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Arene borylation through C-H activation using $Cu_3(BTC)_2$ as heterogeneous catalyst

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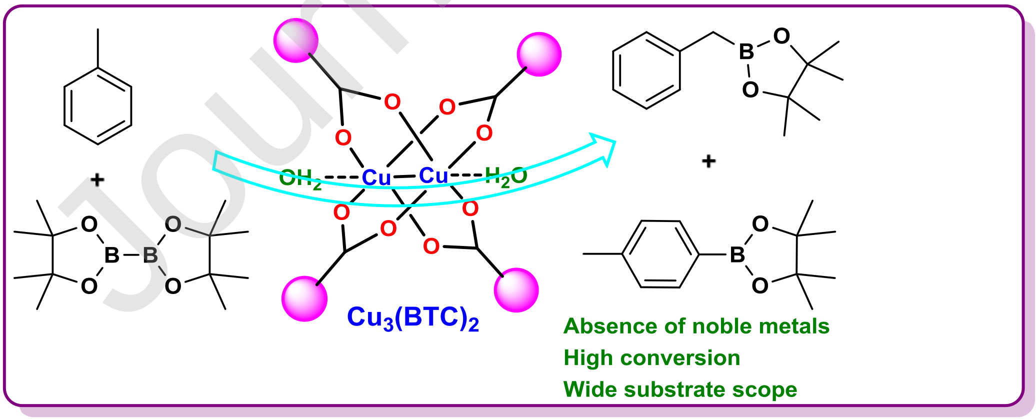
Graphical abstract

TOC Graphic



Absence of noble metals
High conversion
Wide substrate scope

Highlights

- Cu3(btc)2 is a suitable catalyst for borylation by pinacolyl diborane
- Cu3(btc)2 exhibits a wide scope promoting aromatic and benzylic borylation
- Cu3(btc)2 can be reused without deactivation
- Other metal-organic frameworks were unable to promote the C-B formation reaction
- Toluene can be borylated at the aromatic and benzylic carbon

Abstract

C-H borylation by diborane is an important process to access organoboron compounds. Noble metals, including Ir and Rh-based complexes either in the form of homogeneous or heterogeneous catalysts, have been reported to promote arene C-H borylation. Recently, metal organic frameworks (MOFs) having Ir and Co as active sites have been used as catalysts, but they require co-catalysts. In the present study, commercially available $Cu_3(BTC)_2$ metal organic framework is reported as an effective catalyst to promote borylation of arenes through C-H activation employing bis(pinacolato)diboron as reagent leading to benzylic and aromatic borylation products. Interestingly, other related MOFs like MIL-101(Cr) and Al(OH)(BDC) do not exhibit catalytic activity under identical conditions. Mechanistic studies using in-situ IR spectroscopy reveal that Cu ions play a crucial role in activating the arene and B-B bond.

Keywords: Heterogeneous Catalysis; Metal organic frameworks as catalysts; Cu3(BTC)2; Borylation Reaction

1. Introduction

Aryl and alkyl boronates are important starting materials in transition-metal catalyzed cross-coupling reactions, resulting in the formation with high yield and selectivity of new C-C and C-heteroatom bonds.[1, 2] Typically, the reaction conditions of cross-couplings involving boronates are compatible with the presence of a large variety of functional groups including hydroxyl, carbonyl, nitro and amino, among others.[3, 4] Due to the importance of organoboron compounds as substrates, development of preparation procedures for this type of substrates is of considerable interest.[4]

One of the general strategies for the preparation of organoboron compounds is based on the catalytic substitution of halides by boronates using copper and other transition metals as catalysts.[5, 6] For the sake of atom economy, it will be much more convenient to obtain the wanted organoboronate by C-H activation of the precursor. In this context, it has been recently reported that iridium and rhodium complexes are homogeneous catalysts able to promote C-H activation of methyaromatics to form a mixture of C-(sp^2)-B (aromatic) and C-(sp^3)-B products (benzylic) products.[7] Rh-based complexes have been reported for the borylation of alkanes, arenes, amines, ethers, ketals, and haloalkanes.[7-9] Although the activity of these Rh-based complexes is lower for alkyl C-H bonds, the combination of bipyridines and iridium(I)-olefin complexes has been reported to be more effective for the borylation of arenes.[10] A highly stable and recyclable single-site solid catalyst was prepared by post-synthetic Ir metalation of the 2,2′-bipyridyl-derived UiO-67 to obtain bpy-UiO-67-Ir and its activity was tested in the borylation of aromatic C–H bonds using B_2pin_2.[11] Very recently, Zr-based metal organic framework (MOF) has been used to stabilize low-coordinate Ir complex to promote active methane borylation to its monoborylated product.[12] These examples have shown the possibility to use MOFs as hosts of active Ir complex developing in this way a heterogeneous catalyst for borylation.

