This article was downloaded by: [Universite Laval] On: 04 March 2015, At: 11:15 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



CrossMark Click for updates

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsyc20</u>

Synthesis of Novel Organosiliconsulfur-Containing Tetrasubstituted Imidazoles Sonocatalyzed by $La_xSr_{1-x}Fe_yCo_{1-y}O_3$ Nanoperovskites

Kazem D. Safa^a, Maryam Allahvirdinesbat^a & Hassan Namazi^b

^a Organosilicon Research Laboratory, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

^b Laboratory of Dendrimers and Nano-Biopolymers, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

Accepted author version posted online: 18 Feb 2015.

To cite this article: Kazem D. Safa, Maryam Allahvirdinesbat & Hassan Namazi (2015): Synthesis of Novel Organosiliconsulfur-Containing Tetrasubstituted Imidazoles Sonocatalyzed by $La_xSr_{1-x}Fe_yCo_{1-y}O_3$ Nanoperovskites, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, DOI: <u>10.1080/00397911.2015.1009552</u>

To link to this article: <u>http://dx.doi.org/10.1080/00397911.2015.1009552</u>

Disclaimer: This is a version of an unedited manuscript that has been accepted for publication. As a service to authors and researchers we are providing this version of the accepted manuscript (AM). Copyediting, typesetting, and review of the resulting proof will be undertaken on this manuscript before final publication of the Version of Record (VoR). During production and pre-press, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal relate to this version also.

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any

form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Synthesis of Novel Organosiliconsulfur-Containing Tetrasubstituted Imidazoles Sonocatalyzed by La_xSr_{1-x}Fe_yCo_{1-y}O₃ Nanoperovskites

Kazem D. Safa¹, Maryam Allahvirdinesbat¹, Hassan Namazi²

¹Organosilicon Research Laboratory, Faculty of Chemistry, University of Tabriz, Tabriz, Iran, ²Laboratory of Dendrimers and Nano-Biopolymers, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

Corresponding author, E-mail: dsafa@tabrizu.ac.ir

Abstract

The one-pot synthesis of tetrasubstituted imidazoles by use of a series of perovskites $La_xSr_{1-x}Fe_yCo_{1-y}O_3$ as catalysts is described. The $La_{0.8}Sr_{0.2}Fe_{0.34}Co_{0.66}O_3$ nanocatalyst had the highest activity in the heterogeneous cyclocondensation of an aldehyde, benzil, ammonium acetate and a primary aromatic amine in water under ultrasonic irradiation. Some of the derivatives generated during this work were utilized as substrates for the synthesis in high yields of novel multifunctional tetrasubstituted imidazoles with Me₃Si, C=S, and SH groups, via nucleophilic attack of tris(trimethylsilyl)methyllithium (TsiLi) at the carbon of carbon disulphide



KEYWORDS: La_xSr_{1-x}Fe_yCo_{1-y}O₃ perovskites, Imidazoles, Ultrasonic irradiation,

MCRs, Organosiliconsulfur

INTRODUCTION

The incorporation of organosilicon moieties into drug structures has been used to improve pharmacological potency, to modify selectivity toward a given target, to change metabolic rates, and to increase lipophilicity. Lipophilicity can provide several physiological benefits, including increased bioavailability and tissue and cell penetration.^[1–3] The chemistry of compounds containing silicon and sulfur attached to the same or neighbouring carbons offers opportunities, particularly in the broad area of organic synthesis, not available if work is restricted to compounds containing only one of these elements.^[4]

Cyclizations via one-pot multicomponent coupling reactions (MCRs) are widely used for the preparation of heterocycles.^[5,6] Imidazoles are important in biological systems, e.g. as histidine, histamine, biotin, and components in drugs (e.g. Losartan, Olmesartan, Eprosartan, and Trifenagrel) and pesticides. Some of these compounds could also be used as organic optical materials, in molecular switches and organic light-emitting diodes (OLEDs). Several methods for their preparation have been reported. Some of these are associated with one or more disadvantages, such as use of expensive reagents, harmful organic solvents, prolonged reaction times, or unsatisfactory yields.^[7–16] Ultrasound techniques are proving to be efficient and selective for improving traditional reactions that require long reaction times.^[11,17–20]

In organic syntheses, metal oxide ^[20,21] catalysts are alternatives for noble metal catalysts. Perovskites are mixed metal oxides with the general formula ABO₃.

