

FULL PAPER

Silica immobilized copper N-heterocyclic carbene: An effective route to 1,2,3-triazoles via azide-alkyne cycloaddition and multicomponent click reaction

Anirban Garg¹ | Nobomi Borah^{1,2} | Jasmin Sultana¹ | Akshay Kulshrestha³ | Arvind Kumar³ | Diganta Sarma¹

¹Department of Chemistry, Dibrugarh University, Dibrugarh, India

²Department of Chemical Sciences, Tezpur University, Napaam, India

³AcSIR, Salt and Marine Chemicals Division, CSIR-Central Salt and Marine Chemicals Research Institute, Bhavnagar, India

Correspondence

Diganta Sarma, Department of Chemistry, Dibrugarh University, Dibrugarh-786004, Assam, India. Email: dsarma22@dibru.ac.in; dsarma22@gmail.com

Funding information

Department of Biotechnology, Ministry of Science and Technology, India, Grant/ Award Number: BT/PR24684/ NER/95/810/2017; Department of Science and Technology, Ministry of Science and Technology, India, Grant/Award Number: EMR/2016/002345 A new silica supported copper N-heterocyclic carbene (Cu-NHC@SiO₂) complex is prepared and characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) analyses. This complex is an efficient and easily retrievable catalyst for 1,2,3-triazole synthesis through direct azide-alkyne cycloaddition reaction as well as one-pot reaction using arylboronic acids. This catalytic system is also suitable for synthesis of 4-aryl-NH-1,2,3-triazoles from diverse benzaldehydes. Further, the catalyst can efficiently be recycled up to fifth cycle for all the three methods of 1,2,3-triazole synthesis through direct azide-alkyne cycloaddition and multi-component reactions.

K E Y W O R D S

1,2,3-triazole, Cu-NHC@SiO2, heterogeneous catalyst, mild condition, reusability

1 | INTRODUCTION

Solid supported catalysts offer innumerable opportunities to recover and reuse catalysts from reacting media. These characteristics of heterogeneous catalysts lead to better process economy and environment compatibility to industrial scale manufacturing. Silica remains preferred alternatives among different heterogeneous supports as silica exhibits good thermal and chemical stability, high surface area and excellent porosity.^[1] Due to the reactive silanol groups in silica surface, different ligand functionality can be robustly anchored onto it. Therefore, ample studies have been carried out in fabricating silica surface^[2] with different ligands and subsequent incorporation of transition metals for their use in various organic transformations.^[3–5]

N-heterocyclic carbenes (NHCs) are widely used as ligands in preparation of transition metal based organometallic catalysts.^[6] With strong σ -donating and Lewis basicity NHCs can easily stabilize metal centers and form metal complexes. Additionally, due to presence of strong σ bonds, NHCs are comparatively stable to hydrolytic conditions than phosphine ligands in similar complexes.^[7] Attributing to the better stability NHCs can form complexes with almost all transition metals and many main group elements.^[8] In 1993, the first NHC coordinated copper complex was reported and after that copper NHC complexes have been widely used as effective catalysts in many organic reactions^[9] including click reaction for 1,4-disubstituted-1,2,3-triazole synthesis. In particular, Nolan et al. reported a good example of three solid ^{2 of 10} WILEY Applied Organometallic_

supported CuNHC complexes for triazoles synthesis.^[10] Further, a few more catalytic protocols based on CuNHC catalyst^[11] including a latent NHC catalyst,^[12] which shows excellent catalytic activity toward triazoles synthesis at slightly elevated temperature were reported. Inspired by the efficiency of these protocols, effort has been made to develop new CuNHC catalyst, which can subsequently be applied for 1,4-disubstituted-1,2,3-triazole synthesis. It is worth mentioning that typical non-supported CuNHC catalysts were stabilized by allowing the metal to make complex with bulky ligands.^[8-10] Therefore, our effort involves use of solid support and functionalization of the support with the NHC and consequently preparation of supported CuNHC catalyst using simple ligand, which is fairly stable for catalytic application.

