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Silica-supported metal acetylacetonate catalysts with a robust and flexible linker constructed by using 2-butoxy-3,4-dihydropyrans as dual anchoring reagents and ligand donors

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Anchoring of a metal complex catalyst onto a solid support with covalent bond has been widely used in designing a recyclable catalyst at molecular level. However, performance of the obtained solid catalyst relies heavily on the stability and flexibility of the linker between metal complex and solid support. A ring-opening reaction of 2-butoxy-3,4-dihydropyrans with mercaptan was known to produce 2-alkylated 1,3-dicarbonyl compounds, which featured also by good atom-economy, excellent yield and mild conditions. With the aid of this reaction, we used, in this work, 2-butoxy-3,4-dihydropyrans as dual anchoring reagents and ligand donors to modify a ready-made SH-functionalized HMS. This opened an easy way to construct a robust and flexible linker for anchoring a metal acetylacetonate complex catalyst onto HMS support. The thereby obtained HMS can be used to immobilize $Cu(acac)_2$, $Zn(acac)_2$ and $Ru(acac)_3$ complexes. The obtained solid catalysts were fully characterized by many physicochemical methods. In the selected reactions, these catalysts not only displayed better or comparable activity in various organic reactions as compared with heir homogeneous counterparts, but also were proved to be quite robust and can be recycled several times without significant loss of their activities.

Introduction

Heterogenizing homogeneous catalysts by immobilization is a trend toward the development of chemically homogeneous but physically heterogeneous catalysts.[1] Anchoring of a metal complex catalyst onto a solid support with covalent bond has been widely used in designing a recyclable catalyst at molecular level.[2] However, performance of the obtained solid catalyst relies heavily on the stability and flexibility of the linker between metal complex and solid support.[3]

Metal complexes of 1,3-diketone have been widely used as catalysts in organic reactions.[4] Because these compounds are readily soluble in organic solvents, the catalytic reactions have long been plagued by the following difficulties: (i) recycling metal complex catalysts; and (ii) removing metal species from organic product. 1,3-Diketones have also been used as ligands in selective extraction of metal ions.[5] However, to increase the efficiency of extraction, the diketone structure has to be finely manipulated and modified. As a result, the prices of these ligands are generally very high, so that their recovery and reuse are in general imperative.[6] Out of these considerations, many immobilization methods of 1,3-diketones have been developed. For example, by using a NH_2-containing solid support, an acetylacetone ligand can be anchored *via* formation of an enamine.[7] Because of the nucleophilicity of C2 position of acetylacetone, this ligand can also be anchored onto a solid support through a nucleophilic substitution reaction.[8] An acetylacetone fragment has also been covalently bonded to an imidazolium-based ionic liquid.[9] These approaches offered in theory possible way to solve the problems of recycling metal complexes of 1,3-diketones. However, as a matter of fact, their practical uses often encountered several obstacles. First, the enamine formation strategy changed the core structure of 1,3-diketone, diminishing thus the catalytic activity of the catalyst. Second, the commonly used anchoring reagents employed to establish a linker between 1,3-diketone ligand and the solid support, such as 3-chloropropyltrimethoxysilane and aminopropyltrimethoxysilane, contain only three carbons. It is therefore conceivable that the immobilized metal complexes are less flexible. As a result, despite the fact that this strategy reached a compromise between accessibility and efficiency, but failed to give a highly active catalyst. The ionic liquid with a 1,3-diketone tail associated however with the use of some reagents that are not easily available and expensive. Their preparations are also hard tasks. Therefore there is a definite need to develop a simple and an efficient method to anchor 1,3-diketone fragment onto solid support with a structurally flexible reagent.

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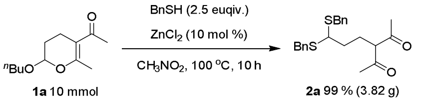
We have recently developed a ring-opening reaction of 2-alkoxy-3,4-dihydropyrans with a nucleophile, which is able to produce 2-substituted 1,3-dicarbonyl compounds under mild conditions.[10] Particularly, when mercaptans were used as nucleophiles, the ring-opening reactions proceeded very smoothly, and almost quantitative yields could be obtained.[11] Taking a cue from these observations, we envisaged that, by using 2-alkoxy-3,4-dihydropyrans as dual anchoring reagents and ligand donors, an easily accessible SH-functionalized silica can be derivatized to a hitherto unreported organic/inorganic hybrid material featured by a robust and flexible 1,3-diketone tail. We have therefore initiated an investigation into the preparation of this novel hybrid material. Herein, we disclose that this method is indeed feasible, and the obtained 1,3-diketone-functionalized material can be used in immobilizing Cu, Zn and Ru complexes. Benefiting from the good flexibility of the ligand linker, the obtained catalysts displayed remarkable catalytic activity in several organic reactions. Taking into account the fact that many 1,3-diketones can be used to prepare the substituted 3,4-dihydropyrans through a simple procedure,[12] this approach should be applicable for implementing the immobilization of many 1,3-diketone ligands.

Results and Discussion

Because a SH-functionalized HMS material that contains a high loading of mercapto group can be easily synthesized through a well-known procedure,[13] our study commenced from verifying the feasibility using a thiol as a nucleophile in the ring-opening reaction of 2-butoxy-3,4-dihydropyran **1a**. Thus, **1a** was treated with benzyl mercaptan in the presence of catalytic amount of $ZnCl_2$. After 10 hours of reaction at 80 ^{o}C, the expected 2-alkylated 1,3-diketone **2a** was obtained in 99 % yield. This result implies that (i) this type of 3,4-dihydropyran can easily react with thiol; and (ii) the generated 1,3-diketone is quite stable under the reaction conditions. In view of the fact that the experimental procedure is quite simple and convenient, and the reaction conditions are amenable to scale-up, we therefore deduced that the ring-opening reaction of **1a** with thiol should be applicable in a solid/liquid interface reaction, with which a 1,3-diketone-functionalized organic/inorganic hybrid material can be prepared.



Scheme 1. Ring-opening reaction of dihydropyran **1a** with benzyl mercaptan.

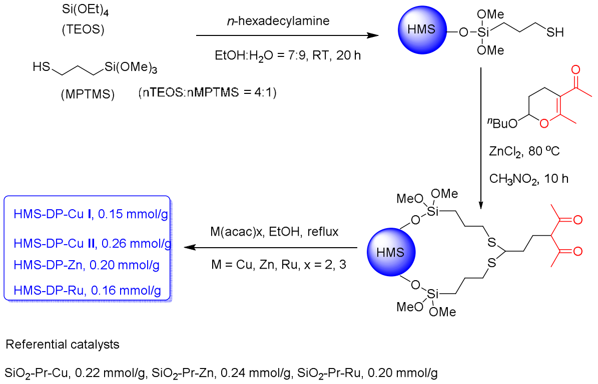


Figure 1. Silica-supported catalysts with different metals in this work.

