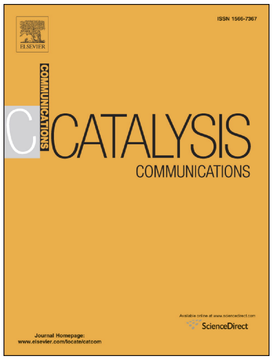

Nickel-catalyzed oxidative hydroxylation of arylboronic acid: Ni(HBTC)BPY MOF as an efficient and ligand-free catalyst to access phenolic motifs

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Nickel-Catalysed Oxidative Hydroxylation of Arylboronic Acid: Ni(HBTC)BPY MOF as an Efficient and Ligand-Free Catalyst to Access Phenolic Motifs

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Abstract:

A straightforward and mild oxidative *ipso*-hydroxylation of arylboronic acids has been achieved using a simple and non-noble metal, nickel-based reusable heterogeneous catalyst Ni(HBTC)BPY MOF (HBTC=benzene-1,3,5-tricarboxylate, BPY=4,4'-bipyridine) in the presence of benign hydrogen peroxide as an oxidant under ambient reaction condition. The Ni(HBTC)BPY MOF exhibits excellent catalytic activity towards the formation of phenols from diverse arylboronic acids within short time and can be reused up to five times without any notable loss in its activity as well as shown high functional group tolerance even in the presence of sensitive functionalities and useful to achieve hydroxyl group in heterocycles.

Keywords: Ni(HBTC)BPY MOF; *ipso*-Hydroxylation; Metal-Organic Frameworks; Heterogeneous catalysis; Boronic acids.

1. Introduction

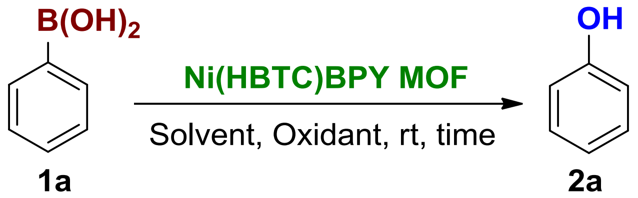
Phenols are one of the important and commonly used fine chemical compounds both in industries and academics.[1] Phenolic compounds and its derivatives exhibit wide biological properties such as antioxidant, antihyperglycemia, antihypertension, antimicrobial and anticancer activities.[2-4] Phenolic motifs are present in numerous natural products such as aryl steroids, macrolides, quinines, terpenoids, and alkaloids.[5] Owing to the prevalent importance of phenolic motifs, a number of methods have been developed for their direct synthesis or through functional group transformations including non-oxidative electrophilic substitution,[6] hydroxylation of aryl halides using hydroxide salts,[7] ligand-assisted, water-mediated hydroxylation of aryl halides[8] and hydrolysis of diazonium salts,[9] etc., Indeed, the development of alternative strategies for the formation of phenolic motifs has continuously attracted more attention in synthetic organic chemistry. Besides, the existing methodologies, *ipso*-hydroxylation of arylboronic acids has widespread gain attraction owing to an extensive abundant of boronic acid derivatives that can be converted to desired moieties even in the presence of other functionalities. Various catalysts and reagents were studied for the *ipso*-hydroxylation of arylboronic acids to corresponding phenols. Metal-based catalyst using both noble and non-noble metals such as copper,[10] iron,[11] palladium,[12] Zinc,[13] silver[14] and gold[15] either in the presence of a strong base or under base-free conditions using thermal or photochemical conditions were explored. Instead, metal-free oxidations were also developed using air[16] and stoichiometric amounts of oxidants such as hydrogen peroxide,[17] TBHP,[18] *m*-CPBA,[19] oxone,[20] hydroxylamine,[21] *N*-oxide,[22] $PhI(OAc)_2$,[23] $NaClO_2$[24] and Na_2SO_3.[25] Recently *ipso*-hydroxylation based on a carbocatalyst was also reported.[26] However some of the above-developed methodologies involved arduous experimental procedure or stochiometric equivalent of oxidants, which are difficult to practice neither in academic nor industrial applications. Thus, identifying a straightforward methodology employing benign catalyst without any waste generation with high selectivity is more desirable, which is still under investigation.

