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Scalable electrochemical synthesis of diaryliodonium salts†

Mohamed Elsherbini and Wesley J. Moran  *

Cyclic and acyclic diaryliodonium are synthesised by anodic oxidation of iodobiaryls and iodoarene/arene mixtures, respectively, in a simple undivided electrolysis cell in MeCN–HFIP–TfOH without any added electrolyte salts. This atom efficient process does not require chemical oxidants and generates no chemical waste. More than 30 cyclic and acyclic diaryliodonium salts with different substitution patterns were prepared in very good to excellent yields. The reaction was scaled-up to 10 mmol scale giving more than four grams of dibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (>95%) in less than three hours. The solvent mixture of the large-scale experiment was recovered (>97%) and recycled several times without significant reduction in yield.

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Introduction

Owing to their ready availability, low toxicity, unique chemical properties and structural diversity, hypervalent iodine reagents have found tremendous applications in organic synthesis.¹ Iodonium salts,² a class of hypervalent iodine reagents with two carbon ligands, have practical synthetic applications as oxidants,³ photosensitisers in photopolymerisation⁴ and electrophilic group transfer reagents in a wide range of metal-catalysed and metal-free cross coupling reactions,⁵ in addition to their medical and pharmaceutical applications.⁶ Diaryliodonium salts $Ar_2I^+X^-$ are, typically, highly stable compounds that have been extensively studied for over a century. Their high electrophilicity and the superior leaving group ability of iodoarenes stand behind their versatility as arylating agents for a wide range of nucleophiles.⁷ In addition, they serve as efficient aryne synthons.⁸ Furthermore, cyclic diaryliodonium salts provide a handle for the rapid construction of polycyclic heterocyclic and carbocyclic compounds of various classes.⁹

Over the long history of diaryliodonium salts, various synthetic routes have been developed and improved over time to achieve high levels of efficiency and selectivity.^{1a,7} Typically, the synthesis of diaryliodonium salts involves oxidation of iodoarenes to the corresponding λ^3 -iodanes followed by ligand exchange with arenes or organometallic arenes and anion exchange if necessary. Extended reaction cascades that involve initial iodination of arenes with molecular iodine are also known.¹⁰ The reaction sequence can be achieved stepwise or

in one-pot.¹¹ Most of these synthetic approaches to iodonium salts are under acidic conditions, although some neutral or basic conditions have been developed. In addition, synthesis under flow conditions has been achieved.¹²

Hypervalent iodine compounds are often lauded in the literature as mild, “green” reagents and are considered eco-friendly alternatives to various chemical oxidants, especially heavy metal oxidising agents. Unfortunately, syntheses typically require the utilisation of toxic and/or hazardous, and sometimes expensive, chemical oxidants, usually in large excess. This is accompanied by the generation of waste, which increases their ecological footprint and reduces the “greenness” of the overall process. This problem can, in theory, be alleviated by the development of electrochemical syntheses of hypervalent iodine reagents.¹³ Unsurprisingly, the electrochemical synthesis¹⁴ of hypervalent iodine reagents is a current hot topic,^{13,15} however the published methods for the electrochemical synthesis of diaryliodonium salts are scarce and suffer from limited substrate scopes and low current efficiencies. In addition, published procedures suffer from the formation of side products and complex mixtures as a result of the reaction medium; usually, a mixture of H_2SO_4 /AcOH/ Ac_2O , that leads to acylation of electron-rich aromatic substrates.¹⁶ Herein, we report a simple, scalable “green” electrochemical synthesis of cyclic and acyclic diaryliodonium salts with wide scope. A very recent report on the electrochemical synthesis of arylidiodine(III) reagents including some diaryliodonium salts emerged during the final preparation of this work.¹⁷

Results and discussion

Diaryliodonium salts are air and moisture stable compounds, but their physical properties and synthetic utility are strongly

Department of Chemistry, University of Huddersfield, Queensgate, Huddersfield HD1 3DH, UK. E-mail: w.j.moran@hud.ac.uk

