# Benzoquinone-Promoted Aerobic Oxidative Hydroxylation of Arylboronic Acids in Water

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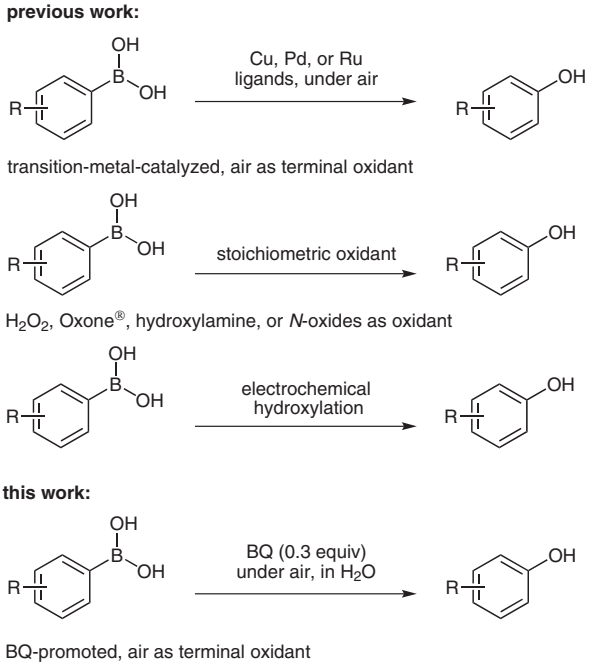
*Received: 10.10.2013; Accepted after revision: 18.11.2013*

**Abstract:** A general and efficient aerobic oxidative hydroxylation of arylboronic acids promoted by benzoquinone in water was realized, and provided phenols in 72–95% yields for 20 examples. The main advantages of this protocol are the use of water as solvent in the presence of a catalytic amount of benzoquinone, and metal-free conditions.

**Key words:** benzoquinone, arylboronic acids, oxidation, oxygen, phenols

Phenols are important industrial chemicals and versatile building blocks in synthetic chemistry,[1] and they frequently exist in natural products and pharmaceuticals.[2] The arylboronic acids have been widely applied in organic synthesis due to their easy operation and stability.[3] Their transformation into phenols was achieved by transition-metal-catalyzed hydroxylation[4] or by oxidative hydroxylation[5] (Scheme 1). Transition-metal catalysts, such as copper,[4a–d] palladium,[4e] ruthenium,[4f,g] and relative ligands are necessary for the former procedure. The latter one requires an external stoichiometric oxidant such as $H_2O_2$,[5a–e] Oxone,[5f,g] hydroxylamine,[5h] or *N*-oxides.[5i] Moreover, the reaction temperature and time need to be carefully controlled to avoid overoxidation. Meanwhile, an electrochemical hydroxylation of arylboronic acids leading to the corresponding phenols was also reported.[6] From the viewpoint of low cost, green chemistry, and low metal contamination in pharmaceutical industry, the development of aerobic oxidative protocol under the metal free conditions is of great significance.[7] Herein, we disclose a highly practical procedure toward phenols from arylboronic acids, in which air and water were used as oxidant and solvent, respectively. The reaction is environmentally friendly and has a general substrate scope.



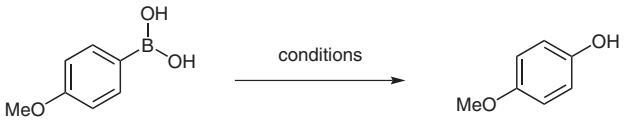

**Scheme 1** Hydroxylation of arylboronic acids

4-Methoxyphenylboronic acid (**1a**; 1 mmol) was initially chosen as a model substrate to optimize the reaction parameters using KOH (3 equiv) as a base in water (5 mL) under air. As shown in Table 1, the first reaction was performed at room temperature using benzoquinone (BQ, 1 equiv) as an oxidant and monitored by TLC. The starting material **1a** was consumed completely within 30 hours. The corresponding phenol **2a** was isolated in 87% yield (Table 1, entry 1), while no desired product was observed with bubbling of $O_2$ in the absence of BQ (entry 2). These results suggested that BQ was a suitable oxidant for this transformation.

