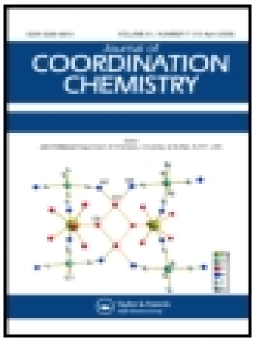

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Construction of polymeric Cu(I) *N*-heterocyclic carbene complex utilizing terpyridine-Fe(II) as linkers: Formation of an efficient and recyclable catalyst

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A metal-coordination-driven self-assembly using the predesigned building block has been developed. Herein, the catalytic active NHC-Cu(I) units were introduced into the terpyridine metal coordination polymers. The self-assembled architecture, as a heterogeneous catalyst, was successfully used to catalyze the A^3-coupling reaction of aldehyde, alkyne, and amine and Huisgen 1,3-dipolar cycloaddition reaction of azide and alkyne in high yields.

Keywords: Polymeric Cu(I) *N*-heterocyclic carbene complexes; Terpyridine-Fe(II); Self-supported catalyst

1. Introduction

The field of metal-coordination-driven functional assembly has been successfully used for the construction of various supramolecular entities, with continuous emergence of exciting applications in the catalysis [1, 2]. In this regard, Ding has shown that coordination polymers incorporating multiple catalytic active sites can be synthesized *via* directed-assembly strategies and the reactive structures have been shown to initiate or enhance catalytic processes [3-7]. Much of the current effort is directed toward the construction of supramolecular systems that are capable of performing a variety of catalytic chemical transformations. In recent years, the use of

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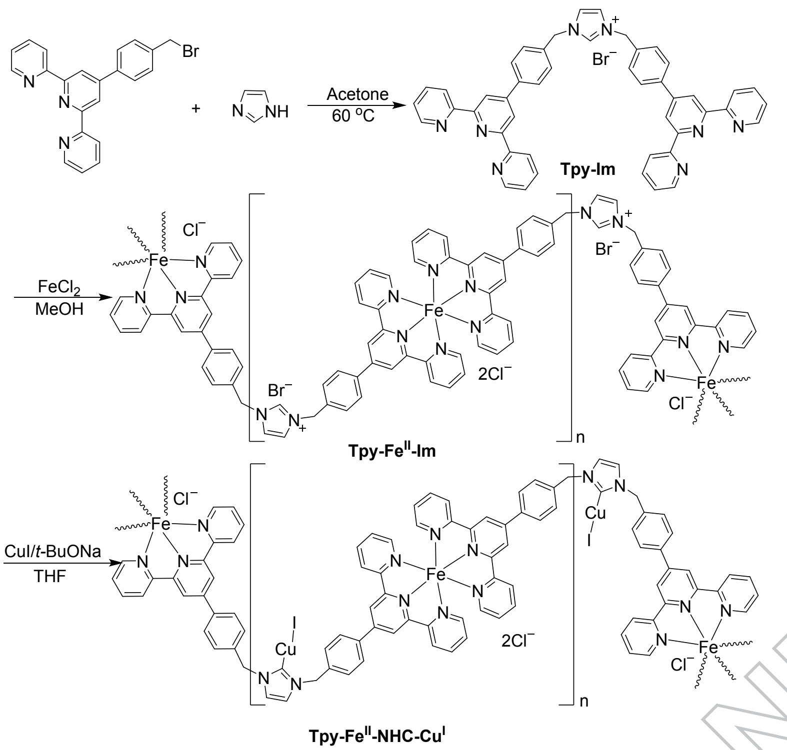
*Corresponding author. Email: yangjinlz@163.com terpyridine as a key-component to the self-assembly of supramolecular network has been comprehensively demonstrated [8]. Terpyridine-metal coordination is especially appealing because of an easy access to back-to-back coordination polymers. In this respect, Fe(II) and Ru(II) were often used as the metal nodes for coordination polymerization [9]. *N*-heterocyclic carbene (NHC) has been extensively studied in the field of organometallics as a ligand capable of coordinating with a wide range of transition metals [10]. Diverse studies for applications of NHC-metal complexes have been conducted and a number of polymeric materials that contain tethered *N*-heterocyclic carbenes have been reported [11, 12]. Over the last decade, the self-supporting strategy, which incorporates ditopic ligands and active metal centers into organometallic assemblies, represents an efficient approach to immobilize specific catalysts. It is also an effective strategy for the immobilization of NHC compounds. For example, the use of di-imidazolium salts as precursors to NHC-based coordination polymers has been explored [13-16]. Moreover, the self-assembly of pyridyl, bipyridyl and carboxylic acid-functionalized imidazolium salts with transition metals to form NHC supramolecular networks were also achieved [17-19]. In contrast, the introduction of the NHC-metal units within supramolecular networks through terpyridine-metal complexes acting as linkers is rare despite the intensive investigation of various NHC complexes [20, 21]. In this paper, we reported the synthesis and self-assembly of a polymeric Cu(I) *N*-heterocyclic carbene complex utilizing terpyridine-Fe(II) as linkers and its catalytic behaviors in A^3-coupling reaction of alkyne, aldehyde, and amine and Huisgen 1,3-dipolar cycloaddition reaction of organic azide and terminal alkyne were comparatively studied.



