

1

Historical Introduction

Viktor V. Zhdankin

Department of Chemistry and Biochemistry, University of Minnesota Duluth, Duluth, MN, USA

1.1 Discovery of Iodine and Early Studies

Iodine was originally isolated and recognized as a new element early in the nineteenth century. The French industrial chemist Bernard Courtois had noticed that the addition of concentrated sulfuric acid to seaweed ashes resulted in the emission of a violet vapor that could be condensed to the deep purple solid with the metal-like appearance of the crystals. These observations were first published in November 1813 in the *Annales de Chimie* [1]. In this original paper, the name “iode,” derived from the Greek word *ιώδης* for violet, was first used for the new substance “due to the beautiful violet color of its vapor.” Soon after, J. L. Gay-Lussac published his initial results on the chemical properties of iodine demonstrating that this was a novel element capable of forming compounds with other elements [2, 3].

Numerous inorganic compounds of polyvalent iodine in the oxidation states +3, +5, and +7 were prepared early in the nineteenth century. In particular, iodine trichloride was first prepared by J. L. Gay-Lussac by reacting iodine or iodine monochloride with an excess of chlorine under gentle heating [4]. In the same 1814 paper [4], the preparation of potassium iodate by the action of iodine on hot potash lye was described. The history of the inorganic chemistry of iodine was summarized in numerous common textbooks and reference sources [5–9]. Iodine history, chemistry, and applications were discussed in detail in the review commemorating two centuries of iodine research [10].

The preparation of first polyvalent organoiodine compound, (dichloroiodo)benzene **1** (Figure 1.1) was reported by the German chemist C. Willgerodt in 1886 in the *Journal fuer Praktische Chemie* [11]. Many other organic iodine(III) and iodine(V) compounds were prepared during the 1890s and at the beginning of the twentieth century. In particular, (diacetoxyiodo)benzene **2**, iodosylbenzene **3**, and iodylbenzene **4** were reported in 1892 [12]; 2-iodoxybenzoic acid (IBX, **5**) in 1893 [13]; and the first example of diaryliodonium salts **6** were reported by C. Hartmann and V. Meyer in 1894 [14].

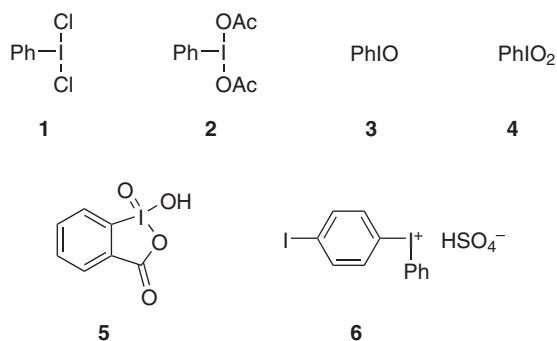


Figure 1.1 First examples of polyvalent organoiodine compounds reported in 1886–1894.

The early research on organoiodine chemistry was summarized by C. Willgerodt in 1914 in a comprehensive book *Die Organischen Verbindungen mit Mehrwertigen Jod* describing nearly 500 polyvalent organoiodine compounds [15].

1.2 Iodine Research in the Twentieth Century

During the period between 1914 and 1970s, research activity in the area of organic chemistry of iodine compounds was relatively low and represented mainly by valuable contributions from the laboratories of I. Masson, R. B. Sandin, F. M. Beringer, K. H. Pausacker, A. N. Nesmeyanov, and O. Neilands. This research, dealing mostly with various iodonium compounds, was summarized in the reviews of R. B. Sandin [16] and D. F. Banks [17] published in 1943 and 1966, respectively. A comprehensive list of known at that time iodine(III) and iodine(V) compounds with their physical properties was published by F. M. Beringer and E. M. Gindler in *Iodine Abstracts and Reviews* in 1956 [18].

Starting from the 1970s, the interest in the chemistry of iodine compounds had significantly increased. At that time, numerous new classes of polyvalent organoiodine compounds were discovered and many useful synthetic applications of these compounds were developed. The concept of hypervalent molecules was originally proposed by J. I. Musher in 1969 [19], and shortly after, the terminologies “hypervalent iodine,” “hypervalent iodine reagents,” “hypervalent iodine compounds,” and “organohypervalent iodine reagents” were broadly introduced in the works of J. C. Martin, R. M. Moriarty, and several other researchers. During the 1980s, polyvalent iodine compounds have achieved the status of valuable synthetic reagents known under the common name of hypervalent iodine reagents.