Downloaded by [Universite Laval] at 11:15 04 March 2015

Lanthanides and/or alkaline earth metal ions usually occupy the A-site position, and first row transition metals the B-site position. Both A and B cations can be partially substituted, leading to multicomponent oxides A_{1-x}A'_xB_{1-v}B'_vO₃. Partial substitution of the A site causes lattice defects and abnormal valences in B site cations that usually enhance catalytic activity. Partial substitution of the B site brings about synergistic effects and influences the stability of the crystalline structure.^[22] For example, $AB_{0.5}B'_{0.5}O_3$ (A₂BB'O₆) is the most common ternary perovskite and Gallagher et al. have reported high activities for LaMn_{0.5}Cu_{0.5}O₃ in the oxidation of CO. The synergistic effect was explained by the combination of two functions, the activation of oxygen by manganese oxide and that of CO by copper ions. Levasseur and Kaliaguine have studied the catalytic combustion of CH₃OH, CO, and CH₄ over La_{1-v}Ce_vCo_{1-x}Fe_xO₃ perovskites.^[23] Herein we describe the effect of the mole fractions of various cations i.e. Fe, Co, and Sr on the catalytic performance of $La_xSr_{1-x}Fe_yCo_{1-y}O_3$ nanoperovskites for synthesis of imidazole derivatives. We report the development of the La_{0.8}Sr_{0.2}Fe_{0.34}Co_{0.66}O₃ catalytic system for convenient and efficient preparation of tetrasubstituted imidazoles in cyclocondensations of aldehyde, benzil, ammonium acetate and primary aromatic amine in water under ultrasonic irradiation and have synthesized a series of new tetrasubstituted imidazoles containing Me₃Si, C=S, and SH groups by use of (Me₃Si)₃CLi and CS₂.

RESULTS AND DISCUSSION

Nanostructured $La_xSr_{1-x}Fe_yCo_{1-y}O_3$ perovskite mixed oxides, prepared by the sol-gel combustion,^[22] were tested as catalysts for the synthesis of tetrasubstituted imidazole

derivatives which are used for preparation of mercaptobis(trimethylsilyl)thiones containing highly substituted imidazoles. A one-pot four-component condensation of 4methylbenzaldehyde (1 mmol) with aniline (1 mmol), benzil (1 mmol) and ammonium acetate (1.1 mmol) was used as a model for the synthesis of 1,4,5-triphenyl-2-p-tolyl-1Himidazole (1a). The reaction was carried out in the presence of catalytic amount (10 wt%) of catalyst in water under high intensity ultrasound irradiation. The desired product (1a) was obtained with 50% yield after 60 min. However, the reaction proceeded rather slowly and no significant catalysis was observed. Incorporation of various metals such as Sr and Co into LaFeO₃ to give the perovskites $La_xSr_{1-x}Fe_yCo_{1-y}O_3$ has led to improved yields. We showed that cyclocondensation was improved significantly by Sr substitution. The highest catalytic activity was observed when the mole fraction of lanthanum was around 0.8 and the mole fraction of strontium about 0.2. The inclusion of iron and cobalt ions at the B site improved catalyst activity further. In addition, cobalt was better than iron incorporation. The catalyst showed highest catalytic activity when the mole fraction of iron was lower than 0.5 (Table 1). The best results (95% yield, after 5 min) were obtained in the presence of 3 wt % of La_{0.8}Sr_{0.2}Fe_{0.34}Co_{0.66}O₃ in aqueous medium under ultrasound irradiation (Table 1, entry 10). This result is in agreement with our working hypothesis that a higher concentration of acidic sites gives higher yields. When other solvents such as acetonitrile, ethanol, THF, and methanol were used, the reactions were slower and the yields lower.

The reactions of various aldehydes, benzil, amines, and ammonium acetate were examined in the presence of $La_{0.8}Sr_{0.2}Fe_{0.34}Co_{0.66}O_3$ (3 mol%) in water under ultrasound

irradiation. In all cases, the requisite imidazole derivatives were obtained within three to six minutes in excellent yields (Table 2). Most of the tetrasubstituted imidazoles are known compounds and their identity was confirmed by IR, NMR, elemental analyses and melting points.^[24, 38-41]

A plausible mechanism for the catalytic activity of $La_{0.8}Sr_{0.2}Fe_{0.34}Co_{0.66}O_3$ is postulated in Scheme 1. $La_{0.8}Sr_{0.2}Fe_{0.34}Co_{0.66}O_3$ activates the carbonyl group of an aldehyde to facilitate the formation of diamine intermediate **A**. This catalyst also activates the diketone to facilitate the condensation with intermediate A to give imidazol-5-ol intermediate **C** which, upon elimination of water, is transformed into the desired 1,2,4,5tetrasubstituted imidazole.

