Green Chemistry

PAPER

View Article Online
View Journal | View Issue

Cite this: *Green Chem.*, 2024, **26**, 3429

Electrochemical bromination of enamides with sodium bromide†

Shinan Luan, Thomas Castanheiro * and Thomas Poisson *

Received 1st December 2023,
Accepted 30th January 2024

DOI: 10.1039/d3gc04723g

rsc.li/greenchem

The electrochemical bromination of enamide derivatives was developed using inexpensive and non-toxic sodium bromide (NaBr). This transformation enabled the direct stereoselective formation of a C(sp^2)–Br bond and was applied to a wide variety of enamides without the need for external hazardous oxidants, reductants or metal catalysts. The protocol showed a general efficiency and tolerance, allowing access to brominated enamides with yields ranging from 56% to 85%. The reaction conditions were applied to the chlorination reaction using sodium chloride (NaCl). The synthetic utility of the products was illustrated through Suzuki and Sonogashira cross-coupling reactions, offering a novel reaction procedure to access complex enamide derivatives.

Introduction

Organohalide compounds play a crucial role in society and are among the most explored chemicals. Their importance not only comes from their prevalence in Nature,[1] with more than 4500 natural products discovered containing at least one halogen atom, but is also a result of their high versatility as synthetic intermediates and building blocks in a plethora of chemical reactions.[2] Furthermore, as a result of the advent of transition-metal-catalyzed cross-coupling reactions, the relevance of aryl and vinyl halides has increased significantly over the past forty years.[3] Moreover, carbon–halogen (C–X) bonds are present in the structural backbone of many chemicals used in materials sciences, as well as in pharmaceuticals and agrochemicals.[4–6]

Organohalides are conventionally synthesized through well-established procedures, including electrophilic functionalization, the Sandmeyer reaction and *ortho*-lithiation methods, for instance.[7] Aware of the limitations of such strategies, including regioselectivity and functional group tolerance, synthetic chemists have developed more efficient methods, such as transition-metal-catalyzed direct C–H halogenation, transition-metal-free oxidative halogenations, visible-light-induced halogenations and enzymatic halogenations, for instance.[8]

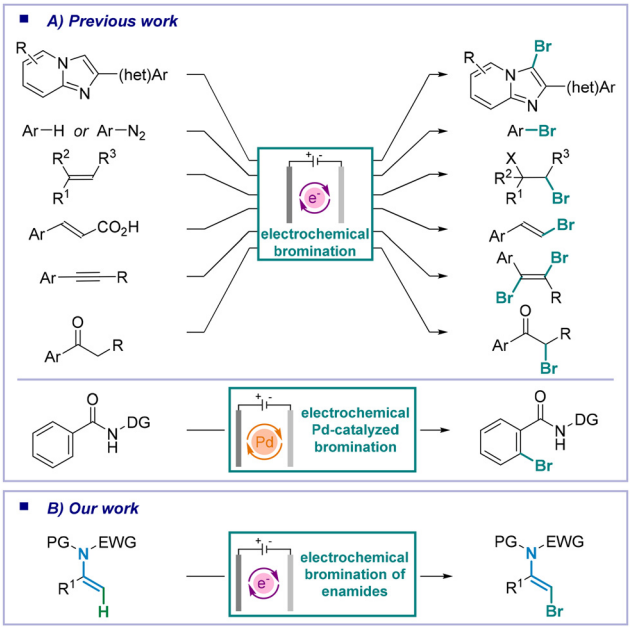
In light of the contemporary concern to discover more sustainable, cost-effective and safe protocols, there is a high demand for the development of procedures that avoid the use of expensive catalysts, hazardous chemical oxidants, and stoichiometric reagents to minimize hazards and synthetic waste. For that purpose, electrochemical transformations provide significant benefits. Organic electrosynthesis offers mild reaction conditions, while providing high chemoselectivity, and minimal waste generation since it relies on the use of electrons as the main reagent.[9] Therefore, synthetic organic electrochemistry has emerged as one of the most important and environmentally benign tools in organic synthesis, particularly when the electricity is produced from renewable sources. Hence, as a part of our ongoing research program dedicated to the functionalization of organic molecules through the addition of electrogenerated radicals,[10] we sought to develop a versatile methodology to access synthetically useful Br-containing building blocks, avoiding the use of harmful brominating agents. With the resurgence of electrochemistry, significant efforts have been invested in the development of sustainable bromination procedures.