We then started to investigate the possibility of preparing a silica-supported metal acetylacetonate (acac) complex with the aid of this ring-opening reaction. The aim of the first series of experiments was to evaluate whether or not the ring-opening reaction of dihydropyran **1a** could be used to anchor an acac fragment onto the surface of HMS-SH. Thus, a SH-functionalized HMS, HMS-SH, was prepared and then treated by **1a**. The XRD patterns show the amorphous texture of these silica materials (**Figure S1**). By means of elemental analysis, the loading of SH group in HMS-SH was confirmed to be 2.21 mmol/g. To facilitate the reaction, excess amount of **1a** was used (SH/**1a** = 1/1). Amount of $ZnCl_2$ catalyst was also doubled. After 10 hours of reaction in nitromethane at 80 ^{o}C, an acetylacetone-modified HMS, HMS-acac, was obtained and submitted to elemental analysis. The carbon and hydrogen contents increased significantly, indicating occurrence of the grafting. Amount of the grafted acac fragment on the HMS is 0.67 mmol/g approximately (calculated based on the carbon context). IR spectroscopy was also used to elucidate the occurrence of the expected grafting reaction. As shown in **Figure 2**, all the hybrid materials showed characteristic peaks of $-CH_2$ stretching band at 2930 cm^{-1}. The disappearance of the S–H stretching band at 2450 cm^{-1}, accompanied by the appearance of a characteristic band of carbonyl group in 1700 cm^{-1}, constitutes strong evidence for the nondestructive tethering of an acac fragment. Characterization with ^{13}C MAS NMR spectra revealed also successful anchoring of acac onto HMS-SH because of the appearance of two peaks around 200 ppm, which can be assigned to the keto-carbonyl group (**Figure 3**). These spectra showed also that the latter contained more aliphatic carbons than the former. Two characteristic carbons of the ring-opening product of **1a** with mercaptan, including (i) a carbon between two sulfur atoms and (ii) C3 carbon of the diketone

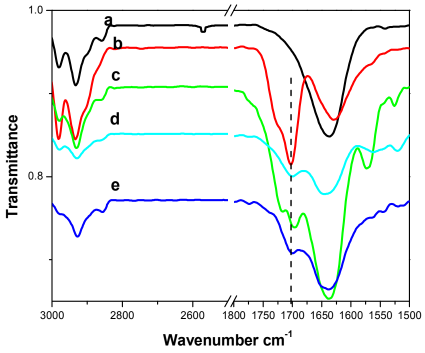


Figure 2. IR spectra of a) HMS-SH, b) HMS-acac, c) HMS-DP-Cu **II**, d) HMS-DP-Ru, e) HMS-DP-Zn.

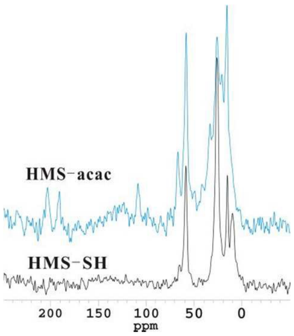


Figure 3. ^{13}C MAS NMR spectra of HMS-SH and HMS-acac.

Table 1. Physicochemical data of the obtained organic/inorganic hybrid materials.

entry	catalyst	loading amount (mmol/g)	BET surface (m^2/g)
1	HMS-HS	0	1316
2	HMS-acac	0	1203
3	HMS-PD-Cu **I**	0.15	1120
4	HMS-DP-Cu **II**	0.26	1038
5	HMS-DP-Zn	0.20	1123
6	HMS-DP-Ru	0.16	1116

fragment, were clearly observed, which appear at 65 to 70 ppm. These results implied that the grafting of acac onto the surface of HMS-SH is indeed successful. Due perhaps to occurrence of over-reactions, some aromatic peaks were also observed in the range of 110 to 140 ppm. These materials were also submitted to TEM, SEM and BET analysis. No significant change in terms of morphology (see **Figure 4**) and surface area (see **Table 1**) was observed before and after implementing the grafting with **1a**. From SEM images of **Figure 4**, the particle size of HMS-SH and HMS-acac is not very uniform, and generally in the range of 0.5 to 1.5 µm. TEM images of HMS-SH and HMS-acac indicate that these hybrid materials have abundant nanoporous structures (**Figure 5**). Grafting of HMS-SH with **1a** occurred probably in the inside of the pore. The incorporation of the organic entities within the silica network can be verified by a color addition of TEM images.

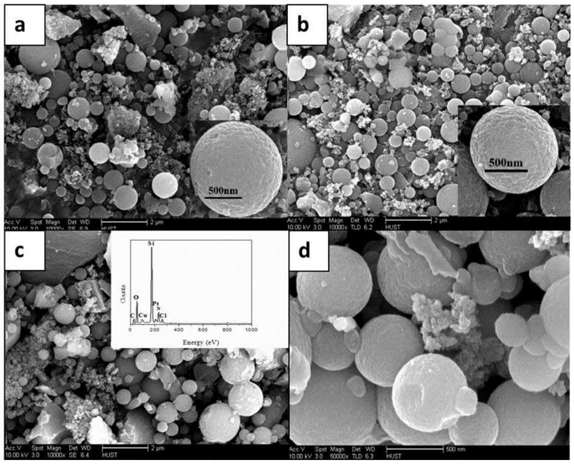


Figure 4. SEM images of functionalized silica materials. a) HMS-SH, b) HMS-acac, c) fresh HMS-DP-Cu **II**, d) recycled HMS-DP-Cu **II**.

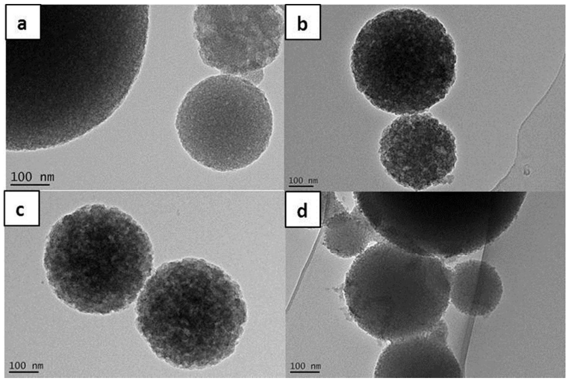


Figure 5. TEM images of functionalized silica materials. a) HMS-SH, b) HMS-acac, c) fresh HMS-DP-Cu **II**, d) recycled HMS-DP-Cu **II**.