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affected by the nature of the anionic part of the molecule. Previously published electrochemical methods for their preparation utilised $\text{H}_2\text{SO}_4/\text{AcOH}/\text{Ac}_2\text{O}$ as the reaction medium but these suffered from low yields and side product formation. In addition, isolation was problematic as the initially formed hydrogen sulfate salts required an additional ion exchange step. Usually this was achieved with halide salts such that the iodonium salts were isolated and characterised as halides, mainly iodides. Unfortunately, the synthetic utility of diaryliodonium salts with halide counterions is limited due to their extremely poor solubility in organic solvents and the nucleophilicity of the halide anions. On the other hand, diaryliodonium triflates are easily soluble in organic solvents and are widely used in organic synthesis.^{9,18} Thereby, this work focuses on the direct electrochemical synthesis of diaryliodonium triflates and hence triflic acid (TfOH) was the acid of choice for the process optimisation.

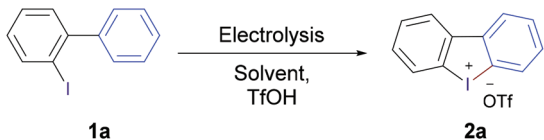
The oxidation of 2-iodobiphenyl (**1a**) to the corresponding cyclic diaryliodonium triflate **2a** was attempted using the Electrasyn device with an undivided cell setup. In accordance with several previous reports on the anodic oxidation of iodoarenes into the corresponding hypervalent iodine reagents, we initiated our studies using a glassy carbon (GC) anode and a platinum (Pt) cathode.¹³ The initial attempt at electrolysis of a solution of **1a** (0.15 mmol) in 2,2,2-trifluoroethanol (TFE, 5 mL) containing TfOH (0.75 mmol, 5 equiv.) applying a constant current of 5 mA (Table 1, entry 1) was unsuccessful as the cell voltage increased rapidly to reach the cell limit (30 V) within a few minutes. Replacing TFE with

1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) enhanced the solution conductivity, and the electrolysis could be completed leading to the formation of the iodonium salt **2a** in 70% yield after passing a charge of 2.5 F (entry 2). Despite this encouraging result, the cell voltage was still high, 12 V at the beginning of the electrolysis which dropped gradually to 5 V at the end of the electrolysis. This problem was alleviated by using a solvent mixture of HFIP and MeCN (4 : 1) leading to the formation of **2a** in excellent yield (95%, entry 3).

Interestingly, running the electrolysis in acetonitrile without fluorinated alcohol (entry 4) led to the isolation of salt **2a** in 80%, which is not significantly different from using a 1 : 1 mixture of HFIP and MeCN (entry 5, see the ESI† for more results of solvent screening). Increasing the current density from 1.8 mA cm⁻² to 2.7 and 3.6 mA cm⁻² whilst maintaining the same total charge transfer (entries 6 and 7) led to a decrease of the reaction yield to 88 and 89%, respectively. Reducing the charge passed to the theoretical amount (2.0 F) led to a significant decrease of the reaction yield (78%, entry 8) while passing a charge of 2.25 F (entry 9) led to the formation of **2a** in 86% yield. Doubling the concentration of **1a** (entry 10) did not negatively affect the reaction yield, as **2a** was isolated in 96% yield, while increasing the concentration to 0.1 M (entry 11) was accompanied by a gradual increase in the cell voltage due to the precipitation of the product during the electrolysis which led to a drop in the yield to 85% (see the ESI† for more experiments). Applying the optimum conditions (entry 10) but using 3 or 4 equivalents of TfOH did not lead to any reduction in the yield (entry 12) but was accompanied by a significant increase in the cell voltage.