The foundation of modern hypervalent iodine chemistry was established in the 1980s in the groundbreaking works of G. F. Koser, J. C. Martin, R. M. Moriarty, P. J. Stang, A. Varvoglis, Y. Kita, M. Ochiai, and N. S. Zefirov. The twentieth-century iodine research was summarized in two books published by A. Varvoglis in 1992 and 1997: a comprehensive monograph *The Organic Chemistry of Polycoordinated Iodine* [20] and a book on the applications of hypervalent iodine compounds in organic synthesis [21]. Numerous general reviews [22–27], book chapters [28–33], and specialized reviews on phenyliodine(III) carboxylates [34, 35],

[hydroxy(tosyloxy)iodo]benzene [36], the chemistry of alkynyliodonium salts [37], electrophilic perfluoroalkylations [38], application of hypervalent iodine in the carbohydrate chemistry [39], carbon–carbon bond formation via hypervalent iodine [40], hypervalent iodine oxidations [41, 42], hypervalent iodine compounds as free radical precursors [43], synthesis of heterocyclic compounds using organohypervalent iodine reagents [44], and the chemistry of benziodoxoles [45] were also published during the 1980s and 1990s.

1.3 Iodine Research in the Twenty-first Century

During the first two decades of the twenty-first century, iodine chemistry has experienced explosive development. Six books [46–51] and hundreds of reviews summarizing various aspects of iodine chemistry and applications have been published between 2001 and 2020. Thousands of research works utilizing iodine reagents in organic and inorganic synthesis are currently published every year. Starting from the beginning of the twenty-first century, the International Conference on Hypervalent Iodine Chemistry (ICHIC) is regularly convened in different countries, the Society of Iodine Science (SIS) holds annual meetings in Japan, and the American Chemical Society presents the National Award for Creative Research and Applications of Iodine Chemistry biennially. The World Iodine Association (www.worldiodineassociation.com) was officially registered in 2017 as an international nonprofit organization established with the main goal of providing information about the purposes, uses, and applications of iodine and its derivatives.

Current surging interest in iodine chemistry is mainly explained by the very useful oxidizing properties of hypervalent iodine reagents, combined with their benign environmental character and commercial availability. Iodine(III) and iodine(V) derivatives are now routinely used in organic synthesis as reagents for various selective oxidative transformations of complex organic molecules. The discovery and utilization of similarities between the transition metal chemistry and the hypervalent iodine chemistry, and in particular, the development of the highly efficient and enantioselective catalytic systems based on the iodine redox chemistry, has added a new dimension to the field of hypervalent iodine chemistry and initiated a major surge of research activity, which is expected to continue in the future.

1.4 Brief History of Iodine Catalysis

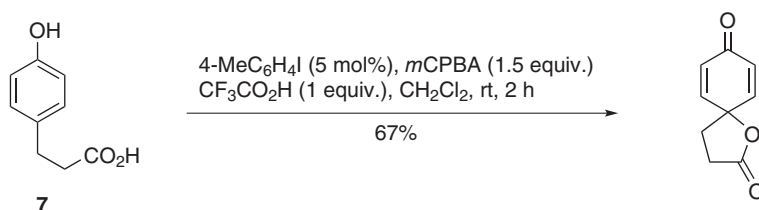
A quick SciFinder search on the concept “iodine catalysts” reveals over 10 000 papers published between 1890 and 2020, including about 300 older papers published during the first half of the twentieth century. The first reliable observations of inorganic and organic reactions catalyzed by iodine date back to the early 1900s. For example, J. Brode [52] and J. H. Walton [53] reported in 1904 the catalytic decomposition of

hydrogen peroxide in the presence of iodine involving hypoiodite as a key intermediate. L. Bruner in 1902 published a mechanistic study of the catalytic action of iodine on the bromination of benzene, in which the catalytic effect of iodine is explained by the formation of iodine bromide, IBr, as active species [54].