We then tried to use the obtained HMS-acac to immobilize some homogeneous metal acetylacetonate complexes. As we expected, HMS-acac is indeed amenable to heterogenizing copper (II) acetylacetonate. Simple treatment of HMS-acac with $Cu(acac)_2$ in ethanol solvent under reflux conditions provided two catalysts, which were denoted as HMS-DP-Cu **I** and HMS-DP-Cu **II**, respectively. Likewise, HMS-DP-Zn and HMS-DP-Ru can also be prepared through a similar procedure. The metal loadings in these materials are in a range from 0.15 mmol/g to 0.26 mmol/g (**Figure 1**). The install of acac fragment onto HMS surface is the key to make the immobilization possible as a very low metal loading, 0.01 mmol/g, was obtained by treating HMS-SH with $Cu(acac)_2$ under the identical conditions. The incorporation of the copper complex with silica support could also be confirmed by energy-dispersive X-ray analysis (EDX) (**Figure 4,** picture **c**), which indicates also the presence of all the other expected elements. SEM image of HMS-DP-Cu **II** indicated that irregular agglomeration of the particles occurred during the immobilization of metal complex (**Figure 4**, picture **c**). The IR spectra revealed that the coordination of metal with the tethered acac ligand induced a weakened C=O bond, resulting in a slight red-shift on the stretch vibration of the carbonyl group. In addition, new peaks appear at 1550 cm^{-1} after loading metal acetylacetonate, which could be attributed to the stretch vibration of C=C band in the enol form of the acac fragment. It is in a good accordance with the IR data of the metal acetylacetone complex (see **Figure S2-S4**).

The hybrid materials were also submitted to XPS analysis, and the results are shown in **Figure 6**. In Cu 2p XPS spectrum of HMS-DP-Cu **II**, no characteristic peak of Cu^{2+} was observed (around 942 eV), indicating that the copper species was reduced in the course of immobilization. Meanwhile, a sharp peak appeared in 932.5 eV, which is a strong evidence to proof the occurrence of a reduction of Cu^{2+}. A strong interaction between the anchored thiol and $Cu(acac)_2$ should be responsible to the reduction,[14] which is able to convert thiol to disulfide. Indeed, the XPS pattern of S 2p region showed a component located at around 163.8 eV, which is attributed to the presence of disulfide on the surface of HMS-DP-Cu **II**. In the XPS pattern of C 1s region, contributions of C-O (286.2 eV), C=O (287.6

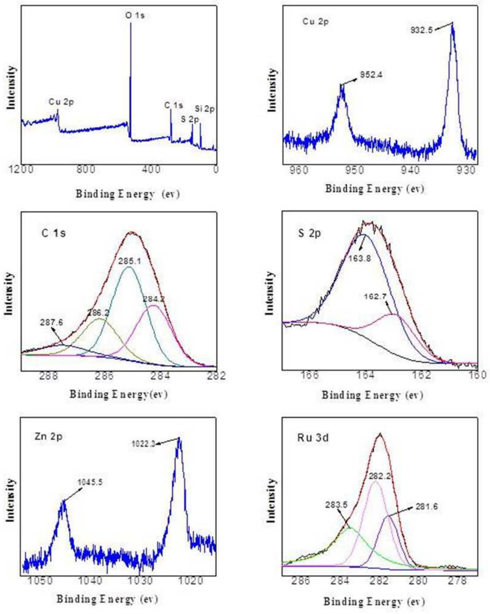


Figure 6. XPS spectra of HMS-DP-Cu **II** in the regions of Cu 2p, C 1s and S 2p, XPS spectrum of HMS-DP-Zn in the region of Zn 2p, and XPS spectrum of HMS-DP-Ru in the region of Ru 3d.

eV), C-C (285.1 eV), C=C (284.2 eV) and C-S (286.5 eV) bonds can all be found. With HMS-DP-Zn, characteristic peaks of Zn^{2+} (1022.3 eV) were clearly observed in the XPS pattern of Zn 2p region. However, in case of HMS-DP-Ru, three ruthenium species could be found in the XPS pattern of Ru 3d region, which involves RuO_4 (283.5 eV), Ru^{4+} (282.2 eV) and Ru^{3+} (281.6 eV).

The obtained organic/inorganic hybrid materials were also submitted thermal gravimetric analysis, and the obtained results are shown in **Figure 7**. HMS-SH was found to be quite stable in temperature below 250 °C. After treatment of **1a**, due to a significant increase of organic component in the obtained hybrid material, a drastic weight loss comes about 100 °C earlier. Loading of Zn and Ru did not change the thermal stability of the hybrid material. But, the congener with Cu is not very stable and it starts to decompose at 130 °C. These results imply that the organic/inorganic hybrid materials synthesized based on the ring-opening reaction of dihydropyran **1a** and thiol have a decent thermal stability, and thus are qualified to be used as catalysts under mild conditions.

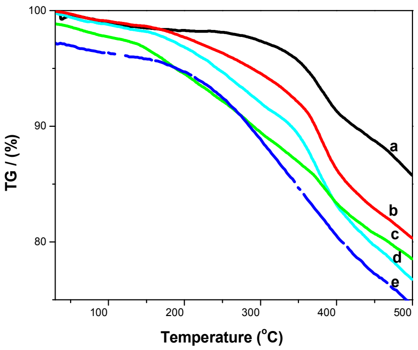


Figure 7. Thermogravimetric weight loss of the obtained hybrid materials. a) HMS-SH, b) HMS-acac, c) HMS-DP-Cu **II**, d) HMS-DP-Ru, e) HMS-DP-Zn.

Having the expected materials in hand, we then started to examine their catalytic activities. In order to compare the efficiency, three referential supported metal acetylacetonate catalysts were also prepared according to a reported enamine formation method (**Figure 1**). Firstly, we examined the supported copper catalysts in a three-component click reaction of NaN_3, phenylacetylene **3a** and benzyl bromide **4a**.

This reaction has been extensively investigated and widely used in chemistry and biology.[15] Generally, homogenous copper salts, such as $Cu(OAc)_2.H_2O$[16] and CuI[17], were used as catalysts. To facilitate the catalyst recovery, various solid copper catalysts, such as ammonium salt-tagged NHC-Cu(I) complexes,[18] cross-linked polymeric ionic liquid material-supported copper,[19] and glutathione bearing nano-ferrites,[20] have been developed in this type of reaction, sometimes with remarkable results.[21] However, these catalyst systems are associated with one or more disadvantages, such as the use of sodium ascorbate as additive,[22] tedious procedure for preparation, hazardous and carcinogenic organic solvents like nitrobenzene, acetonitrile, dioxane for reactions. Hence, a simple, green, and efficient procedure avoiding these drawbacks will be of much use. HMS-DP-Cu **II** was proved to be highly active for catalyzing this reaction, and the desired cycloaddition product **5a** was obtained in almost quantitative yield with exclusive 1,4-regioselectivity (**Table 2**, entry 7). The

