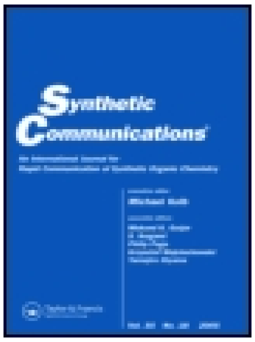

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Synthesis of Novel 1,4-Disubstituted 1,2,3-triazoles Bearing Organosilicon-sulfur Groups via the Click Reaction Sonocatalyzed by $LaCu_xMn_{1-x}O_3$ Nanoparticles

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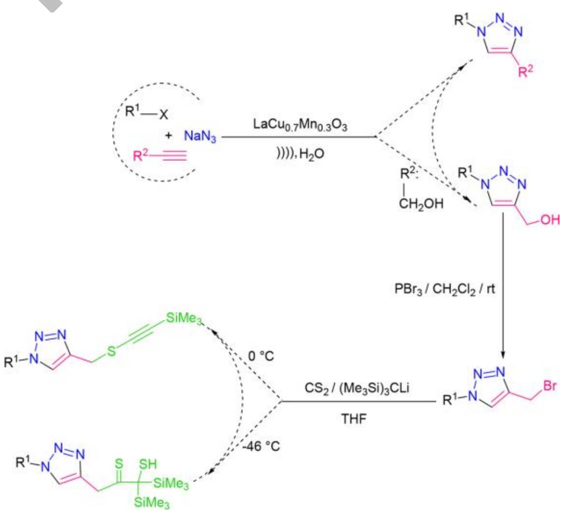
Abstract

A high efficient and environmentally friendly one-pot procedure for the synthesis of 1,2,3-triazoles by 1,3-dipolar cycloaddition of benzyl halides, terminal alkynes and sodium azide over $LaCu_xMn_{1-x}O_3$ perovskite oxides was developed. $LaCu_{0.7}Mn_{0.3}O_3$ was found to be active with low catalyst loading under ultrasonic irradiation in aqueous media. The reaction was performed efficiently in the presence of the nanocatalyst in the absence of any additive or base with a noticeable reduction in the reaction time. The catalyst could be recycled and reused at least five times without any significant effect on the results of the reaction. Moreover, a series of novel organosilicon-sulfur substituted 1,2,3-triazole derivatives was synthesized using carbon disulfide and tris(trimethylsilyl)methylithium.

Graphical abstract



KEYWORDS: 1,2,3-Triazole, $LaCu_{0.7}Mn_{0.3}O_3$ perovskite, Organosilicon, Carbon disulfide, Ultrasonic irradiation

INTRODUCTION

Organosilicon compounds provide opportunities to design and control stability, solubility, and pharmacokinetic properties.[1] The incorporation of organosilicon moieties into known drug scaffolds changes the geometric and electronic aspects, chemical reactivity and lipophilicity of the molecule.[2] Lipophilicity can provide several biological benefits, including an increase bioavailability and better tissue and cell penetration. Organosilicon compounds of sulphur-containing ligands have known to be important due to their useful applications as pharmaceutical agents, e.g. anticarcinogenic, antibacterial, antifungal, insecticidal and acaricidal activities.[3,4] However, the chemistry of these compounds is still underdeveloped. As five-membered heterocyclic compounds, 1,2,3-triazoles have received increasing attention over the past few years, because of their wide range of applications in pharmaceuticals, agrochemicals, dyes, photographic materials, corrosion inhibition, photostabilizers and etc.[5–8] The copper(I) catalyzed Huisgen cycloaddition reaction has been recognized as a regioselective method for the synthesis of 1,4-disubstituted 1,2,3-triazoles.[9,10] Recently, various catalytic systems such as copper nano particles[11], copper immobilized on various supports,[12–15] Cu(I) directly[9,10] or Cu(II) in the presence of reductants [16] and etc, have been reported for the synthesis of 1,2,3-triazoles. However, few reports have been dedicated to mixed metal oxides in organic synthesis. Metal oxide[17] catalysts appear to be a promising alternative to noble metal catalysts in organic syntheses. Metal oxides are developed both for their acid-base and redox properties and constitute the largest family of catalysts in heterogeneous catalysis.[18] The catalytic activity of some of the mixed metal oxides is better than component oxides in various reactions due to increasing acidic and basic sites, and increasing surface area.[19]