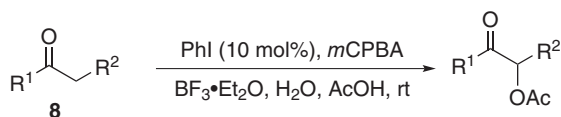
The vast majority of papers on iodine catalysis published between 1900 and 2005 did not involve the oxidation of iodine to the hypoiodite or hypervalent iodine-active species. These papers almost exclusively deal with the catalytic application of iodine as a Lewis acid or as a radical initiator. In some catalytic reactions, iodide anion is utilized as a strong nucleophile, generating organic iodides RI as intermediate species incorporating the excellent iodide-leaving group. Such catalysis involving the generation of organic iodides has been employed in the important Monsanto–Cativa industrial process for the production of acetic acid. In this process, the catalytic hydroiodic acid converts the methanol feedstock into methyl iodide, which undergoes Rh- or Ir-catalyzed carbonylation. Hydrolysis of the resulting acetyl iodide regenerates hydroiodic acid and gives acetic acid [55]. The carbonylation of methanol, catalyzed by rhodium in the presence of hydroiodic acid, was originally invented by Monsanto company in the 1960s. In the 1990s, Eastman Chemical Company developed a modification of this industrial process based on the use of lithium iodide as the cocatalyst [56].

A new era in iodine catalysis was opened in 2005 by the discovery of reactions catalyzed by hypervalent iodine species. The similarities between hypervalent iodine species and transition metal-organic complexes had been widely recognized in the works of many researchers since the end of the twentieth century. At that time, the terminologies “oxidative addition,” “reductive elimination,” “ligand exchange,” and “ligand coupling” became common in mechanistic discussions of the reactions of hypervalent molecules [57]. However, catalytic reactions, typical of transition metals, remained unknown for hypervalent iodine compounds until the beginning of the twenty-first century.

In 2005, Kita and Ochiai independently reported the catalytic use of aryl iodides, in the presence of stoichiometric *m*-chloroperoxybenzoic acid, to perform oxidative dearomatization of phenolic substrates **7** (Scheme 1.1) [58], or α -acetoxylation of carbonyl compounds **8** (Scheme 1.2) [59], respectively. These reactions involved selective generation of the highly reactive hypervalent iodine(III) species (e.g. **9** in Scheme 1.2) *in situ* from aryl iodide and terminal oxidant.

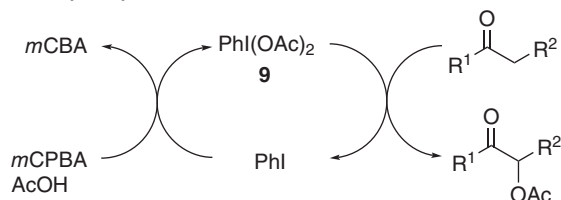


Scheme 1.1 Catalytic oxidative spirocyclization reaction of a phenolic substrate in the presence of 4-iodotoluene.



$\text{R}^1, \text{R}^2 = \text{alkyl, aryl, etc.}$

Catalytic cycle:



Scheme 1.2 Catalytic α -acetoxylation of carbonyl compounds in the presence of iodobenzene.

First examples of the catalytic application of the iodine(V) species in the oxidation of alcohols using Oxone[®] ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) as a stoichiometric oxidant at 70 °C were independently reported by the groups of Vinod [60] in 2005 and Giannis [61] in 2006. A few years later, Ishihara and coworkers discovered that 2-iodoxybenzenesulfonic acid (IBS) can act as an extremely active catalyst for the selective oxidation of alcohols to aldehydes, ketones, carboxylic acids, and enones with Oxone [62]. While chemical reactions catalyzed by hypervalent iodine species were discovered only in 2005, the electrochemical generation of iodine(III) species *in situ* from catalytic amounts of iodoarenes (0.05–0.2 equiv), and the use of these species as the in-cell mediators in electrochemical fluorination reactions, had been known since 1994 [63].

First examples of enantioselective reactions catalyzed by chiral aryl iodides [64–69] or chiral ammonium iodides [70] were reported by several research groups in 2007–2010. These groundbreaking initial reports were followed by a huge wave of publications describing various enantioselective oxidative transformations catalyzed by hypervalent iodine species. A brief historical overview of enantioselective iodine catalysis can be found in the 2019 review of Muñiz and coauthors [71].

References

- 1 Courtois, B. (1813). Découverte d'une substance nouvelle dans le Vareck. *Ann. Chim.* 88: 304–310.
- 2 Gay-Lussac, J.L. (1813). Sur la combinaison de l'iode avec l'oxygène. *Ann. Chim.* 88: 319–321.
- 3 Gay-Lussac, J.L. (1813). Sur un nouvel acide formé avec la substance découverte par M. Courtois. *Ann. Chim.* 88: 311–318.
- 4 Gay-Lussac, J.L. (1814). Sur l'iode. *Ann. Chim.* 91: 5–160.