To explore the scope of substrates, a wide range of iodobiaryls with various substitution patterns in both rings were synthesised and subjected to the optimised reaction conditions (Table 1, entry 10). The results (Scheme 1) showed that the reaction proceeded smoothly in most cases giving the desired cyclic diaryliodonium salts **2** in very good to excellent yields. Under the standard reaction conditions 2-iodobiphenyl afforded the corresponding iodonium triflate **2a** in 96% yield, replacing triflic acid with tosylic acid and trifluoroacetic acid afforded the tosylate and trifluoroacetate analogues in 93% and 70%, respectively, showing the flexibility of the method for producing the desired iodonium salts with different counter anions. The relatively lower yield in the case of trifluoroacetic acid could be attributed to the poor conductivity of the reaction solution; the addition of water (150 µL) was required to improve the conductivity and complete the electrolysis. Substrates without substituents on the ArI moiety furnished the desired products (**2b–k**) in very good to excellent yields regardless of the nature of the substituent in the arene part, with excellent tolerance of cyano, ketone, halogen, alkyl, and aryl substituents. 2-Fluorodibenzo[*b,d*]iodol-5-ium trifluoro-methanesulfonate (**2b**) was obtained in 88% using 3'-fluoro-2-iodo-1,1'-biphenyl (**1b**), containing the fluorine in the arene moiety, while the analogous substrate 5-fluoro-2-iodo-1,1'-biphenyl (**1b'**) containing the fluorine in the ArI moiety led to a slight decrease in the yield (82%). Highly electron-rich

Table 1 Optimization of the electrochemical oxidation of 2-iodobiphenyl (**1a**) to the corresponding iodonium triflate **2a**^a

					
Entry	Solvent	1a [mol L ⁻¹]	Current [mA]	Charge [F]	2a yield [%]
1	TFE	0.03	5	—	—
2	HFIP	0.03	5	2.5	70
3	HFIP–MeCN (4 : 1)	0.03	5	2.5	95
4	MeCN	0.03	5	2.5	80
5	HFIP–MeCN (1 : 1)	0.03	5	2.5	83
6	HFIP–MeCN (4 : 1)	0.03	7.5	2.5	88
7	HFIP–MeCN (4 : 1)	0.03	10	2.5	89
8	HFIP–MeCN (4 : 1)	0.03	5	2.0	78
9	HFIP–MeCN (4 : 1)	0.03	5	2.25	86
10	HFIP–MeCN (4 : 1)	0.06	5	2.5	96
11	HFIP–MeCN (4 : 1)	0.1	5	2.5	85
12 ^b	HFIP–MeCN (4 : 1)	0.06	5	2.5	95

^a Electrolyses were carried out with an Electrasyn 2.0, using a 5 mL glass vial equipped with a glassy carbon (GC) anode and a Pt cathode; electrode immersed area: 2.8 cm². Reaction conditions: 2-iodobiphenyl (**1a**) dissolved in 5 mL solvent, TfOH (5 equiv.), constant current electrolysis. ^b TfOH (3 or 4 equiv.). TFE: 2,2,2-trifluoroethanol; HFIP: 1,1,1,3,3,3-hexafluoro-2-propanol.





Scheme 1 Reaction scope of the electrochemical synthesis of cyclic diaryliodonium salts **2**. ^a TfOH replaced with TsOH·H₂O (2 equiv.). ^b TfOH replaced with CF₃CO₂H (5 equiv.). ^c Using substrate **1b'**. ^d Obtained using Pt–Pt with alternating polarity.

substrates were problematic. The methoxy-substituted product **2l** was obtained in just 44% yield, as the experiment could not be completed. Electrolysis was stopped after passing only 1.25 F due to unwanted polymerisation and electrode passivation that led to the gradual increase of the cell voltage till the cell limit; a problem that has been reported previously for electrolysis of electron-rich aryl iodides.^{13a,19} The same problem was observed in the case of **2m** and **2o**. Fortunately, this problem was alleviated by replacing the glassy carbon anode with platinum and alternating the polarity of the electrolysis each 20 seconds. Under these modified conditions, the electrolysis could be completed without problems and product **2l** was obtained in a very good yield (87%). Also, product **2o** was obtained in very good yield (81%) under the modified conditions, however product **2m** was not obtained and decompo-

