RESEARCH ARTICLE

A waste valorization strategy for the synthesis of phenols from (hetero)arylboronic acids using pomegranate peel ash extract

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ABSTRACT
Phenols are prominent in organic reactions and highly significant biologically active substances. We report a versatile and sustainable CuI-catalyzed protocol for their synthesis through an oxidative ipso-functionalization (hydroxy deborylation) strategy of (hetero)arylboronic acids [(H)ABAs] using the water extract of pomegranate peel ash (WEPA) in open-air. They are formed at room temperature (RT). This process shows high significance toward the environmental sustainability over the reported procedures of ipso-hydroxylation of (H)ABAs. The application of a waste-derived biorenewable basic reaction medium, air as an oxidant, wide substrate scope, high functional group tolerance, reusability of the catalyst, ambient conditions, less expensive and safer catalyst with low loading, aqueous medium, avoidance of volatile organic solvents, and external oxidant, and tremendous further scope are the noteworthy features of this protocol.

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1. Introduction

The development of technologies/methods to explore organic solid waste as vital feedstocks/reagents/catalysts for synthetically and commercially valuable chemical transformations is urgently required in synthetic chemistry. This seems to be the perfect ladder of sustainable development (1). It controls the environmental pollution caused by solid organic waste in accordance with the current rate of development and by the huge consumption of non-renewable resources and avenues toward a circular economy (1). The pomegranate peels are the household/industrial waste widely used as highly nutritious cattle feed (2,3). Furthermore, the pomegranate peels are used in water remediation (4–6), generation of feedstocks (7,8), a diverse range of organic transformations (1,9–11), healthcare and biological applications (12–15), stabilization of oils (16–18), obtaining the useful phenolics and polysaccharides (19,20), etc. This article discusses the application of pomegranate peel ash derivative for the CuI-catalyzed synthesis of phenols through ipso-hydroxylation of (hetero)arylboronic acids [(H)ABAs]. Moreover, the invention of sustainable protocols for efficient access to fine chemicals is a highly potential and urgently
required assignment to replace the traditional organic procedures (1).

Phenols are the highly significant and valuable compounds, widely present in the structures of natural products and pharmaceuticals. They are occupied as versatile precursors to access polymers, herbicides, drugs, and antioxidants in a polyphenolic form (1,20–23). Up to now, several classes of phenols have been isolated from various natural resources that are structurally characterized, including lignans, flavonoids, and cardanols (20,24–26). These natural substances and synthetic phenols are frequently applied in dietary regimes and display several biological activities, including antioxidant, antimicrobial, antitumor, antibiotic, antiviral, and cardiovascular protective effects (20,24–27). For these reasons, phenols are the principal substances for therapeutic design and drug innovation and other functional applications. The biological activities of natural and unnatural phenols can also be regulated by metabolism in cell via oxidative enzymatic systems, such as human liver microsomes/NAD(P)H oxidoreductase (28), prostaglandin synthase/arachidonic acid, horse-radish peroxidase/H2O2, dioxygenases, and myeloperoxidase/H2O2 systems (29). Due to this significance, the synthesis of phenols is an ever progressing process in synthetic chemistry laboratories.

Structures of some important phenols have been provided in Figure 1. Chlorogenic acid (1), tannic acid (2), and eugenol (3) are the naturally abundant phenols, with one of the major use as food additives during food processing. These compounds show promising antioxidant, anti-inflammatory, hepatitis C virus (HCV) infection inhibition, and lysozyme-binding properties and the like (30–37). Paracetamol (4) is used for treating aches and pains, showing several other pharmacological properties (38–40). Vitamin E (5) lowers the cancer risk and maintains healthy eyes and prevents heart diseases (41–42). L-tyrosine (6) is a metabolite for the biosynthesis of several alkaloids (43) that have several biologically significant properties (44–45). Moreover, the phenolic groups are the common units in flavonoids, xanthones, aurones, isoaurones, and several other naturally available and biologically important aromatic compounds (46–49).

