ORGANOHYPERVALENT HETEROCYCLES

Journal:	*Chemical Society Reviews*
Manuscript ID	CS-SYN-12-2022-001055.R3
Article Type:	Review Article
Date Submitted by the Author:	12-Mar-2024
Complete List of Authors:	Kumar, Ravi; JC Bose University of Science and Technology, Chemistry Dohi, Toshifumi; Ritsumeikan University, Zhdankin, Viktor; University of Minnesota-Duluth, Department of Chemistry

ARTICLE

Organohypervalent Heterocycles

Ravi Kumar,*[a] Toshifumi Dohi*[b] and Viktor V Zhdankin*[c]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

This review summarizes the structural and synthetic aspects of heterocyclic molecules incorporating an atom of a hypervalent main-group element. The term "hypervalent" has been suggested for derivatives of main-group elements with more than eight valence electrons, and the concept of hypervalency is commonly used despite some criticism from theoretical chemists. The significantly higher thermal stability of hypervalent heterocycles, as compared to their acyclic analogs, adds special feature to their chemistry, particularly for bromine and iodine. Heterocyclic compounds of elements with double bonds are not categorized as hypervalent molecules owing to the zwitterionic nature of such bonds that results in the conventional 8-electron species. The review is focused mainly on hypervalent heterocyclic derivatives of nonmetal main-group elements, such as, boron, silicon, nitrogen, carbon, phosphorus, sulfur, selenium, bromine, chlorine, iodine(III) and iodine(V).

Keywords

Hypervalent, hypervalency, hypervalent heterocycles, hypervalent boron, hypervalent sulfur, hypervalent carbon, hypervalent chlorine hypervalent bromine, hypervalent iodine(III), hypervalent iodine(V)

Table of Contents

1. Introduction

A hypervalent molecule is generally defined as main group element compound which contains number of formally assignable electrons exceeding than the octet in a valence shell around the central atom.[1–4] The expansion of electronic valence shell beyond the classical Lewis-Langmuir octet, in particular the non-metallic elements, opens an important era in the chemistry of these elements. Jeremy I. Musher,[3] in 1969, originally defined hypervalent molecules as those formed by the non-metals of groups 15-18 in any of their stable valence states higher than 3, 2, 1, and 0, respectively; however, recently this terminology has been extended to the group 13 and 14 elements also.[5] The special structural features and reactivity pattern of hypervalent compounds are explained by hypervalent bonding that involves a 3c-4e bond.[5–7] Sugden explained for the subsistence of a two-centre one-electron (2c-1e) bond in hypervalent molecules and thus rationalized bonding in these molecules without the need for expanded octets or ionic bond character; which was not widely accepted at the time.[8] In 1951, the molecular orbital description of a 3c-4e model was independently developed by G.C. Pimentel[9] and R.E. Rundle[10]. Recently, Parkin made a clear distinction between the main-group element compounds that attribute to 3c-4e interactions from those featuring the 3c-2e interactions.[11] The former are termed as ‘electron-rich hypervalent molecules’ while the latter ones are called as ‘electron-deficient hypercoordinate molecules’.[12–20] Moreover, Braïda and Hiberty claimed the role of charge-shift bonding in hypervalent prototypes.[21] Further,Crabtree recently pointed out the similarity among hypervalency and other kinds of weak bonding.[22] The valence shell of the central atom is essentially

---

[a] Department of Chemistry, J C Bose University of Science and Technology, YMCA, NH-2, Sector-6, Mathura Road, Faridabad-121006 (Haryana) INDIA; ravi.dhamija@rediffmail.com; ravi.dhamija@jcboseust.ac.in
[b] Graduate School of Pharmaceutical Sciences, Ritsumeikan University 1-1-1 Nojihigashi, Kusatsu, Shiga, 525-8577 JAPAN; td1203@ph.ritsumei.ac.jp
[c] Department of Chemistry and Biochemistry, 1038 University Drive, 126 HCAMS University of Minnesota Duluth, Duluth, Minnesota 55812, USA; vzhdanki@d.umn.edu

an octet and the electrons beyond eight electrons (8e) are mainly located on the ligands, not on the central atom.

Hypervalent heterocycles are the cyclic compounds containing a hypervalent main-group element in the ring. Typically, these heterocyles include the polycoordinated heteroatoms bearing 10 electrons or 12 electrons and either distorted trigonal-bipyramidial or pseudo-octahedral geometry. However, heterocycles with elements having double bonds are not categorized as hypervalent compounds due to the zwitterionic nature that result in the eight electron species.[23] Cyclic hypervalent molecules possess higher thermal stability as compared to their acylic analogues. Enhnaced thermal stability of cyclic hypervalent molcules can be refereed to the fact that hypervalent molelcules for carbon, boron and nitrogen are possible only in cyclic strucutres. Further, the enhanced thermal stability of the cyclic versions may be attributed to the linking/bridging between equitiorial and apical ligands[24] which restricts the Berry pseudorotation and makes ligand coupling more difficult. Further, overlap of lone pair of pi-electrons on the hypervalent atom (such as iodine) with the aromatic ring (π-conjugation) may also enhance the stability.[25-26] Despite the fact that hypervalent heterocycles are associated with significantly higher thermal stability as compared to their acyclic analogs, a systematic presentation on the chemistry of these compounds is still in its infacy.[27] This review is primarily focused on the chemistry of the hypervalent heterocycles of non-metal main group elements, such as, boron, carbon, silicon, nitrogen, phosphorous, sulfur, selenium, chlorine, bromine and iodine. As there are no siginificant reports on the synthetic applications of some of the cyclic hypervalent molecules; in some cases, only synthesis and characterization of hypervalent heterocycles are discussed.

2. General Overview of Hypervalent Compounds

In 1980, the research groups of Martin, Arduengo and Kochi introduced the 'N-X-L' nomenclature to classify the hypervalent compounds of main-group elements, where 'N' represents the number of valence electrons present on the hypervalent atom 'X', and 'L' denotes the number of ligands around the central atom 'X'.[28] Parkin proposed $ML_lX_xZ_zH_h$nomenclature, which gives a more comprehensive description of this 'N-X-L' terminology.[11] However, compounds of elements containing double bonds are, in general, not included in the category of hypervalent species due to the presence of zwitterionic nature of these bonds leading to the classical 8e-species.[23] The hypervalent bonding and geometry have noteworthy implications in numerous existing growing areas of synthetic organic chemistry, such as hypervalent iodine(III) and iodine(V) reagents/catalysts, use of sterically constrained T-shaped phosphorus(III) compounds in small molecule activation and catalysis,[29-36] and utilization of novel heavier group Lewis acids in the frustrated Lewis pair chemistry.[37-44] According to the IUPAC recommendations,[45] the position and valency of a 'hypervalent atom' in a molecule is indicated by using the Greek letter 'λ'. Here, the symbol λ^n represents the heteroatom present in the non-standard valence state 'n' in a formally neutral molecule. Early considerations about the geometry of hypervalent molecules were described by the 'VSEPR model' for atomic bonding. Accordingly, AB_5 and AB_6 type molecules would acquire trigonal bipyramidal and octahedral geometry, respectively. However, the bond lengths, bond angles and violation of the octet rule were not fully justified, and hence alternative models were proposed. Further, the argument on the basic bonding descriptions of hypervalent species to recognize why they do not fulfil to the conventional Lewis octet rule has almost come to end on the theoretical front.[4,13-16,46-57]

The widely used '3c-4e' bond explained the structural features and high reactivity of the hypervalent compounds. The molecular description of the 3c-4e bond, developed by Rundel[10] and Pimentel[9], involved the formation of three molecular orbitals by the combination of p-orbital on the central atom and one atomic orbital from each of the two ligands. The three molecular orbitals obtained by the combination of these atomic orbitals are bonding, non-bonding, and anti-bonding molecular orbitals. The bonding and non-bonding molecular orbitals each contain one pair of electrons. A representative example of such type **1** of presentation from 10-I-3 is shown in **Figure 1**. The interaction of the 5p orbital of the iodine atom and the half-filled orbitals of the two ligands forms three molecular orbitals. The node present in the non-bonding molecular orbitals results in the charge distribution of almost +1.0 on the iodine atom and -0.5 on each ligand. Further, a normal covalent bond exists between the carbon substituent and the iodine atom, and this carbon substituent occupies the equatorial position. Both the ligands are attached by the hypervalent bond and occupy the apical positions leading to distorted trigonal bipyramidal geometry. Besides, the 12-I-5 species, RIL_4 has overall a square bipyramidal (or pseudooctahedral) geometry.

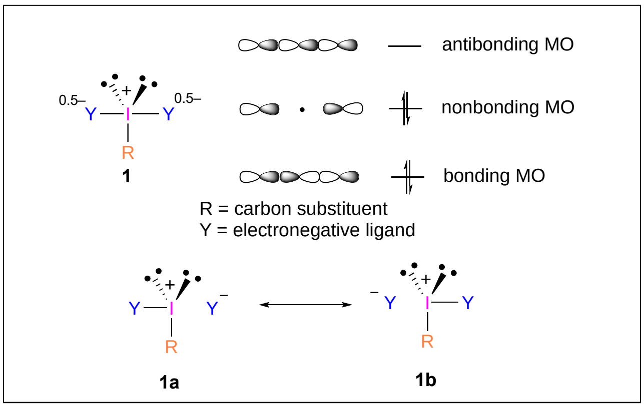


Figure 1 Molecular orbital description of the 3c-4e bond in hypervalent 10-I-3 species **1**

It is pertinent to mention here that hypervalent F, O, N, C and B componds are rarely stable. In a recent report on computational studies pertaining to the hypervalent bonding in these elements, Machsdo and coworkers suggest that synthesis of stable hypervalent second-period molecules may be achieved by destabilizing the competing non-covalent interations.[58] Further, computational studies suggest that hypervalent bonding in such molecules is considerably weaker and has less covalency than the classisal 2c-2e bonds.

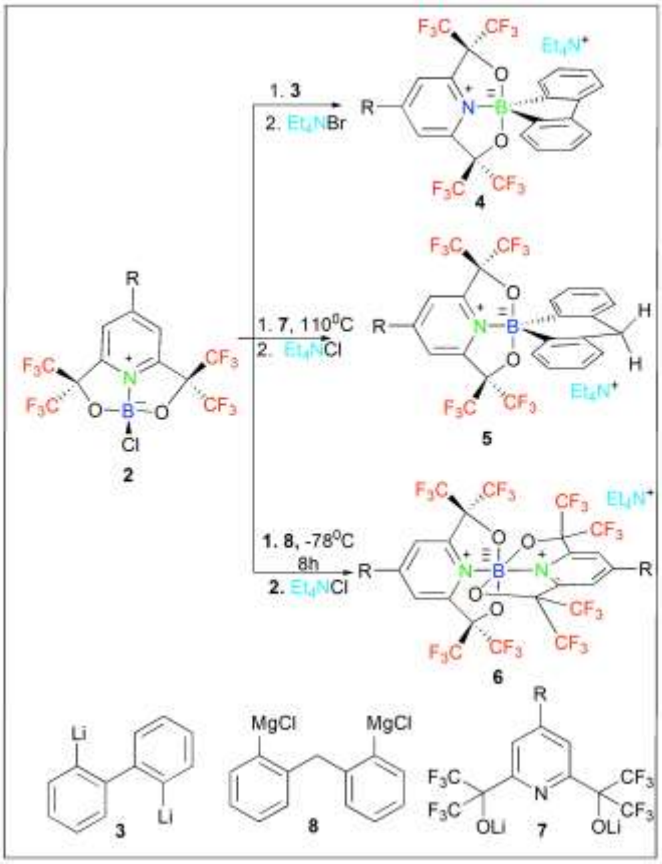
In nutshell, the structure and reactivity of hypervalent species can be best summarized as: (i) pentacoordinated hypervalent compounds, 10-X-5, 10-X-4, and 10-X-3 possess trigonal pyramidal geometry with ligand at apical positions; (ii) hexacoordinated species, 12-X-6 and 12-X-5 exists as square bipyramidal (or pseudooctahedral); (iii) hypervalent bond, in general, is longer than the sum of the covalent radii of the bonded atoms, but shorter than ionic bonds; (iv) intramolecular positional isomerisation (known as 'Berry pseudorotation') significantly explain the reactivity of hypervalent species; (v) ligand exchange and reductive elimination (ligand coupling) are typical for hypervalent compounds.

3. Hypervalent Heterocyclic Compounds of Group 13 Elements

Main group elements present in and below the third row of the periodic table are capable of expanding their valency to form hypervalent species, and numerous stable compounds with atoms formally containing 10 valence electrons have been reported in the literature.[5] As far as the second row elements such as carbon and boron are concerned, the corresponding electron state lies in the transition state of the S_N2 reaction, which leads to the general conception about these elements that these are reluctant to form stable hypervalent compounds. Synthesis and isolation of such hypervalent compounds seems to be a challenging task.[1,59-62] Despite the challenges associated with the synthesis and isolation, numerous hypervalent heterocycles of 10-electron structures for the Group 13 elements have been reported in the literature.[63] This section of the review elaborates the synthesis and structural aspects of hypervalent heterocycles of boron and aluminium, respectively.

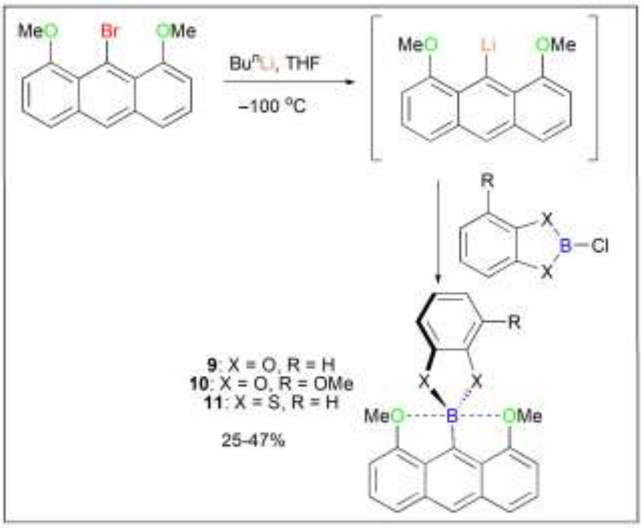
3.1. Hypervalent Boron Heterocycles

Lee and Martin first reported the anionic pentacoordinated and hexacoordinated boron species of the type **10-B-5** and **12-B-6** **(Scheme 1),** stabilized in a heterocyclic system by complexation.[61] Chloroborate **2** on reaction with dilithiobiphenyl-(**4**)[64] gives the yellow anion of **3**, stabilized as tetrabutylammonium salt as shown in **Scheme 1**. Reaction of chloroborate **2** with Grignard reagent (**8**) in THF at -78°C, followed by addition of tetrabutylammonium chloride in dioxane gives another pentacoordinated boron species **5**. Further, the hexacoordinated boron **6** was isolated as a white crystalline solid, by the reaction of **7** with dilithio derivative at 110°C followed by cation exchange.



Scheme 1 First report on anionic pentacoordinated and hexacoordinated hypervalent boron species of the type **10-B-5** and **12-B-6** by Lee and Martin

Synthesis of pentacoordinated hypervalent boron species **9-11,** bearing 1,8-disubstitued anthracene skeleton was reported by Akiba and coworkers in 2000 as outlined in **Scheme 2**.[65,66] The structures of these species and the intramolecular hypervalent interactions were elucidated on the basis of X-ray and DFT calculations. The central boron atom is found to be planar in **9-11** with sp^2 hybridization as the sum of the bond angles around the central boron atom is 360^0. Thus, one of the lone pairs on the oxygen atoms present at the 1,8-positions in **9-11** interacts with empty p-orbital of the central boron atom, to form a 3c-4e bond, and the overall structure can be regarded as slightly distorted trigonal bipyramid. Further, the two hypervalent B–O bond lengths are 2.379 and 2.441 Å in **9**, 2.398 and 2.412 Å in **10**, and identical (2.436 Å) in **11**. The lengths are longer than covalent B–O bonds (1.39 to 1.40 Å) but shorter than the sum of the van der Waals radii (3.48 Å).[65] The small difference in the B-O bond in **9** may be either due to packing effect or may be linked to the electrophilicity of boron atom, since **9**, bearing more electron-donating methoxy (OMe) group, exhibited a more symmetrical structure.



Scheme 2 Synthesis of pentacoordinated hypervalent boron species **9-11** bearing 1,8-disubstitued anthracene skeleton

In another example, Yamamoto and coworkers reported the similarly coordinated 10-methylacridinium-based hypervalent boron species **12** and confirmed the hypervalent nature by X-ray structural data **(Figure 2)**.[67] Further, hypervalent 10-B-5 species **13-15 (Figure 2),** bearing a flexible tridentate ligand based on 2,6-bis(*p*-tolyloxymethyl)benzene, were synthesized from the corresponding aryl bromides, and their structures were confirmed by single crystal X-ray analysis.[68] As revealed from the X-ray analysis, the boron atoms of the diphenyl (**14**) and the catecholato derivative (**15**) were pentacoordinated, however in case of the pinacolato derivative (**13**), it was found to be tricoordinated. Moreover, the catecholato derivative (**15**) was found to have the strongest B-O interactions indicating close to the ideal trigonal bipyramidial structure typical of hypervalent 10-B-5 species.

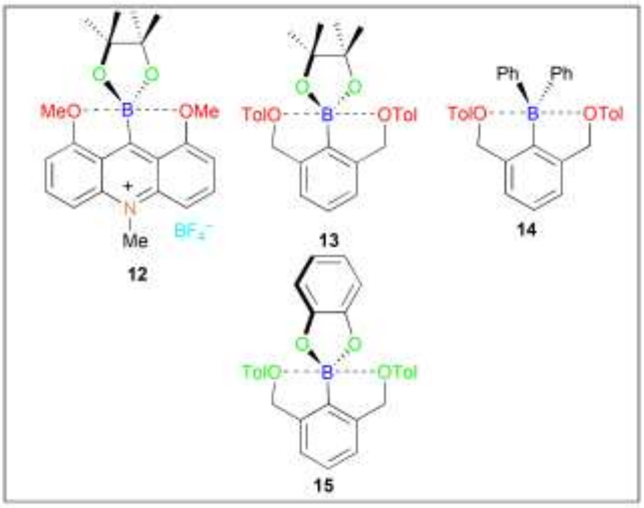


Figure 2 Structures of 10-methylacridinium-based hypervalent boron species **12** and 2,6-bis(*p*-tolyloxymethyl)benzene-based hypervalent 10-B-5 species **13-15**

In two representative examples, hypervalent boron-nitrogen heterocycles **16** and **17** have been reported.[69,70] The first hypervalent boron compound **16** (**Figure 3**) with apical N coordination was synthesized by Yamamoto and coworkers using tridentate ligand bearing two pyrimidine rings.[69] X-ray analysis and molecular orbital calculations indicated that the compound **16** possess a hypervalent pentacoordinate structure with hypervalent N-B-N bond (**Figure 3**). The crystal structure of **16** showed the 1,3,2-dioxaborolane ring to be planar indicating that the boron atom is sp^2 hybridized and is perpendicular to the phenyl rings to which it is linked. The central boron atom and two nitrogen atoms of the pyrimidine rings were nearly colinear. The B-N distances (equal to 2.537 Å in both cases) are shorter as compared to the sum of the vander Waals radii (3.62 Å). In another example, terpyridine-based hypervalent boron-nitrogen compound, [(β-diketiminate)B(terpy)](OTf)$_2$ **(17)** (**Figure 3)** has been synthesized in 85% yield by Vidovic, Findlater and coworkers.[70] X-ray analysis of the compound **17** suggested the pentacoordination with four shorter B-N bonds (bond lengths between 1.50 and 1.63 Å) and one B-N bond having bond length 2.94 Å. The authors describe this molecule **17** as hypervalent; however, the geometry provided in X-ray picture is not convincing. In particular, the boron atom is best described as tetrahedral and the N5 lone pair is not even directed toward boron. Boron is likely too small to sit in the terpy pocket and have a bonding interaction with all three nitrogen atoms.