Metal-organic frameworks (MOFs) as a new class of crystalline micromesoporous hybrid materials which recently attracted significant attention that has been used in diverse synthetic applications.[27] Owing to their inherent large surface areas, uniform and easy tunable pore make MOFs as a promising heterogeneous catalyst for a variety of organic reactions.[28] Though nickel-based catalysis is well recognized in synthetic transformations, as like other transition metal-based MOFs, the catalytic potential of nickel-based MOFs are not much explored. Scarcely, nickel-based MOFs reported as a heterogeneous catalyst for the oxidative coupling of alkynes and arylboronic acids,[29] cyanosilylation of aromatic aldehydes[30] and synthesis of cyclic carbonates.[31] Ni(HBTC)BPY MOF (HBTC = benzene-1,3,5-tricarboxylate, BPY = 4,4'-bipyridine) is explicit in the *ipso*-hydroxylation of arylboronic acids. Previously this MOF was used as a heterogeneous catalyst for the arylation of aldehydes.[32] To the best of our knowledge there is only one report was available in homogeneous nickel salt with BODIPY used as a photocatalyst for the synthesis of phenol from aryl halides.[33] Herein we are reporting the Ni(HBTC)BPY MOF as a significant heterogeneous catalyst for the *ipso*-hydroxylation of arylboronic acids to phenols. The present methodology utilizes the environment-friendly hydrogen peroxide as an oxidant in minimal equivalent, under a greener renewable ethanolic medium within short reaction time. This non-noble metal-based nickel MOF catalyst is highly stable and quickly recovered from the reaction medium by simple filtration and reused several times. To our delight, this work is the first report on the heterogeneous nickel as a catalyst employed for the *ipso*-hydroxylation of arylboronic acids.

2. Results and Discussion

To develop a benign and environmental friendly methodology for the *ipso*-hydroxylation of arylboronic acids, using Ni(HBTC)BPY MOF as a heterogeneous catalyst, the required primary reaction parameters such as solvent, temperature, time and catalyst loading are screened using phenylboronic acid (**1a**) as a model substrate. Initially to screen the catalytic activity of the catalyst in different solvents and choose the best medium, a spectrum of solvents were tested using 30% aqueous hydrogen peroxide as an oxidant at room temperature for the period of 60 mins. From the solvent screening results, we could observe the fact that the solvent plays a critical role in the Ni(HBTC)BPY MOF catalyzed formation of phenol. The reactions involving non-polar solvents such as toluene, DCM and DCE proceed with moderate yield. In the case of polar solvents such as THF, chloroform, 1,4-dioxane, acetone, acetonitrile and DMF resulted in moderate to good yield, meanwhile the protic polar solvents such as methanol, ethanol and isopropyl alcohol afforded good to excellent yield, where ethanol gave the maximum yield (Table 1, entry 11). With the green chemistry perspective, water also tested as one of the solvents (Table 1, entry 2), albeit it provided a good yield, the catalyst is not stable which turned as a paste and stacked on the walls of reaction vessel, further analysis revealed that the catalyst was decomposed. Among the solvent screening results, the catalyst was more efficient in ethanol medium and as per green chemistry recommendations, ethanol is greener and renewable solvent.[34] Finally, ethanol was fixed as a medium for the *ipso*-hydroxylation of phenylboronic acid which gave phenol as a sole product with 98% yield. Furthermore, to elucidate the role of oxidants in the *ipso*-hydroxylation, other oxidants such as $K_2S_2O_8$, molecular oxygen, TBHP and TEMPO were tested. Molecular oxygen does not initiate the reaction, even after using azobisisobutyronitrile (AIBN) as an external initiator. Similarly, reaction was inert with the $K_2S_2O_8$ and TEMPO.

Table 1. Effect of solvent on the oxidation of phenylboronic acid.[a]



Entry	Solvents	Oxidants	Yield (%)[b]
1	IPA	H_2O_2	68
2	H_2O	H_2O_2	82
3	MeCN	H_2O_2	60

4	$CHCl_3$	H_2O_2	58
5	DCM	H_2O_2	50
6	DCE	H_2O_2	60
7	Acetone	H_2O_2	72
8	Toluene	H_2O_2	69
9	1,4-dioxane	H_2O_2	90
10	THF	H_2O_2	56
11	Ethanol	H_2O_2	98, 98[c], 98[d]
12	Methanol	H_2O_2	83
13	DMF	H_2O_2	50
14	Ethanol	-	-
15	Ethanol	TBHP	48[e]
16	Ethanol	$K_2S_2O_8$	-
17	Ethanol	O_2	-
18	Ethanol	O_2, AIBN	-
19	Ethanol	TEMPO	25

[a] Reaction conditions: Phenylboronic acid (0.4 mmol), 30% H_2O_2 (0.4 mmol), Ni(HBTC)BPY (30 wt%), solvent (1 mL) at 60 min., RT. [b] Isolated yield. [c] 10 min., [d] 2.0 eq of TEMPO was added, [e] 2 mmol of TBHP used.

