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Green Chemistry

From Waste Biomass to Solid Support: Lignosulfonate as a Cost-Effective and Renewable Supporting Material for Catalysis

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Abstract: Lignosulfonate (LS) is an organic waste generated as a byproduct of the cooking process in sulfite pulping in the manufacture of paper. In this paper, LS was used as an anionic supporting material for immobilizing cationic species, which can then be used as heterogeneous catalysts in some organic transformations. With this strategy, three lignin-supported catalysts were prepared including 1) lignin-$SO_3Sc(OTf)_2$, 2) lignin-$SO_3Cu(OTf)$, and 3) lignin-IL@NH_2 (IL = ionic liquid). These solid materials were then examined in many organic transformations. It was finally found that, compared with its homogeneous counterpart as well as some other solid catalysts that are prepared by using different supports with the same metal or catalytically active species, the lignin-supported catalysts showed better performance in these reactions not only in terms of activity but also with regard to recyclability.

Introduction

The synthesis of novel catalysts with well-designed composition and structure tailored to the requirements of a particular application is one of the most active fields in catalysis research. The relationship between structure, organized environment, and catalytic properties of active species tells us how to establish a new strategy for the rational design of heterogeneous catalysts. However, to realize this goal, diversity of solid support has to be extended as much as possible because the chemical properties of the support have been shown to play an important role in determining catalyst activity and selectivity.[1] Although researchers are now able to manipulate, to some extent, the morphology and surface character of some supporting materials, such as metal oxides[2] and resins,[3] with the increasing demand on task-specific catalysis, especially in the area of sustainable energy and environmental science, preparation of new supporting materials with unique properties that enable researchers to conduct rational design of a catalytic system still remains a big challenge.

On the other hand, conversion of waste biomass to value-added materials has gained the attention of academia and industry. Particularly, in the last five years, a lot of effort has been devoted to converting lignin, which is one of the major parts of inedible biomass to valuable materials.[4] Although many kinds of lignin-based biomass are available, most of the efforts have been spent on valorization of natural lignin, and the rational utilization of the other lignin derivatives is far less studied. The salt of lignosulfonic acid is one of the most important lignin derivatives that is produced from an eluted solution (black liquor) obtained as a byproduct of the cooking process in sulfite pulping. The sulfonic group of lignosulfonate (LS) is usually introduced into the α-position of the phenylpropane structure of lignin by cleavage of the side chain.[5] Molecular mass of LS ranges from several hundred to several million according to the preparation conditions. Since LS consists of a C_6–C_3 hydrophobic basic structure with hydrophilic groups, such as sulfonic, hydroxyl, and carboxyl groups, an aqueous solution of LS shows amphiphilic properties. In this account, metal salts of LS have often been used as dispersants in a wide range of industrial fields.[6] Because LS salts are very cheap and largely available in the market,[7] value-added conversions of sodium lignosulfonate (NaLS, 800 000 tons per year) into fine chemicals have also been explored.[8] However, existence of sulfur in lignosulfonate precluded the possible application of novel metal-based catalysts, such as Pd and Pt, in its value-added conversions. Strong acid strength of lignosulfonic acid also allowed its use as either a proton-transfer material for fuel cells or a Brønsted acid catalyst for hydrolysis of biomass.[9] Unfortunately, until now, preparation of the acid form of lignosulfonate has had to rely on an energy-intensive procedure.

Recently, we have been interested in rational utilizations of bio-based chemicals. In a continuation of our research to explore organic reactions by using bio-based chemicals as alternatives to conventional solvents or auxiliaries,[10] we thought it

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would be worthwhile to investigate the possibility of using LS as catalyst support. The reasons are multifold: 1) NaLS is a fine powder that is quite stable at moderately high temperature (<200 °C) under neutral conditions, and insoluble in most of the organic solvents; this will facilitate the use and the following recycling of the LS-immobilized metal catalyst; 2) a large amount of sulfonic group in LS enables its use as an anionic support that can load some cationic species by means of ion exchange; 3) the skeleton of LS contains various polar functional groups, such as hydroxyl and carboxyl groups, which might be able to affect the catalytic efficiency synergistically; and importantly, this kind of synergistic effect, if exists, cannot be easily attained with some other supporting materials. Out of these considerations, we have recently started a research program on this topic. Herein, we disclose the successful outcome of this endeavor in which lignosulfonate-based support not only displays an excellent ability to immobilize the selected cationic species, but also confers the formed catalysts an outstanding performance including high catalytic activity and good recyclability. This observation opens a new way for rational utilization of this waste biomass while making benefit of the heterogenization of homogeneous metal catalysts.

Results and Discussion

To demonstrate the feasibility of using LS as a solid support to immobilize cationic species, our initial studies started with immobilization of Sc^{III} by using $Sc(OTf)_3$, which has been extensively used as a Lewis acid catalyst in many organic transformations thanks to a series of original works of Kobayashi in the 1990s,[11] as the metal source. As $Sc(OTf)_3$ is very expensive and normally soluble in the reaction mixture, recycling of $Sc(OTf)_3$ after its use is practically difficult. Therefore, much effort has recently been paid to the immobilization of this species onto solid supports.[12] However, immobilizing Sc^{III} with solid supports while maintaining the high catalytic activity of the homogeneous counterpart is not easy because catalytic activity of the heterogeneous Sc^{III} catalyst was also affected by many factors, such as accessibility of substrate to the catalyst and diffusion of the product into the solvents. Generally, preparation of a highly active solid-supported scandium(III) catalyst not only needs sophisticated ability on the structural tuning of the supporting materials, but also requires a good control on the balance of steady immobilization and maintenance of the catalytic activity. For these reasons, the reported solid-supported Sc^{III} catalysts, so far, were only used in some high-end applications, although some of them are commercially available. In searching for a more practical and efficient approach to the immobilization of the scandium(III) catalyst, we were attracted by the unique properties of NaLS. Because it is a cheap and largely available organic waste product, the strategy of immobilizing Sc^{III} with NaLS, if established, will be a huge incentive for both academia and industry to use the obtained catalysts.

NaLS was provided by Shanghai Jingchun Industry. Implementation of our study was started with a simple ion exchange of NaLS with $Sc(OTf)_3$ in ethanol. The thereby obtained solid materials were thoroughly washed with ethanol, and then dried under vacuum at 80 °C. By means of changing the mass ratio of NaLS/$Sc(OTf)_3$, two Sc^{III}-modified lignin materials were obtained, which possess different Sc loadings as shown in Figure 1. A control experiment, ion exchange of lignin with

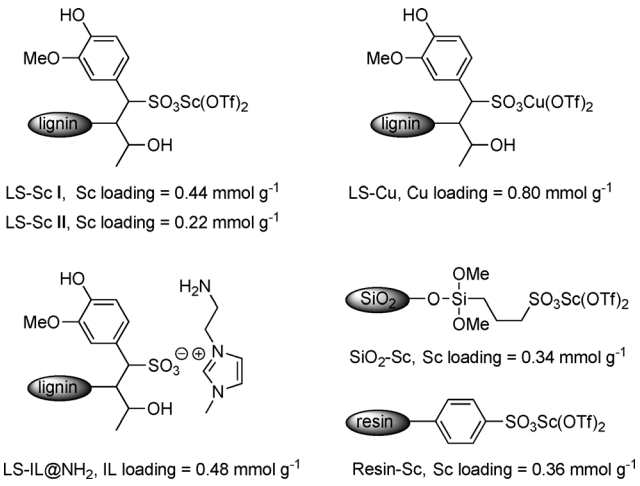


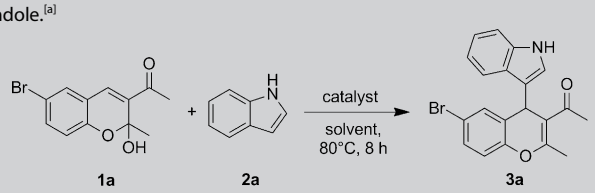
Figure 1. Solid-supported catalysts prepared in this work.