Copper catalyzed azide-alkyne cycloaddition reaction (CuAAC), also popularly known as click reaction, is the most accessed route for 1.2.3-triazole synthesis.^[13] After its discovery in 2001, click reaction has frequently found designing,^[14] material bioconjugation usage in application,^[15] and most importantly in medicinal chemistry owing to broad-spectrum biological activity of 1,2,3-triazoles.^[16] However, many catalytic systems have been developed to improvise this system.^[17] Especially, Ramachary et al. have developed the first ever organocatalyzed [3+2]-cycloaddition of unsaturated ketones and azides. Subsequently, various research groups have reported transition metals other than copper and many metal free systems for 1,2,3-triazole synthesis. Interestingly, Na ascorbate/CuSO₄ system still remains the most favorite route for synthetic chemists to introduce 1,2,3-triazole moiety in various molecules owing to the simplicity of the protocol. Hence, we are interested in developing simple protocol for 1,2,3-triazole synthesis, which is not only efficient but also versatile and easily retrievable in nature.

Usually, organic azides that are cyclized with terminal alkyne to yield 1,2,3-triazoles are prepared prior to cycloaddition. Through multicomponent reaction (MCR), azides can be generated in situ from easily available reacting materials. Therefore, MCR offers convenient route to access complex molecular architecture without going through multistep reactions. A number of one-pot systems have been developed recently, highlighting the use of different copper catalysts.^[18] Although many efficient methods are present for synthesis of 1,2,3-triazole further improvement in terms of selectivity, environment issue related to use of solvents, high temperature needed to be addressed. Herein, we have developed a new CuI-NHC catalyst anchored on silica and its catalytic application for azide-alkyne cycloaddition reaction and NH-triazoles using aromatic aldehydes, nitromethane and sodium azide.

2 | PREPARATION OF THE CATALYST

The preparation of the catalyst was carried out by following the method reported by Wang et al. for synthesis of silica immobilized Cu-NHC complex for A³-coupling reaction.^[19] The synthesis of the catalyst involves following steps:

- a. Synthesis of CPTMS functionalized silica CPTMS@SiO₂: 2-g silica (pre-activated at 120°C for 4 h) was added to a two neck round bottom flask containing 50 ml dry toluene, which was followed by addition of 2-mmol 3-chloropropyl trimethoxy silane (CPTMS). The resultant mixture was stirred under N₂ atmosphere at 80°C for 8 h and was allowed to cool. The solids were separated by filtration and washed repeatedly through Soxhlet extraction with toluene. The resulting material was then dried at 120°C for 24 h to obtain CPTMS@ SiO₂.
- b. Synthesis of Imidazole-CPTMS@SiO₂: 1.5-g CPTMS@SiO₂ was added to a two neck round bottom flask containing 50 ml dry toluene followed by addition of 2-mmol N-methylimidazole. The resultant mixture was stirred under N₂ atmosphere at 80°C for 6 h and was allowed to cool. The solids were separated by filtration and washed repeatedly through Soxhlet extraction with toluene. The resulting material was then dried at 120°C for 24 h to obtain Imidazole-CPTMS@SiO₂.
- c. Synthesis of Cu-NHC@SiO₂: To a suspension of 1-g Imidazole-CPTMS@SiO₂ in THF 0.5 mmol of CuI and 1 mmol of KO^tBu were added and stirred overnight under N₂ atmosphere at room temperature. The solids were separated by filtration and washed several times with methanol followed by THF. The filtrate was dried in hot air oven for 6 h to obtain a gray–green powder.