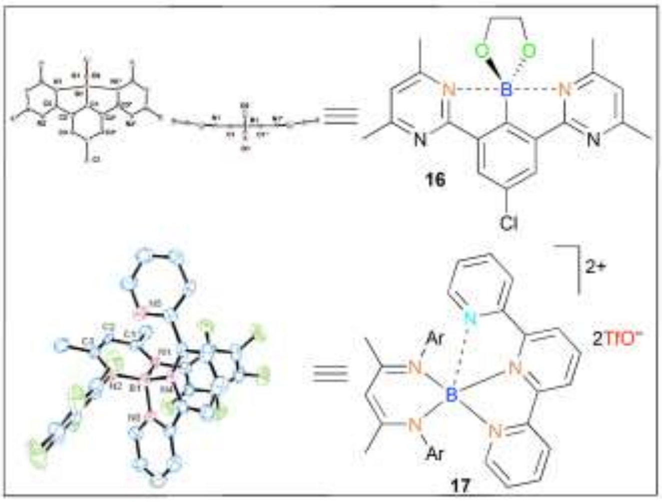
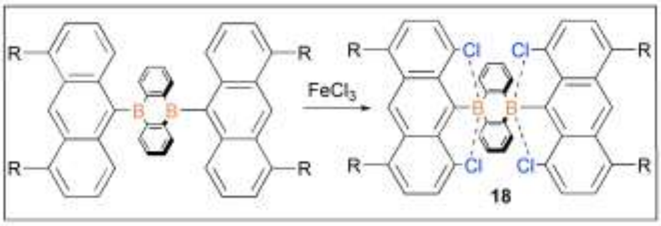


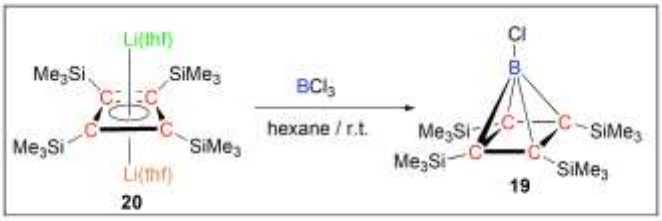
Figure 3 X-ray structures of hypervalent boron-nitrogen heterocycles **16-17**

A pentacoordinate organoboron compound, B,B-bis(1,8-dichloro-9-anthryl)-substituted 9,10-dydro-9,10-diboraanthracene (**18**) was developed by Yamaguchi and coworkers as outlined in **Scheme 3**.[71] in these compounds, orthogonal arrangement of the anthryl substitutents might push the boron and chlorine atoms to form a 3c-4e bond.



Scheme 3 Synthesis of pentacoordinate organoboron compound, B,B-bis(1,8-dichloro-9-anthryl)-substituted 9,10-dydro-9,10-diboraanthracene (**18**)

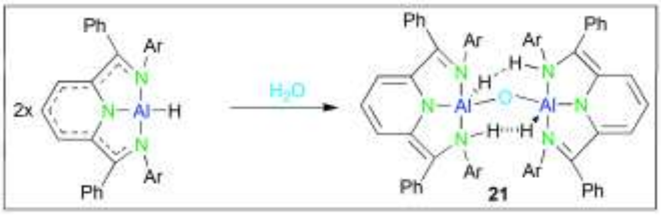
Lee, Sekiguchi and coworkers reported the first representative example of the pyramidal compounds with the group 13 elements, chloroborapyramidane (**19**) (**Scheme 4**).[72] Reaction of $\mathbf{20}^{2-}[\mathrm{Li(thf)}^{+}]_2$ with BCl$_3$ in hexane afforded compound **19** as pale-yellow crystals in 51% yield. B-Cl bond of 1.766 Å in **19** is shorter than the sum of the single bond covalent radii of boron and chlorine atoms of 1.84 Å. Crystal structure of **19** suggested an unprecedented square pyramidal geometry with the central boron atom pulled above the centre of the carbon ring base.



Scheme 4 Synthesis of chloroborapyramidane **19**

3.2. Hypervalent Aluminium Heterocycles

One of the representative examples of hypervalent aluminium heterocycles can be illustrated by the alumoxane **21**, which is obtained by the aluminium-amido-mediated heterolytic addition of water as shown in **Scheme 5**.[73]



Scheme 5 Aluminium-amido-mediated heterolytic addition of water affords alumoxane **21**

In 2009, Huang group demonstrated various deprotonation and reductive addition reactions of hypervalent aluminium dihydride compounds with primary and secondary amines, phenols, ketones, and phenyl isothiocyanate leading to the synthesis of various hypervalent heterocycles **22-25** (**Figure 4**).[74]

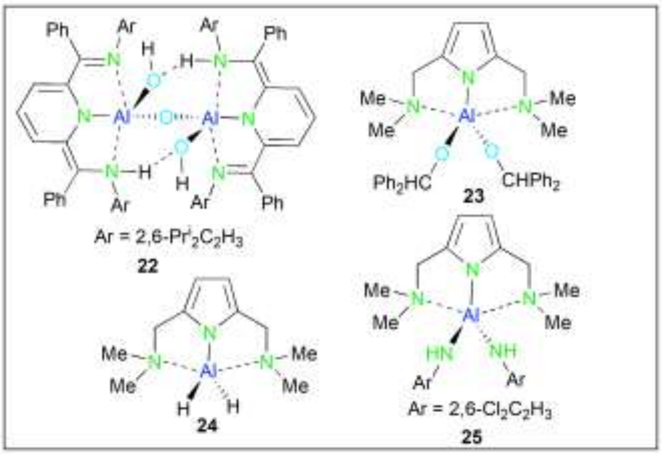


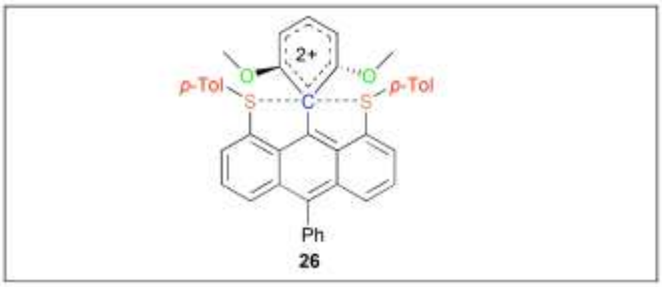
Figure 4 Structures of hypervalent aluminium heterocycles **22-25**

4. Hypervalent Heterocyclic Compounds of Group 14 Elements

In recent years, research interest in the group 14 compounds with non-classical chemical bonds has augmented extensively.[5,75] These include the derivatives of carbon, silicon, germanium, tin, and lead. The extension in the coordination sphere in these elements is generally due to the additional intra- or intermolecular coordination interactions. In case of the hypervalent compounds of group 14 elements, the donor lone pair of electrons is usually provided by the ligand as the central atom has no ns^2 lone pair. In the early 1960s, organotin compounds were shown to have the ability to expand their coordination spheres.[76-77] Hulme reported the first structurally characterized pentacoordinated organotin compound PyMe$_3$SnCl, in 1963.[78] In the last three decades, five (TBP, SP) and six (Oh) coordinated Sn have been extensively studied. Interestingly, some studies on hypervalent carbon compounds are also reported mainly by the Martin group, as well by Akiba, Yamamoto and coworkers.

4.1. Hypervalent Carbon Heterocycles

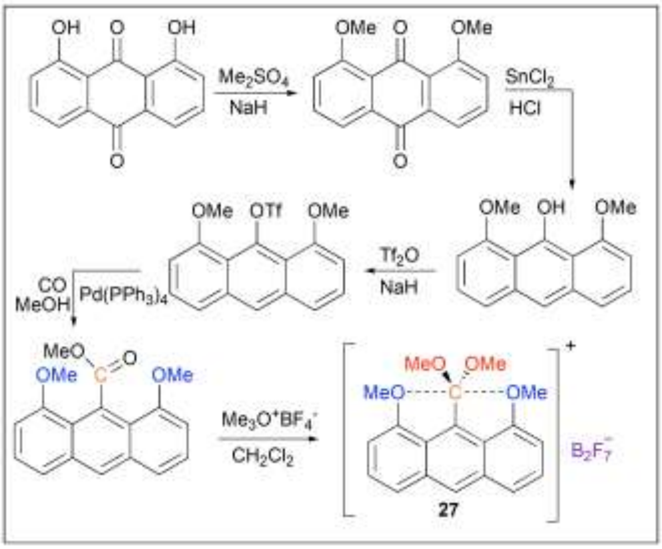
Pentacoordinate carbon compounds, termed as electron-deficient and electron-rich species depending on the number of formal valence electrons around the central carbon, have distinct structures and properties. Electron-rich species such as 10-C-5, generally found as the transition state of a fundamental bimolecular nucleophilic substitution, usually consist of an interaction of a vacant 2p orbital of the central carbon atom with two lone-pair electrons or an interaction between a vacant C-X σ^*orbital and a lone pair of a nucleophile. These pentacoordinate carbon compounds bearing a 3c-4e bond are termed as hypervalent carbon compounds. Although hypervalent compounds of heavy main group elements are widespread, however, in case of the light second row elements, synthesis and isolation always presents a big challenge. Earlier syntheses of hypervalent carbon compounds include significant work done by Martin and coworkers;[1,59,61,79-81] however, lack of solid-state X-ray crystallographic data couldn't confirm the existence of 3c–4e bonding in these compounds. Martin and coworkers reported synthesis of hypervalent carbon species **26** through the coordination of two sulfide moieties to a carbocation (**Figure 5**)[60] The group presented the evidence of the existence of hypervalent 10-C-5 using NMR study[4] and electrochemistry[5].



26

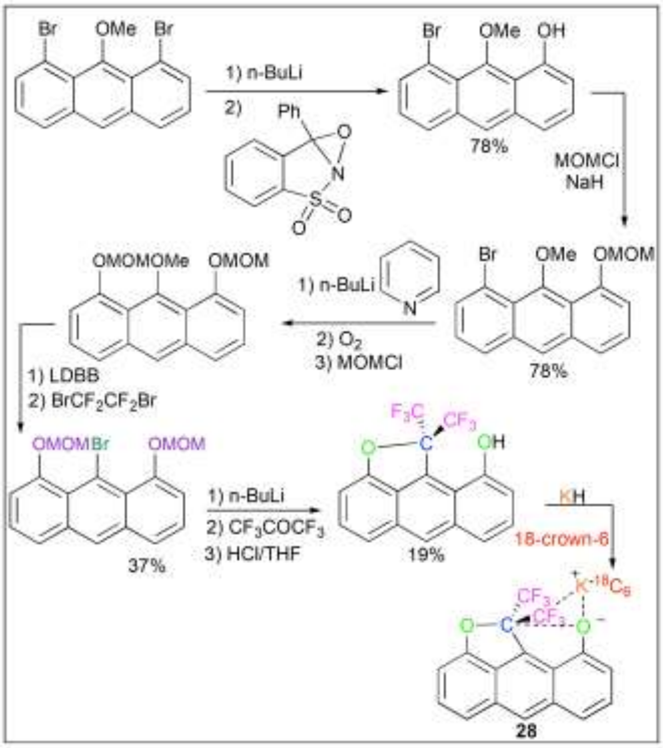
Figure 5 Structure of hypervalent carbon species **26** bearing two sulfide linkages

Last two decades witnessed the substantial efforts by Akiba, Yamamoto and coworkers in this area, and handful examples of isolated and structurally confirmed penta-/hexa-coordinated carbon have been reported.[66,82-87] In this series, the first X-ray crystallographically characterized solid-state structure of a stable pentacoordinate carbon species, 1,8-dimethoxy-9-dimethoxymethyl anthracene monocation was reported in the year 1999.[82] The group reported the synthesis and X-ray analysis of hypervalent carbon compound **27** bearing tridentate anthracene ligand with two coordinating oxygen sites at the 1,8-positions (**Scheme 6**).[66,82] The distances of the apical 'C-O' bonds (2.44 Å) were found shorter than the distances between the ipso carbon atoms of the anthracene backbone linked to these three atoms (2.51 Å).The sum of the C-O covalent radii was found to be 1.39 Å. Further, the atoms in molecule (AIM) analysis indicated the presence of bond paths between the central carbon and the two oxygen atoms present at 1,8-positions. However, the 'ρ' values indicate very weak interactions between carbon and oxygen atoms.



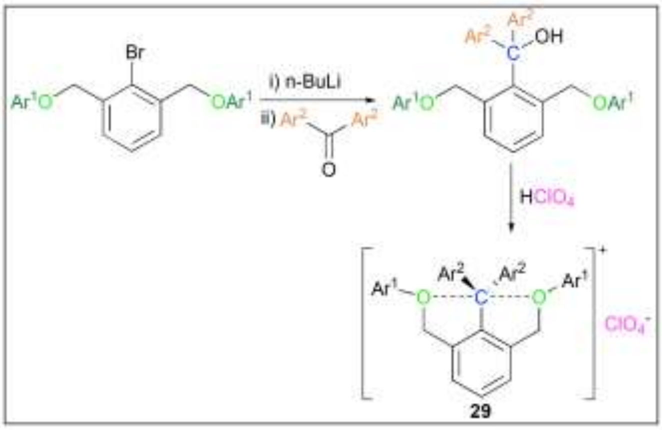
Scheme 6 Synthesis of hypervalent carbon compound **27** bearing tridentate anthracene ligand with two coordinating oxygen sites at the 1,8-positions

An anionic hypervalent pentacoordinate carbon compound **28** was synthesized by utilizing a ligand bearing two deprotectable methoxymethoxy groups as depicted in **Scheme 7**.[83]



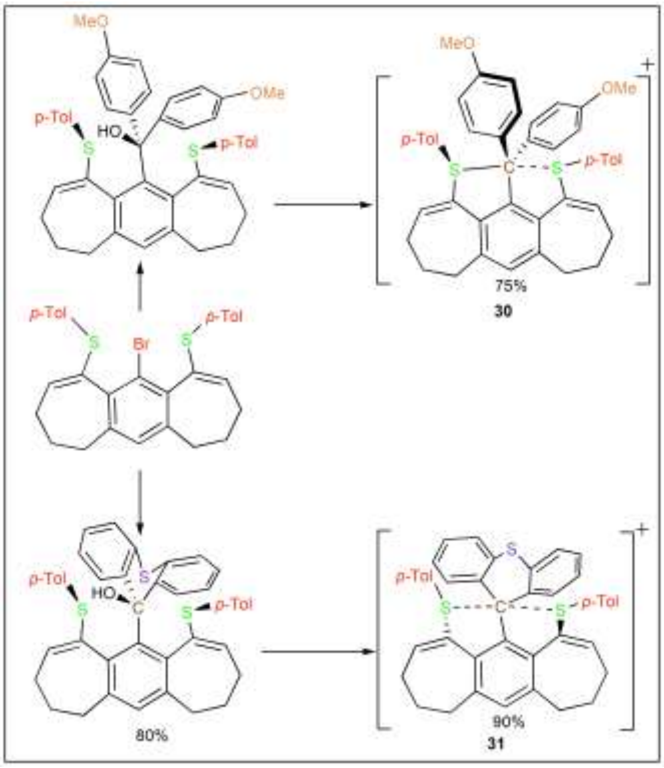
Scheme 7 Synthesis of anionic hypervalent pentacoordinate carbon compound **28**

Yamamoto and Akiba group also developed certain other hypervalent carbon species **29,** bearing 2,6-bis(*p*-substituted phenyloxymethyl)benzene, utilizing the van Koten-type framework (**Scheme 8**).[84] These species bears flexible side arms supporting the apical donors, which result in significantly longer and weaker apical interactions. X-ray analysis of bis(*p*-fluorophenyl)methyl cation bearing a 2,6-bis(*p*-tolyloxymethyl)benzene ligand displayed a symmetrical structure in which the two C-O distances are identical, although the distance (2.690Å) is longer than those (2.43 and 2.45 Å) of 1,8-dimethoxy-9-dimethoxymethylanthracene monocation. Further, synthesis and experimental charge density analysis and DFT calculations of a hexacoordinate carbon species, 12-C-6, have also been reported by the same group.[86,87]



Scheme 8 Synthesis of cations **29** bearing 2,6-bis(*p*-substituted phenyloxymethyl)benzene

Recently, synthesis and X-ray characterization of hypervalent pentacoordinate carbon compounds **30** and **31** bearing a 7-6-7 ring skeleton has been reported by Yamamoto and coworkers. Synthesis of compounds **30** and **31** is outlined in **Scheme 8**.[83] In case of compounds **30**, bearing *para*-OMe substitutent, and compound **31** with thioxanthylium moiety, hypervalent pentacoordinate structures were observed.



Scheme 9 Synthesis of hypervalent pentacoordinate carbon compounds **30** and **31** bearing a 7-6-7 ring skeleton

Both structures featured a sp^2 hybridized central carbon atom with the sulfur atoms aligned at apical positions to form trigonal bipyramidal geometry (**Figure 6**). In both compounds **30** and **31**, a pair of nearly identical S/C distances (3.154/3.069 Å) and 3.020/3.041 Å) were observed, which are considerably shorter than the sum of the vander Waals radii of the two atoms (3.50 Å).

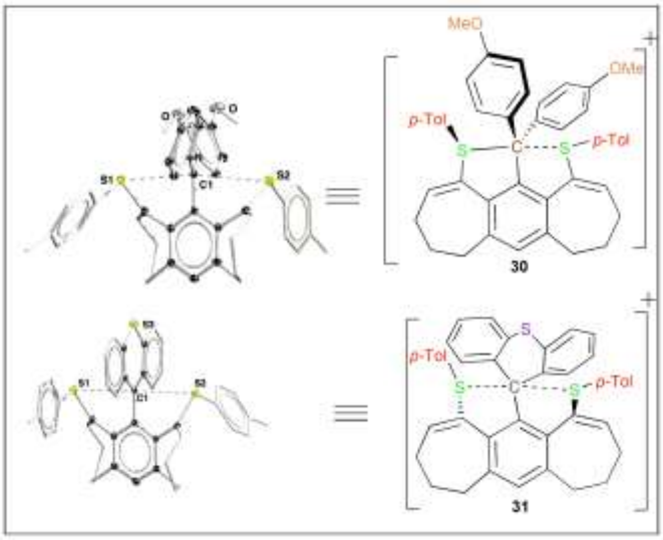


Figure 6 X-ray structures of carbon heterocycles **30** and **31**

4.2. Hypervalent Silicon Heterocyles

Martin and coworkers reported the synthesis of stable, anionic hypervalent 10-Si-5 heterocycles **32-33** **(Figure 7)**.[89-90] The highelectronegativity of the apical oxygen present in the fluoroalkoxy ligand and the electropositive carbon equatorial to the central atom increases the difference in electronegativity between central atom and apical ligand that makes for a stable hypervalent bond.[91-92] The ligand also provides stabilization through a 5-membered ring effect[93] and a gem-dialkyl (Thorpe-Ingold) effect[94-96] which favors the ring-closed hypervalent species.