- 5 Greenwood, N.N. and Earnshaw, A. (1997). *Chemistry of the Elements*. Oxford: Butterworth-Heinemann.
- 6 Mellor, J.W. (1922). *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*. London: Longmans, Green and Co.
- 7 (1933). *Gmelins Handbuch der Anorganischen Chemie, 8 Auflage*. Berlin: Verlag Chemie.
- 8 Brasted, R.C. (1954). Iodine. In: *Comprehensive Inorganic Chemistry*, vol. 3 (eds. M.C. Sneed, J.L. Maynard and R.C. Brasted). Princeton, NJ: D. Van Nostrand Co., Inc.
- 9 Gutmann, V. (1967). *Halogen Chemistry*. New York: Academic Press.
- 10 Kuepper, F.C., Feiters, M.C., Olofsson, B. et al. (2011). Commemorating two centuries of iodine research: an interdisciplinary overview of current research. *Angew. Chem. Int. Ed.* 50: 11598–11620.
- 11 Willgerodt, C. (1886). Découverte d'une substance nouvelle dans le Vareck. *J. Prakt. Chem. (Weinheim, Germany)* 33: 154.
- 12 Willgerodt, C. (1892). Zur Kenntniss aromatischer Jodidchloride, des Jodoso- und Jodobenzols. *Ber. Dtsch. Chem. Ges.* 25: 3494–3502.
- 13 Hartmann, C. and Meyer, V. (1893). Ueber Jodobenzoësäure. *Ber. Dtsch. Chem. Ges.* 26: 1727–1732.
- 14 Hartmann, C. and Meyer, V. (1894). Ueber eine neue Klasse jodhaltiger, stickstofffreier organischer Basen. *Ber. Dtsch. Chem. Ges.* 27: 426–432.
- 15 Willgerodt, C. (1914). *Die Organischen Verbindungen mit Mehrwertigen Jod*. Stuttgart: Ferdinand Enke Verlag.
- 16 Sandin, R.B. (1943). Organic compounds of polyvalent iodine. *Chem. Rev.* 32: 249–276.
- 17 Banks, D.F. (1966). Organic polyvalent iodine compounds. *Chem. Rev.* 66: 243–266.
- 18 Beringer, F.M. and Gindler, E.M. (1956). Organic compounds of polyvalent iodine. *Iodine Abstr. Rev.* 3: 70. pp.
- 19 Musher, J.I. (1969). Chemistry of hypervalent molecules. *Angew. Chem. Int. Ed.* 8: 54–68.
- 20 Varvoglis, A. (1992). *The Organic Chemistry of Polycoordinated Iodine*. New York: VCH Publishers, Inc.
- 21 Varvoglis, A. (1997). *Hypervalent Iodine in Organic Synthesis*. London: Academic Press.
- 22 Varvoglis, A. (1997). Chemical transformations induced by hypervalent iodine reagents. *Tetrahedron* 53: 1179–1255.
- 23 Merkushev, E.B. (1987). Organic compounds of polyvalent iodine. Derivatives of iodobenzene. *Russ. Chem. Rev.* 56: 826.
- 24 Moriarty, R.M. and Prakash, O. (1986). Hypervalent iodine in organic synthesis. *Acc. Chem. Res.* 19: 244–250.
- 25 Stang, P.J. and Zhdankin, V.V. (1996). Organic polyvalent iodine compounds. *Chem. Rev.* 96: 1123–1178.

