Res Chem Intermed
DOI 10.1007/s11164-016-2787-1

Synthesis of silyl-protected terminal thioalkyne-substituted tetraaryl imidazoles: utilization of Ag–Fe/ZSM-5 bimetallic nanooxides for cyclocondensation of polysubstituted imidazoles

Maryam Allahvirdinesbat[1] · Mohaddeseh Fozi[1] · Kazem D. Safa[1] · Maryam Alyari[1] · Parvaneh Nakhostin Panahi[2] · Aligholi Niaei[3]

Received: 20 May 2016 / Accepted: 14 October 2016

Abstract An improved one-pot and ecofriendly approach to tri- and tetraaryl imidazoles through three- and four-component coupling reactions under neutral and solvent-less solid-phase conditions is presented. A series of nanosized Ag/metal oxide species on H–ZSM-5 support were tested in this procedure, with Ag–Fe/ZSM-5 bimetallic oxide nanoparticles exhibiting excellent catalytic activity for improved efficiency of the one-pot, multicomponent cyclocondensation reaction. The obtained bromoimidazole derivatives were converted into silyl-protected terminal alkynyl thiolate-substituted tetraaryl imidazoles by treatment with lithium 2,2,2-tris(trimethylsilyl)ethanedithioate, produced by reaction of organolithium reagent $(Me_3Si)_3CLi$ with CS_2 at 0 °C. These novel and stable synthetic intermediates are potential compounds for functionalization of imidazoles.

Keywords Imidazole · MCRs · Alkynyl thiolation reaction · Silyl protecting group · Triple bond · Ag/metal nanooxides

Electronic supplementary material The online version of this article (doi:10.1007/s11164-016-2787-1) contains supplementary material, which is available to authorized users.

✉ Kazem D. Safa
dsafa@tabrizu.ac.ir

[1] Organosilicon Research Laboratory, Faculty of Chemistry, University of Tabriz, Tabriz 5166614766, Iran

[2] Department of Chemistry, Faculty of Science, University of Zanjan, Zanjan, Iran

[3] Department of Applied Chemistry and Chemical Engineering, Faculty of Chemistry, University of Tabriz, Tabriz 5166614766, Iran

Published online: 28 October 2016

Introduction

Silicon-containing analogs have diverse uses in organic chemistry from the most common application as protecting groups to essential building blocks in natural products [1]. Silylacetylenes are useful conduits for the most versatile terminal alkynes in a number of chemical reactions such as Diels–Alder reactions, and [2 + 2] and [2 + 3] cycloadditions [2]. On the other hand, alkynyl thiolates have emerged as powerful and versatile intermediates in a variety of synthetic transformations. This is based on the combination of the enhanced reactivity of the triple bond with a sulfur atom, frequently encountered in biological systems and materials [3]. S–C_{sp} bonds undergo a large number of reactions such as copper-catalyzed azide–alkyne cycloaddition and cross-coupling processes [4]. Due to the applications of Si–C_{sp} and S–C_{sp} bonds as key units in preparation of natural products and chemical compounds, we focus on biologically important heterocycles that contain a silyl-protected terminal alkynyl thiolate unit.

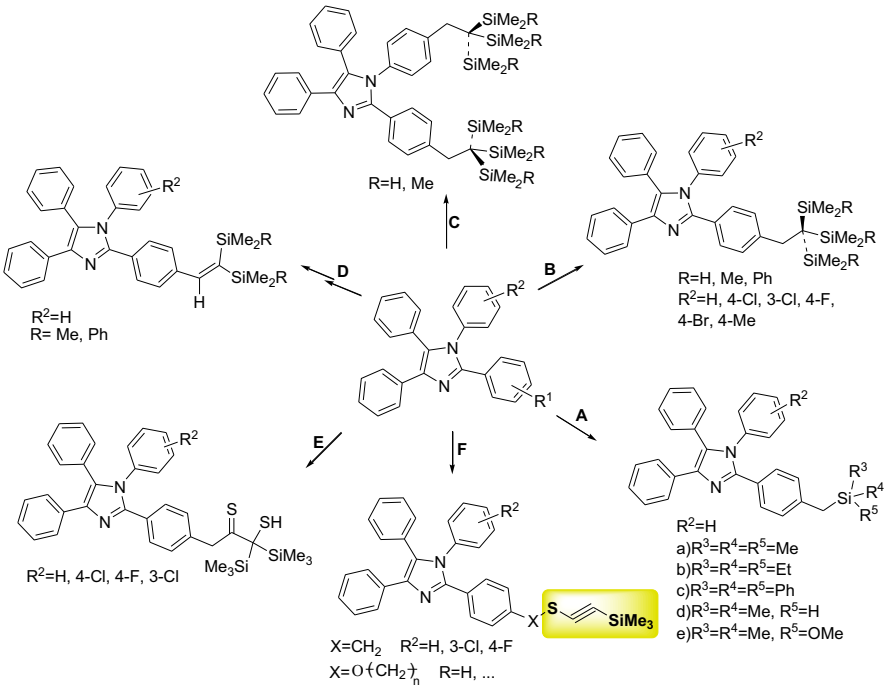
Zeolite-catalyzed multicomponent reactions (ZCMCRs) are efficient, environmentally friendly, and economic tools in organic and medicinal chemistry for synthesis of bioactive systems [5]. The imidazole scaffold has emerged as an active backbone in natural products (viz. biotin, the essential amino acid histidine, histamine, and pilocarpine alkaloids) and several drugs (e.g., naamidine a, olmesartan, losartan, trifenagrel, and eprosartan). Some imidazole-based derivatives have extensive applications in many fields, e.g., as organic optical materials, in anion sensors, and as ionic liquids [6–8]. This versatile applicability in materials science, and organic and medicinal chemistry highlights the importance of access to convenient synthetic methods for benign imidazole ring-containing derivatives. Several new routes have been reported for their synthesis. Cyclizations via one-pot multicomponent coupling reactions (MCRs) [9] represent a useful synthetic route for preparation of heterocyclic compounds. In recent years, design of cyclocondensation reactions under neutral and solvent-free solid-phase catalytic conditions has received enormous attention in the area of green MCR protocols [8, 10, 11].

Silver has long been recognized as a useful and convenient catalyst for a variety of reactions of commercial and environmental importance [12, 13]. Ag-loaded catalysts are active and durable at high reaction temperatures, especially in presence of water and sulfur dioxide [14].

As part of our work devoted to synthesis of highly substituted imidazoles, we report herein, for the first time, development of an Fe/Ag-modified ZSM-5 nanocatalyst for simple preparation of tri- and tetraaryl imidazoles using an MCR strategy under solvent-free conditions and synthesis of a series of imidazole derivatives terminated by trimethylsilylethynylthiolato groups via nucleophilic reaction of $(Me_3Si)_3CLi$ with carbon disulfide at 0 °C.

Results and discussion

Due to the significance of imidazole-based derivatives and silicon-containing analogs as useful building blocks in the chemical and pharmaceutical industry, we recently prepared a series of highly substituted imidazoles including carbosilane and silyl ether moieties [15] (route **A**, Scheme 1).