sition/polymerisation was observed under both conditions. Substrates with one methyl group in the ArI moiety led to products **2n** and **2p–r** in excellent yields, higher than 90% in all cases regardless of the nature of the substituent in the arene moiety. In addition, electron-deficient substrates with electron-withdrawing groups in both parts of the molecule performed very well and gave the corresponding iodonium salts (**2u–2x**) in high yields (79%–91%). All substrates containing chlorine substituents gave the desired iodonium salts in excellent yields (>90%). The lowest yields obtained (59% and 75%) for products **2k** and **2j** having Ph and *t*Bu substituent, respectively maybe attributed to the low solubility of the corresponding substrates in the reaction medium.

Electron-rich heterocyclic substrates proved challenging. Compounds **S1y**, **S1z**, and **S1aa** for example underwent poly-



merisation/decomposition and the corresponding heterocyclic iodonium salts were not obtained under either the standard or the modified reaction conditions. The anodic oxidation of pyrrole typically leads to deposition to pyrrole black and other polymeric materials.²⁰ In addition, these electron-rich heterocyclic systems are prone to polymerisation under acidic conditions.²¹

Although the original focus of this work was the electrochemical synthesis of cyclic diaryliodonium salts, the excellent results achieved encouraged us to explore the general applicability of the developed method and extending the reaction scope to acyclic diaryliodonium salts (Scheme 2). Under the same reaction conditions (Table 1, entry 10), diphenyliodonium trifluoromethanesulfonate (**5a**) was obtained in 55% yield from the reaction of iodobenzene and 1.0 equivalent of benzene. Increasing the amount of benzene to 1.2, 1.5 and 2.0 equivalents led to a gradual improvement of the reaction outcome, forming **5a** in 67%, 80% and 88% yield, respectively. The reaction scope was studied using 1.5 equivalents of the arene. Electrolysis of iodobenzene without addition of any other arene component led to the isolation of (4-Iodophenyl)(phenyl)iodonium trifluoromethanesulfonate (**5b**) in excellent yield (91%).

Anodic oxidation of the relatively electron-deficient 4-fluoroiodobenzene in the presence of benzene, toluene and mesitylene furnished the corresponding diaryliodonium salts **5c,d,f** in high yields, while using electron-deficient arene counterpart, namely, benzonitrile did not lead to successful formation of the desired iodonium salt **5e**. The electrochemical oxidation of

1-bromo-4-iodobenzene in the presence of toluene gave **5g** in a relatively lower yield (70%). Replacing toluene with mesitylene achieved the corresponding iodonium salt **5h** in higher yield (81%), which was formed in lower yield (58%) when using iodo-mesitylene and bromobenzene. Using a more electron rich aryl-iodide (4-iodotoluene) and electron-rich arene (mesitylene) led to the formation of **5j** in excellent yield (97%). Like the methoxy-containing cyclic product **2m**, the acyclic product **5k** was not obtained and decomposition/polymerisation was observed upon electrolysis of 2-methoxyiodobenzene in the presence of benzene as the arene counterpart. The competition between oxidation/intramolecular coupling and oxidation/intermolecular coupling was studied by anodic oxidation of 2-iodobiphenyl (**1a**) in the presence of one equivalent of each of benzene and mesitylene. The experiment using benzene showed the exclusive formation of the cyclic iodonium salt **2a** in 95% yield without any trace of the acyclic product **5l**. While the reaction using mesitylene led to the formation of the acyclic product **5m** as a major product along with a small percentage of the cyclic product **2a** in a 10 : 1 ratio.