$Sc(OTf)_3$, revealed that only a trace amount of Sc was absorbed onto the unmodified natural lignin, which implied the fact that the presence of sulfonic groups in NaLS is the key to render the immobilization possible. Two conventional solid-supported Sc^{III} reagents were also prepared through an ion exchange method, which included a silica-supported scandium (SiO_2–Sc) and a resin-supported scandium (Resin–Sc), to understand well the catalytic efficiency of the LS–Sc materials.

With all the solid-supported scandium catalysts in hand, we then examined the catalytic efficiency of these materials in some organic reactions. In the beginning, we undertook this study with the implementation of a Michael addition/dehydration tandem reaction of 3-acetyl-2-hydroxy-2-methylchromene and indole that might be able to provide densely functionalized 4*H*-chromene derivatives, which have showed various interesting pharmacological properties.[13] Although 3-acetyl-2-hydroxy-2-methylchromene could be easily obtained through condensation of salicylaldehyde and acetoacetone,[14] its use as a Michael acceptor has not been evaluated before. In continuation of our research to synthesize substituted 4*H*-chromenes,[15] we envisioned that Michael addition/dehydration tandem reaction of 3-acetyl-2-hydroxy-2-methylchromene with a nucleophile should be a possible way for constructing these heterocycles.

Initial experimentation was undertaken in ethanol by using **1a**, **2a**, and catalytic amounts of toluenesulfonic acid (PTSA) under an atmospheric environment, the mixture being heated at 80 °C for 8 h (Table 1, entry 1). After reaction, a pale-yellow solid was obtained by means of isolation with preparative TLC. The following spectrometric analysis of the sample with NMR and IR spectroscopy, and HRMS analysis confirmed the structure of **3a**. However, the yield only reached 70% in this case. No product was obtained under catalyst-free conditions, which indicated the fact that a catalyst is necessary for this reaction

Table 1. Michael addition/dehydration tandem reaction of **1a** with indole.[a]



1a **2a** **3a**

Entry	Cat.	Cat. amount [mol%]	Solvent	Yield [%]
1	PTSA	1.2	EtOH	70
2	–	0	EtOH	0
3	$ZnCl_2$	1.2	EtOH	15
4	LiBr	1.2	EtOH	26
5	$FeCl_3$	1.2	EtOH	80
6	$Sc(OTf)_3$	1.2	EtOH	90
7	LS–Sc **I**	1.2	EtOH	93 (90)[b]
8	lignin	–	EtOH	0
9	NaLS	–	EtOH	0
10	LS–Sc **II**	1.2	EtOH	34
11	LS–Sc **I**	1.2	CH_3NO_2	81
12	LS–Sc **I**	1.2	CH_3CN	75
13	LS–Sc **I**	1.2	1,4-dioxane	65
14	LS–Sc **I**	1.2	DCE	84
15	LS–Sc **I**	1.2	toluene	30
16	LS–Sc **I**	0.6	EtOH	41
17[c]	LS–Sc **I**	1.2	EtOH	43
18[d]	LS–Sc **I**	1.2	EtOH	65
19	SiO_2–Sc	1.2	EtOH	92 (50)[b]
20	Resin–Sc	1.2	EtOH	87 (63)[b]
21	LS–Sc **I**	1.2	EtOH	91[e]

[a] **1a**: (0.5 mmol), **2a**: (0.6 mmol), solvent: (1 mL). [b] The yield in parenthesis showed reuse of the catalyst in the third run. [c] Reaction temperature: 50 °C. [d] Reaction time: 4 h. [e] The reaction was performed in 10 mmol scale. DCE = dichloroethane.

(entry 2). In the presence of weak Lewis acids, such as $ZnCl_2$ and LiBr, the reaction proceeded sluggishly, and **3a** was obtained in less than 30% of yields (entries 3 and 4). The reaction rate can be significantly improved by using strong Lewis acids, such as $FeCl_3$ and $Sc(OTf)_3$, as catalysts, and the reaction yields reached 80 and 90%, respectively, under identical conditions (entries 5 and 6). Some solid catalysts were examined later on. Interestingly, a maximum yield, 93%, was obtained with a heterogeneous scandium catalyst, LS–Sc **I** (entry 7). The reaction was also performed over lignin and NaLS systems, and no **3a** was detected in these cases (entries 8 and 9). All these results indicated that the immobilized scandium is responsible for the good performance of LS–Sc **I**. When LS–Sc **II**, which possesses a lower Sc loading than that of LS–Sc **I**, was used in the reaction, only a moderate yield was obtained under the identical conditions (entry 10), which implied the fact that scandium loading on the NaLS support was also able to significantly affect the catalytic activity of the prepared lignin-immobilized metal catalyst. The effect of the organic solvents on the model reaction was also examined, in which ethanol and acetonitrile gave high yields (entries 11–15). For safety and environmental reasons, we continued the reactions with ethanol. Further investigation revealed that the reaction was also affected by the other parameters including catalyst amount, temperature, and reaction time, and the optimal conditions should be 1.2 mol% of LS–Sc **I**, 80 °C, and 8 h (entries 16–18).

Because LS–Sc is solid, recycling of the catalyst is very easy. After reaction, the recovered LS–Sc **I** was washed with ethanol and dried under vacuum conditions at 60 °C, and then, subjected to the next run. After three times of reuse, the LS–Sc **I** catalyst is still capable of catalyzing the model reaction in 90% of yield (Table 1, entry 7), which indicates that the present LS–Sc catalyst is quite robust under the reaction conditions. We also investigated Sc leaching during the reaction. The heterogeneous catalyst was isolated by centrifugation after 4 h of reaction (ca. 65% yield) and the solution phase was allowed to react for a further 4 h under the same conditions. The yield of **3a** was only 66% after that time, which confirmed that there was hardly any leaching of Sc into the reaction mixture. ICP-MS showed that the Sc 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. Replacing LS–Sc **I** with other solid-supported scandium catalysts, such as SiO_2–Sc and Resin–Sc, gives also good results with the fresh catalysts. However, in the second round of recycling the catalysts, only moderate yields were obtained (entries 19 and 20). ICP-MS analysis revealed that Sc loadings of the recovered SiO_2–Sc and Resin–Sc catalysts decreased to 0.27 and 0.30 mmol g^{-1} after its use. Although the linkage is the same in all the supported Sc^{III} catalysts, because of the presence of a lot of hydoxy and carboxyl groups in the NaLS support, immobilizing Sc^{III} onto this support was naturally affected by the possible interaction of Sc^{III} with these polar functional groups. This kind of interaction might play a role in culling, in which only tightly bonded Sc^{III} can remain in the support, and some Sc^{III} species trapped by the support through relatively weak interactions were removed; this behavior ensures the immobilized Sc^{III} stays steadily in the support even under the reaction conditions; however, in the case of SiO_2 and resin supports, due to a lack of such a kind of culling effect, a part of the immobilized Sc^{III} species might break away from the support with the aid of an interaction with polar substrates, thus resulting in leaching of Sc^{III}. All these results indicated that 1) the properties of supporting materials are indeed crucial for maximizing the catalytic efficiency of the scandium catalyst and 2) NaLS is a preferable support, compared with silica and resin, for immobilizing $Sc(OTf)_3$ when the obtained catalyst was utilized in the model reaction. It is worth noting that the reaction can also be effectively scaled up with similar efficiency. For example, the 10 mmol scale reaction of **1a** with **2a** gave the corresponding 4*H*-chromene **3a** in 91% yield (entry 21) by using the same catalyst, LS–Sc **I**. This result not only demonstrated the feasibility of using lignin-supported metal as a practical catalyst, but also manifested the great potential of the model reaction in organic synthesis.

