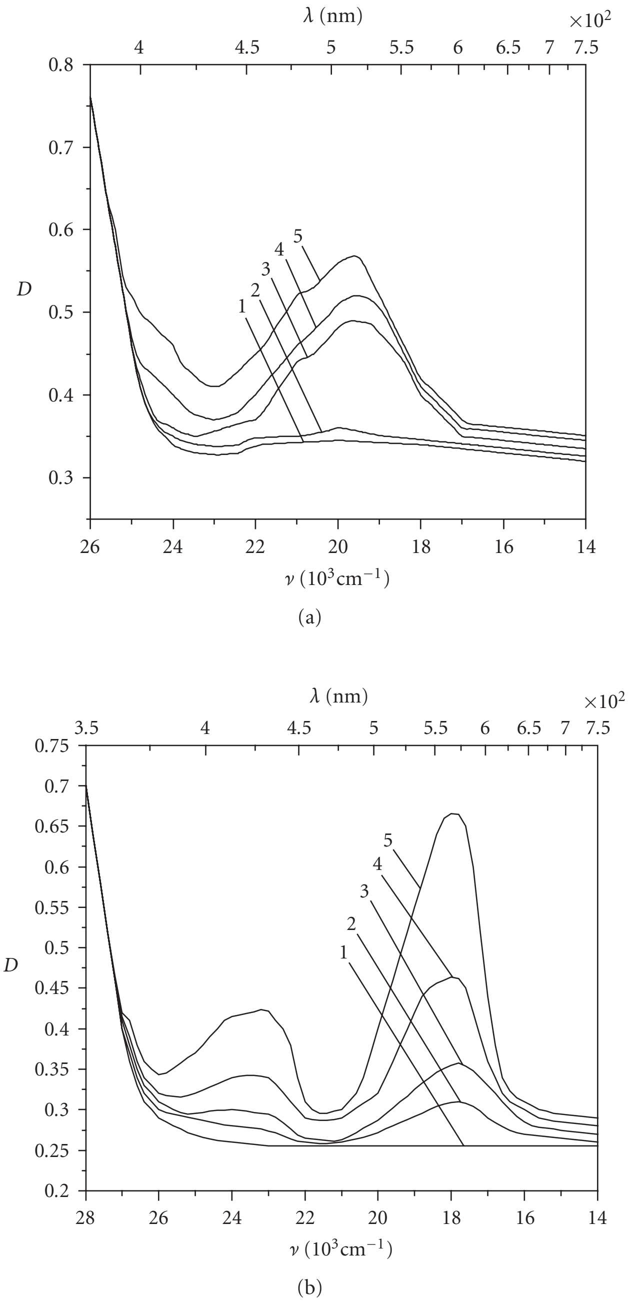
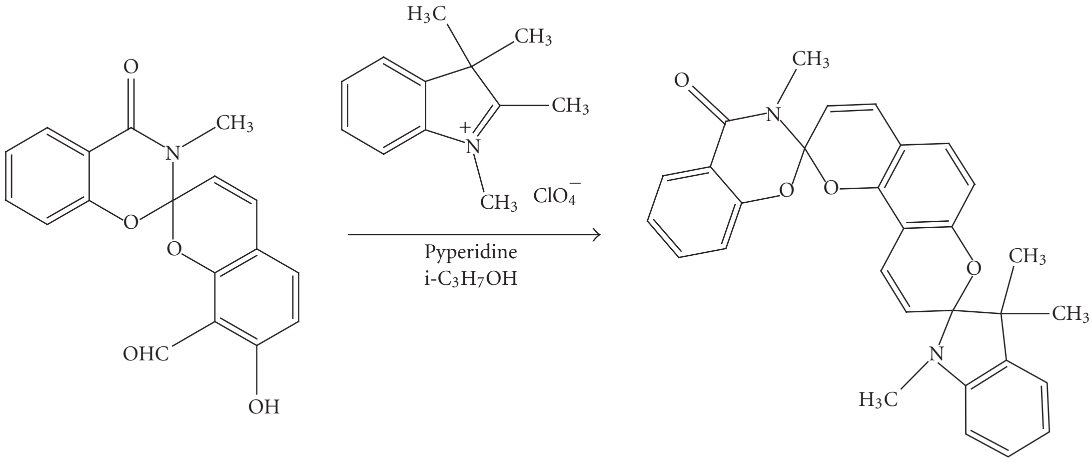


