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Benzylic C–H arylation with dicyanoarenes *via* convergent paired electrolysis†

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We describe the convergent paired electrolysis of methylarene derivatives and 1,4-dicyanoarenes to perform the arylative functionalization of a benzylic $C(sp^3)$–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.
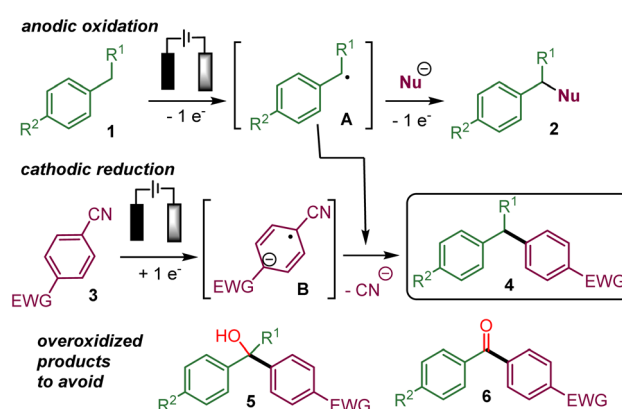
Introduction

In recent years, several electrochemical methods for the functionalization of benzylic $C(sp^3)$–H bonds have been reported that form C–N, C–O, C–halogen or even C–C bonds.[1,2] These processes usually involve the oxidation of the benzylic position of **1** directly at the anode *via* single electron transfers (SET) or indirectly with an electro mediator. The resulting benzylic radical **A** could react with a radical acceptor or be further oxidized into a carbocation that could be intercepted by a nucleophile already present in the reaction media to yield **2** (Scheme 1).

For example, we have performed the addition of an isocyanide to the electrogenerated benzylic carbocation.[3] Most of the time, the cathodic counter-reaction, such as the reduction of protons into hydrogen, does not produce species reacting with the benzylic substrate. An attractive refinement of the electrochemical benzylic $C(sp^3)$–H functionalization would be to take advantage of the cathodic reduction to generate a nucleophilic intermediate that would add to the anodically oxidized benzylic substrate in a convergent paired-electrolysis process.[4]

In this context, we turned our attention to developing an electrochemical benzylic arylation using this concept to form the 1,1-biarylmethane motif,[5] which can be found in several drugs or biologically active compounds such as diisopromine, fenpiprane, prozapine, fendilline, milverine, indatraline, sertraline and elvitegravir among others (Fig. 1).[5,6]

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[7] or in the absence of electric current (cation-pool method)[8] to deliver triarylmethane derivatives. Anodically generated less stable benzylic carbocations from monoarylmethane 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).[9] Electrogenerated benzylic radicals could also react in a Minisci-type process with heteroarenes to achieve a C–H bond functionalization of the latter.[10]

On the other hand, the electrochemical nickel-catalysed arylation of electron-rich primary benzylic $C(sp^3)$–H bonds with electron-deficient arylbromides were deployed in a paired-elec-

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Scheme 1 The proposed electrochemical benzylic arylation *via* convergent paired electrolysis.
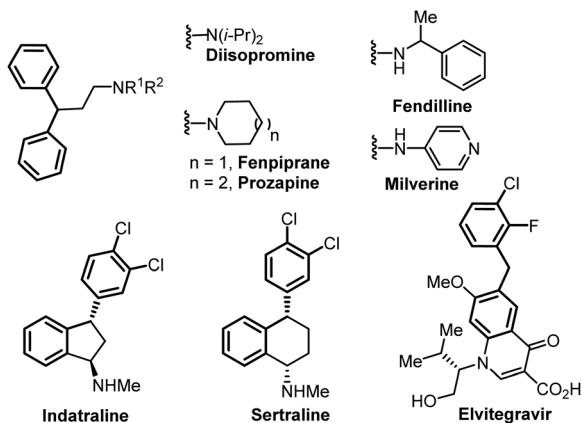
Fig. 1 Biologically active compounds containing a 1,1-diarylmethane motif.

trolysis process *via* the reductive regeneration of the nickel catalyst at the cathode.[11]