Table 2. Optimization of the conditions of the three-component click reaction of NaN_3, phenylacetylenes and benzyl halides.[a]

entry	catalyst	solvent	yield(%)[b)]
1	HMS–DP- Cu **II**	—	19
2	HMS–DP- Cu **II**	1,4-Dioxane	trace
3	HMS–DP- Cu **II**	CH_3NO_2	20
4	HMS–DP- Cu **II**	DCE	trace
5	HMS–DP- Cu **II**	toluene	trace
6	HMS–DP- Cu **II**	H_2O	70
7	HMS–DP- Cu **II**	EtOH	99 (98[f)])
8	HMS–DP- Cu **I**	EtOH	70
9	$Cu(acac)_2$	EtOH	57
10	SiO_2-Pr-Cu	EtOH	64
11[c)]	HMS–DP- Cu **II**	EtOH	63
12[d)]	HMS–DP- Cu **II**	EtOH	75
13[e)]	HMS–DP- Cu **II**	EtOH	98

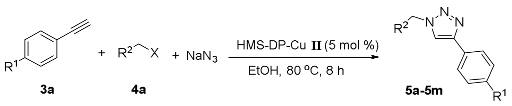
[a] **3a**: 0.2 mmol, **4a**: 0.2 mmol, NaN_3: 0.24 mmol, solvent: 1.0 ml. [b] Isolated yield. [c] 40 °C. [d] 6 h. [e] The catalyst was reused in the third time. [f] 10.0 mmol scale reaction.

reaction was performed in the absence of sodium ascorbate. Taking this together with the results obtained from the XPS pattern of Cu 2p region, we deduced that, during the preparation of HMS-DP-Cu II, Cu^{2+} was reduced to Cu^+, which was considered to have higher catalytic activity in this type of reaction that the former one.[17] Among the various solvents that were screened, ethanol was recognized to be the best medium for this reaction (entries 1 to 7). HMS-DP-Cu **I** can also catalyze this reaction, but the efficiency is much lower as compared with HMS-DP-Cu **II** (entry 8). Interestingly, with a homogeneous counterpart of these catalysts, $Cu(acac)_2$, only 57 % yield was obtained under the identical conditions (entry 9). When a referential copper catalyst, SiO_2-Pr-Cu, which was prepared through a reported enamination reaction, was used, the yield of **5a** is rather poor (entry 10). This result demonstrates that this immobilization method is able to offer us a better catalyst than the conventional route. The reaction was also affected by temperature and reaction time, and the optimal conditions were finally confirmed to be the followings: ethanol solvent, 5 mol % of HMS-DP-Cu **II**, 80 °C and 8 hours (entries 11 and 12). It is worth noting that the reaction can also be effectively scaled up with the similar efficiency. For example, the reaction of **3a** (10 mmol) with **4a** (10 mmol) and NaN_3 (12 mmol) gave the corresponding cycloaddition product **5a** in 98% yield (2.3 g).

The aim of this study is to develop a new catalyst system that not only is capable of catalyzing three-component click reactions efficiently, but also could be recycled easily and steadily. To test the recyclability of HMS-DP-Cu **II** catalyst, after reaction, the recovered solid catalyst was washed with ethanol and dried under vacuum condition at 60 °C, and then, subjected to the next run. After four consecutive runs, HMS-DP-Cu **II** catalyst is still capable of catalyzing the model reaction in 98 % of yield (**Table 2**, entry 13), indicating the fact that the present HMS-DP-Cu catalyst is quite robust under the reaction conditions. SEM and TEM images of the recycled HMS-DP-Cu **II** showed that the particle size does not changed significantly, and the integrity of the catalyst remained very well (**Figure 4** and **Figure 5**). We also investigated Cu leaching during the reaction. The heterogeneous catalyst was isolated by centrifugation after 4 hours of reaction (ca. 65 % yield) and the solution phase was allowed to react for a further 4 hours under the same conditions. The yield of **5a** was only 66 % after that time, which confirmed that there was hardly any leaching of Cu into the reaction mixture. ICP-MS showed that the Cu content of the catalyst did not change appreciably after the reaction. The slight decrease in catalytic activity in subsequent runs may be due to the unavoidable loss of solid catalyst during recovery and washing.

With the optimized conditions in hand, we probed the scope of the reaction with respect to both the phenylacetylene and the alkylhalide components. As evidenced by the results in **Table 3**, phenylacetylenes with different substituents smoothly reacted with **4a**, producing the corresponding cycloaddition products in generally excellent yields (entries 1 to 9). Various benzyl bromides were then utilized in this reaction (entries 10 to 13). In all cases, excellent yields were obtained, whatever the nature of the substituent present on the phenyl ring (electron-donating or electron-withdrawing). Compound **5a** can also be synthesized with the same efficiency by using benzyl chloride as substrate instead of benzyl bromide (entry 2). Ethyl iodide participated readily in this reaction as well, and the expected product, **5m**, was obtained in 70 % yield (entry 14).

Table 3. The substrate scope of HMS-DP-Cu-catalyzed three-component click reaction of NaN_3, phenylacetylenes and benzyl halides.[a]

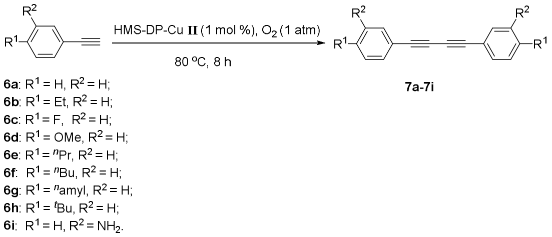


entry	R^1	X	R^2	product	yield(%)[b]
1	H	Br	Ph	**5a**	99
2	H	Cl	Ph	**5a**	99
3	F	Br	Ph	**5b**	99
4	OMe	Br	Ph	**5c**	93
5	*t*-Bu	Br	Ph	**5d**	80
6	Et	Br	Ph	**5e**	85
7	*n*-Pr	Br	Ph	**5f**	90
8	*n*-Bu	Br	Ph	**5g**	99
9	*n*-amyl	Br	Ph	**5h**	90
10	H	Br	4-NO_2-C_6H_4	**5i**	95
11	H	Br	*n*-heptyl	**5j**	99
12	H	Br	*n*-amyl	**5k**	99
13	H	Br	Bn	**5l**	99
14	H	I	Me	**5m**	70

[a] Reaction conditions: **3a/4a/**NaN_3 = 1:1:1.2, solvent: EtOH: l.0 ml. [b] Isolated yield.

