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Journal Name

COMMUNICATION

Metallomicelle Catalyzed Aerobic Tandem Desilylation/Glaser Reaction in Water

Shanyu Tang, Longjia Li, Xuanhe Ren, Jiao Li, Guanyu Yang, Heng Li, and Bingxin Yuan*

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PEG-grafted nitrogen ligands were synthesized. The corresponding copper complexes serve as metallomicellar nanoreactors for the aerobic tandem desilylation/Glaser coupling of TMS-protected alkynes in water. The protocol is also suitable for base-free homocoupling of terminal alkynes. The metallomicellar catalyst could be recycled 5 times with minor loss of reactivity.

From the prospects of green chemistry, water is an ideal solvent for organic synthesis since it is naturally abundant, environmentally benign, and inexpensive.[1-3] Since Breslow's discovery of the acceleration of Diels-Alder reaction in water,[4] aqueous media has shown to improve the selectivity and reactivity.[5-8] Water as solvent is promising to provide the possibility of catalyst recycling and work-up simplification as most organic products are insoluble in aqueous media.[9, 10] However, the low solubility of most organic compounds and catalysts also is the hindrance to conduct organic synthesis in water. Inspired by enzymes as highly active water soluble catalysts in nature, the usage of surfactants under micellar conditions represents one of the simplest methods to achieve catalysis in aqueous media.[11-15] Aiming at exploring the recyclability of catalysts, covalently surfactant-modified catalytic systems were endowed with metallo-surfactants.[16-21] Covalent conjugation of surfactant scaffold to a ligand-metal species bestows interesting surfactant-type features to catalysts, such as the spontaneous aggregation to form micelles and act as nanoreactors in water.[22] More importantly, such amphiphilic ligands can produce a highly concentrated catalytic active species inside the hydrophobic core of the micelles. The hydrophobic substrates turn to self-enrich inside the micellar core and increase the chance of substrate to interact with catalytic center. Metallo-surfactants have been used as green alternatives to traditional homogeneous catalysts in organic synthesis.[23] Despite those prominent advances, metallomicelles catalyzed dehydrogenative coupling reactions in water are quite rare.

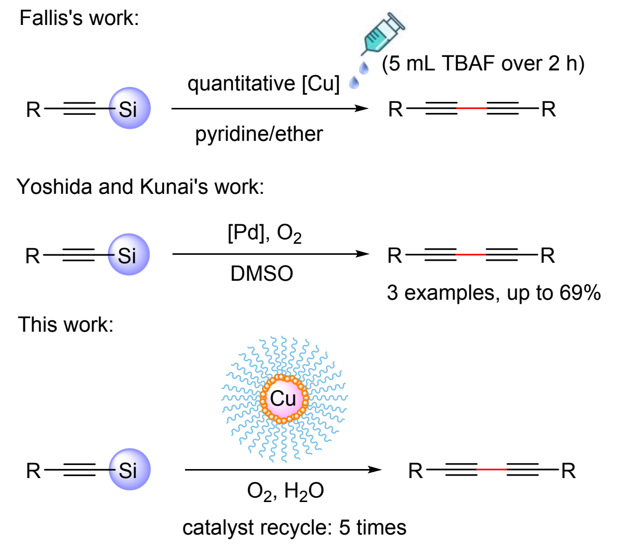

Figure 1. Pathways for tandem desilylation/Glaser reaction.

1,3-Diynes are a class of conjugated diynes with unique structures and properties.[24] The rod-like molecular shape with high rigidness enabled both stability and reactivity.[25] Diynes can be widely found in nature and serves as important building blocks in material chemistry, synthetic chemistry and pharmaceuticals.[26-31] Glaser-Hay coupling of terminal alkynes in the presence of oxidants represents a typical pathway to synthesize 1,3-diynes.[29, 32-34] The instability of some simple terminal alkynes and higher polyynes becomes a major challenge in Glaser coupling as they are prone to decomposition and polymerization.[35, 36] Tandem desilylation/dimerization of trialkylsilyl-arylacetylene has been developed. The higher stability of organosilanes compared to the corresponding terminal alkynes would benefit the synthetic process by utilizing

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† The authors declare no interest conflict.