A: if R^1=CH_3, a) LDA/THF/r.t; b)R_3SiCl/THF/0°C or r.t
B: if R^1:CH_3, a) NBS,CCl_4/AIBN/50-52 °C; $(RMe_2Si)_3CLi$/THF/r.t
C: if R^1 and R^2:CH_3, a) NBS,CCl_4/AIBN/50-52 °C; $(RMe_2Si)_3CLi$/THF/r.t
or if R^1 and R^2: OH, a) $Br(CH_2)_4Br/K_2CO_3$/DMF; b) $RMe_2Si)_3CLi$/THF/r.t
D: if R^1=CH_3, a) DMSO-H_2O/IBX/EtOAc; b) $RMe_2Si)_3CLi$/THF/r.t
E: if R^1:CH_3, a) NBS,CCl_4/AIBN/50-52 °C; $(RMe_2Si)_3CLi/CS_2$/THF/-46°C
F: if R^1:CH_3, a) NBS,CCl_4/AIBN/50-52 °C; $(RMe_2Si)_3CLi$/THF/0°C
or if R^1 and R^2: OH, a) $Br(CH_2)_4Br/K_2CO_3$/DMF; b) $RMe_2Si)_3CLi$/THF/0°C

Scheme 1 Some of the synthetic strategies for construction of silicon-containing imidazoles

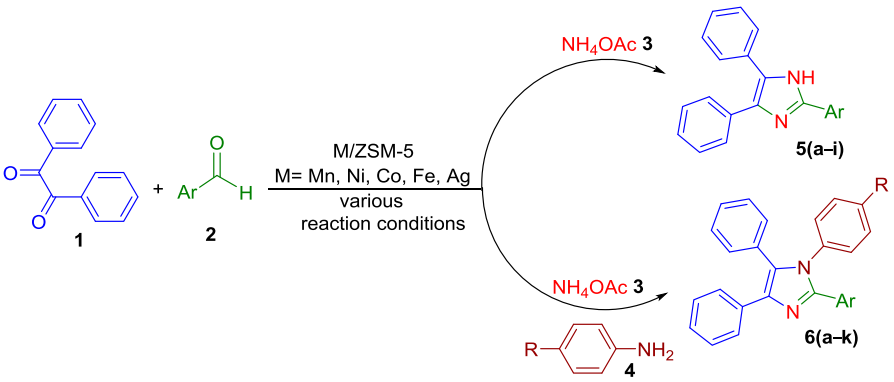
In previous work, silyl-substituted organometallic reagents $(RMe_2Si)_3CLi$ were studied for generation of synthetically useful multisubstituted imidazoles containing bulky organosilicon groups and organosilylvinyl substituent [16] (routes **B**, **C**, **D**, Scheme 1). In the other paper in this series, we reported the new type of chemistry of mixed organosulfur-silicon compounds with Me_3Si, SH, and C=S groups proceeding via nucleophilic attack of organometallic reagent $(Me_3Si)_3CLi$ at carbon atom of carbon disulfide in presence of several alkyl and benzyl halides possessing highly substituted imidazole core at −46 °C [17] (route **E**, Scheme 1). In another development, we investigated preparation of thioalkyne-substituted thiazolidine-2-thione derivatives using $(Me_3Si)_3CLi$ and CS_2 at temperature ranging from 0 to 25 °C [4]. In continuation of our investigations on synthesis of novel organosulfur-silicon compounds, we set out to study the generality of this reaction with several alkyl and benzyl bromides possessing polysubstituted imidazole core (route **F**, Scheme 1). Pursuing this matter further, initially, we optimized the reaction

conditions for synthesis of fully substituted imidazoles for use in synthesis of imidazole-based silyl-protected terminal alkynyl thiolates.

Due to the wide application of nanosized metal oxides on different supports as catalysts for a variety of chemical purposes and during the course of our studies towards development of facile and clean synthetic methodologies for biologically active compounds [15, 16, 18], we report herein an efficient green MCR protocol for synthesis of a variety of 2,4,5-triaryl and 1,2,4,5-tetraaryl imidazoles via cyclocondensation reactions under solvent-free conditions (Scheme 2).

Nanosized Ag/metal-modified ZSM-5 catalysts were tested for preparation of imidazole-based derivatives. The X-ray power diffraction (XRD) patterns of the H–ZSM-5 support, Ag/ZSM-5 monometallic catalyst, and Ag–Fe/ZSM-5 bimetallic catalyst are shown in Fig. 1. All the characteristic peaks corresponding to H–ZSM-5 appeared in the patterns of Ag/ZSM-5 and Ag–Fe/ZSM-5, suggesting that the original structure of the support was not destroyed during impregnation and calcination. No peaks due to metal oxides or metal could be detected in the diffractograms registered for all the metal-promoted samples. This implies that the metal oxide species are very small and are well dispersed in the support. The results of Transmission electron microscopy (TEM) analysis of H–ZSM-5 and Ag–Fe/ZSM-5 catalyst are shown in Fig. 2. The TEM images of the Ag–Fe/ZSM-5 catalyst indicate that nanooxide species (dark area) are uniformly distributed over H–ZSM-5.

To the best of the authors' knowledge, use of Ag-based catalysts for synthesis of triaryl imidazoles has not been reported to date. Thus, we sought to optimize the reaction condition for formation of 2-(4-fluorophenyl)-4,5-diphenyl-1*H*-imidazole (**5b**) as model reaction via one-pot three-component reaction of 1,2-diketone (1 mmol), ammonium acetate (2.2 mmol), and 4-fluorobenzaldehyde (1 mmol), examining the catalytic effect of nanosized Ag/metal-ZSM-5 oxide species, the weight loadings of transition metal (wt%), the amount of catalysts, temperature, and time. We first tested this reaction in presence of pure H–ZSM-5 under solvent-free condition at 120 °C; however, the yield of **5b** was low (Table 1, entry 10). Table 1 shows that, when the model reaction was studied in presence of M/ZSM-5 (M: Ag,



Scheme 2 Preparation of 2,4,5-triaryl and 1,2,4,5-tetraaryl imidazoles using metal-supported nanocatalysts under various reaction conditions

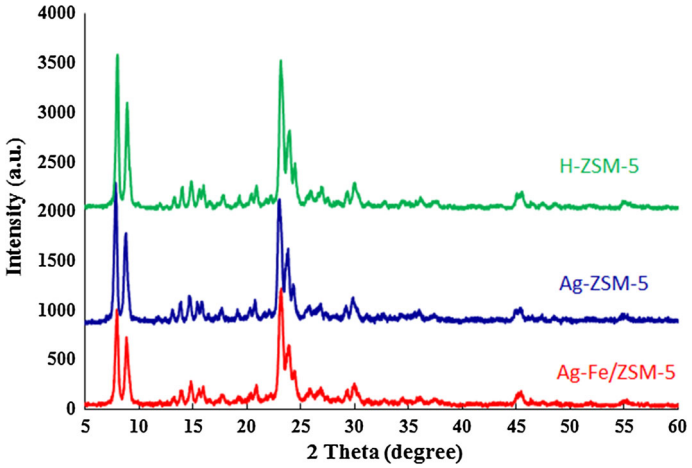


Fig. 1 XRD patterns of H–ZSM-5 support, Ag/ZSM-5 monometallic nanostructure, and Ag–Fe/ZSM-5 bimetallic nanostructure