Electron-deficient aryl nitrile derivatives appeared to be pertinent partners to develop a benzylic arylation *via* convergent paired electrolysis[4a] and related transformations have been achieved under photochemical irradiation.[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.[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,[15] such as the α-arylation of amines,[15a,b] alkenes,[15b] benzylic alcohols[15c] and benzylic ethers,[15d] the decarboxylative arylation of carboxylic acid[15b] and the deboronative arylation of trifluoroborate salts.[15b] In addition, the α-hydroxylation-α-arylation of benzylic C(sp^3)–H substrates to afford **5** has also been very recently reported *via* preliminary oxidation into a benzylic alcohol.[16]
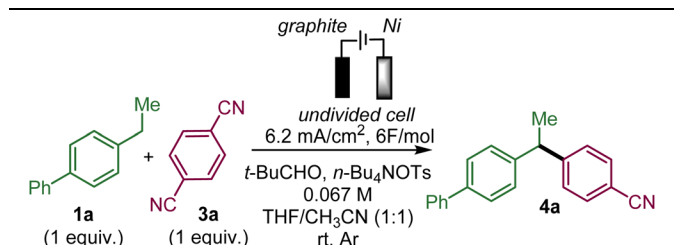
Therefore, it appears that the present challenge would be to favour the coupling of the persistent aryl nitrile radical anion with the transient benzylic radical over the evolution of the latter into the corresponding benzylic alcohol that could lead to overoxidized products **5** or **6**.[16,17] Indeed, conducting the reaction in the absence of water or oxygen should prevent the evolution of **A** into a benzylic alcohol or ketone leading to **5** or **6**. However, the risk is that the highly reactive benzylic 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).
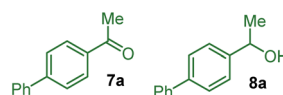
Upon evaluation of the parameters of the reaction, the optimal conditions appear to be those of the electrolysis in an

Table 1 Optimisation of the electrochemical reaction between ethylbiphenyl and 1,4-dicyanobenzene

Entry	Deviation from standard conditions[a]	Yield **4a**[b]
1	None	58%
2	2 equiv. of **1a**	60%
3	Under air instead of argon	12%[c]
4	No *t*-BuCHO	48%
5	CH$_3$CN instead of THF/CH$_3$CN (1 : 1), no *t*-BuCHO	27%
6	THF instead of THF/CH$_3$CN (1 : 1), no *t*-BuCHO	8%
7	2Me-THF instead of THF, no *t*-BuCHO	22%[d]
8	THF/CH$_3$CN (2 : 1) instead of (1 : 1), no *t*-BuCHO	44%
9	THF/CH$_3$CN (1 : 2) instead of (1 : 1), no *t*-BuCHO	46%
10	DMF instead of THF/CH$_3$CN (1 : 1), no *t*-BuCHO	39%
11	*n*-Bu$_4$NClO$_4$ instead of *n*-Bu$_4$NOTs, no *t*-BuCHO	Traces
12	*n*-Bu$_4$NBF$_4$ instead of *n*-Bu$_4$NOTs, no *t*-BuCHO	Traces
13	*n*-Bu$_4$NOTf instead of *n*-Bu$_4$NOTs, no *t*-BuCHO	0%
14	Et$_4$NOTs instead of *n*-Bu$_4$NOTs, no *t*-BuCHO	37%
15	C(+)/C(−) instead of C(+)/Ni(−), no *t*-BuCHO	37%
16	C(+)/Pt(−) instead of C(+)/Ni(−), no *t*-BuCHO	53%
17	Pt(+)/Ni(−) instead of C(+)/Ni(−), no *t*-BuCHO	Traces

[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$_4$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.