Figure 2: Absorption spectra of spiropyrans **III** (a) and **IV** (b). Spectra 1,2,3,4,5, were recorded after 0, 5,15,20,30 min irradiation, respectively.

3.3. Spiropyrans of the naphthoxazinone series

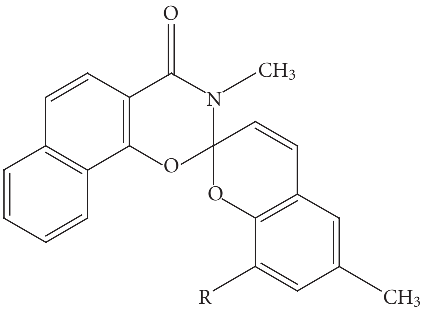
It was of interest to synthesize analogues of benzoxazinone spiropyran **III** containing a fused benzene ring suitable for studying the structure of spiropyran compounds and their photochromic properties. Compounds **VI** (a), (b) (see Scheme 6) [16] and **VII** (see Scheme 7) were synthesized and their photochromic behaviours were investigated.

Spiropyrans **VI** (a) and **VI** (b) dissolved in ethanol are not light sensitive at −70°C under the same condition as



III **V**

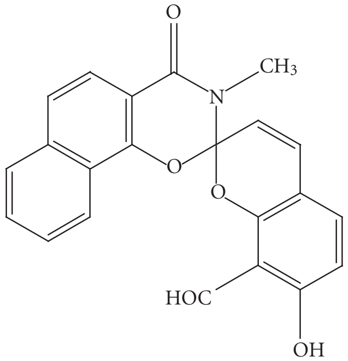
Scheme 5



VI (a), (b)

a) R = H
b) R = CHO

Scheme 6



VII

Scheme 7

compound **I** (the stationary irradiation with UV light $\lambda_{\max} = 365\,\text{nm}$) [17]. However, compound **VI** (b) shows the photochromic properties in toluene solution ($t = 25^\circ\text{C}$, $\lambda_{\max} = 365\,\text{nm}$) (Figure 3).

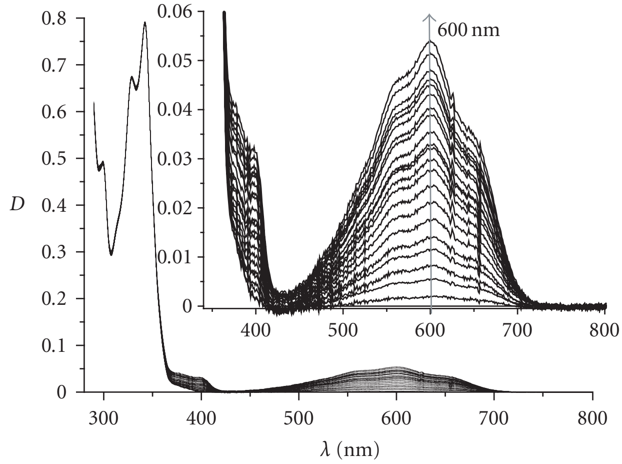


Figure 3: Absorption spectra of spiropyran **VI** (b) in toluene at $t = 10^\circ\text{C}$: (a) before irradiation; (b) after irradiation with UV light $\lambda_{\max} = 365\,\text{nm}$.

This phenomenon is unexpected due to the fact that the polarity of toluene is less than that of ethanol and temperature conditions of this experiment look unsuitable for observing the open form in the electronic absorption spectra.