In order to extend the utility of this immobilized metal acetylacetonate catalyst, we then examined some other reactions with HMS-DP-Cu. The second reaction we investigated is Glaser oxidative homo-coupling of phenylacetylene, which is an important organic transformation that can produce, in a direct way, diyne derivatives.[23] Recently, a plethora of methods have flourished around Glaser coupling reactions by using Cu species as catalyst.[24] It is pertinent to note here that, in this type of reaction, solid catalysts showed not only a good performance but also, in some cases, a robust activity. Unfortunately, the costs of many solid catalysts are generally high, and thus restrict its application in practical synthesis. On the contrary, homogeneous Cu catalysts are very cheap, but often suffer from inefficiency in recycling the catalysts. Therefore, a new system that can combine both advantages of homogeneous and heterogeneous systems is appealingly needed. Although $Cu(acac)_2$ has been used in this reaction as catalyst, but no successful result was obtained.[25] HMS-DP-Cu **II** was found again to be an active catalyst for the homo-coupling of phenylacetylene **6a**. The reaction was performed at 80 °C with a balloon of oxygen. The solvent effect indicated that better result was obtained with ethanol (**Table 4**, entries 1 to 6). Various organic bases could promote the reaction, to some extent, and the best result was obtained when using pyridine as a base (entries 7 to 9). While good to excellent yields was obtained with HMS-DP-Cu **II** catalysts, the reaction over its homogeneous counterpart, $Cu(acac)_2$, proceeded sluggishly (entry 10). The use of a referential catalyst, SiO_2-Pr-Cu, resulted in the recovery of the most unreacted phenylacetylene (entry 11). We then investigated the recyclability of this catalyst, and it was found that HMS-DP-Cu **II** could be recycled in the model Glaser coupling reaction at least three times without significant loss of its activity (entry 12). Some other terminal alkynes can also be converted to the corresponding dikynes in excellent yields with the aid of HMS-DP-Cu **II** catalyst (entries 13 to 19). 2-Ethynyl aniline can also be converted smoothly to the corresponding product albeit the yield is slightly inferior as compared with **6a** (entry 20). These results demonstrated that HMS-DP-Cu is indeed a robust and an efficient catalyst for Glaser coupling reactions.

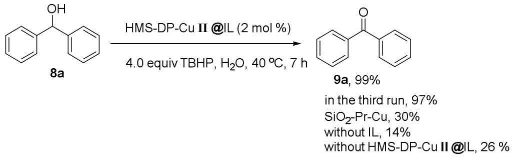
Table 4. HMS-DP-Cu **II** catalyzed Glaser coupling reaction of alkyne.[a]



entry	alkyne	solvent	product	yield (%) [b)]
1	**6a**	—	**7a**	60
2	**6a**	EtOH	**7a**	99
3	**6a**	H_2O	**7a**	38
4	**6a**	DCE	**7a**	13
5	**6a**	Toluene	**7a**	56
6	**6a**	CH_3NO_2	**7a**	43
7[c)]	**6a**	EtOH	**7a**	60
8[d)]	**6a**	EtOH	**7a**	50
9[e)]	**6a**	EtOH	**7a**	trace
10[f)]	**6a**	EtOH	**7a**	29
11[g)]	**6a**	EtOH	**7a**	N.D
12[h)]	**6a**	EtOH	**7a**	97
13	**6b**	EtOH	**7b**	99
14	**6c**	EtOH	**7c**	94
15[i)]	**6d**	EtOH	**7d**	90
16	**6e**	EtOH	**7e**	90
17	**6f**	EtOH	**7f**	90
18	**6g**	EtOH	**7g**	85
19	**6h**	EtOH	**7h**	80
20[j)]	**6i**	EtOH	**7i**	60

[a] alkyne: 0.4 mmol, pyridine: 0.4 mmol, solvent: 1.0 ml. [b] Isolated yield. [c] TMEDA was used as base. [d] Morpholine was used as base. [e] Triethylamine was used as base. [f] $Cu(acac)_2$ was used as catalyst. [g] SiO_2-Pr-Cu was used as catalyst. [h] The catalyst was reused in the third time. [i] 12 h, catalyst loading: 2 mol %. [j] 10 h, catalyst loading: 2 mol %.

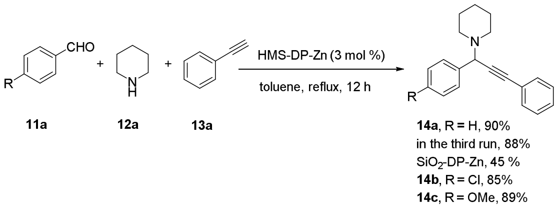
$Cu(acac)_2$ has been used as catalyst in oxidation of secondary alcohols in an ionic liquid [BMIm]BF_4.[26] Taking a cue from this report, we then used HMS-DP-Cu catalyst in the oxidation of benzhydrol by using TBHP as oxidant. As expected, in an ionic liquid [OMIm]NTf_2, benzhydrol can be converted to benzophenone in almost quantitative yield over HMS-DP-Cu **II** catalyst. Because the solvent, [OMIm]NTf_2, is rather expensive, to decrease the cost, we then turned to a concept of supported catalyst with ionic liquid.[27] The HMS-DP-Cu catalyst was therefore coated by 30 wt % of [OMIm]NTf_2, and the obtained fine powder was denoted as HMS-DP-Cu **II**@IL. Gratifyingly, this IL-decorated catalyst showed also an excellent catalytic activity in the oxidation of benzhydrol, and benzophenone could be obtained in 99 % yield after 7 hours of reaction at 40 °C. Direct use of HMS-DP-Cu **II** as catalyst under the identical conditions resulted in an insufficient conversion of benzhydrol. Therefore, coating of [OMIm]NTf_2 onto this ready-made solid catalyst is critical to achieve a good efficiency. The reaction over a referential catalyst, SiO_2-Pr-Cu, sluggishly proceeded, and benzophenone was obtained only in 30 % of yield. Because the reaction was performed in water, considering also the fact that [OMIm]NTf_2 is a hydrophobic fluid, we therefore deduced that the reaction might be accelerated by a hydrophobic microenvironment created by loading this ionic liquid onto the solid.[28] HMS-DP-Cu **II**@IL can be easily recovered and reused. As shown in **Scheme 2**, its catalytic activity persisted very well, and the desired benzophenone could be obtained in 97 % yield in the third run.



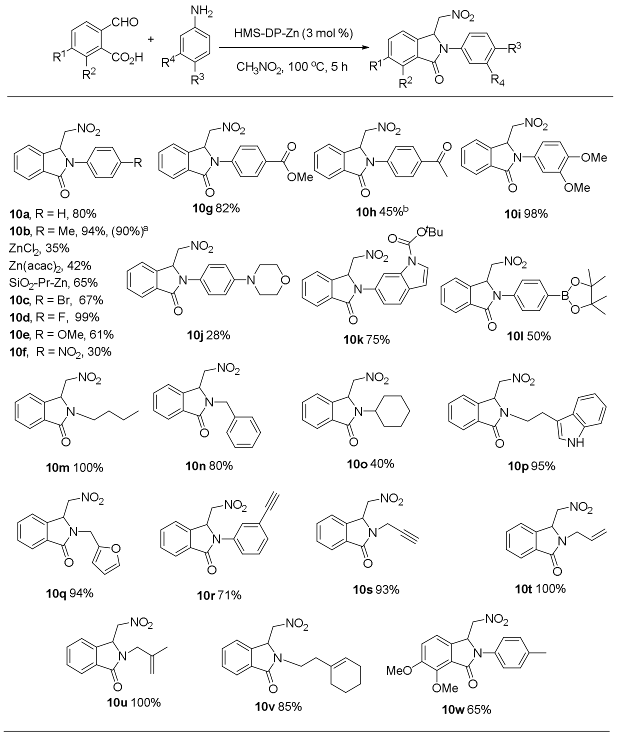
Scheme 2. HMS-DP-Cu **II**@IL catalyzed alcohol oxidation reaction.