Various C(sp^2)– and C(sp^3)–Br bonds formed on heteroaryl, aryl, alkene, alkyne, alkyl and carboxylic acid derivatives were successfully developed through an electrochemical process (Scheme 1A).[11–15]

In addition, the enamide scaffold is ubiquitous in a wide range of pharmaceuticals and natural products and is widely recognized as a linchpin in organic synthesis.[16] Quite surprisingly, the synthesis of halogenated enamides has been underexplored and has relied on elaborate reaction systems. Indeed, to our knowledge, access to halogenated enamides has focused on transition-metal-catalyzed or transition-metal-free amido-halogenation of alkynes,[17,18] radical addition onto alkynes,[19] hydroamidation of halogenated alkynes,[20] or haloolefination of formamides.[21] Hence, in light of the conspicuous absence of a practical, sustainable and direct approach toward

INSA Rouen Normandie, Univ. Rouen Normandie, CNRS, Normandie Univ., COBRA UMR 6014, INC3M FR 3038, F-76000 Rouen, France.
E-mail: thomas.castanheiro-matias@univ-rouen.fr, thomas.poisson@insa-rouen.fr

† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d3gc04723g



Scheme 1 State of the art and present work.

halogenated enamides, we surmised that the electrochemical generation of bromide radicals through anodic oxidation would offer smooth and sustainable access to these interesting scaffolds in a single operation from enamides (Scheme 1B).

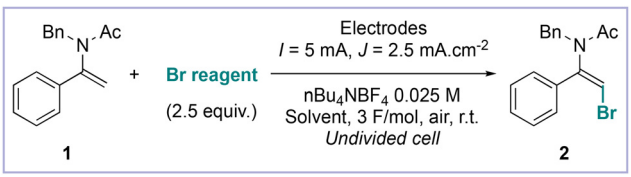
Results and discussion

At the outset of our investigations, enamide **1** was chosen as the model substrate and ammonium bromide was used as the bromine source to initiate the reaction (Table 1, entry 1). Pleasingly, **2** was obtained with a 37% NMR yield by using a carbon graphite anode and a platinum cathode, under a constant current of 5 mA with a total charge of 3 F mol^{-1} in acetonitrile (CH_3CN) under an air atmosphere in an undivided cell. Variation of the solvent of the reaction showed that DMA allowed a slight increase in the yield, reaching 43%. Thus, we pursued the optimization using DMA as the solvent. The use of NaBr in place of NH_4Br as the bromine source resulted in a better yield (55%), while the use of nBu_4NBr as both the electrolyte and the bromine source was deleterious for the outcome of the reaction. We then tried to replace the platinum cathode with a glassy carbon (entry 5), a stainless-steel (entry 6) or a carbon graphite (entry 7) cathode.

Pleasingly, **2** was isolated in 81% and 83% yields, respectively, using a stainless-steel or a carbon graphite cathode (entries 6 & 7). Moreover, the use of a carbon graphite anode was crucial for the formation of product **2** (entry 8). Then, to increase the atom economy and the sustainability of the process, the electrolyte was removed from the reaction conditions (entry 9). Unfortunately, its absence was deleterious for the reaction outcome, since a moderate 50% NMR yield was obtained. Although NaBr could be used as an electrolyte, increasing the amount to 8.0 equiv. did not result in a decent yield. To showcase the added value of our electrochemical bromination protocol, we compared its efficiency with classical electrophilic bromination conditions (Table 2). The reaction of **1** with NBS (*N*-bromosuccinimide) under classical conditions gave the product **2** in a modest yield of 36% along with a significant amount of side products (Table 2, entry 2).[22] Likewise, the use of pyridinium tribromide did not improve the reaction efficiency and **2** was isolated in a modest 23% NMR yield (Table 2, entry 3).[23] Overall, the electrochemical bromination outcompetes the classical brominating reagents. These results clearly highlight the added value of our electrochemical bromination protocol. In addition, it offers a sustainable approach as it avoids the use of an electrophilic brominating agent and uses the eco-friendly and harmless sodium bromide.

Having delineated the optimal reaction conditions (see Table 1, entry 7), the scope of this electrochemical bromination of α-aryl enamides was investigated (Scheme 2). The reac-

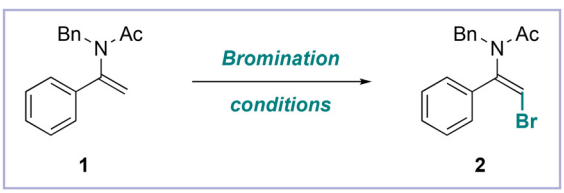
Table 1 Optimization of the electrochemical bromination of **1**



Entry	Br reagent	Solvent	Electrodes	Yields[a] (%)
1	NH_4Br	CH_3CN	C(+)IPt(−)	37
2	NH_4Br	DMA	C(+)IPt(−)	43
3	nBu_4NBr	DMA	C(+)IPt(−)	55
4	NaBr	DMA	C(+)IPt(−)	0
5	NaBr	DMA	C(+)IGC(−)	70
6	NaBr	DMA	C(+)ISST(−)	81[b]
7	NaBr	DMA	C(+)IC(−)	83[b]
8	NaBr	DMA	SST(+)IC(−)	0
9[c]	NaBr	DMA	C(+)IC(−)	50