The scalability of the developed method was demonstrated using a beaker-type cell equipped with three parallel 5 × 5 cm electrodes [anode (GC)-cathode (Pt)-anode (GC), see the ESI† for details]. Electrolysis of 10 mmol of 2-iodobiphenyl (**1a**) applying a total current of 92 mA (46 mA on each anode, 1.84 mA cm⁻²) led to the isolation of 4.17 g of product **2a** (97%) in 5.8 hours (2.5 F) with excellent purity (99.9%) (Fig. 1, experiment 1). Clearly demonstrating the practicality of the developed method at the gram-scale. Performing the same experiment using *m*-chloroperbenzoic acid (*m*CPBA) on the same scale requires 3.5 g *m*CPBA (15.0 mmol) and produces equivalent amount of benzoic acid as chemical waste.²² To improve the “greenness” of the whole process and to reduce its ecological footprint more, the solvent system of the first large-scale experiment was collected using a rotary evaporator and recycled several times. The solvent recovery efficiency was very



Scheme 2 Substrate scope of acyclic diaryliodonium triflates **5**. ^a Using iodomesitylene and bromobenzene. ^b Product **2a** was obtained instead.



Fig. 1 Scale-up/solvent recycling data. Purity of product **2a** was determined by ¹H NMR using 1,4-dibromobenzene as an internal standard; experiment 6: the recovered solvent was dried over MS before use; experiment 7 was performed applying 92 mA on each anode (double current density: 3.68 mA cm⁻²) and fresh solvent mixture.



high (97–99%) and the recovered solvent was used for three more cycles. In these cases, the formation of **2a** was observed in excellent yield and purity (Fig. 1, experiments 2–4).

A subsequent fifth cycle showed a significant reduction of the product purity (85%), but without significant reduction of the actual yield (yield \times purity %). We supposed that this reduction of purity could be due to the increase of the water content of the solvent with recycling and collection. To test this hypothesis, the solvent recovered from experiment number five was dried using molecular sieves prior to use, which led to a regain of the high purity and yield of the product **2a** (Fig. 1, experiment 6). In addition, doubling the current density from 1.84 mA cm⁻² to 3.68 mA cm⁻², applying a total current of 184 mA (92 mA on each anode), did not have a significant negative impact on the reaction outcome and furnished **2a** in high purity and yield, while cutting the reaction time in half to 2.9 hours (Fig. 1, experiment 7).