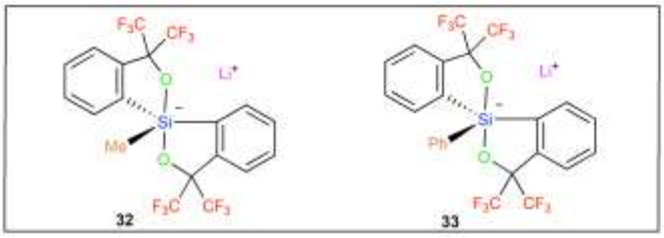
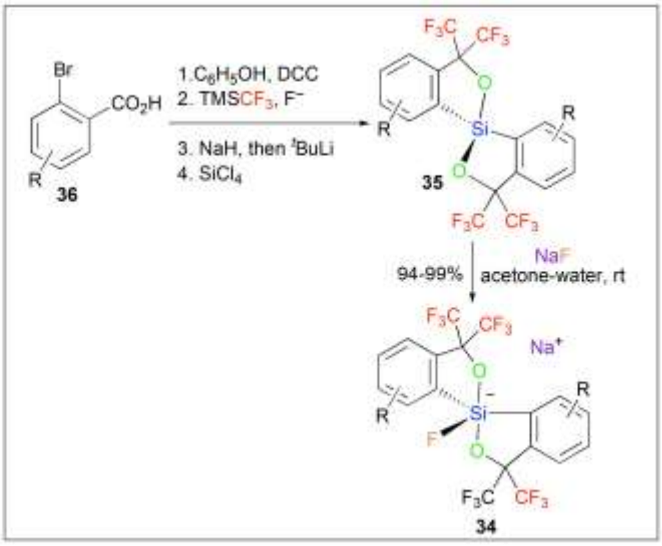


Figure 7 Structures ofanionic hypervalent 10-Si-5 heterocycles **32-33**

A new synthetic route to access Martin's spirosilanes **34** has been developed by Goddard, Fensterbank and coworkers (**Scheme 10**).[97] Hypervalent fluorosilicated **34** have been prepared by the reaction of sodium fluoride with tetracoordinated silicates **35** in acetone-water at room temperature, while the tetracoordinated silicates **35** can be easily obtained from the corresponding 2-bromobenzoic acids **36** by simple synthetic sequence.



Scheme 10 Synthetic route to access Martin's spirosilanes **34**

Further, X-ray analysis of spirosilane **34-OMe** bearing methoxy substituent revealed the trigonal pyramidal structure of silicon with apical oxygen atoms and presence of aromatic ring and fluorine atoms occupying the equatorial positions (**Figure 8**).[97]

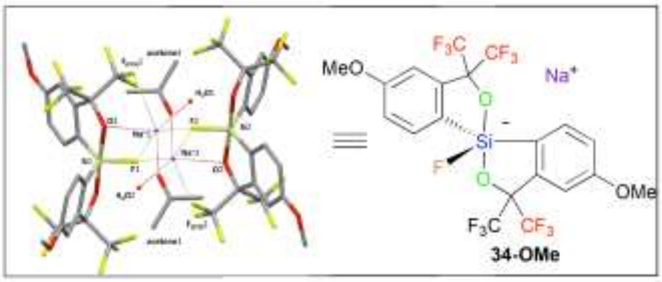


Figure 8 X-ray structure of silicon hypervalent heterocycle **34-OMe**

During the catalytic cross-Aldol reactions of aldehydes mediated by chlorosilanes, intermediate formation of unstable 10-Si-5 silicon-oxygen heterocycles has been proposed.[98-99] Further, Ikeda and Inagaki investigated theoretically (electron-pair bond model) the structures and stabilities of three-membered rings containing hypervalent atoms X (X= Si, S or P).[100]

Another important class of cyclic hypervalent silicon compounds are, triptych siloxazolidines (5-aza-2,8,9-trioxa-1-silabicyclo[3.3.3] undecane) (**37**), later termed as silatranes (**Figure 9**). Silatranes {X-Si(OCH_2CH_3)$_3$N}, and their derivatives, are a class of pentacoordinated silicon compounds with unique stereoelectronic and crystal structure. Several reviews have appeared in the literature highlighting synthesis, structure and reactivity of these compounds.[101-105] Besides, the unique chemical reactivity pattern, diverse biological activities, such as, antiviral, anti-inflammatory, anti-tumor as well as seed germination properties have been well investigated.[102]

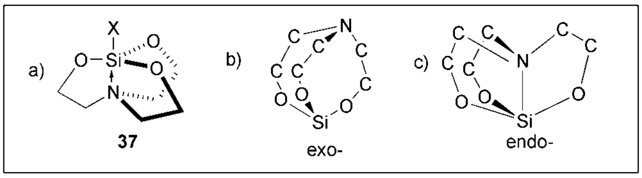


Figure 9 Structures of silatranes (**37**)

X-ray diffraction suggests a tricyclic cage structure for silatranes that possess hypervalent silicon having a trigonal bipyramidal arrangement surrounded with three endocyclic oxygens placed at equatorial position. Silatranes can exist in two conformations, exo- and endo-conformations (**Figure 9**).[106-107] The concept of 3c-4e bonding in these compounds was established in 1977.[108] In case of exo-conformation, the lone pair of electrons present on the nitrogen atom are directed out of the cage while in endo-form the lone pair is directed towards the silicon atom as depicted in **Figure 9**. The transannular Si-N interactions may lead to the endo form that results into 3c-4e hypervalent bond.[108] A significant dipole moment (μ= 5.3-7.1D) is present in these compounds due to the transfer of electron-density from N-atom to Si-R bond. This dipole moment in conjunction with the strong electron-donating effect of the silatranyl group contributes towards high reactivity of these compounds.[109] The transannular Si-N dative bond distance is in between sum of their covalent and non-bonded radii (1.89Å and 2.69 Å). This bond length indicates weak interaction between silicon and nitrogen.[110]

4.3. Hypervalent Germanium, Tin, and Lead Heterocycles

The chemistry of the hypervalent germanium, tin, and lead compounds has been elaborated in several reviews and monographs. The inter- and intramolecular donor-acceptor bonds are usual characteristics of these compounds, in particular for the tin(IV) compounds. In general, a trigonal bipyramid or more rarely a square pyramid as well as an octahedral arrangement of the metal atom, are distinctive for germanium, tin, and lead in pentacoordinate '10-M-5' and hexacoordinate '12-M-6' compounds, respectively.

According to the Musher's classification, in view of 10-M-5 and 12-M-6, hypervalent compounds of germanium, tin and lead include hypervalent bonding of the second kind, in which the central atom has no ns^2 lone pair electrons. This model implies that the trigonal bipyramidal metal atom could utilize its nsp^2 orbitals for bond formation with the equatorial ligands to form two-center bonds, while its npz orbital could get involved in the interaction with an appropriate orbital of the axial substituent 'X' and a lone pair of electrons of the donor atom to form a hypervalent, 3c-4e bond in the axial moiety D → M–X. Baukov and Tandura[111] discussed the hypervalent compounds of germanium, tin and lead classifying these compounds as self associates[112-113] of the type **38-39**, pentacoordinate anionic compounds **40-46,**[114-120] pentacoordinate neutral compounds **47-51**,[121-127] pentacoordinate cationic **52-53**,[128-130] and hexacoordinate anionic **54**[131], neutral **55-56**[132-134] and cationic **57**[135] compounds (F**igure 10**).

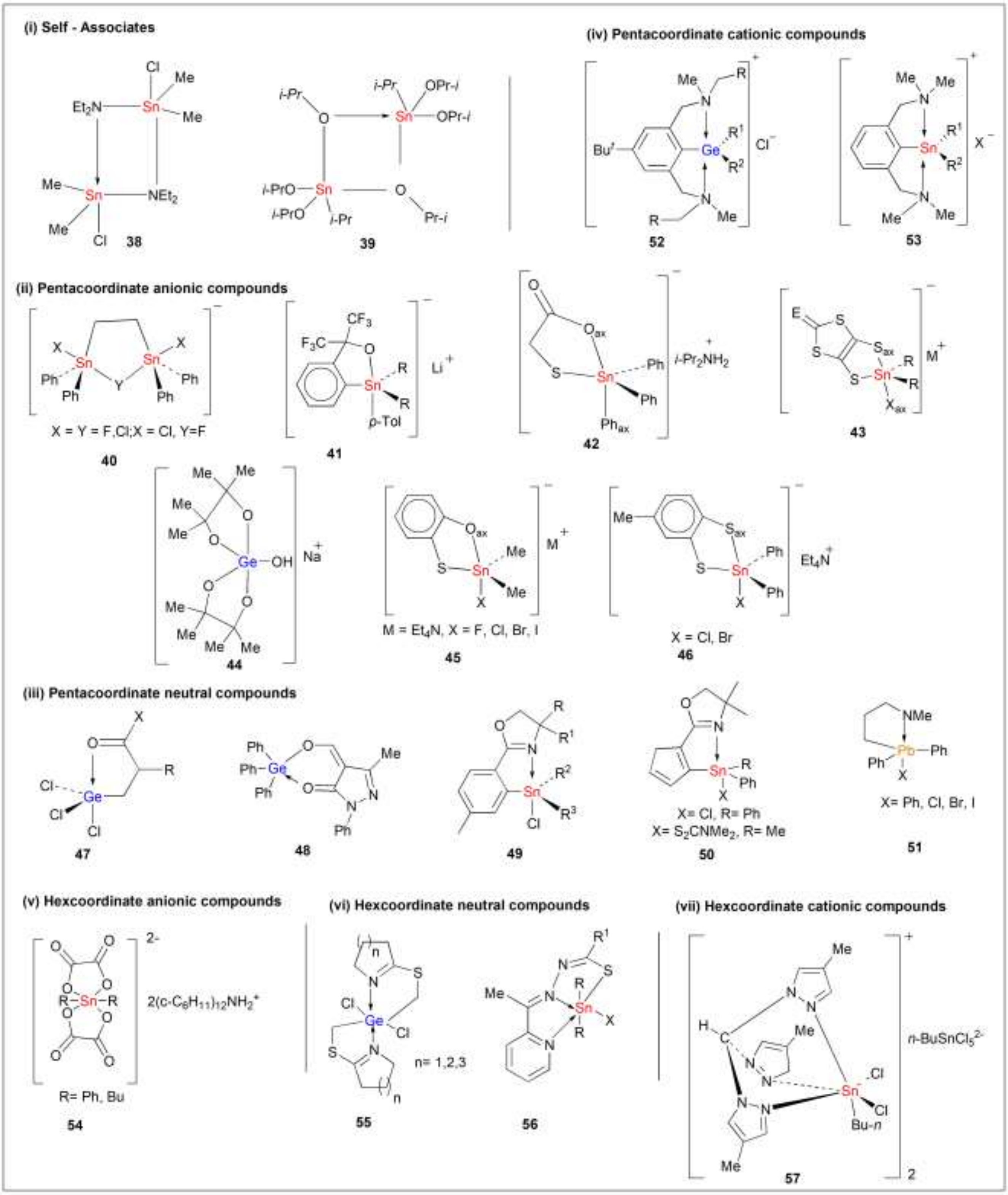

(i) Self - Associates
38
39
(iv) Pentacoordinate cationic compounds
52
53
(ii) Pentacoordinate anionic compounds
X = Y = F,Cl;X = Cl, Y=F
40
41
42
43
44
M = Et$_4$N, X = F, Cl, Br, I
45
X = Cl, Br
46
(iii) Pentacoordinate neutral compounds
47
48
49
X= Cl, R= Ph
X= S$_2$CNMe$_2$, R= Me
50
X= Ph, Cl, Br, I
51
(v) Hexcoordinate anionic compounds
2(c-C$_6$H$_{11}$)$_2$NH$_2^+$
R= Ph, Bu
54
(vi) Hexcoordinate neutral compounds
n= 1,2,3
55
56
(vii) Hexcoordinate cationic compounds
n-BuSnCl$_5^{2-}$
57

Figure 10 Selected examples of hypervalent germanium, tin, and lead heterocycles **38-57**

Other representative examples of such heterocyclic compounds are illustrated by germanium cyclic oxamide complexes **58**[136] and cyclic pentaorganostannate **59**[137] as shown in **Figure 11**.

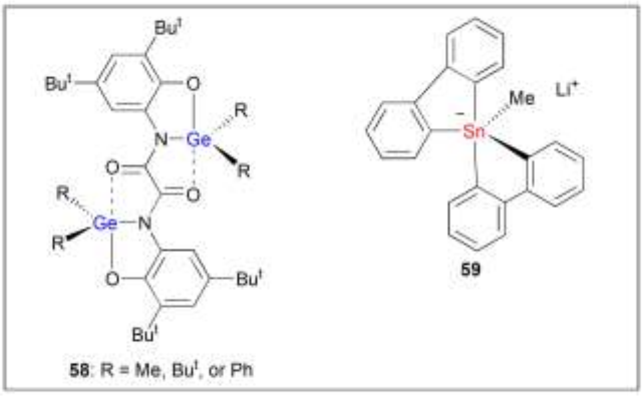
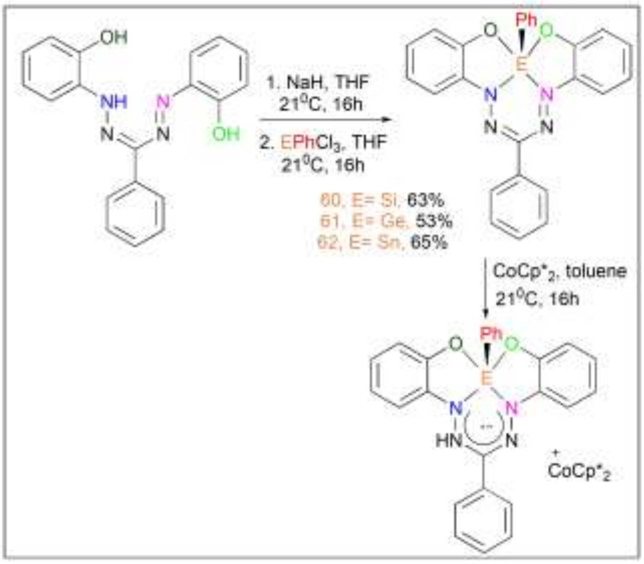


Figure 11 Germanium cyclic oxamide complexes**54** and cyclic pentaorganostannate **55**

In 2018, Gilroy and coworkers reported the preparation and characterization of a family of formazanate complexes **60-62** of hypervalent group 14 elements (Ge, Sn, Si) (**Scheme 11**).[138] Chemical reduction of these complexes using bis(pentamethylcyclopentadienyl)cobalt (CoCp*$_2$) afforded radicals stabilized specifically by the square-pyramidal coordination geometry within the framework of the heteroatom-rich formazanate ligands.



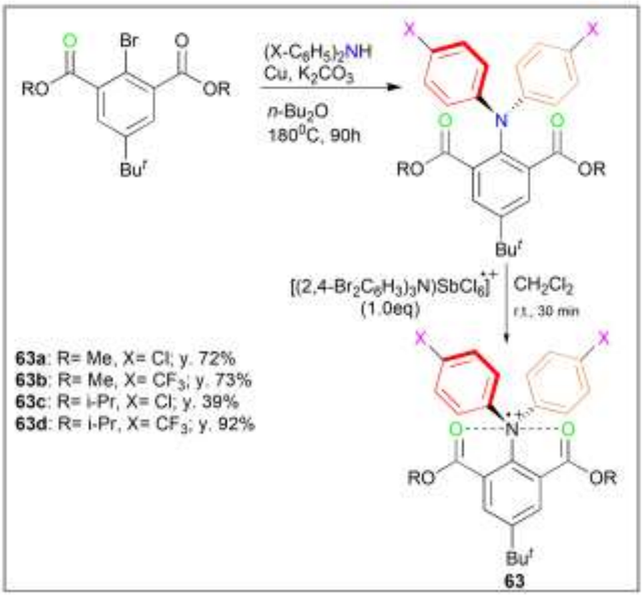
Scheme 11 Preparation of formazanate complexes **60-62** of hypervalent group 14 elements (Ge, Sn, Si)

5. Hypervalent Heterocyclic Compounds of Group 15 Elements

Among the hypervalent heterocycles of group 15 elements, hypervalent nitrogen species have been recently characterized, while various types of hypervalent phosphorous compounds are described in the literature. As far as other elements of this group are concerned, a large number of reports on the organobismuth and organotin compounds showing hypervalent coordination/hypercoordination have been reported.[139-141]

5.1. Hypervalent Nitrogen Heterocycles

Hypervalent pentacoordinated nitrogen species (10-N-5) have been some of the fundamental hypervalent compounds, with their synthetic attempts traced back to 1916.[142-150] Regardless of the theoretical calculations about the existence and stability,[151-156] synthesis and isolation of thermally stable hypervalent nitrogen compounds of the type, N–N–L; (N>10, L>4) could not be achieved until 2020.[148,150,157-158] However, detection,[159-163] isolation and structural characterization of transient, as well as stable[164-166] hypervalent tetracoordinate nitrogen radical species (9-N-4) have been reported. Recently, in 2020, Shang, Yamamoto and coworkers synthesized stable hypervalent pentacoordinate nitrogen cationic radical (11-N-5) species **63** as depicted in **Scheme 12**.[167]



Scheme 12 Synthesis of stable hypervalent pentacoordinate nitrogen cationic radical (11-N-5) species **63**

Furthermore, the N–O bond distance in cationic radical species **63a** is shorter than the sum of N–O van der Waals radii, which indicates the attractive interactions between N and O atoms. Single crystal X-ray analysis and computational studies revealed that the nitrogen centre adopts a trigonal bipyramidal geometry that features a 3c-5e hypervalent attractive interaction (**Figure 12**).