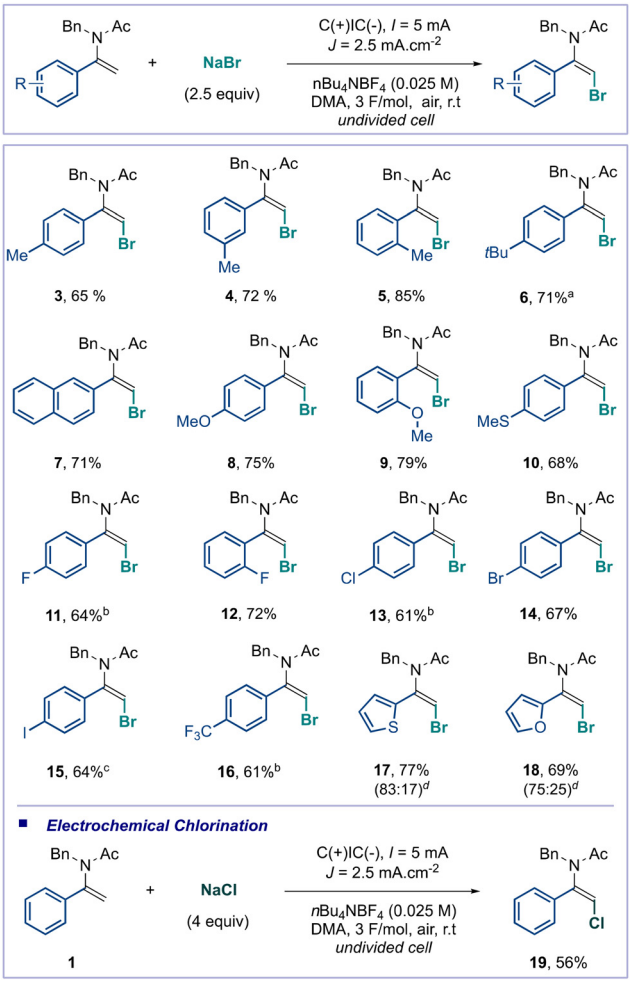
[a] ^1H NMR yield using dibromomethane as an internal standard. [b] Isolated yield. [c] Reaction without electrolyte. C: carbon graphite. GC: glassy carbon. SST: stainless steel.

Table 2 Added-value of the electrochemical bromination of **1**



Entry	Br reagent	Yields[a] (%)
1	NaBr, C(+)IC(−), I = 5 mA, 3 F mol^{-1}, air, r.t.	83[b]
2	NBS (1.5 equiv.), DMF, r.t., 14 h	36
3	PyrH;Br_3 (1.5 equiv.), DMF, r.t., 14 h	23

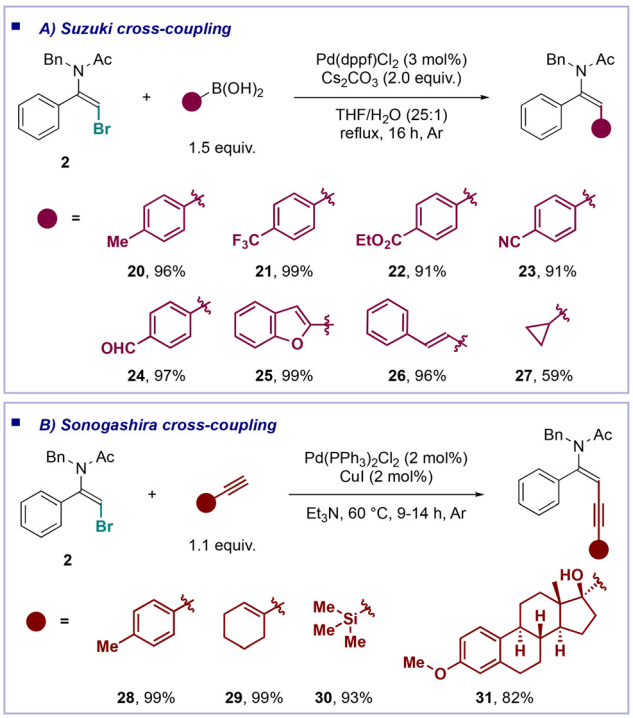
[a] ^1H NMR yield using dibromomethane as an internal standard. [b] Isolated yield.



Scheme 2 Electrochemical direct C–H bromination of enamides. [a] 3.5 F mol^{-1} charge was applied. [b] 5 F mol^{-1} charge was applied. [c] 4.5 F mol^{-1} charge was applied. [d] *E*/*Z* ratio determined on the crude reaction mixture.