Only when TBHP used as an oxidant, reaction ended up with 48% yield after using 2 mmol equivalents, which is five times higher than that of H_2O_2 used in the present study. Further to understand the mechanistic pathway of the Ni(HBTC)BPY MOF catalyzed oxidative *ipso*-hydroxylation of arylboronic acid, with the optimized condition along with hydrogen peroxide, TEMPO was used which gave the excellent phenol formation without any drop in the yield (Table 1, entry 11), which clearly demonstrate the reaction does not proceed through radical pathway.

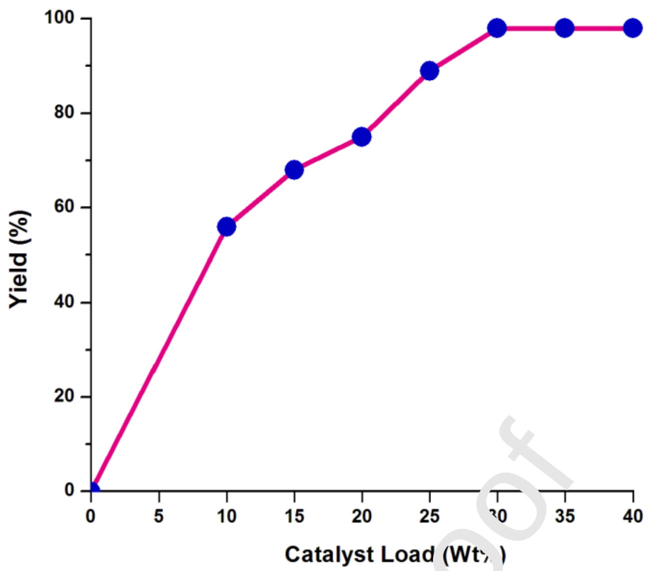


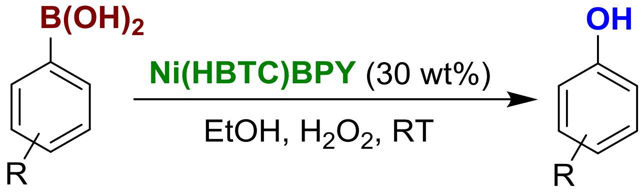
Fig. 1 Effect of catalyst load on the Ni(HBTC)BPY catalyzed *ipso*-hydroxylation of arylboronic acids.

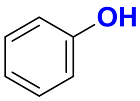
After optimized the above parameters, the exact quantity of the catalyst required for the hydroxylation of boronic acid was systematically focused by controlling the catalyst load. Though the optimization studies were performed up to 40 wt% of the catalyst, initially it was started from a minimum value of 10 wt%, which resulted only in 56% yield (Fig. 1). Upon increasing the catalyst load, a remarkable increase in the yield was observed. The desired complete conversion with the maximum yield 98% was reached with 30 wt% of catalyst and on further enhancing the catalyst load does not show any improvement in the yield.

The preliminary screening studies revealed that the Ni(HBTC)BPY MOF acts as an efficiently heterogeneous catalyst with 30% H_2O_2 as an oxidant in the ethanolic medium is a suitable condition for the *ipso*-hydroxylation of phenylboronic acid (**1a**). Furthermore, to extend the scope of the catalyst, various arylboronic acids were subjected to *ipso*-hydroxylation under the above-optimized conditions and the results were depicted in table 2.

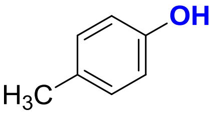
Almost all the tested arylboronic acids smoothly undergo the *ipso*-hydroxylation under the optimized condition within 10 min., without the formation of any other by-products such as hydroquinone, quinine, and homocoupled products of arylboronic acids. The electronic nature of the substituents present on the arylboronic acid does not influence much in this oxidative *ipso*-hydroxylation. When the electron releasing substituents like methyl, methoxy and isopropyl (**2b, 2d, 2n**) are present in the *para*- position gave excellent yield of corresponding phenols (94-96%); meanwhile arylboronic acids possessing substituents on *ortho* position (**2c**) resulted with a mild drop in the yield (88%). Similarly, boronic acids with electron-withdrawing groups like chloro, bromo, iodo and nitro groups on the *para* position (**2f, 2h-2j**) gave excellent yield 93-97%, albeit when they present on the *ortho* or *meta* position (**2g, 2k, 2l, 2m**) there was a mild decrease in the yield (84-88%) was noted. In the case of di-substituted arylboronic acid (**2e**) with methoxy groups at *para* and *meta* positions gave good yield (87%). Aryl substituents like biphenyl (**2o**), diphenyl ether (**2q**), and terphenyl (**2r**) were also produced excellent yields of 89-92%. Fused ring system like naphthyl gave good yield of 90%. Considering arylboronic acids containing heteroatoms (**2x-2z**) a notable decrease in the yield (72-79%) was observed. It might be owing to the coordination of the hetero atom with the active metal sites present in the catalyst which prevents the further progress of the reaction. In the case of hydroxylation of 1,4-phenyldiboronic acid (**2w**), it required two-fold excess of oxidant with extended reaction time up to 30 min producing 91% of yield without prone to further oxidation. Remarkably, the catalyst is chemoselective towards *ipso*-hydroxylation even in the presence of sensitive functional groups such as nitrile (**2n**), formyl (**2v**), secondary amine (**2z, 2aa**) and multiple functional groups like carbonyl with secondary amine (**2ab**) is also stable under the optimized condition gave the corresponding hydroxylated product with a reasonable yield of 72-89%. Finally, the optimized system was also well suitable for the alicyclic compound