Currently, we are planning to explain the photochromic behaviour of this compound by using computer modeling.

A formyl group in the [2*H*]-chromene moiety can enhance photochromism in the solid state. Unfortunately, compounds **VI** (a), (b) did not show photochromic properties in the thin solid films obtained by the thermal vacuum deposition onto glass or quartz surfaces in contrast to spiropyran **I** [9].

Compound **VII** similar to spiropyran **III** was used to obtain new bispiropyran **VIII** (see Scheme 8) [18].

The structure of this compound was determined by IR and NMR ^{1}H spectroscopy as well as X-ray analysis (Figure 4).

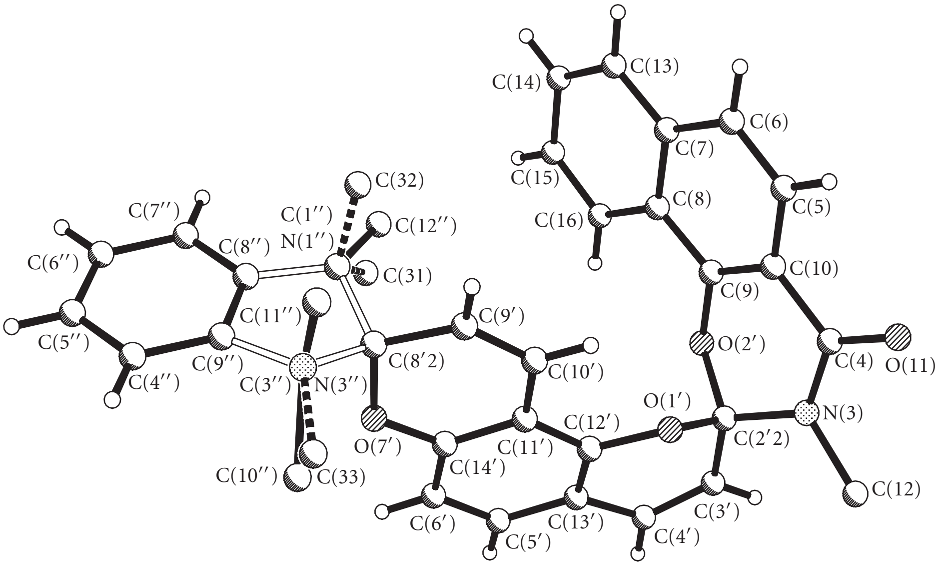
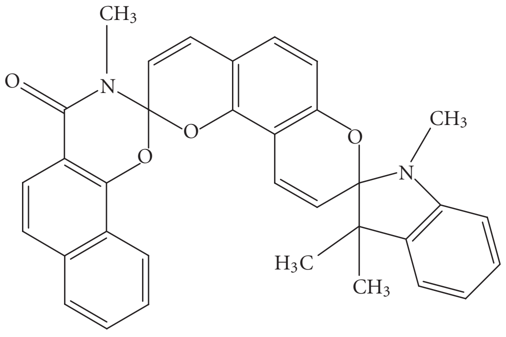


Figure 4: Data of the X-ray analysis of compound **VIII**.



VIII

Scheme 8

4. CONCLUSION

We tested the phenomenon of photochromism in some previously synthesized spiropyrans containing a formyl group in the [2*H*]-chromene fragment and a derivative obtained recently (spiropyrans **VII**). Moreover, other derivatives (hydrazones, azomethines, as well as bispiropyrans) of some spirocompounds were obtained based on the reactivity of the formyl group located in the benzene ring of the [2*H*]-chromene moiety. The results are qualitatively compared with reported results of model compound **I**. It has been noticed that introduction of reactive formyl group in the [2*H*]-chromene fragment results in enhanced photochromism in solution and/or solid thin films.

