Supporting Information:

Bio-based green solvent for the catalyst free oxidation of arylboronic acids into phenols

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Experimental section:
All reactions were performed under open air atmosphere at room temperature (~30°C). Solvents and chemicals were purchased from commercial sources and used without further purifications. The NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer and JEOL 300 MHz NMR Spectrometer. The column chromatography was performed on silica gel (60-120 mesh) using a mixture of ethylacetate and hexane as eluent. Thin layer chromatography was performed using pre-coated plates obtained from E. Merck (TLC silica gel 60 F254). The proton NMR was recorded for the phenols and compared with literature reports.1-4

A general experimental procedure for the oxidation reaction:
To a stirred solution of aryl boronic acid (or) aliphatic boronic acid (0.5 mmol) in lactic acid (or) acetic acid (1.0 mL) was added 1.0 equivalent of 30% aqueous hydrogen peroxide at room temperature and the progress of the reaction was monitored by TLC. In case of acetic acid, after completion of the reaction (as seen by TLC), solvent was evaporated to dryness and the residue was subjected to column chromatography to obtain pure phenols. In case of lactic acid, after completion, the reaction mixture was diluted with water and extracted with petroleum ether-ethyl acetate mixture (2:1, 5x5mL). The companied organic layer was dried over sodium sulphate (Na2SO4), evaporated and subjected to chromatography to obtain pure products.

Analytical data for the products:
2a: Phenol was obtained as brown oil (Yield: 45 mg (95%) in both lactic acid and acetic acid). 1H NMR (400 MHz, CDCl3): δ 7.27 (m, 2H), 6.97 (m, 1H), 6.87 (m, 2H), 6.16 (br, 1H).

2b: 1-Naphthol was obtained as a white solid (Yield: 67 mg (93%) in lactic acid; 68 mg (95%) in acetic acid). 1H NMR (400 MHz, CDCl3): δ 8.20 (m, 1H), 7.80 (m, 1H), 7.57-7.42 (m, 3H), 7.32 (t, J = 7.8 Hz, 1H), 6.82 (d, J = 7.3 Hz, 1H), 5.40 (br, OH).
2c: 2-Naphthol was obtained as a white solid (Yield: 68 mg (94%) in lactic acid; 69 mg (96%) in acetic acid). $^1$H NMR (400 MHz, CDCl$_3$)$^1$: $^6$ 7.77 (t, $J = 9.2$ Hz, 2H), 7.67 (d, $J = 8.2$ Hz, 1H), 7.44 (t, $J = 7.3$ Hz, 1H), 7.35 (t, $J = 8.2$ Hz, 1H), 7.17-7.08 (m, 2H).

2d: 4-Methoxyphenol was obtained as colorless oil. (Yield: 56 mg (90%) in lactic acid; 59 mg (95%) in acetic acid). $^1$H NMR (400 MHz, CDCl$_3$)$^1$: $^6$ 6.82-6.75 (m, 4H), 3.77 (s, 3H).

2e: 4-Methylphenol was obtained as colorless oil (Yield: 51 mg (95%) in lactic acid; 50 mg (93%) in acetic acid). $^1$H NMR (400 MHz, CDCl$_3$)$^1$: $^6$ 7.05 (d, $J = 8.0$ Hz, 2H), 6.81 (d, $J = 8.2$ Hz, 2H), 2.31 (s, 3H).

2f: 2-Methylphenol was obtained as colorless oil (Yield: 51 mg (95%) in lactic acid; 51 mg (95%) in acetic acid). $^1$H NMR (400 MHz, CDCl$_3$)$^2$: $^6$ 7.27 (m, 2H), 7.10-6.85 (m, 2H), 5.80 (br, OH), 2.42 (3H, s).

2g: 4-Ethylphenol was obtained as a white solid (Yield: 57 mg (93%) in lactic acid; 58 mg (95%) in acetic acid). $^1$H NMR (400 MHz, CDCl$_3$)$^3$: $^6$ 7.03 (d, $J = 8.4$, 2H), 6.73 (d, $J = 8.8$ Hz, 2H), 4.89 (br, OH), 2.58 (q, $J = 7.59$ Hz, 2H), 1.22 (t, $J = 7.6$ Hz, 3H).

2h: 4-tert-Butylphenol was obtained as a colourless solid (Yield: 72 mg (96%) in lactic acid; 70 mg (93%) in acetic acid). $^1$H NMR (400 MHz, CDCl$_3$)$^1$: $^6$ 7.27-7.23 (m, 2 H), 6.79-6.74 (m, 2H), 4.84 (br, OH), 1.29 (s, 9 H).