Conclusions

In conclusion, the synthesis of a wide range of cyclic and acyclic diaryliodonium salts was achieved in high to excellent yields *via* anodic oxidation of iodobiaryls and iodoarene/arene mixtures using a simple undivided cell. The reaction proceeds smoothly in a mixture of HFIP, MeCN and TfOH under constant current electrolysis, avoiding the use of added salts such as Bu₄NBF₄, Bu₄NClO₄ or LiClO₄ typically used in batch-type electrolyses as supporting electrolytes. Using triflic acid as a volatile added electrolyte in addition to its role as a reactant rendered the isolation of the formed iodonium salts very simple and efficient. The flexibility of the method was proven by obtaining iodonium salts with other counterions by simply replacing triflic acid with the desired acid. Electrolysis of electron-rich heterocyclic substrates was unsuccessful with this setup and led to polymerisation/decomposition of the starting materials without the isolation of the desired heterocyclic iodonium salts. The easy scalability of the developed method was demonstrated by running a large-scale experiment (10 mmol, 33 folds) leading to the isolation of more than four grams of product **2a** (>97%) with excellent purity (>99%). In addition, the solvent system of the large-scale experiment was easily recovered (>97%) using a rotary evaporator and recycled several times without significant reduction of the reaction yield, improving the overall efficiency, economy, and the ecological impact of the developed method.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- (a) V. V. Zhdankin, *Hypervalent Iodine Chem*, John Wiley & Sons Ltd, Chichester, UK, 2013, pp. 21–143; (b) *Hypervalent Iodine Chemistry: Modern Developments in Organic Synthesis*, ed. T. Wirth, [in: *Top. Curr. Chem.*, 2016, 373], Springer-Verlag, 2016; (c) A. Parra, *Chem. Rev.*, 2019, **119**, 12033–12088.
- (a) M. S. Yusubov, A. V. Maskaev and V. V. Zhdankin, *ARKIVOC*, 2011, **2011**, 370–409; (b) K. Kepski, C. R. Rice and W. J. Moran, *Org. Lett.*, 2019, **21**, 6936–6939.
- (a) J. Qurban, M. Elsherbini, H. Alharbi and T. Wirth, *Chem. Commun.*, 2019, **55**, 7998–8000; (b) A. Yoshimura, K. C. Nguyen, S. C. Klasen, A. Saito, V. N. Nemykin and V. V. Zhdankin, *Chem. Commun.*, 2015, **51**, 7835–7838.
- (a) A. Baralle, P. Garra, F. Morlet-Savary, C. Dietlin, J. Fouassier and J. Lalevée, *Macromol. Rapid Commun.*, 2020, **41**, 1900644; (b) J. Kabatc, J. Ortyl and K. Kostrzewska, *RSC Adv.*, 2017, **7**, 41619–41629; (c) T. Brömme, D. Oprych, J. Horst, P. S. Pinto and B. Strehmel, *RSC Adv.*, 2015, **5**, 69915–69924.
- (a) N. R. Deprez and M. S. Sanford, *Inorg. Chem.*, 2007, **46**, 1924–1935; (b) D. R. Stuart, *Chem. – Eur. J.*, 2017, **23**, 15852–15863; (c) D. P. Hari, S. Nicolai and J. Waser, in *PATAI'S Chem. Funct. Groups*, John Wiley & Sons, Ltd, Chichester, UK, 2018, pp. 1–58; (d) E. Zawia, D. J. Hamnett and W. J. Moran, *J. Org. Chem.*, 2017, **82**, 3960–3964; (e) A. Rodríguez and W. J. Moran, *J. Org. Chem.*, 2016, **81**, 2543–2548.
- (a) V. W. Pike, *J. Labelled Compd. Radiopharm.*, 2017, 1–32; (b) P. Das, E. Tokunaga, H. Akiyama, H. Doi, N. Saito and N. Shibata, *Beilstein J. Org. Chem.*, 2018, **14**, 364–372; (c) N. Nguyen, D. W. Wilson, G. Nagalingam, J. A. Triccas, E. K. Schneider, J. Li, T. Velkov and J. Baell, *Eur. J. Med. Chem.*, 2018, **148**, 507–518.
- E. A. Merritt and B. Olofsson, *Angew. Chem., Int. Ed.*, 2009, **48**, 9052–9070.
- D. R. Stuart, *Synlett*, 2017, **28**, 275–279.
- (a) D. Zhu, Z. Wu, L. Liang, Y. Sun, B. Luo, P. Huang and S. Wen, *RSC Adv.*, 2019, **9**, 33170–33179; (b) A. Boelke, P. Finkbeiner and B. J. Nachtsheim, *Beilstein J. Org. Chem.*, 2018, **14**, 1263–1280; (c) M. Wang, Q. Fan and X. Jiang, *Org. Lett.*, 2018, **20**, 216–219.
- E. Lindstedt, M. Reitti and B. Olofsson, *J. Org. Chem.*, 2017, **82**, 11909–11914.
- N. Soldatova, P. Postnikov, O. Kukurina, V. V. Zhdankin, A. Yoshimura, T. Wirth and M. S. Yusubov, *Beilstein J. Org. Chem.*, 2018, **14**, 849–855.
- (a) G. Laudadio, H. P. L. Gemoets, V. Hessel and T. Noël, *J. Org. Chem.*, 2017, **82**, 11735–11741; (b) N. S. Soldatova,



