We describe the convergent paired electrolysis of methylarene derivatives and 1,4-dicyanoarenes to perform the arylative functionalization of a benzylic C(sp³)–H bond to form 1,1-biarylmethane derivatives that are found in several drugs and biologically active compounds. This electrochemical process proceeds via the coupling of a benzylic radical or a benzylic carbocation with a 1,4-dicyanoarene radical anion to form the desired C–C bond followed by elimination of the cyanide anion which could be trapped as a cyanhydrin by an aldehyde. These reactive species are produced, respectively, by the oxidation of the benzylic substrate at the anode and the reduction of the dicyanoarene at the cathode. One of the key challenges that we have overcome is avoiding the formation of overoxidized coupling products at the bis-benzylic position of the biarylmethane products obtained.

Indeed, the anodic oxidation of biarylmethane derivatives delivered a particularly stabilized carbocation in which an electron-rich arene could be added during the electrolysis in a few cases or in the absence of electric current (cation-pool method) to deliver triarylmethane derivatives. Anodically generated less stable benzylic carbocations from monoaryl-methane derivatives could be trapped in situ by a stabilizing agent during the electrolysis and then an electron-rich arene could be added to deliver biarylmethanes (stabilized cation pool method). Electrogeneated benzylic radicals could also react in a Minisci-type process with heteroarenes to achieve a C–H bond functionalization of the latter.

On the other hand, the electrochemical nickel-catalysed arylation of electron-rich primary benzylic C(sp³)–H bonds with electron-deficient arylbromides were deployed in a paired-elec-

![Scheme 1](https://doi.org/10.1039/d3gc00866e)

**Scheme 1** The proposed electrochemical benzylic arylation via convergent paired electrolysis.
trolysis process via the reductive regeneration of the nickel catalyst at the cathode.\(^\text{11}\)

Electron-deficient aryl nitrile derivatives appeared to be pertinent partners to develop a benzylic arylation via convergent paired electrolysis\(^\text{4a}\) and related transformations have been achieved under photochemical irradiation.\(^\text{12}\)

The cathodic reduction of an electron-deficient aryl nitrile 3, such as 1,4-dicyanobenzene, is known to produce a persistent radical-anion B, which could add to a radical or an electrophilic species.\(^\text{13,14}\) Indeed, such a concept has been recently employed in convergent paired electrolysis involving the arylation of electron-deficient intermediates produced by anodic oxidation,\(^\text{15}\) such as the α-arylation of amine,\(^\text{15a,b}\) alkenes,\(^\text{15b}\) benzyl alcohol\(^\text{15c}\) and benzyl ethers,\(^\text{15d}\) the decarboxylative arylation of carboxylic acid\(^\text{15b}\) and the deboronative arylation of trifluoroborate salts.\(^\text{15b}\) In addition, the α-hydroxylation-α-arylation of benzyl C(sp\(^3\))–H substrates to afford 5 has also been very recently reported via preliminary oxidation into a benzyl alcohol.\(^\text{16}\)

Therefore, it appears that the present challenge would be to favour the coupling of the persistent aryl nitrile radical anion with the transient benzyl radical over the evolution of the latter into the corresponding benzyl alcohol that could lead to oxidized products 5 or 6.\(^\text{16,17}\) Indeed, conducting the reaction in the absence of water or oxygen should prevent the evolution of A into a benzyl alcohol or ketone leading to 5 or 6. However, the risk is that the highly reactive benzyl radical A and the corresponding carbocation resulting from further anodic oxidation would be involved in undesired reaction processes instead of reacting with the radical anion B.

**Results and discussion**

To test the feasibility of this approach, we selected ethylbiphenyl 1a and 1,4-dicyanobenzene 3a as substrates to generate 4a (Table 1).