tion efficiency was not affected by the substitution pattern. α-Aryl enamides substituted by a methyl group at the *para*-, *meta*- or *ortho*-position afforded the desired products (**3–5**) in good yields as a single stereoisomer, showing no impact of the steric hindrance. The reaction with enamides bearing electron-donating groups on the aryl residue such as tertbutyl, methoxy and thiomethyl ether, as well as the naphthyl derivative, proceeded well, producing the corresponding products (**6–10**) in high yields. Pleasingly, no further oxidation of the sulfur atom was observed under our electrochemical conditions. It should be noted that once again the steric hindrance did not impact the reaction outcome as a larger methoxy group was installed at the *ortho*-position, allowing for electrochemical bromination with 79% yield (see product **9**). Halogen atoms were well tolerated under our electrochemical conditions as the aryl moiety substitution with fluorine (**11** and **12**), chlorine (**13**), bromine (**14**) and iodine (**15**) gave the corresponding products with good yields, enabling opportunities for further transformations through metal-catalyzed cross-coupling, for instance. The reaction with the trifluoromethyl group at the *para*-position of the aryl moiety efficiently afforded the desired brominated enamides with a good yield of 61% at the cost of an increased charge from 3 F mol^{-1} to 4.5 F mol^{-1}. Due to the high interest in heteroaromatic compounds in medicinal chemistry and crop science, heteroaryl enamides were also reacted under our optimal reaction conditions and were proved to be efficient substrates, yielding two valuable heteroaromatic molecules (**17** and **18**). In these cases, the bromoenamides were obtained as a separable *E*/*Z* mixture of stereoisomers, the *E* being the major one. To showcase the versatility of our transformation, sodium bromide was replaced by sodium chloride. To our delight, the electrochemical chlorination occurred under similar reaction conditions with a slightly lower efficiency, giving access to the unknown chlorinated enamide **19**, with a good yield of 56%. Importantly, the reaction was highly stereoselective, as all substrates were exclusively obtained as (*E*)-isomers, except the heteroaromatic derivatives **17** and **18**. Unfortunately, some enamide substrates remained reluctant or poorly reactive under our reaction conditions. Aliphatic enamides showed no reactivity, highlighting the importance of the formation of a stabilized benzylic radical in our transformation, and enamides derived from cyclic olefins were poorly reactive, leading to trace formation of the desired products.[24]

Then, to highlight the synthetic utility of the obtained products, we envisioned taking advantage of a halogen atom to develop original C–C bond formation on the enamide scaffold (Scheme 3). To the best our knowledge, no report dealing with the functionalization of halogenated enamides has been

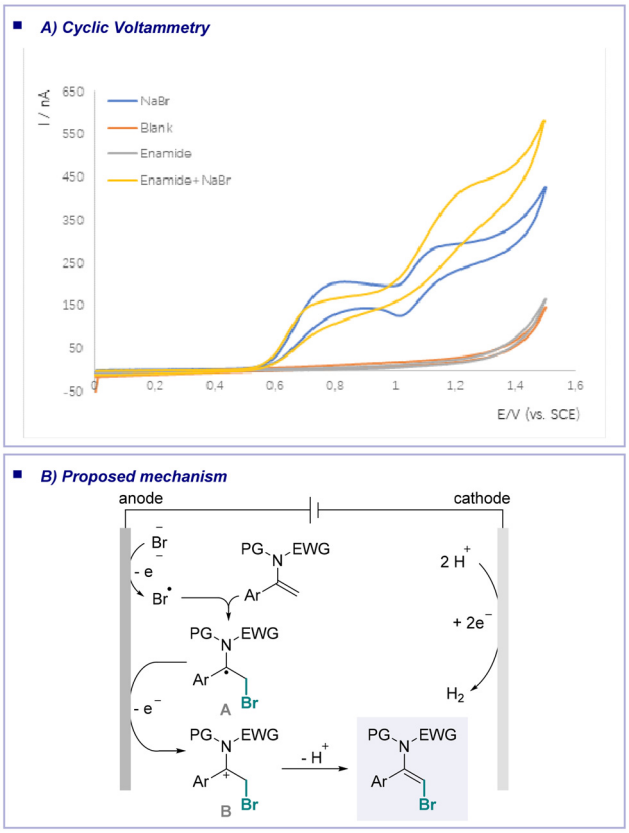


Scheme 3 Synthetic utility of the brominated enamides.

reported to date. Thus, we took advantage of the bromide atom to develop a protocol for the Suzuki cross-coupling reaction, a pivotal transformation in medicinal chemistry and API manufacturing.[25] Pleasingly, with our developed reaction conditions, excellent yields were obtained using aryl boronic acids bearing electron-donating or -withdrawing substituents. Methyl, trifluoromethyl, ethyl ester, cyano and aldehyde substituents were very well tolerated, affording the desired products (**20–24**) with yields ranging from 91% to 99%. In addition, an excellent yield of 99% was obtained by reacting **2** with an heteroaryl boronic acid, *i.e.* benzofuran-2-ylboronic acid. Then, the reaction with β-styrylboronic acid afforded the corresponding (*E*,*E*)-dienes in a very good yield of 96%, with a complete stereoretention of the starting olefins. Finally, we showcased the possible use of alkyl boronic acid, through the reaction with cyclopropyl boronic acids, which afforded the product **27** in a fairly decent yield of 59%.

Finally, we developed a procedure for the Sonogashira cross-coupling reaction to access enyne derivatives. The use of standard reaction conditions ($Pd(PPh_3)_2Cl_2$, CuI in Et_3N) allowed the reaction of **2** with ethynyl-4-methylbenzene, 1-ethynylcyclohexene and ethynyltrimethylsilane. The corresponding enynes **28**, **29** and **30** were obtained with excellent yields ranging from 93% to more than 99%. Finally, we applied our protocol to the reaction of **2** with mestranol, a complex bioactive molecule. The reaction proceeded smoothly and the product **31** was obtained in an excellent yield of 82%, showcasing the versatility of the transformation toward complex structures. Overall, these novel transformations highlighted the synthetic utility of these building blocks. Then, to gain insights into the reaction mechanism, cyclic voltammetry measurements were carried out (Scheme 4A).