- 26 Kitamura, T. and Fujiwara, Y. (1997). Recent progress in the use of hypervalent iodine reagents in organic synthesis. A review. *Org. Prep. Proced. Int.* 29: 409–458.
- 27 Wirth, T. and Hirt, U.H. (1999). Hypervalent iodine compounds. Recent advances in synthetic applications. *Synthesis*: 1271–1287.
- 28 Nguyen, T.T. and Martin, J.C. (1984). Heterocyclic rings containing halogen. In: *Comprehensive Heterocyclic Chemistry*, vol. 1 (eds. A.R. Katritzky and C.W. Rees), 563. Oxford: Pergamon Press.
- 29 Koser, G.F. (1983). Hypervalent halogen compounds. In: *The Chemistry of Functional Groups, Suppl. D: Chemistry of Halides, Pseudo-Halides, Azides* (eds. S. Patai and Z. Rappoport), 721–811. Chichester: Wiley-Interscience.
- 30 Koser, G.F. (1983). Halonium ions. In: *Chemistry of Halides. Halides, Pseudo-Halides Azides*, vol. 2 (eds. S. Patai and Z. Rappoport), 1265–1351. Chichester: Wiley-Interscience.
- 31 Koser, G.F. (1995). Halonium ions. In: *Chemistry of Halides, Pseudo-Halides and Azides, Suppl. D2* (eds. S. Patai and Z. Rappoport), 1173–1274. Chichester: Wiley-Interscience.
- 32 Zhdankin, V.V. and Stang, P.J. (1999). Polycordinate iodine compounds. In: *Chemistry of Hypervalent Compounds* (ed. K.-Y. Akiba), 327–358. New York: VCH Publishers.
- 33 Ochiai, M. (1999). Organic synthesis using hypervalent organoiodanes. In: *Chemistry of Hypervalent Compounds* (ed. K.Y. Akiba), 359–387. New York: VCH Publishers.
- 34 Varvoglis, A. (1981). Aryliodine(III) dicarboxylates. *Chem. Soc. Rev.* 10: 377–407.
- 35 Kirschning, A. (1998). (Diacetoxyiodo)benzene DIB. A multi-talented oxidant in organic synthesis. *J. Prakt. Chem.* 340: 184–186.
- 36 Moriarty, R.M., Vaid, R.K., and Koser, G.F. (1990). [Hydroxy(organosulfonyloxy)iodo]arenes in organic synthesis. *Synlett*: 365–383.
- 37 Zhdankin, V.V. and Stang, P.J. (1998). Alkynyliodonium salts in organic synthesis. *Tetrahedron* 54: 10927–10966.
- 38 Umemoto, T. (1996). Electrophilic perfluoroalkylating agents. *Chem. Rev.* 96: 1757–1778.
- 39 Kirschning, A. (1998). Hypervalent iodine and carbohydrates. A new liaison. *Eur. J. Org. Chem.*: 2267–2274.
- 40 Moriarty, R.M. and Vaid, R.K. (1990). Carbon-carbon bond formation via hypervalent iodine oxidations. *Synthesis*: 431–447.
- 41 Moriarty, R.M. and Prakash, O. (1999). Oxidation of carbonyl compounds with organohypervalent iodine reagents. *Org. React.* 54: 273–418.
- 42 Kita, Y., Takada, T., and Tohma, H. (1996). Hypervalent iodine reagents in organic synthesis: nucleophilic substitution of *p*-substituted phenol ethers. *Pure Appl. Chem.* 68: 627–630.
- 43 Muraki, T., Togo, H., and Yokoyama, M. (1997). Hypervalent iodine compounds as free radical precursors. *Rev. Heteroatom Chem.* 17: 213–243.
- 44 Moriarty, R.M. and Prakash, O. (1998). Synthesis of heterocyclic compounds using organohypervalent iodine reagents. *Adv. Heterocycl. Chem.* 69: 1–87.