Among the metal oxides, perovskites as mixed metal oxides have received wide attention, due to their low-cost, appropriate redox properties, stability of mixed oxidation, high thermal stability and high catalytic activity. This material is introduced by the general formula of ABO_3, where A is lanthanide or alkaline earth metal ion and B is a transition metal ion. The partial substitution of cations in both places A and B, provided multicomponent oxides ($A_{1-x}A'_xB_{1-y}B'_yO_3$) with unusual valence in cation sites that usually increased catalytic activity of the perovskite systems.[20, 21] For example, the synergistic effect manganese oxide and copper ions in the $LaMn_{0.5}Cu_{0.5}O_3$ increased the activity of perovskite system in the oxidation of CO.[22] The attractive catalytic activity of perovskite-type oxides related to their acid-base, adsorption as well as redox properties.[23] In this work, we described the effect of the mole fractions of Mn and Cu on the catalytic performance of $LaCu_xMn_{1-x}O_3$ perovskite oxides in the 1,3-dipolar azide-alkyne cycloaddition reaction. Our results demonstrate that the $LaCu_{0.7}Mn_{0.3}O_3$ perovskite is an efficient, environmentally heterogeneous nanocatalyst for the synthesis of 1,4-disubstituted 1,2,3-triazoles in high yields in aqueous media. The 1,3-dipolar cycloaddition reaction of benzyl halides, terminal alkynes and sodium azide over $LaCu_{0.7}Mn_{0.3}O_3$ nanocatalyst was followed in aqueous media under ultrasonic irradiation.

Moreover, a series of novel 1,2,3-triazoles bearing organosilicon-sulfur groups was synthesized using carbon disulfide and tris(trimethylsilyl)methyllithium.

RESULTS AND DISCUSSION

$LaCu_xMn_{1-x}O_3$ nano perovskite oxides were prepared by sol-gel procedure.[24–26] In this sense, the results of the investigations showed that the ratio of $x = 0.7$ of mixed metal oxides is the ideal ratio for 1,3-dipolar azide-alkyne cycloaddition reaction. The structure of the nanocatalyst was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM). According to the Scherrer's equation from the XRD pattern and the result of SEM photograph, the average particle size of $LaCu_{0.7}Mn_{0.3}O_3$ nano perovskite is around 20 nm. The EDX spectrum of the perovskite system confirmed the presence of copper and manganese (Fig. 1).

Initially, we explored the catalytic activity of $LaCu_{0.7}Mn_{0.3}O_3$ perovskite in the 1,3-dipolar cycloaddition reaction of phenylacetylene, benzyl bromide and sodium azide in aqueous media. As shown in Table 1, incorporation of Mn into the $LaCuO_3$ improved the catalytic activity of the perovskite system and the optimum catalytic activity was obtained for $LaCu_{0.7}Mn_{0.3}O_3$ (3 mol %) at room temperature under ultrasound-irradiation condition. It is noteworthy that the corresponding 1,2,3-triazole **1a** was obtained in high yield after 5 min. When the Cu catalyst loading increased to 5 mol %, the reaction was completed without any observable change in the cycloaddition reaction time. The use of ultrasound irradiation as compared to conventional stirring or heating conditions significantly decreased reaction times. Acoustic cavitation-induced sonochemistry lead to high local temperatures and pressures and increase in the rate of reaction.[27] On the other hand, decreasing the ratio of copper in catalyst system resulted in an increase in the cycloaddition reaction time. The cycloaddition reaction was not completed using $LaMnO_3$ even after 24 hours reaction time. Similarly, no 1,2,3-triazole was isolated in the absence of copper mixed catalyst system even after 2 h of sonication.