3 | CHARACTERIZATION OF THE CATALYST

Cu-NHC@SiO₂ was characterized by Fourier transform infrared (FTIR), thermo gravimetric analysis (TGA), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), and solid ultraviolet (UV) analyses. The FTIR spectra of the samples (Figure 1) revealed important information about formation of NHC complex and its successful immobilization onto the support. For all the samples, the bands around 1639 and 3430 cm⁻¹ correspond to ν O–H stretching and bending vibrations of the adsorbed water, while the absorption peaks around

Applied Organometallic_WILEY 3 of 10 Chemistry

FIGURE 1 Fourier transform infrared (FTIR) spectra (a) SiO₂, (b) NHC@SiO₂, and (c) Cu-NHC@SiO₂



FIGURE 2 Scanning electron microscopy (SEM) images of (a) silica (c) catalyst; energy dispersive X-ray spectroscopy (EDX) pattern of (b) silica (d) catalyst

802 and 1087 cm⁻¹ were attributed to Si–O–Si structure of silica framework. Appearance of a band at 967 cm⁻¹ was assigned to silanol group of silica. Intensity of this particular band decreases as silica is functionalized with CPTMS and 1-methyl imidazole. This observation indicates formation of Si–O bond as a result of interaction between silanol groups of silica with the $(CH_3O)_3Si$ -group of CPTMS.

Furthermore, presence of peaks at 3447 (sp² C–H stretching vibration of the imidazole moiety), 3342 (N–CH₂ stretching vibration) and 1567 cm⁻¹ (C–N and C=C vibrations of the imidazole ring) in FTIR spectrum of Cu-NHC@SiO₂ relative to raw silica sample suggests functionalization of silica with desired ligands and metal complex.^[20] Appearance of a peak at 664.7 cm⁻¹ is observed due to Cu–C stretching, which

indicates probable formation of silica anchored CuNHC complex.

The scanning electron microscopic images (Figure 2a,c) of silica and the catalyst suggest smaller particle size of the catalyst following reaction of silica particles, silane and CuI.^[21] Furthermore, the Cu-immobilized silica surface shows more roughness than the non-functionalized silica (Figure 2b,d). The grav-green color of silica gel and observation of a rougher surface indicates the binding of copper to the silica gel. To further confirm the structure, EDX was performed. EDX study shows presence of different elements along with copper in the highly uniform surface of the catalyst (Figure 2b,d). The inductively coupled plasma atomic emission spectroscopy (ICP-AES) results also reveal successful attachment of metal on the silica surface. The amount of metal content in the Cu-NHC@SiO2 catalyst was found to be 37.67 mol% per gram of the catalyst.

The electronic properties of the catalyst were probed by XPS analysis. Binding energies ($\pm 0.1 \text{ eV}$) of the elements were determined with respect to the position C 1s peak at 283.78 eV. Calibration of the binding energy (BE) scale was done by using the C 1s (BE = 284.8 eV) signal. Figure 3a depicts full scan profile of the catalyst, which shows presence of N, O, I, and Cu along with Si and C in the catalyst. The binding energies of Cu $2p_{3/2}$ and $2p_{1/2}$ at 934.82 and 954.56 eV with strong satellite peak at 941.96 and 943.65 eV indicates presence of copper mostly in +2 oxidation state, while two peaks at 932.87 and 952.20 eV are suggestive of fraction of copper catalyst present at +1 oxidation state. Similarly, from the XPS profile binding energies of N (1s) and O (1s) were found at 404.4 and 532.2 eV, respectively, owing to presence of imidazole moiety attached to the silane. Moreover, I 3d curve could be fitted with peak at the BE of 618.2 eV that confirms I $3d_{5/2}$ component in the catalyst.

To examine the thermal stability of the catalyst TGA was performed from 35 °C to 780°C at scanning rate of 20°C/min with Perkin Elmer STA 8000 instrument under nitrogen atmosphere (N₂ gas flow rate: 20 ml/min) taking empty alumina as reference. The TGA curve (Figure 4) of the catalyst demonstrates the superior thermal stability of the catalyst up to 541°C, indicating wide temperature range usefulness of prepared catalyst for any chemical reaction.