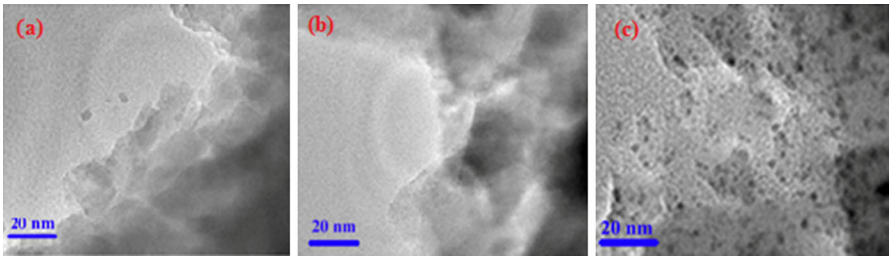


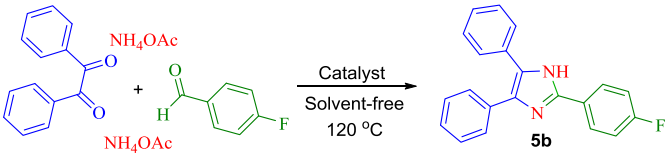
Fig. 2 TEM images of H–ZSM-5 support (**a**), Ag/ZSM-5 monometallic nanostructure (**b**), and Ag– Fe/ZSM-5 bimetallic nanostructure (**c**)

Mn, Co, Ni, and Fe) supported nanocatalysts (10 wt%) in the same conditions, the corresponding product **5b** was isolated in 40–65 % yield after 3 h. The behavior of Ag and Fe is very similar, having higher activity than Mn, Co or Ni (Table 1, entries 1–5).

Ag/ZSM-5 monometallic nanooxide was prepared with different Ag loadings (3, 5, and 8 wt%). The results showed that the cyclocondensation increased with increasing silver loading, passing through a maximum at loading of 5 wt%. Additional increase in the Ag loading had no further effect on the cyclocondensation. This can be attributed to excessive Ag agglomeration that blocked the pores inside and inhibited access of reactants to active sites of the support. Therefore, Ag loading of 5 wt% on H–ZSM-5 was found to be the optimum loading in this investigation. However, the proposed reaction proceeded rather slowly, and no remarkable acceleration was observed.

In the present study, an attempt was made to prepare a series of Ag–M/ZSM-5 (M = Co, Mn, Fe, and Ni) zeolite-supported Ag-based multicomponent catalysts that would improve the catalytic ability of the heterogeneous catalyst for

Table 1 Optimization of reaction conditions



Entry	Catalyst (wt%)	Time (h)	Yield (%)[a]
1	Mn/ZSM-5 (10)	3	40
2	Co/ZSM-5 (10)	3	45
3	Ni/ZSM-5 (10)	3	50
4	Fe/ZSM-5 (10)	3	63
5	Ag/ZSM-5 (10)	3	65
6	Ag–Mn/ZSM-5 (5)	1	60
7	Ag–Co/ZSM-5 (5)	1	74
8	Ag–Ni/ZSM-5 (5)	1	82
9	Ag–Fe/ZSM-5 (5)	1	95
10	H–ZSM-5 (10)	1 day	30
11	No catalyst	1 day	Trace

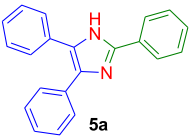
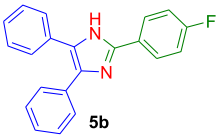
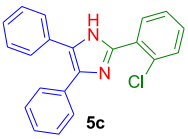
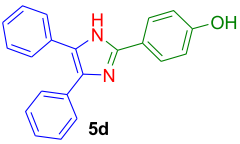
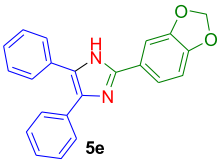
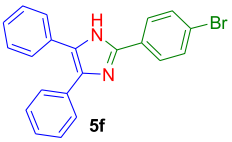
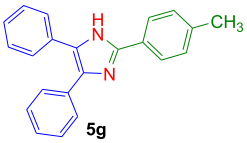
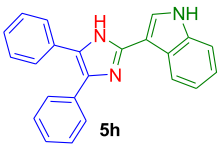
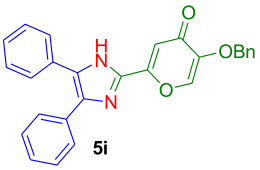
Reaction conditions: 1,2-diketone (1 mmol), ammonium acetate (2.2 mmol), and 4-fluorobenzaldehyde (1 mmol). The metal content was kept at 5 wt% for M/ZSM-5 catalysts and 2 wt% for Ag–M/ZSM-5 catalysts

[a] Indicated yields refer to isolated products

preparation of 2,4,5-trisubstituted imidazoles. Furthermore, study of the catalytic ability of the Ag–Fe/ZSM-5 catalyst showed that incorporating Fe over Ag/ZSM-5 increased the product yield to 95 % and reduced the reaction time (1 h) with decreased catalyst loading (5 wt%) under solvent-free condition at 120 °C (Table 1, entry 9). The highest activity of Ag–Fe/ZSM-5 for preparation of triaryl imidazoles can be attributed to the favorable synergetic effects of silver and iron over H–ZSM-5, acidity, and reactant adsorption ability on the catalyst surface. Also, we studied the effect of various solvents such as EtOH, EtOAc, and CH_2Cl_2 on the model reaction. Polar solvents and solventless conditions afforded better yield than nonpolar solvent, with the best result obtained under solvent-free condition with Ag–Fe/ZSM-5 catalyst.

To further show the applicability of this protocol, 5-(benzyloxy)-4-oxo-4*H*-pyran-2-carbaldehyde was tested in the previous reaction. Unfortunately, the corresponding triaryl imidazole was isolated in poor yield due to formation of byproducts (Table 2, entry 9). In comparison, synthesis of derivatives **5a**–**i** with a wide range of substituted diverse aldehydes bearing either electron-withdrawing or electron-donating groups and heterocyclic substrates was studied under the same experimental conditions, and the desired derivatives were obtained in high yield

Table 2 Synthesis of 2,4,5-triaryl imidazoles[a]

 **5a**	 **5b**	 **5c**
[Time: 1 h/Yield: 92%] MP: 272–274 °C (272–273 °C)[19]	[Time: 1 h/Yield: 95%] MP: 200–202 °C (201–202 °C)[19]	[Time: 1 h/Yield: 93%] MP: 190–192 °C (192–193 °C)[19]
 **5d**	 **5e**	 **5f**
[Time: 1 h/Yield: 92%] MP: 243–244 °C (242–243°C)[19]	[Time: 1 h/Yield: 95%] MP: 251–253 °C	[Time: 1 h/Yield: 93%] MP: 264–266 °C (265–266 °C)[19]
 **5g**	 **5h**	 **5i**
[Time: 1 h/Yield: 92%] MP: 236–237 °C (236–238 °C)[20]	[Time: 1 h/Yield: 95%] MP: 281–283 °C	[Time: 4 h/Yield: trace]