Moving towards less costly transition metal catalysts, noble metal-free catalysts for promoting the formation of borylated products have been subsequently developed, although the reaction mechanism still remains unknown. Cobalt-based homogeneous catalysts are also able to activate borylation at the benzylic positions, but it results in polyborylation through the multiple activation of sp^3-H bonds.[13] MOFs can also be used as hosts of Co^{2+} complexes, obtaining solid catalysts for borylation. In this way, metal-organic layers stabilized with Co-terpyridine diradical complexes promoted borylation of arenes.[14] Also, cobalt-metalated PCN-308 (PCN: porous coordination network) has been reported as noble metal free, air-stable heterogeneous solid catalyst for the C-H borylation of arenes.[15] In addition, UiO-68-Co was shown to promote C-H borylation of arenes under solvent-less conditions.[16]

Considering the interest of organoboron compounds, it is herein reported that a readily available commercial $Cu_3(BTC)_2$ is an efficient heterogeneous catalyst to activate C-H bond in arenes (sp^2) and benzylic positions (sp^3 carbons) leading to the formation of the corresponding organoboranes. Some of the salient features of this method are the absence of noble metal, catalyst availability, no need of post-synthetic modification or external reducing agent and stability of catalyst under the present experimental conditions. Although it has been frequently observed a poor $Cu_3(BTC)_2$ stability as catalyst, it has been found that $Cu_3(BTC)_2$ can be reused as catalyst for C-H borylation.

The structure of $Cu_3(BTC)_2$ (commercially known as Basolite C 300) is constructed by clusters of two Cu^{2+} ions coordinated with four carboxylate groups of

1,3,5-benzenetricarboxylate (BTC) forming a paddle-wheel building unit that acts as structural nodes interconnected by tripodal BTC linkers. The pore dimensions of $Cu_3(BTC)_2$ are around 16 Å, with pore windows of around 11 and 6 Å. Further, each Cu^{2+} ion is coordinated to one water molecule which can be removed upon thermal activation of the material, generating a Lewis acid site. These coordinatively unsaturated Cu^{2+} ions exhibit catalytic activity for a large variety of reactions including Knoevenagel condensation,[17] ring opening of epoxides,[18] heterocycle synthesis,[19-21] oxidation reactions[22, 23] and others.[24-26] As it will be shown below, these Cu^{2+} ions are also responsible for borylation with B_2pin_2.

2. Experimental Section

As previously commented, C-H borylation of arenes promoted by transition metals is becoming increasingly important due to its synthetic versatility to synthesize borylated aromatic compounds under mild reaction conditions.[27-32] In this aspect, MOFs have been employed as heterogeneous catalysts in different ways, like as a scaffold to stabilize metal nodes within the framework, as a host to immobilize organometallic complex and to anchor organometallic complex in the satellite position of the linkers.

2.1 Materials

$Cu_3(BTC)_2$ also commercially known as Basolite C300 and Al(OH)(BDC) also commercially known as A100 were supplied by Sigma Aldrich. MIL-101(Cr) was synthesised following a reported procedure.[33] CuCl, $Cu(NO_3)_2.3H_2O$ and bis(pinacoloto)diboron (**1**) were obtained from Sigma Aldrich. All the starting materials employed in Table 2, including solvents like toluene and acetonitrile were also purchased from Sigma Aldrich and used as received without further purification.

2.2 Raman spectra measurements

Raman spectra were recorded with a Renishaw Raman Spectrometer (“Reflex”) equipped with a CCD detector. A 514 nm laser operating at 25 mW and acquiring a total of 20 acquisitions for each spectra has been used. For the in situ studies a Linkam CCR 1000 catalytic cell has been used. The sample has been ex situ impregnated with B_2Pin_2 at 100 °C and dried at 60°C. Raman spectra has been acquired at 100°C in N_2 flow, followed by flowing a N_2 feed saturated with toluene. At similar acquisition conditions, reference spectra of toluene, B_2Pin_2 and BPin have been acquired.

2.3 FT-IR spectra measurements

The FTIR spectra were collected with a Thermo “Nexus” IR spectrometer equipped with a DTGS detector (4 cm^{-1} resolution, 32 scans). A home-made IR cell allowing in situ treatments in controlled atmospheres and temperatures has been connected to a vacuum system with gas dosing facility. Self-supporting pellets (ca. 10 mg cm^{-2}) were prepared from the sample powders and treated in vacuum (10^{-4} mbar) at 100 °C for 0.5 h. 5mbar of toluene has been adsorbed at 100 °C , kept 0.5h and evacuated at 10^{-4} mbar at the same temperature. After it, the sample temperature has been decreased to 25 °C, and CO has been adsorbed at 4mbar. IR spectra were recorded after each dosage.

2.4 Experimental Procedure

In a 25 mL round bottom flask, toluene (1 mL), $Cu_3(BTC)_2$ (30 mg), **1** (127 mg, 0.5 mmol) were charged and this slurry was stirred at 100 °C. The borylation of toluene was monitored by gas chromatography (GC) and the conversion of **1** was determined at different time intervals. Similar experimental procedures were performed with radical quenchers like TEMPO and 2,6-di-t-butyl-4-methylphenol with appropriate amount mentioned in the table. The product identity was confirmed by analyzing the reaction mixture by GC-MS.

Conversion of the borylation reaction and selectivity of the products were determined by Agilent gas chromatography.