With the optimized conditions in hand, we probed the scope of the reaction with respect to both the 3-acetyl-2-hydroxy-2-methylchromene and the indole components. As evidenced by the results in Figure 2, 3-acetyl-2-hydroxy-2-methylchromenes with different substituents smoothly reacted with

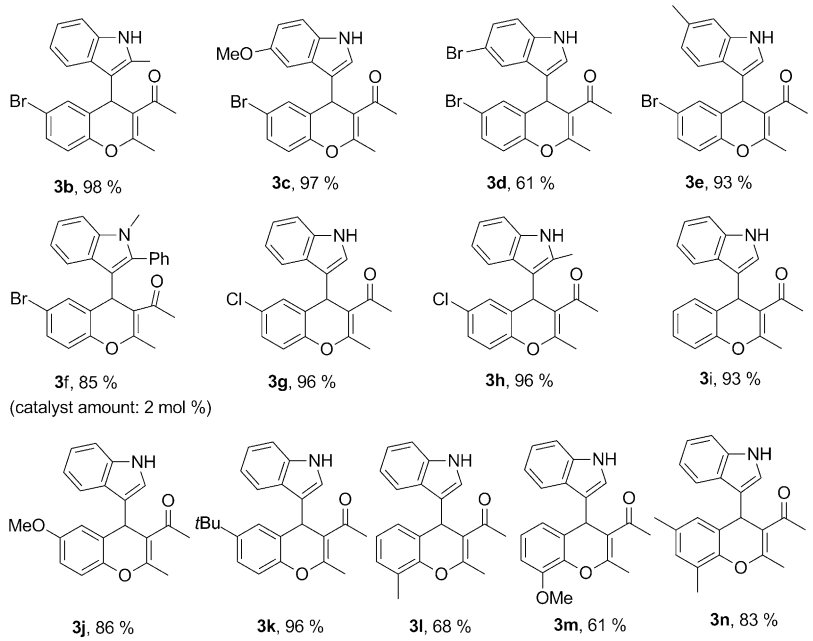
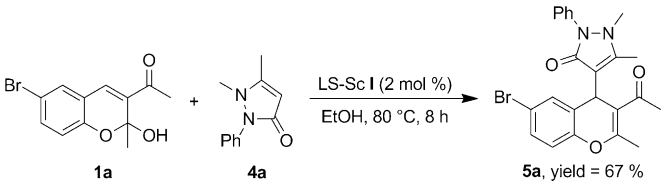


Figure 2. Substrate scope for the model Michael/dehydration tandem reaction catalyzed by LS–Sc **I**.

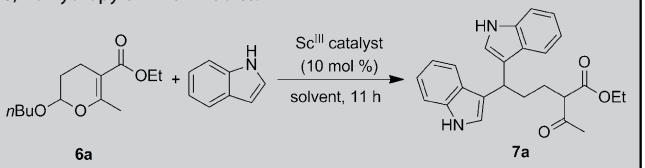
indoles, producing the corresponding densely substituted 4*H*-chromene products in generally good to excellent yields. Both electron-rich and moderately electron-poor indoles readily participated in the reaction. However, indoles containing a strongly electron-withdrawing group, such as carboxyl, failed to participate in the reaction, likely due to their poor reactivity. This sequential reaction can also be extended, over LS–Sc **I** catalyst, to another carbon-based nucleophile, antipyrine, affording the hitherto unreported 4-(3-acetyl-2-methyl-4*H*-chromen-4-yl)antipyrine **5a** in good yield (Scheme 1).



Scheme 1. LS–Sc-catalyzed Michael addition/dehydration tandem reaction of **1a** and antipyrine.

To extend the utility of this catalyst, we then examined some other reactions with LS–Sc catalyst. The second reaction we investigated was electrophilic ring-opening reactions of 2-butoxy-3,4-dihydropyran with indoles. This type of reaction is an acid-catalyzed reaction, but proved to be very sensitive to the acid strength of the catalyst.[16] Previously, it has been successfully performed in the presence of manganese(II) halides, such as $MnCl_2$ and $MnBr_2$.[17] However, these catalysts cannot be recycled after the reaction. We examined the performance of the LS–Sc catalyst in this type of reaction, and the results are listed in Table 2. To our delight, LS–Sc **I** can indeed effectively catalyze the model ring-opening reaction and an 89% yield could be obtained (Table 2, entry 1). Although LS–Sc **II** gave only a moderate yield, the selectivity to the ring-opening product, **7a**, over this catalyst was very high (entry 2). Decrease of the catalyst amount from 10 to 5 mol% resulted in a significant loss of the reaction yield (entry 3). Remarkably, because the model ring-opening reaction was known to be susceptible to the acid strength of the catalyst, applying the homogeneous counterpart of the LS–Sc **I** catalyst, $Sc(OTf)_3$, in this reaction resulted in formation of a very messy mixture. As a result, the yield of **7a** obtained in this case was only 23% under identical conditions (entry 4). This result also indicated that immobilizing $Sc(OTf)_3$ onto the NaLS support might either be able to tune the Lewis acidity of the Sc^{III} species, or be capable of offering a synergistic effect between the support and Sc^{III} species that is responsible for the enhancement of the reaction selectivity. This point deserves further investigation. Screening of the reaction solvents revealed that the best one is nitromethane. In this solvent, LS–Sc **I** is insoluble at the end of the reaction, thus facilitating the recovery of the catalyst (entries 5 to 8). Reuse experiments demonstrated that LS–Sc **I** can be reused at least twice in the model ring-opening reaction without significant loss of its activity (entries 9 and 10). However, it should be noted that nitromethane is toxic and explosive solvent, which diminished to some extent the greenness of this system. Fortunately, green

Table 2. LS–Sc-catalyzed electrophilic ring-opening reactions of 2-butoxy-3,4-dihydropyran with indoles.[a]



Entry	Cat.	Solvent	T [°C]	Yield [%]
1	LS–Sc **I**	CH_3NO_2	100	89
2	LS–Sc **II**	CH_3NO_2	100	45
3[b]	LS–Sc **I**	CH_3NO_2	100	69
4	$Sc(OTf)_3$	CH_3NO_2	100	23
5	LS–Sc **I**	EtOH	80	trace
6	LS–Sc **I**	CH_3CN	80	trace
7	LS–Sc **I**	1,4-dioxane	100	< 10%
8	LS–Sc **I**	DCE	80	trace
9[c]	LS–Sc **I**	CH_3NO_2	100	88

[a] **6a**: (0.5 mmol, indole: 1.25 mmol, Sc catalyst, 10 mol%, solvent: 1 mL, 100 °C, 11 h. [b] Sc catalyst: 5 mol%. [c] The catalyst was used in the third time.