The CV measurements of NaBr (blue curve) showed two successive oxidative waves (Scheme 4A), while no oxidation of enamide (grey curve) was observed in the potential range studied (up to +1.5 V). Moreover, the analysis of a mixture of NaBr and enamide demonstrated a similar profile without any increase of oxidative potential, meaning that there is no bromine mediation in the plausible enamide oxidation (Scheme 4). With all these data to hand, we suggested a plausible reaction mechanism, starting with the anodic oxidation of bromine from sodium bromide (Scheme 4B). The resulting electrophilic bromine radical could then add onto the enamide, leading to a stabilized nucleophilic carbon centered radical **A**. A subsequent anodic oxidation of this open-shell intermediate generated the carbocation **B**, which then readily underwent E1 elimination to furnish the desired and less congested brominated enamide. A final cathodic reduction of H^+, resulting from the elimination, would release H_2, equilibrating the redox balance.



Scheme 4 Control experiments, cyclic voltammetry and suggested mechanism.

Conclusions

In conclusion, we depicted herein the unprecedent electrochemical bromination of enamide derivatives using non-toxic and inexpensive sodium bromine as a precursor of Br•. The reaction conditions proved to be tolerant to various electron-donating or -withdrawing chemical substituents and provided the resulting products with excellent (*E*)-stereoselectivity in good to excellent yields (56–85%). The standard reaction conditions proved to be efficient for the electrochemical chlorination of enamide upon the simple replacement of NaBr by NaCl. The synthetic utility of the products was highlighted through Suzuki and Sonogashira cross-coupling reactions. Pleasingly, excellent yields were obtained, and the tri-substituted enamides were stereoselectively obtained from the brominated (*E*)-enamide under simple and practical reaction conditions. The efficiency of these novel reaction manifolds on enamide demonstrated their versatility toward the expansion of the chemical space. A mechanistic analysis of the reaction supported a plausible reaction pathway involving a Br• radical, generated from the anodic oxidation of bromide. We hope that the sustainable synthesis of these novel building blocks will offer new opportunities to expand the chemical space, particularly in medicinal chemistry.

Author contributions

S. L., T. C. and T. P. conceived and designed the experiments. S. L. performed the experiments. S. L., T.C. and

T.P. analyzed the data. T. C. wrote the manuscript with the input from all authors.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was partially supported by Normandie Université (NU), Région Normandie, the Centre National de la Recherche Scientifique (CNRS), Université de Rouen Normandie (URN), INSA Rouen Normandie, Labex SynOrg (ANR-11-LABX-0029), the Graduate School for Research XL-Chem (ANR-18-EURE-0020 XLCHEM) and Innovation Chimie Carnot (I2C). This work is part of the EFLUX program supported by the European Union through the operational program FEDER/FSE 2014-202. T. P. thanks the Région Normandie for support (RIN TREMPLIN EFLUX). S. L. thanks the Chinese Scholarship Council (CSC) for a doctoral fellowship.

References

1 (*a*) G. W. Gribble, *Acc. Chem. Res.*, 1998, **31**, 141–152; (*b*) G. W. Gribble, *J. Chem. Educ.*, 2004, **81**, 1441–1449.

2 (*a*) S. Caron, in *Practical Synthetic Organic Chemistry: Reactions, Principles, and Techniques*, Wiley, Hoboken, New Jersey, 2011; (*b*) R. C. Larock, *Comprehensive Organic Transformations, 2nd ed*, Wiley-VCH, New York, 1999; (*c*) H. House, in *Modern Synthetic Reactions, 2nd ed*, W. A. Benjamin, New York, 1972, pp. 459–478; (*d*) N. De Kimpe and R. Verhé, *The Chemistry of α-Haloketones, α-Haloaldehydes, and α-Haloimines*, John Wiley & Sons, New York, 1988; (*e*) R. Lin, A. P. Amrute and J. Pérez-Ramírez, *Chem. Rev.*, 2017, **117**, 4182–4247.

3 (*a*) S. Bräse and A. De Meijere, in *Metal-Catalyzed Cross-Coupling Reactions*, Wiley-VCH, New York, 2004; (*b*) N. Kambe, T. Iwasaki and J. Terao, *Chem. Soc. Rev.*, 2011, **40**, 4937–4947.

4 (*a*) K. Müller, C. Faeh and F. Diederich, *Science*, 2007, **317**, 1881–1886; (*b*) S. Purser, P. R. Moore, S. Swallow and V. Gouverneur, *Chem. Soc. Rev.*, 2008, **37**, 320–330; (*c*) P. Jeschke, in *Modern Crop Protection Compounds*, Wiley-VCH, Weinheim, 2013; (*d*) P. Jeschke, *Pest Manage. Sci.*, 2017, **73**, 1053–1066; (*e*) R. Wilcken, M. O. Zimmermann, A. Lange, A. C. Joerger and F. M. Boeckler, *J. Med. Chem.*, 2013, **56**, 1363–1388; (*f*) Y. Lu, T. Shi, Y. Wang, H. Yang, X. Yan, X. Luo, H. Jiang and W. Zhu, *J. Med. Chem.*, 2009, **52**, 2854–2862; (*g*) M. J. Dagani, H. J. Barda, T. J. Benya and D. C. Sanders, *Bromine Compounds In Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co, KGaA, 2000; (*h*) B. R. Smith, C. M. Eastman and J. T. Njardarson, *J. Med. Chem.*, 2014, **57**, 9764–9773.