Reaction conditions: aldehyde (1 mmol), benzil (1 mmol), ammonium acetate (2.2 mmol), and 5 wt% Ag–Fe/ZSM-5 for preparation of **5a–i** under solvent-free condition at 120 °C

[a] Indicated yields refer to isolated products

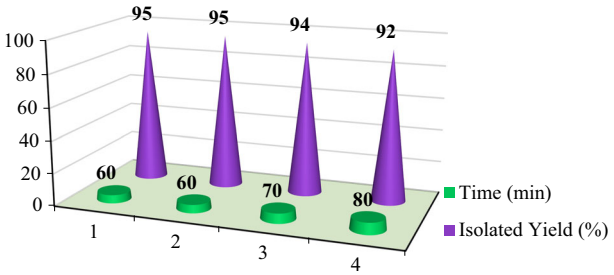


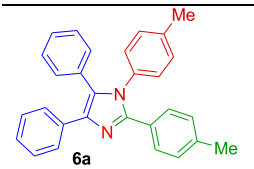
Fig. 3 Reusability results for Ag–Fe/ZSM-5 in preparation of **5b**

without significant amounts of undesirable byproducts (Table 2). Furthermore, the reaction conditions are mild enough not to react with acid-sensitive moieties, such as ethers, which often undergo cleavage in highly acidic media (**5e**).

In addition to the benefits from the economical point of view, easy recovery and reusability of catalyst is very significant to avoid waste. Consequently, we tested the catalytic performance of recycled Ag–Fe/ZSM-5 in the model reaction. As shown in Fig. 3, the recovered catalyst could be reused three times without appreciable loss of its activity during storage.

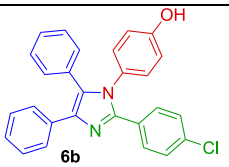
Following the optimized conditions, an array of tetraaryl imidazoles were synthesized using the same reaction conditions. The substrate scope of the reaction was evaluated using a variety of amines and aromatic aldehyde derivatives (Table 3). In all cases, corresponding products were prepared in excellent yield

Table 3 Synthesis of 1,2,4,5-tetraaryl imidazoles[a]



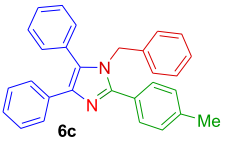
6a

[Time 1h/Yield: 82%]
MP: 189–191°C(189-19 °C)[19]



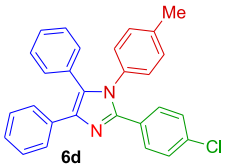
6b

[Time 1h/Yield: 85%]
MP: >280 °C(>280 °C)[19]



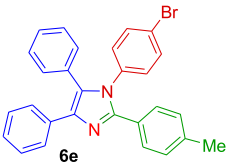
6c

[Time 1h/Yield: 83%]
MP: 190-192 °C(190-192 °C)[19]



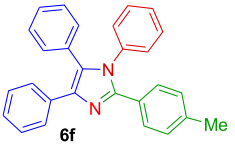
6d

[Time 1h/Yield: 84%]
MP:167-169 °C (167-169 °C)[20]



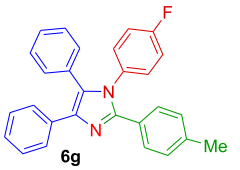
6e

[Time 1h/Yield: 83%]
MP: 190-192 °C(190-192 °C)[20]



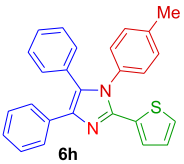
6f

[Time 1h/Yield: 83%]
MP: 183–184 °C(183-185 °C)[20]



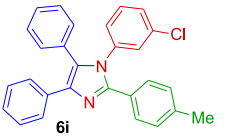
6g

[Time 1h/Yield: 83%]
MP: 188-190 °C (188-190 °C)[20]



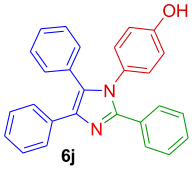
6h

[Time 1h/Yield: 85%]
MP:177-179 °C (177-179 °C)[19]



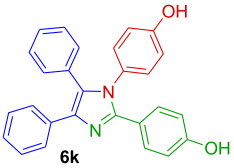
6i

[Time 1h/Yield: 84%]
MP: 198-200 °C(198-200 °C)[19]



6j

[Time 1h/Yield: 84%]
MP: >280 °C(>280 °C)[19]



6k

[Time 1h/Yield: 84%]
MP: >280 °C (>280 °C)[19]

Reaction conditions: aldehyde (1 mmol), benzil (1 mmol), ammonium acetate (1.1 mmol), amine (1 mmol), and 5 wt% Ag–Fe/ZSM-5 for synthesis of **6a–k** under solvent-free condition at 120 °C

[a] Indicated yields refer to isolated products

(Table 3) without preparation of any byproducts such as 2,4,5-triaryl imidazoles, oxidized products of aniline and aldehyde derivatives, which are generally observed in strong acid media.

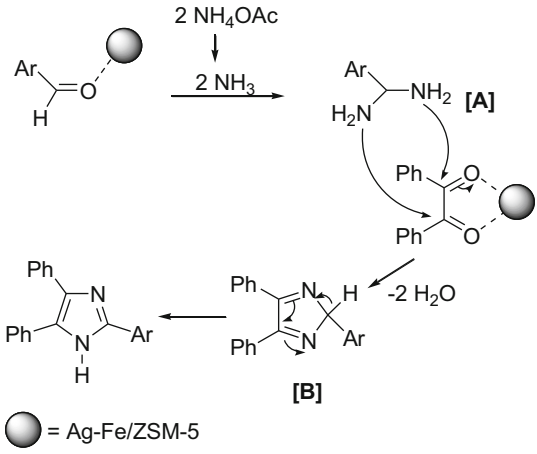
A plausible route for the catalytic activity of Ag–Fe/ZSM-5 is postulated in Scheme 3. Ag–Fe/ZSM-5 nanocatalyst facilitates formation of diamine intermediate [**A**] by increasing the electrophilicity of the aldehyde's carbonyl group. Intermediate [**A**], in presence of Ag–Fe/ZSM-5, condenses with diketone to form intermediate [**B**], which in turn rearranges to the 2,4,5-triaryl imidazole by a [1, 5] hydrogen shift (Scheme 3).