ACKNOWLEDGMENTS

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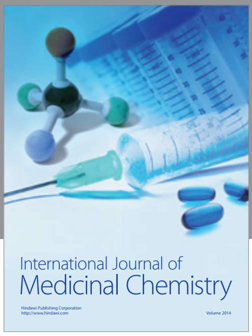
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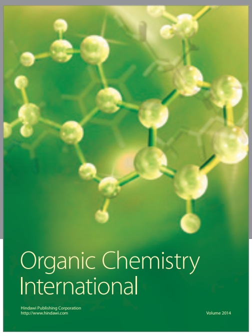
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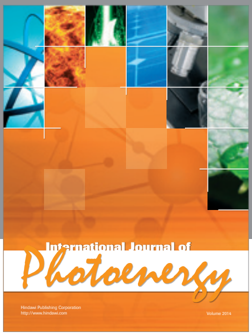
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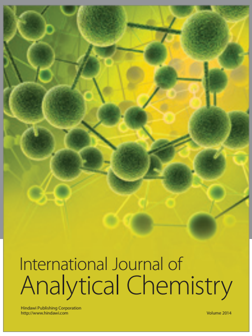
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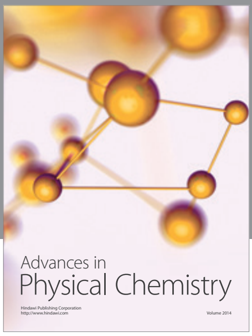
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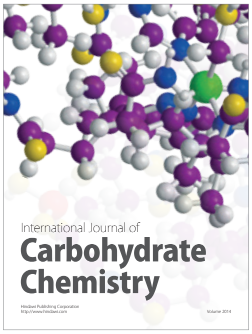
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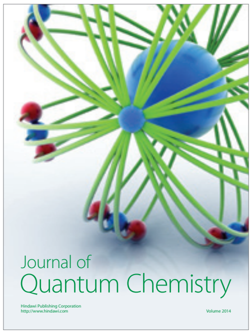
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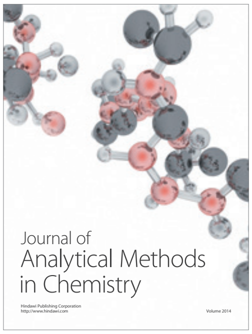
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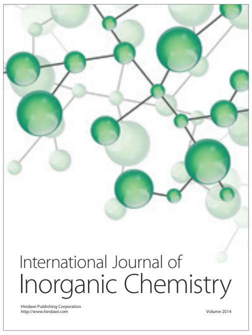
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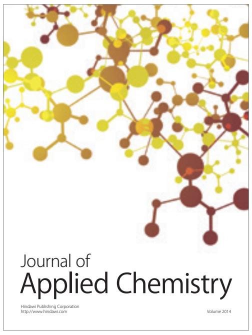
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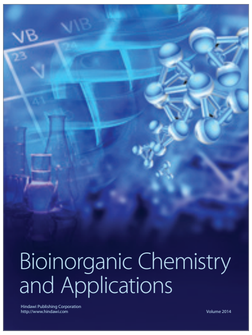
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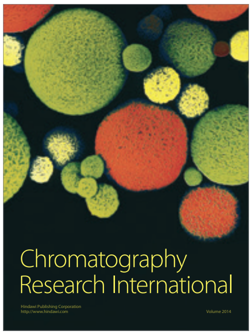
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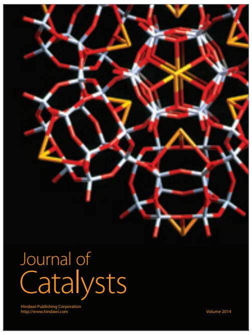
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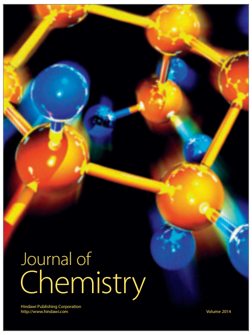
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