We have recently used bulky tris(trimethylsilyl)methyllithium (TsiLi) as a reagent for the preparation of vinylsilanes, epoxysilanes, halovinylsilanes, silyl ethers, etc.^[25–31] To show the usefulness of the imidazoles generated during this study, imidazoles containing three different functional groups viz –mercapto, trimethylsilyl and thiocarbonyl–, have been made via nucleophilic attack of TsiLi at the carbon of CS₂ at -46 °C. (Bromomethyl)phenyl-imidazoles **2a–2d** were synthesized according to Scheme 2. **B**romination of the benzylic methyl group(s) in compounds **1a–1d** was achieved by use of *N*-bromosuccinimide (NBS) in CCl₄ in the presence of a catalytic amount of α , α - azobisisobutyronitrile (AIBN) at 50–52 °C. The crude products were used directly for the synthesis of thiones **3a–3d** by reaction with tris(trimethylsilyl)methyllithium and CS₂ at -46 °C, in short reaction times and with excellent yields. Furthemore, treatment of TsiLi

and CS_2 with bromopropoxy-imidazoles **2f** and **2g** was investigated. These compounds were synthesized by treatment of the hydroxyl-imidazoles **1f** and **1g** with K₂CO₃ and dibromopropane in DMF (Scheme 2). Reaction of TsiLi and CS_2 with **2f** and **2g** proceeded slowly and after 1h gave a poor yield. In contrast, the reactions of iodopropoxy-imidazoles were rapid and quantitative. Iodopropoxy-imidazoles were obtained by addition of potassium iodide (1.1 eq) to **2f** or **2g** in boiling acetone (Scheme 2). The crude products were directly used for the synthesis of thiones **3f** and **3g**.

The pathway for the formation of organosiliconsulfur-containing tetrasubstituted imidazoles is assumed to be by C-to-S migration of the SiMe₃ group, the formation of a carbanion (**b**) as in a Brook rearrangement and then conversion to the enethiolate (**c**). The resulting product **3** shows that the migration of sulfur to the central carbon of C(SiMe₃)₂ has occurred. It seems likely that the product **3** forms through the intermediates (**d**)–(**g**) and after hydrolysis of (**g**) (Scheme 3).^[32-36]

CONCLUSION

We have reported $La_{0.8}Sr_{0.2}Fe_{0.34}Co_{0.66}O_3$ -catalyzed four-component one-pot syntheses of multi-substituted imidazoles in water under ultrasound irradiation in excellent yields. The simple procedures combined with easy recovery and reuse of this catalyst make this method economically and environmentally benign. The organosiliconsulfur-containing tetrasubstituted imidazoles **3a–3d**, **3f** and **3g** were obtained in good yields. These synthetic intermediates are potential compounds for incorporation into silver

nanoparticles (AgNPs) by reaction with terminal-thiol groups. We shall investigate this possibility and discuss our results in future communications.

EXPERIMENTAL

Chemicals were either prepared in our laboratory or purchased from Merck, Fluka and Aldrich. Commercial products were used without further purification. The ¹H NMR and ¹³C NMR spectra were recorded with a Bruker FT-400 MHz spectrometer at room temperature and with CDCl₃ and/or DMSO- d_6 as solvent. The FT-IR spectra were recorded on a Bruker Tensor 270 spectrometer. The reactions were carried out using an ultrasonic processor probe (SONOPULS Ultrasonic homogenizers). The Elemental analyses were carried out with an Elementar vario EL III instrument. The abbreviations used for NMR signals are: s = singlet, d = doublet, t = triplet and m = multiplet. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes and are uncorrected.