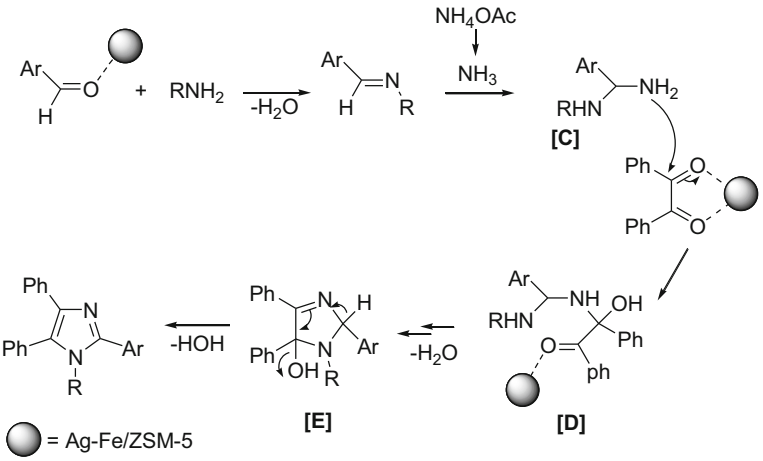
Similarly, a plausible mechanism for the preparation of the tetraaryl imidazole involves the formation of intermediate [**C**] by reaction of an aldehyde, primary amine, and ammonium acetate using Ag–Fe/ZSM-5 as catalyst. Intermediate [**C**] condenses with diketone to form intermediate [**D**], to obtain imidazol-5-ol intermediate [**E**] that, upon elimination of water, is transformed into the desired products (Scheme 4).

To extend our investigation, some tetraaryl imidazoles containing triple bond including sulfur atom and trimethylsilyl group were synthesized through nucleophilic reaction of $(Me_3Si)_3CLi$ with carbon disulfide at 0 °C.

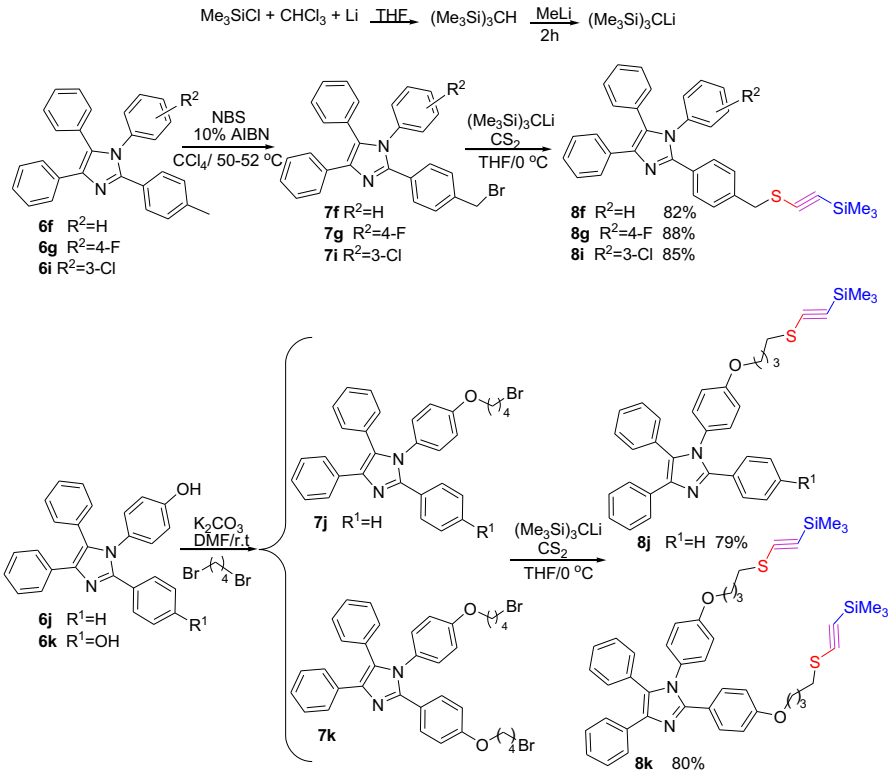
(Bromomethyl)phenyl-imidazoles **7f**, **g**, **i** were synthesized according to Scheme 5. Following use of *N*-bromosuccinimide (NBS) in CCl_4 in presence of catalytic amount of α,α′-azobisisobutyronitrile (AIBN) at 50–52 °C, bromination products were obtained, to which we assign the structures **6f**, **g**, **i**. The crude products were used directly for preparation of compounds **8f**, **g**, **i** by reaction with tris(trimethylsilyl)methyllithium and CS_2 at 0 °C, in short reaction time and high yield. In addition, treatment of TsiLi and CS_2 with bromobutoxy-imidazoles **7j**, **k** was investigated. These compounds were synthesized by treatment of the hydroxyl-imidazoles **6j**, **k** with K_2CO_3 and 1,4-dibromobutane in Dimethylformamide (DMF) (Scheme 5). Reaction of TsiLi and CS_2 with **7j**, **k** gave compounds

Scheme 3 Proposed route for preparation of 2,4,5-triaryl imidazoles using Ag–Fe/ZSM-5

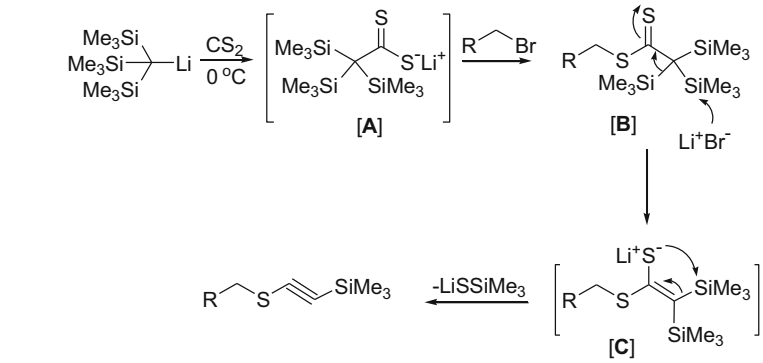




Scheme 4 Proposed route for preparation of 1,2,4,5-tetraaryl imidazoles by Ag–Fe/ZSM-5



Scheme 5 Preparation of organosulfur-silicon-containing tetraaryl imidazoles



Scheme 6 Plausible mechanism for reaction of TsiLi, CS_2, and bromoimidazoles

8j, **k** at 0 °C. All spectroscopic results indicated that the nucleophilic substitution on bromoimidazoles was complete.

The precursor $(Me_3Si)_3CH$ was prepared by reaction of Li, chloroform, and trimethylsilyl chloride in tetrahydrofuran (THF). The solvated organolithium reagent $(Me_3Si)_3CLi$ was obtained by treatment of $(Me_3Si)_3CH$ with methyllithium under reflux conditions in THF (Scheme 5).

A possible mechanism for the synthesis of trimethylsilylethynylthiolato group-containing tetraaryl imidazoles is depicted in Scheme 6. First, addition of carbon disulfide to tris(trimethylsilyl)methyllithium at 0 °C produced lithium 2,2,2-tris(trimethylsilyl)ethanedithioate $(Me_3Si)_3C(S)SLi$ (**A**) as intermediate, which subsequently reacted with alkyl and benzyl bromides possessing highly substituted imidazole core (**7f**, **g**, **i**–**k**) to give $(Me_3Si)_3C(S)SCH_2R$ (**B**). E_2 elimination from **B** with nucleophilic attack of Br^- at Me_3Si, which leads to loss of $BrSiMe_3$ group, produced **C**. Intermediate **C** was unstable with respect to loss of $LiSSiMe_3$ group, resulting in final products **8f**, **g**, **i**–**k** (Scheme 6).