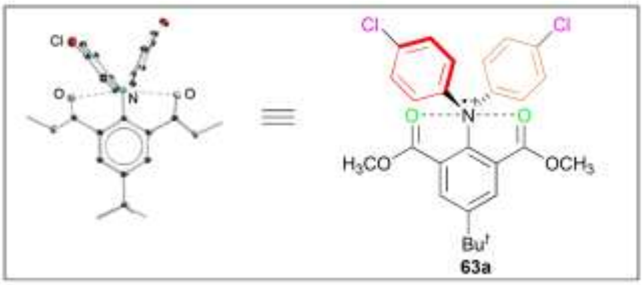


Figure 12 X-ray structure of the nitrogen hypervalent heterocycle **63a**

5.2. Hypervalent Phosphorous Heterocycles

Various structural types of hypervalent phosphorus compounds are reported in the literature.[5] Representative examples of stable hypervalent phosphorus heterocycles are, 10-P-3 compounds **64**,[33] anionic 10-P-4 species **65**,[168] pentacovalent 10-P-5 compounds **66**,[169] and anionic hexacoordinated 12-P-6 species **67**[170] (**Figure 13**). The first two structural types **64** and **65** are usually classified as the low-coordinate hypervalent phosphorus compounds.[33]

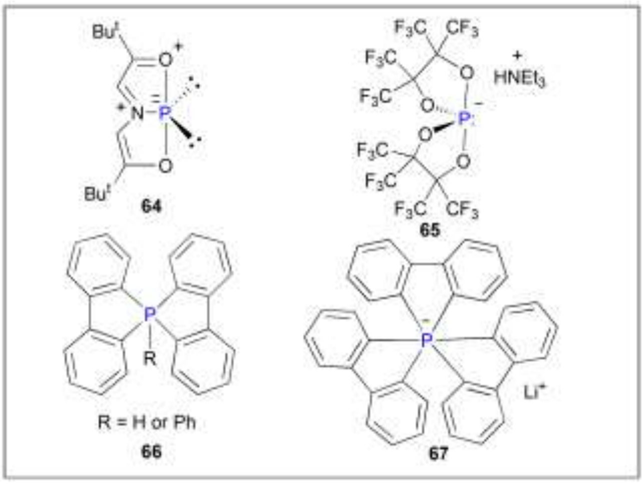
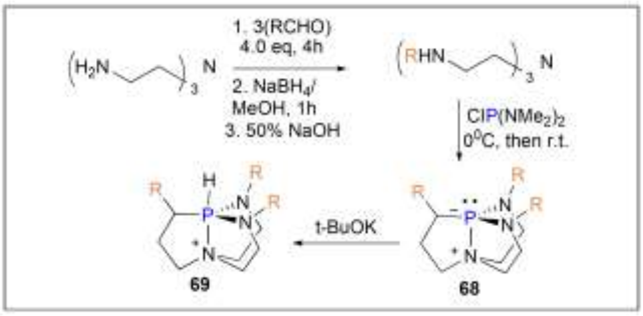


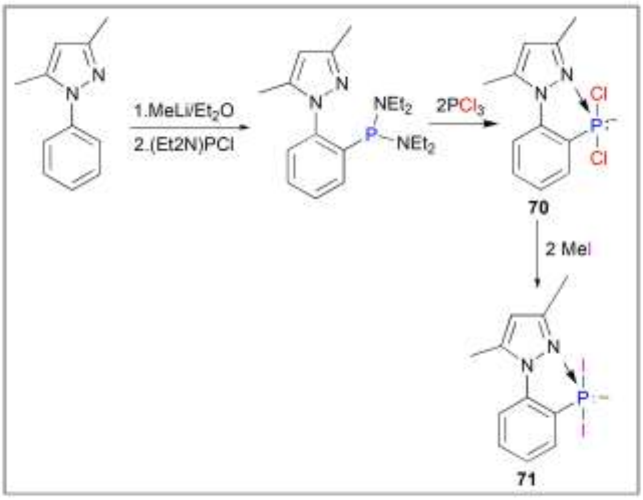
Figure 13 Representative examples of stable hypervalent phosphorus heterocycles **64-67**

Pentacovalent 10-P-5 compound, shown by the protonated form of proazaphosphatrane **69,** have been reported by Kishanga and Verkade as depicted in **Scheme 13**. Compounds **68**, a class of strong nonionic bases (Verkade bases, also known as superbases), serves as efficient catalysts and promoters of many chemical transformations.[171] X-ray analyses showed that the P-Nax distance (2.047 Å) in cation **69** was within experimental error (i.e. within 3×esds) Further, the NeqPNeq angles of 118-119° were also comparable to those in the aforementioned analogs reported previously. Another important class of hypervalent phosphorous heterocycles includes hypervalent 10-P-3 compounds. 3,7-Di-tert-butyl-5-aza-2,8-dioxa-1-phosphabicyclo[3.3.0]octa-2,4,6-triene (ADPO, **64**), is one of the important examples of this class which possesses unique chemical properties.[33]



Scheme 13 Preparation of pentacovalent 10-P-5 compound **69**

Kornev and coworkers reported the preparation and structural investigation of certain low-coordinate hypervalent phosphorus heterocycles, phenylpyrazole-based hypervalent phosphorus compounds **70** and **71** (**Scheme 14**).[172] X-ray analysis revealed that the phosphorus atom in molecule **70** has overall trigonal bipyramidal geometry with both chlorine atoms present at the apical position, and the N- and C-substituents as well as the lone pair of electrons occupies the equatorial positions. Further the P–N and P–C bond distances are of 1.771 Å and 1.831 Å bond lengths, respectively.



Scheme 14 Synthesis of Phenylpyrazole-based hypervalent phosphorus heterocycles **70** and **71**

Yamamoto and coworkers reported the first stereo-pure isolation of pair of O-*facial* and O-*meridional* isomers of 12-P-6 oxaphosphates **72** and **73** using a modified Martin ligand[173-176] with two bulky C_2F_5 groups to slow down the Berry pseudorotation (BPR) of the precursors (**Figure 14**).[177]

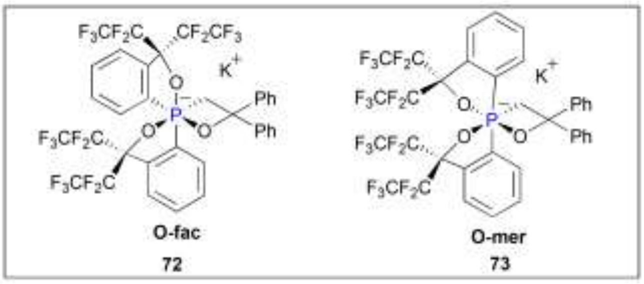


Figure 14 Pair of O-*facial* and O-*meridional* isomers of 12-P-6 oxaphosphates **72** and **73**

Single-crystal X-ray crystallographic strutures of both oxaphosphates **72** and **73** are given in **Figure 15.** X-ray crystallographic analysis of **72** revealed a hexacoordinate O-facial geometry, while the solid-state structure displays a facial coordination of the potassium to all oxygen atoms.

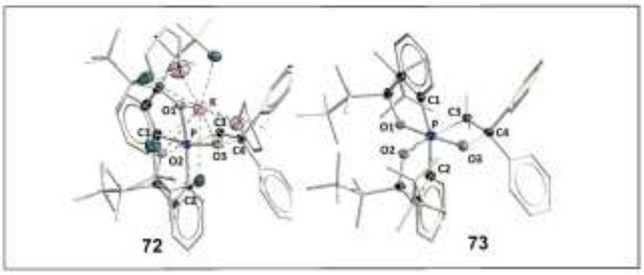


Figure 15 X-ray crystallographic strutures of oxaphosphates **72** and **73**

5.3. Hypervalent Arsenic, Antimony, and Bismuth Heterocycles

Hypervalent structures are typical of arsenic, antimony, and bismuth heterocycles. The chemistry of these compounds has been overviewed by K.-y. Akiba[2] and Romanenko and Sotiropoulos.[178] Certain representative examples of these compounds are illustrated by structures **74** and **75** (**Figure 16**).

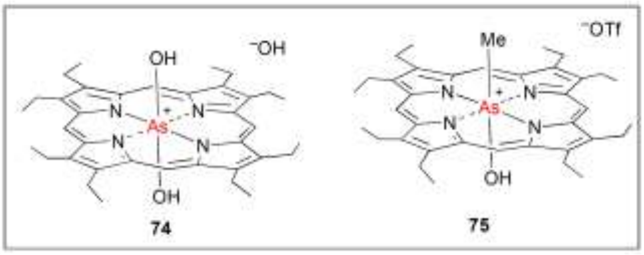


Figure 16 Representative examples of hypervalent arsenic heterocycles **74** and **75**

Further, selected examples of hypervalent heterocycles of antimony and bismuth elements **76-86** are given in Figure **17.**

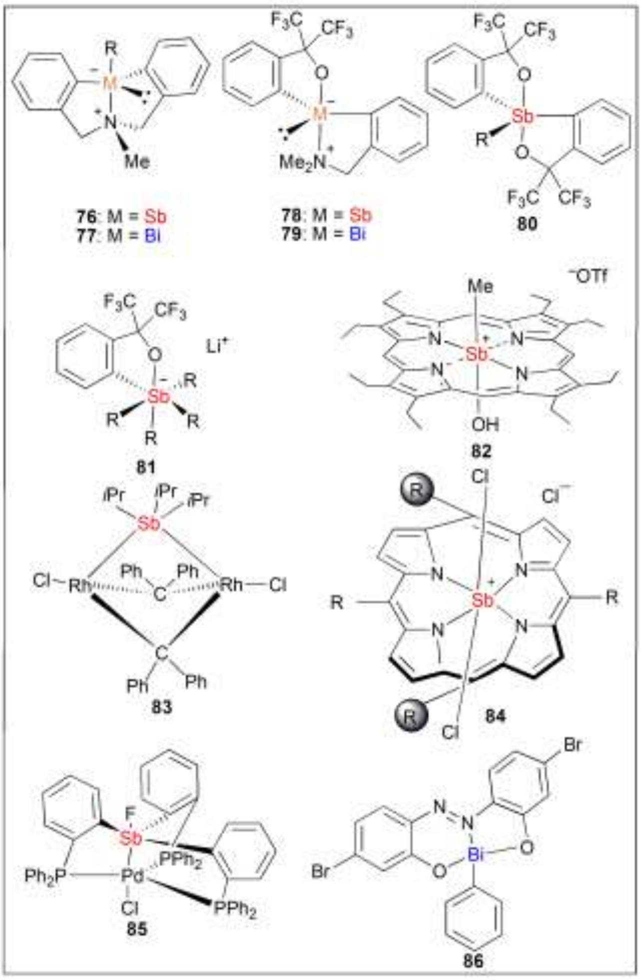


Figure 17 Examples of hypervalent heterocycles of antimony and bismuth elements **76-86**

6. Hypervalent Heterocyclic Compounds of Group 16 Elements

Recent few decades have witnessed a tremendous growth in the organochalcogen (S, Se, and Te) chemistry amongst chemists due to their immense utilization in the field of synthetic organic chemistry,[179-188] dyes,[189] as well as biological applications[190–195]. Certain hypervalent heterocycles of these elements have been synthesized and well-characterized. The hypervalent compounds of Se and Te have similar structures as that of sulfur.

6.1. Hypervalent Sulfur Heterocycles

Certain structural types of hypervalent compounds of sulfur(IV) and sulfur(VI) are known.[5.] Representative examples of stable hypervalent sulfur heterocycles reported in the literature are: anionic 10-S-3 sulfuranes **87**,[196] 10-S-4 species **88**,[197] **89**,[198] pentacoordinated 10-S-5 sulfuranes **90**[199] and **91**[200] and, hexacoordinated 12-S-6 species **92** (also known as persulfuranes)[201] (**Figure 18**).

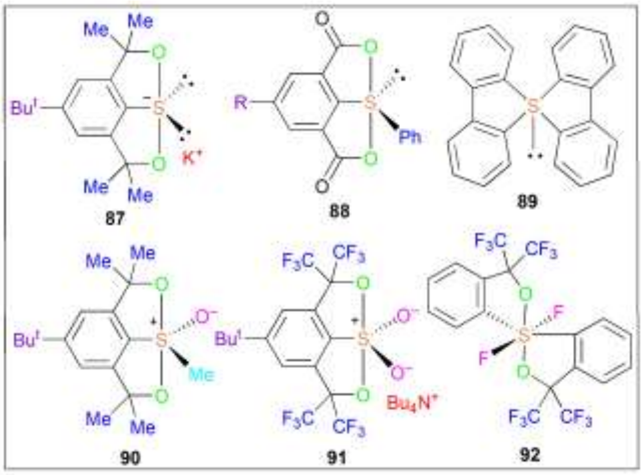


Figure 18 Representative examples of stable hypervalent sulfur heterocycles **87-92**

Kawashima reported the preparation and structural studies of various four-membered 10-S-4 and 10-S-5 heterocycles **93-96** (**Figure 19**).[202]

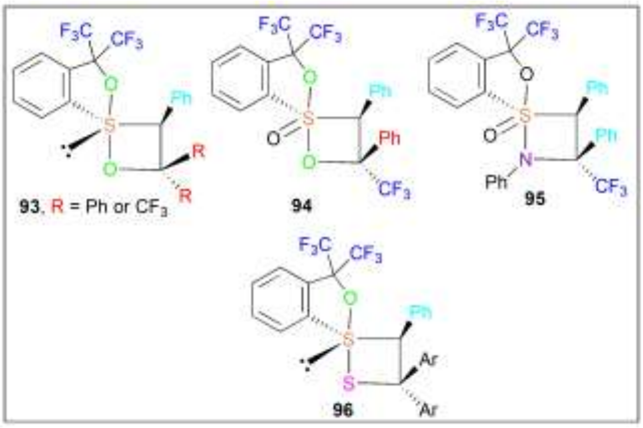
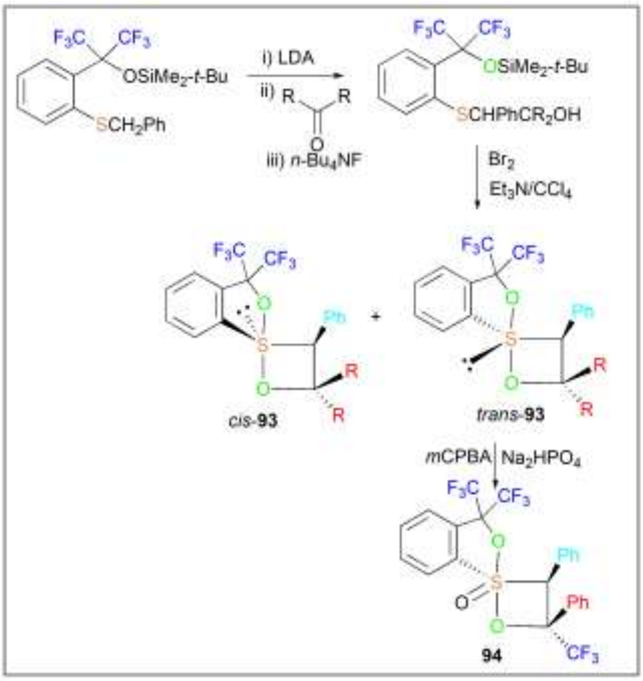


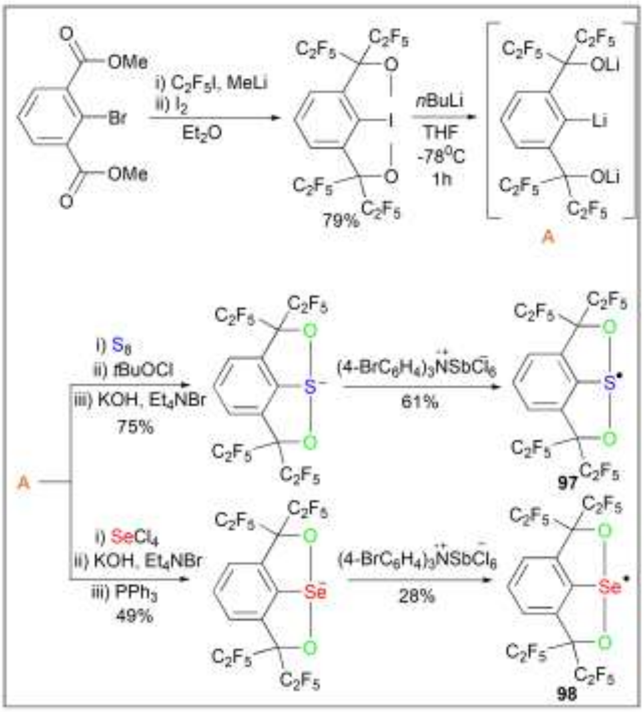
Figure 19 Four-membered 10-S-4 and 10-S-5 heterocycles **93-96**

In particular, the group synthesized tetracoordinated and pentacoordinated 1,2-oxathietanes **93** and **94** as shown in **Scheme 15** and reported their thermolyses. These compounds having a tetracoordinated or pentacoordinated hypervalent sulfur atom collectively with other heteroatoms were isolated as thermally stable products and were structurally characterized through single crystal XRD. X-ray crystallographic analyses revealed that the hypervalent sulfur centers in these molecules possesses distorted trigonal bipyramidal geometry.



Scheme 15 Synthesis of tetracoordinated and pentacoordinated 1,2-oxathietanes **93** and **94**

Isolation of hypervalent group 16 radicals and their applications in organic-radical batteries was reported by Yamamoto and coworkers.[203] Utilizing a tridentate ligand bearing C_2F_5 groups, hypervalent sulfur **97** and selenium radicals **98** have been isolated for the first time (**Scheme 16**). The structures were characterized by X-ray crystallography, electron spin resonance spectroscopy, and density functional theory calculations that revealed a three-coordinate hypervalent structure. Furthermore, by making use of reversible redox reactions between the hypervalent radicals and corresponding anions, organic radical batteries as cathode-active materials were developed.