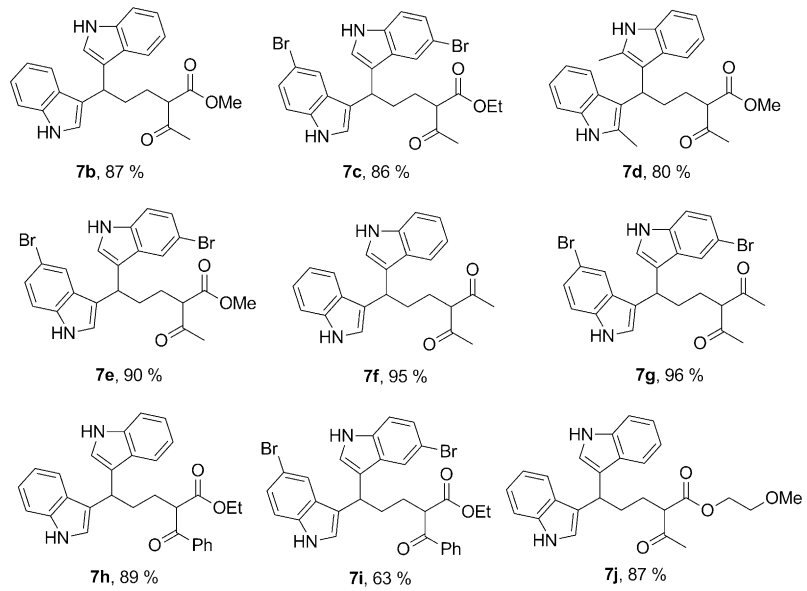
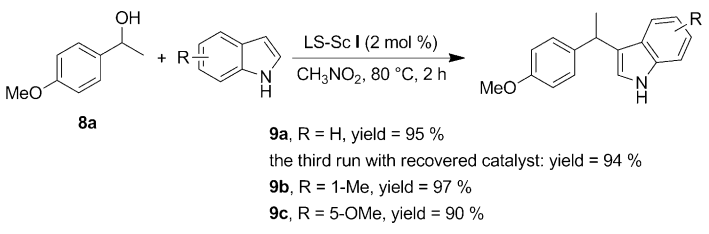


Figure 3. Substrate scope of ring-opening of 2-butoxy-3,4-dihydropyrans with indoles catalyzed by LS–Sc **I**.

chemists already started to work on the replacement of nitromethane with environmentally benign solvents, and a recent advance is a class of nitrofunctionalized imidazolium salts that was proved to be able to replace nitromethane while keeping its efficiency in acid catalysis.[18] Although the reported imidazolium salts are not compatible with LS–Sc catalyst (suffer from a solubility problem), we believe that this problem can be overcome in the future because of the rapid development of green solvents.

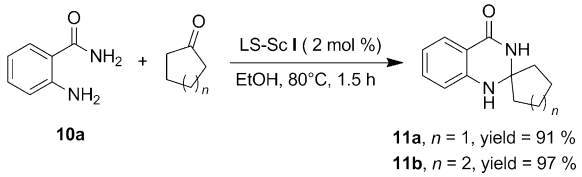
Later on, substrate scope was also investigated under the optimized conditions. As shown in Figure 3, all the examined 2-butoxy-3,4-dihydropyrans and indoles readily participated in the ring-opening reactions, and random combination of the starting materials could give the final products with up to 96% yield. These results indicated again the usefulness of the LS–Sc catalyst for organic transformations.

Similarly, a Friedel–Crafts-type reaction of α-methyl-4-methoxybenzyl alcohol, **8a**, and indoles performed also very well in the presence of LS–Sc **I** catalyst, providing 3-benzylindole derivatives, **9a**–**c**, in high yields (Scheme 2). LS–Sc **I** catalyst could be reused at least twice without significant loss of its activity. Although many catalyst systems have been used in these types of reactions before, most of which are homogeneous Brønsted or Lewis acids that cannot be recycled and reused, some of the reported systems lack efficiency. For example, for the synthetic reaction of **9a**, only a 66% yield was obtained with triflic acid.[19c] By using sulfamic acid as a catalyst, the yield reached 83%; however, a longer reaction time, 8 h, was needed.[19f] Although gluconic acid gave a comparable yield with that of LS–Sc **I**, it was used, unfortunately, as a solvent.[10a] Some solid catalysts have also been evaluated,[20] however, because their preparations are not always easy, our present system thus offers a cost-effective and easily accessible alternative to the previously reported solid catalysts.



Scheme 2. Friedel–Crafts-type reaction of **8a** with indoles catalyzed by LS–Sc **I**.

The LS–Sc catalyst also showed a good catalytic activity in ethanol in the condensation of anthranilamide and cyclic ketones, thus providing an ecofriendly route for the synthesis of 2-substituted-2,3-dihydroquinazolin-4(1*H*)ones (Scheme 3).[21]

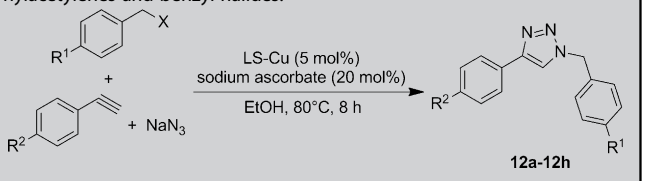


Scheme 3. Condensation of anthranilamide and cyclic ketones catalyzed by LS–Sc **I**.

All the above-mentioned examples demonstrated that LS–Sc can indeed be used as an efficient and recyclable solid catalyst for organic transformations. Considering the fact that previous methods for immobilizing $Sc(OTf)_3$ onto solid support were generally associated with some supporting materials that were either expensive or not commercially available, the present method thus provided a cost-effective and practically feasible route for heterogenizing $Sc(OTf)_3$ catalyst.

To further explore the potential utility of our strategy for use of NaLS as an anionic solid support, we then applied this material to the immobilization of copper(II) catalyst. As we expected, NaLS support is indeed amenable to heterogenizing Cu^{II} species when $Cu(OTf)_2$ was used as the copper source. The obtained LS–Cu catalyst was proved to be highly active for catalyzing the three-component click reaction of NaN_3, phenylacetylenes, and benzyl halides along with 20 mol% of sodium ascorbate (Table 3). The desired cycloaddition products were obtained in yields ranging from 88 to 99% with exclusive 1,4-regioselectivity. Previously, various solid copper catalysts, such as ammonium salt-tagged N-heterocyclic carbene (NHC)–Cu^{I} complexes,[22g] cross-

Table 3. LS–Cu-catalyzed three-component click reaction of NaN_3, phenylacetylenes and benzyl halides.[a]

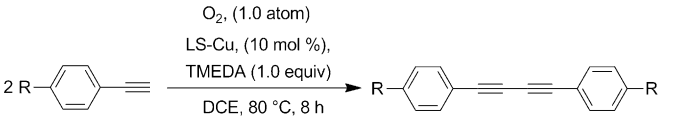


12a-12h

entry	X	R^1	R^2	Product	Yield [%]
1	Br	H	H	**12a**	96 (94)[b]
2	Cl	H	H	**12a**	88
3	Br	NO_2	H	**12b**	96
4	Br	H	Me	**12c**	99
5	Br	H	Et	**12d**	99
6	Br	H	*n*-Pr	**12e**	98
7	Br	H	*n*Bu	**12f**	97
8	Br	H	*n*-amyl	**12g**	99
9	Br	H	OMe	**12h**	96
10	Br	H	*t*Bu	**12i**	60

[a] (Bromomethyl)benzene: 0.30 mmol, ethynylbenzene: 0.36 mmol, NaN_3: 0.40 mmol, Cu catalyst, 5 mol%, sodium ascorbate: 20 mol%, ethanol: 1 mL, 80 °C, 8 h. [b] Cu catalyst was used the third time.

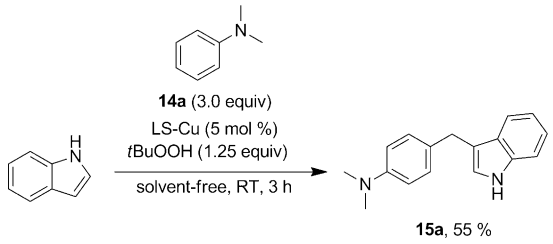
linked polymeric ionic liquid material supported copper,[22h] and glutathione bearing nanoferrites,[22i] have been developed in this type reaction, sometimes with remarkable results.[22] Our LS–Cu catalyst showed, however, its inherent advantages in the following aspects: 1) cost-effectiveness of the supporting material and 2) simple operation for preparing the catalyst. Besides, taking the fact that $Cu(OTf)_2$ is now an easily available copper salt into account, it is not unreasonable to expect that LS–Cu catalyst might be a preferable choice for researchers who needed a heterogenized copper(II) catalyst. With this in mind, two other reactions were then examined by using LS–Cu as the catalyst. As shown in Scheme 4, more than 90% of



13a, R = H, yield = 92% (2nd run, 90 %)
13b, R = *n*Bu, yield = 98 %.