4 | APPLICATION OF PREPARED CU CATALYST IN TRIAZOLE SYNTHESIS

CuAAC is known to be a powerful reaction, which is applied in complex molecular synthesis, bioconjugation, drug development, and so forth. Therefore, the scope of the synthesized Cu catalyst was tested for triazole synthesis. In our initial investigations, benzyl azide (**1a**) with



FIGURE 3 X-ray photoelectron spectroscopy (XPS) analysis of Cu-NHC@SiO₂ for (a) full scan, (b) Cu 2p, (c) N 1s, (d) I 3d, and (e) O 1s

phenyl acetylene (2a) was chosen as the probe. At first, the reaction was conducted in open air at 60° C with 15 mg of the Cu catalyst in water with 10 mol% Na



FIGURE 4 Thermo gravimetric analysis (TGA) and DTG curve of the catalyst

TABLE 1	Optimization of reaction
condition	

Applied Organometallic_WILEY 5 of 10 Chemistry

ascorbate, which successfully led to the formation of 1-benzyl-4-phenyl-1H-1,2,3-triazole (3a) with 91% yield (Table 1, Entry 1), while using water and ethylene glycol as solvent system in ratio 10:1 for the triazole synthesis gave 3a in almost quantitative yield (Table 1, Entry 2). It is assumed that the larger and less polar ethylene glycol molecules enhance solubility of the organic substrates in water. It is worth mentioning that in ethylene glycol alone the reaction does not produce good result. Further screening of solvents showed no improvement to existing best condition (Table 1, Entries 4-10). To estimate optimum temperature for the triazole synthesis under present condition, a reaction was performed at 50°C and the yield of 3a was found to be decreased (Table 1, Entry 11). The reaction mixture needed to be stirred for considerably longer time under room temperature to achieve convenient yield (Table 1, Entry 12). These observations suggested the need of small thermal energy to activate catalytic property of the catalyst. A catalyst-free reaction was performed under similar condition that showed no product formation at all which suggests requirement of the catalyst (Table 1, Entry 13). Furthermore, decreasing

	N ₃ + a 2a	CuNHC Na-ascorbate Solvent 60 °C	N ^N N 3a
Sl. no.	Reaction medium	Time (h)	Isolated yield (%)
1	H ₂ O	1	91
2	H ₂ O/EG (10:1)	0.5	99
3	EG	1	trace
4	H ₂ O/DMSO (1:1)	1	56
5	H ₂ O/t-BuOH	1	60
6	H ₂ O/ACN	1	trace
7	Toluene	1	trace
8	DMF	1	32
9	THF	1	trace
10	DMSO	1	<10
11	H ₂ O/EG (10:1)	1.5	93 ^[a]
12	H ₂ O/EG (10:1)	3	75 ^[b]
13	H ₂ O/EG (10:1)	4	0 ^[c]
14	H ₂ O/EG (10:1)	0.5	87 ^[d]

Note: Reaction condition: Benzyl azide (0.5 mmol), phenyl acetylene (1.2 equiv), CuNHC 15 mg (1.13 mol%) and Na-ascorbate (10 mol%) was stirred in 1-ml solvent (ratio in case of binary mixture) at 60°C. ^aReaction mixture was stirred at 50°C.

^bReaction was carried out at room temperature.

^cReaction was performed without catalyst.

^d12 mg of CuNHC was used.

6 of 10 WILEY Organometallic

catalyst loading greatly affects the reaction resulting decreased yield of **3a** (Table 1, Entry 14). Thus, the optimized catalytic system was established; **1a** (0.5 mmol), **2a** (0.6 mmol), catalyst (15 mg, 1.13 mol%), Na ascorbate (10 mol%), and water/ethylene glycol (10:1) at 60° C.

With the optimized condition in hand, we next investigated the scope of the catalytic system (Scheme 2). An array of benzyl and aromatic azide could be cyclized to corresponding 1,4-disubstituted-1,2,3-triazoles using this protocol with excellent yields (**3a–3k**, 84–99% yields). Benzyl, phenyl, or 4-substituted phenyl azides smoothly reacted to furnish corresponding triazoles **3a–3h.** Similarly, 3- or 2-substituted phenyl azides and aliphatic azide could also be tolerated under present catalytic system affording corresponding triazoles in excellent yields (**3i–3k**).