2.5 Product Analysis

Aliquots of the reaction mixture (100 µL) were collected at increasing time intervals and diluted with 2 mL of acetonitrile. Later, this slurry was subjected to filtration with Nylon filter of 0.2 µm adapted to a syringe and the clear filtrate analyzed by GC using a flame ionization detector and a methyl-phenyl silicone column (TRB-5MS;30m x0.32mm x 0.25 µm) with the following conditions: initial column temperature, 30 °C; initial dwelling time, 3 min, rate of temperature ramp, 10 °C/min, final temperature 280 °C. Quantification was performed with calibration curves to obtain the relative response factors (RF) of the products and starting materials compared to the nitrobenzene as the internal standard. The product identities were ascertained by injecting the reaction mixture in a GC-MS (Agilent 5973) model. The percentage of metal leaching from the catalyst to the liquid phase at the end of the reaction was determined by quantitative ICP-OES analysis. In brief, the catalyst was filtered at the end of the reaction by using 0.2 µm Nylon filter. Then, 30 mL of 3 M aqueous nitric acid solution was added to the organic phase and stirred for 20 h at 80 ^{o}C. Then, the aqueous phase was analyzed by ICP-OES to determine the leached Cu from the solid to solution.

Furthermore, the conversion of **1** and selectivity of products formed, namely compounds **2, 3** and **4,** were determined using the following formulae:

RF was obtained with the following equation

RF= Area of nitrobenzene X moles of **1**/Area of **1** X moles of nitrobenzene

Moles of remaining **1** and product were calculated using the following equation

Moles of **1** = RF X moles of nitrobenzene X Area of **1**/ Area of nitrobenzene

Conversion (%) = moles of **1** reacted/initial moles of **1**

Selectivity (%) = moles of **2** formed/total moles of **2, 3** and **4**

3. Results and discussion

Recently, we have shown that borasiloxanes can be facilely synthesised by oxidative hydrolysis of silanes with pinacolborane using $Cu_3(BTC)_2$ as a heterogeneous solid catalyst.[25] Continuing with this research line to develop a simple and readily available transition metal based catalyst, $Cu_3(BTC)_2$ is used as solid catalyst for the promotion of C-H borylation of arenes.

The activity of $Cu_3(BTC)_2$ in the C-H borylation of arenes was screened by selecting toluene as a model compound. The C-H borylation of toluene was performed by **1** under solvent-free conditions at 100 ^oC. It was observed that C-H borylation of toluene occurs at four different positions, namely at benzylic and aromatic positions either in ortho, meta or para. The observed results are summarized in Table 1. A blank control experiment using **1** and toluene in the absence of catalyst resulted in no conversion at 100 ^oC. On other hand, the reaction between toluene and **1** using $Cu_3(BTC)_2$ as catalyst did not provide any product at 60 and 80 ^oC under identical conditions. Both control results are in agreement with earlier reports.[14, 32] Interestingly, $Cu_3(BTC)_2$ reached 27 % conversion of **1** with 68 % of **2** and 26 % of **3** at 100 ^oC after 5 h (entry 1, Table 1). Under identical conditions, the conversion of **1** reached to 87 % after 24 h with a selectivity of 70 and 22 % for compounds **2** and **3**, respectively (entry 2, Table 1). Figure 1 shows the time-conversion profile for the C-H borylation of toluene using $Cu_3(BTC)_2$ at 100 ^oC. Further, the selectivities of the products (**2**, **3** and **4**) remained constants with the conversion. When the C-H borylation of toluene was performed under similar experimental conditions with HBpin instead of **1**, conversion was negligible (4 %) without observing the formation of any desired product (entry 3, Table 1). It should be commented that $Cu_3(BTC)_2$ is not stable in the presence of HBpin that apparently causes a prompt chemical reduction of Cu^{2+} under these experimental conditions.

After identifying $Cu_3(BTC)_2$ as a suitable catalyst to promote C-H borylation of toluene, a series of reactions were performed to gain insight into the nature of intermediates involved in the C-H borylation. Initially, the C-H borylation of toluene with **1** using $Cu_3(BTC)_2$ as solid catalyst was performed in the presence of TEMPO as radical scavenger. The experimental results shown in Table 1 indicated that the addition of TEMPO to the reaction medium completely arrests the reaction, no borylation occurring neither at benzylic nor at aromatic positions (entries 4-5, Table 1). This hypothesis was further confirmed by another control experiment. The C-H borylation of toluene with **1** using $Cu_3(BTC)_2$ was performed at 100 ^oC under identical conditions and 20 mg of TEMPO was added to the reaction mixture at around 27 % conversion of **1** after 5 h. The time-conversion profile indicated that the progress of the reaction is significantly quenched upon addition of TEMPO, thus supporting the involvement of C-centred radical intermediates. These results are shown in Figure 1. Furthermore, the C-H borylation of toluene was also performed using 2,6-di-t-butyl-p-cresol as radical quencher, no C-H borylation products being observed (entry 6, Table 1). The C-H borylation of toluene with **1** using $Cu_3(BTC)_2$ as heterogeneous catalyst in inert atmosphere was also very low (3%) after 24 h (entries 7-8, Table 1). These series of control experiments in the presence of radical scavengers clearly suggest that the reaction mechanism involves as reaction intermediate benzyl radicals originated from toluene by $Cu_3(BTC)_2$. Furthermore, the C-H borylation of toluene with **1** using

$Cu_3(BTC)_2$ was also quenched by the addition of methanol suggesting that electrophilic species intercepted by methanol are also formed.