Scheme 1. Schematic presentation for preparation of the terpyridine-Fe(II) linked polymeric Cu(I) *N*-heterocyclic carbene complex.

2. Results and discussion

The [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst was readily prepared in a three-step procedure (scheme 1). The reaction of 4'-(4-(bromomethyl)phenyl)-2,2':6',2''-terpyridine and 1*H*-imidazole in acetone gave the desired product as a white powder in 70% yield. The as-synthesized imidazole salt ([Tpy-Im][Br]) is insoluble in common solvent and only slightly soluble in DMSO. Due to the poor solubility of the ligand, the characterization of [Tpy-Im][Br] was performed *via* the imidazole salt with BF_4^- ion as counteranion through anion metathesis. The iron complex [Tpy-Fe^{II}-Im] was synthesized by mixing the [Tpy-Im][Br] with $FeCl_2$ in methanol in reflux. After purification, a violet-purple powder was obtained, wherein the Fe^{2+} ion binds two tpy units from two ligands while leaving the imidazole salt sites untouched. This coordination mode leads to the supramolecular compounds of $\{[Fe\text{-}(tpy)_2]^{2+}\}_n$ incorporating the imidazolium salt as a potential active site. The [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst was then obtained by treating [Tpy-Fe^{II}-Im] with

CuI in the presence of NaO^t-Bu in dry THF. The thermal stability of the complex was studied by TGA. [Tpy-Fe^{II}-NHC-Cu^{I}] showed a relative gradual thermal stability from room temperature to 300 °C, and a major weight loss from 300 to 450 °C due to combustion of the organic part of the framework. The exact composition of [Tpy-Fe^{II}-NHC-Cu^{I}] was determined by combined elemental analysis, TGA, EDX and ICP analysis. The crystallized particles of [Tpy-Fe^{II}-NHC-Cu^{I}] revealed by EDX that the Fe:Cu ratio appears to be 1:1. Furthermore, the EDX spectra of [Tpy-Fe^{II}-NHC-Cu^{I}] have also shown that only Cl and I elements exist in the system, which indicates that the Br anion is completely removed in this reaction process. ICP analysis also indicated that a weight loading of 0.88 mmol g^{-1} copper in [Tpy-Fe^{II}-NHC-Cu^{I}], corresponding to all of the carbenes, have been coordinated to Cu ions. The new class of NHC-Cu catalyst should then be of catalytic interest due to the presence of well-defined isolated NHC-Cu active sites.

The catalytic activity of [Tpy-Fe^{II}-NHC-Cu^{I}] was first examined in one of the representative Cu-catalyzed reactions, the A^3-coupling (aldehyde-alkyne-amine) reaction. The A^3-coupling reaction has attracted attention for the coupling product, propargylamine, which is a major skeleton for the preparation of nitrogen-containing biologically active compounds. However, its potential application in industry is still limited due to the difficulty in separating and recycling the Cu-catalysts from the product mixture. Using heterogeneous and recyclable copper catalysts is, therefore, a promising solution to this problem. In order to evaluate the catalytic activity of the obtained catalyst, the coupling of *para*-formaldehyde, phenylacetylene and piperidine was chosen as standard substrates to optimize the reaction conditions. Initially, the solvent effect was examined using the [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst (2 mol %) at room temperature. Among the solvents tested, CH_3CN, $CHCl_3$ and CH_2Cl_2 were the most suitable reaction media for the reaction, whereas THF and toluene afforded moderate yields. However, the highest yield was achieved under neat conditions. Then the influence of the amount of the catalyst on the reaction was examined, and it was found that catalyst loading affected the reaction significantly. The use of 1.0 mol% Cu catalyst only gave the product in moderate yield.