Next, the scope of alkyne substrates was tested with our catalytic system (Scheme 3). It was pleasing to see that all the alkynes under study reacted well affording corresponding triazoles in good to excellent yields. Initially, two naphthyl derivatized alkynes were allowed to cyclize with benzyl azide, and the products were obtained in excellent yields (3I-3m). Likewise, reaction of phenyl ether and phenyl thioether containing alkynes with benzyl azide produced 1,4-disubstituted triazoles quantitatively (3n-3o). Further, other alkyne substrates with 2,4-disubstituted phenyl, ester, carboxylic groups, and aliphatic chain also tolerated well under current catalytic condition (3p-3u). It is worth mentioning that internal alkynes and heterocyclic alkynes also reacted readily to furnish desired triazoles (3v-3x).

MCRs are always helpful in accessing seemingly difficult products that cannot be synthesized otherwise. In order to expand accessibility of our system towards broader range of triazoles, we have put emphasis on accessing 1-aryl-1,2,3-triazoles using aryl boronic acids as azide precursor. The same reaction condition was maintained for this MCR of 3-methoxy phenylboronic acid, sodium azide, and phenyl acetylene, which led successfully to desired product **3y** in 1 h with 92% yield. Similarly, seven different triazoles are synthesized (Scheme 4). It was observed that the triazoles (Scheme 4,



SCHEME 3 Reaction of benzyl/phenyl azide with various alkynes^a. ^aReaction conditions: Benzyl or phenyl azide (0.5 mmol), alkyne (0.6 mmol), Cu-NHC@SiO₂ (15 mg, 1.13 mol%), and Na ascorbate (10 mol%) were stirred in H₂O/EG (10:1, 2 ml) at 60°C for 0.5–1 h. Isolated vields



SCHEME 4 Reaction of various arylboronic acids, sodium azide, and different alkynes^a. ^aReaction condition: arylboronic acids (0.5 mmol), NaN₃ (1. mmol), alkynes (0.6 mmol), Cu-NHC@SiO₂ (15 mg, 1.13 mol%), and Na ascorbate (10 mol%) were stirred in H₂O/ EG (10:1, 2 ml) at 60°C for 1–3 h. Isolated yields

3c-3x) were produced as efficiently by multicomponent strategy as it had been done by typical azide-alkyne cyclo-addition discussed earlier.

Under the hood of 1,2,3-triazole family, the NH-1, 2,3-triazole is an important class showing promising applications in many fields, particularly in postalkylation or arylation of NH-1,2,3-triazole for synthesis of N²-substituted 1,2,3- triazoles.^[22] It is worth mentioning, however, that their synthesis is still remaining a challenge compared to the direct synthesis of substituted 1,2,3-triazoles. Initially introduced by Zefirov, condensation of nitroalkenes and NaN₃ was a popular method for the synthesis of NH-1,2,3-triazoles but usually alkenes undergo polymerization and overall yield of triazole product gets decreased.^[23] This problem can be overcome through one-pot reaction of aryl aldehyde, sodium azide, and nitroalkane by employing Cu or Pd catalysts.^[24] Therefore, as an expansion of scope of our catalytic system, ability of Cu-NHC@SiO₂ to catalyze one-pot synthesis of NH-1,2,3-triazole was studied. For standardization purpose 4-bromobenzaldehyde, NaN₃ and nitromethane were selected as model substrates and allowed to react in presence of 15 mg copper catalyst in water at 100°C, which resulted formation of **3aa** with 37% yield (Table 2, Entry 1). To improve yield of NH-triazole, different solvents were tried and PEG 400 was found to produce the best result (Table 2, Entries 2–5). After that, catalyst loading and temperature were optimized while only trace of

TABLE 2 Standardization of reaction condition for NH-1,2,3-triazole synthesis



Note: Reaction conditions: 4-Bromobenzaldehyde (0.5 mmol), nitromethane (0.75 mmol), NaN3 (1 mmol), and Cu-NHC@SiO2 were stirred in solvent (2 ml) for 2 h.