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the former as starting material. Furthermore, organosilanes are mostly synthesized by Sonogashira-type coupling between trialkylsilylacetylene and aromatic halides, followed by the deprotection of the trialkylsilyl group. The usage of *in situ* generated terminal alkynes can avoid the purification procedures and any stability concern. Fallis and coworkers reported a copper-mediated in situ desilylation/dimerization of TIPS-acetylenes in pyridine/ether, using TABF as a fluoride source.[37] In this protocol, 3 equivalents of Cu(OAc)$_2$ were used and the TBAF solution was added to the reaction mixture via syringe pump (5 mL over 2 h). Yoshida and Kunai developed a palladium-DPPP complex catalyzed homocoupling of organosilanes in DMSO under oxygen atmosphere.[38] However, only three examples of diynes were obtained in modest yields. Other progresses have been made by utilizing Pd and Cu as co-catalytic system to produce 1,3-butadiynes via two steps in moderate yields.[39, 40]

Our group has been working on the aerobic dehydrogenative coupling reaction in aqueous media.[41-44] Herein, we considered synthesizing poly(ethylene glycol)-functionalized nitrogen ligands and using their copper complex as catalysts to achieve catalytic transformation of trialkylsilyl-arylacetylenes into the corresponding diynes via tandem desilylation/dimerization in one-pot. The amphiphilic instincts of the PEG-modified complex tend to aggregate and form metallomicelles in aqueous media. We speculate that metallomicelles can act as nanoreactors and highly increase the catalyst performance, thus accomplish the copper-catalyzed instead of copper-mediated tandem desilylation/dimerization. Herein, in this context, we address the use of amphiphilic nitrogen ligands (Figure 2), poly(ethylene glycol)-functionalized 1,10-phenanthrolines (**L_1** and **L_2**) and poly(ethylene glycol)-functionalized2,2'-bipyridines (**L_3** and **L_4**). We report an efficient and recyclable metallomicelle catalyzed tandem desilylation/Glaser reaction with molecular oxygen as the sole oxidant in water. Moreover, the usage of water as solvent enables the potential to recycle the metallomicellar catalyst system and simply the work-up procedure as the product could be easily collected via filtration. All ligands could be prepared in high yields in one step (see supporting information).

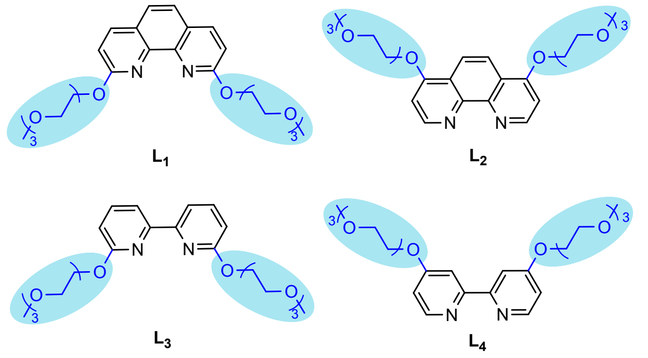
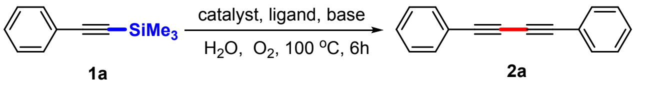


Figure 2. PEG-functionalized nitrogen ligands for disiylation/Glaser couplingin aqueous media.

Table 1. Optimization of reaction reagents.[a]



Entry	Catalyst	Base	Ligand	Yield (%)[b]
1	CuI	NaOH	/	0
2	CuI	NaOH	**L_1**	Trace
3	CuI	NaOH	**L_2**	98
4	CuI	NaOH	1,10- phenanthroline	43
5	CuI	NaOH	**L_3**	11
6	CuI	NaOH	**L_4**	63
7	CuI	NaOH	2,2'-bipyridine	30
8	CuI	NaOH	pyridine	Trace
9	/	NaOH	**L_2**	0
10	CuCl	NaOH	**L_2**	41
11	CuBr	NaOH	**L_2**	39
12	Cu(OAc)$_2$	NaOH	**L_2**	Trace
13	CuPcS	NaOH	**L_2**	Trace
14	CoPcS	NaOH	**L_2**	0
15	Pd(OAc)$_2$	NaOH	**L_2**	0
16	CuI	/	**L_2**	0
17	CuI	NaF	**L_2**	33
18	CuI	KF·2H$_2$O	**L_2**	36
19	CuI	CsF	**L_2**	40
20	CuI	K$_2$CO$_3$	**L_2**	23
21	CuI	TBAF	**L_2**	77

[a] Reaction conditions: **1a** (0.3 mmol), Catalyst (10 mol%), Ligand (10 mol%), Base (1.0 equiv.), H$_2$O (2 ml), 0.3 MPa O$_2$, 100 °C, 6 h. [b] Isolated yields.