Scheme 16 Hypervalent sulfur **97** and selenium radicals **98** utilizing tridentate ligand bearing C_2F_5 groups

'π-Hypervalent' heterocyclic systems have attracted substantial attention because of their remarkable structure and reactivity.[204] A variety of sulfur heterocycles with endocyclic double bonds on sulfur are usually referred to as the 10-S-3 "π-hypervalent heterocyclic systems". Compounds containing a 10-S-3 sulfurane species have extensively been studied. Further, these compounds can be represented as canonical structures with tetracovalent sulfur; for example, tetraazathiapentalenes **99** and trithiapentalenes **100** (Figure **20**).[205-206] However, a more precise illustration of these compounds involves 'non-hypervalent betaine structures' with eight electrons on the sulfur atom. These compounds are associated with extensive theoretical and synthetic interest[207-209] and a discussion on heterocyclic mesomeric betaines including sulfur or other elements has been well-reviewed.[210-211]

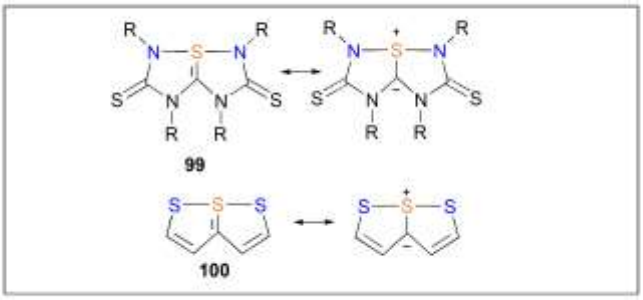
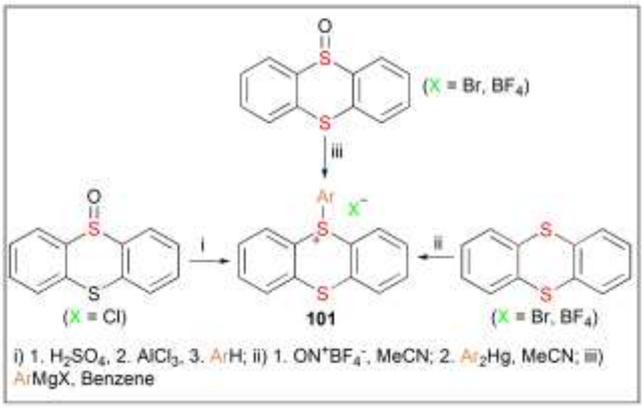


Figure 20 Canonical structures of tetracovalent sulfur heterocycles, tetraazathiapentalenes **99** and trithiapentalenes **100**

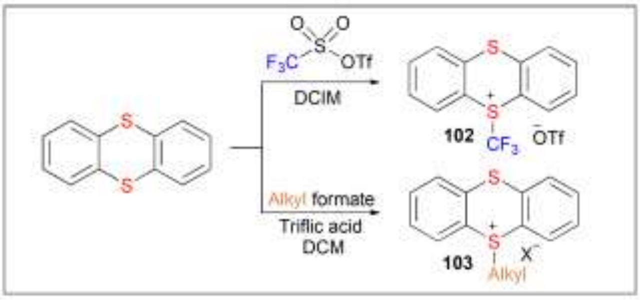
Thianthrenium salts represent a typical class of organosulfur compounds with exceptional potential applications in organic synthesis. These compounds have emerged as versatile precursors in variety of chemical transformations.[211-227] Shu and co-workers recently summarized the synthesis and applications of aryl, alkyl, and alkenyl salts.[227] The seminal work reported by Calvin and coworkers,[228] Lucken[229] and Shine group[230] became the foundations for the development of different organothianthrenium salts. Shine developed the synthesis of aryl thianthrenium perchlorates by the treatment of thianthrenium perchlorates with e⁻-rich aromatics.[213-215] Other methods for the synthesis of aryl thianthrenium salts (**101**) include reaction of thianthrene *S*-oxide with: (i) $AlCl_3$ followed by arenes;[215,217] and (ii) aryl Grignard reagents or Ar_2Hg (**Scheme 17**). Recently, Ritter[231] and Wang[232] research groups independently developed efficient protocols for the synthesis of aryl thianthrenium salts using thianthrene sulfoxides.



i) 1. H_2SO_4, 2. $AlCl_3$, 3. ArH; ii) 1. $ON^+BF_4^-$, MeCN; 2. Ar_2Hg, MeCN; iii) ArMgX, Benzene

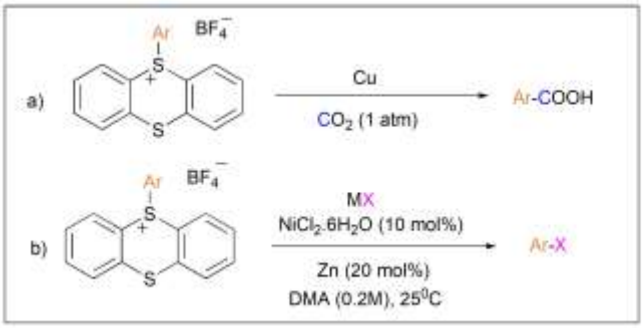
Scheme 17 Synthesis of aryl thianthrenium salts (**101**) including thianthrene *S*-oxide

Besides, synthetic methods to access alkenyl thianthrenium salts have been developed through: (i) treatment of thianthrene with acetic anhydride followed by appropriate alkenes[225]; (ii) stereoselective C(sp²-H) thianthrenation of aliphatic alkenes using trifluoroacetic anhydride (TFAA) followed by alkaline workup[226]; (iii) thianthrene sulfoxides reaction with alkenes using triflic anhydride and alkaline workup[233]; and (iv) electrochemical strategy developed by Wickens and coworkers[234]. Ritter group reported an excellent example for the synthesis of trifluoromethyl thianthrenium salt (**102**) using trifluomethyl sulfonic anhydride (CF_3SO_3Tf)[235], while Shine and coworkers made excellent access to alkyl thianthrenium salts (**103**) utilizing alkyl formates and triflic anhydride[236] (**Scheme 18**). Recently, Shi group achieved the synthesis of diverse range of alkyl thianthrenium salts using trifilic anhydride and aliphatic alcohols.[237]



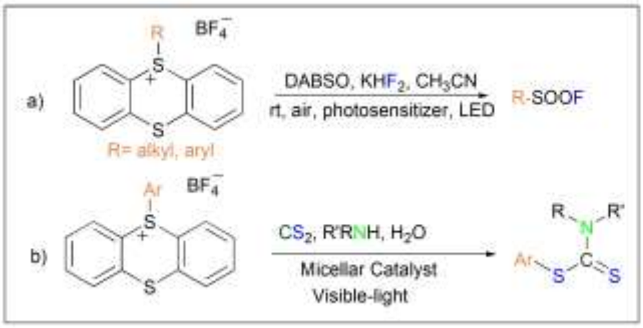
Scheme 18 Synthesis of trifluoromethyl thianthrenium salt (**102**) and alkyl thianthrenium salts (**103**)

Apart from the significant achievements in the area of synthesis of thianthrenium salts, various reports pertaining to the versatile utilization of these salts have appeared in the literature.[222,227] An overview of their potential applications is presented here. A variety of aryl substituted compounds can be effectively accessed through transition-metal catalyzed cross-coupling reactions of aryl thianthrenium salts, majority of these are Palladium catalyzed reactions. Examples of Pd- catalyzed coupling reactions are, sulfination of arenes,[238] Suzuki-Miyaura coupling reaction,[239] one-pot conversion of C-H bond of arenes into C-Si bond bond,[240] α-arylation of carbonyl compounds,[241] reduction alkylation,[242] reductive deuteration/tritiation,[243] phosphination,[244] esterification,[245] and deuterated formylation[246]. Apart from these applications, copper-catalyzed carboxylation of aryl thianthrenium salts has been reported by Wang and coworkers recently[247] **(Scheme 19a)**. This example provides an elegant illustration of site-selective C–H carboxylation, which may be utilized for the late-stage carboxylation modification. Moreover, Ritter group developed an unusual Ni(I)/Ni(III)-catalyzed regioselective late-stage arene halogenation method (**Scheme 19b)**[248]



Scheme 19 (a) copper-catalyzed carboxylation of aryl thianthrenium salts; (b) Ni(I)/Ni(III)-catalyzed regioselective late-stage arene halogenation of aryl thianthrenium salts

Besides, several photoredox-catalyzed cross-coupling reactions of aryl thianthrenium salts have been explored highlighting the versatility of these salts under free-radical pathways. First report of Ritter, in 2019, gave a breakthrough in the development of numerous photoredox cross-coupling transformations of aryl thianthrenium salts.[249] Photoredox-catalysis involving aryl thianthrenium salts has been reported for the regioselective hydroxylation,[250] arene fluorination,[251] *para*-selective orylation of monosubstituted arenes,[252] Sonogashira-type reaction,[253] late-stage heteroarylation,[254] (hetero)arylation,[255] radical hydroarylation of azine-substituted enamides,[256] thioetherification,[257] sulfonylation,[258] α-sulfonylation of carbonyl compounds,[259] C-H arylation of heterocycles,[260] and three-component synthesis of aryl sufonohydrazides[261]. Other recent examples in this area include visible-light-mediated fluorosulfonylation reaction for the synthesis of sulfonyl fluorides[262] (**Scheme 20a**) and synthesis of *S*-aryl dithiocarbamates *via* an electron donor-acceptor photoactivation strategy[263] (**Scheme 20b**). Besides, Kong and Cao group developed a practical method for the sluorosulfonylation of thianthrenium salts (alkyl and alryl) without the use of any external redox reagent ot metal catalyst.[264]



Scheme 20 (a) visible-light-mediated fluorosulfonylation reaction of thianthrenium salts (b) synthesis of *S*-aryl dithiocarbamates from thianthrenium salts

In addition to aryl thianthrenium salts, applications of alkyl as well as alkenyl thianthrenium salts have also been well explored towards various transformations. Alkenyl thianthrenium salts can be utilized for the olefinic carbon-phosphorous cross-coupling,[265] Cu-catalyzed silyation and borylation,[233] vinylation reactions,[266] electrochemical synthesis of aziridines,[234] allylic C-H functionalization,[267] electrochemical synthesis of allyamines,[268] aziridination and cyclopropanation,[269] etc. Applications of alkyl thianthrenium salts include, trifluoromethylations,[235,270] Cu-catalyzed Sonogashira coupling reactions,[237] thermal and photochemical borylation reactions,[271] visible-light promoted hydroalkylation,[272] etc.

6.2. Hypervalent Selenium and Tellurium Heterocycles

The chemistry of hypervalent selenium (generally named as selenuranes) and tellurium (known as telluranes) is similar to that of sulfur compounds.[5] Representative examples of stable hypervalent heterocyclic derivatives of selenium and tellurium include: anionic 10-Se-3 **104** and 10-Te-3 species **105**,[273] 10-Se-4 selenuranes **106**[274] and 10-Te-4 telluranes **107**[275] and hexacoordinated 12-Te-6 species **108** (pertellurane)[276] (**Figure 21**). Mlochowski and coauthors gave a comprehensive review on the chemistry of selenaheterocycles.[277]

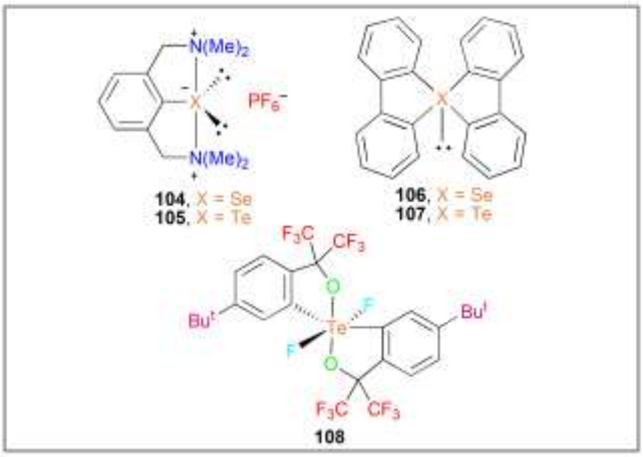
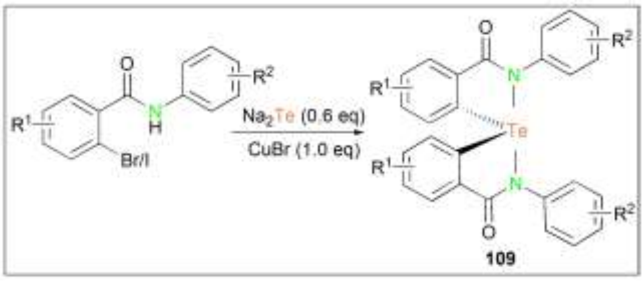


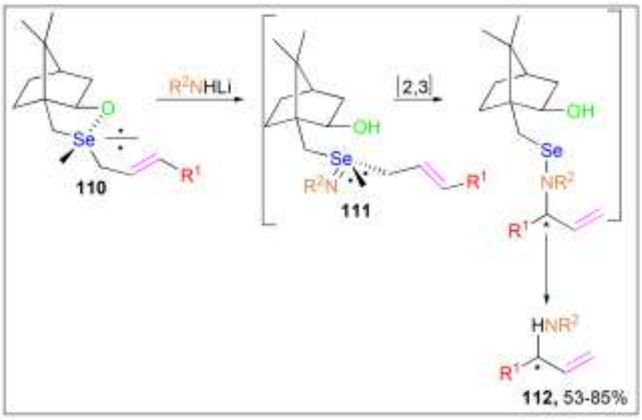
Figure 21 Examples of hypervalent heterocycles selenium and tellurium **104-108**

A one pot Cu(I)-assisted synthetic approach has been reported by Batabyal and coworkers for the preparation of biologically important benzoxytelluranes **109** from 2-bromo-N-aryl benzamides and the tellurium dianion (Te_2) under base-free conditionsas depicted in **Scheme 21**.[278]



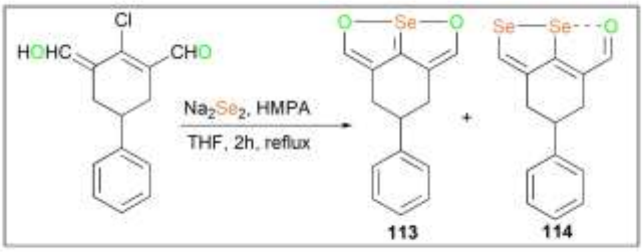
Scheme 21 One pot Cu(I)-assisted synthesis of benzoxytelluranes **109**

An interesting synthetic utilization of cyclic chloroselenurane **110** has been reported to afford chiral allylic selenimides **111** on nucleophilic reaction with lithium N-protected amides as intermediates with retention of configuration. A sigmatropic [2,3]-rearrangement of **111** yielded chiral N-protected allylic amides **112** up to 93 % ee (**Scheme 22**).[279-281]



Scheme 22 Synthetic utilization of cyclic chloroselenurane **110** to afford chiral allylic selenimides **111** and further chiral N-protected allylic amides **112**

Similar to the ‘π-hypervalent’ heterocyclic systems in sulfur, Butcher group synthesized organoselenium compounds **113** and **114** stabilized by the intramolecular coordination as shown in **Scheme 23.**[282]



Scheme 23 Synthesis of ‘π-hypervalent’organoselenium compounds **113** and **114**

7. Hypervalent Heterocyclic Compounds of Group 17 Elements

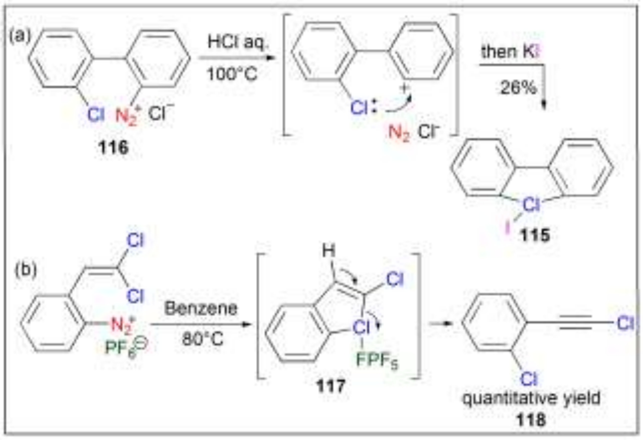
7.1. Hypervalent Heterocyclic Compounds of Group 17 Elements

Hypervalent halogen compounds are generally classified into halogen(III), halogen(V), and halogen(VII) derivatives, and have been utilized as reagents for a variety of selective organic transformations. These compounds have always been a centre of attraction for the researchers due to their exceptional chemical reactivity, in particular, electrophilic and oxidative reactions of organoiodine(III) and organoiodine(V) compounds have been extensively used in organic synthesis.[283] Besides the enormous development in the area of hypervalent iodine chemistry, the chemistry of organobromanes and organochloranes has been relatively much less investigated. Only a few researchers have been actively involved in the development of these compounds and their synthetic utilization, which limits their primacy in the literature. Even after the first ever report on the synthesis of hypervalent iodine compound by Wilgerodt in 1886,[284] it took more than 60 years for the preparation of first hypervalent bromine and chlorine compounds. The first preparation of λ^3-chlorane and λ^3-bromane was reported back in 1952 by Sandin and Hay;[285] however, the physicochemical properties of these compounds received little attention for many years, which may be broadly attributed to the lack of user-friendly preparation methods. In this section, an overview of the synthesis and synthetic applications of cyclic hypervalent halogens, highlighting some recent examples, is provided.

7.1. Hypervalent Heterocyclic Compounds of Chlorine(III)

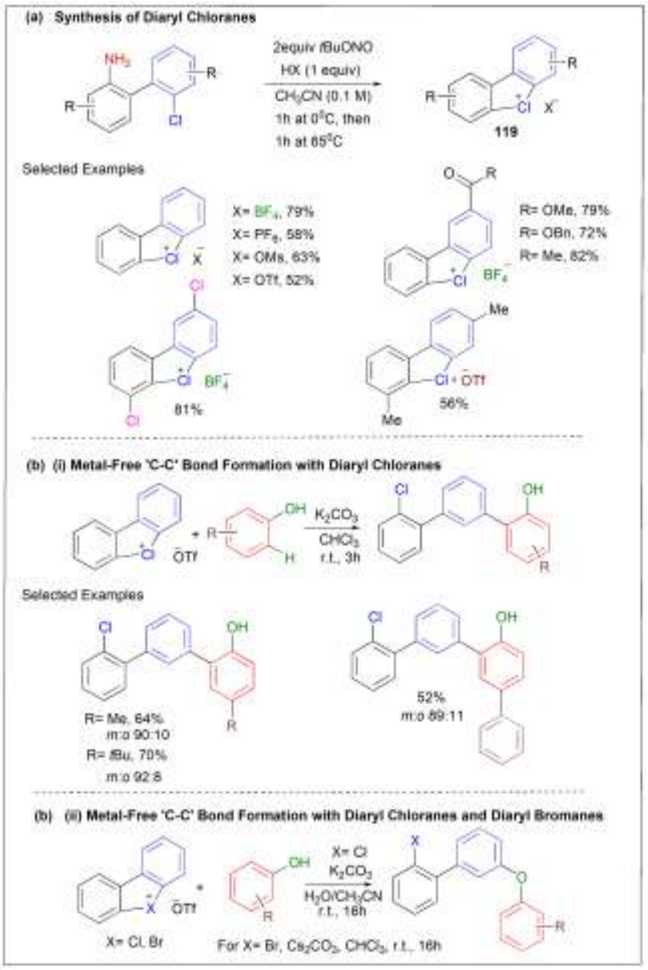
Despite the fact that inorganic λ^3-chloranes, such as, sodium chlorite ($NaClO_2$) and chlorine trifluoride (ClF_3)[286] were discovered in 1922 and 1930, respectively; yet, the organo λ^3-chloranes were not revealed until 1952. Even after 70 years of the first ever synthesis of organochlorine(III) compound, the development of the chemistry of organochloranes is still in its infancy.[287] In 1957, Nesemyanov gave a prediction about the utilization of diarylchloronium and diarylbromonium salts as excellent arylating agents, subject to the discovery of possible conditions for the production of these salts in higher yields.[288] The chemistry of organo λ^3-chloranes seems quite promising considering the higher ionization potential and electronegativity of chlorine atom that tends to a decreased positive charge in the hypervalent chloranes, accounting for an enhanced reactivity of these compounds. Their distinctive electronic properties present reactivity that is complementary to that of the iodanes and the promising bromanes.