SCHEME 5 Reaction of different aromatic aldehydes, nitromethane, and sodium azide^a. ^aReaction conditions: Aldehyde (0.5 mmol), nitromethane (0.75 mmol), NaN₃ (1 mmol), and Cu-NHC@SiO₂ (20 mg, 1.5 mol%) were stirred in PEG-400 (2 ml) at 100°C for 1.5–3 h. Isolated yields

triazole product was obtained through catalyst-free reaction (Table 2, Entries 6–10). Thus, PEG 400, 20 mg (1.5 mol%) Cu-NHC@SiO₂ catalyst at 100°C was found to be the best condition for the synthesis of NH-1,2,3-triazoles. After standardizing the reaction condition, various aryl aldehydes were subsequently tested with the catalytic system (Scheme 5). Aromatic aldehydes with electron donating functional groups ($-OCH_3$, -OH, and $-CH_3$) reacted satisfactorily affording NH-triazoles in

FIGURE 5 Reusability of the catalyst



excellent yields (**3ab–3ad**). Moreover, benzaldehyde (**3ae**), halogen substituted aryl aldehydes (**3af–3ah**) and nitro benzaldehydes (**3ai–3aj**) also furnished corresponding NH-triazole with excellent yields. It should be noted that heterocycle containing NH-triazoles **3ak–3al** were obtained in good yields from corresponding heterocyclic aldehydes using this method. Similarly, after variation of nitroalkane part desired triazole was obtained in high yield (**3am**).

Reusability of Cu-NHC@SiO2 catalyst was investigated for all the three reactions, that is, (I) direct AAC for synthesis of triazoles, (II) one-pot synthesis of 1,2,3-triazole from arylboronic acids, and (III) one-pot NH-1,2,3-triazole synthesis; discussed here. For Reaction (I), reusability test was performed with benzyl azide and phenyl acetylene as substrate using our established standard condition. It was observed that the copper catalyst can be reused with ease for at least up to fifth cycle with only small decrease in product yield from 99% to 90%. Similarly, reusability test for Reaction (II) was performed taking 3-methoxyphenylboronic acid, NaN₃, and phenyl acetylene as substrate while for reaction (III) 4-bromo benzaldehyde, NaN₃ and nitromethane as reactants. The catalyst again stands out to be efficient for both these reactions and desired products were obtained without significant loss of product yield up to fifth cycle (for Reaction [II], decrease of yield from 92%-85%; for Reaction [III], yield decreases from 91% to 83%, Figure 5).

This small decrease in product yield during reusability test may be due to physical loss of the catalyst during repetitive steps or leaching of the metal from the catalyst. ICP-AES analysis was performed for the reused catalyst that showed only a very small decrease in metal loading. Moreover, SEM and EDX analyses (Figure S1) also showed no significant change in surface morphology and composition of the catalyst. The solid UV–Visible spectrum of the catalyst is typical for the Cu (II) metal, while the UV spectrum of the catalyst after fifth cycle of reuse showed very little change indicating persistence in metal content after repetitive use (Figure S2). All these results were representative of strong binding of the metal with anchored ligand and efficiency of the heterogeneous catalyst for 1,2,3-triazole synthesis.

Applied Organometallic_WILEY Chemistry

9 of 10

5 | CONCLUSION

In conclusion, a silica supported copper catalyst has been developed that combined with excellent reusability shows remarkable catalytic efficiency towards direct azidealkyne cycloaddition as well as one-pot triazole synthesis from arylboronic acids. This catalyst can also be used in one-pot synthesis of 4-aryl-NH-1,2,3-triazoles from various benzaldehydes. This method offers advantage over other catalytic protocol in terms of broad substrate scope with electronically diverse substrates for three different reactions, easy recovery and use of green solvents as reaction media.