Typical Procedure For The Synthesis Of 1-(4-Fluorophenyl)-4,5-Diphenyl-2-*P*-Tolyl-1*H*-Imidazole (1b)

The perovskite-type oxides were prepared as described by Niaei and co-workers.^[22] In a typical procedure, a mixture of benzil (1 mmol), 4-methylbenzaldehyde (1 mmol), amine (1 mmol), and ammonium acetate (1.1 mmol) as ammonia source and 3 mol% of $La_{0.8}Sr_{0.2}Fe_{0.34}Co_{0.66}O_3$ in 3 mL water was introduced in a 20 mL heavy walled pearshaped two necked flask with nonstandard tapered outer joint. The flask was attached to a 12 mm tip diameter probe and the reaction mixture was sonicated at ambient temperature

at 20% power of the processor. After completion of the reaction (monitored by TLC, within 3–6 min), the solid product was filtered off, washed with water, dried and recrystallized from ethanol. The supported reagent was washed three times with ethanol and dried under vacuum before reuse. The product was identified as 1-(4-fluorophenyl)-4,5-diphenyl-2-*p*-tolyl-1*H*-imidazole (**1b**) by spectral data.

White powder (96%), mp 188–190 °C, IR (KBr,cm⁻¹): $v_{max} = 3058$ (Ar–H), 2962 (C–H), 1602, 1508, 1444 (C=C), 960, 775, 730. ¹H NMR (CDCl₃, 400 MHz) δ_{H} : 2.36 (s, 3H, CH₃), 6.96–7.00 (m, 2H, Ar–H), 7.03–7.07 (m, 2H, Ar–H), 7.11 (d, 2H, J = 8.0 Hz, Ar–H), 7.14–7.17 (m, 2H, Ar–H), 7.21–7.32 (m, 6H, Ar–H), 7.35 (d, 2H, J = 8.0 Hz, Ar–H), 7.63 (d, 2H, J = 7.2 Hz, Ar–H). ¹³C NMR (CDCl₃, 100 MHz) δ_{C} : 20.24 (CH₃), 114.95, 115.17, 125.58, 126.32, 126.41, 127.01, 127.12, 127.41, 127.79, 127.88, 128.99, 129.08, 129.50, 129.58, 130.07, 132.19, 133.30, 137.16, 137.31, 146.12, 159.59, 162.06 (Ar). Anal.Calc. for C₂₈H₂₁FN₂: C, 83.14; H, 5.23; N, 6.93%. Found: C, 83.09; H, 5.14; N, 6.81%.

Typical Procedure For The Synthesis Of 2-(4-(Bromomethyl)Phenyl)-1-(4-Fluorophenyl)-4,5-Diphenyl-1*H*-Imidazole (2b)

Compound **2b** was prepared by reacting compound **1b** (1 mmol) with *N*bromosuccinimide (NBS) (1 mmol) in 70 mL of carbon tetrachloride under argon atmosphere. To initiate the reaction, 10 mol % of α, α' -azobisisobutyronitrile (AIBN) was added and the reaction mixture was stirred at 50–52 °C. The optimum reaction time for **2b** was observed to be 2 days. Then the reaction mixture was cooled to 10 °C, and the precipitated succinimide was filtered off. The solution was washed with water three times, the organic phase dried over Na_2SO_4 , and the solvent evaporated under vacuum. For example, crude product **2b** was purified by column chromatography (silica gel, hexane/ethylacetate mixture (10:1, v/v)) to afford bromo-methyl imidazole **2b**.

White powder (73%), mp 152–154 °C, IR (KBr, cm⁻¹): $v_{max} = 3058$ (Ar–H), 2924 (C–H), 1603, 1509, 1446 (C=C), 1225, 825, 777, 733, 698, 532. ¹H NMR (CDCl₃, 400 MHz) $\delta_{\rm H}$: 4.49 (s, 2H, CH₂–Br), 6.99–7.09 (m, 4H, Ar–H), 7.16 (dd, J = 1.6 Hz, J = 7.8 Hz, 2H, Ar–H), 7.24–7.34 (m, 8H, Ar–H), 7.44 (d, J = 8.3 Hz, 2H, Ar–H), 7.60–7.63 (m, 2H, Ar– H). ¹³C NMR (CDCl₃, 100 MHz) $\delta_{\rm C}$: 31.98 (CH₂–Br), 115.165, 115.39, 125.77, 126.32, 127.19, 127.48, 127.94, 128.01, 128.12, 128.99, 129.07, 129.22, 130.05, 131.95, 133.03, 136.78, 159.75, 162.23 (Ar). Anal.Calc. for C₂₈H₂₀BrFN₂: C, 69.57; H, 4.17; N, 5.80%. Found: C, 69.45; H, 4.09; N, 5.72%.