Table 2. Ni(HBTC)BPY MOF Catalyzed *ipso*-hydroxylation of arylboronic acids.[a]

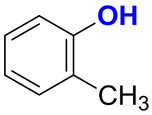




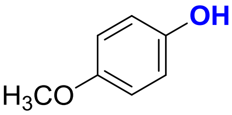
2a, 98%, 97%^{b}
(2054,^{c} 205^d)



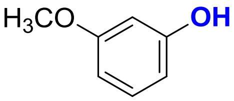
2b, 94%
(1971,^{c} 197^d)



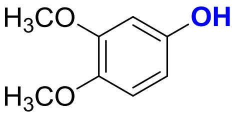
2c, 88%
(1845,^{c} 184^d)



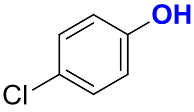
2d, 95%
(1992,^{c} 199^d)



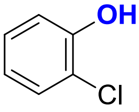
2e, 95%
(1992,^{c} 199^d)



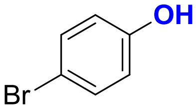
2f, 87%
(1824,^{c} 182^d)



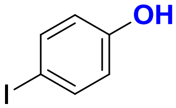
2g, 97%
(2033,^{c} 203^d)



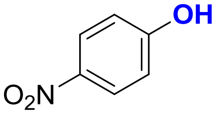
2h, 86%
(1803,^{c} 180^d)



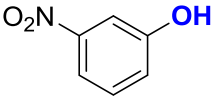
2i, 96%
(2013,^{c} 201^d)



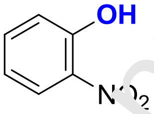
2j, 95%
(1992,^{c} 199^d)



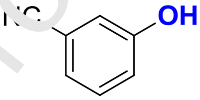
2k, 93%
(1950,^{c} 195^d)



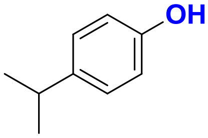
2l, 90%
(1887,^{c} 189^d)



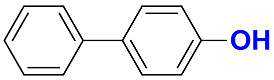
2m, 84%
(1761,^{c} 176^d)



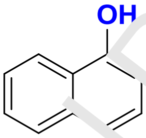
2n, 88%
(1845,^{c} 184^d)



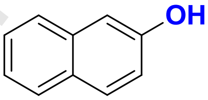
2o, 96%
(2013,^{c} 201^d)



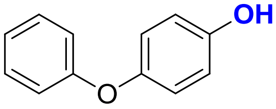
2p, 92%
(1929,^{c} 193^d)



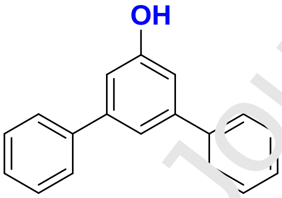
2q, 82%
(1719,^{c} 172^d)



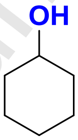
2r, 90%
(1887,^{c} 189^d)



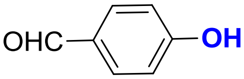
2s, 89%
(1866,^{c}187^d)



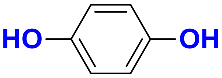
2t, 87%
(1824,^{c} 182^d)



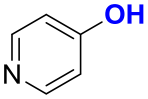
2u, 90%
(1887,^{c} 189^d)



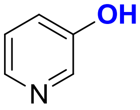
2v, 84%
(1761,^{c} 176^d)



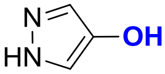
2w, 91%
(1908,^{c} 191^d)



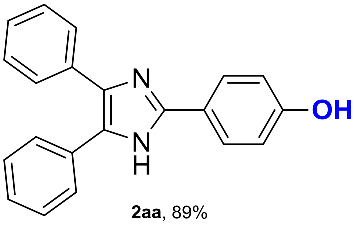
2x, 79%
(1656,^{c} 166^d)