In order to gain understanding in the role of Cu in $Cu_3(BTC)_2$, and particularly the oxidation state involved in the process, a series of control experiments were performed under identical conditions using CuCl and $Cu(NO_3)_2.3H_2O$ as homogeneous catalysts. The observed results are also given in Table 1. CuCl as homogeneous catalyst for the C-H borylation of toluene with **1** reached complete conversion with 70 and 26 % selectivity to **2** and **3**, respectively after 8 h at 100 ^oC (entry 10, Table 1). Under identical conditions, the C-H borylation of toluene using $Cu(NO_3)_2.3H_2O$ as homogeneous catalyst afforded also complete conversion of **1** with 68 and 37 % selectivity to compounds **2** and **3**, respectively after 5 h (entry 11, Table 1). Comparing the initial reaction rates of CuCl and $Cu(NO_3)_2.3H_2O$ as homogeneous catalysts that are related to the nature of the initial Cu^+ or Cu^{2+} ion, the later catalyst exhibits much higher activity. These experiments suggest that C-H borylation can occur both with Cu(I) or Cu(II) salts as active sites, although the latter is more efficient. These results with partially soluble Cu salts can serve to rationalize the activity observed for $Cu_3(BTC)_2$ that may contain in its framework both Cu(II) and Cu(I) sites.[34] On other hand, the activity of CuCl and $Cu(NO_3)_2.3H_2O$ was comparatively much higher with $Cu_3(BTC)_2$ that is mainly due to the easy accessibility of active sites in the former soluble Cu catalysts, while the reactants encounter some diffusion limitations with $Cu_3(BTC)_2$ as catalyst, resulting in lower activity. This relative catalytic activity of homogeneous versus heterogeneous catalysts has been frequently observed when the catalytic active sites in the mechanism are similar and diffusion is the main differential factor. On the other hand, solid catalysts offer a simple separation from the reaction mixture that usually requires a more elaborated workup for homogeneous catalysts.

Further, the activity of $Cu_3(BTC)_2$ was also compared with other related MOFs that are frequently employed as catalysts for liquid phase reactions. Hence, the C-H borylation of toluene with **1** was also studied with MIL-101(Cr) and Al(OH)(BDC) (BDC: 1,4-benzenedicarboxylate). These two solids afforded negligible conversion of **1** even after prolonged time (entries 12-15, Table 1). These results clearly indicate that C-H borylation of toluene with **1** is highly dependent on the nature and coordination of metal ion. Furthermore, these data imply that Cu^{2+} plays a catalytic role activating **1** and toluene to promote C-H borylation of arene.

Heterogeneity of the catalytic process under the present reaction conditions was ascertained by performing the hot-filtration test. The C-H borylation of toluene was started in the presence of $Cu_3(BTC)_2$ and after 5 h at 27 % conversion of **1**, the solid catalyst was removed by filtration at the reaction temperature. Then, the reaction in the absence of solid was continued for 24 h. The experimental results indicated that upon removal of solid the conversion of **1** increased to 32 % after 24 h which suggest that the progress of the reaction is much slower in the absence of $Cu_3(BTC)_2$. These results are consistent with the reaction being mainly catalysed by the active sites on the solid, confirming the heterogeneity of the reaction (Figure 1). Further, ICP-OES analysis of the fresh and the recovered $Cu_3(BTC)_2$ solids showed identical copper content, thus supporting the absence of Cu leaching. Furthermore, the activity of $Cu_3(BTC)_2$ was retained for two consecutive runs without change in the product distribution. The structural integrity of reused solid was almost identical to the fresh solid based on XRD (Figure 2).

In order to understand the role of $Cu_3(BTC)_2$ in promoting the C-H borylation of toluene, in-situ IR spectroscopy studies were performed. The results are given in Figure 3. Initially, toluene was adsorbed on dehydrated $Cu_3(BTC)_2$ observing the appearance of a species at 1944 cm^{-1} that can be attributed to Cu-H (Figure 3, blue spectra).[35] Formation of Cu(I), by hydride reduction of Cu(II) was further confirmed by CO titration measurements that indicate that Cu(II) is reduced to Cu(I) as it can be deduced from the wavenumber of the CO stretching band at 2124 cm^{-1}.[36] Spontaneous formation of less active Cu(I) justifies the beneficial effect of the atmospheric oxygen promoting reoxidation of possible Cu(I) to Cu(II). Thus, FT-IR spectra indicate that $Cu_3(BTC)_2$ produced benzyl radicals from toluene by undergoing the reduction of the oxidation state of copper from divalent to monovalent, which can be detected by CO titration. As commented earlier, these benzyl radical intermediates were trapped with radical scavengers like TEMPO and BHT that quench the reaction due to the radical scavenging.

Besides adsorption of toluene, it was also observed that activated $Cu_3(BTC)_2$ can also interact with **1** (Figure 4). The interaction between $Cu_3(BTC)_2$ with **1** leads to the formation of Bpin appearing in the Raman spectra at a wavenumber of 289 cm^{-1} (Figure 4). This monomer becomes adsorbed on the MOF structure as evidenced by the shift of the 502, 449 and 190 cm^{-1} bands to 506, 460 and 229 cm^{-1}, respectively (compare green and blue IR spectra in Figure 4). The initial band at 190 cm^{-1} is shifted to 229 cm^{-1} after Bpin interaction with the lattice. This band has been ascribed to Cu-Cu stretching vibration of the two Cu(II) ions of the $Cu_2C_4O_8$ nodes[37] and the remarkable shift indicates the involvement of the Cu atoms in the process resulting in the cleavage of **1**. The shift in the characteristic Cu-Cu vibration band suggests that the Cu-Cu bond distance is shortened upon interaction with

Bpin. Furthermore, the two bands at 506 and 460 cm^{-1} are attributed to Cu-O stretching modes.[38] They are also shifted from the original ones at 502 and 449 cm^{-1} to higher frequencies after Bpin interaction. A new band at 596 cm^{-1} is clearly formed, which disappears after toluene adsorption (Figure 4, red spectra), suggesting the formation of a reaction intermediate species. In addition, after toluene adsorption, the band at 229 cm^{-1} decreased slightly by restoring partially the band at 190 cm^{-1} band. This change would agree with the partial release of the Bpin adsorbed on the Cu(II) ions and the restoring of the initial Cu-Cu interaction.