Then, a catalytic amount of BQ was screened to evaluate the reaction efficiency. Interestingly, 0.7 equivalent of BQ could give an acceptable yield (84%, entry 3). The yield dropped to 33% when 0.3 equiv of BQ was used (entry 4). However, increasing the reaction temperature improved this transformation dramatically (entries 5, 6). A temperature of 100 °C proved to be crucial to obtaining a satisfactory result, probably because the oxidation of hydroquinone (HQ) to BQ could proceed smoothly at an elevated temperature. The effect of base was subsequently examined (entries 7−10). KOH gave the best result (entry 6). No phenol was observed without KOH (entry 11) and 3 equiv of KOH was enough for this transformation (entries 12 and 13) since monopotassium trihydroxy(4-methoxy)phenylborate salt served as a real active intermediate.[4a] The loading of BQ was screened from 0.3 to 0.2, 0.1, and 0.05 equivalent under $O_2$ atmosphere. Yields amounting to 60%, 61%, and 56% were obtained in the presence of 0.2, 0.1, and 0.05 equivalent of BQ, respec-

**SYNTHESIS** 2014, 46, 0295–0300
Advanced online publication: 05.12.2013
DOI: 10.1055/s-0033-1338571; Art ID: SS-2013-H0668-OP

**Table 1** Screening of Reaction Parameters for the Oxidative Hydroxylation of 4-Methoxyphenylboronic Acid (**1a**)[a]




**1a** **2a**

| Entry | Catalyst | Base | Temp (°C) | Time (h) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | BQ (1.0) | KOH | r.t. | 30 | 87 |
| 2[c] | – | KOH | r.t. | 30 | 0 |
| 3 | BQ (0.7) | KOH | r.t. | 30 | 84 |
| 4 | BQ (0.3) | KOH | r.t. | 96 | 33 |
| 5 | BQ (0.3) | KOH | 60 | 30 | 72 |
| **6** | **BQ (0.3)** | **KOH** | **100** | **30** | **90** |
| 7 | BQ (0.3) | NaOH | 100 | 30 | 83 |
| 8 | BQ (0.3) | $K_3PO_4$ | 100 | 48 | 76 |
| 9 | BQ (0.3) | $Cs_2CO_3$ | 100 | 48 | 56 |
| 10 | BQ (0.3) | $K_2CO_3$ | 100 | 48 | 55 |
| 11 | BQ (0.3) | – | 100 | 30 | 0 |
| 12[d] | BQ (0.3) | KOH | 100 | 30 | 84 |
| 13[e] | BQ (0.3) | KOH | 100 | 30 | 87 |
| 14 | BQ (0.2) | KOH | 100 | 30 | 81 |
| 15 | BQ (0.4) | KOH | 100 | 25 | 89 |
| 16[f] | BQ (0.3) | KOH | 100 | 30 | 33 |
| 17[g] | BQ (0.3) | KOH | 100 | 5 | 65 |
| 18 | DDQ (0.3)[h] | KOH | 100 | 30 | 49 |
| 19 | NQ (0.3)[i] | KOH | 100 | 30 | 88 |

[a] Reactions conditions: Unless otherwise noted, the reaction was carried out on a 1 mmol scale. 4-Methoxyphenylboronic acid (**1a**; 1 mmol), catalyst (0.3 equiv), base (3.0 equiv), $H_2O$ (5 mL), 100 °C, under air atmosphere.
[b] Isolated yield based on **1a**.
[c] With bubbling of $O_2$.
[d] Base: 2 equiv.
[e] Base: 4 equiv.
[f] Under $N_2$.
[g] $O_2$: 1 atm.
[h] DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.
[i] NQ = 1,4-naphthoquinone.

tively. Further investigation showed that 0.3 equivalent of BQ, 3 equivalent of KOH, and air atmosphere provided the optimal result (entries 14−16). An $O_2$ balloon can accelerate the reaction.