ACKNOWLEDGMENTS

DS is thankful to DST, New Delhi (Department of Science and Technology, Ministry of Science and Technology, India) for a research grant [No. EMR/2016/002345] and DBT, New Delhi, (Department of Biotechnology, Ministry of Science and Technology, India) for a research grant [No. BT/PR24684/NER/95/810/2017]. AG thanks DST, New Delhi, for Research Fellowship and CSIR, New Delhi, for Senior Research Fellowship (CSIR-SRF). The financial assistance of DST-FIST and UGC-SAP program to the Department of Chemistry, Dibrugarh University is also gratefully acknowledged.

AUTHOR CONTRIBUTIONS

Anirban Garg: Conceptualization; data curation; investigation; methodology. Nobomi Borah: Data curation; methodology. JASMIN SULTANA: Data curation; formal analysis; methodology. AKSHAY KULSHRESTHA: Data curation; formal analysis. Arvind Kumar: Data curation; formal analysis. Diganta Sarma: Conceptualization; supervision; visualization.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the supporting information of this article.

ORCID

Anirban Garg b https://orcid.org/0000-0002-8623-3440 Nobomi Borah b https://orcid.org/0000-0002-6921-0992 Jasmin Sultana b https://orcid.org/0000-0002-3154-492X Akshay Kulshrestha b https://orcid.org/0000-0003-4468-5526

Arvind Kumar ⁽¹⁾ https://orcid.org/0000-0001-9236-532X Diganta Sarma ⁽¹⁾ https://orcid.org/0000-0001-5174-418X

REFERENCES

- a) M. Opanasenko, P. Stepnicka, J. Cejka, *RSC Adv.* 2014, 4, 65137; b) V. Polshettiwar, C. Len, A. Fihri, *Coord. Chem. Rev.* 2009, 253, 2599.
- [2] D. Brunel, N. Bellocq, P. Sutra, A. Cauvel, M. Lasperas, P. Moreau, F. di Renzo, A. Galarneau, F. Fajula, *Coord. Chem. Rev.* 1998, 1085, 178.
- [3] P. M. Price, J. H. Clark, D. J. Macquarrie, J. Chem. Soc. Dalton Trans. 2000, 101.
- [4] D. E. de Vos, P. E. Jacobs, Catal. Today 2000, 57, 105.
- [5] a) W. J. Sommer, M. Weck, *Coord. Chem. Rev.* 2007, 251, 860.
 b) R. Zhong, A. C. Lindhorst, F. J. Groche, F. E. Kühn, *Chem. Rev.* 2017, 117, 1970.
- [6] F. Glorius, *Topics in Organometallic Chemistry*, Vol. 21, Springer, Berlin 2007.
- [7] R. Tonner, G. Heydenrych, G. Frenking, *Chem. Asian J.* 2007, 2, 1555.
- [8] a) J. Cheng, L. Wang, P. Wang, L. Deng, *Chem. Rev.* 2018, 118, 9930.
 b) Y. Wang, G. H. Robinson, *Inorg. Chem.* 2014, 53, 11815.
- [9] J. D. Egbert, C. S. J. Cazin, S. P. Nolan, *Cat. Sci. Technol.* 2013, 3, 912.
- [10] a) S. Diez-Gonzalez, A. Correa, L. Cavallo, S. P. Nolan, *Chem. A Eur. J.* 2006, *12*, 7558; b) S. Diez-Gonzalez, E. D. Stevens, S. P. Nolan, *Chem. Commun.* 2008, 4747.
- [11] a) J. Broggi, S. Díez-González, J. L. Petersen, S. Berteina-Raboin, S. P. Nolan, L. A. Agrofoglio, *Synthesis* 2008, 1. 0141-0148; b)
- [12] S. Diez-Gonzalez, E. D. Stevens, S. P. Nolan, *Chem. Commun.* 2008, 4747.
- [13] a) C. W. Tornøe, C. Christensen, M. Meldal, J. Org, *Chem* 2002, 67(9), 3057; b) V. V. Rostovtsev, L. G. Green, V. V.

Fokin, K. B. Sharpless, Angew. Chem. Int. Ed. 2002, 41, 2596.