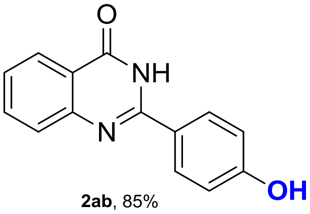
2y, 78%
(1635,^{c} 163^d)



2z, 72%
(1509,^{c} 151^d)



2aa, 89%
(1866,^{c} 187^d)

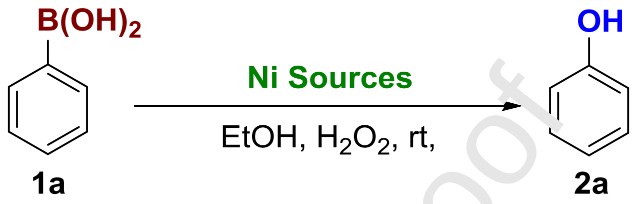


2ab, 85%
(1782,^{c} 178^d)

[a]Reaction conditions: Phenylboronic acid (0.4 mmol), H_2O_2 (0.4 mmol), Ni(HBTC)BPY MOF (30 wt%), EtOH (1 mL), 10 min., RT, All are isolated yields. [b]Gram scale' [c]TON, [d]TOF (min.$^{-1}$)

which also produced the corresponding cyclohexanol (**2u**) in a good yield of 90% confirmed that the developed protocol is not only restricted to arylboronic acids. The potential of the catalyst Ni(HBTC)BPY MOF has also been tested for the gram scale *ipso*-hydroxylation of phenylboronic acid which produced 97% yield.

Table 3. Effect of nickel sources on the oxidation of phenylboronic acid.[a]



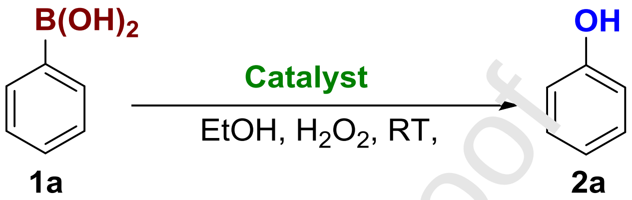
Entry	Catalyst	Yield(%)[b]
1	-	trace
2	$Ni(NO_3).6H_2O$	25[c]
3	$NiCl_2.6H_2O$	30[c]
4	$Ni(OAc)_2.4H_2O$	35[c]
5	$Ni(OH)_2$	30[c]
6	Ni(HBTC)BPY MOF	98[d]

[a] Reaction conditions: Phenylboronic acid (0.4 mmol), H_2O_2 (0.4 mmol), catalyst (0.4 mmol), EtOH (1 mL), 10 min., RT, [b] Isolated yield. [c] After 120 min., [d] Catalyst (30 wt%).

To figure out the role of nickel present in the framework and to ascertain its true catalytic efficiency, various other homogeneous nickel sources were also examined under the identical condition, and the results were given in table 3. All the homogeneous nickel salts reacted almost, in the same manner, resulted in the poor formation of phenol even after longer reaction time (120 min.). These results are strongly emphasizing the role of nickel ions supported by the framework which enhances its catalytic efficiency than the free metal ions. Further to understand the competence of the framework nickel ions in the *ipso*-hydroxylation, other Lewis acidic MOFs such as Cu(tpa), Cu(BTC), Fe(BTC), Fe-

MIL-53 and Ni(BDC)DABCO were compared under the optimized condition. Other metals present in the framework such as copper (Table 4, entries 1, 2) and iron (Table 4, entries 3, 4) are not competent under the present screened condition and shown inferior performance, which resulted in the poor formation of phenol (25-35%).

Table 4. Effect of catalyst on the oxidation of phenylboronic acid.[a]



Entry	Catalyst	Yield(%)[b]
1	Cu(tpa) MOF	30
2	$Cu_3(BTC)_2$ MOF	38
3	Fe(BTC) MOF	25
4	Fe-MIL 53	32
5	Ni(BDC)(DABCO) MOF	69
6	Ni(HBTC)BPY MOF	98
7	$Ni(NO_3).6H_2O$:BTC:BPY	18[c]