However, the yield decreased to 65% at shorter reaction time (entry 17). Other commercially available quinones, such as DDQ and NQ, were also examined, which gave **2a** in 49% and 88% yield, respectively (entries 18, 19).

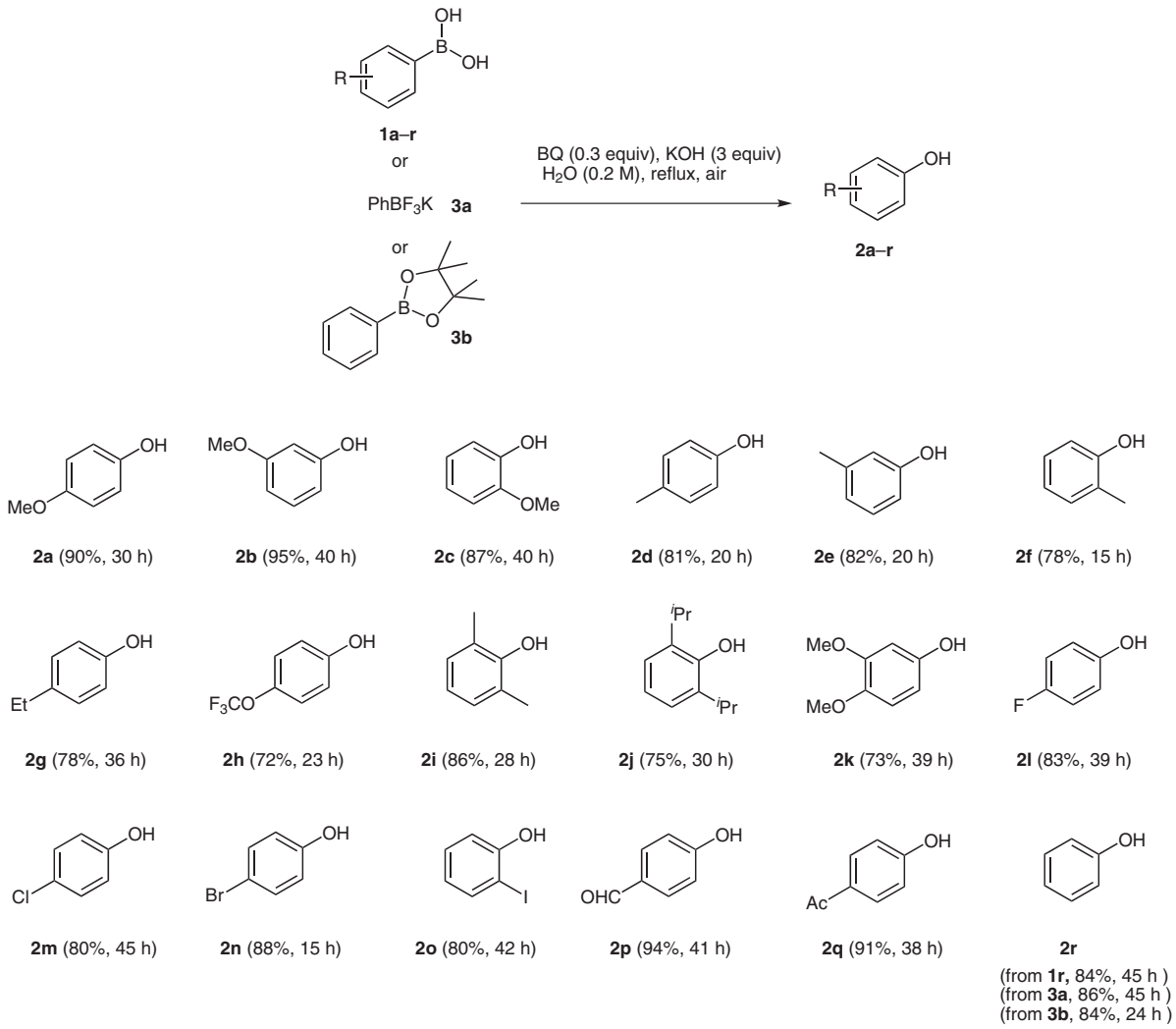
With the optimized reaction parameters in hand, the generality of substrates was explored. As illustrated in Scheme 2, this catalytic system was applied to a large variety of substrates and was found not significantly affected by the electron-donating and -withdrawing groups and the bulk. A series of phenols with electron-donating group **2a**–**k** as well as electron-withdrawing group **2l**–**q** were obtained practically in good to excellent yields. The aerobic oxidative hydroxylation of arylboronic acids **1c**, **1f**, and **1o** with larger bulk, including the highly blocked substrates **1i** and **1j**, proceeded smoothly. Compared with the palladium-[8] or copper-catalyzed[9] hydroxylation of aryl halides, this protocol tolerated halide in the substrates and gave higher yields. The major drawback of oxidative hydroxylation is the less tolerance of oxidation-sensitive functional group, such as aldehyde. However, our catalytic system was also suitable to aldehyde derivatives. For example, product **2p** could be obtained in 94% yield. Furthermore, pinacol phenylboronate (**3a**) and potassium phenyltrifluoroborate (**3b**) were also suitable substrates for this transformation and gave corresponding phenol **2r** in good yield.[10]