- [14] a) D. Döhler, P. Michael, W. H. Binder, Acc. Chem. Res. 2017, 50, 2610; b) P. K. Behera, P. Mondal, N. K. Singha, Macromolecules 2018, 51, 4770.
- [15] V. K. Tiwari, B. B. Mishra, K. B. Mishra, N. Mishra, A. S. Singh, Xi Chen.
- [16] a) S. Haider, M. Sarwar Alam, H. Hamid, *Inflamm Cell Signal* 2014, 1, e95; b) P. Thirumurugan, D. Matosiuk, K. Jozwiak, *Chem. Rev.* 2013, 113, 4905.
- [17] a) D. L. J. Broere, R. Plessius, J. Tory, S. Demeshko, B. de Bruin, M. A. Siegler, F. Hartl, J. I. van der Vlugt, *Chem. A Eur. J.* **2016**, *22*, 13965; b) Z. Chen, Z. Liu, G. Cao, H. Li, H. Rena, *Adv.Synth. Catal.* **2017**, *359*, 202.
- [18] a) R. B. N. Baig, R. S. Varma, Green Chem. 2012, 14, 625;
 b) H. Sharghi, R. Khalifeh, M. M. Doroodmand, Adv. Synth. Catal. 2009, 351, 207; c) F. Alonso, Y. Moglie, G. Radivoy, M. Yus, Adv. Synth. Catal. 2010, 352, 3208; d) B. S. P. A. Kumar, K. H. V. Reddy, B. Madhav, K. Ramesh, Y. V. D. Nageswar, Tetrahedron Lett. 2012, 53, 4595; e) Y.-B. Zhao, Z.-Y. Yan, Y.-M. Liang, Tetrahedron Lett. 2006, 47, 1545; f) J. Yan, L. Wang, Synthesis 2010, 447; g) J.-A. Shin, Y.-G. Lim, K.-H. Lee, J. Org. Chem. 2012, 77, 4117; h) N. Mukherjee, S. Ahammed, S. Bhadra, B. C. Ranu, Green Chem. 2013, 15, 389; i) A. Garg, A. A. Ali, K. Damarla, A. Kumar, D. Sarma, Tetrahedron Lett. 2018, 59, 4031.
- [19] M. Wang, P. Li, L. Wang, Eur. J. Org. Chem. 2008, 2255.
- [20] T. Begum, M. Mondal, M. P. Borpuzari, R. Kar, G. Kalita, P. K. Gogoi, U. Bora, *Dalton Trans.* 2017, 46, 539.
- [21] a) J.-M. Collinson, J. D. E. T. Wilton-Ely, S. Dıéz-González, *Chem. Commun.* 2013, 49, 11358; b) J. D. S. Newman, J. M. Roberts, G. J. Blanchard, *Anal. Chem.* 2007, 79, 3448.
- [22] a) S. Ueda, M. Su, S. L. Buchwald, Am. Ethnol., Angew. Chem., Int. Ed. 2011, 123, 8944; b) W. Yan, T. Liao, O. Tuguldur, C. Zhong, J. L. Petersen, X. Shi, Chem. Asian J. 2011, 6, 2720.
- [23] N. S. Zefirov, N. K. Chapovskaya, V. V. Kolesnikov, J. Chem. Soc., D 1971, 1001.
- [24] a) T. Jin, S. Kamijo, Y. Yamamoto, *Eur. J. Org. Chem.* 2004, 3789; b) J. Kalisiak, K. B. Sharpless, V. V. Fokin, *Org. Lett.* 2008, 10, 3171; c) A. E. Cohrt, J. F. Jensen, T. E. Nielsen, *Org. Lett.* 2010, 12, 5414; d) J. Barluenga, C. Valdeś, G. Beltrań, M. Escribano, F. Aznar, *Angew. Chem. Int. Ed.* 2006, 45, 6893. e) X. Wang, C. Kuang, Q. Yang, *Eur. J. Org. Chem.* 2012, 424.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: A. Garg, N. Borah,

J. Sultana, A. Kulshrestha, A. Kumar, D. Sarma, Appl Organomet Chem **2021**, e6298. <u>https://doi.org/</u> 10.1002/aoc.6298