The classical methods of phenol preparation include Cu-promoted transformations of diazonium salts (50–51) and transition-metal catalyzed C–X bond hydroxylations of aryl halides (52–55). These have limitations, such as less availability of starting materials and the requirements of harsh reaction conditions, such as high-temperature and hazardous chemicals. The diazotization of the amino arenes to diazoarenes is often not compatible when the substrate has many other functional groups. Consequently, the synthesis of phenols from (H)ABAs via ipso-hydroxylation receives vast attention for higher stability, easy availability of precursors, and a greater diversity of the functional groups (21,22). Fewer Cu-catalyzed oxidative ipso-hydroxylations of (H)ABAs have appeared in the literature, which include CuSO4–phen–KOH (56),

![Figure 1. Structures of some prominent phenolic compounds.](image-url)
CuCl₂–O₂–Brij S-100 (57), Cu-electrode–aq. NH₃–sat. aq. KNO₃–Ag/AgCl reference electrode (58), CuFe₂O₄ NPs–NaOH (59), CuSO₄–MeOH–ellagic acid–60 °C (60), Cu₂O–(BTC)₂–Acetone–H₂O₂ (61), Cu₂O NPs–60°C (62), CuCl₂–cryptand-[2.2.2benzo] complex (63), Cu₃O NPs–H₂O₂ (64), Cu₂O–KOH–CTS-Py (65), Cu@C₃N₄–NaOH–blue LEDs (66) and Cu₂O–TiO₂–K₂CO₃–white LED (67) systems. Many of these procedures require 1–3 equivalent non-renewable base, unconventional catalysts, ligands, or heating conditions or take a considerable reaction time. A detailed comparison of reported Cu-mediated methods of ipso-hydroxylation of (H)ABAs has been provided in Table 3 in the results and discussion section (Section 3), and Scheme 1 is a glimpse of the reported advantageous methods for this purpose.

Although some efficient methods were reported in the literature for the ipso-hydroxylation of (H)ABAs, these require stoichiometric amounts of reagents or oxidants, problematic solvents, and photocatalytic activations (21,22,68–72). As part of our continuous efforts in green and sustainable chemistry (1,3,9–11,73,74), we disclose here a sustainable method for the Cu-catalyzed ipso-hydroxylation of (H)ABAs at RT shows tremendous benefits, such as the avoidance of stoichiometric amounts of oxidants/reagents with very low catalyst loading to access phenols from (H)ABAs using air as a sustainable oxidant. Scheme 1 shows the advantages of this protocol compared to some of the reported methods in this area (65,66). The present method uses biorenewable and waste-originated base and reaction media, and the reactions are quicker to give excellent yields of phenols (Scheme 1).

2. Materials and methods

2.1. General information

The aryl/heteroarylboronic acids were purchased from Sigma-Aldrich, Alfa Aesar, and the AVRA synthesis was used with no further purification. The progress of reactions has been monitored by TLC (Thin layer chromatography) using precoated Merck silica gel plates (60F-254). Visualization of reactants and products was accomplished under UV light. The ¹H/¹³C NMR spectra were recorded on a JEOL, JNM ECS NMR spectrometer operating at 400/100 MHz using CDCl₃ or DMSO-d₆ and tetramethylsilane (TMS) as a solvent and internal standards,

![Scheme 1](image-url)
and chemical shifts (δ) are quoted in ppm while coupling constants (J) in Hz.

2.2. Procedure for the preparation of WEPA

WEPA has been prepared from a new collection of pomegranate peels using our previous reports (3,9–11,73,74).

2.3. Procedure for the synthesis of phenols using WEPA

A solution of aryl/heteroaryl boronic acid (1) (1.0 mmol) 3 mL of WEPA was added to 3 mol% of CuI, and the reaction allowed for stirring at RT for an appropriate time, as displayed in Table 2. The reaction mixture was added with 5 mL of water to quench the reaction after its completion as indicated by TLC, 3 × 5 mL of EtOAc was used to extract the crude product, and the combined EtOAc portion was evaporated used for the purification of phenol via column chromatography. The structures of phenols (2) were assigned using their 1H NMR and 13C NMR data. These data well matched with the reported data. The copies of 1H NMR and 13C NMR spectra have been provided in the supplementary material.

2.3.1. Phenol (2a) (56). Yield: >99%; 1H NMR (400 MHz, CDCl3): δ (ppm) 7.24 (t, J = 8.5 Hz, 2H), 6.93 (t, J = 7.8 Hz, 1H), 6.83 (d, J = 8.3 Hz, 2H), 5.48 (brs, 1H); 13C NMR (100 MHz, CDCl3): δ (ppm) 155.4, 129.7, 120.8, 115.3.