2i: 4-Phenylphenol was obtained as a white solid (Yield: 79 mg (93%) in lactic acid; 83 mg (97%) in acetic acid). $^1$H NMR (400 MHz, CDCl$_3$)$^2$: $^6$ 7.56–7.53 (m, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.32 (t, $J = 7.4$ Hz, 1H), 6.90 (d, $J = 8.8$ Hz, 2H), 5.00 (br, OH).

2j: 2,4,6-Trimethyl phenol was obtained as a white solid (Yield: 64 mg (94%) in both lactic acid and acetic acid). $^1$HNMR (400 MHz, CDCl$_3$)$^4$: $^6$ 6.79 (s, 2H), 4.47 (s, 1H), 2.22 (m, 9H).

2k: 3-Nitrophenol was obtained as a pale yellow solid (Yield: 63 mg (91%) in lactic acid; 66 mg (95%) in acetic acid). $^1$H NMR (400 MHz, CDCl$_3$)$^2$: $^6$ 7.81-7.78 (m, 1H), 7.72 (t, $J = 2.3$ Hz, 1H), 7.41 (t, $J = 8.2$ Hz, 1H), 7.21–7.17 (m, 1H), 5.96 (br, OH).

2l: 4-Nitrophenol was obtained as a yellow solid (Yield: 64 mg (92%) in lactic acid; 65 mg (94%) in acetic acid). $^1$HNMR (400 MHz, CDCl$_3$) $^1$: $^6$ 8.19-8.15 (m, 2H), 6.96-6.91 (m, 2H), 6.57 (s, OH).

2m: 4-Fluorophenol was obtained as a white solid (Yield: 52 mg (92 %) in both lactic acid and acetic acid). $^1$H NMR (400MHz, CDCl$_3$)$^1$: $^6$ 6.95-6.88 (m, 2H), 6.80-6.75 (m, 2H).

2n: 4-Chlorophenol was obtained as a white solid (Yield: 61 mg (95%) in both lactic acid and acetic acid). $^1$H NMR (400MHz, CDCl$_3$)$^2$: $^6$ 7.21-7.17 (m, 2H), 6.79-6.74 (m, 2H), 5.58 (br, OH).
2o: 2,4-Dichlorophenol was obtained as a white solid (Yield: 76 mg (93%) in lactic acid; 73 mg (90%) in acetic acid). $^1$H NMR (CDCl$_3$, 400 MHz)$^3$: $\delta$ 7.33 (s, 1H), 7.18 (d, $J$=8.0 Hz, 1H), 6.95 (d, 1H, $J$=8.0 Hz), 5.57 (br, OH).

2p: 4-Bromophenol was obtained as a semisolid (Yield: 81 mg (94%) in lactic acid; 83 mg (96%) in acetic acid). $^1$H NMR (400 MHz, CDCl$_3$)$^1$: $\delta$ 7.32 (m, 2H), 6.72 (m, 2H), 5.36 (br, OH).

2q: 4-Iodophenol was obtained as a semisolid (Yield: 103 mg (94%) in lactic acid; 100 mg (91%) in acetic acid). $^1$H NMR (400 MHz, CDCl$_3$)$^1$: $\delta$ 7.51 (m, 2H), 6.62 (m, 2H), 5.15 (br, OH).

2r: 4-Hydroxyphenol was obtained as a white solid (Yield: 52 mg (95%) in both lactic acid and acetic acid). $^1$H NMR (400 MHz, CDCl$_3$)$^3$: $\delta$ 6.72 (4H, s), 3.47 (2H, s).

2s: 4-Hydroxyacetophenone was obtained as white solid. (Yield: 65mg (95%) in both lactic acid and acetic acid). $^1$H NMR (400 MHz, CDCl$_3$)$^1$: $\delta$ 7.91 (d, $J$ = 8.6 Hz, 2H), 6.91 (d, $J$ = 8.6 Hz, 2H), 2.57 (s, 3H).

2t: 2-Phenylethanol was obtained as colorless oil (Yield: 57 mg (94%) in lactic acid). $^1$H NMR (300 MHz, CDCl$_3$)$^5$: $\delta$ 7.30-7.34 (m, 3H), 7.24 (t, $J$ = 7.4 Hz, 2H), 3.85 (t, $J$ = 6.4 Hz, 2H), 2.87 (t, $J$ = 6.4 Hz, 2H).

2u: Cyclohexanol was obtained as colorless oil (Yield: 43 mg (86%) in lactic acid). $^1$H NMR (400 MHz, CDCl$_3$)$^5$: $\delta$ 3.61 (m, 1H), 2.00-1.50 (m, 6H), 1.35-1.10 (m, 4H).

References


1H NMR Spectrum of Phenols and aliphatic alcohols