Scheme 4. LS–Cu-catalyzed Glaser reaction of phenylacetylenes.

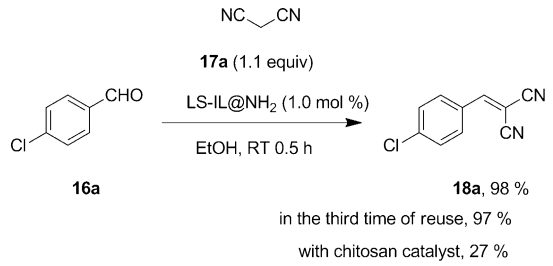
yields could be obtained in Glaser reactions of phenylacetylenes, in which LS–Cu catalyst is also recyclable. Oxidative coupling of *N*,*N*-dimethylaniline and indole proceeded also very well in the presence of LS–Cu catalyst (Scheme 5) bearing in mind the fact that only 73% of yield was obtained over expensive ruthenium porphyrins catalysts.[23] The mechanism of this reaction most likely involves the formation of formaldehyde through oxidation of the methyl group of *N*,*N*-dimethylaniline **14a**, which followed by an electrophilic alkylation reaction.[23] All these results demonstrated that LS–Cu is indeed a versatile heterogeneous catalyst for organic transformations.



15a, 55 %

Scheme 5. LS–Cu-catalyzed oxidative coupling of *N*,*N*-dimethylaniline and indole.

Finally, another lignosulfonate, ammonium lignosulfonate (NH_4LS), was used to immobilize an amine-functionalized imidazolium-based ionic liquid by the ion exchange method, and the obtained material was defined as LS-IL@NH_2 (see Figure 1). LS-IL@NH_2 showed a good catalytic ability to promote a Knoevengal reaction between 4-chlorobenzaldehyde **16a** and malononitrile **17a**. As before, LS-IL@NH_2 catalyst could be reused many times without significant loss of its catalytic activity. Interestingly, with LS-IL@NH_2 catalyst, the yield of the desired product **18a** is much higher than that of another commercially available natural base catalyst, chitosan, under the identical conditions. This is quite reasonable considering the fact the ion-exchange procedure ensures all the imidazolium cations stay on the positions that are easily accessible in the support, which allows the substrate contact easily with the NH_2 group in LS-IL@NH_2. However, most of the NH_2 groups of chitosan were blocked by a hard backbone constructed by multiple hydrogen bond interaction between the glucose monomers.[24] This example not only manifested the effectiveness of LS-IL@NH_2, but also demonstrated that LS is indeed a versatile support for immobilizing homogeneous catalysts (Scheme 6).



16a **18a**, 98 %
in the third time of reuse, 97 %
with chitosan catalyst, 27 %

Scheme 6. LS–AIL-catalyzed Knoevenagel reaction of 4-chlorobenzaldehyde and malononitrile.

Conclusion

Lignosulfonates were used, for the first time, as a solid support of cationic catalysts. This protocol was proved to be amenable to the immobilizations of $Sc(OTf)_3$, $Cu(OTf)_2$, and an amine-functionalized imidazolium-based ionic liquid. The obtained catalysts were then successfully applied to many organic transformations, in which the catalysts showed not only high activity but also good recyclability. In some cases, synergistic effects between the metal species and lignosulfonate support were also observed, which conferred the catalyst a salient ability

that cannot be attained with other supporting materials. Because LS is a cheap waste biomass, the use of LS as the supporting material ensures a bonus of practicability, sustainability, and safety to the processes which deals with the LS-based catalysts. In fact, our strategy stems upon the unexpected capacity of LS material for cationic exchange. Inspired by this observation, some other technologies might be developed with the aid of using metal salts of lignosulfanic acid as anionic supports.

However, the use of NaLS support is also suffering from some limitations: 1) because LS is soluble in water, the catalysts prepared with this strategy may not be suitable to use in aqueous conditions taking into consideration their recycling, 2) due to the possible degradation, durability of the obtained catalysts needed to be further improved, especially when the catalysts were used in harsh conditions; condensation of lignosulfonate with formalin under acidic conditions can be one of the suitable methods to strengthen the stability of the lignosulfonate catalyst,[25] 3) in some cases, special attention should be paid to the reactivity of lignosulfanate support because there are a large amount of functionalities in the matrix of LS, which otherwise will affect negatively the reaction outcomes under appropriate conditions. Furthermore, the structure of lignin may change according to the season and its origin, the potential effects of these factors on the catalytic behavior of lignin support should also be considered.

Despite these drawbacks, by means of a careful control on balancing every important factor, LS support has been proved to be a potential candidate to be applied in many organic reactions in combination with immobilizing cationic catalysts. In the future, these problems might be partially solved by compositing LS with some other materials. If such methods were established, considering the low cost and the unique capacity of LS, it is not unreasonable to expect that the use of LS as a supporting material or one component of supporting materials will constitute a new facet of catalysis research. We are now actively working on this line.

Experimental Section

General

Typical procedure for the preparation of LS–Sc catalyst: Sodium ligninsulfonate (1.5 g) and $Sc(OTf)_3$ (700 mg, 1.4 mmol) was mixed with anhydrous ethanol (30 mL) in a 100 mL round-bottomed flask. The mixture was then stirred at 80 °C for 36 h. After the reaction was completed, the solid was obtained by filtration and then washed with ethanol (50×5 mL). After drying, the loading of scandium was measured by ICP-MS, and the value was 0.44 mmol g^{-1} (LS–Sc **I**).

Typical procedure for catalytic reaction: All reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, the prepared starting material **1a** (0.50 mmol) was mixed with **2a** (0.60 mmol) and LS–Sc **I** (1.2 mol%) in anhydrous ethanol (1.0 mL) for 8 h at 80 °C. After reaction, the mixture was cooled to room temperature, and then centrifuged. The supernatant organic phase was isolated and the bottom solid was washed with ethanol (1.0 mL×2). All organic phases were then combined together and concentrated under reduced pressure. Then, the desired product, **3a**, was obtained in 93% yield (177.6 mg) by isolation with preparative TLC (eluting solvent: ethyl acetate/petroether = 1:5 (v/v)). Tests for substrate scope were all performed with an analogous procedure. The recovered catalyst was dried in air and directly used in the next run. The large-scale reaction was also performed in the same procedure.

Spectroscopic data of new compounds

1-[6-Bromo-4-(1*H*-indol-3-yl)-2-methyl-4*H*-chromen-3-yl]ethanone (3a): Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.13 (s, 3H), 2.42 (s, 3H), 5.27 (s, 1H), 6.87 (d, J = 8.8 Hz, 1H), 6.93 (d, J = 2.4 Hz, 1H), 7.09–7.19 (m, 3H), 7.26 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 2.4 Hz, 1H), 7.62 (d, J = 2.4 Hz, 1H), 8.31 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.7, 29.6, 33.0, 111.5, 113.6, 116.4, 117.9, 118.5, 120.0, 120.4, 122.2, 122.6, 125.5, 127.1, 130.4, 131.5, 136.5, 148.1, 157.5, 199.6 ppm; IR: $\tilde{\nu}$ = 3401, 3351, 3057, 2923, 2247, 1884, 1677, 1618, 1569, 1477, 1738, 1240, 1185, 1041, 941, 907, 816, 737, 651, 626, 524, 424 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{20}H_{16}BrNNaO_2$: 404.0262 $[M+Na]^+$; found: 404.0251.