The activity of $Cu_3(BTC)_2$ on the borylation of toluene with **1** encouraged us to expand the scope of this solid catalyst to other arenes. The observed results are shown in Table 2. The borylation of diphenylmethane with **1** using $Cu_3(BTC)_2$ exhibited complete conversion with 50 % benzylic and 42 % aromatic borylations after 24 h (entry 1, Table 2). On other hand, the reactivity of ethylbenzene with **1** was also complete within 24 h with 29 and 62 % for benzylic and aromatic borylations, respectively under identical conditions (entry 2, Table 2). Furthermore, the borylation of anisole with **1** afforded exclusively aromatic borylation under similar reaction conditions (entry 3, Table 2). In contrast, borylation of *p*-xylene resulted in low conversion of **1** with 6 and 4 % of benzylic and aromatic borylation, respectively (entry 4, Table 2). This notably lower reactivity of *p*-xylene compared to toluene under the present experimental conditions may be due to the close packing of *p*-xylene within the pores of $Cu_3(BTC)_2$ that can cause diffusion limitations to **1** to reach the active sites. Similarly, 4-bromotoluene also afforded low conversion with almost equal selectivity between benzylic and aromatic positions (entry 5, Table 2). An attempt to borylate aniline using $Cu_3(BTC)_2$ was unsuccessful under the present experimental conditions. This may be ascribed due to the coordination of amine groups to the active Cu(II) sites. Finally, the borylation of benzyl bromide using $Cu_3(BTC)_2$ was attempted, but no borylated products were detected. However, the solid catalyst turned its colour to black, suggesting the decomposition of $Cu_3(BTC)_2$ by benzyl bromide. One of the probable reasons for this deactivation may be the high reactivity of this benzylic halide with Cu(II) that could result in formation of copper halides and favouring the reduction to lower oxidation state or metallic state.

4. Conclusions

In conclusion, it has been shown that $Cu_3(BTC)_2$ is able to activate C-H bond in arenes to promote borylation at benzylic and aromatic positions using **1** as borylating agent. This work demonstrates the ability of Cu(II) to act as active sites for C-H bond activation under mild reaction conditions as evidenced by IR study. The present study illustrates C-H borylation with readily available MOF without the requirement of noble metals. Among the series of analogous MOFs tested under identical conditions for C-H borylation, $Cu_3(BTC)_2$ is the only solid exhibiting activity. The activity of $Cu_3(BTC)_2$ was maintained for two runs with no changes in the conversion and product distribution. $Cu_3(BTC)_2$ as catalyst offers some advantages, like the absence of noble metal catalysts, ready availability, no need of post-synthetic modification or addition of external reducing agent and catalyst stability.

Author's contribution:

Experimental work and catalytic tests were carried out by Amarajothi Dhakshinamoorthy, and Cristina Vallés García. Sample characterization was performed by Patricia Concepcion The concept of the paper and writing were carried out by Amarajothi Dhakshinamoorthy and Hermenegildo Garcia. All the authors read and agreed on the manuscript.

Conflicts of interest

There are no conflicts to declare.

The authors declare that they do not incur in any conflict of interest.