The above-mentioned results demonstrated that the use of dihydropyran **1a** as dual anchoring reagent and ligand donor is indeed feasible for the immobilization of $Cu(acac)_2$. Good results obtained by using HMS-DP-Cu as catalyst encouraged us to scrutinize the performance of other support metal acetylacetonate catalysts. Gratifyingly, a hitherto unreported three-component reaction of 2-carboxybenzaldehyde, aniline and nitromethane was established by using HMS-DP-Zn as catalyst, which produced a 2,3-dihydroisoindol-1-one derivative **10a** (**Scheme 3**). The reaction might proceed through a tandem nitro-Mannich and amidation reaction.[29] HMS-DP-Zn works very well for promoting this reaction, and the expected product, **10a**, was obtained in 80 % yield. The homogeneous counterpart, $Zn(acac)_2$, and a commonly used Lewis acid, $ZnCl_2$, can also be used as decent catalysts, but the yields obtained are inferior. It should be noted that, by increasing either the reaction time to 24 hours or the catalyst loading to 10 mmol %, good yields can be obtained with these homogeneous catalysts. When a referential catalyst, SiO_2-Pr-Zn, the yield of **10a** reached 65 %. We thus believe that the support in HMS-DP-Zn catalyst played to some extent the role of concentration amplifier of the metal catalyst. The support tethered all the metal species onto its surface, thanks to the adequate banding manner, a good flexibility of the metal species was achieved, ensuring thus a good activity of the immobilized catalyst. In this three-component reaction, HMS-DP-Zn catalyst can be recycled at least two times without significant loss of its activity.

Anilines with electron-donating groups, such as methyl, methoxy and fluoro, participated readily in the condensation reactions, providing the corresponding 2,3-dihydroisoindol-1-ones in good to excellent yields (**10b**, **10d**, **10i**, and **10j**). Anilines with electron-withdrawing groups, such as methoxycarbonyl, acetyl and nitro, can also be used in the reaction (**10f** to **10h**). But, in some cases, the reaction time has to be increased to 12 hours. Even though, the yields of **10f** and **10h** are rather inferior. Heterocycle-containing anilines, N-(Boc)-6-aminoindole and 4-morpholinoaniline can also be smoothly converted without affecting the stability of these moieties (**10j** and **10k**). It should be noted that although a three-component reaction of 2-carboxybenzaldehyde, aniline and indole has been reported,[30] the reaction of N-(Boc)-6-aminoindole selectively occurred in the site of NH_2 group under the present conditions. 4-Aminophenylboronic acid pinacol ester reacted readily also with 2-carboxybenzaldehyde and nitromethane, producing the corresponding product **10l** in 50 % of yield. Aliphatic amines, such as *n*-butylamine and benzylamine, have also been examined, and the desired products were obtained in almost quantitative yields (**10m** and **10n**). However, due perhaps to steric hindrance, cyclohexylamine participated in this reaction reluctantly (**10o**). Tryptamine and furfurylamine can be converted to the expected product without damage of the heterocyclic fragments (**10p** to **10q**). Double and triple bonds in the starting substrates can all be delivered uneventfully into the skeletons of the products (**10r** to **10v**). 2-Carboxy-3,4-dimethoxybenzaldehyde can also be used as a viable substrate of this three-component reaction (**10w**).



Scheme 4. HMS-DP-Zn catalyzed A^3 reaction.



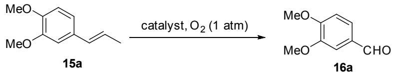
^{a} The catalyst was used in the third run. ^{b} Reaction time was 12 h.

Scheme 3. HMS-DP-Zn catalyzed three-component reaction of 2-carboxybenzaldehyde, amine and nitromethane.

HMS-DP-Zn can also be used as a recyclable catalyst in a three-component reaction of phenylacetylene, benzaldehyde and piperidine (**Scheme 4**).[31] While good yield of **14a** (90 %) was obtained with this catalyst, only 45 % of yield was obtained by using SiO_2-Pr-Zn as catalyst. Likewise, **14b** and **14c** can also be synthesized in excellent yields under the identical conditions.

Finally, HMS-DP-Ru was used in the oxidation of isoeugenol methyl ether, which can be used to produce veratraldehyde. Previously, this type reaction has been investigated by many systems, such as methyltrioxorhenium/H_2O_2,[32] H_2O_2/*n*-Bu_4NVO_3/pyrazine-2-carboxylic acid,[33] VCl_2(salen)/TBHP,[34] $KMnO_4/CuSO_4{\cdot}5H_2O$,[35] $NaIO_4/OsO_4$,[36] $PhI(OAc)_2$-NaY,[37] and so on. A ruthenium salt, $RuCl_3$, has been used as catalyst in this type of reaction in conjunction with $NaIO_4$ oxidant, but the yield obtained is rather low.[38] Cleavage of a C=C double bond adjacent to an aromatic ring to yield the corresponding carbonyl compounds can also use molecular oxygen as the oxidant, which however, associated with a biocatalytic method.[39] In view of the increasing synthetic importance of the target aldehydes as synthons in various organic transformations, the development of simple, convenient, and environmentally friendly oxidation systems are desirable. We found unexpectedly that $Ru(acac)_3$ is a potent catalyst for promoting the oxidation of isoeugenol methyl etherto veratraldehyde. In the presence of 1 mol% of $Ru(acac)_3$, after 4 hours reaction at 120 °C in a sealed tube, veratraldehyde could be obtained in 85 % yield (**Table 5**, entry 1). Among the various solvents that were screened, DMSO was recognized to be the best one for this reaction (entries 2 to 8). In the absence of $Ru(acac)_3$, the reaction proceeded sluggishly, and only 34 % yield was obtained under the identical conditions (entry 9). With an increase of reaction time from 4 hours to 6 hours, yield of **16a** could be increased from 85 % to 95 % (entry 10). Gratifyingly, in the oxidation of isoeugenol methyl ether, catalyst load as low as 0.4 mol % can be used to lead to high yield (entry 11). To facilitate the recycling of catalyst, HMS-DP-Ru and SiO_2-Pr-Ru were used instead of the homogeneous catalyst, $Ru(acac)_3$. While almost the same yield was obtained with the former, only 60 % yield was obtained with the latter (entries 12 and 13). It is conceivable that the immobilization allows all the metal species stay steadily on the silica surface, increasing thus the catalyst concentration of local reaction domain. Considering the good flexibility conferred by the unique linker structure, it is quite reasonable to have a good catalytic activity with HMS-DP-Ru. Under optimal conditions, TON of this catalyst in the model oxidation reaction reached 234, which is quite remarkable. To test the recyclability of HMS-DP-Ru, this catalyst was recycled 6 times, as shown in **Figure 8**. The high activities were preserved throughout recycling. It is noteworthy that, after 6 runs, the TOF decreased by only about 10% with respect to that of the fresh catalyst (29 vs 26 h^{-1}), giving a total TON of 1338.