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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
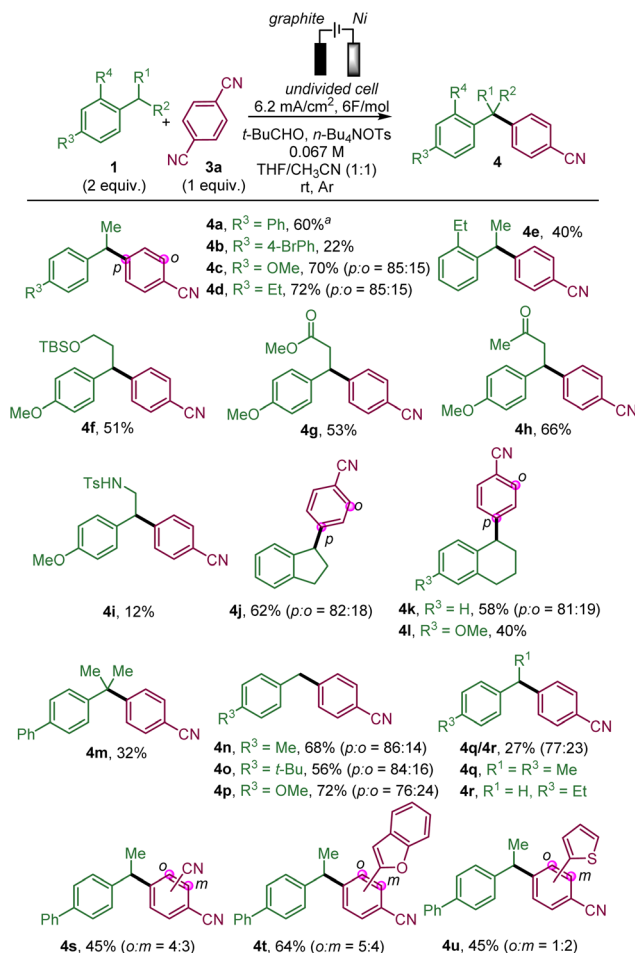
decrease in the yield and formation of undesired bisbenzylic alcohol **5a** (entry 7). The ratio of THF and acetonitrile also had an influence on the yield (entries 8 and 9). DMF is also a suitable solvent and can promote the reaction but with a moderate yield of 39% (entry 10), while other solvents, 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 *n*-BuNOTs 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 **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 afforded a similar yield of 53% (entries 15 and 16). On the other hand at the anode, switching graphite to platinum led only to trace amounts of **4a** due to very poor conversion of **1a** (entry 17). It should be noted that the use of an electrochemical mediator to generate the benzyl radical **A** was ineffective (see the ESI†).

Overall, we were able to attain our goal, *i.e.* the arylation of benzylic C(sp³)–H bonds without overoxidation or other undesired reactions.

We then studied the scope of this benzylic arylation with *para*-dicyanobenzene (Scheme 2).

We began by arylating secondary benzylic positions. In addition to *para*-ethylbiphenyl **1a**, *para*-substituted ethyl benzene derivatives were able to deliver the desired targets in modest yields for the *para*-bromo bipenyl **4b** but with more success with electron-donating groups, such as *para*-methoxy **4c** or *para*-ethyl **4d**. Symmetrical *ortho*-ethyl benzene also led to the arylated product **4e**. We further showed the compatibility of this benzylic electrochemical arylation with *para*-methoxy alkyl benzenes bearing a functional group on the alkyl chain, such as a protected alcohol (**4f**), an ester (**4g**) or a ketone (**4h**). The reaction proceeded affording a modest yield in the presence of a tosyl amide on the ethyl chain (**4i**). Cyclic substrates fused with the aromatic ring proved to be amenable for producing the desired arylation products, such as indane **4j**, and tetrahydronaphthalene derivatives **4k** and **4l**. The tertiary benzylic position of iso-propyl-biphenyl could also be arylated (**4m**) albeit in moderate yield probably due to steric hindrance. The primary benzylic position of *para*-substituted toluene derivatives is also prone to react with the formation of *para*-methyl, *t*-butyl and methoxy biarylmethane products **4n–p**. *para*-Ethyl toluene reacts mainly to afford the ethyl-substituted compound (**4q**) over the methyl-substituted compound (**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 (**4c,d,j,k** and **4n–p**), a minor amount of the *ortho*-substituted arylation product relative to the cyanobenzene part has been formed, as it has been observed previously.[14e] Subsequently, 1,4-dicyanobenzene derivatives, which have an additional substituent such as a cyano group (**4s**), and hetero-

Scheme 2 Electrochemical benzylic arylation with dicyanoarenes *via* convergent paired electrolysis. Reaction conditions: an undivided cell, a graphite-SK50 anode (1.5 cm × 0.8 cm × 0.2 cm submerged), a nickel cathode (1.5 cm × 0.8 cm × 0.2 cm submerged), 7.5 mA, 6 F mol⁻¹, **1a** (0.4 mmol), **2a** (0.2 mmol), *n*-Bu₄NOTs (0.2 mmol), 3 mL of CH₃CN/THF (1:1), room temperature, under an argon atmosphere; isolated yield of **4**; *a* 55% yield on a 1 mmol scale.

aromatic substituents (benzofurane and thiophene) (**4t** and **4u**), could also deliver the arylation products as a mixture of two regioisomers from *para*-ethylbiphenyl.