Typical Procedure For The Synthesis Of 1-(4-(3-Bromopropoxy)Phenyl)-2-(4-Chlorophenyl)-4,5-Diphenyl-1*H*-Imidazole (2f)

A mixture of (1 mmol) imidazole derivative (**1f**) and (1 mmol) 1,3-dibromopropane in the presence of K_2CO_3 in 100 mL of dry DMF was stirred at room temperature for 24 h. Then DMF solvent was evaporated in vacuum, and the residue was taken up in CH₂Cl₂ (50 mL) and the extract was washed with brine (30 mL) and then dried (Na₂SO₄). After filtration, the solvent evaporated, and the residue was purified by silica gel column chromatography using hexane/ethylacetate (75:25, v/v). Fraction containing bromopropoxy-imidazole was collected then the solvent was removed under reduced pressure.

Yellow powder (64%), mp 175–177 °C, IR (KBr, cm⁻¹): $v_{max} = 3059$ (Ar–H), 2925 (C–H), 1637, 1510, 1468 (C=C), 1239, 1169, 1090, 930, 694. ¹H NMR (CDCl₃, 400 MHz) δ_{H} : 2.02–2.09 (m, 2H, CH₂–CH₂–CH₂), 3.48 (t, *J* = 6.5 Hz, 2H, CH₂–Br), 3.94 (t, *J* 6.0 Hz, 2H, O–CH₂), 6.73–6.76 (m, 2H, Ar–H), 6.91–6.95 (m, 2H, Ar–H), 7.11–7.14 (m, 2H, Ar–H), 7.16-7.26 (m, 8H, Ar–H), 7.36–7.39 (m, 2H, Ar–H), 7.55–7.57 (m, 2H, Ar–H). ¹³C NMR (CDCl₃, 100 MHz) δ_{C} : 28.35 (CH₂–CH₂–CH₂), 31.36 (CH₂–Br), 65.97 (O–CH₂), 113.73, 125.54, 125.63, 126.29, 126.97, 127.16, 127.34, 127.36, 128.05, 128.34, 128.57, 129.01, 129.47, 130.05, 130.30, 133.16, 133.28, 137.24, 144.84, 157.49 (Ar). Anal.Calc. for C₃₀H₂₄BrClN₂O: C, 66.25; H, 4.45; N, 5.15%. Found: C, 66.33; H, 4.38; N, 5.31%.

Typical Procedure For The Synthesis Of 3-(4-(1-(4-Fluorophenyl)-4,5-Diphenyl-1*H*-**Imidazol-2-Yl)Phenyl)-1-Mercapto-1,1 Bis(Trimethylsilyl)Propane-2-Thione (3b)** Tris(trimethylsilyl)methyllithium, (Me₃Si)₃CLi was prepared as described by Gröbel and co-worker.^[37] To a stirred solution of tris(trimethylsilyl)methyllithium (1 mmol) in THF, carbon disulfide (1.2 mmol) in 2 mL THF was added at -46 °C (cyclohexanone/N₂) under argon atmosphere. The mixture was stirred for 5 min and then 2-(4-

(Bromomethyl)phenyl)-1-(4-fluorophenyl)-4,5-diphenyl-1*H*-imidazole (**2b**) (1 mmol) was added at this temperature and the stirring is maintained (-46 °C \rightarrow 0 °C) to the end of the reaction that followed by TLC. The mixture was poured into water and extracted with

 CH_2Cl_2 . The organic layer was washed with water, dried with Na_2SO_4 and filtered. The solvent was evaporated and the residue was purified by preparative TLC on silica gel using n-hexane/ethylacetate (v/v: 10:2) as eluent to give the product (**3b**).