5 https://www.essentialchemicalindustry.org/chemicals/bromine.html.

6 (*a*) D. Ioffe and A. Kampf, in *Kirk-Othmer Encyclopedia of Chemical Technology, 5th ed*, John Wiley &Sons, Inc., New York, 2004, Vol. 4, pp 340–345; (*b*) D. L. Turner, *J. Food Sci.*, 1972, **37**, 791–792; (*c*) D. A. Laskowski, *Rev. Environ. Contam. Toxicol.*, 2002, **174**, 49–170; (*d*) J. Green, *J. Fire Sci.*, 1996, **14**, 426–442; (*e*) G. W. Gribble, *Chem. Soc. Rev.*, 1999, **28**, 335–346; (*f*) S. J. Decanio, *Contemp. Econ. Policy*, 2005, **23**, 376–393; (*g*) J. Kaspersma, C. Doumen, S. Munro and A.-M. Prins, *Polym. Degrad. Stab.*, 2002, **77**, 325–331.

7 (*a*) H. Gilman, in *Organic Chemistry: An Advanced Treatise*, Wiley, New York, 1938, Vol. 1, pp. 36–43; (*b*) P. B. D. de la Mare, in *Electrophilic Halogenation*, Cambridge University Press, New York, 1976; (*c*) I. Saikia, A. J. Borah and P. Phukan, *Chem. Rev.*, 2016, **116**, 6837–7042; (*d*) Y. Xiang, P.-Y. Caron, B. M. Lillie and R. Vaidyanathan, *Org. Process Res. Dev.*, 2008, **12**, 116–119; (*e*) Z. Wang, in *Comprehensive Organic Name Reactions and Reagents*, Wiley, 2010; (*f*) V. Snieckus, *Chem. Rev.*, 1990, **90**, 879–933; (*g*) H. Hodgson, *Chem. Rev.*, 1947, **47**, 251–277.

8 Selected reviews: (*a*) A. Paik, S. Paul, S. Bhowmik, R. Das, T. Naveen and S. Rana, *Asian J. Org. Chem.*, 2022, **11**, e202200060; (*b*) R. Das and M. Kapu, *Asian J. Org. Chem.*, 2018, **7**, 1524–1541; (*c*) F. H. Vaillancourt, E. Yeh, D. A. Vosburg, S. Garneau-Tsodikova and C. T. Walsh, *Chem. Rev.*, 2006, **106**, 3364–3378; (*d*) A. Podogoršek, M. Zupan and J. Iskra, *Angew. Chem., Int. Ed.*, 2009, **48**, 8424–8450; (*e*) X.-W. Liang, C. Zheng and S.-L. You, *Chem. – Eur. J.*, 2016, **22**, 11918–11933; (*f*) S. E. Denmark, W. E. Kuester and M. T. Burk, *Angew. Chem., Int. Ed.*, 2012, **51**, 10938–10953; (*g*) C. Crove, S. Molyneux, S. V. Sharma, Y. Zhang, D. S. Gkotsi, H. Connaris and R. J. M. Goss, *Chem. Soc. Rev.*, 2021, **50**, 9443–9481; (*h*) H. Tu, S. Zhu, F.-L. Qing and L. Chu, *Tetrahedron Lett.*, 2018, **59**, 173–179; (*i*) S. France, A. Weatherwax and T. Lectka, *Eur. J. Org. Chem.*, 2005, 475–479; (*j*) A. M. Arnold, A. Ulmer and T. Gulder, *Chem. – Eur. J.*, 2016, **22**, 8728–8739.

9 (*a*) *Organic Electrochemistry, 5th Ed*, ed. O. Hammerich and B. Speiser, CRC Press, Taylor and Francis, New-York, 2016; (*b*) C. Kingston, M. D. Palkowitz, Y. Takahira, J. C. Vantourout, B. K. Peters, Y. Kawamata and P. S. Baran, *Acc. Chem. Res.*, 2020, **53**, 72–83; (*c*) D. Pollok and S. R. Waldvogel, *Chem. Sci.*, 2020, **11**, 12386–12400; (*d*) K. Yamamoto, M. Kuriyama and O. Onomura, *Acc. Chem. Res.*, 2020, **53**, 105–120; (*e*) S. Cembellin and B. Batanero, *Chem. Rec.*, 2021, **21**, 2453–2471; (*f*) C. Zhu, N. W. J. Ang, T. H. Meyer, Y. Qiu and L. Ackermann, *ACS Cent. Sci.*, 2021, **7**, 415–431; (*g*) Y. Yuan and A. Lei, *Acc. Chem. Res.*, 2019, **52**, 3309–3324; (*h*) K. Mitsudo, Y. Kurimoto, K. Yoshioka and S. Suga, *Chem. Rev.*, 2018, **118**, 5985–5999; (*i*) S. R. Waldvogel, S. Lips, M. Selt, B. Riehl and C. J. Kampf, *Chem. Rev.*, 2018, **118**, 6706–6765; (*j*) M. Yan, Y. Kawamata and P. S. Baran, *Chem. Rev.*, 2017, **117**, 13230–13319; (*k*) A. Wiebe, T. Gieshoff, S. Möhle, E. Rodrigo, M. Zirbes and S. R. Waldvogel, *Angew. Chem.,*