Upon evaluation of the parameters of the reaction, the optimal conditions appear to be those of the electrolysis in an undivided cell at a constant current of 6.2 mA cm\(^{-2}\) with a graphite anode and a nickel cathode in a 1 : 1 mixture of acetonitrile and THF with tetrabutylammonium tosylate as the electrolyte and pivaldehyde as a trap for the released cyanide ion at room temperature; a 58% yield of 4a was obtained from equimolar amounts of 1a and 3a (entry 1 with 19% recovery of 1a) while 60% yield was obtained with an excess of 1a (entry 2). Performing the reaction under argon is critical since under air, only 12% of 4a was obtained along with 47% of unreacted 1a with 14% and 4% ketone 7a and benzyl alcohol 8a, respectively, which are supposedly the products of the reaction of benzyl radical A with oxygen (entry 3). In the absence of pivaldehyde as a scavenger for the toxic cyanide ion, the yield diminished to 48% (entry 4). The screening of solvents indicated that the association of THF and acetonitrile indeed played a crucial role in this electrochemical arylation protocol. Lower yields were obtained when pure acetonitrile (47% of 1a recovered) or THF (85% recovery of 1a) were used (entries 5 and 6). Interestingly, replacing THF by 2-MeTHF resulted in a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Deviation from standard conditions(^a)</th>
<th>Yield 4a (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>58%</td>
</tr>
<tr>
<td>2</td>
<td>2 equiv. of 1a</td>
<td>60%</td>
</tr>
<tr>
<td>3</td>
<td>Under air instead of argon</td>
<td>12%(^c)</td>
</tr>
<tr>
<td>4</td>
<td>No t-BuCHO</td>
<td>48%</td>
</tr>
<tr>
<td>5</td>
<td>CH(_3)CN instead of THF/CH(_3)CN (1 : 1), no t-BuCHO</td>
<td>27%</td>
</tr>
<tr>
<td>6</td>
<td>THF instead of CH(_3)CN (1 : 1), no t-BuCHO</td>
<td>8%</td>
</tr>
<tr>
<td>7</td>
<td>2Me-THF instead of THF, no t-BuCHO</td>
<td>22%(^d)</td>
</tr>
<tr>
<td>8</td>
<td>THF/CH(_3)CN (2 : 1) instead of (1 : 1), no t-BuCHO</td>
<td>44%</td>
</tr>
<tr>
<td>9</td>
<td>THF/CH(_3)CN (1 : 2) instead of (1 : 1), no t-BuCHO</td>
<td>46%</td>
</tr>
<tr>
<td>10</td>
<td>DMF instead of THF/CH(_3)CN (1 : 1), no t-BuCHO</td>
<td>39%</td>
</tr>
<tr>
<td>11</td>
<td>n-Bu(_2)NClO(_4) instead of n-Bu(_2)NOTs, no t-BuCHO</td>
<td>Traces</td>
</tr>
<tr>
<td>12</td>
<td>n-Bu(_2)NBF(_4) instead of n-Bu(_2)NOTs, no t-BuCHO</td>
<td>Traces</td>
</tr>
<tr>
<td>13</td>
<td>n-Bu(_2)NOT instead of n-Bu(_2)NOTs, no t-BuCHO</td>
<td>60%</td>
</tr>
<tr>
<td>14</td>
<td>Et(_2)NCl instead of n-Bu(_2)NOTs, no t-BuCHO</td>
<td>37%</td>
</tr>
<tr>
<td>15</td>
<td>C(+)\slash{C}(−) instead of C(+)\slash{Ni}(−), no t-BuCHO</td>
<td>37%</td>
</tr>
<tr>
<td>16</td>
<td>C(+)\slash{Pt}(−) instead of C(+)\slash{Ni}(−), no t-BuCHO</td>
<td>53%</td>
</tr>
<tr>
<td>17</td>
<td>Pt(+)\slash{Ni}(−) instead of C(+)\slash{Ni}(−), no t-BuCHO</td>
<td>Traces</td>
</tr>
</tbody>
</table>