$LaCu_{0.7}Mn_{0.3}O_3$ as a heterogeneous nanocatalyst can be recovered by simple filtration and reused at least five times without any loss in acceptable catalytic activity (Table 1, entry 9).

In order to further investigate, the reaction was also carried out for a series of other substrates under the optimized conditions and the related products were obtained (Table 2, entries 1-18). The results showed that the reaction in the presence of electron withdrawing substituents (Table 2, entries 4, 12, 18) and less reactive benzyl chlorides (Table 2, entries 2, 9) processed in good yield. Also benzyl and alkyl halides, aromatic and hydroxyl functionalized alkynes obtained the desired products in high yield, revealing the efficacy of the catalytic system. The known products are confirmed by making a comparison with melting point in the literature.[28–31]

Additionally, a series of novel 1,2,3-triazoles bearing organosilicon-sulfur groups was synthesized using carbon disulfide and tris(trimethylsilyl)methylithium. Recently, successful synthesis of a variety of organosilicon-sulfur derivatives was reported in our laboratory.[32–35] The tris(trimethylsilyl)methyllithium substance was organized using published methodologies (Scheme 1).[36] The reaction of the hydroxyl group of 1,2,3-triazole derivatives **1h-q** with phosphorus tribromide (PBr_3) obtained the desired bromomethyl derivatives **2h–q** in good yields (Scheme 2).[37] After this successful synthesis, the crude products **2h-p** were added dropwise to the stirred solution of carbon disulfide and tris(trimethylsilyl)methyllithium in tetrahydrofuran at 0 °C. The 1,2,3-triazole substitute thioalkynes **3h-p** (Table 3, entries 1-9) were obtained in good yield at 0 °C. Nucleophilic attack of tris(trimethylsilyl)methyllithium at the carbon of carbon disulfide at –46 °C furnished the other organosilicon-sulfur containing triazoles **4h**, **4i**, **4j** and **4q** in high yields and short reaction times (Table 3, entries 9-13).

CONCLUSION

A one-pot procedure was introduced for the synthesis of 1,4-disusbtitude 1,2,3-triazoles through 1,3-dipolar cycloaddition of benzyl halides, terminal alkynes and sodium azide using $LaCu_{0.7}Mn_{0.3}O_3$ recyclable nanocatalyst in aqueous media. The $LaCu_{0.7}Mn_{0.3}O_3$ as an effective and inexpensive catalyst showed high catalytic activity with low catalyst loading under ultrasonic irradiation in aqueous media. Using this methodology, the corresponding 1,2,3-triazole derivatives obtained in high yields and very short reaction times. In continuous, the organosilicon-sulfur substituted 1,2,3-triazole derivatives were synthesized using carbon disulfide and tris(trimethylsilyl)methylithium in high yields. These synthetic compounds are valuable intermediates in synthetic chemistry, chemical biology, and material science.

EXPERIMENTAL

Chemicals were either prepared in our laboratory or purchased from Merck, Fluka and Aldrich. ^{1}H and ^{13}CNMR spectra of all samples were obtained using Bruker 400 MHz spectrometer in $CDCl_3$. Elemental analyses were performed on Elementar Vario EL III apparatus. The reactions were carried out using an ultrasonic processor probe (SONOPULS Ultrasonic homogenizers). The structure of the nanocatalyst was characterized by X-ray diffraction (Bruker AXS model D8Advance diffractometer using CuKα radiation (= 1.542 A°), with the Bragg angle ranging from 10° to 70° and scanning electron microscopy using LEO 1430VP instrument. The elemental chemical composition of the prepared catalyst was determined by EDX (VEGA\\TESCAN-LMU, Czech Republic).