Int. Ed., 2018, **57**, 5594–5619; (*l*) D. Pollok and S. R. Waldvogel, *Chem. Sci.*, 2020, **11**, 12386–12400.

10 (*a*) S. Luan, T. Castanheiro and T. Poisson, *Org. Lett.*, 2023, **25**, 1678–1682; (*b*) M. Aelterman, M. Sayes, P. Jubault and T. Poisson, *Chem. – Eur. J.*, 2021, **27**, 8277–8282; (*c*) T. Biremond, P. Jubault and T. Poisson, *ACS Org. Inorg. Au*, 2022, **2**, 148–152; (*d*) T. Cantin, A. B. Charette, T. Poisson and P. Jubault, *Synthesis*, 2023, **55**, 2943–2950; (*e*) M. Aelterman, P. Jubault and T. Poisson, *Eur. J. Org. Chem.*, 2023, e202300063; (*f*) M. Aelterman, T. Biremond, P. Jubault and T. Poisson, *Chem. – Eur. J.*, 2022, **28**, e2022002194; (*g*) S. Luan, T. Castanheiro and T. Poisson, *Adv. Synth. Catal.*, 2022, **364**, 2741–2747.

11 (*a*) T. Yuan, A. Yao, Y. Zheng, M. Gao, Z. Zhou, J. Qiao, J. Hu, B. Ye, J. Zhao, H. Wen and A. Lei, *iScience*, 2019, **12**, 293–303; (*b*) W. Xie, S. Ning, N. Liu, Y. Bai, S. Wang, S. Wang, L. Shi, X. Che and J. Xiang, *Synlett*, 2019, **30**, 1313–1316; (*c*) P. Zhang, J. Chen, W. Gao, Y. Xiao, C. Liu, S. Xu, X. Yan and D. Qin, *Molecules*, 2019, **24**, 696; (*d*) J. Wu, H. Abou-Hamdan, R. Guillot, C. Kouklovsky and G. Vincent, *Chem. Commun.*, 2020, **56**, 1713–1716; (*e*) L. Sun, X. Zhang, Z. Li, J. Ma, Z. Zeng and H. Jiang, *Eur. J. Org. Chem.*, 2018, 4949–4952; (*f*) X. Liu, Z. Wu, C. Feng, W. Liu, M. Li and Z. Shen, *Eur. J. Org. Chem.*, 2022, e202200262; (*g*) Z. Zhou, Y. Yuan, Y. Cao, J. Qiao, A. Yao, J. Zhao, W. Zuo, W. Chen and A. Lei, *Chin. J. Chem.*, 2019, **37**, 611–615; (*h*) Z. Tan, Y. Liu, R. Helmy, N. R. Rivera, D. Hesk, S. Tyagarajan, L. Yang and J. Su, *Tetrahedron Lett.*, 2017, **58**, 3014–3018.

12 (*a*) K. Kulangiappar, G. Karthik and M. Anbu Kulandainathan, *Synth. Commun.*, 2013, **39**, 2304–2309; (*b*) T. Raju, K. Kulangiappar, M. Anbu Kulandainathan, U. Uma, R. Malini and A. Muthukumaran, *Tetrahedron Lett.*, 2006, **47**, 4581–4584; (*c*) T. Raju, K. Kulangiappar, M. Anbu Kulandainathan and A. Muthukumaran, *Tetrahedron Lett.*, 2005, **46**, 7047–7050; (*d*) X. Yang, Q.-L. Yang, X.-Y. Wang, H.-H. Xu, T.-S. Mei, Y. Huang and P. Fang, *J. Org. Chem.*, 2020, **85**, 3497–3507; (*e*) Q. Liu, B. Sun, Z. Liu, Y. Kao, B.-W. Dong, S.-D. Jiang, F. Li, G. Liu, Y. Yang and F. Mo, *Chem. Sci.*, 2018, **9**, 8731–8737.

13 (*a*) K. Kulangiappar, M. Ramprakash, D. Vasudevan and T. Raju, *Synth. Commun.*, 2015, **46**, 145–153; (*b*) C. Wan, R.-J. Song and J.-H. Li, *Org. Lett.*, 2019, **21**, 2800–2803; (*c*) T.-T. Zhang, M.-J. Luo, Y. Li, R.-J. Song and J.-H. Li, *Org. Lett.*, 2020, **22**, 7250–7254; (*d*) M.-X. Bi, P. Qian, Y.-K. Wang, Z.-G. Zha and Z.-Y. Wang, *Chin. Chem. Lett.*, 2017, **28**, 1159–1162.