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References

[1] J.Z. Deng, D.V. Paone, A.T. Ginnetti, H. Kurihara, S.D. Dreher, S.A. Weissman, S.R. Stauffer and C.S. Burgey, Org. Lett., 11 (2009) 345.
[2] E.G. Occhiato, F.L. Galbo and A. Guarna, J. Org. Chem., 70 (2005) 7324.
[3] M. Blangetti, H. Rosso, C. Prandi, A. Deagostino and P. Venturello, Molecules, 18 (2013) 1188.
[4] D.M. D'Souza and T.J. Müller, Chem. Soc. Rev., 36 (2007) 1095.
[5] G.A. Molander, S.L.J. Trice and S.D. Dreher, J. Am. Chem. Soc., 132 (2010) 17701.
[6] C. Diner and K.J. Szabo, J. Am. Chem. Soc., 139 (2017) 2−14.
[7] J.F. Hartwig, Acc. Chem. Res. , 45 (2012) 864.
[8] H. Chen and J.F. Hartwig, Angew. Chem., Int. Ed., 38 (1999) 3391.
[9] H. Chen, S. Schlecht, T.C. Semple and J.F. Hartwig, Science 287 (2000) 1995.
[10] T. Ishiyama, J. Takagi, K. Ishida, N. Miyaura, N. Anastasi and J.F. Hartwig, J. Am. Chem. Soc. , 124 (2002) 390.
[11] K. Manna, T. Zhang and W. Lin, J. Am. Chem. Soc. , 136 (2014) 6566.
[12] X. Feng, Y. Song, Z. Li, M. Kaufmann, Y. Pi, J.S. Chen, Z. Xu, Z. Li, C. Wang and W. Lin, J. Am. Chem. Soc., (2019) doi.org/10.1021/jacs.9b04285.
[13] W. Neil Palmer, J.V. Obligacion, I. Pappas and P.J. Chirik, J. Am. Chem. Soc., 138 (2016) 766−769.
[14] Z. Lin, N.C. Thacker, T. Sawano, T. Drake, P. Ji, G. Lan, L. Cao, S. Liu, C. Wang and W. Lin, Chem. Sci., 9 (2018) 143.
[15] Y. Zhang, J. Li, X. Yang, P. Zhang, J. Pang, B. Li and H.-C. Zhou, Chem. Commun., 55 (2019) 2023.
[16] K. Manna, P. Ji, Z. Lin, F.X. Greene, A. Urban, N.C. Thacker and W. Lin, Nature Commun. , 7 (2016) 12610.
[17] V.N. Panchenko, M.M. Matrosova, J. Jeon, J.W. Jun, M.N. Timofeeva and S.H. Jhung, J. Catal., 316 (2014) 251.
[18] N. Anbu and A. Dhakshinamoorthy, J. Ind. Eng. Chem., 58 (2018) 9.
[19] A. Nikseresht, S. Ghasemi and S. Parak, Polyhedron 151 (2018) 112.
[20] M.J. Kim, B.R. Kim, C.Y. Lee and J. Kim, Tetrahedron Lett., 57 (2016) 4070.
[21] E. Perez-Mayoral and J. Cejka, ChemCatChem 3(2011) 157.
[22] C. Guo, Y. Zhang, L. Zhang, Y. Guo, N. Akram and J. Wang, ACS Applied Nano Materials, 1 (2018) 5289.
[23] G.-Q. Song, Y.-X. Lu, Q. Zhang, F. Wang, X.-K. Ma, X.-F. Huang and Z.-H. Zhang, RSC Adv., 4 (2014) 30221.
[24] B. Qi, T. Zhang, M. Li, C. He and C. Duan, Catal. Sci. Technol., 7 (2017) 5872.
[25] A. Dhakshinamoorthy, A.M. Asiri, P. Concepcion and H. Garcia, Chem. Commun., 53 (2017) 9998.
[26] M. Vandichel, F. Vermoortele, S. Cottenie, D.E. De Vos, M. Waroquier and V. Van Speybroeck, J. Catal., 305 (2013) 118.
[27] Z.H. Syed, Z. Chen, K.B. Idrees, T.A. Goetjen, E.C. Wegener, X. Zhang, K.W. Chapman, D.M. Kaphan, M. Delferro and O.K. Farha, Organometallics, 39 (2020) 1123.
[28] H. Vardhan, Y. Pan, Z. Yang, G. Verma, A. Nafady, A.M. Al-Enizi, T.M. Alotaibi, O.A. Almaghrabi and S. Ma, APL Mater., 7 (2019) 101111.
[29] B. Yang, X.-P. Wu, L. Gagliardi and D.G. Truhlar, Theo. Chem. Acc., 138 (2019) 107.
[30] T. Zhang, K. Manna and W. Lin, J. Am. Chem. Soc., 138 (2016) 3241.

[31] M.I. Gonzalez, E.D. Bloch, J.A. Mason, S.J. Teat and J.R. Long, Inorg. Chem., 54 (2015) 2995.
[32] K. Manna, T. Zhang, F.X. Greene and W. Lin, J. Am. Chem. Soc., 137 (2015) 2665.
[33] G. Ferey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble and I. Margiolaki, Science 309 (2005) 2040.
[34] J. Szanyi, M. Daturi, G. Clet, D.R. Baer and C.H.F. Peden, Phys. Chem. Chem. Phys., 14 (2012) 4383.
[35] E. Bennett, T. Wilson, P.J. Murphy, K. Refson, A.C. Hannon, S. Imberti, S.K. Callear, G.A. Chass and S.F. Parker, Inorg. Chem., 54 (2015) 2213.
[36] K.I. Hadjiivanov and G.N. Vayssilov, Adv. Catal., 47 (2002) 307.
[37] C. Prestipino, L. Regli, J.G. Vitillo, F. Bonino, A. Damin, C. Lamberti, A. Zecchina, P.L. Solari, K.O. Kongshaug and S. Bordiga, Chem. Mater., 18 (2006) 1337.
[38] N.R. Dhumal, M.P. Singh, J.A. Anderson, J. Kiefer and H.J. Kim, J.Phys.Chem.C., 120 (2016) 3295.