A yellow sticky solid (96%), IR (KBr, cm⁻¹): $v_{max} = 3060$ (Ar–H), 2955 (C–H), 1605, 1561, 1508, 1482, 1447 (C=C), 1409, 1151 (C=S), 1253, 916, 855 (C–Si), 1028 (C–S). ¹H NMR (CDCl₃, 400 MHz) δ_{H} : 0.18 (s, 18H, SiMe₃), 3.14 (bs, 1H, S–H), 4.45 (s, 2H, CH₂), 6.94–7.00 (m, 4H, Ar–H), 7.11 (d, *J* = 6.8 Hz, 2H, Ar–H), 7.13–7.28 (m, 10H, Ar–H), 7.61 (d, *J* = 7.1 Hz, 2H, Ar–H). ¹³C NMR (CDCl₃, 100 MHz) δ_{C} : -1.18 (SiMe₃), 41.27 (CH₂), 55.40 (C(SiMe₃)₂SH), 115.04, 115.27, 126.33, 127.17, 127.31, 127.46, 127.59, 127.77, 127.84, 127.89, 127.96, 127.98, 128.95, 129.04, 129.96, 130.05, 130.25, 132.00, 137.56, 146.28, 159.66, 162.13 (Ar), 214.28 (C=S). Anal. Calc. for C₃₆H₃₉FN₂S₂Si₂: C, 67.67; H, 6.15; N, 4.38%. Found: C, 67.44; H, 6.29; N, 4.53%.

5-(4-(2-(4-Chlorophenyl)-4,5-Diphenyl-1H-Imidazol-1-Yl)Phenoxy)-1-Mercapto-1,1 Bis(Trimethylsilyl)Pentane-2-Thione (3f)

A yellow sticky solid (95%), IR (KBr, cm⁻¹): $v_{max} = 3060$ (Ar–H), 2955 (C–H), 1592, 1481, 1423 (C=C), 1410, 1149 (C=S), 1251, 915, 852 (C–Si), 1029 (C–S). ¹H NMR (CDCl₃, 400 MHz) $\delta_{\rm H}$: 0.19 (s, 18H, SiMe₃), 2.11–2.17 (m, 2H, CH₂–CH₂–CH₂), 3.17 (bs, 1H, S–*H*), 3.37 (t, *J* = 7.1 Hz, 2H, (CH₂–C(SiMe₃)₂S)), 4.01(t, *J* = 6.10 Hz, 2H, O–CH₂), 6.80 (d, *J* = 7.9 Hz, 2H, Ar–H), 6.98 (d, *J* = 8.1 Hz, 2H, Ar–H), 7.16 (d, *J* = 6.2 Hz, 2H, Ar–H), 7.23–7.32 (m, 8H, Ar–H), 7.43 (d, *J* = 7.9 Hz, 2H, Ar–H), 7.61 (d, *J* = 7.4, 2H, Ar–H). ¹³C NMR (CDCl₃, 100 MHz) $\delta_{\rm C}$: -1.18 (SiMe₃), 28.69 (CH₂), 38.43 (CH₂–

C(SiMe₃)₂S), 54.09 (C(SiMe₃)₂SH), 65.35 (O–CH₂), 113.84, 125.68, 126.35, 126.82, 127.02, 127.18, 127.39, 128.36, 128.13, 128.77, 128.89, 129.09, 129.59, 129.63, 130.09, 133.42, 137.13, 145.79, 157.67 (Ar), 213.95 (C=S). Anal. Calc. for C₃₈H₄₃ClN₂OS₂Si₂: C, 65.25; H, 6.20; N, 4.00%. Found: C, 65.31; H, 6.41; N, 3.88%.

ACKNOWLEDGMENT

We thank Dr. J.D. Smith for his helpful comments. The authors are thankful to those who contributed to enhancing this project, especially Dr. A. Niaei, Dr. D. Salari and Mrs Samira Arefi Oskoui.

SUPPLEMENTAL MATERIAL

Full experimental detail, and ¹H and ¹³C NMR spectra, for this article can be accessed on the publisher's website.

REFERENCES

1. Showell, G. A.; Mills, J. S. Drug Discov Today 2003, 8, 551.

2. Ziaee, M.; Samini, M.; Bolourtchian, M.; Ghaffarzadeh, M.; Ahmadi, M.; Egbal,

M. A.; Khorrami, A.; Andalib, S.; Maleki-Dizaji, N.; Garjani, A. *Iranian Journal of Pharmaceutical Research* **2012**, *11*, 91.

3. Li, Y.; Kock, d. C.; Smith, P. J.; Guzgay, H.; Hendricks, D. T.; Naran, K.;

Mizrahi, V.; Warner, D. F.; Chibala, K.; Smith, G. S. Organometallic 2013, 32, 141.