1-[6-Bromo-2-methyl-4-(2-methyl-1*H*-indol-3-yl)-4*H*-chromen-3-yl]ethanone (3b): Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.10 (s, 3H), 2.33 (s, 3H), 2.37 (s, 3H), 5.33 (s, 1H), 6.87 (d, J = 8.0 Hz, 1H), 7.02–7.09 (m, 3H), 7.16–7.20 (m, 2H), 7.45 (d, J = 7.2 Hz, 1H), 8.06 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.8, 19.5, 29.8, 31.7, 110.4, 113.0, 115.5, 116.4, 117.5, 117.7, 119.8, 121.1, 126.5, 127.2, 130.4, 131.7, 131.8, 135.0, 149.1, 156.2, 199.7 ppm; IR: $\tilde{\nu}$ = 3396, 3057, 3025, 2978, 2921, 2247, 1880, 1679, 1619, 1570, 1477, 1380, 1237, 940, 814, 738, 433 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{21}H_{18}BrNNaO_2$: 418.0419 $[M+Na]^+$; found: 418.0416.

1-[6-Bromo-4-(5-methoxy-1*H*-indol-3-yl)-2-methyl-4*H*-chromen-3-yl]ethanone (3c): Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.16 (s, 3H), 2.42 (s, 3H), 3.82 (s, 3H), 5.22 (s, 1H), 6.81 (dd, J_a = 2.4, J_b = 8.8 Hz, 1H), 6.92–6.94 (m, 2H), 7.03–7.05 (m, 2H), 7.13–7.17 (m, 2H), 8.32 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.7, 29.6, 33.1, 55.7, 100.5, 112.1, 112.1, 113.4, 117.4, 120.1, 123.2, 125.8, 126.6, 127.5, 128.5, 128.9, 131.7, 147.7, 154.1, 157.6 ppm; IR: $\tilde{\nu}$ = 3353, 3055, 2996, 2939, 2249, 1873, 1679, 1623, 1576, 1482, 1379, 1241, 1220, 1043, 941, 908, 818, 732, 651, 552, 474, 429 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{21}H_{18}BrNNaO_3$: 434.0368 $[M+Na]^+$; found: 434.0360.

1-[6-Bromo-4-(5-bromo-1*H*-indol-3-yl)-2-methyl-4*H*-chromen-3-yl]ethanone (3d): Brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS):δ = 2.15 (s, 3H), 2.42 (s, 3H), 5.23 (s, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.97 (d, J = 2.4 Hz, 1H), 7.14 (d, J = 8.0 Hz, 1H), 7.18–7.32 (m, 5H), 7.71 (d, J = 1.2 Hz, 3H), 7.71 (d, J = 8.0 Hz, 1H), 8.42 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.8, 29.8, 32.8, 112.9, 113.3, 113.6, 116.5, 118.1, 120.3, 121.0,123.8, 125.2, 126.7, 127.2, 130.6, 131.4, 135.0, 148.1, 157.7, 199.3 ppm; IR: $\tilde{\nu}$ = 3344, 3066, 2926, 2249, 1673, 1620, 1567, 1476, 1238, 908, 817, 733, 644, 587, 420 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{20}H_{15}Br_2NNaO_2$: 481.9367 $[M+Na]^+$; found: 481.9355.

1-[6-Bromo-2-methyl-4-(6-methyl-1*H*-indol-3-yl)-4*H*-chromen-3-yl]ethanone (3e): Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.12 (s, 3H), 2.39 (s, 3H), 2.41 (d, J = 1.2 Hz, 3H), 5.21 (s, 1H), 6.83–6.86 (m, 2H), 6.94 (d, J = 8.4 Hz, 1H), 7.03 (s, 1H), 7.15 (dd, J_a = 4.0, J_b = 8.0 Hz, 1H), 7.29 (s, 1H), 7.49 (d, 1H), 8.25 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.7, 21.5, 29.5, 33.0, 111.4, 113.5, 116.3, 117.8, 118.0, 120.2, 121.7, 121.9, 123.3, 127.1, 130.3, 131.5, 132.0, 136.9, 148.0, 157.5, 199.7 ppm; IR: $\tilde{\nu}$ = 3402, 2919, 2861, 2248, 1876, 1677, 1621, 1568, 1476, 1378, 1240, 1219, 908,

802, 733, 647, 484, 430 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{21}H_{18}BrNNaO_2$: 418.0419 $[M+Na]^+$; found: 418.0417.

1-[6-Bromo-2-methyl-4-(1-methyl-2-phenyl-1*H*-indol-3-yl)-4*H*-chromen-3-yl]ethanone (3 f): Brown liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.98$ (s, 3H), 2.01 (s, 3H), 3.41 (s, 3H), 5.36 (s, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 7.01 (d, $J = 4.0$ Hz, 1H), 7.07 (s, 1H), 7.11–7.31 (m, 5H), 7.42 (s, 3H), 7.71 ppm (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.2$, 29.8, 30.3, 31.9, 109.5, 112.5, 116.9, 117.2, 118.2, 120.0, 121.8, 126.3, 126.7, 127.4, 128.2, 128.5, 128.6, 130.7, 131.5, 136.4, 138.9, 147.4, 155.7, 199.5 ppm; IR: $\tilde{\nu} =$ 3055, 2928, 2248, 1882, 1683, 1610, 1574, 1477, 1359, 1240, 1218, 908, 817, 735, 546 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{27}H_{22}BrNNaO_2$: 494.0732 $[M+Na]^+$; found: 494.0714.

1-[6-Chloro-4-(1*H*-indol-3-yl)-2-methyl-4*H*-chromen-3-yl]ethanone (3 g): Brown liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 2.13 (s, 3H), 2.42 (s, 3H), 5.27 (s, 1H), 6.91–6.93 (m, 2H), 7.03 (dd, $J_a = 2.4$, $J_b = 8.8$ Hz, 1H), 7.10–7.16 (m, 3H), 7.26 (d, $J = 7.6$ Hz, 1H), 7.62 (d, $J = 7.6$ Hz, 1H), 8.36 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.7$, 29.6, 33.0, 111.5, 113.5, 117.5, 118.4, 119.9, 120.4, 122.2, 122.6, 125.5, 126.6, 127.5, 128.5, 128.8, 136.5, 147.6, 157.7, 199.7 ppm; IR: $\tilde{\nu} =$ 3403, 3354, 3058, 2924, 2248, 1883, 1677, 1619, 1572, 1480, 1357, 1241, 1221, 907, 818, 737, 654, 424 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{20}H_{16}ClNNaO_2$: 360.0767 $[M+Na]^+$; found: 360.0755.

1-[6-Chloro-2-methyl-4-(2-methyl-1*H*-indol-3-yl)-4*H*-chromen-3-yl]ethanone (3 h): Brown liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.09$ (s, 3H), 2.30 (s, 3H), 2.37 (s, 3H), 5.32 (s, 1H), 6.90–6.95 (m, 2H), 7.00–7.08 (m, 3H), 7.17 (d, $J = 7.6$ Hz, 1H), 7.46 (d, $J =$ 7.6 Hz, 1H), 8.09 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 11.8$, 19.5, 29.7, 31.8, 110.4, 112.9, 115.5, 117.3, 117.5, 119.7, 121.1, 127.2, 127.5, 128.8, 128.8, 131.8, 134.9, 147.5, 156.4, 199.9 ppm; IR: $\tilde{\nu} =$ 3395, 3058, 2922, 2247, 1879, 1679, 1619, 1573, 1479, 1225, 907, 817, 735, 652, 428 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{21}H_{18}ClNNaO_2$: 374.0924 $[M+Na]^+$; found: 374.0910.