- 45 Zhdankin, V.V. (1997). Chemistry of benziodoxoles. *Rev. Heteroatom Chem.* 17: 133–151.
- 46 Wirth, T. (ed.) (2003). *Hypervalent Iodine Chemistry: Modern Developments in Organic Synthesis, Topics in Current Chemistry*, vol. 224.
- 47 Preedy, V.R., Burrow, G.N., and Watson, R.R. (eds.) (2009). *Comprehensive Handbook of Iodine: Nutritional, Biochemical, Pathological and Therapeutic Aspects*. Elsevier Inc.
- 48 Zhdankin, V.V. (2013). *Hypervalent Iodine Chemistry: Preparation, Structure, and Synthetic Applications of Polyvalent Iodine Compounds*. Chichester UK: Wiley.
- 49 Kaiho, T. (ed.) (2015). *Iodine Chemistry and Applications*. Chichester, UK: John Wiley & Sons, Inc.
- 50 Wirth, T. (ed.) (2016). *Hypervalent Iodine Chemistry: Modern Developments in Organic Synthesis, Topics in Current Chemistry*, vol. 373. Springer.
- 51 Olofsson, B., Marek, I., and Rappoport, Z. (eds.) (2019). *Patai's Chemistry of Functional Groups: The Chemistry of Hypervalent Halogen Compounds*. Wiley.
- 52 Brode, J. (1904). Oxidation of the iodine ion to hypiodite as an intermediate stage in several reactions. *Z. Phys. Chem.* 49: 208–216.
- 53 Walton, J.H. (1904). Catalysis of hydrogen peroxide by iodine ions. *Z. Phys. Chem.* 47: 185–222.
- 54 Bruner, L. (1902). Mechanism of the catalytic action of iodine on the bromination of benzene. *Bull. Int. Acad. Sci. Cracovie*: 181–200.
- 55 Jones, J.H. (2000). The Cativa process for the manufacture of acetic acid. *Platin. Met. Rev.* 44: 94–105.
- 56 Zoeller, J.R., Agreda, V.H., Cook, S.L. et al. (1992). Eastman Chemical company acetic anhydride process. *Catal. Today* 13: 73–91.
- 57 Akiba, K.-Y. (ed.) (1999). *Chemistry of Hypervalent Compounds*. New York: VCH Publishers.
- 58 Dohi, T., Maruyama, A., Yoshimura, M. et al. (2005). Versatile hypervalent-iodine(III)-catalyzed oxidations with m-chloroperbenzoic acid as a cooxidant. *Angew. Chem. Int. Ed.* 44: 6193–6196.
- 59 Ochiai, M., Takeuchi, Y., Katayama, T. et al. (2005). Iodobenzene-catalyzed alpha-acetoxylation of ketones. *In situ* generation of hypervalent (diacetoxyiodo)benzenes using m-chloroperbenzoic acid. *J. Am. Chem. Soc.* 127: 12244–12245.
- 60 Thottumkara, A.P., Bowsher, M.S., and Vinod, T.K. (2005). *In situ* generation of o-iodoxybenzoic acid (IBX) and the catalytic use of it in oxidation reactions in the presence of oxone as a co-oxidant. *Org. Lett.* 7: 2933–2936.
- 61 Schulze, A. and Giannis, A. (2006). Oxidation of alcohols with catalytic amounts of IBX. *Synthesis*: 257–260.
- 62 Uyanik, M., Akakura, M., and Ishihara, K. (2009). 2-Iodoxybenzenesulfonic acid as an extremely active catalyst for the selective oxidation of alcohols to aldehydes, ketones, carboxylic acids, and enones with oxone. *J. Am. Chem. Soc.* 131: 251–262.
- 63 Fuchigami, T. and Fujita, T. (1994). Electrolytic partial fluorination of organic compounds. 14. The first electrosynthesis of hypervalent iodobenzene difluoride

- derivatives and its application to indirect anodic gem-difluorination. *J. Org. Chem.* 59: 7190–7192.
- 64 Richardson, R.D., Page, T.K., Altermann, S. et al. (2007). Enantioselective α -oxytosylation of ketones catalyzed by iodo arenes. *Synlett*: 538–542.
- 65 Dohi, T., Maruyama, A., Takenage, N. et al. (2008). A chiral hypervalent iodine(III) reagent for enantioselective dearomatization of phenols. *Angew. Chem. Int. Ed.* 47: 3787–3790.
- 66 Altermann, S.M., Richardson, R.D., Page, T.K. et al. (2008). Catalytic enantioselective α -oxysulfonylation of ketones mediated by iodoarenes. *Eur. J. Org. Chem.*: 5315–5328.
- 67 Quideau, S., Lyvinec, G., Marguerit, M. et al. (2009). Asymmetric hydroxylative phenol dearomatization through *in situ* generation of iodanes from chiral iodoarenes and *m*-CPBA. *Angew. Chem. Int. Ed.* 48: 4605–4609.
- 68 Uyanik, M., Yasui, T., and Ishihara, K. (2010). Enantioselective Kita oxidative spirocyclization catalyzed by *in situ* generated chiral hypervalent iodine(iii) species. *Angew. Chem. Int. Ed.* 49: 2175–2177.
- 69 Uyanik, M., Yasui, T., and Ishihara, K. (2010). Chiral hypervalent iodine-catalyzed enantioselective oxidative Kita spirocyclization of 1-naphthol derivatives and one-pot diastereo-selective oxidation to epoxyspirolactones. *Tetrahedron* 66: 5841–5851.
- 70 Uyanik, M., Okamoto, H., Yasui, T., and Ishihara, K. (2010). Quaternary ammonium (hypo)iodite catalysis for enantioselective oxidative cycloetherification. *Science* 328: 1376–1379.
- 71 Flores, A., Cots, E., Berges, J., and Muñiz, K. (2019). Enantioselective iodine(I/III) catalysis in organic synthesis. *Adv. Synth. Catal.* 361: 2–25.