This protocol could be scaled-up to provide almost 1 g of **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 **1a** in a mixture of THF and acetonitrile is sharply lower than that of 1,4-dicyanobenzene (Fig. 2), which indeed implies that the benzylic substrate is preferentially oxidized directly at the anode. In the cathodic process, 1,4-dicyanobenzene displays a reduction peak, which is reversible and corresponds to the formation of the persistent radical anion **B**, while the benzylic substrate is not reduced in the range studied as well as pivaldehyde.
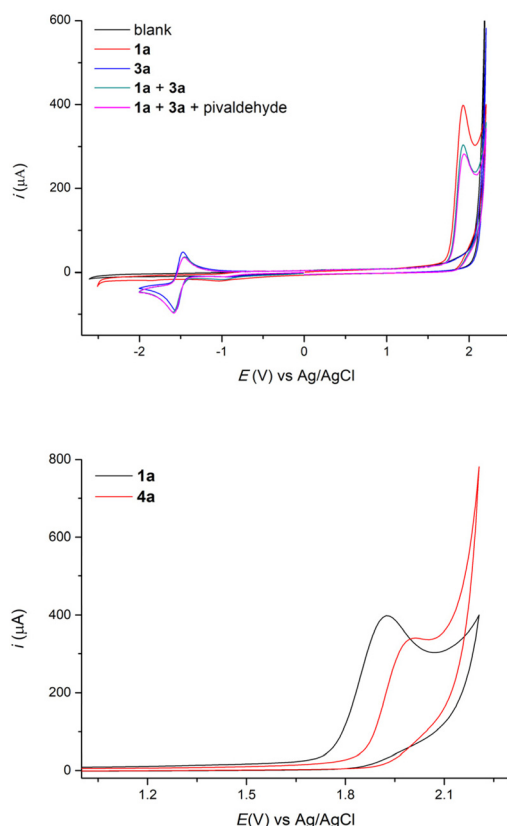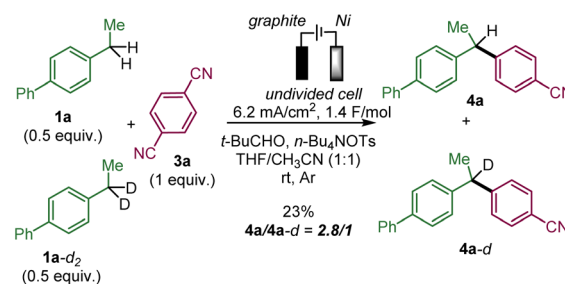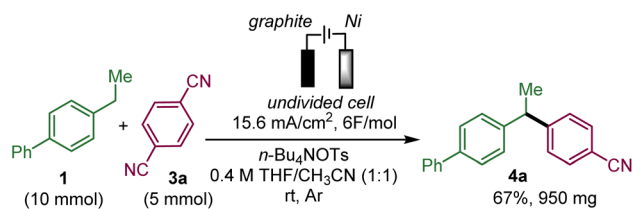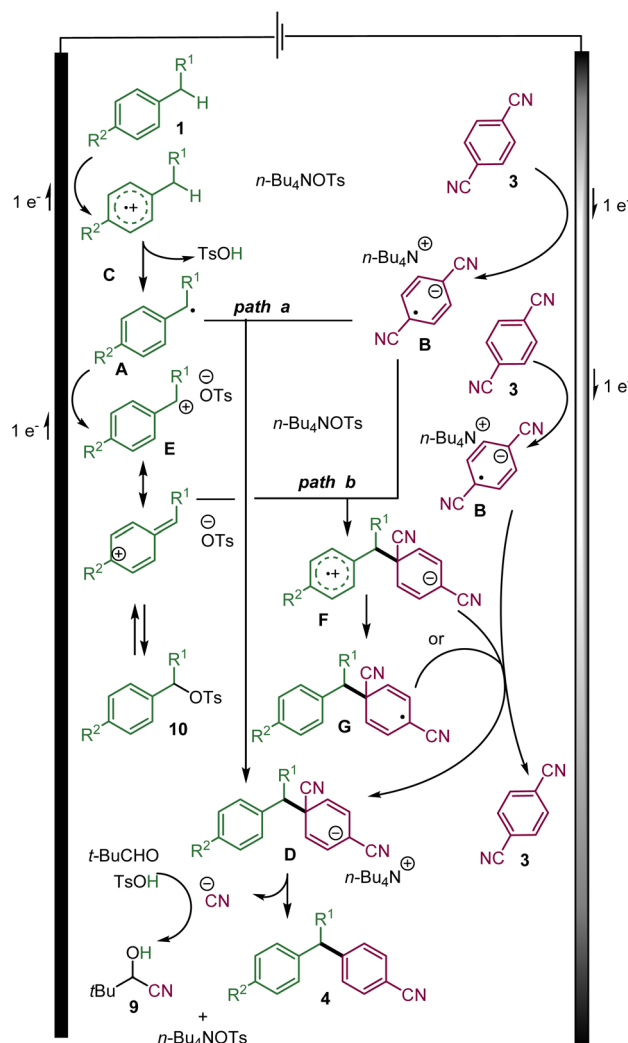
Scheme 3 Scale-up experiment. Reaction conditions: an undivided cell, a graphite-SK50 anode (3 cm × 0.8 cm × 0.2 cm submerged), a nickel cathode (3 cm × 0.8 cm × 0.2 cm submerged), 37.5 mA, 6 F mol^{-1}, **1a** (10 mmol), **2a** (5 mmol), n-Bu$_4$NOTs (5 mmol), 12 mL of CH$_3$CN/THF (1:1), room temperature, under an argon atmosphere.