Sandin and Hay prepared the first hypervalent chloronium compound, namely, *o,o'*-diphenylene(iodo)-λ^3-chlorane **115** through the intramolecular nucleophilic chlorine attack on aryldiazonium salt **116** (**Scheme 24a**).[285] The same synthetic strategy was applied for the synthesis of benzochlorole **117**, however, the compound **117** underwent ring opening to give alkyne derivative **118** in quantitative yield (**Scheme 24b**).[289] It is pertinent to mention here that similar strategy performed under intermolecular fashion to access acyclic diaryl-λ^3-chloranes, gave relatively low yields of the desired products.[290–293] Improved synthetic strategy, in terms of yields, for acyclic diaryl-λ^3-chloranes has been recently reported using weakly coordinating anions.[294-295]



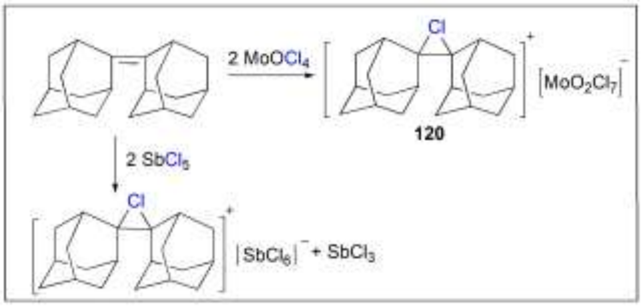
Scheme 24 (a) Synthesis of cyclic diaryl- λ^3-chlorane **115**; (b) attempted synthesis of benzochlorole **117**

Recently, a simple and robust synthetic method for the preparation (**Scheme 25a)** of a series of cyclic diaryl-λ^3-chloranes **119** and their synthetic potential as versatile aryne precursors {**Scheme 25b (i)** have been reported.[296] The enhanced reactivity of these λ^3-chloranes accounts for the unparalleled metal-free arylation reactions of phenols under base-mediated reaction conditions. Further, the chemo- and regio- selectivity observed in the reactions of these chloranes as well as the intermediacy of arynes is supported by the DFT calculations and experimental mechanistic investigations. Cyclic diaryl-λ^3-bromanes were also utilized in a similar fashion for the metal-free 'C-O' coupling with phenols as outlined in **Scheme 25b (ii).**



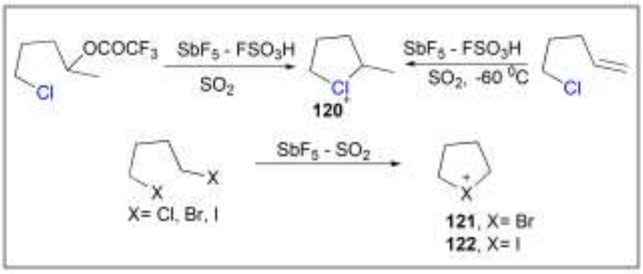
Scheme 25 (a) Synthesis of a series of cyclicdiaryl-λ^3-chloranes; (b)metal-free 'C-C' and 'C-O' coupling of cyclicdiaryl-λ^3-chloranes with phenols *via* aryne intermediates

In addition to the diaryl-λ^3-chloranes, many researchers have demonstrated the participation of diaryl-λ^3-chloranes as intermediates *via* kinetic studies, product identification, and/or by the direct observation.[297-298] Olah and coworkers provided the first spectroscopic evidence of a bridged chloronium ion[299] and later synthesized the sterically crowded cyclic chloronium salt,[300] which was further isolated by Nugent[301] (**Scheme 26**). The solid-state structure of the salt was in contrast to that of corresponding cyclic bromonium and iodonium salts and showed an unsymmetrical three-membered chloronium moiety.



Scheme 26 Synthesis of three-membered chloronium salts

Further, Olah and Peterson reported the formation of cyclic chloronium ions **120** *via* 1,4-halogen participation through ionization using antimony pentafluoride (SbF_5) - sulfur dioxide (SO_2) solution as outlined in **Scheme 27**.[302] Other cyclic halonium ions, bromonium **121** and iodonium **122** ions were also formed using similar synthetic strategy. Certain five-membered halonium ions were revealed to be stable by NMR investigation for short periods of time at temperatures in the range –30 - 0˚C, depending on their structure.



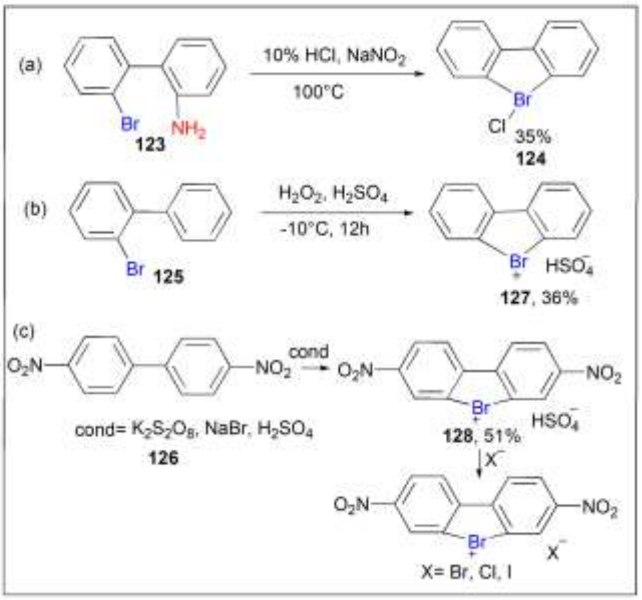
Scheme 27 Formation of five-membered cyclic halonium ions **120-122**

7.2. Hypervalent Heterocyclic Compounds of Bromine (III)

Among the hypervalent halogen compounds, the hypervalent iodine compounds have been the centre of attraction for the researchers due to their unique characteristic properties, such as, mild in reactivity, easy to handle, and environmentally benign class of compounds. Their hypervalent bromine analogues can attribute to higher reactivity pattern due to the higher nucleofugality, ionization potential and strong electrophilicity associated with them.[303-305] These properties of hypervalent bromine compounds have been the mainstay for the development of various synthetically useful transformations using bromanes, such as, Bayer-Villiger-like oxidation,[303-304] oxidative coupling reactions of alkynes with primary alcohols,[306] metal-free C-O as well as C-N couplings,[307] amination of unactivated alkanes,[308] etc. Despite the fact that the hypervalent bromine compounds offer superior reactivity pattern, synthesis of these compounds always remains a challenge owing to the inherent thermodynamic barrier for the oxidation of Br(I) to Br(III) in comparison to the conversion of I(I) to I(III). This disadvantage limits the synthetic utilization of these compounds. In this series, synthesis of certain cyclic λ^3-bromanes (diaryl-/dialkyl-/Br-O) has been reported using various oxidizing agents. Recently, electrochemical oxidation was also developed by Francke, Suna and coworkers as an alternative approach for the preparation of these compounds.[309]

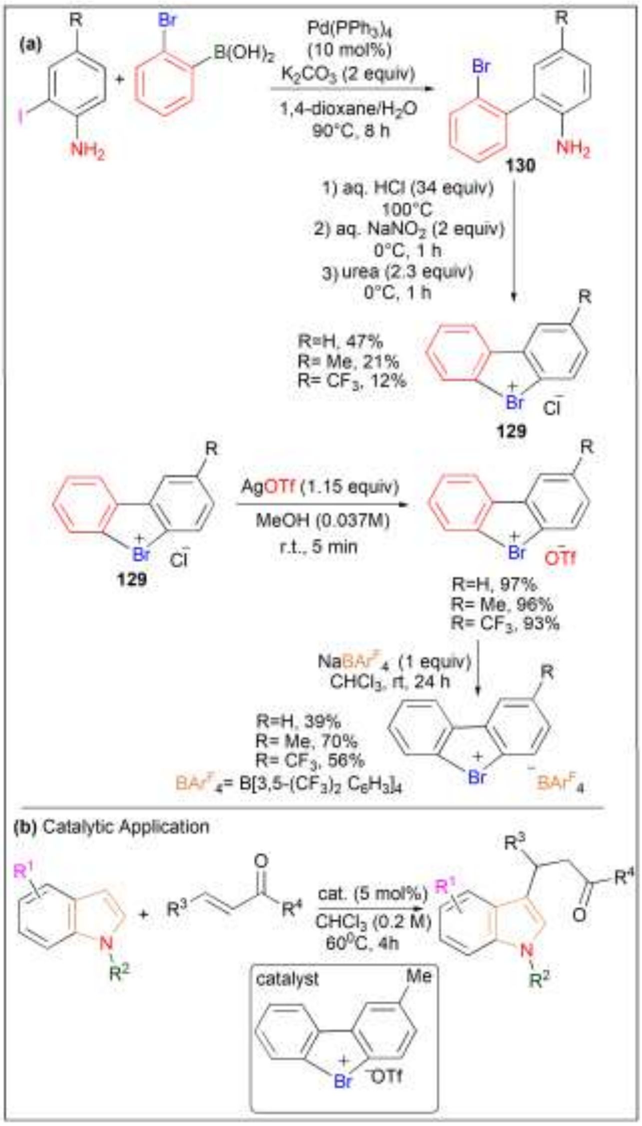
7.2.1. Cyclic diaryl-λ^3-bromanes

The first hypervalent bromonium compound **124** was prepared by Sandin and Hay through the thermal decomposition similar to the preparation of cyclic diaryl-λ^3-chloranes *via* intramolecular nucleophilic bromine attack on an aryldiazonium salt as outlined in **Scheme 28 (a)**.[285] 2-Amino-2′-bromobiphenyl (**123**) on diazotization using 10%HCl/$NaNO_2$ at 100˚C afforded the hypervalent bromonium compound **124** in 35% yield as outlined in **Scheme 28 (a)**. Oxidative cyclization of 2-bromobiphenyl (**125)** using hydrogen peroxide[310] and that of 4,4′-dinitrobiphenyl (**126**) using $K_2S_2O_8$[311] in sulfuric acid afforded corresponding cyclic diaryl λ^3-bromanes **127** and **128**, respectively as shown in **Scheme 28(b) and (c)**.



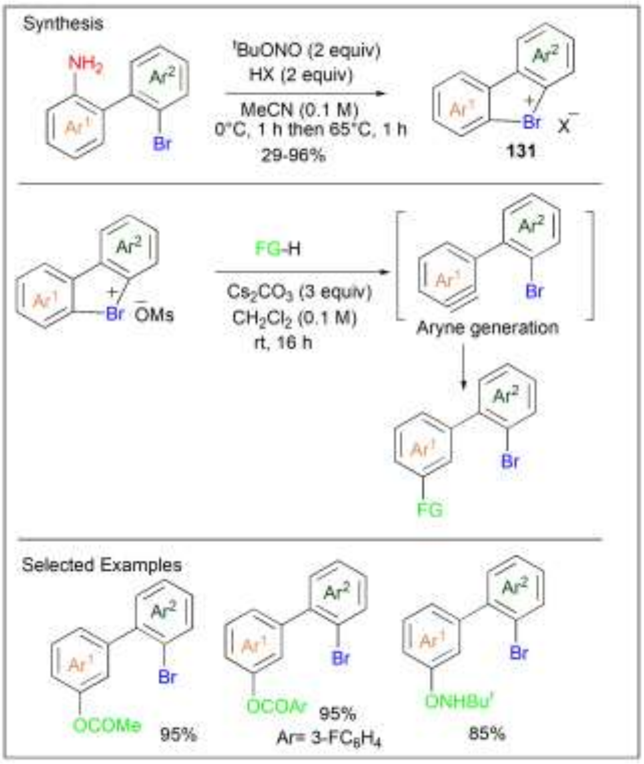
Scheme 28 Synthesis of cyclicbromonium compounds **124, 127** and **128**

Yoshida and coworkers synthesized the cyclic bromonium salts **129** and evaluated their potential as excellent halogen-bonding organocatalysts.[2312] Functionalized 2-amino-2′-bromobiphenyl derivatives **130**, obtained through palladium-catalyzed Suzuki coupling reactions, were cyclized to produce the corresponding cyclic diaryl λ^3-bromanes **129** as chloride salts in 12-47% yield (**Scheme 29**). These salts were further converted to their triflates in up to 97% yield, which were then treated with $BAr^F{}_4$ anions. X-ray analysis of the cyclic λ^3-bromanes **129** revealed ion-pair structure rather than the covalently bonded form.[313] These cyclic bromonium salts were evaluated for their catalytic applications as halogen-bonding organocatalysts towards Michael addition reaction of indoles with α,β-unsaturated ketones with final product yield upto 96% as shown in **Scheme 29 (b)**.



Scheme 29 (a) Synthesis of cyclic diaryl λ^3-bromanes **129** and related λ^3-bromanes**;** (b)catalytic applications of cyclic diaryl λ^3-bromanes as halogen-bonding organocatalysts

A series of cyclic diaryl λ^3-bromanes **131** has been reported using *t*-butyl nitrite (^{t}BuONO) as a mild oxidant in the presence of Brønsted acid, and being utilized as aryne precursors (**Scheme 30**).[307]



Scheme 30 Synthesis of cyclic diaryl λ^3-bromanes **131** using *t*-butyl nitrite (^{t}BuONO) and their synthetic utilization as aryne precursors

Further, the X-ray analysis of **131-OMs** revealed tricyclic planar structure with a dihedral angle of -1.04(4)° and the carbon-bromine bonds slightly longer (1.928 Å and 1.932 Å respectively) with respect to the bromobenzene (1.850 Å). Moreover, the angle between C-Br-C reflected a T-shape structure typical for 3c-4e bonding **(Figure 22)**.[207,238–243]

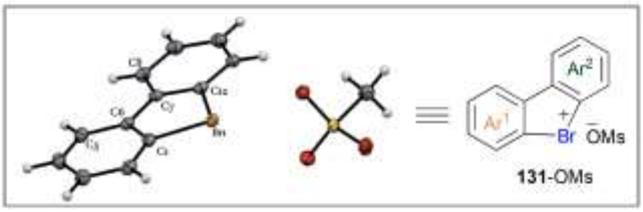
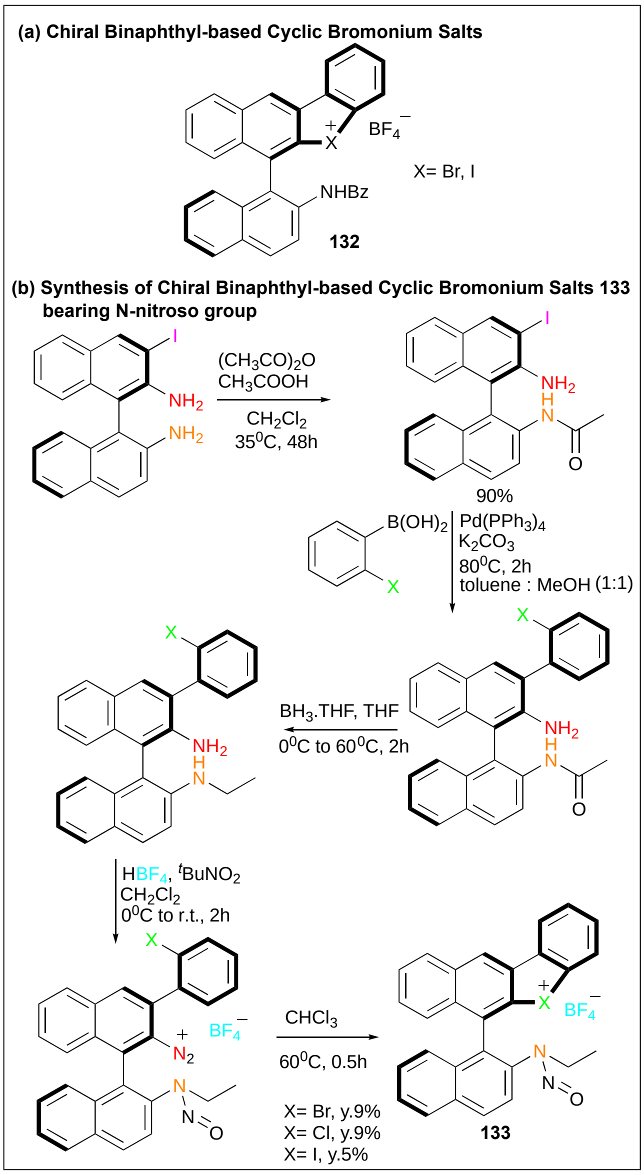


Figure 22 X-ray structure of cyclic diaryl λ^3-bromanes **131-OMs**

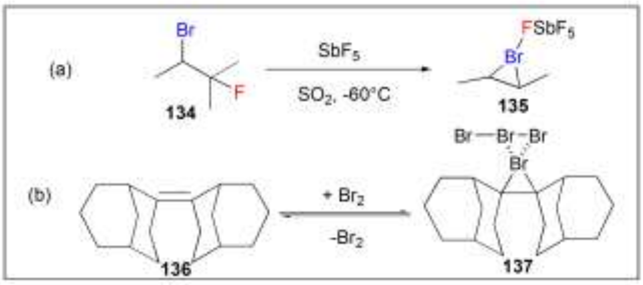
In addition to the achiral version, synthesis and applications of chiral bromonium salts as asymmetric halogen-bonding donor catalysts have been recently reported in the literature. Yoshida and coworkers developed chiral binaphthyl-based cyclic bromonium salts **132 {Scheme 31 (a)}** with amide functionalities and utilized these salts for the vinylogous Mannich reaction of cyanomethyl coumarins with imines upto 99% yield and 96% *ee*.[320] The corresponding iodonium salts were explored for the thiol addition reaction to isatin derived ketimines which gave the products with up to 99% yield and 97% *ee*.[320] Further, the chiral bromonium salts **133** bearing N-nitroso group were prepared through multi-step synthetic sequence as shown in **Scheme 31(b)** and their reactivity was studied in the Mannich reaction of isatin derived ketimines with malonic esters.



Scheme 31 Structure of binaphthyl-based chiral bromonium salts **132** and multi-sequence synthesis of **133**

7.2.2. Cyclic dialkyl-λ^3-bromanes

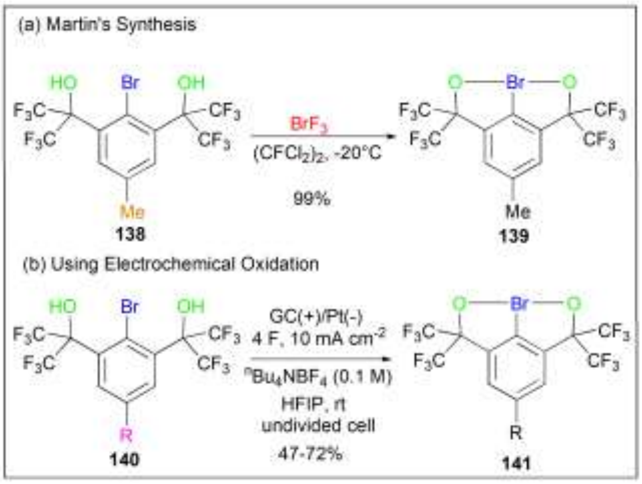
Olah and Bollinger reported that the ionization of 2-fluoro-3-bromo-2-methylbutane (**134**) in antimony pentafluoride (SbF_5)-sulfur dioxide solution at -78°C gave stable solution of cyclic dialkyl λ^3-bromane **135 {Scheme 32 (a)}.**[322] Later, in 1985, Brown and coworkers presented the synthesis and X-ray analysis of cyclic diakylbromanes **136 {Scheme 32 (b)}.**[323] The compound **137**, was obtained as bright yellow solid by the addition of bromine to adamantylideneadamantane (**136**) in dichloromethane.