\(^a\) Undivided cell, graphite-SK50 anode (1.5 cm × 0.8 cm × 0.2 cm submerged), nickel cathode (1.5 cm × 0.8 cm × 0.2 cm submerged), 7.5 mA, 6 F mol\(^{-1}\), 1a (0.2 mmol), 2a (0.2 mmol), n-Bu\(_2\)NOTs (0.2 mmol), 3 mL of CH\(_3\)CN/THF (1 : 1), room temperature, under an argon atmosphere. \(^b\) Isolated yield of 4a. \(^c\) 7a and 8a were obtained in 14% and 4% yields. \(^d\) 5a was obtained in 13% yield.
decrease in the yield and formation of undesired bisbenzylic alcohol \textit{5a} (entry 7). The ratio of THF and acetonitrile also had an influence on the yield (entries 8 and 9). DMF is also a suitable solvent and can promote the reaction but with a moderate yield of 39\% (entry 10), while other solvents, such as DMA, NMP or DMSO, are ineffective (see the ESI†). The nature of the electrolyte was critical, particularly that of the anion, since replacing the tosylate anion of \textit{n-Bu}NO\textsubscript{T}s by a perchlorate, a tetrafluoroborate or a triflate led to almost no formation of the desired product, which is explained by the non-reactivity of \textit{1a} (entries 11–13). On the other hand, the tetrabutylammonium cation could be substituted by a tetraethylammonium cation with a moderately decreased yield (entry 14). The effect of the material of the electrodes was also investigated. Replacing nickel with graphite at the cathode was less effective affording a 37\% yield, while a more expensive platinum cathode led only to trace amounts of \textit{4a} due to very poor conversion of \textit{1a} (entry 17). It should be noted that the use of an electrochemical mediator to generate the benzylic radical \textit{A} was ineffective (see the ESI†).

Overall, we were able to attain our goal, \textit{i.e.} the arylation of benzylic C(sp\textsuperscript{3})–H bonds without overoxidation or other undesired reactions.

We then studied the scope of this benzylic arylation with \textit{para}-dicyanobenzene (Scheme 2).

We began by aryling secondary benzylic positions. In addition to \textit{para}-ethylbiphenyl \textit{1a}, \textit{para}-substituted ethyl benzene derivatives were able to deliver the desired targets in modest yields for the \textit{para}-bromo bipenyl \textit{4b} but with more success with electron-donating groups, such as \textit{para}-methoxy \textit{4c} or \textit{para}-ethyl \textit{4d}. Symmetrical \textit{ortho}-ethyl benzene also led to the arylated product \textit{4e}. We further showed the compatibility of this benzylic electrochemical arylation with \textit{para}-methoxy alkyl benzenes bearing a functional group on the alkyl chain, such as a protected alcohol (\textit{4f}), an ester (\textit{4g}) or a ketone (\textit{4h}). The reaction proceeded affording a modest yield in the presence of a tosyl amide on the ethyl chain (\textit{4i}). Cyclic substrates fused with the aromatic ring proved to be amenable for producing the desired arylation products, such as indane \textit{4j}, and tetrahydro-naphthalene derivatives \textit{4k} and \textit{4l}. The tertiary benzylic position of iso-propyl-biphenyl could also be arylated (\textit{4m}) albeit in moderate yield probably due to steric hindrance. The primary benzylic position of \textit{para}-substituted toluene derivatives is also prone to react with the formation of \textit{para}-methyl, \textit{t}-butyl and methoxy biaryl methane products \textit{4n–p}. \textit{Para}-Ethyl toluene reacts mainly to afford the ethyl-substituted compound (\textit{4q}) over the methyl-substituted compound (\textit{4r}), which could be explained by the stabilisation of the secondary radical being favoured over the primary one. It should be noted that in some cases (\textit{4c,d,j,k} and \textit{4n–p}), a minor amount of the \textit{ortho}-substituted arylation product relative to the cyanobenzene part has been formed, as it has been observed previously.\textsuperscript{1ae} Subsequently, \textit{1,4}-dicyanobenzene derivatives, which have an additional substituent such as a cyano group (\textit{4s}), and hetero-aromatic substituents (benzofuran and thiophene) (\textit{4t} and \textit{4u}), could also deliver the arylation products as a mixture of two regioisomers from \textit{para}-ethylbiphenyl.

This protocol could be scaled-up to provide almost 1 g of \textit{4a} in 67\% yield, which proved the synthetic utility of this protocol (Scheme 3). In order to shorten the reaction time, the current density and concentration were increased compared to the standard conditions.