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-Bu$_4$N·BF$_4$ in a 1:1 mixture of THF and acetonitrile.

In addition, we demonstrated that the benzylic substrate **1a** is oxidized at a lower potential than the obtained 1,1-biarylethane 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-d**2 (Scheme 4), which resulted in a 2.8/1 ratio of **4a** and **4a-d** corresponding to a

Scheme 4 The competitive experiment between **1a** and **1a-d$_2$**.

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

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

C.[1e] 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,[15,16] the radical anion **B** could react with the transient benzyl 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**.[1e,3]

Upon its diffusion into the solution, the carbocation **E** could react with the radical anion **B** leading to the zwitterionic 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(sp^3)–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 biarylmethane derivatives **4**.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

References

1 For a review, see: (*a*) M. Oliva, G. A. Coppola, E. V. V. der Eycken and U. K. Sharma, *Adv. Synth. Catal.*, 2021, **363**, 1810–1834. For selected examples of C–N bonds, see: (*b*) T. Morofuji, A. Shimizu and J. Yoshida, *J. Am. Chem. Soc.*, 2014, **136**, 4496–4499; (*c*) R. Hayashi, A. Shimizu, Y. Song, Y. Ashikari, T. Nokami and J. Yoshida, *Chem. – Eur. J.*, 2017, **23**, 61–64; (*d*) L. Niu, C. Jiang, Y. Liang, D. Liu, F. Bu, R. Shi, H. Chen, A. D. Chowdhury and A. Lei, *J. Am. Chem. Soc.*, 2020, **142**, 17693–17702; (*e*) Z.-W. Hou, D.-J. Liu, P. Xiong, X.-L. Lai, J. Song and H.-C. Xu, *Angew. Chem., Int. Ed.*, 2021, **60**, 2943–2947; (*f*) T. Shen and T. H. Lambert, *J. Am. Chem. Soc.*, 2021, **143**, 8597–8602; (*g*) Y. Yu, X.-B. Zhu, Y. Yuan and K.-Y. Ye, *Chem. Sci.*, 2022, **13**, 13851–13856. C–O bonds: (*h*) Y. Ashikari, T. Nokami and J. Yoshida, *Org. Lett.*, 2012, **14**, 938–941; (*i*) H. Wang, K. Liang, W. Xiong, S. Samanta, W. Li and A. Lei, *Sci. Adv.*, 2020, **6**, eaaz0590. C–Halogen bonds: (*j*) T. Raju, K. Kulangiappar, M. A. Kulandainathan and A. Muthukumaran, *Tetrahedron Lett.*, 2005, **46**, 7047–7050; (*k*) M. Rafiee, F. Wang, D. P. Hruszkewycz and S. S. Stahl, *J. Am. Chem. Soc.*, 2018, **140**, 22–25. C–C bonds: (*l*) X.-H. Ho, S. Mho, H. Kang and H.-Y. Jang, *Eur. J. Org. Chem.*, 2010, 4436–4441; (*m*) N. Fu, L. Li, Q. Yang and S. Luo, *Org. Lett.*, 2017, **19**, 2122–2125; (*n*) Y.-Z. Yang, Y.-C. Wu, R.-J. Song and J.-H. Li, *Chem. Commun.*, 2020, **56**, 7585–7588; (*o*) Q. Zhang, X. Chang, L. Peng and C. Guo, *Angew. Chem., Int. Ed.*, 2019, **58**, 6999–7003.