Increasing the amount of catalyst loading up to 2.0 mol%, high yield of the product was obtained. However, the yields of the product were not improved greatly upon increasing the amount of catalyst loading. Thus, the optimized reaction condition for the A^3-coupling reaction is [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst (2 mol %) in the neat condition at room temperature for 24 h.

To examine the scope of the reaction, the combinations of various aldehydes, alkynes and amines were studied. At the beginning of the search for amine substrate scope, phenylacetylene was used as the model substrate and various amines were examined. The results indicated that secondary aliphatic amines gave high yields of the products (table 1, entries 1-4). To the aldehyde substrates, aliphatic aldehydes, cyclic or acyclic, displayed high reactivity under the reaction condition (entries 5-7). Aromatic aldehydes with both *ortho*, *meta* and *para*-substitutions also afforded the corresponding propargylamines in good yields (entries 8-10). Subsequently, the alkyne substrates were examined. Aromatic alkynes, including those bearing functional groups, were able to undergo the coupling reaction and generate the corresponding products in excellent yields (entries 11 and 12).

It is known that one of the disadvantages of supported catalysts is the leaching of metals into solution, resulting in the contamination of the product and the loss of the activity of the supported catalyst. For these reasons, leaching of the metal from the [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst has been examined. After the workup, inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis showed that the amount of Cu leaching into the reaction mixture was very low (< 0.3 ppm). There was also no detectable leaching of Fe to the reaction mixture due to the high stability of Fe(tpy)$^{2+}$ complexes, so the support will not contaminate the product. Furthermore, the hot filtration experiment was performed to investigate the heterogeneity of the [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst. The catalyst was removed after 20% of conversion and the resulting filtrate was monitored under identical reaction condition for another 24 h, however, no further conversion was detected. Advantages of the [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst are the fact that the catalytic reactions can be conveniently carried out and that the separation of the catalyst can be achieved easily by centrifugation. After being recycled for six runs of the reaction of *para*-formaldehyde, phenylacetylene, and piperidine, the [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst still exhibits a remarkable activity (the yield decreased only for 5%) (table 2). These results indicate that the reaction proceed is really in a heterogeneous fashion.

To further investigate the scope of this catalyst recycling procedure, a second copper(I)-catalyzed reaction, Huisgen 1,3-dipolar cycloaddition reaction was performed. For this reaction, the [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst was proved to be well-suited for the cycloaddition reaction and the desired product was isolated in 93% yield under the optimized conditions. To examine the scope of the reaction, the reaction of phenylethyne with different azides was first tested under solvent-free conditions. The results indicated that benzyl azides and aromatic azides with both electron-donating and electron-withdrawing functionalities gave high yields of the products (table 3, entries 1-5). However, the reactions of alkyl azides with phenylacetylene led to slower reactions and needed a prolonged reaction time (entries 6 and 7). Subsequently, a variety of alkynes were also examined by using benzyl azide-terminal alkynes combination (entries 8-12). As it can be seen from table 3, the reactivity of aliphatic and aromatic alkynes was all observed, in which aromatic alkynes were often much more reactive than aliphatic alkynes.

The recycle use of [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst (2.0 mol%) for Huisgen 1,3-dipolar cycloaddition reaction was further examined in the reaction of benzyl-azide with phenylacetylene (table 4). The results demonstrated that [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst could be reused at least six times without loss of catalytic activity. Meanwhile, copper leaching in the catalyst was determined. ICP analyses of the clear filtrates obtained by filtration after the reaction indicated that Cu content is < 0.2 ppm.

3. Experimental

3.1. *General procedures*

^{1}H and ^{13}C NMR spectra were recorded on a Bruker FT-NMR spectrometer at 400 and 100 MHz using tetramethylsilane as internal standard. FT-IR spectra were measured by a Nicolet AVATAR 360 FT-IR spectrometer as KBr disks. Elemental analyses were performed on a

VarioEL from Elementar Analysensysteme GmbH. ESI-MS measurements were carried out using a Waters ZQ4000 spectrometer. The metal content was determined by a Jarrell-Ash 1100 ICP analysis. The elemental concentration distribution on the sample was verified by energy dispersive X-ray analysis (EDX, Horiba 7593H). 4'-(*p*-Tolyl)-2,2':6',2''-terpyridine and 4'-(phenyl-*p*-bromomethyl)-2,2':6',2''-terpyridine were synthesized according to the literature [22]. All other reagents were commercial purchased and used as received. Products were purified by flash chromatography on 230-400 mesh silica gel, SiO_2.