Table 5. HMS-DP-Ru catalysed oxidation of isoeugenol methyl ether to veratraldehyde.[a]



entry	catalyst	solvent	temp. (^{o}C)	time (h)	yild[b]
1	$Ru(acac)_3$ (1 %)	DMSO	120	4	85
2	$Ru(acac)_3$ (1 %)	EtOH	60	4	NR
3	$Ru(acac)_3$ (1 %)	CH_3NO_2	100	4	10
4	$Ru(acac)_3$ (1 %)	DCE	80	4	20
5	$Ru(acac)_3$ (1 %)	Toluene	100	4	Trace
6	$Ru(acac)_3$ (1 %)	CH_3CN	80	4	NR
7	$Ru(acac)_3$ (1 %)	1,4-Dioxane	100	4	50
8	$Ru(acac)_3$ (1 %)	THF	60	4	40
9	—	DMSO	120	4	34
10	$Ru(acac)_3$ (1 %)	DMSO	120	6	95
11	$Ru(acac)_3$ (0.4 %)	DMSO	120	8	94
12	HMS-DP-Ru (0.4 %)	DMSO	120	8	93
13	SiO_2-Pr-Ru (0.4 %)	DMSO	120	8	60
14[c]	HMS-DP-Ru (0.4 %)	DMSO	120	8	93

[a] The reaction was performed with 0.4 mmol, solvent: 1.0 ml. [b] Isolated Yield. [c] 10.0 mmol scale reaction.

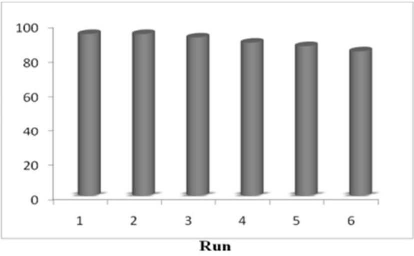


Figure 8. Reuse of HMS-DP-Ru catalyst.

Conclusions

A new method for grafting acetylacetone ligand onto HMS support is described, which stems upon a ring-opening reaction of 2-alkoxy-3,4-dihydropyran with thiol. The use of easily accessible dihydropyran as dual anchoring reagent and ligand donor not only enables successful tethering of acetylacetone fragment onto the surface of a ready-made SH-functionalized HMS, but also ensures a good flexibility, maximizing thus catalytic activity of the immobilized metal acetylacetonate complex. Three supported metal catalysts were prepared and characterized by many physicochemical methods including FT-IR, elemental analysis, ^{13}C MAS NMR, SEM, TEM, EDX, XPS, and TG. Their catalytic applications in the selected organic reactions demonstrated a great success of this immobilization strategy. This method is also characterized by some other advantages, such as simple operational procedure, the use of easily available reagents, and mild conditions. All these alluring properties conferred the present protocol a great potential to be applied in practical uses.

Experimental Section

General

Melting points were determined on a microscopic melting point apparatus and are uncorrected. IR spectra were recorded on a Bruker FT-IR (EQUINOX 55) using KBr pellets or neat liquid technology. Thermogravimetric analysis (TGA) was performed under a flow of nitrogen by heating from room temperature to 500 ^{o}C at a rate of 10 ^{o}C/min. The catalysts surface areas, N_2 adsorption isotherm (77.3 K) were measured using Micromeritics ASAP 2020 M surface area. Before analysis, the samples were degassed at 110 ^{o}C for 8 h under vacuum (10^{-5} bar). Elemental analysis (EA) was determined using a Vario Micro cube Elemental Analyser (Elementar, Germany). AES data were recorded on an Agilent Technologies 4100 MP-AES. Field emission scanning electron microscope (FSEM) and energy-dispersive X-ray spectroscopy (EDX) analyses were carried out on a Holland FEI Instruments Sirion 200 operating at 30 kV. FTEM samples were prepared by placing drops of the catalysts suspension dispersed in ethanol on a carbon-coated copper grid. X-ray diffraction (XRD) patterns were recorded on a PANalytical B.V. X'Pert PRO diffractometer. ^{13}C CP MAS NMR experiments were performed on a Varian Infinity Plus-400 spectrometer working at 9.39T, corresponding to a ^{1}H frequency of 399.5 MHz and a ^{13}C frequency of 100.5 MHz. A 5 mm double resonance MAS probe was used. For CP, a ^{1}H 90^{o} pulse of 8 µs length was followed by a contact time of 2.0 ms. Field strengths for high-power decoupling during acquisition were in the range 70-80 kHz. The spinning frequencies were 5.0 kHz during the measurements of all samples, the -CH_3 of the standard sample with the external standard is 17.35 ppm. X-ray photoelectron spectra (XPS) were recorded on a SHIMADZU -Kratos AXIS-ULTRA DLD-600W X-ray photoelectron spectrometer at a base pressure of 2×10^{-9} Pa in the analysis chamber using Al Kα radiation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400. Chemical shifts are expressed in ppm relative to Me_4Si in solvent. All chemicals used were of reagent grade and were used as received without further purification. All reactions were conducted in a 10-mL V-type flask equipped with triangle magnetic stirring.

Typical procedure for the preparation of HMS-DP-M (M = Cu, Zn, Ru) catalysts, for example (HMS-DP-Cu II). To a 50 ml round bottle, 3.2 g (0.013mol) of *n*-hexadecylamine was dissolved at room temperature in aqueous ethanol (ethanol/water = 7/9 v/v). Then, 8.3 g of tetraethoxysilane (TEOS, 0.039mol) and 1.97 g of 3-mercaptopropyltrimethoxysilane (MPTMS, 0.01 mol) was simultaneously but separately added to the template mixture. The resulting solution was stirred for 20 hours at room temperature and the white solid was recovered by filtration. Removal of *n*-hexadecylamine was carried out by soxhlet extraction over boiling ethanol for 18 hours affording an organic/inorganic hybrid material, HMS-SH. Then, HMS-SH was dried in an oven at 60 ^{o}C (10^{-1} mmHg) for 18 hours. After that, 2 g of the obtained HMS-SH was treated with excess amount of **1a** (0.85 g, SH/**1a** = 1/1). After 10 hours of reaction in nitromethane at 80 ^{o}C, the acetylacetone-modified HMS, HMS-acac, was obtained by filtration and then washed with ethanol

(50 ml ×3). Then the HMS-acac was dried in an oven at 60 ^{o}C for 18 hours. After that, 2 g of acetylacetone-modified HMS and excess amount of Cu(acac)$_2$ (0.5 mmol, 0.13g, HMS-acac/Cu(acac)$_2$ = 2/1 (n/n)) were added to a 100 ml round bottom flask in 30 ml ethanol, the solution was reflux for 48 hours, then the HMS-DP-Cu solid was obtained by filtration and then washed with ethanol (50 ml × 5), then catalyst was dried in an oven at 60 ^{o}C for 24 hours. The loading of copper was measured by AES, and the value was 0.26 mmol/g^{-1}.