2.3.2. 4-Methoxyphenol (2b) (56). Yield: 94%; 1H NMR (400 MHz, CDCl3): δ (ppm) 6.80–6.77 (m, 4H), 6.40 (brs, 1H); 13C NMR (100 MHz, CDCl3): δ (ppm) 153.3, 149.4, 116.1, 114.9, 55.8.

2.3.3. 4-Methylphenol (2c) (75). Yield: 93%; 1H NMR (400 MHz, DMSO-d6): δ (ppm) 9.07 (brs, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.63 (d, J = 8.0 Hz, 2H), 2.14 (s, 3H); 13C NMR (100 MHz, DMSO-d6): δ (ppm) 155.6, 130.2, 127.7, 115.5, 20.6.

2.3.4. 3-Methoxyphenol (2f) (56). Yield: 94%; 1H NMR (400 MHz, DMSO-d6): δ (ppm) 9.35 (brs, 1H), 7.06–6.92 (m, 1H), 6.38–6.16 (m, 3H), 3.64 (s, 3H); 13C NMR (100 MHz, DMSO-d6): δ (ppm) 161.0, 159.1, 130.4, 108.3, 105.1, 101.7, 55.3.

2.3.5. 3-Methylphenol (2g) (75). Yield: 92%; 1H NMR (400 MHz, DMSO-d6): δ (ppm) 9.17 (brs, 1H), 7.03–6.87 (m, 1H), 6.63–6.42 (m, 3H), 2.16 (s, 3H); 13C NMR (100 MHz, DMSO-d6): δ (ppm) 157.8, 139.2, 129.6, 120.1, 116.4, 112.8, 21.6.

2.3.6. 2-Methylphenol (2j) (75): Yield: 89%; 1H NMR (400 MHz, DMSO-d6): δ (ppm) 9.16 (brs, 1H), 7.10–6.42 (m, 4H), 2.06 (s, 3H); 13C NMR (100 MHz, DMSO-d6): δ (ppm) 155.9, 131.0, 127.2, 124.2, 119.2, 115.0, 16.5.

2.3.7. 4-Formylphenol (2l) (56). Yield: >99%; 1H NMR (400 MHz, CDCl3): δ (ppm) 9.84 (s, 1H), 7.79 (d, J = 8.2 Hz, 2H), 6.97 (d, J = 8.2 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 2.46 (s, 3H); 13C NMR (100 MHz, CDCl3): δ (ppm) 155.9, 149.4, 116.1, 114.9, 55.8.

2.3.8. 4-Acetylphenol (2m) (75). Yield: 97%; 1H NMR (400 MHz, DMSO-d6): δ (ppm) 10.34 (brs, 1H), 7.82 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 2.46 (s, 3H); 13C

Table 1. Optimization of reaction conditions.

| Entry | Catalyst (mol%) | Condition | Time (h) | Isolated yield (%) |
|-------|----------------|-----------|----------|--------------------|
| 1     | Cu(1)          | WEPA (1 mL) | 6        | 29                 |
| 2     | Cu(1)          | WEPA (2 mL) | 4        | 40                 |
| 3     | Cu(1)          | WEPA (3 mL) | 4        | 53                 |
| 4     | Cu(1)          | WEPA (4 mL) | 4        | 52                 |
| 5     | Cu(2)          | WEPA (3 mL) | 2        | 69                 |
| 6     | Cu(3)          | WEPA (3 mL) | 0.4      | >99b               |
| 7     | Cu(4)          | WEPA (3 mL) | 0.4      | >99b               |
| 8     | Cu(3)          | Water (3 mL) |          | –                  |
| 9     | Cu(3)          | WEPA (3 mL) | 24       | –                  |
| 10    | Cu(3)          | Neutral WEPA (~3 mL)c | 3        | –                  |
| 11    | Cu(3)          | Acidified WEPA (~3 mL)d | 8        | –                  |
| 12    | CuBr(3)        | WEPA (3 mL) | 10       | 25                 |
| 13    | CuCl2·2H2O (3) | WEPA (3 mL) | 12       | 39                 |
| 14    | Cu(OAc)2 (3)   | WEPA (3 mL) | 8        | 9                  |
| 15    | CuSO4 (3)      | WEPA (3 mL) | 8        | –                  |
| 16    | FeCl3 (3)      | WEPA (3 mL) | 24       | –                  |
| 17    | Ni(OAc)2 (3)   | WEPA (3 mL) | 24       | –                  |