From a mechanistic point of view, cyclic voltammetry results show that the oxidation potential of 4-ethylbiphenyl \textit{1a} in a mixture of THF and acetonitrile is sharply lower than that of \textit{1,4}-dicyanobenzene (Fig. 2), which indeed implies that the benzyl substrate is preferentially oxidized directly at the anode. In the cathodic process, \textit{1,4}-dicyanobenzene displays a reduction peak, which is reversible and corresponds to the formation of the persistent radical anion \textit{B}, while the benzyl substrate is not reduced in the range studied as well as pivaldehyde.
In addition, we demonstrated that the benzylic substrate 1a is oxidized at a lower potential than the obtained 1,1-biaryl-ethane product 4a (Fig. 2) and this explains why we do not observe any noticeable amount of 5.

We performed a competitive experiment between 1a and its bisbenzylic deuterated analogue 1a-d2 (Scheme 4), which resulted in a 2.8/1 ratio of 4a and 4a-d corresponding to a primary KIE similar to a previously reported anodic benzylic functionalization.1e

Based on this study and previous works, the following mechanisms are proposed involving a convergent paired-electrolysis process (Scheme 5).15,16 The benzylic substrate 1 is presumably oxidized directly at the anode to the radical cation.

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**Scheme 3** Scale-up experiment. Reaction conditions: an undivided cell, a graphite-SK50 anode (3 cm × 0.8 cm × 0.2 cm submerged), a nickel cathode (3 cm × 0.8 cm × 0.2 cm submerged), 37.5 mA, 6 F mol⁻¹, 1a (10 mmol), 2a (5 mmol), n-Bu₄NOTs (5 mmol), 12 mL of CH₃CN/THF (1:1), room temperature, under an argon atmosphere.

**Scheme 4** The competitive experiment between 1a and 1a-d2.

**Scheme 5** The proposed mechanism of the convergent paired electrolysis of benzylic substrates and dicyanoarenes.

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**Fig. 2** Cyclic voltammetry studies of the reactants of the electrochemical benzylic arylation. CV scans were performed using a glassy carbon disk (d = 3 mm) as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl electrode as the reference electrode at a scan rate of 0.1 V s⁻¹ at 20 °C in 5 mL of a 2 mM solution of each substrate and 0.1 M of n-Bu₄N·BF₄ in a 1:1 mixture of THF and acetonitrile.
C. Upon the elimination of a proton, the transient benzylic radical A could be generated. On the other hand, the cathodic reduction of 3a produces a persistent radical anion B. According to previously proposed mechanisms of related transformations, the radical anion B could react with the transient benzylic radical A via radical-radical recombination to form the desired C-C bond and the anionic intermediate D (path a). The desired arylated benzylic product could be obtained via aromatization through the elimination of a cyanide ion, which could be trapped by pivaldehyde to probably yield cyanohydrin 9.

Nevertheless, it is more plausible that before leaving the double layer and reacting with a radical anion B, benzylic radical A could rapidly be oxidized at the anode into the corresponding benzylic carbocation E.

Upon its diffusion into the solution, the carbocation E could react with the radical anion B leading to the zwiterionic radical F that could evolve into radical G via a fast intramolecular electron transfer. Either radical F or G could be reduced by the radical anion B into anion D with the regeneration of 1,4-dicyanoarene 3 (path b).

The role of a tosylate as the counter-anion of the tetrabutylammonium electrolyte is the key to the success of the reaction. It might be explained by its basicity, which helps in eliminating a proton from the radical cation C. In addition, the benzylic carbocation E (in the case of path b) might also be trapped by the tosylate anion to form the rather stable benzylic tosylate 10.

Conclusions

In conclusion, we report the direct electrochemical arylation of benzylic C(sp3)–H bonds via a convergent paired electrolysis. We merged the anodic benzylic C–H bond oxidation and the cathodic reduction of dicyanobenzenes to produce two reactive intermediates that can merge to form the desired biaryl-methane derivatives 4.

Conflicts of interest

There are no conflicts to declare.

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