2 For general reviews on benzylic C(sp^3)–H functionalization, see: (*a*) R. Yazaki and T. Ohshima, *Tetrahedron Lett.*, 2019, **60**, 151225; (*b*) R. Vanjari and K. N. Singh, *Chem. Soc. Rev.*, 2015, **44**, 8062–8096.

3 S. Tang, R. Guillot, L. Grimaud, M. R. Vitale and G. Vincent, *Org. Lett.*, 2022, **24**, 2125–2130.

4 For selected reviews, see: (*a*) A. Claraz and G. Masson, *ACS Org. Inorg. Au*, 2022, **2**, 126–147; (*b*) S. Zhang and M. Findlater, *Chem. – Eur. J.*, 2022, **28**, e202201152; (*c*) N. Sbei, T. Hardwick and N. Ahmed, *ACS Sustainable Chem. Eng.*, 2021, **9**, 6148–6169; (*d*) W. Zhang, N. Hong, L. Song and N. Fu, *Chem. Rec.*, 2021, **21**, 2574–2584; (*e*) F. Marken, A. J. Cresswell and S. D. Bull, *Chem. Rec.*, 2021, **21**, 2585–2600.

5 (*a*) Md. Belal, Z. Li, X. Lu and G. Yin, *Sci. China: Chem.*, 2021, **64**, 513–533; (*b*) T. Jia, P. Cao and J. Liao, *Chem. Sci.*, 2018, **9**, 546–559; (*c*) S. Mondal and G. Panda, *RSC Adv.*, 2014, **4**, 28317–28358.

6 D. Ameen and T. J. Snape, *MedChemComm*, 2013, **4**, 893–907.

7 (*a*) B. Wei, J.-H. Qin, Y.-Z. Yang, Y.-X. Xie, X.-H. Ouyang and R.-J. Song, *Org. Chem. Front.*, 2022, **9**, 816–821; (*b*) X. Chen, H. Liu, H. Gao, P. Li, T. Miao and H. Li, *J. Org. Chem.*, 2022, **87**, 1056–1064; (*c*) H. Gao, X. Chen, P.-L. Wang, M.-M. Shi, L.-L. Shang, H.-Y. Guo, H. Li and P. Li, *Org. Chem. Front.*, 2022, **9**, 1911–1916.

8 (a) M. Okajima, K. Soga, T. Nokami, S. Suga and J. Yoshida, *Org. Lett.*, 2006, **8**, 5005–5007; (b) T. Nokami, K. Ohata, M. Inoue, H. Tsuyama, A. Shibuya, K. Soga, M. Okajima, S. Suga and J. Yoshida, *J. Am. Chem. Soc.*, 2008, **130**, 10864–10865.

9 (a) R. Hayashi, A. Shimizu and J. Yoshida, *J. Am. Chem. Soc.*, 2016, **138**, 8400–8403; (b) Y. Imada, J. L. Röckl, A. Wiebe, T. Gieshoff, D. Schollmeyer, K. Chiba, R. Franke and S. R. Waldvogel, *Angew. Chem., Int. Ed.*, 2018, **57**, 12136–12140.