aConditions: 1.0 mmol of 1a at RT in open-air.
bYield of the pure product after extraction without column chromatography.
cWEPA was neutralized using HCl.
dWEPA was acidified using HCl.
Table 2. Substrate feasibility studies.

| Substrate | T (h) | Yield (%) | δ (ppm) CDCl₃ | δ (ppm) CDCl₃ |
|-----------|-------|-----------|----------------|----------------|
| 2a | 0.4 h | >99% | 198.4, 161.2, 131.2 | 198.4, 161.2, 131.2 |
| 2b | 1.1 h | 94% | 129.8, 115.8, 26.3 | 129.8, 115.8, 26.3 |
| 2c | 1.2 h | 93% | 198.4, 161.2, 131.2 | 198.4, 161.2, 131.2 |
| 2d | 1.2 h | 93% | 129.8, 115.8, 26.3 | 129.8, 115.8, 26.3 |
| 2e | 1 h | 96% | 198.4, 161.2, 131.2 | 198.4, 161.2, 131.2 |
| 2f | 1.3 h | 94% | 129.8, 115.8, 26.3 | 129.8, 115.8, 26.3 |
| 2g | 1.5 h | 92% | 198.4, 161.2, 131.2 | 198.4, 161.2, 131.2 |
| 2h | 1.3 h | 90% | 129.8, 115.8, 26.3 | 129.8, 115.8, 26.3 |
| 2i | 1.9 h | 90% | 198.4, 161.2, 131.2 | 198.4, 161.2, 131.2 |
| 2j | 2.0 h | 89% | 129.8, 115.8, 26.3 | 129.8, 115.8, 26.3 |
| 2k | 2.0 h | 89% | 198.4, 161.2, 131.2 | 198.4, 161.2, 131.2 |
| 2l | 1.3 h | >99% | 129.8, 115.8, 26.3 | 129.8, 115.8, 26.3 |
| 2m | 1.2 h | 97% | 198.4, 161.2, 131.2 | 198.4, 161.2, 131.2 |
| 2n | 1.0 h | >99% | 129.8, 115.8, 26.3 | 129.8, 115.8, 26.3 |
| 2o | 2.0 h | 91% | 198.4, 161.2, 131.2 | 198.4, 161.2, 131.2 |
| 2p | 1.5 h | 93% | 129.8, 115.8, 26.3 | 129.8, 115.8, 26.3 |
| 2q | 1.5 h | 96% | 198.4, 161.2, 131.2 | 198.4, 161.2, 131.2 |
| 2r | 2.0 h | 85% | 129.8, 115.8, 26.3 | 129.8, 115.8, 26.3 |
| 2s | 2.0 h | 94% | 198.4, 161.2, 131.2 | 198.4, 161.2, 131.2 |
| 2t | 2.5 h | 89% | 129.8, 115.8, 26.3 | 129.8, 115.8, 26.3 |
| 2u | 3.0 h | 86% | 198.4, 161.2, 131.2 | 198.4, 161.2, 131.2 |
| 2v | 3.5 h | 82% | 129.8, 115.8, 26.3 | 129.8, 115.8, 26.3 |
| 2w | 3.5 h | 86% | 198.4, 161.2, 131.2 | 198.4, 161.2, 131.2 |
| 2x | 3.0 h | 88% | 129.8, 115.8, 26.3 | 129.8, 115.8, 26.3 |

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2.3.9. 4-Hydroxybiphenyl (2o) (56). Yield: 91%; Colorless solid; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.57–7.54 (m, 2H), 7.48 (d, J = 8.7 Hz, 2H), 7.41 (t, J = 7.8 Hz, 2H), 7.32–7.28 (m, 1H), 6.90 (d, J = 8.5 Hz, 2H), 4.90 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.1, 140.8, 134.1, 128.8, 128.5, 126.8, 126.8, 115.7.