General procedure for the ring-opening reaction of a dihydropyran 1a with benzyl mercaptan for the synthesis 2a: A solution of **1a** (10 mmol, 2.1 g) in nitromethane (25 ml) was mixed with benzyl mercaptan (25 mmol, 3.1 g), then ZnCl$_2$ (20 mol %, 2.0 mmol, 273 mg) was added. The mixture was stirred at 80 °C for 10 h. After the reaction, the product **2a** was obtained in 99% yield (9.9 mmol, 3.82 g) by column chromatography (elutent: petroleum ether/ethyl acetate = 10/1 (v/v)).

General procedure for the click reaction of sodium azides, alkynes and benzyl halides. To a reactor containing alkyne (0.2 mmol), alkyl halide (0.2 mmol), sodium azide (0.24 mmol) and EtOH (1.0 ml), HMS-DP-Cu (5 mol %, 0.01 mmol) was added. The mixture was stirred for 8 hours at 80 ^{o}C. After the reaction completed, the solution was centrifuged, and the upper organic phase was isolated. The bottom solid was washed with ethyl acetate (0.5 ml × 3). The acquired organic layer was concentrated *in vacuo*. The pure product was obtained by preparative TLC using a mixture of ethyl acetate and petroleum ether as eluent (EA/PE=1/3 v/v).

General procedure for the Glaser coupling reaction. *Reaction conditions*: alkyne (0.4 mmol), EtOH, 1.0 ml, HMS-DP-Cu (1 mol %, 0.002 mmol) and piperidine (1.0 equivalent, 0.2 mmol). The mixture was stirred for 8 hours at 80 ^{o}C under O$_2$ atomosphere. After completion of the reaction, the solution was centrifuged, and the upper organic phase was isolated. The bottom solid was washed with ethyl acetate (0.5 ml × 3). The acquired organic layer was concentrated *in vacuo*. The pure product was obtained by preparative TLC using petroleum ether.

General procedure for the sec-alcohol oxidation reaction. *Reaction conditions***:** benzhydrol (0.4 mmol), H$_2$O, 1.0 ml, HMS-DP-Cu **II**@IL (2 mol %, 0.004 mmol) and TBHP (4.0 equivalent, 0.8 mmol). The reaction mixture was stirred at 40 ^{o}C for 7 hours. After completion of the reaction, the solution was centrifuged, and the upper organic phase was isolated. The bottom solid was washed with ethyl acetate (0.5 ml × 3). The acquired organic layer was concentrated *in vacuo*. The pure product was obtained by preparative TLC using a mixture of ethyl acetate and petroleum ether as eluent (EA/PE = 1/3 $_{v/v}$).

General procedure for the reaction of 2-carboxybenzaldehyde, amine and nitromethane. A solution of 2-carboxybenzaldehyde (0.3 mmol) in nitromethane (1.0 ml) was mixed with amine (0.3 mmol) and HMS-DP-Zn (3 mol %, 0.009 mol). The mixture was stirred at 100 ^{o}C for 5 hours. After completion of the reaction, the solution was centrifuged, and the upper organic phase was isolated. The bottom solid was washed with ethyl acetate (0.5 ml × 3). The acquired organic layer was concentrated *in vacuo*. The pure product was obtained by preparative TLC using a mixture of ethyl acetate and petroleum ether as eluent (EA/PE = 1/3 $_{v/v}$).

General procedure for A^3 reaction. A stirred solution of alkyne (0.75 mmol), HMS-DP-Zn (3 mol %, 0.015 mmol), aldehyde (0.5 mmol) and amine (0.65 mmol) in toluene (2.0 ml) was taken into a preheated oil bath (120 °C). After 12 hours of refluxing, the solution was centrifuged, and the upper organic phase was isolated. The bottom solid was washed with ethyl acetate (0.5 ml × 3). the organic layer was concentrated *in vacuo*. The pure product was obtained by preparative TLC using a mixture of ethyl acetate and petroleum ether as eluent (EA/PE = 1/5 v/v).

General procedure for oxidation of isoeugenol methyl ether to veratraldehyde. *Reaction conditions*: Isoeugenol methyl ether (0.4 mmol), DMSO, 1ml, HMS-DP-Ru (0.1 mol %, 0.0002 mmol). The reaction was performed at 120 ^{o}C under O$_2$ atmosphere for 8 hours. After completion of the reaction, water (1 ml) was added. The solution was centrifuged and extracted with EA (3 ml × 2). The acquired organic layer was concentrated *in vacuo*. The pure product was obtained by preparative TLC using a mixture of ethyl acetate and petroleum ether as eluent (EA/PE = 1/5 $_{v/v}$).

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Silica-supported metal acetylacetonate catalysts with a robust and flexible linker constructed by using 2-butoxy-3,4-dihydropyrans as dual anchoring reagents and ligand donors

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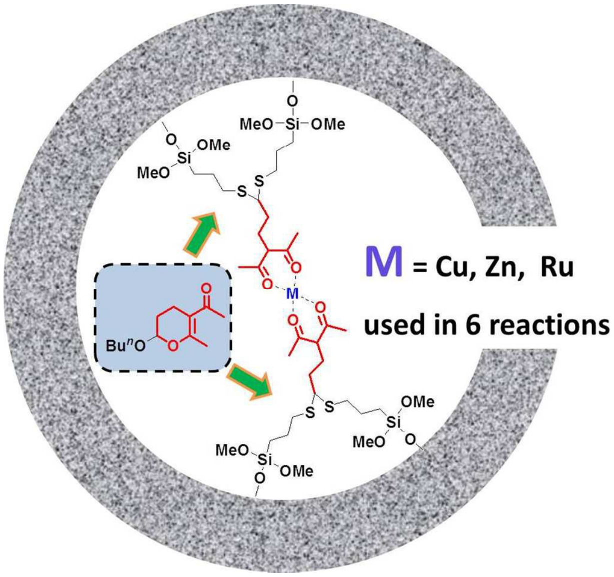

2-Butoxy-3,4-dihydropyrans were used, for the first time, as dual anchoring reagents and ligand donors to modify a ready-made SH-functionalized HMS. The obtained acac-functionalized silica was demonstrated to be an excellent support to immobilize homogeneous metal acetylacetonate catalysts.