This disiylation/Glaser coupling protocol was investigated by using trimethyl(phenylethynyl)silane **1a** as the model substrate in the presence of a copper catalyst, ligand, and base. The reaction was carried out under 0.3 MPa O$_2$ in neat water. In the absence of ligand, no product was formed (Table 1, Entry 1). Interestingly, PEG-functionalized 1,10-phenanthroline ligands **L_1** and **L_2** showed tremendously different catalytic activity. 2,9-DiMPEG3-1,10-phenanthroline (**L_1**) led to trace amount of desired product **2a** (Table 1, Entry 2), while 4,7-diMPEG3-1,10-phenanthroline (**L_2**) was able to furnish **2a** in nearly quantitive yield (Table 1, Entry 3, the conversion of substrate was monitored by GC to get the appropriate reaction hour). A control experiment with 1,10-phenanthroline as ligand was performed, producing **2a** in 43% yield (Table 1, Entry 4). Speculatively, when the two PEG chains were grafted on 2,9-positions of the 1,10-phenanthroline, oxygen atoms on the chains could also serve as chelates to the transition metal center, affecting the catalytic performance as well as the approaching of substrates to the copper center. Also, steric effect of the PEG chains may hinder the substrate approaching. Similar outcomes were obtained in the case of PEG-functionalized 2,2'-bipyridine ligands. Although 6,6'-DiMPEG3-2,2'-bipyridine **(L$_3$)** resulted in low yield (Table 1, Entry 5), 4,4'-diMPEG3-2,2'-bipyridine (**L_4**) and 2,2'-bipyridine led to 63% and 30% of product (Entry 6, 7), respectively. Pyridine as sole ligand did not work well (Table 1, Entry 8). Screening of transitional metal salts revealed CuI to be the optimal catalyst (Table 1, Entry 10-15). The control experiment performed in the absence

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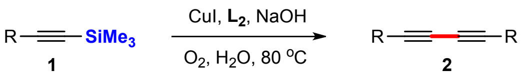
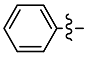
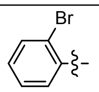
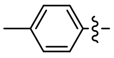
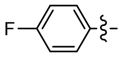
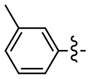
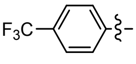
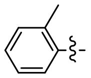
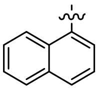
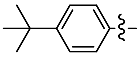
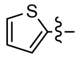
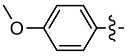
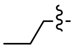
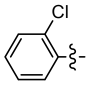
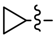
of catalyst indicated the necessity of Cu (Table 1, Entry 9). Fluoride sources and bases were tested as well, and NaOH turned to be the optimal desilyation agent (Table 1, Entry 16-21).

Other reaction parameters, such as catalyst/ligand amount, base equivlents, temperature and oxygen pressure, were studied (Table S1 in the supporting information). By keeping the ratio of catalyst/ligand at 1:1, the evaluation of various amount of catalyst/ligand showed 10 mol% to be optimal (Table S1, Entry 1-5). Increasing relative quantity of either CuI or **L$_2$** reduced the product yiled evidently (Table S1, Entry 6, 7). The reaction atmoshpere evaluation showed that the lowering O$_2$ pressure led to decresed raction effeciency (Table S1, Entry 8, 9). The control experiment under N$_2$ led to no product (Entry 8), demonstrating the necessity of O$_2$ as oxidant for the dehydrogenative coupling. The varition of temperature parameters stated 80 °C to be the most suitable reaction temperature (Table S1, Entry 11, 12). Furthermore, one equivalent NaOH proved to be sufficient enough for desilylation (Table S1, Entry 13-17).