Typical Procedure For The Preparation Of $Lacu_xmn_{1-X}o_3$ Oxides

$LaCu_xMn_{1-x}O_3$ oxides were prepared by the sol-gel method. The citric acid was added to an aqueous stirred solution of $La(NO_3)_3.6H_2O$, $Cu(NO_3)_2.3H_2O$ and $Mn(NO_3)_2.4H_2O$ in the stoichiometric amount at 70 °C. The ratio of citric acid to nitrates was 0.4 for complete complexation of the cations. The solution was heated to 80 °C and the extra water was evaporated. Then, the gel-like substance was dried at 200 °C overnight and calcined at 700 °C for 3 h.[24–26]

Typical Procedure For The Preparation Of 1-Benzyl-4-Phenyl-1H-1,2,3-Triazole (1a)

In a 20 ml thick-walled flax a mixture of sodium azide (1.2 mmol), benzyl halide (1 mmol), terminal alkyne (1 mmol), $LaCu_{0.7}Mn_{0.3}O_3$ (3% mol) and 2 ml water was added.

The flask was attached to a 12-mm-tip-diameter Probe. The reaction mixture was then sonicated at room temperature at 20 % power of the processor. After completion the reaction (TLC monitoring), the crude product was extracted using EtOAC. The recovered catalyst by simple filtration was washed three times with ethanol and dried under vacuum. The product was identified as 1-benzyl-4-phenyl-1H-1,2,3-triazole (**1a**) by spectral data.

A yellowish white solid, m.p. 128-130 °C [34]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.57 (s, 2H, CH_2), 7.26-7.48 (m, 8H, Ar), 7.68 (s, 1H, triazole), 7.79-7.81 (m, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.83, 118.55, 124.43, 126.74, 126.89, 127.43, 127.51, 127.84, 129.36, 133.55, 146.84 ppm; Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86%; Found: C, 76.54; H, 5.61; N, 17.83%.

Preparation Of Tris(Trimethyl)Methyllithium

The reagent was prepared as described by Grobel and coworkers [36].

Typical Procedure For The Synthesis Of 4-((2-(Trimethylsilyl)Ethynylthio)Methyl)-1-Benzyl-1H-1,2,3-Triazole (3h)

Carbon disulfide (1.2 mmol) was added dropwise to a stirred solution of $(Me_3Si)_3CLi$ (1 mmol) in THF at 0 °C under an argon atmosphere. Immediately, an orange-red solution was formed. Then bromomethyl derivative **2h** (1 mmol) was added in this temperature. The reaction was completed within 10 min (TLC monitoring) and the color of the solution changed to red dark. Finally, the mixture was extracted with CH_2Cl_2 and was purified by preparative column chromatography using (*n*-hexane/EtOAc 3:1) to give the pure products **3h.**

A yellow sticky solid (96%); ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.08 (s, 9H, SiMe$_3$), 4.53 (s, 2H, CH$_2$), 5.48 (s, 2H, CH$_2$), 7.19-7.22 (m, 2H, Ar), 7.33-7.36 (m, 3H, Ar), 7.44 (s, 1H, triazole); ^{13}C NMR (100 MHz, CDCl$_3$): δ -1.22 (SiMe$_3$), 30.89, 53.14, 90.86, 101.33, 121.19, 126.92, 127.01, 127.66, 127.79, 128.07, 128.13, 143.29; Anal. Calcd for $C_{15}H_{19}N_3SSi$: C, 59.76; H, 6.35; N, 13.94%; Found: C, 59.83; H, 6.39; N, 13.89%.