To clarify the reaction mechanism, some controlled experiments were carried out. A 33% yield was obtained when the reaction was performed under $N_2$ atmosphere (Scheme 3, equation 1). HQ was also isolated in 40% yield (based on BQ). However, only 15% yield was obtained in the absence of BQ (Scheme 3, equation 2). Obviously, both air and BQ were crucial for this transformation, which suggested that air served as an oxidant, and a catalytic cycle between BQ and HQ was involved. To examine this hypothesis, HQ was used instead of BQ for this reaction, and the desired product **2a** was isolated in 89% yield (Scheme 3, equation 3). Moreover, the amount of HQ slowly decreased during the reaction process and only trace amount of HQ was detected at the end of the reaction. It was reported in the literature that the autoxidation of hydroquinone was accompanied by the formation of hydrogen peroxide. Then, the oxidation of quinone by peroxide led to the decomposition of BQ.[11] Based on this literature, we propose that hydrogen peroxide was produced in our catalytic process. To verify this hypothesis, the condensation of α,β-unsaturated ketone **4** with 1 equiv of HQ was carried out under air atmosphere, which provided the epoxy product **5** in 35% yield (Scheme 3, equation 4).[12]

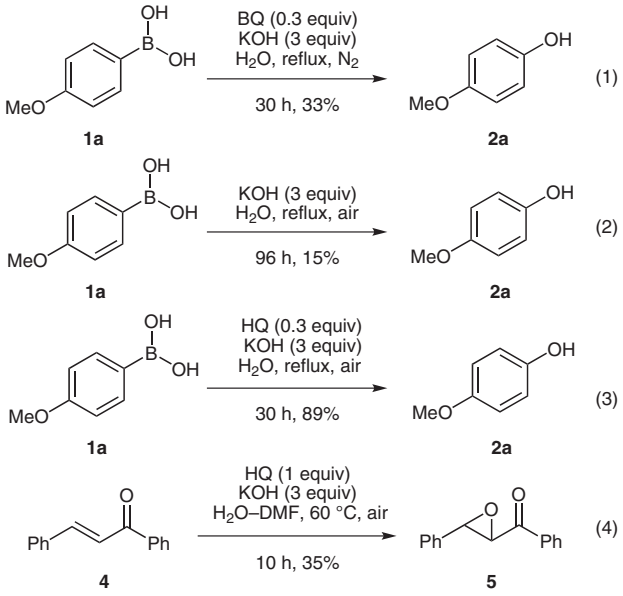
On the basis of the results obtained, a plausible mechanism was proposed as illustrated in Scheme 4. Initially, trihydroxyboronate salts **A** are formed by the treatment of arylboronic acids **1** with base (Scheme 4, equation 1). Subsequent oxidation of **A** with BQ yields phenols **2** and HQ (Scheme 4, equation 2). Then, BQ was regenerated by the autoxidation of HQ accompanied by the formation of hydrogen peroxide (Scheme 4, equation 3). Meanwhile, BQ was partially decomposed by the oxidation of the in situ generated hydrogen peroxide (Scheme 4, equation 4),