1-[4-(1*H*-Indol-3-yl)-2-methyl-4*H*-chromen-3-yl]ethanone (3 i): Brown liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.11$ (s, 3H), 2.43 (s, 3H), 5.30 (s, 1H), 6.82 (d, $J = 2.4$ Hz, 1H), 6.87 (t, 1H), 6.98 (d, $J = 8.0$ Hz, 1H), 7.04 (d, $J = 7.6$ Hz, 1H), 7.09–7.11 (m, 2H), 7.19 (t, 2H), 7.67–7.69 (t, 1H), 8.34 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.8$, 29.4, 32.9, 111.4, 113.7, 116.0, 118.5, 119.6, 121.1, 121.9, 122.6, 124.2, 125.1, 125.6, 127.3, 128.7, 136.4, 148.9, 158.0, 200.1 ppm; IR: $\tilde{\nu} =$3408, 3057, 2924, 2247, 1798, 1675, 1619, 1574, 1486, 1378, 1218, 939, 908, 739, 647, 597, 425 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{20}H_{17}NNaO_2$: 326.1157 $[M+Na]^+$; found: 326.1154.

1-[4-(1*H*-Indol-3-yl)-6-methoxy-2-methyl-4*H*-chromen-3-yl]ethanone (3 j): Brown liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 2.14 (s, 3H), 2.44 (s, 3H), 3.60 (s, 3H), 5.29 (s, 1H), 6.62–6.65 (m, 1H), 6.74–6.75 (m, 1H), 6.91–6.94 (m, 2H), 7.09–7.13 (m, 2H), 7.22–7.25 (m, 1H), 7.67–7.69 (m, 1H), 8.37 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.9$, 29.5, 33.4, 55.3, 111.3, 112.8, 113.0, 113.1, 116.8, 118.5, 119.7, 121.0, 122.0, 122.4, 125.6, 125.8, 136.4, 143.1, 155.9, 158.4, 199.7 ppm; IR: $\tilde{\nu} =$3409, 3349, 3057, 2930, 2836, 2248, 1675, 1582, 1495, 1427, 1215, 1036, 928, 742, 640, 601, 424 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{21}H_{19}NNaO_3$: 356.1263 $[M+Na]^+$; found: 356.1255.

1-[6-(*tert*-Butyl)-4-(1*H*-indol-3-yl)-2-methyl-4*H*-chromen-3-yl]ethanone (3 k): Brown liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.16$ (s, 9H), 2.15 (s, 3H), 2.45 (s, 3H), 5.31 (s, 1H), 6.86 (d, $J =$ 2.8 Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 7.10–7.13 (m, 3H), 7.19–7.22 (m, 1H), 7.32 (d, $J = 2.0$ Hz, 1H), 7.75–7.77 (m, 1H), 8.34 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.9$, 29.4, 31.2, 33.5, 34.1, 111.3, 113.6, 115.6, 118.7, 119.5, 121.1, 121.9, 122.4, 124.4, 125.2, 125.7, 136.6, 147.0, 147.1, 158.8, 199.8 ppm; IR: $\tilde{\nu} =$3413, 3056, 2961, 2869, 2247, 1674, 1575, 1496, 1359, 1218, 916, 824, 739, 605, 425 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{24}H_{25}NNaO_2$: 382.1783 $[M+Na]^+$; found: 382.1775.

1-[4-(1*H*-Indol-3-yl)-2,8-dimethyl-4*H*-chromen-3-yl]ethanone (3 l): Brown liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.12$ (s, 3H), 2.23 (s, 3H), 2.47 (s, 3H), 5.30 (s, 1H), 6.79–6.84 (m, 2H), 6.91 (d, $J = 7.2$ Hz, 1H), 7.06–7.12 (m, 3H), 7.18–7.20 (m, 1H), 7.69–7.71 (m, 1H), 8.28 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 15.3$, 19.5, 29.1, 32.8, 111.0, 113.4, 118.2, 119.3, 121.0, 121.6, 122.6, 123.3, 124.5, 124.9, 125.3, 125.8, 128.3, 136.1, 147.0, 158.0, 199.7 ppm; IR: $\tilde{\nu} =$3412, 3346, 3055, 2922, 2247, 1676, 1578, 1467, 1378, 1247, 1197, 1091, 936, 909, 739, 649, 425 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{21}H_{19}NNaO_2$: 340.1313 $[M+Na]^+$; found: 340.1305.

1-[4-(1*H*-Indol-3-yl)-8-methoxy-2-methyl-4*H*-chromen-3-yl]ethanone (3 m): Brown liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.15$ (s, 3H), 2.50 (s, 3H), 3.87 (s, 3H), 5.32 (s, 1H), 6.67–6.69 (m, 1H), 6.84–6.86 (s, 2H), 6.93 (d, $J = 2.4$ Hz, 3H), 7.12–7.14 (m, 2H), 7.25–7.27 (m, 1H), 7.70–7.72 (m, 1H), 8.27 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.8$, 29.5, 33.0, 56.0, 109.6, 111.3, 113.8, 118.6, 119.8, 120.3, 121.3, 122.0, 122.6, 123.9, 125.7, 126.2, 136.4, 138.7, 147.5, 157.9, 199.7 ppm; IR: $\tilde{\nu} =$3403, 3056, 2933, 2840, 2248, 1675, 1576, 1483, 1330, 1204, 1094, 910, 738, 646, 600, 425 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{21}H_{19}NNaO_3$: 356.1263 $[M+Na]^+$; found: 356.1255.

1-[4-(1*H*-Indol-3-yl)-2,6,8-trimethyl-4*H*-chromen-3-yl]ethanone (3 n): Brown liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.01$ (s, 3H), 2.14 (s, 3H), 2.27 (s, 3H), 2.47 (s, 3H), 5.26 (s, 1H), 6.74 (s, 1H), 6.86–6.90 (m, 2H), 7.10–7.13 (m, 2H), 7.22–7.23 (m, 1H), 7.70–7.71 (m, 1H), 8.28 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 15.2$, 19.6, 20.2, 29.1, 32.8, 110.9, 113.3, 118.3, 119.3, 121.2, 121.5, 122.1, 124.1, 124.6, 125.3, 125.9, 132.6, 136.0, 145.0, 158.1, 199.5 ppm; IR: $\tilde{\nu} =$3411, 3347, 2921, 2247, 1675, 1584, 1482, 1378, 1212, 1150, 932, 909, 739, 652, 552, 423 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{22}H_{21}NNaO_2$: 354.1470 $[M+Na]^+$; found: 354.1462.

4-(3-Acetyl-6-bromo-2-methyl-4*H*-chromen-4-yl)-5-methyl-2-phenyl-1*H*-pyrazol-3(2*H*)one (5 a): Yellow liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.11$ (s, 3H), 2.31 (s, 3H), 2.36 (s, 3H), 3.01 (s, 3H), 5.16 (s, 1H), 6.86 (d, $J = 8.0$ Hz, 1H), 7.23–7.28 (m, 2H), 7.36 (d, $J = 6.4$ Hz, 3H), 7.43 ppm (t, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 10.7$, 19.5, 29.6, 29.7, 35.4, 111.6, 113.5, 116.6, 117.6, 123.9, 125.3, 126.5, 129.1, 130.7, 131.5, 134.7, 148.4, 153.4, 157.8, 164.4, 199.6 ppm; IR: $\tilde{\nu} =$3062, 2923, 2240, 1733, 1660, 1478, 1239, 940, 730, 648, 591, 500 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{23}H_{21}BrN_2NaO_3$: 475.0633 $[M+Na]^+$; found: 475.0619.

Ethyl 2-acetyl-5,5-bis(5-bromo-1*H*-indol-3-yl)pentanoate (7 c): Brown liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.20$ (t, $J =$ 7.2 Hz, 3H), 1.84–1.96 (m, 2H), 2.06–2.12 (m, 2H), 2.14 (s, 3H), 3.47 (t, $J = 6.0$ Hz, 1H), 4.15 (dd, $J_a = 7.2$, $J_b = 14.4$ Hz, 2H), 4.27 (t, $J =$ 7.2 Hz, 1H), 6.86 (d, $J = 6.8$ Hz, 2H), 7.12 (dd, $J_a = 8.8$, $J_b = 26.0$ Hz, 4H), 7.60 (s, 2H), 8.22 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 14.0, 26.6, 28.9, 32.5, 33.7, 59.5, 61.5, 112.1, 112.8, 118.0, 118.2, 121.6, 122.9, 124.5, 128.2, 128.2, 135.1, 169.8, 203.8 ppm; IR $\tilde{\nu} =$ 3421, 3076, 2981, 2933, 2251, 1855, 1731, 1708, 1559, 1459, 1214, 1097, 909, 884, 796, 732, 585, 422 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{25}H_{24}Br_2N_2NaO_3$: 581.0051 $[M+Na]^+$; found: 581.0032.