Typical Procedure For The Synthesis Of 3-(1-Benzyl-1H-1,2,3-Triazol-4-Yl)-1-Mercapto-1,1-Bis(Trimethylsilyl)Propane-2-Thione (4h)

Carbon disulfide (1.2 mmol) was added dropwise to a stirred solution of $(Me_3Si)_3CLi$ (1 mmol) in THF at -46 °C under an argon atmosphere. Then bromomethyl derivative **2h** (1 mmol) was added in this temperature. The reaction was followed by TLC and completed within 5 min. Finally, the mixture was extracted with CH_2Cl_2 and was purified by preparative column chromatography using (*n*-hexane/EtOAc 10:2) to give the pure products **4h.**

A yellow sticky solid (95%); ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.078 (s, 18H, SiMe$_3$), 3.11 (bs, 1H, S-H), 4.53 (s, 2H, CH$_2$), 5.48 (s, 2H, CH$_2$), 7.19-7.22 (m, 2H, Ar) 7.33-7.36 (m, 3H, Ar) 7.44 (s, 1H, triazole); ^{13}C NMR (100 MHz, CDCl$_3$): δ -1.22 (SiMe$_3$), 30.89, 53.13, 57.07, 121.19, 126.92, 127.01, 127.66, 127.79, 128.07, 128.127, 143.26, 230.53;

Anal. Calcd for $C_{18}H_{29}N_3S_2Si_2$: C, 53.02; H, 7.17; N, 10.31%; Found: C, 53.16; H, 7.23; N, 10.33%.

SUPPLEMENTARY INFORMATION

Supporting information associated with this article can be found via the “Supplementary Content” section of this article’s webpage.

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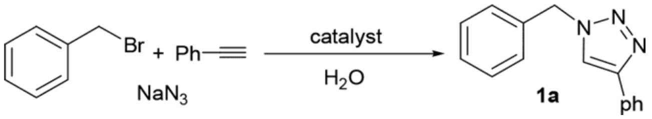
Table 1. Optimization of the reaction conditions[a]

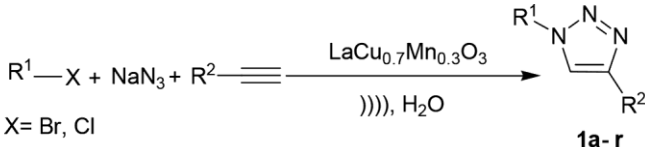


Entry	**Catalyst (mol %)**	**Ultrasound irradiation Time (min)/yield[b] (%)**		**Stirring conditions Temp. (°C)/time (h)/yield[b] (%)**		
1	$LaCuO_3$ (3)	30	70	70	12 h	72
2	$LaCu_{0.5}Mn_{0.5}O_3$ (3)	10	90	70	2 h	92
3	$LaCu_{0.7}Mn_{0.3}O_3$ (3)	5	98	70	2 h	96
4	$LaCu_{0.7}Mn_{0.3}O_3$ (5)	5	98	70	2 h	95
5	$LaCu_{0.7}Mn_{0.3}O_3$ (3)	10	98	100	2 h	96
6	$LaCu_{0.3}Mn_{0.7}O_3$ (3)	20	87	70	6 h	85
7	$LaMnO_3$ (3)	2 h	Trace	70	24 h	Trace
8	Neat	2 h	Trace	70	24 h	Trace
9	$LaCu_{0.7}Mn_{0.3}O_3$ (3) (Recycled)	5	95	70	2 h	96

[a] Reactions were carried out on a scale of 1.0 mmol of benzyl bromide, 1.0 mmol of phenylacetylene, 1.2 mmol of sodium azide, and 2 ml of H_2O.

[b] Isolated yield.

Table 2. $LaCu_{0.7}Mn_{0.3}O_3$ catalyzed 1,3-dipolar azide-alkyne cycloaddition reaction[a]