3.2. ***Synthesis of N,N'-bis[4-([2,2':6',2''-terpyridin]-4'-yl)benzyl]imidazolium bromide ([Tpy-Im][Br])***

4'-(Phenyl-*p*-bromomethyl)-2,2':6',2''-terpyridine (0.80 g, 1.99 mmol) and imidazole (0.27 g, 4.00 mmol) were heated under reflux in dry acetone (10 mL) for 18 h. The reaction mixture was cooled to room temperature and the precipitate was collected from the filtration and purified and washed sequentially with acetone to give [Tpy-Im][Br] as white powder (0.55 g, 70%). Then the compound was dissolved in a large amount of hot DMSO to give a clear solution and treated with a 2-fold excess of the aqueous solution of $NaBF_4$. The white precipitate formed was filtered off and washed successively with H_2O, EtOH and Et_2O, and dried under high vacuum to yield [Tpy-Im][BF_4]. Anal. Calc for [Tpy-Im][BF_4]$\cdot 3H_2O$ ($C_{47}H_{41}BF_4N_8O_3$): C, 66.20; H, 4.85; N, 13.14. Found: C, 66.33; H, 4.92; N, 13.19%. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 9.55 (s, 1H), 8.77-8.67 (m, 12H), 8.05-7.97 (m, 10H), 7.69-7.55 (m, 8H), 5.61 (s, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 156.09, 155.26, 149.69, 149.04, 138.42, 137.81, 137.06, 136.22, 129.86, 128.06, 124.93, 123.56, 121.37, 118.37, 52.30. IR (KBr, cm^{-1}): 3420, 1603, 1586, 1566, 1517, 1470, 1422, 1390, 1155,789, 687. ESI-MS: *m*/*z* 711.29518 ([M−BF_4]$^+$) (calcd 711.29792).

3.3. ***Synthesis of complex [Tpy-Fe^{II}-Im]***

To a stirred suspension of [Tpy-Im][Br] (791 mg, 1.00 mmol) in 2 mL of methanol was added dropwise an aqueous solution of $FeCl_2\cdot 4H_2O$ (220 mg, 1.10 mmol). An immediate color change from colorless to violet-purple marked the complex formation. The resulting violet-purple solution was stirred for 30 min at 60 °C and concentrated in vacuum; a violet-purple precipitate was filtered off, washed with acetone and ether, and dried. [Tpy-Fe^{II}-Im] was obtained as a violet-purple powder in 97% yield. Anal. Calc for [Tpy-Fe^{II}-Im]·6H$_2$O ($C_{47}H_{43}BrCl_2FeN_8O_4$): C, 56.99; H, 4.38; N, 11.31. Found: C, 55.13; H, 4.64; N, 11.19 %. IR (KBr, cm^{-1}): 3406, 1613, 1558, 1468, 1435, 1409, 1364, 1153, 1086, 791, 757.

3.4. *Synthesis of [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst*

In an oven-dried Schlenk flask, freshly prepared CuI (190 mg, 1.0 mmol), NaO^{t}Bu (96.0 mg, 1.0 mmol), [Tpy-Fe^{II}-Im] (1.00 g) and THF (10 mL) were added. The resulting suspension was stirred at room temperature under an inert gas for 6 h. Then the solution was filtered, and the solid was washed with THF (5×2 mL), Et$_2$O (5×2 mL), and dried under vacuum at 60 °C for 12 h. [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst was obtained as a violet-purple powder in 95% yield. Anal. Calc for [Tpy-Fe^{II}-NHC-Cu^{I}]·6H$_2$O ($C_{47}H_{46}Cl_2CuFeIN_8O_6$): C, 49.69; H, 4.08; N, 9.86. Found: C, 49.43; H, 4.29; N, 9.79%. IR (KBr, cm^{-1}): 3411, 1612, 1558, 1467, 1435, 1410, 1364, 1285, 1246, 1153, 1086, 880, 790, 755.