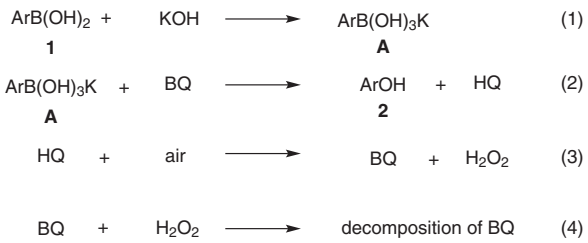
 




**Scheme 2** BQ-catalyzed aerobic oxidative hydroxylation of arylboronic acids in water




**Scheme 3** Controlled experiments




**Scheme 4** Proposed mechanism

which probably accounts for the high loading of the catalyst precursor BQ (30 mol%).

In summary, we have developed an efficient, practical, and green approach for the benzoquinone-promoted aerobic oxidative hydroxylation of arylboronic acids. A wide range of phenols with both electron-donating and electron-withdrawing groups were obtained in good to excellent yields. The great attractiveness of this transformation

is the use of water as solvent and air as environment-friendly oxidant, avoiding transition-metal catalyst, and external stoichiometric oxidant.

All reagents were used directly without further purification. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. $^1$H and $^{13}$C NMR spectra were recorded at 400 and 100 MHz for $CDCl_3$ solutions. Petroleum ether (PE) used refers to the fraction boiling at 60−90 °C.

**Phenols 2a–r; General Procedure**

A mixture of 1,4-benzoquinone (32.4 mg, 0.3 mmol), boronic acid **1** (1 mmol), and KOH (168 mg, 3.0 mmol) in $H_2O$ (5 mL) was stirred at reflux temperature under air for 15−45 h. After the full consumption of **1** (monitored by TLC, eluent: PE–EtOAc, 10:1), the reaction was quenched carefully with aq 2 M HCl (15 mL). The resulting mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with $H_2O$ (30 mL) and brine (10 mL), and dried ($Na_2SO_4$). After the removal of the solvent, the resulting residue was purified by chromatography (silica gel, 20% EtOAc in PE) to give the respective products **2**.

**4-Methoxyphenol (2a)**[4a]

Yield: 112 mg (90%); colorless solid; mp 58 °C (EtOAc–PE)

$^1$H NMR (400 MHz, $CDCl_3$): δ = 6.86–6.70 (m, 4 H), 5.30 (br, 1 H), 3.78–3.69 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 153.6, 149.5, 116.1, 115.0, 55.8.

**3-Methoxyphenol (2b)**[4a]

Yield: 118 mg (95%); colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.11 (t, *J* = 8.1 Hz, 1 H), 6.57–6.37 (m, 3 H), 6.27 (br, 1 H), 3.75 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 160.7, 156.8, 130.1, 108.0, 106.3, 101.6, 55.3.

**2-Methoxyphenol (2c)**[4a]

Yield: 108 mg (87%); colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 6.88–6.81 (m, 1 H), 6.81–6.61 (m, 3 H), 5.60 (br, 1 H), 3.79 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 146.5, 145.6, 121.4, 120.1, 114.5, 110.7, 55.8.