Scheme 32 Formation of cyclic dialkyl λ^3-bromanes **135** and **137**

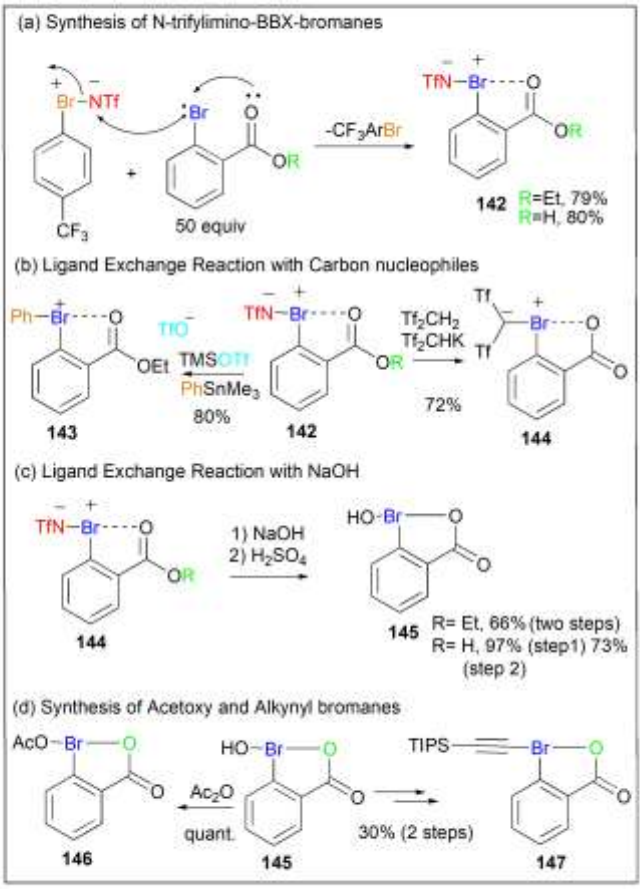
7.2.3. Cyclic λ^3-bromanes containing Br-O bonds

In addition to the diaryl- and dialkyl- cyclic λ^3-bromanes, examples of cyclic bromanes containing Br-O bonds were also reported. In this series, as a representative example, cyclic bromine **139** was prepared in 99% yield for the first time by Martin group through the oxidative cyclization of compound **138** using BrF_3 (**Scheme 33a**).[324] The concern of using highly reactive BrF_3 in this synthetic methodology was recently resolved by utilizing the electrochemical oxidation. Various cyclic bromanes **141** have been synthesized by electrochemical oxidation of aryl bromides **140** in yields upto 72% and have been utilized for the C-C coupling of arenes {**Scheme 33b**}.[309]



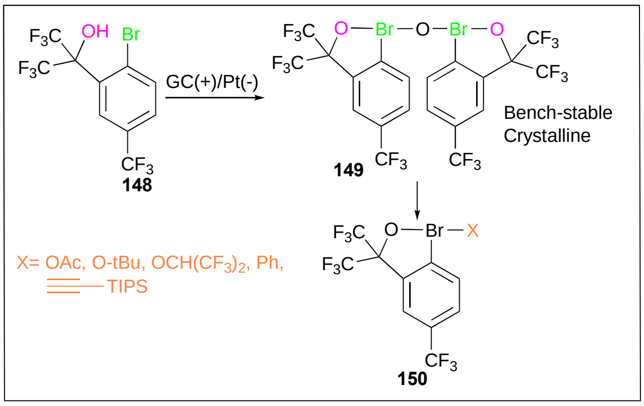
Scheme 33 Synthesis ofcyclic bromanes **139** and **141** containing Br-O bonds through (i) Martin's synthesis using BrF_3 and (ii) electrochemical oxidation, respectively

In another recent example, bench-stable cyclic λ^3-bromanes (**142**), were prepared using cyclic 1,2-benzobromoxol-3-one (BBX) strategy.[325] Ligand exchange reaction of N-triflylimino-λ^3-bromane (**142**) with carbon nuleophiles and NaOH afforded diverse cyclic bromanes **143-145** in good yields as depicted in **Scheme 34**. Two other, cyclic bromanes **146** and **147**, were also prepared from **145** in quantitative yield and 30% yield (2 steps) respectively. Synthetic utilization of these cyclic bromanes was investigated by reaction with various nucleophiles to get arylation of benzene, oxidation of alkanes, sulfides, enones and alcohols.



Scheme 34 Synthesis of various cyclic λ^3-bromanes **142-147**

Recently, Sokolovs and Suna developed an excellent example of electrochemical synthesis of a range of diverse cyclic hypervalent bromine (III) compounds (**150**).[326] The dimeric benzobromoxole (**149**), obtained through anodic oxidation of aryl bromide (**148**), can be converted to numerous synthetically useful Br(III) compounds (**150**) (**Scheme 35**).



Scheme 35 Electrochemical synthesis of cyclic hypervalent bromanes **150**

7.3. Hypervalent Heterocyclic Compounds of Iodine(III)

Hypervalent iodine compounds have been widely utilized as reagents as well as catalysts in organic synthesis due to their environmentally benign and unique characteristic properties.[283,327-339] These compounds are associated with excellent oxidizing and electrophilic properties and reported to show similar structural properties and reactivity pattern as that of transition metals, such as Ag(I), Hg(II) and Tl(III). The low toxicity, high bench stability and easy handling make the hypervalent iodine compounds as excellent alternatives to these heavy metals for diverse organic transformations. The hypervalent iodine compounds have emerged as reagents of choice for various selective oxidative transformations and have shown paramount significance in organic synthesis for the development of organic transformations which are otherwise difficult to access. In particular, the diverse reactions of hypervalent iodine compounds include couplings,[340] oxidative rearrangements,[341] oxidations,[342] cyclizations,[343] atom-transfer reactions,[344] alkene functionalizations,[345] C-H bond functionalization,[346] photochemical transformations,[347] α-functionalization of carbonyl compounds,[348] organocatalysis[349] etc. A range of acyclic hypervalent iodine(III) (λ^3-iodanes) and hypervalent(V) (λ^5-iodanes) compounds has been reported in the literature, some representative examples are given in Figure **23.**

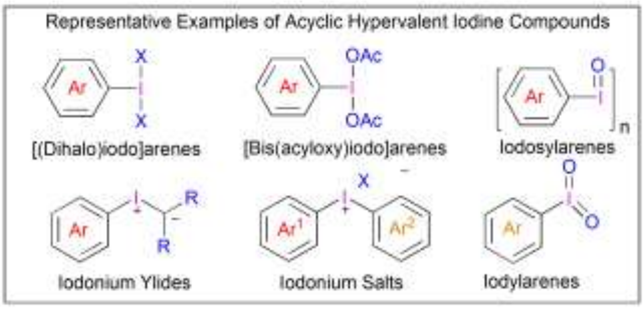


Figure 23 Representative examples of acyclic hypervalent compounds

Cyclic hypervalent iodine compounds are particularly vital reagents because of their higher thermal stability and modified reactivity as compared to that of their acyclic analogues.[344,350-352] The higher thermal stability associated with the cyclic iodanes can be attributed to the link between apical and equatorial ligands present at the iodine centre that makes pseudorotation and reductive elimination leading to thermal decomposition quite difficult.[24-27] The synthetically significant classes of cyclic iodanes have been shown in **Figure 24.** The cyclic hypervalent λ^3-iodanes can be generally classified as: (i) cyclic aryliodonium salts and (ii) benziodoxole derivatives.

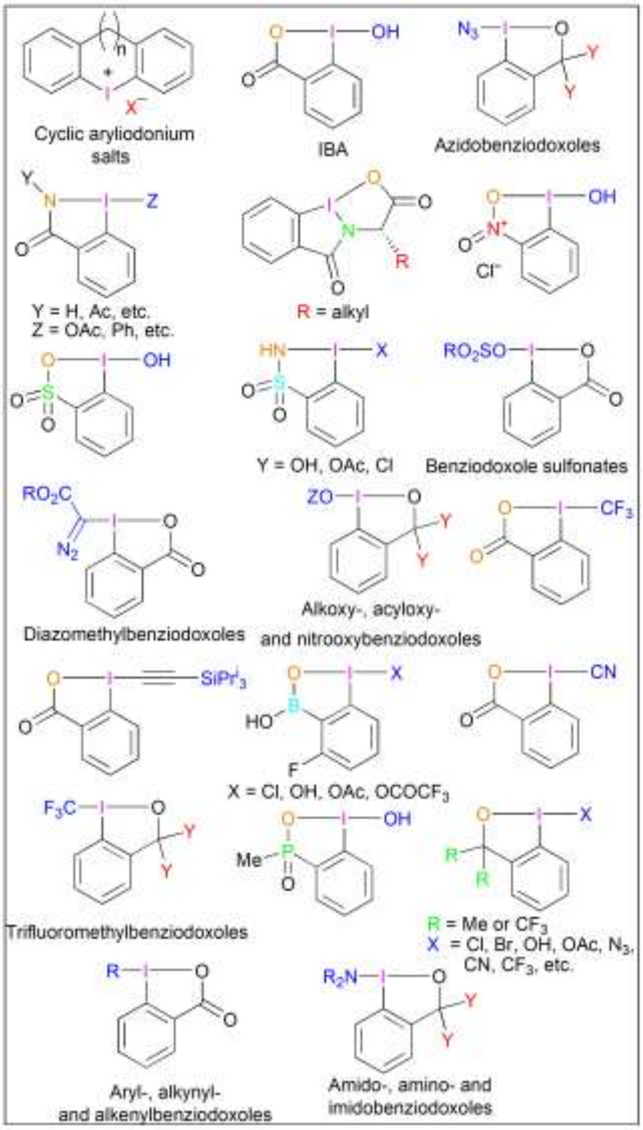
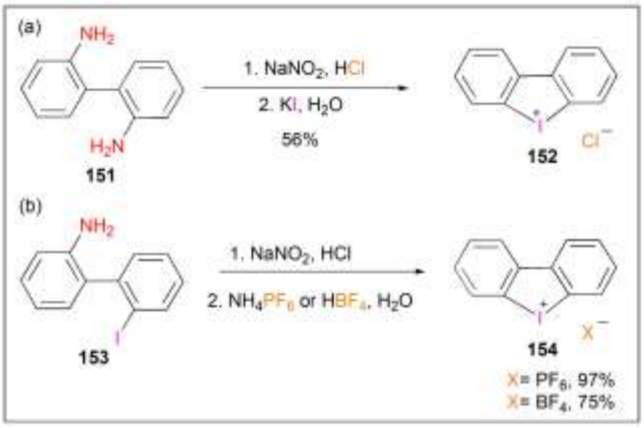


Figure 24 Representative examples of cyclic hypervalent λ^3-iodanes

Aryliodoniums have emerged as important synthons to access diverse structural motifs since the discovery of the iodonium salts in 1890s.[353-360] Iodonium salts having two carbon atoms and a closely associated anionic part, possess a pseudo-trigonal bipyramidal geometry with experimentally found 'C-I-C bond angle close to 90^0. These compounds are also referred to as 'λ^3-iodanes'. Usually, these salts have substantial bonding between the anion and central atom rendering these salts as 'hypervalent'.[361] Despite the fact that the acyclic aryliodoniums have made tremendous advancements, in particular as arylating agents, their cyclic counterparts have been reported to be more atom-economical due to the fact that the iodoarene, generated as byproduct/waste, remains part of the arylated products.[358,362-363] The reactivity patterns and thermal decomposition of cyclic iodonium salts, in concert with their reactions with diverse nucleophiles, was elaborated in review articles by Grushin.[364-365] Recently, Wen, Gu and coworkers have comprehensively reviewed the chemistry and synthetic applications of cyclic aryliodonium salts.[352] Prior to this, Han and coworkers[366] and Fu group[367] provided brief illustration on these compounds. Goswami and coworkers[368] and Jiang et al[369] presented the advancements of cyclic aryliodonium salts focusing on their applications for the synthesis of polycyclic compounds and functionalized molecules. The preparation of the cyclic diaryliodonium salts is well established. Mascarelli and Benati reported the first preparation of cyclic diaryliodonium salt **152** in 1909 *via* diazotization of 2,2'-diaminobiphenyl (**151**) followed by addition of potassium iodide {(**Scheme 36** (**a**)}.[370] Similarly, diazotization of 2-amino-2'-iodobiphenyl (**153**) followed by addition of NH$_4$PF$_6$ (or HBF$_4$) gave dibenziodonium compounds **154** {**Scheme 36 (b)}**.[371]



Scheme 36 Synthesis of cyclic diaryliodonium salts **152** and **154**

The conventional synthetic strategies for the production of cyclic diaryliodoniums are, in general, associated with the disadvantages, such as, wastage of reagents, time-consuming, and requiring multiple synthetic sequences. A number of synthetic routes reducing the above disadvantages have been developed either using electrochemistry or one-pot sequences. Methods involving oxidation of the corresponding precursor by an appropriate oxidant and then by ring closure using a suitable acid to afford cyclic aryliodoniums of the type **155** are well-documented (**Scheme 37**). General methods include: (i) peracetic acid and sulfuric acid,[372-381] (ii) PhI(OH)OTs (Koser's reagent) as oxidant and *p*-toluenesulfonic acid (TsOH),[382] (iii) *m*-CPBA and then TfOH,[353,358] (iv) oxone and sulfuric acid,[383] (v) He's method employing electrolysis in the presence of TfOH,[384] (vi) Moran's method involving oxidation *via* electrolysis and TfOH,[385](vii) Oxone and TfOH,[386] (viii) Selectfluor and TfOH[387].

Scheme 37 General methods involving oxidative cyclization for the synthesis of cyclic diaryliodonium salts **155**

Design and synthesis of several other types of cyclic diaryliodonium salts have also been well established. Representative examples of heterocyclic iodoniums **156-161**,[388–392] vinyl(aryl)iodoniums **162-**

163,[393-394] and polycyclic aryliodoniums **164-167**[395-398] are shown in **Figure 25.**

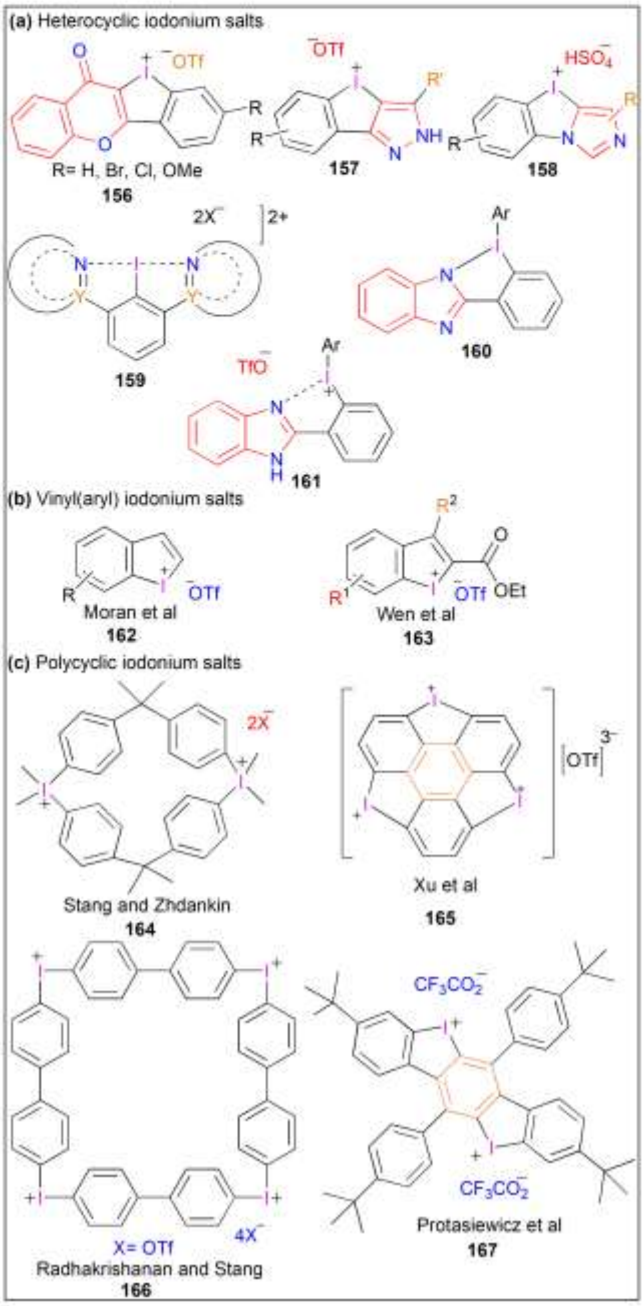


Figure 25 Examples of (a) heterocyclic iodonium salts **156-161**; (b) vinyl(aryl)iodoniums **162-163**; (c) polycyclic aryliodoniums **164-167**

Chiral hypervalent iodine reagents have attracted huge attention in asymmetric synthesis.[399-400] The chiral hypervalent iodine-catalyzed reactions are proved to be an excellent method to access enantioenriched molecules and intermediates that possess a broad array of applications in medicinal chemistry. In this series, synthesis of binaphthyl-based chiral cyclic iodoniums **168** has been reported by Ochiai and co-workers **(Figure 26)**,[302] while Yoshida *et al* prepared the new chiral iodoniums **169** *via* a three-step procedure.[401]

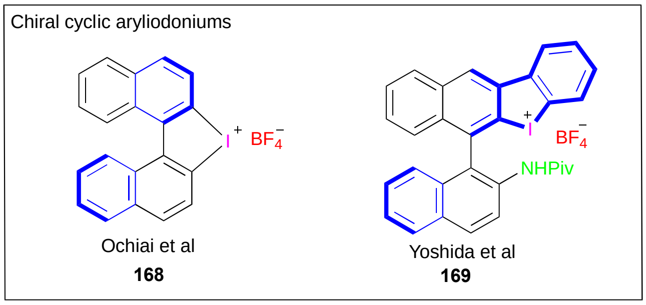
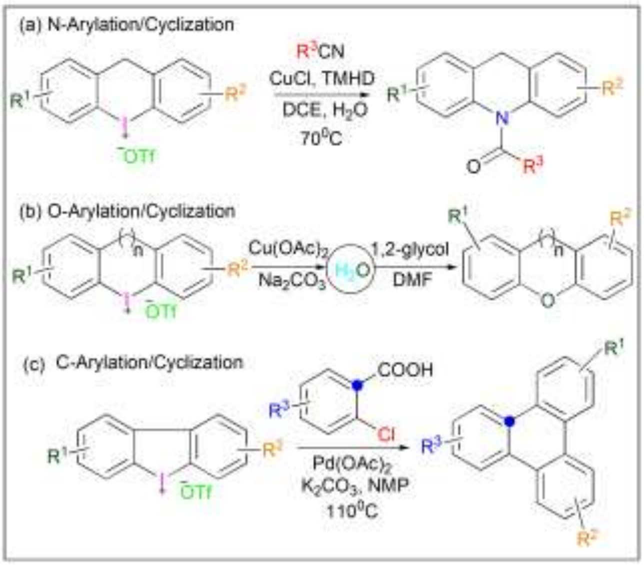