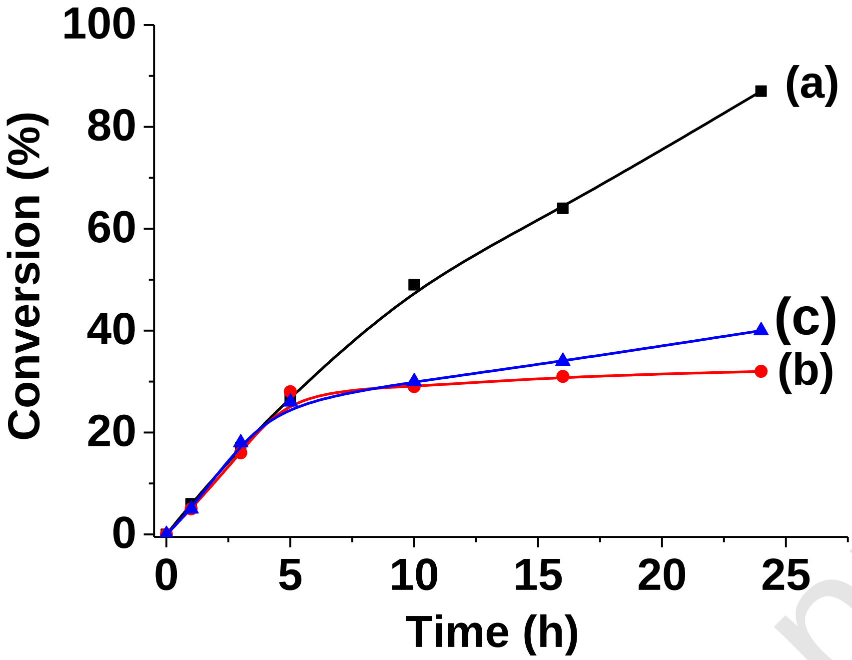


Figure 1. (a) Time conversion plot for the C-H borylation of toluene with **1** using $Cu_3(BTC)_2$ as heterogeneous solid catalyst, (b) hot filtration test upon removal of $Cu_3(BTC)_2$ after 5 h at reaction temperature and (c) addition of TEMPO as radical scavenger after 5 h.

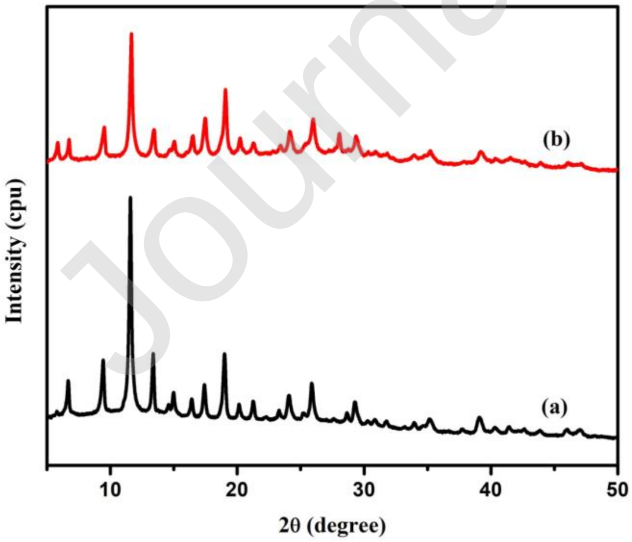


Figure 2. Powder XRD of (a) fresh and (b) two times reused $Cu_3(BTC)_2$ solid.

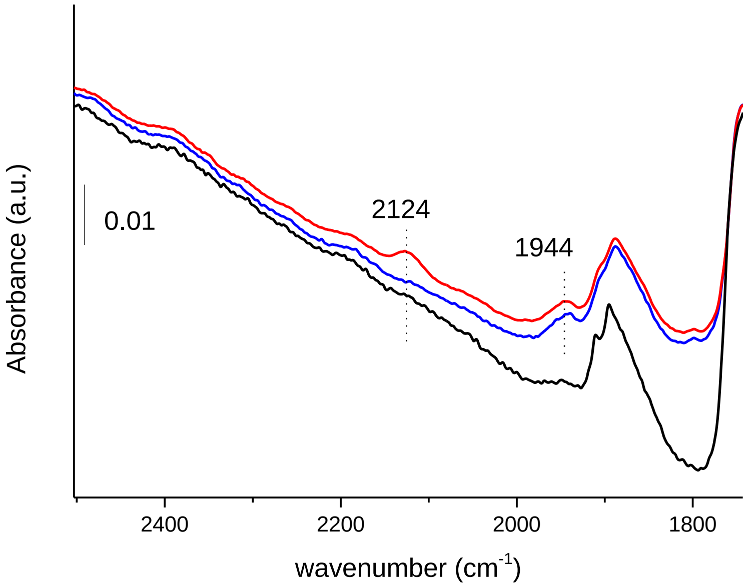


Figure 3. IR spectra of dehydrated $Cu_3(BTC)_2$ (black spectra), after toluene adsorption at 100 °C followed by evacuation (blue spectra) and after CO titration at 25 °C (red spectra).