10 P. Xu, P.-Y. Chen and H.-C. Xu, *Angew. Chem., Int. Ed.*, 2020, **59**, 14275–14280.

11 (a) L. Zhang and X. Hu, *Chem. Sci.*, 2020, **11**, 10786–10791; (b) K.-J. Jiao, D. Liu, H.-X. Ma, H. Qiu, P. Fang and T.-S. Mei, *Angew. Chem., Int. Ed.*, 2020, **59**, 6520–6524.

12 (a) R. Bernardi, T. Caronna, S. Morrocchi, P. Traldi and B. M. Vittimberga, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1607–1609; (b) T. Hoshikawa and M. Inoue, *Chem. Sci.*, 2013, **4**, 3118–3123; (c) K. Qvortrup, D. A. Rankic and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2014, **136**, 626–629; (d) J. D. Cuthbertson and D. W. C. MacMillan, *Nature*, 2015, **519**, 74–77; (e) H. Tanaka, K. Sakai, A. Kawamura, K. Oisaki and M. Kanai, *Chem. Commun.*, 2018, **54**, 3215–3218.

13 For a review on the reductive and decyanative functionalization of cyanoarenes, see: S. Tong, K. Li, X. Ouyang, R. Song and J. Li, *Green Synth. Catal.*, 2021, **2**, 145–155.

14 (a) D. Lehnherr, Y. Lam, M. C. Nicastri, J. Liu, J. A. Newman, E. L. Regalado, D. A. DiRocco and T. Rovis, *J. Am. Chem. Soc.*, 2020, **142**, 468–478; (b) S. Zhang, L. Li, X. Li, J. Zhang, K. Xu, G. Li and M. Findlater, *Org. Lett.*, 2020, **22**, 3570–3575; (c) X. Zhang, C. Yang, H. Gao, L. Wang, L. Guo and W. Xia, *Org. Lett.*, 2021, **23**, 3472–3476; (d) H. Xu, J. Liu, F. Nie, X. Zhao and Z. Jiang, *J. Org. Chem.*, 2021, **86**, 16204–16212; (e) S. Zhang, W. Gao, J. Shi, J. Li, F. Li, Y. Liang, X. Zhan and M.-B. Li, *Org. Chem. Front.*, 2022, **9**, 1261–1266; (f) H.-J. Zhou and J.-M. Huang, *J. Org. Chem.*, 2022, **87**, 5328–5338; (g) W.-M. Zeng, Y.-H. He and Z. Guan, *Org. Lett.*, 2022, **24**, 7178–7182; (h) L. Yang, M. Sun, L. Cao, C. Liang, J. Yang, J. Yi, R. Cheng, Y. Ma and J. Ye, *Chem. Commun.*, 2022, **58**, 13345–13348; (i) W. Yu, S. Wang, M. He, Z. Jiang, Y. Yu, J. Lan, J. Luo, P. Wang, X. Qi, T. Wang and A. Lei, *Angew. Chem., Int. Ed.*, 2023, **62**, e202219166.

15 (a) Y. Ma, X. Yao, L. Zhang, P. Ni, R. Cheng and J. Ye, *Angew. Chem., Int. Ed.*, 2019, **58**, 16548–16552; (b) Y. Mo, Z. Lu, G. Rughoobur, P. Patil, N. Gershenfeld, A. I. Akinwande, S. L. Buchwald and K. F. Jensen, *Science*, 2020, **368**, 1352–1357; (c) S. Zhang, L. Li, J. Li, J. Shi, K. Xu, W. Gao, L. Zong, G. Li and M. Findlater, *Angew. Chem., Int. Ed.*, 2021, **60**, 7275–7282; (d) A. F. Zahrt, Y. Mo, K. Y. Nandiwale, R. Shprints, E. Heid and K. F. Jensen, *J. Am. Chem. Soc.*, 2022, **144**, 22599–22610.

16 X.-W. Wang, R.-X. Li, Y. Deng, M.-Q.-H. Fu, Y.-N. Zhao, Z. Guan and Y.-H. He, *J. Org. Chem.*, 2023, **88**, 329–340.

17 C. Yu, R. Huang and F. W. Patureau, *Angew. Chem., Int. Ed.*, 2022, **61**, e202201142.