Conclusions

We successfully developed a straightforward and atom-economic green approach for synthesis of structurally diverse 2,4,5-triaryl and 1,2,4,5-tetraaryl imidazoles, employing nanosized Ag/metal oxide species on H–ZSM-5 as promoter under solvent-less condition. The protocol has several advantages such as excellent yield combined with ease of recovery and reuse of the catalyst, being a waste-free chemical process with methodological ease due to formation of carbon–carbon and carbon–nitrogen bonds in a single step. We also describe an efficient synthetic strategy for silyl-protected terminal alkynyl thiolates from alkyl and benzyl bromides possessing highly substituted imidazole core at 0 °C. Imidazoles bearing trimethylsilylethynylthiolato groups are key intermediates for functionalization of

imidazoles through preparation of alkynyl thiolate units. We will study this possibility and discuss our results in future communications.

Experimental

Materials and techniques

Chemicals were either synthesized in our laboratory or purchased from Fluka, Merck, and Aldrich. Commercial products were used without further purification. All yields refer to isolated products. The Fourier transform infrared spectroscopy (FTIR) spectra of the compounds were obtained on a Bruker Tensor 270 spectrometer. ^{1}H and ^{13}C Nuclear magnetic resonance spectroscopy (NMR) spectra were measured with a Bruker FT-400 MHz spectrometer at room temperature with $CDCl_3$ and/or Dimethyl sulfoxide (DMSO)-d_6 as solvent. The abbreviations used for NMR signals are: s = singlet, d = doublet, t = triplet, and m = multiplet. Elemental analyses were performed using an Elementar Vario EL III instrument. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes and are uncorrected.

Preparation of catalysts

Ag/ZSM-5 nanooxides with various loadings of Ag (3, 5, and 8 wt%) and other monometallic nanooxides (with metal content 5 %) were prepared by the incipient wetness impregnation technique, and other all bimetallic nanooxides with 5 wt% Ag and 2 wt% transition metal were obtained by the simultaneous impregnation procedure. The precursors for metals were $AgNO_3$, $Co(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, and $Mn(NO_3)_2{\cdot}4H_2O$. H–ZSM-5 support obtained from Zeochem Int with $SiO_2/Al_2O_3 = 50$ was used to fabricate the catalysts. Typically, 1 g H–ZSM-5 zeolite was added to aqueous solution containing calculated amounts of silver nitrate and transition-metal nitrate, followed by continuous stirring at 45 °C until the slurry was completely dry. The prepared samples were dried at 110 °C overnight and calcined at 600 °C for 4 h in air.

Characterization of catalysts

Powder X-ray diffraction patterns of the prepared catalysts were obtained at room temperature using a D500 diffractometer (Siemens) with Cu K_α radiation ($\lambda = 0.154050$ nm) in the 2θ range of 5–70° at scan rate of 0.016 s^{-1}. The morphology of the obtained catalysts was observed by transmission electron microscopy using a JEOL 2000 (JEOL, Japan) operated at 200 kV.

General procedure for synthesis of 2,4,5-triaryl imidazoles 5a–i

A mixture of benzil (1 mmol), aldehyde (1 mmol), ammonium acetate (2.2 mmol), and Ag–Fe/ZSM-5 (3 wt%) was heated at 120 °C within 50–70 min. After completion of the reaction as indicated by thin-layer chromatography (TLC), the

reaction mixture was cooled to room temperature. The mixture was dissolved in ethanol, and supported reagent was separated by filtration. The crude product was recrystallized from ethanol to afford the pure products. The catalyst was washed three times with ethanol and dried under vacuum before reuse. The spectroscopic data of some of the new products are given below.

*2-(2-Chlorophenyl)-4,5-diphenyl-1H-imidazole (**5c**)*

White powder; yield 94 %; m.p. = 190–192 °C; FTIR (KBr, cm^{-1}): 3437, 3062, 2956, 1599, 1501, 1477, 1445, 1386, 971, 763, 695, 518. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.24–7.45 (m, 9H, Ar–H), 7.56–7.58 (m, 4H, ArH), 8.39 (d, $J = 7.4$ Hz, 1H, ArH), 10.11 (s, 1H, N–H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 126.43, 126.51, 126.73, 126.86, 126.90, 127.42, 127.62, 128.55, 129.40, 129.81, 142.16. Anal. Calcd. for $C_{21}H_{15}ClN_2$: C 76.24, H 4.57, N 8.47 %. Found: C 76.01, H 4.78, N 8.19 %.

*4-(4,5-Diphenyl-1H-imidazol-2-yl)phenol (**5d**)*

White powder; yield 96 %; m.p. = 243–244 °C; FTIR (KBr, cm^{-1}): 3616, 3359, 3056, 2976, 1648, 1608, 1546, 1497, 1447, 1359, 1250, 835, 767, 739, 695. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 6.80 (d, $J = 8.4$ Hz, 2H, ArH), 7.16 (t, $J = 7.0$ Hz, 1H, ArH), 7.25 (t, $J = 7.4$ Hz, 2H, ArH), 7.31 (t, $J = 7.0$ Hz, 1H, ArH), 7.38 (t, $J = 7.5$ Hz, 2H, ArH), 7.44 (d, $J = 7.1$ Hz, 2H, ArH), 7.48 (d, $J = 8.0$ Hz, 2H, ArH), 7.85 (d, $J = 8.5$ Hz, 2H, ArH), 9.77 (s, 1H, O–H), 12.38 (s, 1H, N–H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 115.46, 121.66, 126.44, 126.91, 127.10, 127.43, 127.61, 128.22, 128.36, 128.70, 131.33, 135.43, 136.63, 146.12, 157.83. Anal. Calcd. for $C_{21}H_{16}N_2O$: C 80.75, H 5.16, N 8.97 %. Found: C 80.95, H 5.01, N 9.08 %.

*2-(Benzo[d][1,3]dioxol-5-yl)-4,5-diphenyl-1H-imidazole (**5e**)*

White powder; yield 96 %; m.p. = 251–253 °C; FTIR (KBr, cm^{-1}): 3415, 3058, 2973, 2884, 1634, 1605, 1481, 1339, 1237, 1159, 1070, 1038, 934, 814, 767, 733, 697. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.93 (s, 1H, N–H), 6.02 (s, 2H, O–CH_2–O), 6.85 (d, $J = 7.8$ Hz, 2H, ArH), 7.29–7.56 (m, 10H, ArH), 7.76 (d, $J = 7.4$ Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 58.29, 100.14, 100.35, 105.21, 106.72, 107.46, 107.54, 118.28, 120.20, 123.18, 126.03, 126.35, 126.79, 127.54, 127.58, 130.79, 144.93, 147.16, 147.22. Anal. Calcd. for $C_{22}H_{16}N_2O_2$: C 77.63, H 4.74, N 8.23 %. Found: C 77.45, H 4.93, N 7.99 %.