**4-Methylphenol (2d)**[4f]

Yield: 87 mg (81%); colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.00 (d, *J* = 8.2 Hz, 2 H), 6.72 (d, *J* = 8.5 Hz, 2 H), 5.84 (s, 1 H), 2.25 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 153.1, 130.0, 129.9, 115.1, 20.3.

**3-Methylphenol (2e)**[4f]

Yield: 89 mg (82%); colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.09 (t, *J* = 7.7 Hz, 1 H), 6.72 (d, *J* = 7.4 Hz, 1 H), 6.63 (d, *J* = 8.8 Hz, 2 H), 6.13 (br, 1 H), 2.26 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 155.3, 139.8, 129.6, 121.58, 116.1, 112.3, 21.2.

**2-Methylphenol (2f)**[4a]

Yield: 84 mg (78%); colorless solid; mp 31–32 °C (EtOAc–PE).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.08 (ddd, *J* = 15.4, 8.5, 4.4 Hz, 2 H), 6.84 (t, *J* = 7.4 Hz, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 5.06 (s, 1 H), 2.24 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 153.7, 131.0, 127.1, 123.8, 120.7, 114.9, 15.7.

**4-Ethylphenol (2g)**[4f]

Yield: 95 mg (78%); colorless solid; mp 45–46 °C (EtOAc–PE).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.02 (d, *J* = 8.5 Hz, 2 H), 6.76 (d, *J* = 8.5 Hz, 2 H), 6.03 (br, 1 H), 2.55 (q, *J* = 7.6 Hz, 2 H), 1.18 (t, *J* = 7.6 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 153.1, 136.6, 128.9, 115.2, 27.9, 15.8.

**4-Trifluoromethoxyphenol (2h)**[13]

Yield: 128 mg (72%); colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.16–7.04 (m, 2 H), 6.88–6.76 (m, 2 H), 6.07 (br, 1 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 154.2, 142.8, 122.6, 120.6 (q, *J* = 256.0 Hz), 116.2.

**2,6-Dimethylphenol (2i)**[4a]

Yield: 105 mg (86%); colorless solid; mp 44–45 °C (EtOAc–PE).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 6.97 (d, *J* = 7.5 Hz, 2 H), 6.75 (t, *J* = 7.5 Hz, 1 H), 4.61 (s, 1 H), 2.24 (s, 6 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 152.1, 128.6, 122.9, 120.2, 15.8.

**2,6-Diisopropylphenol (2j)**[9b]

Yield: 134 mg (75%); yellowish oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.06 (d, *J* = 7.6 Hz, 2 H), 6.96–6.82 (m, 1 H), 4.77 (s, 1 H), 3.16 (m, 2 H), 1.27 (d, *J* = 6.9 Hz, 12 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 149.9, 133.6, 123.4, 120.6, 27.1, 22.7.

**3,4-Dimethoxyphenol (2k)**[9k]

Yield: 112 mg (73%); yellow solid; mp 36–38 °C (EtOAc–PE).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 6.73 (d, *J* = 8.6 Hz, 1 H), 6.47 (d, *J* = 2.8 Hz, 1 H), 6.35 (dd, *J* = 8.6, 2.8 Hz, 1 H), 5.51 (br, 1 H), 3.81 (s, 3 H), 3.81 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 150.2, 149.9, 143.1, 112.6, 105.9, 100.7, 56.6, 55.8.

**4-Fluorophenol (2l)**[4a]

Yield: 93 mg (83%); white solid; mp 45–46 °C (EtOAc–PE).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 6.95–6.87 (m, 2 H), 6.81–6.72 (m, 2 H), 5.80 (s, 1 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 157.2 (d, *J* = 237.7 Hz), 151.3 (d, *J* = 2.1 Hz), 116.2 (d, *J* = 8.0 Hz), 116.0 (d, *J* = 23.3 Hz).

**4-Chlorophenol (2m)**[4a]

Yield: 103 mg (80%); white solid; mp 45–46 °C (EtOAc–PE).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.18–7.10 (m, 2 H), 6.82–6.66 (m, 2 H), 6.29 (s, 1 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 153.9, 129.5, 125.6, 116.7.