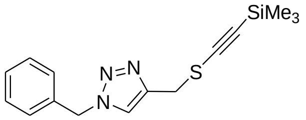
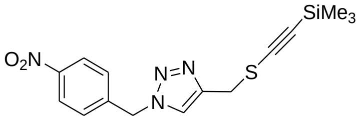
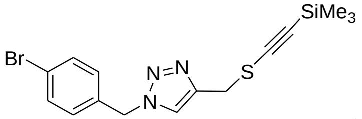
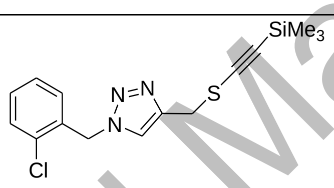
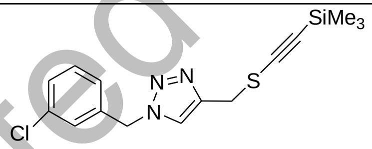
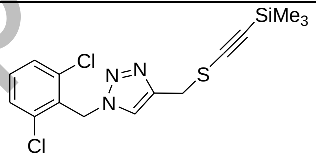
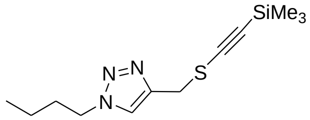
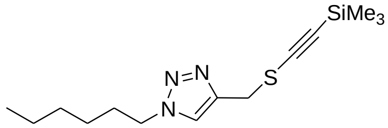
Entry	*Alkyl halide*	*Alkyne*	*Product 1*	*Yield*	
	R^1	X	R^2		(%)[b]
1	$C_6H_5CH_2$	Br	Ph	**1a**	98
2	$C_6H_5CH_2$	Cl	Ph	**1b**	95
3	$C_6H_5CH_2CH_2$	Br	Ph	**1c**	92
4	$4\text{-}O_2NC_6H_4CH_2$	Br	Ph	**1d**	90
5	$C_6H_5COCH_2$	Br	Ph	**1e**	92
6	$CH_3(CH_2)_4CH_2$	Br	Ph	**1f**	90
7	5-(benzyloxy)-2 methyl-4-pyran-4-one	Br	Ph	**1g**	85
8	$C_6H_5CH_2$	Br	CH_2OH	**1h**	93
9	$C_6H_5CH_2$	Cl	CH_2OH	**1i**	92
10	$C_6H_5CH_2CH_2$	Br	CH_2OH	**1j**	92
11	$4\text{-}BrC_6H_4CH_2$	Br	CH_2OH	**1k**	92
12	$4\text{-}O_2NC_6H_4CH_2$	Br	CH_2OH	**1l**	85
13	$2\text{-}ClC_6H_4CH_2$	Br	CH_2OH	**1m**	93
14	$3\text{-}ClC_6H_4CH_2$	Br	CH_2OH	**1n**	92
15	$2,6\text{-}ClC_6H_3CH_2$	Br	CH_2OH	**1o**	94
16	$CH_3(CH_2)_4CH_2$	Br	CH_2OH	**1p**	92

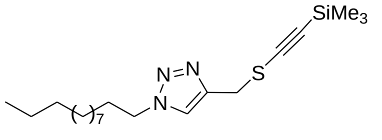
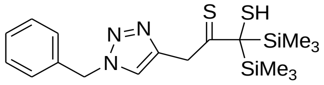
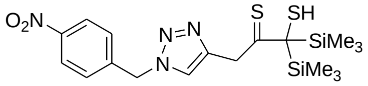
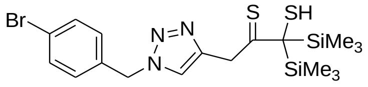
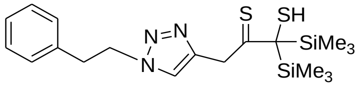
17	$CH_3(CH_2)_{10}CH_2$	Br	CH_2OH	**1q**	90
18	$4\text{-}BrC_6H_4CH_2$	Br	$4\text{-}CHOC_6H_4OCH_2$	**1r**	90

[a] Reactions were carried out on a scale of 1.0 mmol of alkyl halide, 1.2 mmol of sodium azide, and 1.0 mmol of alkyne, $La_3Cu_{0.7}Mn_{0.3}O_3$ (3% mol) in 2 ml H_2O.

[b] Isolated yield.