14 R. Jagatheesan, K. Joseph Santhana Raj, S. Lawrence and C. Christopher, *RSC Adv.*, 2016, **6**, 35602–35608.

15 Q.-L. Yag, X.-Y. Wang, T.-L. Wang, X. Yang, D. Liu, X. Tong, X.-Y. Wu and T.-S. Mei, *Org. Lett.*, 2019, **21**, 2645–2649.

16 For selected reviews, see: (*a*) K. Gopalaiah and H. B. Kagan, *Chem. Rev.*, 2011, **111**, 4599–4657; (*b*) R. Matsubara and S. Kobayashi, *Acc. Chem. Res.*, 2008, **41**, 292–301; (*c*) T. Courant, G. Dagousset and G. Masson, *Synthesis*, 2015, **47**, 1799–1826; (*d*) G. Bernadat and G. Masson, *Synlett*, 2014, **25**, 2842–2867; (*e*) D. R. Carbery, *Org. Biomol. Chem.*, 2008, **6**, 3455–3460; (*f*) N. Gigant, L. Chausset-Boissarie and I. Gillaizeau, *Chem. – Eur. J.*, 2014, **20**, 7548–7564.

17 (*a*) J. Qian, Y. Liu, J. Zhu, B. Jiang and Z. Xu, *Org. Lett.*, 2011, **13**, 4220–4223; (*b*) T. Xu and G. Liu, *Org. Lett.*, 2012, **14**, 5416–5419; (*c*) C. Jonasson, A. Horvath and J.-E. Backvall, *J. Am. Chem. Soc.*, 2000, **122**, 9600–9609; (*d*) S. Karur, S. R. S. S. Kotti, X. Xu, J. F. Cannon, A. Headley and G. Li, *J. Am. Chem. Soc.*, 2003, **125**, 13340–13341; (*e*) X. Ji, H. Huang, W. Wu and H. Jiang, *J. Am. Chem. Soc.*, 2013, **135**, 5286–5289; (*f*) C. Liu and F. Yang, *Eur. J. Org. Chem.*, 2019, 6867–6870; (*g*) W. Wang, L. Liu, W. Chang and J. Li, *Chem. – Eur. J.*, 2018, **24**, 8542–8547; (*h*) X. Ji, H. Huang, W. Xiong, K. Huang, W. Wu and H. Jiang, *J. Org. Chem.*, 2014, **79**, 7005–7011.

18 (*a*) J. Chai, W. Ding, C. Wang, S. Ito, J. Wu and N. Yoshikai, *Chem. Sci.*, 2021, **12**, 15128–15133; (*b*) T. Wang, Z. Tang, H. Luo, Y. Tian, M. Xu, Q. Lu and B. Li, *Org. Lett.*, 2021, **23**, 6293–6298; (*c*) S. Arepally, A. Chamuah, N. Katta and D. S. Sharada, *Eur. J. Org. Chem.*, 2019, 1542–1547; (*d*) M. Li, H. Yuan, B. Zhao, F. Liang and J. Zhang, *Chem. Commun.*, 2014, **50**, 2360–2363.

19 U. Wille, O. Krüger, A. Kirsch and U. Lüning, *Eur. J. Org. Chem.*, 1999, 3185–3189.

20 (*a*) M. Yamagishi, K. Nishigai, T. Hata and H. Urabe, *Org. Lett.*, 2011, **13**, 4873–4875; (*b*) M. Yamagishi, K. Nishigai, A. Ishii, T. Hata and H. Urabe, *Angew. Chem., Int. Ed.*, 2012, **51**, 6471–6474.

21 A. E. Pasqua, J. J. Crawford, D.-L. Long and R. Marquez, *J. Org. Chem.*, 2012, **77**, 2149.

22 R. H. Mitchell, Y.-H. Lai and R. W. Williams, *J. Org. Chem.*, 1979, **44**, 4733.

23 D. Bliman, M. Pettersson, M. Bood and M. Grotli, *Tetrahedron Lett.*, 2014, **55**, 2929.

24 See ESI† for details.

25 (*a*) A. J. J. Lennox and G. C. Lloyd-Jones, *Chem. Soc. Rev.*, 2014, **43**, 412–443; (*b*) N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457–2483; (*c*) S. Namirembe and J. P. Morken, *Chem. Soc. Rev.*, 2019, **48**, 3464–3474; (*d*) J. W. B. Fyfe and A. J. B. Watson, *Chem*, 2017, **3**, 31–55; (*e*) J. Carreras, A. Caballero and P. J. Pérez, *Chem. – Asian J.*, 2019, **14**, 329–343; (*f*) L. Xu, S. Zhang and P. Li, *Chem. Soc. Rev.*, 2015, **44**, 8848–8858; (*g*) G. Duret, R. Quinlan, P. Bisseret and N. Blanchard, *Chem. Sci.*, 2015, **6**, 5366–5382.