Table 2. Desilyation/Homocoupling of TMS-alkynes.[a]

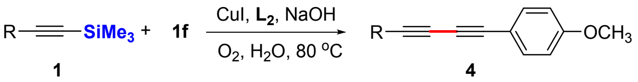


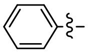
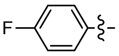
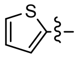
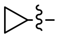
R	pdt	Yield[b]	R	pdt	Yield[b]
	**2a**	99		**2h**	93
	**2b**	94		**2i**	46(94[c])
	**2c**	84		**2j**	68 (87[d])
	**2d**	90		**2k**	87
	**2e**	90		**2l**	95
	**2f**	91		**2m**	5 (61[c])
	**2g**	92		**2n**	74

[a] Reaction conditions: **1** (0.3 mmol), CuI (10 mol%), **L$_2$** (10 mol%), NaOH (1.0 equiv), H$_2$O (2 mL), 0.3 MPa O$_2$, 80 °C, 6 h. [b] Isolated yields. [c] TBAF (1.0 M solution in THF) as desilylation agent. [d] NaOH (2.0 equiv).

With the optimal conditions in hand, we explored its applicability for desilylation/homocoupling of TMS-protected alkynes (Table 2). Organosilanes with various aromatic and heteroaromatic groups smoothly underwent coupling reaction and gave the corresponding symmetrical products in up to 99% yields (**2a-l**). Arylethynylsilanes bearing electron-donating substituents at the *para*- and *othro*-positions of the aromatic ring (**1b**, **1d-h**) are more favorable than that with substituent at the *meta*-position (**1c**). Electron-withdrawing groups on para-position, such as trifluoromethyl and fluoro goups, led to modest yields under the optimal reaction condition (**2i, j**). GCMS results indicated the starting material didn't undergo desilyation thoroughly. The yield of **2i** reached 94% by the replacement of NaOH with TBAF (1.0M solution in THF). The attemptation to increase the amount of NaOH to 2 equiv achieved **2j** in 94% yield. The homocoupling of alkylethynylsilanes (**1m** and **1n**) proceeded to provided corresponding 1,3-butadiynes (**2m** and **2n**) in moderate yields. The desilyation/heterocoupling of organosilanes was attempted by using (p-anisylethynyl)trimethylsilane **1e** as model substrate (Table 3). The asymmetric products were obtained in 52-71% yields (**4a-d**).

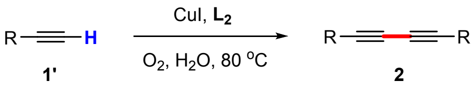
Table 3. Desilyation/ Heterocoupling of TMS-alkynes.[a]

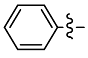
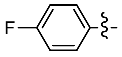
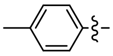
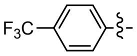
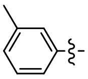
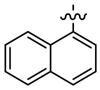
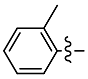
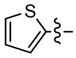
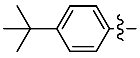
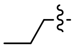
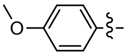
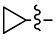
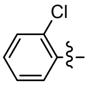
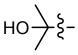
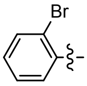


R	pdt	Yield[b]	R	pdt	Yield[b]
	**4a**	67		**4c**	63
	**4b**	71		**4d**	52

[a] Reaction conditions: **1f**(0.3 mmol), **1** (0.9 mmol), CuI (10 mol%), **L$_2$** (10 mol%), NaOH (1.0 equiv.), H$_2$O (2 mL), 0.3 MPa O$_2$, 80 °C, 6 h. [b] Isolated yields.

Table 4. Homocoupling of terminal alkynes.[a]



R	pdt	Yield[b]	R	pdt	Yield[b]
	**2a**	99		**2i**	87
	**2b**	94		**2j**	93
	**2c**	83		**2k**	93
	**2d**	96		**2l**	81
	**2e**	91		**2m**	75
	**2f**	97		**2n**	72
	**2g**	98		**2o**	84
	**2h**	87	Me_3Si-	**2p**	84

[a] Reaction conditions: **1'** (0.3 mmol), CuI (10 mol%), **L$_2$** (10 mol%), H$_2$O (2 mL), 0.3 MPa O$_2$, 80 °C, 6 h. [b] Isolated yields.