*4,5-Diphenyl-2-p-tolyl-1H-imidazole (**5g**)*

White powder; yield 97 %; m.p. = 236–238 °C; FTIR (KBr, cm^{-1}): 3335, 3056, 2948, 2916, 1634, 1576, 1526, 1489, 1453, 1348, 1296, 820, 722, 693, 595. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.26 (s, 3H, CH_3), 5.55 (s, 1H, N–H), 7.04 (d, $J = 7.5$ Hz, 2H, ArH), 7.16 (d, $J = 7.5$ Hz, 2H, ArH), 7.26–7.38 (m, 7H, ArH),

7.43 (d, $J = 6.9$ Hz, 1H, ArH), 7.73 (d, $J = 7.7$ Hz, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 20.12, 126.00, 126.49, 127.53, 128.41, 130.61, 134.74. Anal. Calcd. for $C_{22}H_{18}N_2$: C 85.13, H 5.85, N 9.03 %. Found: C 85.35, H 5.70, N 9.25 %.

*3-(4,5-Diphenyl-1H-imidazol-2-yl)-1H-indole (**5h**)*

Red powder; yield 96 %; m.p. = 281–283 °C; FTIR (KBr, cm^{-1}): 3630, 3412, 3053, 2965, 2889, 1665, 1598, 1492, 1449, 1335, 1267, 751, 697, 512. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 7.12–7.23 (m, 3H, ArH), 7.30–7.37 (m, 3H, ArH), 7.42–7.46 (m, 3H, ArH), 7.51 (d, $J = 7.3$ Hz, 2H, ArH), 7.63 (d, $J = 7.4$ Hz, 2H, ArH), 7.99 (d, $J = 2.4$ Hz, 1H, ArH), 8.46 (d, $J = 7.4$ Hz, 1H, ArH), 11.39 (s, 1H, N–H (indol)), 12.30 (s, 1H, N–H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 38.83, 39.08, 39.29, 39.50, 39.71, 39.92, 40.12, 106.86, 111.70, 119.80, 121.56, 121.96, 123.85, 125.1, 125.82, 126.28, 126.95, 127.49, 128.23, 128.27, 128.79, 131.66, 135.77, 136.32, 143.80. Anal. Calcd. for $C_{23}H_{17}N_3$: C 82.36, H 5.11, N 12.53 %. Found: C 82.08, H 5.32, N 12.35 %.

General procedure for synthesis of 1,2,4,5-tetraaryl imidazoles 6a–k

A mixture of benzil (1 mmol), aldehyde (1 mmol), ammonium acetate (1.1 mmol), amine (1 mmol), and Ag–Fe/ZSM-5 (3 wt%) was heated at 120 °C within 50–70 min. After completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature. The mixture was dissolved in ethanol, and supported reagent was separated by filtration. The crude product was recrystallized from ethanol to afford the pure products. The catalyst was washed three times with ethanol and dried under vacuum before reuse. The spectroscopic data of some of the products were given in Refs. [19, 20].

General procedure for bromination of imidazole derivatives was described in Refs. [16, 17]; they were used for preparation of silyl-protected terminal alkynyl thiolates containing tetraaryl imidazoles.

General procedure for preparation of silyl-protected terminal alkynyl thiolates containing tetraaryl imidazoles

Tris(trimethylsilyl)methyllithium $(Me_3Si)_3CLi$ was synthesized as described by Gröbel and coworkers [21]. Carbon disulfide (1.2 mmol) in 2 mL THF was added to a stirred solution of tris(trimethylsilyl)methyllithium (1 mmol) in THF at 0 °C under argon atmosphere. The mixture was stirred for 5 min, alkyl and benzyl bromides possessing tetraaryl imidazole core (1 mmol) or bis(bromobutoxy)imidazole (0.5 mmol) was added at this temperature, and the stirring was maintained to the end of the reaction as followed by TLC. The mixture was poured into water and extracted with EtOAc. The organic layer was washed with water, dried with $MgSO_4$, and filtered. The solvent was removed in vacuum, 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. Characterization data for the new products are given below:

*2-(4-((2-(Trimethylsilyl)ethynylthio)methyl)phenyl)-1,4,5-triphenyl-1H-imidazole (**8f**)*

Yellow sticky solid (82 %). FTIR (KBr, cm^{-1}): 3059, 2957, 2923, 2853, 2091 (C≡C), 1740, 1681, 1600, 1495, 1450 (C=C), 1250, 841 (C–Si), 759, 697, 539. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.13 (s, 9H, $SiMe_3$), 3.87 (s, 2H, CH_2), 6.98–7.15 (m, 4H, Ar–H), 7.17–7.48 (m, 11H, Ar–H), 7.58 (dd, $J = 1.8$ Hz, $J = 7.3$ Hz, 2H, Ar–H), 7.66–7.69 (m, 2H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 1.08 ($SiMe_3$), 38.98 (CH_2), 90.85 and 100.92 (C≡C), 126.21, 126.36, 126.80, 127.16, 127.33, 127.38, 127.41, 127.54, 127.85, 127.95, 128.15, 128.19, 131.32, 136.34, 138.16. Anal. Calcd. for C_{33} $H_{30}N_2SSi$: C 77.00, H 5.87, N 5.44 %. Found: C 77.31, H 5.94, N 5.82 %.

*2-(4-((2-(Trimethylsilyl)ethynylthio)methyl)phenyl)-1-(4-fluorophenyl)-4,5-diphenyl-1H-imidazole (**8g**)*

Yellow sticky solid (88 %). FTIR (KBr, cm^{-1}): 3055, 2956, 2090 (C≡C), 1602, 1507, 1444 (C=C), 1250, 843 (C–Si), 774, 699, 657, 528. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.13 (s, 9H, $SiMe_3$), 3.88 (s, 2H, CH_2), 6.97 (d, $J = 8.2$ Hz, 2H, Ar–H), 7.02–7.03 (m, 2H, Ar–H), 7.11 (d, $J = 6.4$ Hz, 2H, Ar–H), 7.20–7.26 (m, 8H, Ar–H), 7.40 (d, $J = 8.1$ Hz, 2H, Ar–H), 7.57 (d, $J = 7.2$ Hz, 2H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −1.11 ($SiMe_3$), 38.94 (CH_2), 90.09 and 101.04 (C≡C), 115.16, 115.39, 125.81, 126.37, 127.04, 127.14, 127.21, 127.50, 127.97, 129.05, 129.13, 129.37, 129.45, 129.58, 130.10, 131.98, 133.35, 136.27, 142.21, 145.00, 160.10, 161.07. Anal. Calcd. for $C_{33}H_{29}FN_2SSi$: C 74.40, H 5.49, N 5.26 %. Found: C 74.28, H 5.54, N 5.02 %.