2.3.10. 3-Formylphenol (2p) (63). Yield: 93%; ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 9.92, 9.86 (s, 1H), 7.36 (t, J = 7.7 Hz, 1H), 7.32–7.29 (m, 1H), 7.21 (s, 1H), 7.08–7.04 (m, 1H); ¹3C NMR (100 MHz, DMSO-d₆): δ (ppm) 193.6, 155.9, 131.7, 129.7, 121.8, 116.3, 115.7.

2.3.11. Ethyl 3-hydroxybenzoate (2q) (76). Yield: 96%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.61 (t, J = 7.7 Hz, 1H), 7.57 (s, 1H), 7.46 (t, J = 7.9 Hz, 1H), 7.07–7.04 (m, 1H), 5.66 (brs, 1H), 4.38 (q, J = 7.3 Hz, 2H), 1.39 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 166.8, 155.9, 131.7, 129.7, 121.8, 120.2, 116.3, 61.3, 14.3.

2.3.12. 2-Acetylphenol (2r) (77). Yield: 85%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 12.26 (brs, 1H), 7.73 (dd, J = 1.6, 8.0 Hz, 1H), 7.50–7.43 (m, 1H), 6.97 (dd, J = 1.1, 8.4 Hz, 1H), 6.93–6.87 (m, 1H), 2.63 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆): δ (ppm) 205.1, 161.5, 136.7, 131.9, 120.6, 119.6, 118.1, 27.8.
2.3.13 1-Naphthanol (2s) (56). Yield: 94%; $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.24–8.19 (m, 1H), 7.87–7.82 (m, 1H), 7.55–7.49 (m, 2H), 7.47 (d, $J$ = 8.3 Hz, 1H), 7.32 (t, $J$ = 7.8 Hz, 1H), 6.80 (d, $J$ = 7.5 Hz, 1H), 5.26 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ (ppm) 151.3, 134.8, 127.8, 126.5, 125.9, 125.4, 124.4, 121.6, 120.8, 108.8.

2.3.14 2-Phenyl-1-ethanol (2u) (78). Yield: 86%; $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.36–7.32 (m, 3H), 3.80 (t, $J$ = 8.4 Hz, 2H), 7.26–7.22 (m, 3H), 3.80 (t, $J$ = 7.2 Hz, 2H), 2.83 (t, $J$ = 7.2 Hz, 2H), 2.00 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ (ppm) 138.7, 129.2, 128.7, 126.6, 63.7, 39.3.

2.3.15 4-Hydroxypyrididine (2v) (79). Yield: 82%; $^1$H NMR (400 MHz, DMSO-d$_6$): δ (ppm) 7.82–7.56 (m, 2H), 6.28–6.07 (m, 2H), 5.75 (brs, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$): δ (ppm) 177.2, 140.1, 116.8.

2.3.16 3-Hydroxypyrididine (2w) (66). Yield: 86%; $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.19 (s, 1H), 8.00 (d, $J$ = 4.3 Hz, 1H), 7.29–7.12 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ (ppm) 155.2, 139.1, 136.5, 125.1, 124.9.

3. Results and discussion

3.1. Characterization of WEPA

Our recent characterizations of WEPA, using EDAX, XPS, XRD, XRF, and FTIR analysis, revealed the followings: K$_2$O and KCl in large quantities, along with SO$_3$, Na$_2$O, CaO, MgO, Al$_2$O$_3$, SiO$_2$ in minor quantities (3,9–11,73,74). The XPS and XRF data of WEPA from our recent reports have been provided in the supporting information for convenience. These constituents of WEPA played a critical role in various organic transformations, including Ullmann coupling of aryl halides, Suzuki–Miyaura coupling, self-coupling of (H)ABAs, aryl bromides, and aryl iodide synthesis (3,9–11,73,74). In these cases, WEPA acted as an aqueous media and biorenewable base [pH was between 11.7 and 12.1 after several repetitions (3)] and (or) catalyst by the reduction/elimination of the requirement of non-renewable resources-based materials including bases/catalysts/volatile organics/oxidants/heatings/conditions, etc. Inspired by the steady, sustainable attributes in the chemical transformations using WEPA, we have investigated the applicability of WEPA to Cu-catalyzed phenol synthesis via ipso-hydroxylation of (H)ABAs.