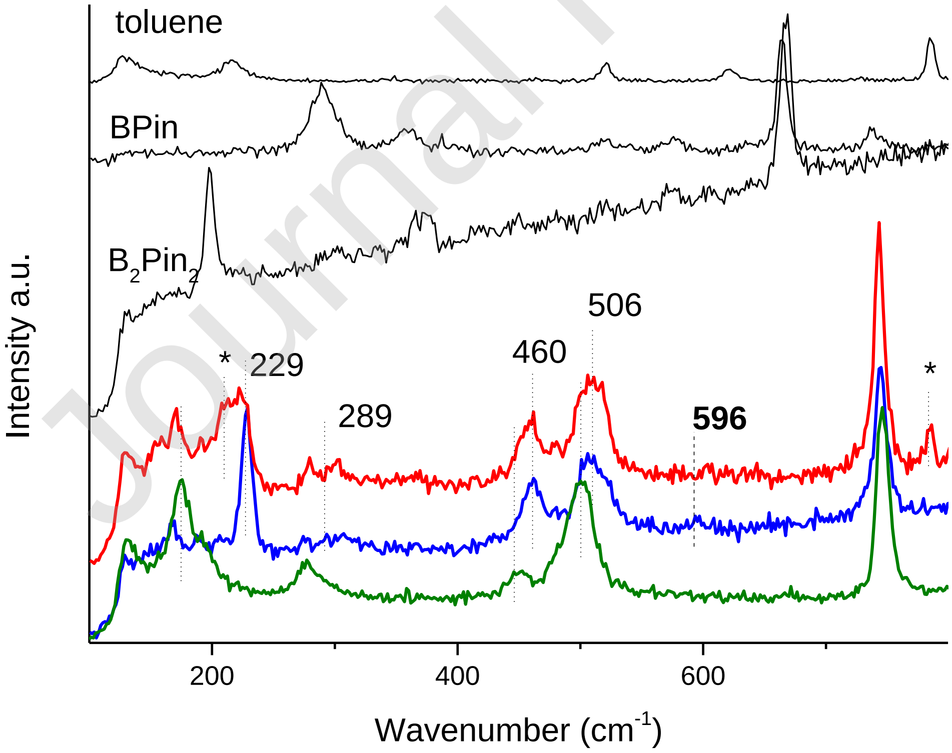
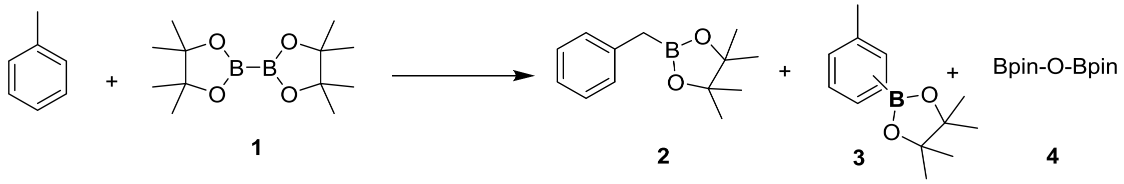


Figure 4. Raman spectra of $Cu_3(BTC)_2$ (green spectra), after adsorbing **1** (blue spectra) and after adding toluene (red spectra), and the reference Raman spectra of B_2Pin_2, HBpin and toluene (black spectra). (*) bands of toluene

Table 1. Optimization of reaction conditions for the borylation of toluene using diboronate **1** as reagent.[a]



S.No	Catalyst	Time (h)	Conversion (%)[b]	Selectivity (%)[b]		
				2	**3**	**4**
1	$Cu_3(BTC)_2$	5	27	68	26	6
2	$Cu_3(BTC)_2$	24	87	70	22	8
3	$Cu_3(BTC)_2$	2[c]	4	-	-	-
4	$Cu_3(BTC)_2$	5[d]	-	-	-	-
5	$Cu_3(BTC)_2$	24[d]	-	-	-	-
6	$Cu_3(BTC)_2$	24[e]	-	-	-	-
7	$Cu_3(BTC)_2$	5[f]	-	-	-	-
8	$Cu_3(BTC)_2$	24[f]	3	50	49	1
9	CuCl	5[g]	63	70	27	3
10	CuCl	8[g]	100	70	26	4
11	$Cu(NO_3)_2.3H_2O$	5[h]	100	68	37	3
12	MIL-101(Cr)	5	<1	-	-	-
13	MIL-101(Cr)	24	3	72	22	6
14	Al(OH)(BDC)	5	<1	-	-	-
15	Al(OH)(BDC)	24	4	72	23	5

[a] Reaction conditions: toluene (1 mL), catalyst (30 mg), **1** (127 mg, 0.5 mmol), 100 ^oC, presence of air.

[b] Determined by GC. Conversion represents of B_2pin_2.

[c] HBpin (0.150 mL)

[d] TEMPO (20 mg) was added.

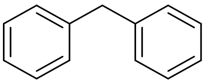
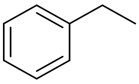
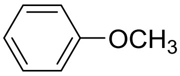
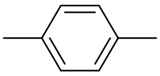
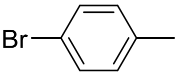
[e] 2,6-di-t-butyl-4-methylphenol (BHT) (50 mg) was added.

[f] Reaction performed under inert atmosphere.

[g] 15 mg was used in respect to the Cu content in $Cu_3(BTC)_2$.

[h] 37 mg was used in respect to the Cu content in $Cu_3(BTC)_2$.

Table 2. Scope of $Cu_3(BTC)_2$ as catalyst for borylation using **1** as reagent.[a]

S.No	Arene	Conversion (%)	Selectivity (%)[b]	
			Benzylic	Aromatic[c]
1		100	50	42(8)[d]
2		100	29	62(9)[d]
3		100	-	92(8)[d]
4		10	6	4(90)[d]
5		50	51	40(9)[d]

[a] Reaction conditions: arene (1 mL), **1**(0.5 mmol), $Cu_3(BTC)_2$ (30 mg), 100 °C, 24 h.

[b] Determined by GC.

[c] Borylation includes ortho/meta/para isomers.

[d] Values in parentheses indicate the selectivity to Bpin-O-Bpin.