Methyl 2-acetyl-5,5-bis(2-methyl-1*H*-indol-3-yl)pentanoate (7 d): Brown liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.88$–1.96 (m, 2H), 2.08 (s, 3H), 2.20 (d, $J = 2.4$ Hz, 6H), 2.36–2.43 (m, 2H), 3.45 (t, $J = 7.6$ Hz, 1H), 3.64 (s, 3H), 4.38 (t, $J = 8.0$ Hz, 1H), 6.95–7.04 (m, 4H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.59 (dd, $J_a = 7.2$, $J_b = 8.0$ Hz, 2H), 7.74 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 12.5$, 12.5,

27.4, 28.7, 32.2, 34.7, 52.3, 59.7, 110.2, 113.8, 113.8, 118.9, 119.0, 119.1, 120.3, 128.0, 128.0, 130.9, 131.0, 135.0, 171.2, 203.4 ppm; IR: $\tilde{\nu}$ = 3396, 3055, 2951, 2866, 2248, 1736, 1709, 1617, 1550, 1487, 1459, 1358, 1301, 1245, 1154, 1046, 911, 741, 652, 591, 494, 430 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{26}H_{28}N_2NaO_3$: 439.1998 $[M+Na]^+$; found: 439.1982.

3-[3,3-Bis(5-bromo-1*H*-indol-3-yl)propyl]pentane-2,4-dione (7g): Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.84–1.89 (m, 2H), 1.99–2.01 (m, 2H), 2.05 (s, 6H), 3.63 (t, *J* = 7.2 Hz, 1H), 4.24 (t, *J* = 7.2 Hz, 1H), 4.87 (s, 2H), 7.09 (s, 1H), 7.12–7.16 (m, 3H), 7.58 (s, 2H), 8.29 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 22.5, 26.7, 32.7, 33.8, 68.1, 112.2, 112.2, 112.8, 112.8, 118.0, 118.4, 121.5, 121.5, 122.7, 122.9, 124.5, 124.6, 128.2, 128.2, 135.1, 191.1, 204.8 ppm; IR $\tilde{\nu}$ = 3417, 3075, 2250, 1722, 1696, 1560, 1457, 1358, 1247, 1099, 908, 796, 732, 587, 421 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{24}H_{22}Br_2N_2NaO_2$: 550.9946 $[M+Na]^+$; found: 550.9933.

Ethyl 2-benzoyl-5,5-bis(5-bromo-1*H*-indol-3-yl)pentanoate (7i): Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.10 (t, *J* = 7.2 Hz, 3H), 2.02 (s, 6H), 2.06–2.13 (m, 2H), 2.18–2.23 (m, 2H), 4.10 (q, J_a = 6.8, J_b = 14.0 Hz, 2H), 4.30–4.37 (m, 2H), 6.88 (s, 2H), 7.08–7.16 (m, 4H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.59–7.61 (m, 2H), 7.88 (d, *J* = 7.6 Hz, 2H), 8.40 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 27.6, 32.7, 33.8, 54.0, 61.5, 112.1, 112.7, 117.9, 118.1, 121.5, 121.6, 123.1, 123.1, 124.4, 128.2, 128.4, 128.6, 133.5, 135.2, 135.9, 170.0, 195.6 ppm; IR $\tilde{\nu}$ = 3418, 3064, 2981, 2934, 2251, 1727, 1679, 1456, 1246, 1097, 1046, 909, 795, 732, 587, 421 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{30}H_{26}Br_2N_2NaO_3$: 643.0208 $[M+Na]^+$; found: 643.0198.

2-Methoxyethyl 2-acetyl-5,5-di(1*H*-indol-3-yl)pentanoate (7j): Yellow solid; m.p: 71–73 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.80–1.99 (m, 2H), 2.01 (s, 3H), 2.05–2.20 (m, 2H), 3.23 (s, 3H), 3.40 (d, *J* = 7.6 Hz, 1H), 3.42–3.46 (m, 2H), 4.15–4.21 (m, 2H), 4.40 (t, *J* = 6.8 Hz, 1H), 6.72 (dd, J_a = 2.0, J_b = 9.6 Hz, 2H), 6.97 (t, *J* = 7.2 Hz, 2H), 7.07 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.95 ppm (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.1, 28.9, 33.3, 34.0, 58.9, 59.7, 64.2, 70.2, 111.4, 119.0, 119.1, 119.2, 119.5, 121.7, 122.0, 126.9, 127.0, 136.7, 170.1, 203.9 ppm.

1-Benzyl-4-(4-propylphenyl)-1*H*-1,2,3-triazole (12e): White solid; m.p. 113–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.23 (t, *J* = 6.8 Hz, 3H), 1.63 (sext, J_a = 7.2, J_b = 14.8, J_c = 22.4 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 5.52 (s, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.25–7.28 (m, 2H), 7.32–7.37 (m, 3H), 7.63 (s, 1H), 7.70 ppm (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 24.5, 37.8, 54.2, 119.3, 125.6, 128.0, 128.0, 128.7, 129.0, 129.1, 134.8, 142.9, 148.3 ppm; IR: $\tilde{\nu}$ = 3095, 2959, 2865, 1748, 1494, 1454, 1214, 1077, 1044, 975, 829, 715, 527, 480 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{18}H_{19}N_3Na$: 300.1477 $[M+Na]^+$; found: 300.1462.

1-Benzyl-4-(4-butylphenyl)-1*H*-1,2,3-triazole (12f): White solid; m.p. 110–112 °C; ^{1}H NMR (400Mz, $[D_6]$DMSO, 25 °C): δ = 0.87 (t, *J* = 7.2 Hz, 3H), 1.24–1.33 (m, 2H), 1.51–1.58 (m, 2H), 2.58 (m, 2H), 5.63 (s, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.32–7.41 (m, 5H), 7.74 (d, *J* = 8.0 Hz, 2H), 8.56 ppm (s, 1H); ^{13}C NMR (100 MHz, $[D_6]$DMSO): δ = 14.2, 22.2, 33.5, 35.0, 53.5, 121.6, 125.6, 128.4, 128.5, 128.7, 129.3, 129.3, 136.4, 142.7, 147.3 ppm; IR: $\tilde{\nu}$ = 3093, 2926, 2856, 1742, 1496, 1379, 1219, 1080, 977, 818, 716, 534, 490 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{19}H_{21}N_3Na$: 314.1633 $[M+Na]^+$; found: 314.1630.

1-Benzyl-4-(4-pentylphenyl)-1*H*-1,2,3-triazole (12g): White solid; m.p. 102–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, *J* = 6.8 Hz, 3H), 1.29–1.34 (m, 4H), 1.57–1.64 (m, 2H), 2.59 (t, *J* = 7.6 Hz, 2H), 5.51 (s, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.25–7.28 (m, 2H), 7.32–7.36 (m, 3H), 7.63 (s, 1H), 7.70 ppm (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.6, 31.1, 31.5, 35.7, 54.2, 119.4, 125.6, 128.0, 128.0, 128.7, 128.9, 129.1, 134.9, 143.1, 148.3 ppm; IR: $\tilde{\nu}$ = 3090, 2953, 2924, 2855, 1714, 1455, 1346, 1219, 1080, 848, 818, 715, 578, 469 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{20}H_{23}N_3Na$: 328.1790 $[M+Na]^+$; found: 328.1785.

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