3.5. *Typical procedure for A^3-coupling reaction (para-formaldehyde, phenylacetylene, and piperidine) catalyzed by [Tpy-Fe^{II}-NHC-Cu^{I}]*

A 10 mL reaction tube was introduced catalyst [Tpy-Fe^{II}-NHC-Cu^{I}] (11 mg, 1.0 mol%), phenylacetylene (61 mg, 0.6 mmol), *para*-formaldehyde (15 mg, 0.5 mmol) and piperidine (47 mg, 0.55 mmol). The mixture was stirred at room temperature for 24 h. After the reaction was completed, Et$_2$O (2×3 mL) was added, and the slurry was stirred. The organic layer was collected by centrifugation, concentrated, and the residue was purified by flash chromatography on silica gel to obtain the desired products. In a recycle test, phenylacetylene (61 mg, 0.6 mmol), *para*-formaldehyde (15 mg, 0.5 mmol), piperidine (47 mg, 0.55 mmol) and [Tpy-Fe^{II}-NHC-Cu^{I}]

(11 mg, 0.01 mmol) were used. After each cycle, the catalyst was dried and then used directly without any further treatment.

3.6. *Typical procedure for Huisgen 1,3-dipolar cycloaddition of phenylacetylene and benzyl azide catalyzed by [Tpy-Fe^{II}-NHC-Cu^{I}]*

A 10 mL reaction tube was introduced catalyst [Tpy-Fe^{II}-NHC-Cu^{I}] (11 mg, 0.01 mmol), phenylacetylene (51 mg, 0.5 mmol) and benzyl-azide (66 mg, 0.5 mmol). The mixture was stirred at room temperature for 4 h. After the reaction was completed (monitored by TLC), the mixture was centrifugated and the solid was washed with dichloromethane (3×5 mL). The combined organic phase was then evaporated under reduced pressure to leave the crude products which were further purified by column chromatography over silica gel to obtain the desired products. In a recycle test, phenylacetylene (51 mg, 0.5 mmol), benzyl-azide (66 mg, 0.5 mmol) and [Tpy-Fe^{II}-NHC-Cu^{I}] (11 mg, 0.01 mmol) were used. After each cycle, the catalyst was dried and then used directly without any further treatment.

4. Conclusion

A self-supporting catalyst has been prepared by construction of polymeric Cu(I) *N*-heterocyclic carbene complex utilizing terpyridine-Fe(II) as linkers. The resulting heterogeneous [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst exhibits high catalytic activities and gives higher catalytic performance in catalyzed A^3-coupling reaction of aldehyde, alkyne, and amine and Huisgen 1,3-dipolar cycloaddition reaction of azides and alkynes. The further construction of the polymeric *N*-heterocyclic carbene complexes and their application in organic reactions is currently underway in our laboratory.

Acknowledgements

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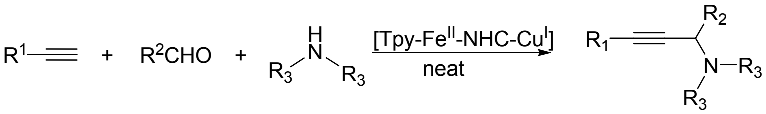
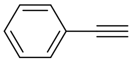
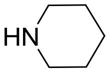
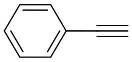
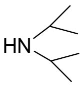
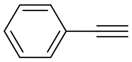
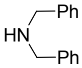
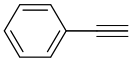
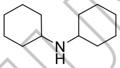
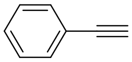
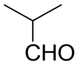
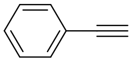
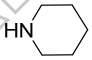
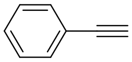
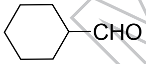
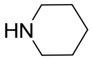
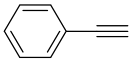
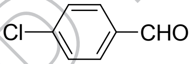
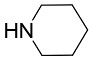
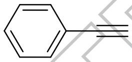
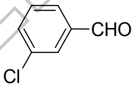
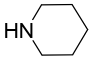
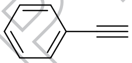
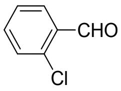
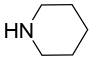
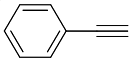
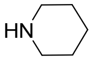
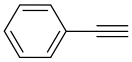
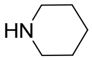
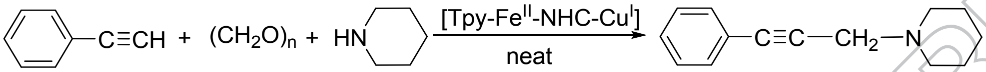
Table 1. A^3-coupling reaction catalyzed by [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst[a].