*2-(4-((2-(Trimethylsilyl)ethynylthio)methyl)phenyl)-1-(3-chlorophenyl)-4,5-diphenyl-1H-imidazole (**8i**)*

Yellow sticky solid (85 %). FTIR (KBr, cm^{-1}): 3030, 2954, 2089 (C≡C), 1652, 1491, 1422, 1365 (C=C), 1246, 841 (C–Si), 772, 697, 528, 500. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.14 (s, 9H, $SiMe_3$), 3.89 (s, 2H, CH_2), 6.98 (d, $J = 8.6$ Hz, 1H, Ar–H), 7.11 (d, $J = 6.5$ Hz, 1H, Ar–H), 7.18–7.32 (m, 14H, Ar–H), 7.57 (d, $J = 6.9$ Hz, 2H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −1.11 ($SiMe_3$), 38.95 (CH_2), 89.88 and 102.59 (C≡C), 125.82, 126.36, 126.48, 127.19, 127.27, 127.55, 127.97, 128.00, 128.34, 128.44, 128.59, 129.85, 130.09, 133.34, 134.54, 135.95, 145.36. Anal. Calcd. for $C_{33}H_{29}ClN_2SSi$: C 72.17, H 5.32, N 5.10 %. Found: C 72.30, H 5.04, N 5.23 %.

*1-(4-(4-(2-(Trimethylsilyl)ethynylthio)butoxy)phenyl)-2,4,5-triphenyl-1H-imidazole (**8j**)*

Yellow sticky solid (79 %). FTIR (KBr, cm^{-1}): 3098, 2926, 2855, 2091 (C≡C), 1608, 1512, 1472, 1400 (C=C), 1250, 838 (C–Si), 1104 (C–O–Ar), 696, 621, 469. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.16 (s, 9H, $SiMe_3$), 1.91–1.92 (m, 4H, $2CH_2$), 2.79 (t, $J = 6.5$ Hz, 2H, CH_2), 3.93 (t, $J = 4.6$ Hz, 2H, CH_2), 6.73 (d, $J = 8.8$ Hz,

2H, ArH) 6.94 (d, $J = 8.8$ Hz, 2H, ArH), 7.11–7.26 (m, 11H, ArH), 7.45 (d, $J = 6.5$ Hz, 2H, ArH), 7.58 (d, $J = 7.1$ Hz, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −1.00 ($SiMe_3$), 24.69, 26.67, 28.69, 34.77, 66.37, 90.95 and 101.05 (C≡C), 113.05, 125.54, 126.37, 126.85, 127.08, 127.22, 128.67, 129.05, 129.31, 129.74, 130.15, 134.05, 138.00, 146.74, 157.66. Anal. Calcd. for $C_{36}H_{36}N_2OSSi$: C 75.48, H 6.33, N 4.89 %. Found: C 75.21, H 6.09, N 5.01 %.

*1,2-Bis(4-(4-(2-(trimethylsilyl)ethynylthio)butoxy)phenyl)-4,5-diphenyl-1H-imidazole (**8k**)*

Yellow sticky solid (80 %). FTIR (KBr, cm^{-1}): 3059, 2925, 2859, 2090 (C≡C), 1675, 1608, 1511, 1469, 1391 (C=C), 1246, 836 (C–Si), 1170, 1100 (C–O–Ar), 738, 695, 469. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.13 (s, 18H, $SiMe_3$), 2.00–2.03 (m, 8H, $4CH_2$), 2.05–2.09 (m, 4H, $2CH_2$), 3.79–3.89 (m, 4H, $2CH_2$), 6.79–6.85 (m, 4H, ArH), 6.98 (d, $J = 6.5$ Hz, 2H, ArH), 7.15–7.30 (m, 8H, ArH), 7.40 (d, $J = 8.4$ Hz, 2H, ArH), 7.62 (d, $J = 7.6$ Hz, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): −1.56 ($SiMe_3$), 25.00, 26.67, 28.68, 35.02, 67.69, 67.90, 90.77 and 100.64 (C≡C), 113.05, 113.64, 125.49, 126.39, 126.80, 127.10, 127.31, 128.47, 129.29, 130.14, 133.57, 133.58, 136.90, 157.77, 158.00. Anal. Calcd. for $C_{45}H_{52}N_2O_2S_2Si_2$: C 69.90, H 6.78, N 3.62 %. Found: C 69.79, H 6.99, N 3.78 %.

Acknowledgments The authors would like to acknowledge the financial support from the University of Tabriz and Iranian Nanotechnology Initiative.

References

1. E. Langkopf, D. Schinzer, Chem. Rev. **95**, 1375 (1995)
2. L.W. Bieber, M.F. Silva, P.H. Menezes, Tetrahedron Lett. **45**, 2735 (2004)
3. K.D. Safa, M. Alyari, J. Sulfur Chem. **37**, 340 (2016)
4. K.D. Safa, M. Alyari, Synthesis **47**, 256 (2015)
5. S.R. Mistry, K.C. Maheria, J. Mol. Catal. A Chem. **355**, 210 (2012)
6. A. Mirjafari, Environ. Chem. Lett. **12**, 177 (2014)
7. M.S. Jourshari, M. Mamaghani, F. Shirini, K. Tabatabaeian, M. Rassa, H. Langari, Chin. Chem. Lett. (2013). doi:10.1016/j.cclet.2013.06.005
8. A.R. Karimi, Z. Alimohammadi, M.M. Amini, Mol. Divers. **14**, 635 (2010)
9. H. Bienayme, C. Hulme, G. Oddon, P. Schmitt, Chem. Eur. J. **6**(18), 3321–3329 (2000)
10. G. Brahmachari, S. Das, Indian J. Chem. **52B**, 387 (2013)
11. J. Safari, S.D. Khalili, S.H. Banitaba, Synth. Commun. **41**, 2359 (2011)
12. X. Yang, F. Ma, K. Li, Y. Guo, J. Hu, W. Li, M. Huo, Y. Guo, J. Hazard. Mater. **175**, 429 (2010)
13. L. Sun, J. Li, C. Wang, S. Li, Y. Lai, H. Chen, C. Lin, J. Hazard. Mater. **171**, 1045 (2009)
14. T. Angelidis, N. Kruse, Appl. Catal. B **34**, 201 (2001)
15. K.D. Safa, M. Allahvirdinesbat, H. Namazi, P. Nakhostin Panahi, C. R. Chim. **18**, 883 (2015)
16. K.D. Safa, M. Allahvirdinesbat, H. Namazi, Mol. Divers. **19**, 29 (2015)
17. K.D. Safa, M. Allahvirdinesbat, H. Namazi, Synth. Commun. **45**, 1205 (2015)
18. K.D. Safa, T. Shokri, H. Abbasi, R. Teimuri-Mofrad, J. Heterocycl. Chem. **51**, 80 (2013)
19. M.R.P. Heravi, E. Vessally, G.R. Behbehani, C. R. Chim. (2013). doi:10.1016/j.crci.2012.12.007
20. A. Khorramabadi-zad, M. Azadmanesh, S. Mohammadi, S. Afr, J. Chem. **66**, 244 (2013)
21. T. Gröbel, D. Seebach, Chem. Ber. **110**, 852 (1977)