Encouraged by the success in desilyation/homocouping of alkynylsilanes, we attempted homocoupling of terminal alkynes. The homocoupling of terminal alkynes was performed in the

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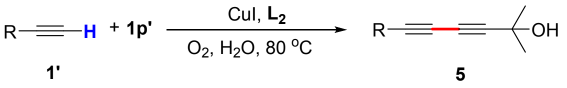
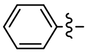
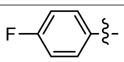
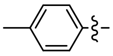
absence of NaOH since the desilylating agent was not needed (Table 4). This base-free aerobic oxidative coupling of terminal alkynes in water displayed high efficiency and extensive versatility. Except the substrates mentioned in Table 3, base-sensitive compounds, 2-methyl-3-butyn-2-ol and ethynyltrimethylsilane can be employed to produce the corresponding diynes (**2o** and **2p**), of which the latters are significant synthetic motifs. The base-free aerobic heterocoupling of terminal alkynes was tested with 2-methyl-3-butyn-2-ol as a fixed substrate (Table 5). The asymmetric products were produced in 59-71% yields.

Table 5. Heterocoupling of terminal alkynes. [a]



R	No.	Yield[b]	R	No.	Yield[b]
	**5a**	67		**5c**	63
	**5b**	71			

[a] Reaction conditions: **1p'** (0.3 mmol), **1'** (0.9 mmol), CuI (10 mol%), L_2 (10 mol%), NaOH (1.0 equiv.), H_2O (2 mL), 0.3 MPa O_2, 80 °C, 6 h. [b] Isolated yields.

UV-Vis studies of L_2 in aqueous solution were carried out (Figure 3). The L_2 solution displayed absorption bands in the range of 200~380 nm. Upon the addition of CuI (1 equiv.), the solution turned bluish and the absorption spectrum showed red shift with an increasing shoulder at 218 nm. This color change and band shift confirms the coordination of phenanthroline-nitrogen atom to the central copper ion.

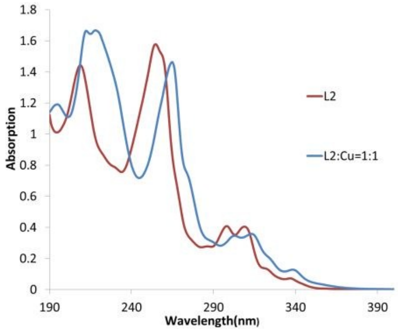


Figure 3. UV-Vis absorption spectra of L_2 solutions.

To study the structure and morphology of aggregates assembled form catalyst L_2-Cu in water, we conducted dynamic light scattering (DLS) and transmission electron microscopy (TEM) studies. DLS experiment with L_2 in the absence of Cu revealed the existence of self-assembled nanostructures (Figure 4a). Upon the addition of 1 equivalent CuI to the L_2 solution, the nanomicelle size increased (Figure 4b), which might be owing to the entering of copper in the micelle center and its coordination to the nitrogen chelates. The spherical shape and average size of nanoscale micelles revealed by TEM was in agreement with that identified by DLS (Figure 4c, 4d).

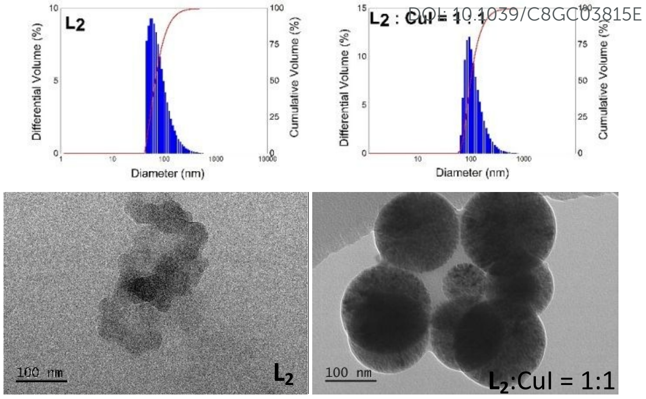


Figure 4. DLS and TEM results of metallomicelle.