Entry	Alkyne	Aldehyde	Amine	Yield (%)[b]
1		$(CH_2O)_n$		94
2		$(CH_2O)_n$		94
3		$(CH_2O)_n$		93
4		$(CH_2O)_n$		93
5				92
6				90
7				90
8[c]				88
9[c]				87
10[c]				82
11		$(CH_2O)_n$		94
12		$(CH_2O)_n$		93

[a] Reaction conditions: aldehyde (0.5 mmol), amine (0.55 mmol), and alkyne (0.6 mmol), [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst (11 mg, containing Cu 0.01 mmol) at r.t. for 24 h. [b] Isolated yields. [c] At 60 °C for 6 h.

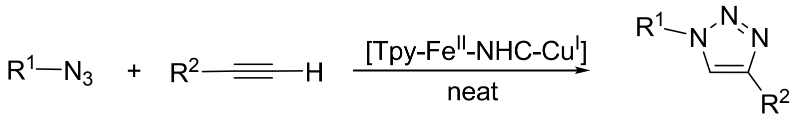
Table 2. Successive runs by using reused [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst [a].

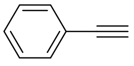
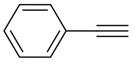
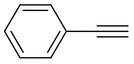
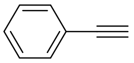
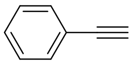
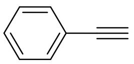
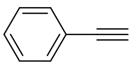
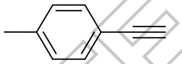
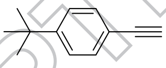
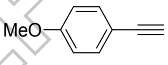
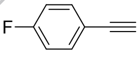


Cycle	**Yield (%)**[b]	**Cycle**	**Yield (%)**[b]
1	94	2	94
3	93	4	92
5	90	6	89

[a] Reaction conditions: *para*-formaldehyde (0.5 mmol), piperidine (0.55 mmol), and penylacetylene (0.6 mmol), [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst (11 mg, containing Cu 0.01 mmol) at r. t. for 24 h. [b] Isolated yields.

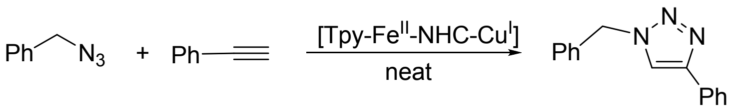
Table 3. Huisgen 1,3-dipolar cycloaddition reaction of azides and alkynes catalyzed by [Tpy-Fe^{II}-NHC-Cu^{I}] [a].



Entry	Alkyne	Organic azide	Yield (%)[b]
1		$C_6H_5CH_2N_3$	95
2		p-$CH_3C_6H_5CH_2N_3$	94
3		p-$NO_2C_6H_5CH_2N_3$	95
4		p-$ClC_6H_5N_3$	91
5		p-$MeOC_6H_5N_3$	90
6		n-$C_6H_{13}N_3$	87
7		n-$C_8H_{17}N_3$	89
8		$C_6H_5CH_2N_3$	94
9		$C_6H_5CH_2N_3$	93
10	 MeO	$C_6H_5CH_2N_3$	91
11	 F	$C_6H_5CH_2N_3$	92
12	n-$C_6H_{13}C\equiv CH$	$C_6H_5CH_2N_3$	84

[a] Reaction conditions: organic azide (0.5 mmol), alkyne (0.5 mmol), [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst (11 mg, containing Cu 0.01 mmol) at r. t. for 6 h. [b] Isolated yields.

Table 4. Successive runs by using reused [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst [a].



Cycle	Yield (%)[b]	Cycle	Yield (%)[b]
1	95	2	95
3	94	4	94
5	92	6	91

[a] Reaction conditions: benzyl azide (0.5 mmol), phenylacetylene (0.5 mmol), [Tpy-Fe^{II}-NHC-Cu^{I}] catalyst (11 mg, containing Cu 0.01 mmol) at r. t. for 6 h.
[b] Isolated yields.

Graphical abstract