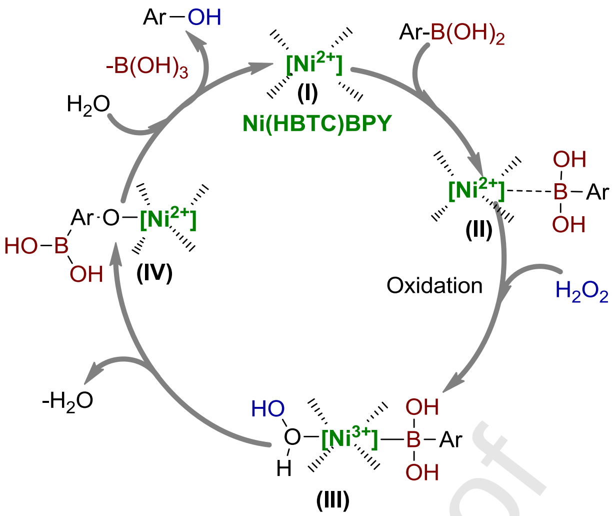
[a] Reaction conditions: Phenylboronic acid (0.4 mmol), H_2O_2 (0.4 mmol), catalyst (30 wt%), EtOH (1 mL) at 10 min., RT, [b] Isolated yield. [c] As a 1:1:1 mixture.

Meanwhile another nickel MOF, Ni(BDC)DABCO catalyzed the *ipso*-hydroxylation under the identical reaction condition, however gave only moderate yield (69%) of phenol. The above reports prove that the Ni^{2+} present in the framework of Ni(HBTC)BPY catalyzes the *ipso*-hydroxylation of arylboronic acid proficiently within the shorter reaction time. The observed results strongly suggest that the presence of high surface area 1232 m^2g^{-1}, (Fig. S4, SI), porous nature, and the coordinatively unsaturated nickel center ligated by the trimesic acid and 4,4'-bipyridine are all together made a potential catalytic center in Ni(HBTC)BPY MOF and shows excellent reactivity towards *ipso*-hydroxylation. Further, in order to confirm the role of framework metal structure in the present hydroxylation reaction, a control experiment was performed using the corresponding precursors of Ni(HBTC)BPY MOF such as $Ni(NO_3).6H_2O$, trimesic acid and bipyridine as a physical mixture in 1:1:1 ratio under the optimized condition, they gave only 18% (Table 4, entry 7) yield and also the product separation from the reaction medium is highly complicated. This control study strongly ascertains the catalytic role of nickel, when it presents in the framework is responsible for the catalysis.

Further, to fortify the true heterogeneity of the Ni(HBTC)BPY MOF catalyst, a filtration test was performed with the optimized reaction parameters (Table S2, SI). This filtration test revealed that the catalyst is high stability in ethanol medium and Ni(HBTC)BPY MOF behaving truly in heterogeneous nature under the optimized reaction conditions without leaching of metal ions due to breaking or deforming the frameworks. Obtained results were endorsed by the inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements of the ethanol filtrate from the reaction mixture, where no proof of metal leaching was observed, manifesting the true heterogeneity of the Ni(HBTC)BPY MOF.

The reusability aspect determines the stability and strength of the heterogeneous catalyst. To ascertain the sustainability, the catalyst was filtered at the end of the reaction, dried under vacuum at 120 °C for 2 h, and reused. This practice was repeated at the end of each cycle, and the catalyst was reused up to five times without any remarkable loss in its activity (Fig. S17, SI). Besides, the stability of the catalyst was confirmed by subjecting the reused catalyst to the analytical tools such as FTIR, Powder XRD and SEM (Fig. S18 to Fig. S20, SI). All the evidence mentioned above strongly endorses the stability of the reused catalyst even after five successive runs.

With these intriguing results, a plausible mechanism was proposed based on the literature reports [29, 35] for the Ni(HBTC)BPY MOF catalyzed *ipso*-hydroxylation of arylboronic acids as shown in scheme 1. MOF based heterogeneous catalysis offers advantages such as large pores, high surface area and porosity together with a high number of active sites and exposed apical coordination sites. Owing to this advantages nickel in Ni(HBTC)BPY MOF promotes *ipso*-hydroxylation of arylboronic acids. Notably, in the present metal-organic framework, the Ni^{2+} ion is coordinated with the two carboxylic groups and one nitrogen from the bipyridine organic linker, which stabilises the variable oxidation states nickel ion during the oxidative addition process through expanding coordination sphere. This phenomenon missing with the other homogeneous nickel salts. Hence, when Ni^{2+} is more reactive and promotes the oxidative hydroxylation when it presents in the framework. It is also revealed by the controlled experiment by a physical mixture of precursors of Ni(HBTC)BPY MOF (Table 4, entry 7). In the proposed mechanism. initially, phenylboronic acid coordinated to the nickel present in the MOF through transmetalation and form **II** which was further oxidized using hydrogen peroxide resulted in the formation of **III** and **IV**. During the oxidation Ni^{2+} gets oxidized into Ni^{3+} and form an intermediate **III**. Then the intermediate **III** undergoes rearrangement by eliminating a water molecule to form **IV**. The rearranged adduct **IV** upon subsequent hydrolysis gives the hydroxylated product. Finally, the metal gets back to its original oxidation state in the framework and ready for next cycle of hydroxylation.