**4-Bromophenol (2n)**[5i]

Yield: 152 mg (88%); colorless solid; mp 65–66 °C (EtOAc–PE).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.27 (m, 2 H), 6.77–6.68 (m, 2 H), 6.13 (s, 1 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 154.6, 132.4, 117.2, 112.8.

**2-Iodophenol (2o)**[5e]

Yield: 176 mg (80%); colorless solid; mp 43–44 °C (EtOAc–PE).



$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.65 (dd, *J* = 7.9, 1.5 Hz, 1 H), 7.32–7.16 (m, 1 H), 6.99 (dd, *J* = 8.1, 1.4 Hz, 1 H), 6.67 (td, *J* = 7.8, 1.4 Hz, 1 H), 5.29 (s, 1 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 154.8, 1383, 130.2, 122.4, 115.2, 85.7.

**4-Hydroxybenzaldehyde (2p)**[4a]
Yield: 115 mg (94%); yellowish solid; mp 113–115 °C (EtOAc–PE).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 9.87 (s, 1 H), 7.82 (d, *J* = 8.7 Hz, 2 H), 6.98 (d, *J* = 8.6 Hz, 2 H), 6.34 (s, 1 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 191.3, 161.7, 132.5, 129.8, 116.0.

**4-Acetylphenol (2q)**[5i]
Yield: 124 mg (91%); white solid; mp 107–108 °C (EtOAc–PE).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.09 (br, 1 H), 7.92 (d, *J* = 8.6 Hz, 2 H), 6.96 (d, *J* = 8.6 Hz, 2 H), 2.59 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 198.7, 161.5, 131.2, 129.5, 115.6, 26.3.

**Phenol (2r)**[4a]
Yield: 79 mg (84%); white solid; mp 40–41 °C (EtOAc–PE).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.24 (t, *J* = 7.7 Hz, 2 H), 6.93 (t, *J* = 7.4 Hz, 1 H), 6.86–6.80 (m, 2 H), 5.13 (br, 1 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 155.4, 129.7, 120.8, 115.3.

**1,3-Diphenyl-2,3-epoxypropan-1-one (5)**[12]
A mixture of hydroquinone (110 mg, 1 mmol), the α,β-unsaturated ketone **4** (208 mg, 1 mmol), and KOH (168 mg, 3.0 mmol) in 1:1 $H_2O$–DMF (5 mL) was stirred at 60 °C under open air for 10 h. After complete consumption of **4** (monitored by TLC, eluent: PE–EtOAc, 20:1), the reaction was quenched carefully by the addition of aq 2 M HCl (15 mL). The resulting mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with $H_2O$ (30 mL) and brine (10 mL) and dried ($Na_2SO_4$). After the removal of the solvent, the resulting residue was purified by chromatography (silica gel, 5% EtOAc in PE) to give **5** as a colorless solid; yield: 78 mg (35%); mp 84–85 °C (EtOAc–PE).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.02 (ddd, *J* = 5.3, 3.1, 1.2 Hz, 2 H), 7.65–7.60 (m, 1 H), 7.53–7.47 (m, 2 H), 7.44–7.36 (m, 5 H), 4.30 (d, *J* = 1.9 Hz, 1 H), 4.08 (d, *J* = 1.9 Hz, 1 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 193.1, 135.5, 134.0, 129.1, 129.0, 128.9, 128.8, 128.4, 125.8, 61.0, 59.4.

## Acknowledgment

This work was supported by National Natural Science Foundation of China (21202048), Program for Minjiang Scholar (10BS216), Science Research Item of Science and Technology of Xiamen City (3502z201014), the Natural Science Foundation of Fujian Province, China (2013J01050), and Promotion Program for Young and Middle-aged Teacher in Science and Technology Research of Huaqiao University (ZQN-PY120).

**Supporting Information** for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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