- 4. Block E.; Aslam, M. *Tetrahedron* **1988**, *44*, 281.
- 5. Hasaninejad, A.; Firoozi, S. *Mol. Divers.* **2013**, *17*, 459.

Downloaded by [Universite Laval] at 11:15 04 March 2015

- 6. Shahrisa, A.; Esmati, S. *Synlett* **2013**, *24*, 595.
- 7. Karimi, A. R.; Alimohammadi, Z.; Amini, M. M. Mol. Divers. 2010, 14, 635.
- 8. Safari, J.; Khalili, S. D.; Banitaba, S. H. Synth. Commun. 2011, 41, 2359.
- 9. Teimouri, A.; Najafi, C. A. J. Mol. Catal. A 2011, 346, 39.
- 10. Safari, J.; Gandomi-Ravandi, S.; Akbari, Z. J. Advanced Res. 2013, 4, 509.
- 11. Ramesh, K.; Murthy, S. N.; Karnakar, K.; Nageswar, Y. V. D.; Vijayalakhshmi,

K.; Prabhavathi, D. B. L. A.; Prasad, R. B. N. Tetrahedron Lett. 2012, 53, 1126.

- Vikrant, K.; Ritu, M.; Neha, S. *Research Journal of Chemical Sciences* 2012, 2,
 18.
- 13. Samai, S.; Nandi, G. C.; Singh, P.; Singh, M. S. Tetrahedron 2009, 65, 10155.
- Kumar, D.; Kommi, D. N.; Patel, A. R.; Chakraborti, A. K. Green Chem. 2012, 14, 2038.
- 15. Wang, X. B.; He, L.; Jian, T. Y.; Ye, S. Chin. Chem. Lett. 2012, 23, 13.
- 16. Marzouk, A. A.; Abbasov, V. M.; Talybov, A. H.; Mohamed, S. K. *World Journal of Organic Chemistry* **2013**, *1*, 6.
- 17. Safari, J.; Zarnegar, Z. Iranian Journal of catalysis 2012, 2, 121.
- Safari, J.; Dehghan Khalili, S.; Banitaba, S. H.; Dehghani, H. *Journal of Korean Chemical Society* 2011, 55, 787.
- 19. Safari, J.; javadian, L. Ultrasonics Sonochemistry 2014, 22, 341.
- 20. Safari, J.; Naseh, S.; Zarnegar, Z.; Akbari, Z. *Journal of Taibah University for Science* **2014**, in Press.
- Bandgar, B. P.; Hote, B. S.; Korbad, B. L.; Patil, S. A. *E-Journal of Chemistry* **2011**, *8*, 1339.

21. Arefi Oskoui, S.; Niaei, A.; Tseng, H-H.; Salari, D.; Izadkhah, B.; Hosseini, S. A. *ACS Comb. Sci.* **2013**, *15*, 609.

22. Hosseini, S. A.; Salari, D.; Niaei, A.; Arefi Oskoui, S. *Journal of Industrial and Engineering Chemistry* **2013**, *19*, 1903-1909.

23. Safa, K. D.; Sarchami, L.; Allahvirdinesbat, M.; Feyzi, A.; Nakhostin Panahi, P. *Journal of chemical research* **2014**, *38*, 571.

24. Safa, K. D.; Hassanpour, A.; Tofangdarzadeh S. Synth. Commun. 2009, 39, 1601.

25. Safa, K. D.; Ghorbanpour, K.; Hassanpour, A.; Tofangdarzadeh, S. J. Organomet. Chem. 2009, 694, 1907.

 Safa, K. D.; Behmagham, F.; Ghorbanpour, K.; J. Organomet. Chem. 2011, 696, 1840.

27. Safa, K. D.; Sharifi, E.; Tofangdarzadeh, S.; Hassanpour, A. *Phosphorus, Sulfur, and Silicon* **2010**, *182*, 2433.

28. Safa, K. D.; Mosaei, O. U. J. Organomet. Chem. 2010, 695, 26.

Safa, K. D.; Namvari, M.; Hassanpour, A.; Tofangdarzadeh, S. J. Organomet.
 Chem. 2009, 694, 2448.