Scheme 1. A plausible mechanism for the Ni(HBTC)BPY MOF-catalyzed *ipso*-hydroxylation of phenylboronic acid.

3. Conclusions

In conclusion, we have demonstrated a simple and efficient protocol for the *ipso*-hydroxylation of arylboronic acids using Ni(HBTC)BPY MOF as a heterogeneous catalyst. Using this catalyst, *ipso*-hydroxylation has been achieved in a shorter time using a minimal amount of H_2O_2 as an environmentally benign oxidant under renewable ethanol medium. This catalyst shows wide functional group tolerance under mild conditions with excellent yield. The present nickel mediated *ipso*-hydroxylation is compatible for the synthesis of phenols possessing electron releasing, electron-withdrawing and heterocyclic substituents an attractive yield. The as-synthesized and reused Ni(HBTC)BPY MOF catalyst was characterized using FTIR, PXRD and SEM analyses, which shows that the catalyst was highly stable even after five consecutive reuses. Besides, this is the first report in heterogeneous nickel catalyzed *ipso*-hydroxylation of arylboronic acids.

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Author Contributions Section

Ganesapandian Latha: Conceptualization, Methodology, Investigation

Nainamalai Devarajan: Methodology, Investigation

Murugan Karthik: Validation, Investigation

Palaniswamy Suresh*: Conceptualization, Supervision, Writing - Review & Editing

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] N. Balasundram, K. Sundram, S. Samman, Food Chem. 99 (2006) 191–203. **DOI: 10.1016/j.foodchem.2005.07.042**

[2] L. G. Ranilla, Y. I. Kwon, E. Apostolidis, K. Shetty, Bioresource Technol. 101 (2010) 4676–4689. **DOI: 10.1016/j.biortech.2010.01.093**

[3] I. Ouerghemmi, I. B. Rebey, F. Z. Rahali, S. Bourgou, L. Pistelli, R. Ksouri, B. Marzouk, M. S. Tounsi, J. Food Drug Anal. 25 (2017) 350–359. **DOI: 10.1016/j.jfda.2016.04.001**

[4] S. Nandi, M. Vracko, M. C. Bagchi, Chem. Biol. Drug Des. 70 (2007) 424–436. **DOI: 10.1111/j.1747-0285.2007.00575.x**

[5] F. Shahidi, C. T. Ho, ACS Symposium Series, 909 (2005) 1–8. **DOI: 10.1021/bk-2005-0909.ch001**

[6] T. George, R. Mabon, G. Sweeney, J. B. Sweeney, A. Tavassoli, J. Chem. Soc., Perkin Trans. 1 (2000) 2529–2574. **DOI: 10.1039/a808133f**

[7] A. Tlili, N. Xia, F. Monnier, M. Taillefer, Angew. Chem. Int. Ed. 48 (2009) 8725–8728. **DOI: 10.1002/anie.200903639**

[8] L. Jing, J. Wei, L. Zhou, Z. Huang, Z. Lia, X. Zhou, Chem. Commun. 46 (2010) 4767–4769. **DOI: 10.1039/C0CC00434K**

[9] J. P. Lambooy, J. Am. Chem. Soc. 72 (1950) 5327–5328. DOI:

[10] S. Priyadarshini, P. J. Amal Joseph, M. L. Kantam, B. Sreedhar, Tetrahedron 69 (2013) 6409–6414. **DOI: 10.1016/j.tet.2013.05.102**

[11] I. Saikia, M. Hazarika, N. Hussian, M. R. Das, C. Tamuly, Tetrahedron Lett. 58 (2017) 4255–4259. **DOI: 10.1016/j.tetlet.2017.09.075**

[12] M. Khazaei, A. Khazaei, M. Nasrollahzadeh, M. R. Tahsili, Tetrahedron 73, (2017) 5613–5623. **DOI: 10.1016/j.tet.2017.04.016**

[13] S. Phukan, A. Mahanta, Md. H. Rashid, Appl. Catal., A. 562 (2018) 58-66. **DOI: 10.1016/j.apcata.2018.05.037**

[14] T. Begum, A. Gogoi, P. K. Gogoi, U. Bora, Tetrahedron Lett. 56 (2015) 95–97. **DOI: 10.1016/j.tetlet.2014.11.018**

[15] J. Zheng, S. Lin, X. Zhu, B. Jiang, Z. Yang, Z. Pan, Chem. Commun. 48 (2012) 6235–6237. **DOI: 10.1039/C2CC31948A**