3.2. Optimization studies of Cul-catalyzed ipso-hydroxylation of ABAs in WEPA

For obtaining the optimized conditions for phenol synthesis, we have used the model reaction of phenylboronic acid (1a) (1 mmol) in 1 mL of WEPA and 1 mol% of Cul, and the phenol (2a) was formed with a 29% yield in 6 h at RT (Table 1, entry 1). The use of 2, 3 and 4 mL of WEPA at this stage was provided 2a in 40%, 53%, and 52% in 4 h (Table 1, entries 2–4), which indicates the present phenol synthesis requires 3 mL of WEPA. Furthermore, the application of Cul in 2, 3, and 4 mol% provided the 2a with 69%, >99%, and >99% in 4, 0.4, and 0.4 h (Table 1, entries 5–7), signifies that this conversion is effective using 3 mol% of Cul. The absence of WEPA (where 3 mL of water was used in the place of WEPA) or Cul showed no progress (Table 1, entries 8 and 9), and hence this conversion requires the Cul and WEPA. The model reaction was not preceded using neutralized WEPA or acidified WEPA under the current reaction conditions (Table 1, entries 10 and 11). Hence, the basicity of WEPA is crucial for this conversion. Furthermore, the pH of WEPA decreased from ~12 to ~8 after the completion of the reaction. The study of other copper salts such as CuCl$_2$·2H$_2$O, CuBr, Cu(OAc)$_2$ and CuSO$_4$, FeCl$_3$, and Ni(OAc)$_2$ showed no improvement in the current transformation (Table 1, entries 12–17). These analyses show that the present reaction requires 3 mol% of Cul and 3 mL of WEPA per 1 mmol of the substrate to obtain phenol with high yields at RT.

3.3. Substrate scope of Cul-catalyzed ipso-hydroxylation of (H)ABAs in WEPA

The optimized conditions were studied for their implementation in synthesizing phenols from various ABAs, heteroarylboronic acids (HABAs), and an alkylboronic acid, and the results are depicted in Table 2. The ABAs with the electron releasing groups, such as –OMe, –Me, –OH, and –SMe at ortho, meta, and para positions (3,9–11,73,74) delivered high yields of phenols (89% to nearly quantitative) in 0.4–2 h (Table 2, products 2a–2k).

The electron-withdrawing groups (such as –CHO, –Ac, –NO$_2$, –Ph, and –CO$_2$Et) containing ABAs were also converted to phenols in high yields (85–>99%) in 1–2 h despite their positions (ortho/meta/para) on aryl moiety (Table 2, products 2l–2r). 1-Naphthylboronic acid and disubstituted 4-formyl-2-methoxyphenylboronic acid provided 94% and 89% yields of their corresponding phenols such as 2s and 2t in 2 and 2.5 h under the optimized Cul-catalyzed conditions. HABAs, such as 4-pyridinylboronic acid, 3-pyridinylboronic acid and 2-furanylboronic acid, were also converted to their related hydroxy compounds with 82–86% yields in 3–3.5 h (Table 2, products 2v–2x). Furthermore, the alkylboronic acids, such as 2-phenylthyl-1-boronic acid, also formed 2-phenyl-1-ethanol (2u) in 86% yield in 3 h under the developed Cul-biorenewable base-assisted conditions.
The electron-withdrawing or electron releasing nature of substituent of ABAs showed no considerable influence on the present synthesis of phenols. However, the ABAs with the substituents at the o-position of the aromatic nucleus showed relatively fewer yields (Table 2, products \(2i-2k, 2r, \text{ and } 2t\)). The reactions of alkylboronic acid (such as 2-phenylethyl-1-boronic acid) and HABAs are slow and display fewer yields (Table 2, products \(2u-2x\)).

3.4. Plausible mechanism of Cul-catalyzed ipso-hydroxylation of (H)ABAs

The mechanism of Cu-catalyzed ipso-hydroxylation of ABAs is not fully understood yet. However, we propose here a plausible mechanism of current ipso-hydroxylation of (H)ABAs in WEPA based on the observations shown in Table 1 along with some control experiments (Scheme 2), reusability studies (Section 3.5), and literature reports (56,63,65,80–82).