- P. S. Postnikov, M. S. Yusubov and T. Wirth, *Eur. J. Org. Chem.*, 2019, 2081–2088.
- 13 (a) M. Elsherbini, B. Winterson, H. Alharbi, A. A. Folguez-Amador, C. Génot and T. Wirth, *Angew. Chem., Int. Ed.*, 2019, **58**, 9811–9815, (*Angew. Chem.*, 2019, **131**, 9916–9920); (b) M. Elsherbini and T. Wirth, *Chem. – Eur. J.*, 2018, **24**, 13399–13407; (c) T. Broese and R. Francke, *Org. Lett.*, 2016, **18**, 5896–5899.
- 14 (a) D. Pollok and S. R. Waldvogel, *Chem. Sci.*, 2020, **11**, 12386–123400; (b) A. L. Rauen, F. Weinelt and S. R. Waldvogel, *Green Chem.*, 2020, **22**, 5956–5960; (c) D. Pletcher, R. A. Green and R. C. D. Brown, *Chem. Rev.*, 2018, **118**, 4573–4591; (d) D. E. Collin, A. A. Folguez-Amador, D. Pletcher, M. E. Light, B. Linclau and R. C. D. Brown, *Chem. – Eur. J.*, 2020, **26**, 374–378; (e) T. H. Meyer, I. Choi, C. Tian and L. Ackermann, *Chem.*, 2020, **6**, 2484–2496; (f) M. C. Leech and K. Lam, *Acc. Chem. Res.*, 2020, **53**, 121–134; (g) F. J. Holzhäuser, G. Creusen, G. Moos, M. Dahmen, A. König, J. Artz, S. Palkovits and R. Palkovits, *Green Chem.*, 2019, **21**, 2334–2344.
- 15 (a) S. R. Waldvogel, S. Arndt, D. Weis and K. Donsbach, *Angew. Chem., Int. Ed.*, 2020, **59**, 8036–8041; (b) A. F. Roesel, T. Broese, M. Májek and R. Francke, *ChemElectroChem*, 2019, **6**, 4229–4237; (c) R. Francke, T. Broese and A. F. Roesel, in *PATAI'S Chem. Funct. Groups*, John Wiley & Sons, Ltd, Chichester, UK, 2018, pp. 1–22; (d) L. Massignan, X. Tan, T. H. Meyer, R. Kuniyil, A. M. Messinis and L. Ackermann, *Angew. Chem., Int. Ed.*, 2020, **59**, 3184–3189; (e) S. Doobary, A. T. Sedikides, H. P. Caldora, D. L. Poole and A. J. J. Lennox, *Angew. Chem., Int. Ed.*, 2020, **59**, 1155–1160.
- 16 (a) L. L. Miller and A. K. Hoffmann, *J. Am. Chem. Soc.*, 1967, **89**, 593–597; (b) M. J. Peacock and D. Pletcher, *Tetrahedron Lett.*, 2000, **41**, 8995–8998; (c) K. Watts, W. Gattrell and T. Wirth, *Beilstein J. Org. Chem.*, 2011, **7**, 1108–1114.
- 17 B. Zu, J. Ke, Y. Guo and C. He, *Chin. J. Chem.*, 2021, **39**, 627–632.
- 18 (a) K. Zhu, Y. Wang, Q. Fang, Z. Song and F. Zhang, *Org. Lett.*, 2020, **22**, 1709–1713; (b) G. Kervefors, L. Kersting and B. Olofsson, *Chem. – Eur. J.*, 2021, **27**, 5790–5795; (c) S. N. Yunusova, A. S. Novikov, N. S. Soldatova, M. A. Vovk and D. S. Bolotin, *RSC Adv.*, 2021, **11**, 4574–4583.
- 19 Y. Amano and S. Nishiyama, *Heterocycles*, 2008, **75**, 1997–2003.
- 20 J. K. Howard, K. J. Rihak, A. C. Bissember and J. A. Smith, *Chem. – Asian J.*, 2016, **11**, 155–167.
- 21 J. K. Laha, M. K. Hunjan, S. Hegde and A. Gupta, *Org. Lett.*, 2020, **22**, 1442–1447.
- 22 (a) D. Zhu, Q. Liu, B. Luo, M. Chen, R. Pi, P. Huang and S. Wen, *Adv. Synth. Catal.*, 2013, **355**, 2172–2178; (b) M. Jiang, J. Guo, B. Liu, Q. Tan and B. Xu, *Org. Lett.*, 2019, **21**, 8328–8333.