Table 3. 1,2,3-triazoles bearing organosilicon-sulfur groups

Entry	**Substrate (2h-p) / R^1**	**Product / (3h-p)**	**Time (min)**	**Yield (%)^c**
1^a	$C_6H_5CH_2$	 **3h**	10	96
2^a	$4\text{-}O_2NC_6H_4CH_2$	 **3i**	15	92
3^a	$4\text{-}BrC_6H_4CH_2$	 **3j**	10	94
4^a	$2\text{-}ClC_6H_4CH_2$	 **3k**	10	95
5^a	$3\text{-}ClC_6H_4CH_2$	 **3l**	10	92
6^a	$2,6\text{-}ClC_6H_3CH_2$	 **3m**	15	90
7^a	$CH_3(CH_2)_2CH_2$	 **3n**	15	85
8^a	$CH_3(CH_2)_4CH_2$	 **3o**	15	89

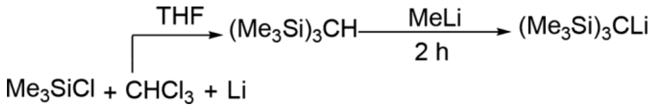
9[a]	$CH_3(CH_2)_{10}CH_2$	 **3p**	20	83
10[b]	$C_6H_5CH_2$	 **4h**	5	95
11[b]	$4-O_2NC_6H_4CH_2$	 **4i**	10	92
12[b]	$4-BrC_6H_4CH_2$	 **4j**	5	94
13[b]	$C_6H_5CH_2CH_2$	 **4q**	5	96

[a] Reactions were carried out in CS_2 /$(Me_3Si)_3CLi$ /THF /0 °C,

[b] in CS_2/$(Me_3Si)_3CLi$ /THF /-46 °C.

[c] Isolated yield.

Scheme 1. Synthesis of the tris(trimethylsilyl)methyllithium.



Scheme 2. Synthesis of the 1,2,3-triazoles bearing organosilicon-sulfur groups.

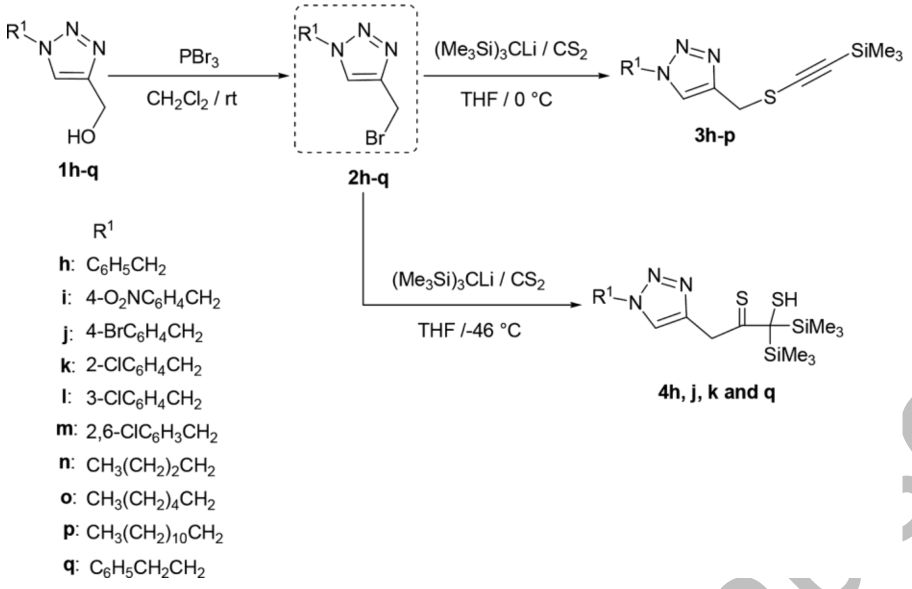


Figure 1 The SEM image (a), the XRD pattern (b) and the EDX of image (c) $LaCu_{0.7}Mn_{0.3}O_3$ nano perovskite.