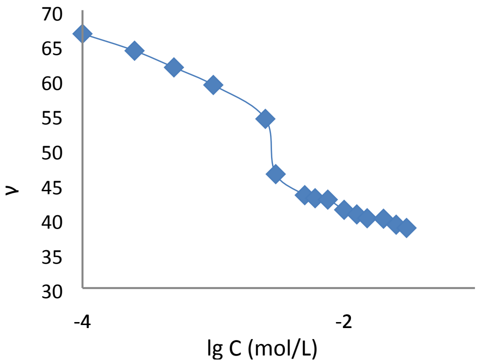
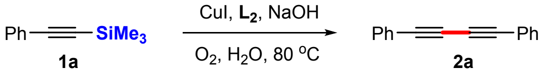


Figure 5. A plot of surface tension γ (mN/m) of the aqueous L_2 solution vs. logarithm of L_2 concentration at 286.15 K.

Table 6. Homocoupling of **1a** at various ligand concentrations.[a]



H_2O (mL)	Conc.(mol/L)[b]	Yield (%)[c]
30.0	0.001	10
15.0	0.002	40
7.5	0.004	99
4.3	0.007	99

[a] Reaction condition: **1a** (0.3 mmol), CuI (10 mol%), L_2 (10 mol%), NaOH (1.0 equiv), H_2O, 0.3 MPa O_2, 80 °C, 6 h. [b] Concentration (mol/L) of L_2. [c] Isolated yield.

The critical micelle concentration (CMC) was determined by plotting the surface tension as a function of L_2 concentration (Figure 5). An abrupt change of slope marked the transition from the pre-micellar state to micellar solution around 0.003 mol/L (CMC). Since the concentration of L_2 used in the optimal reaction condition is 0.015 mol/L, it is reasonable to conclude the presence of metallomicelle in the reaction mixture. Furthermore, the aerobic tandem desilylation/Glaser reaction of TMS-alkyne **1a** was performed beyond and below the CMC. Low yields were obtained at 0.001 and 0.002 mol/L of L_2 when no micelles formed (Table 6, Entry 1, 2), while 99% yields could be achieved beyond the CMC (Table 6, Entry 3, 4). This might be a reflection of the micellar effect contributed by the surfactant-type ligand **L$_2$**.

The sustainability of the metallomicelle enabled transformation was assessed by performing recycle studies of trimethyl(phenylethynyl)silane **1a** and ethynylbenzene **1a'** under the optimal reaction conditions, respectively (Figure 6). The recovery of micelle solution and product collection could be completed by simple filtration. The metallomicellar catalytic system could be reused five times with minor loss of reactivity.

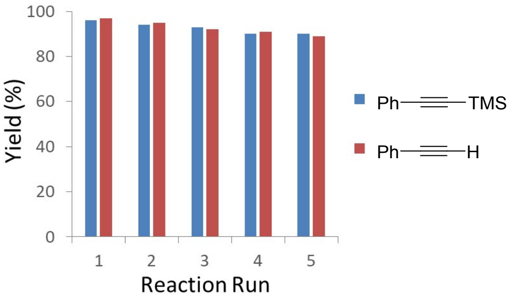


Figure 6. Catalyst recycle.

Conclusions

In conclusion, a series of PEG-grafted nitrogen ligands were synthesized via one-step procedure in excellent yields. The corresponding water-soluble amphiphilic copper complexes turn to form nano-sized metallomicelles. An effective and recyclable metallomicellar catalyst for tandem desilylilation/ Glaser reaction in water with molecular oxygen as the sole oxidant has been developed. This protocol avoids the work-up procedure and instability caused by the deprotection of the trialkylsilyl group to achieve the corresponding terminal alkynes. At the meantime, these nanoreactors are highly efficient for base-free aerobic oxidative of terminal alkynes as well. DLS and TEM studies demonstrate the existence of round-shaped nanomicelles. The catalytic performance is highly affected by the size and morphology of metallomicelles. The recyclability of metallomicellar catalyst could run 5 times in the homocoupling of TMS-protected and terminal alkynes, respectively.

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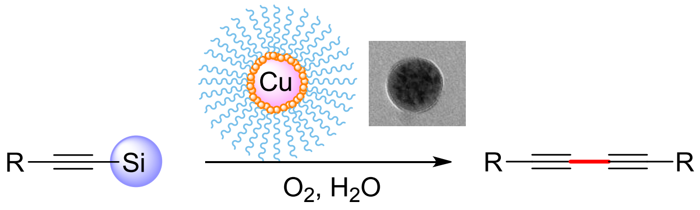
Metallomicelle Catalyzed Aerobic Tandem Desilylation/Glaser Reaction in Water



Metallomicelle as nanoreactor