Supporting Information
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Supporting information

Metal-free [3+2] Oxidative Coupling of Phenols with Alkenes:

Synthesis of Dihydrobenzofurans

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1. General information

All reagents were purchased from commercial sources unless otherwise noted. Substituted styrenes were prepared following standard literature procedures[1]. Solvents were dried according to standard procedures prior to use. $^1$H NMR (400MHz) and $^{13}$C NMR (100 MHz) spectra are recorded on a Bruker AV-400 spectrometer in CDCl$_3$. For $^1$H NMR (400MHz), tetramethylsilane (TMS) served as internal standard ($\delta = 0$ ppm) and data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (in Hz), and integration. For $^{13}$C NMR (100 MHz), CDCl$_3$ was used as internal standard ($\delta = 77.23$ ppm) and spectra were obtained with complete proton decoupling. HR-MS spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization.

2. Procedure for the scale up synthesis of corsifuran A

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{OTMS} & \quad \text{OTMS} \\
1a, 500\text{mg} & \quad 2f & \quad \text{Na}_2\text{S}_2\text{O}_8 \\
\end{align*}
\]

\[50^\circ\text{C} \quad \text{MeCN} \]

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{OTMS} & \quad \text{OTMS} \\
1a, 500\text{mg} & \quad 2f & \quad \text{Na}_2\text{S}_2\text{O}_8 \\
\end{align*}
\]

In an oven-dried 100 mL round bottom flask equipped with magnetic stir bar, Na$_2$S$_2$O$_8$ and 1a was combined. Then the reaction flask was allowed to be vacuumed and charged with nitrogen, added 2f dissolving in MeCN under nitrogen, and then heating to 50 $^\circ$C. After reaction for 72h, the resulting mixture was cooled to room temperature, washed twice with water. Extracted the aqueous layer with EtOAc. Then combined the organic phase, dried over MgSO$_4$, filtered and concentrated. The oil residue was then purified by flash column chromatography to give the final product.

Under this standard reaction conditions, we also tested many other substituted phenols and alkenes (Table S1). However, no desired cyclization products have been obtained
in the systems of styrene and \( p \)-Cl, \( p \)-Me substituted phenol (3ca and 3da). Phenols with \( m \)- and \( o \)-methoxyl groups did not provide the cyclization products either (3ea or 3fa). Aliphatic unsaturated compounds with C-C double bond were also applied to

**Table S1: Additional testing scope of phenols and alkenes**

<table>
<thead>
<tr>
<th>Phenols</th>
<th>Alkenes</th>
</tr>
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<tbody>
<tr>
<td>3ca, 0 %</td>
<td>3ap, 0 %</td>
</tr>
<tr>
<td>3da, 0 %</td>
<td>3aq, 0 %</td>
</tr>
<tr>
<td>3ea, 0 %</td>
<td>3ar, 0 %</td>
</tr>
<tr>
<td>3fa, 0 %</td>
<td>3as, 0 %</td>
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<tr>
<td></td>
<td>3at, 0 %</td>
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<tr>
<td></td>
<td>3au, 0 %</td>
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<tr>
<td></td>
<td>3av, 0 %</td>
</tr>
<tr>
<td></td>
<td>3aw, 0 %</td>
</tr>
<tr>
<td></td>
<td>3ax, 0 %</td>
</tr>
<tr>
<td></td>
<td>3ay, &lt;5 % ![h]</td>
</tr>
<tr>
<td></td>
<td>3az, &lt;5 %</td>
</tr>
</tbody>
</table>
All reactions were performed with 1 (0.15 mmol), 2 (0.6 mmol), Na₂S₂O₈ (0.45 mmol) in MeCN (0.1 M), unless otherwise noted. Isolated yields.

this cyclization reaction, but no detecting of desired products as a result (3ap, 3aq and 3ar). Moreover, we examined styrenes bearing electron-withdrawing groups at β-position of double bond. No desired product has been detected in this reaction system (3as, 3at and 3au). When heterocycle compounds such as benzothiophene and indole were subjected to this reaction system, no cycloadducts were observed (3aw and 3ax). α- or β- Di-substituted alkenes and 3,5-di-methoxyl styrene provided trace to no cyclization products (3av, 3ay and 3az).

3. The Procedure for Radical Trapping Experiment

To a 10 mL round bottom flask equipped with magnetic stir bar was charged with TMS protected phenols (0.15 mmol), alkenes (0.6 mmol), Na₂S₂O₈ (0.45 mmol), TEMPO (1.5eq, 0.22 mmol) and dried CH₃CN (1.5 mL). Then the flask was allowed to be vacuumed, purged with nitrogen for three times and heated at 50°C for reaction. After 72h, the reaction system was filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography to give a small amount of 3aa and other two by-products which were unconcern with TEMPO.
4. $^1$H and $^{13}$C NMR spectra