30. Safa, K. D.; Abbasi, H.; Teimuri-Mofrad, R.; Charandabi, F. Aust. J. Chem. 2014,
67, 784.

31. Seyferth, D.; Hui, R. C. Tetrahedron Lett. 1984, 25, 2623.

32. Fleming, L.; Floyd, C. D. J. Chem. Soc. Perkin (1) **1981**, 1981, 969.

33. Wright, A.; Ling, D.; Boudjouk, P.; West, R. J. Am. Chem. Soc. 1972, 94, 4784.

34. Takeda, K.; Sumi, K.; Hagisawa, S. J. Organomet. Chem. **2000**, *611*, 449.

35. Kawashima, T. Chinese J. Chem. 2005, 23, 1267.

- 36. Gröbel, T.; Seebach, D. Chem. Ber. 1977, 110, 852.
- 37. Mahmoodi, N.O., Mamaghani, M., Behzadi, T. Mol. Divers. 2012, 16, 737.
- 38. Karami, B., Eskandari, K., Ghasemi, A. Turk. J. Chem. 2012, 36, 601.
- 39. Reddy, P.P., Mukkanti, K., Purandhar, K. RASAYAN. J. Chem. 2010, 3, 335.
- 40. Wang, X.B., He, L., Jian, T.Y., Ye, S. Chinese Chem. Lett. 2012, 23, 13.

Accepted Manus

Table 1 Optimization of the reaction conditions

$\begin{array}{c c} & & & & \\ & & & & \\ & & & \\ & & &$							
Entry	Catalyst (mol %)	Time (min)	Yield (%) ^a				
1	LaFeO ₃ (10)	60	50				
2	$La_1Fe_{0.5}Co_{0.5}O_3(5)$	40	57				
3	$La_1Fe_{0.66}Co_{0.34}O_3(5)$	40	60				
4	$La_{0.9}Sr_{0.1}Fe_{0.5}Co_{0.5}O_{3}(5)$	30	71				
5	$La_{0.9}Sr_{0.1}Fe_{0.82}Co_{0.18}O_3(5)$	30	65				
6	$La_{0.9}Sr_{0.1}Fe_{0.66}Co_{0.34}O_{3}(5)$	30	67				
7	$La_{0.8}Sr_{0.2} Fe_{0.66}Co_{0.34}O_{3}(5)$	10	78				
8	$La_{0.8}Sr_{0.2} Fe_{0.34}Co_{0.66}O_{3}(5)$	10	87				
9	$La_{0.8}Sr_{0.2} Fe_{0.34}Co_{0.66}O_{3}(3)$	10	95				
10	$La_{0.8}Sr_{0.2} Fe_{0.34}Co_{0.66}O_{3}(3)$	5	95				
11		120	20				

Reaction conditions: 4-methylbenzaldehyde (1.0 mmol), benzil (1.0 mmol), aniline (1.0 mmol), ammonium acetate (1.1 mmol), and 3 mol% $La_{0.8}Sr_{0.2}$ Fe_{0.34}Co_{0.66}O₃ in water under ultrasonic irradiation at ambient temperature at 20% power of the processor ^aIsolated yield





	[~] R ¹		R'	*
Entry ^a	Product	R ¹	R^2	Yield(%) ^b
1 ³⁹	1a	4-Me	Н	95
2^{24}	1b	4-Me	4-F	96
3 ⁴⁰	1c	4-Me	4-Cl	95
4 ²⁴	1d	4-Me	3-Cl	94
5 ²⁴	1e	Н	4-OH	95
6 ²⁴	1f	4-Cl	4-OH	93
7 ²⁴	1g	4-Me	4-OH	94
8 ²⁴	1h	4-OH	4-OH	92
9 ³⁸	1i	4-OH	4-Me	94
10^{41}	lj	Н	4-Me	94
11^{24}	1k	4-Cl	4-Me	94
12 ²⁴	11	4-Me	4-Br	93
1340	lm	4-Me	4-Me	95

^aReference

^bIsolated yield

Scheme 1 Plausible mechanism for the formation of 1,2,4,5-tetrasubstituted imidazoles in the presence of $La_{0.8}Sr_{0.2}Fe_{0.34}Co_{0.66}O_3$.





Scheme 2 Synthesis of organosiliconsulfur-containing tetrasubstituted imidazoles

Scheme 3 The proposed mechanism of the reaction of TsiLi, CS_2 and halo-methyl derivatives of imidazoles