The versatility of the Cu-catalyzed process is that it can undergo very quickly into one- or two-electron processes and shows easy access to its four oxidation states from 0 to +3 (82,83). The reaction of \(1a\) in the presence of Cul (3 mol%), WEPA (3 mL) and 1 eq. of radical scavenger such as TEMPO was proceeded to give >99% of \(2a\) in 0.4 h (Scheme 2), indicating no influence of TEMPO on the current reaction; hence, the reaction is not proceeding through a radical mechanism. The reaction of \(1a\) did not proceed in the presence of an inert (\(N_2\)) atmosphere, but it shows similar results in open-air and in the presence of oxygen (Scheme 2), and these control experiments indicate that the current transformation requires oxygen to proceed, but the oxygen from the air is enough. Furthermore, the reusability studies (Section 3.5), a decrease in pH of WEPA after the reaction (Section 3.2) and no progress of the reaction in the presence of neutralized or acidified WEPA (Table 1, entries 10 and 11) indicates that the basic nature of WEPA is crucial for this transformation. Furthermore, the copper catalyst can be recycled and reused.

According to the above observations and the literature reports, initially, an ionic species, \(A\), formed from the ABA and base of WEPA (i.e. MB) (82), may react with Cul to generate the intermediates \(i\) and \(B\) via the oxidative addition process (I) in the presence of molecular oxygen (\(O_2\), from the air) (Scheme 3). Further oxidative addition (II) of intermediates \(i\) and \(B\) in the presence of water may result the intermediate \(ii\) and \(C\). Finally, intermediate \(ii\) may participate in reductive elimination (III) to produce phenol \(2\) and the catalyst, Cul. The other chemical substances of WEPA may also participate in this process by acting as promoters or phase transfer agents (3).

3.5. Reusability studies

After the completion of the reaction of \(1a\) (Section 2.3), the product formed was extracted using \(Et_2O\), and 1 mmol of \(1a\) was added to the resultant WEPA-Cul system for understanding the reusability of the WEPA-Cul mixture, but the reaction gave < 5% yield of \(2a\) after 8 h. However, the evaporation of the resultant WEPA-Cul mixture to \(\sim 0.3 \text{ mL}\) followed by the addition of 3 mL of WEPA and 1 mmol of \(1a\) was proceeded at RT to give a 96% yield of \(2a\) in 0.4 h, and further repetition of this process showed 93%, 90% and 81% yields of \(2a\) in 0.4 h during the third to fourth cycles.
This study reveals that the WEPA cannot be reused for this transformation since the base components of WEPA may be consumed during the reaction process. However, WEPA is based on biorenewable organic waste. This study also indicates that the copper catalyst can be reused for up to 3 cycles, and a considerable loss of its activity in the fourth cycle may be accountable for the loss of catalyst during the extraction process.
3.6. Comparison of results
For identifying the effectiveness of the current protocol, a concise review of the existing Cu-catalyzed protocols of *ipso*-hydroxylation of phenylboronic acid (1a) has been provided in Table 3. This method avoids the non-renewable resources-based bases, ligands, problematic solvents, promoters, heating conditions, significant reaction times, and tedious preparation of catalysts. The current method is significant to the scientific community, as we believe that the next generation of catalysis would use green and sustainable catalysts in organic synthesis. This process also becomes an attractive alternative to the protocols based on the application of stoichiometric amounts of green oxidants such as H₂O₂ (21,84).

4. Conclusions
We have developed a Cu-catalyzed, room temperature protocol for synthesizing phenols from (H)ABAs using biorenewable and waste-originated WEPA as a primary reaction medium. This protocol shows broad substrate feasibility, vast functional group tolerability, and good catalyst reusability in the biorenewable base. A systematic comparison of the previously reported methods of the *ipso*-hydroxylation of (H)ABAs has displayed the advantages of this protocol as the use of biorenewable catalyst, ambient conditions, good yields of products, and ease of synthesis and purification of the end-products. Finally, this method could be one of the forefront sustainable procedures for the *ipso*-hydroxylation of (H)ABAs in the industry in the near future.

Disclosure statement
No potential conflict of interest was reported by the author(s).

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