[16] A. Gualandi, A. Savoini, R. Saporetti, P. Franchi, M. Lucarini, P. G. Cozzi, Org. Chem. Front. 5 (2018) 1573–1578. **DOI: 10.1039/C8QO00061A**

[17] N. Mulakayala, Ismail, K. M. Kumar, R. K. Rapolu, B. Kandagatla, P. Rao, S. Oruganti, M. Pal, Tetrahedron Lett. 53, (2012) 6004–60010. **DOI: 10.1016/j.tetlet.2012.08.087**

[18] S. Guo, L. Lu, H. Cai, Synlett 24 (2013) 1712–1714. **DOI: 10.1055/s-0033-1339303**

[19] D. S. Chen, J. M. Huang, Synlett 24 (2013) 499–501. **DOI: 10.1055/s-0032-1318197**

[20] G. A. Molander, L. N. Cavalcanti, J. Org. Chem. 76 (2011) 623–630. **DOI: 10.1021/jo102208d**

[21] E. Kianmehr, M. Yahyaee, K. Tabatabai, Tetrahedron Lett. 2007, 48, 2713–2715. **DOI: 10.1016/j.tetlet.2007.02.069**

[22] C. Zhu, R. Wang, J. R. Falck, Org. Lett. 2012, 14, 3494–3497. **DOI: 10.1016/j.tetlet.2007.02.069**

[23] N. Chatterjee, H. Chowdhury, K. Sneh, A. Goswami, Tetrahedron Lett. 56 (2015) 172–174. **DOI: 10.1016/j.tetlet.2014.11.058**

[24] P. Gogoi, P. Bezboruah, J. Gogoi, R. C. Boruah, Eur. J. Org. Chem. (2013) 7291–7294. **DOI: 10.1002/ejoc.201301228**

[25] W. D. C. -Godoy, L. C. Schmidt, J. E. Arguello, Eur. J. Org. Chem. 19(2019) 3035–3039. **DOI: 10.1002/ejoc.201900311**

[26] M. Karthik, P. Suresh, ACS Sustainable Chem. Eng. 7 (2019), 9, 9028-9034. **DOI: 10.1021/acssuschemeng.9b01361**

[27] H. C. Zhou, S. Kitagawa, Chem. Soc. Rev. 43 (2014) 5415–5418. **DOI: 10.1039/C4CS90059F**

[28] Y. Wen, J. Zhang, Q. Xu, X. -T. Wu, Q. -L. Zhu, Coord. Chem. Rev. 376 (2018) 248–276. **DOI: 10.1016/j.ccr.2018.08.012**

[29] T. Truong, C. K. Nguyen, T. V. Tran, T. T. Nguyen, N. T. S. Phan, Catal. Sci. Technol. 4 (2014) 1276–1285. **DOI: 10.1039/C3CY01053H**

[30] X. -M. Zhang, C. -W. Zhao, J. -P. Ma, Y. Yu, Q. -K. Liu, Y. -B. Dong, Chem. Commun. 51 (2015) 839–842. **DOI: 10.1039/C4CC08003C**

[31] Y. Ren, Y. Shi, J. Chen, S. Yang, C. Qi, H. Jiang, RSC Adv. 2013, 3, 2167–2170. **DOI: 10.1039/C2RA22550F**

[32] N. T. S. Phan, T. T. Nguyen, A. H. Ta, J. Mol. Catal. A: Chem. 365 (2012) 95–102. **DOI: 10.1016/j.molcata.2012.08.015**

[33] L. Yang, Z. Huang, G. Li, W. Zhang, R. Cao, C. Wang, J. Xiao, D. Xue, Angew. Chem. Int. Ed. 57 (2018) 1968–1972. **DOI: 10.1002/anie.201710698**

[34] D. Prat, J. Hayler, A. Wells, Green Chem. 16 (2014) 4546–4551. **DOI: 10.1039/c4gc01149j**

[35] R. Borah, E. Saikia, S. J. Bora, B. Chetia, Tetrahedron Lett. 58 (2017) 1211–1215. **DOI: 10.1016/j.tetlet.2017.02.028**

Graphical abstract:

Highlights

- The first report on heterogeneous nickel as a catalyst for *ipso*-hydroxylation of arylboronic acids
- Ni(HBTC)BPY MOF was used as a heterogeneous catalyst for *ipso*-hydroxylation under mild condition
- Chemoselective towards *ipso*-hydroxylation in the presence of sensitive functional groups
- Short reaction time with a minimum oxidant load and renewable ethanol as a greener solvent
- Ni(HBTC)BPY MOF is stable and reusable for several cycles with excellent catalytic efficiency