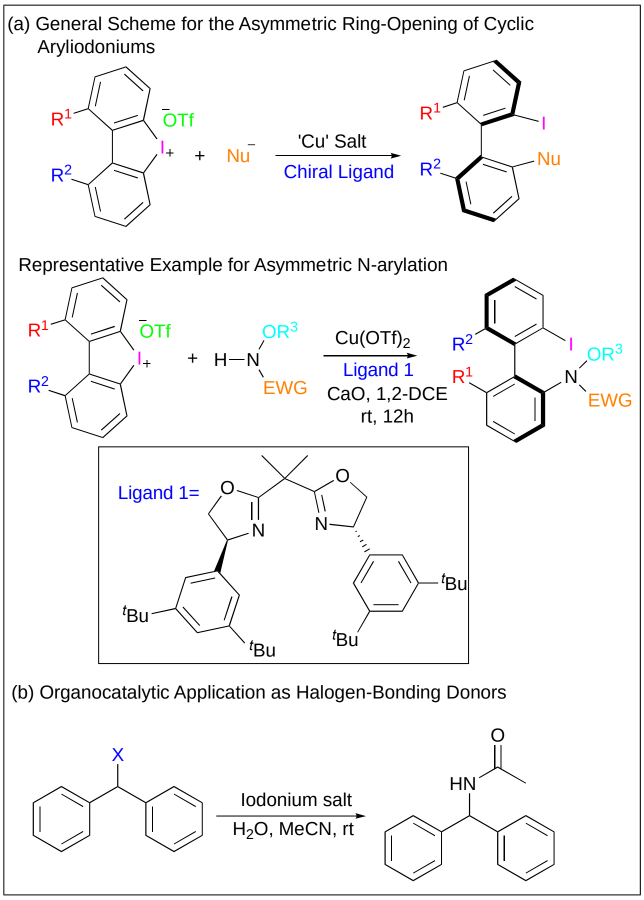
Figure 26 Chiral cyclic aryliodoniums **168** and **169**

Cyclic aryliodoniums, due to their unique ring system and high electron-deficient properties can be efficiently used for the construction of various polycyclic scaffolds.[402-407] Besides,cyclic aryliodoniums have been utilized in diverse transformations, and the past decade witnessed a high demand in the design and synthesis of a broad range of cyclic aryliodoniums with varying substitutents.[408–413] Certain recently selected arylation approaches for the construction of diverse compounds through C-N,[414] C-O,[415] and C-C[416] bond formation are highlighted in **Scheme 38.**



Scheme 38 Arylation approaches for the construction of diverse compounds using cyclic aryliodoniums

In recent years, much attention has also been directed toward the enantioselective ring-opening reactions of cyclic aryliodoniums with different nucleophiles to obtain axially chiral atropisomers.[417-421] **Scheme 39(a)** depicts some recently developed protocols for the synthesis of chiral biarylatropisomers. Besides, the efficient exploration of cyclic aryliodoniums as versatile halogen-bonding organocatalysts is shown in **Scheme 39(b)**.[422-423]



Scheme 39 (a) General scheme for asymmetric ring opening of cyclic aryliodoinum salts (asymmetric N-arylation); (b) Cyclic aryliodonium salts as halogen-bonding donors

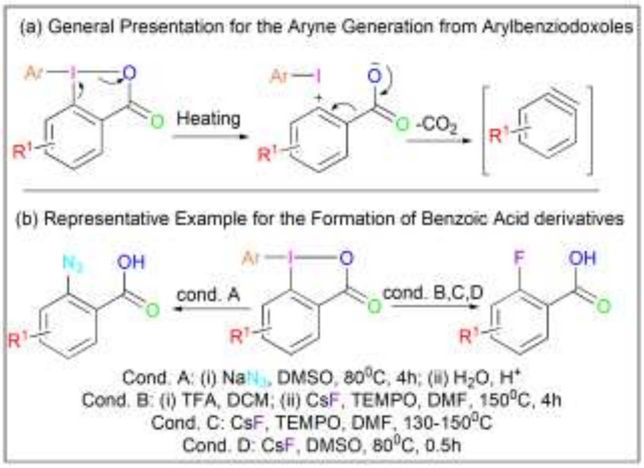
Other cyclic hypervalent iodine reagents are represented by cyclic compounds, which incorporate iodine, oxygen, nitrogen, and some other elements in the ring (**Figure 24**). In general, the name 'benziodoxoles' is used for the cyclic iodanes that contain iodine and oxygen in the five-membered ring and different substituents are attached to the iodine. The most important compound of this class is 2-iodosobenzoic acid, abbreviated as 'IBA' (1-hydroxy-1,2-benziodoxol-3-(1*H*)-one), that was prepared for the first time over 100 years ago.[424] According to the X-ray analysis, the five-membered ring in benziodoxoles is quite distorted with almost linear arrangement of two electronegative ligands. The endocyclic iodine-oxygen bond length in iodine-substituted benziodoxoles varies from 2.11 Å (in carboxylates) to 2.48 Å (in 1-phenyl benziodoxolone).

Benziodoxoles are extensively utilized in organic synthesis as the umpolung iodine(III) reagents for the introduction of diverse functional groups, such as alkynyl, alkenyl, cyano, SCN, azido, CF_3, Hal, etc., and are generally termed as 'atom-transfer reagents'.[344,425–428] Further, benziodoxole reagents that contain carbon-based functional groups at the iodine center (such as aryl-, alkynyl-, and alkenylbenziodoxoles) permit C-C and C-heteroatom bond-forming reactions under metal-free conditions, or under mild and easy-to-handle catalytic conditions. Preparation, structural aspects, and recent synthetic applications of aryl-, alkynyl-, and alkenylbenziodoxoles for direct arylation, alkynylation and alkenylation of various organic substrates have been comprehensively reviewed recently.[429-430] We herein present some of the representative examples in order to showcase their synthetic applications in organic synthesis.

Arylbenziodoxoles **170** can be easily prepared from the appropriate 2-iodobenzoic acids **171** and substituted benzenes[431-439] (**Scheme 40**). Moreover, such compounds can also be obtained from suitable hypervalent iodine reagents through ligand exchange reaction.[440-442] Single-crystal X-ray structures of several arylbenziodoxoles have been published.[436,443-445] Arylbenziodoxoles have shown to possess a zwitterionic structure as evidenced by the presence of a short internal interaction between iodine and oxygen atoms.[436-438,440-443] Further, the average distance of the intramolecular I⋯O bonds (2.5 Å) is longer as compared to the average covalent I-O bond length (2.14 Å),[446-447] however, shorter than the sum of van der Waals radii for iodine atom and oxygen atoms (3.5 Å),[448] indicating a significant increase in the ionic nature of this bond.

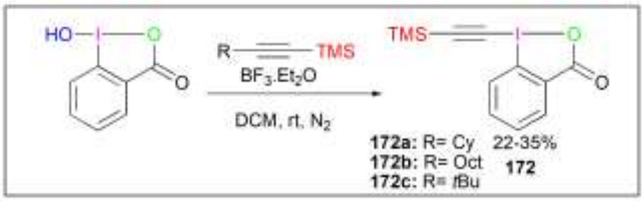
Scheme 40 Synthesis of arylbenziodoxoles **171** from 2-iodobenzoic acids **170** and substituted benzenes

Arylbenziodoxoles can be used as versatile aryne precursors,[449] as well as for the formation of benzoic acid derivatives.[450-454] A general schematic presentation for aryne generation and representative example for the benzoic acid formation are outlined in **Scheme 41(a)** and **41(b)**, respectively.



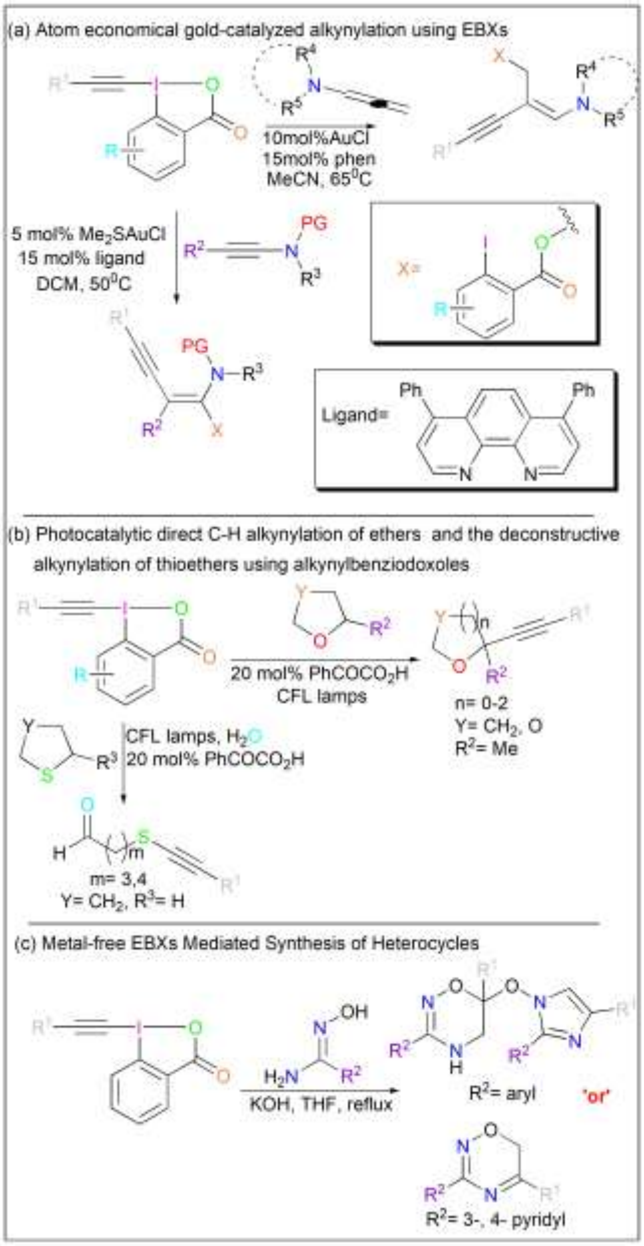
Scheme 41 (a) General presentation for the aryne generation; (b) representative example for the benzoic acid formation from arylbenziodoxoles

Besides, alkynylbenziodoxoles, also termed as ethynylbenziodoxoles (EBXs), evolved as excellent alkyne transfer reagents. These reagents can be successfully applied as electrophilic alkynylating reagents to wide range of organic substrates and their utilization is usually preferred over the classical methods.[344,426-427,455-460] The first example of EBX **172** was prepared by Ochiai and coworkers in 1991 (**Scheme 42**).[384]



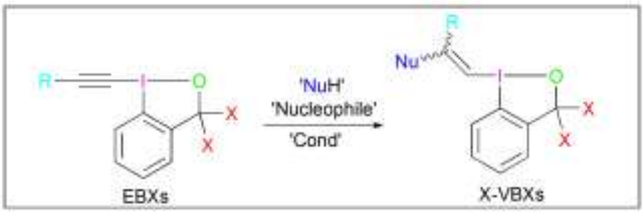
Scheme 42 First example of preparation of ethynylbenziodoxoles (EBXs)

The same group established the structure of cyclohexyl-EBX **172a** by X-ray diffraction analysis.[461] X-ray structural data showed the presence of a distorted T-shaped geometry with an endocyclic C(sp^2)-I-O angle of 75.28° and a C(sp^2)-I-C(sp) angle of 90.9°. Later on, many X-ray structures of various aromatic and aliphatic alkynylbenziodoxoles, and silyl alkynylbenziodoxoles, were reported with almost the same bond lengths and angles at the iodine atom.[462] EBXs can be conveniently used in direct alkynylation or complex reactions involving the formation of several bonds in a single transformation.[344,426-427,455-460,463] The alkyne transfer reactions can be performed effectively under metal-catalyzed conditions using gold,[464-470] copper,[471-478] palladium,[479-483] etc. Ethynylbenziodoxoles have also been utilized for the radical alkynylation reactions under photoredox conditions.[459,484-496] Besides, several metal-free alkynylation reactions are also reported for the synthesis of numerous synthetically important targets, including heterocycles.[497-507] Representative examples for the metal-catalyzed, photoredox and metal-free alkynylation reactions using EBXs are given in **Scheme 43.**



Scheme 43 (a) Atom economical gold catalyzed alkynylation using EBXs; (b) photocatalytic direct C-H alkynylation of ethers and the deconstructive alkynylation of thioethers using alkynylbenziodoxoles; (c) metal-free EBXs mediated synthesis of heterocycles

Vinylbenziodoxoles (VBXs), also termed as alkenylbenziodoxoles, have recently received much attention. Formation of VBXs as products in various addition reactions of alkynylbenziodoxoles has been reported in earlier reports.[508–510] Waser and coworkers described the synthetic approaches to access various VBX reagents and their reactivity in detail in 2020[427] and recently elaborated by Zhdankin et al.[429] In general, the VBXs are categorized X-VBX and C-VBX, depending upon the presence of heteroatom 'X' or carbon substituent at the β-carbon of the vinyl group, respectively. C-VBXs can be easily synthesized by coupling of vinylboronic acids and suitable hypervalent iodine compounds,[511–514] whereas several synthetic methods have been reported recently for the synthesis of 'X-VBXs' through the addition reaction of S-, N-, O-, and X-nucleophiles to ethynylbenziodoxoles (EBXs).[515-524] A common approach for the preparation of X-VBXs starting from EBXs is outlined in **Scheme 44**.



Scheme 44 A common approach for the preparation of X-VBXs starting from EBXs

The cyclic structure of the styrylbenziodoxole (**173**) was confirmed by X-ray analysis (**Figure 27**).[511] The molecular structure of VBXs showed a distorted T-shape with an O-IC(sp^2) angle of 165.88 Å, similar to that of reported arylbenziodoxoles[436,443-445] and alkynylbenziodoxolones[461-462,525] The endocyclic I-O bond length of 2.51 Å was considerably longer than in case of alkynylbenziodoxoles, and in general, close to the I-O bond in the structure of arylbenziodoxolones.[436,443-445] This bond length trend is indicative of the higher trans influence exerted by the vinyl and aryl groups in comparison to the alkynyl- and trifluoromethyl- groups.

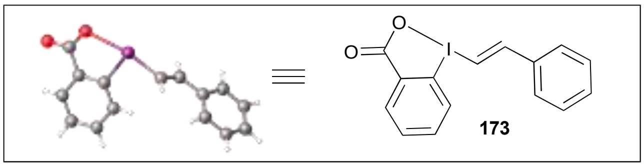
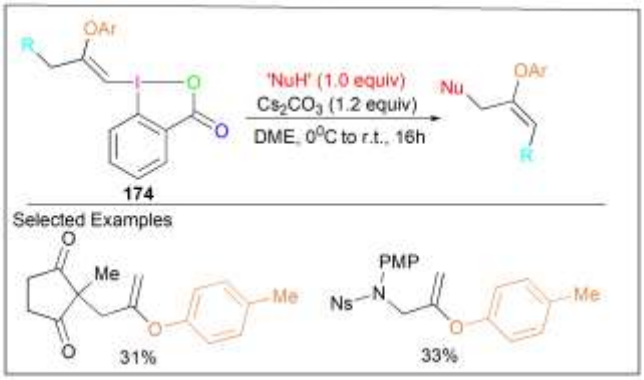


Figure 27 X-ray structure of styrylbenziodoxole (**173**)

Further, VBXs are efficiently utilized as synthetic equivalents of the alkenyl group.[427,429] As one of the representative recent examples, an umpolung strategy of enol ethers to generate oxy-allyl cation equivalents from O-VBXs **174** is outlined in **Scheme 45**.[372]



Scheme 45 Generation of oxy-allyl cation equivalents from O-VBXs **174**

The chemistry of benziodoxole sulfonates as oxidants and electrophiles has been discussed in detail recently by Zhdankin and coworkers.[526] Iodine(III) benziodoxoles **175-178** and pseudobenziodoxoles **179 -180** are powerful electrophiles as well as mild oxidants towards a range of unsaturated compounds. Pseudocyclic benziodoxole-derived triflate (IBAOTf) **179,** in particular, has been shown to be an efficient reagent for oxidative heteroannulation reactions. Benziodoxole-derived organosulfonates **179-180** are shown in **Figure 28**. Single crystal X-ray diffraction of IBA-OTf (**179**) showed that hydroxy(aryl)iodonium ion in **179** possesses distorted T-shaped intramolecular geometry around the hypervalent iodine atom with an O–I–O angle of ~167°. Further, the I–OH bond of 1.92 Å is notably shorter than the dative secondary interaction between iodine and a carboxylate oxygen atom (2.34 Å), which is in concurrence with the proposed pseudocyclic structure of **179.**

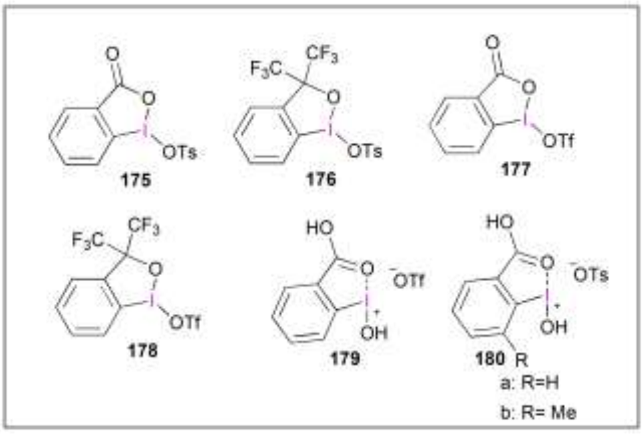
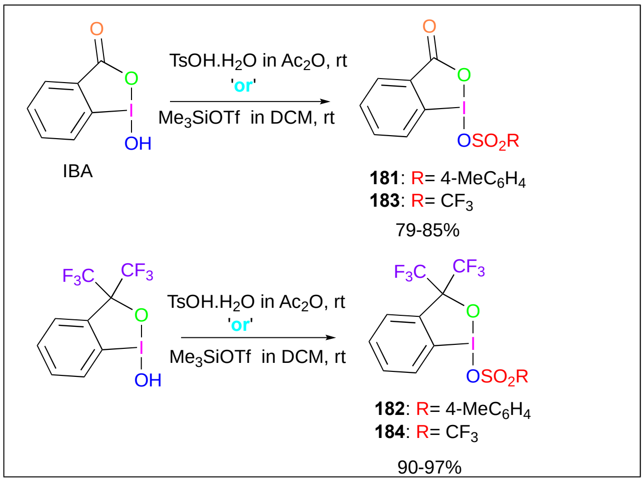


Figure 28 Benziodoxole-derived organosulfonates **175-180**

Benziodoxole-based tosylates **181**-**182** and triflates **183**-**184** were prepared by the reactions of 2-iodosylbenzoic acid (IBA) or 1-hydroxy-3,3-bis(trifluoromethyl)-3(1H)-1,2- benziodoxole (**185**) with *p*-toluenesulfonic acid or trimethylsilyl triflate, respectively (**Scheme 46**).[527-528] The cyclic structure of **175** and **177** was in agreement with the IR absorption at about 1615 cm^{-1}.[529] Further, the structures of the benziodoxole based tosylates were independently confirmed by X-ray structural analysis by Stuart and coworkers.[530] Further,preparation, structure, and reactions of 2-iodosylbenzoic acid triflate (IBA-OTf, **179**) have been recently investigated by Zhdankin and coworkers.[531-532] Synthetic applications of IBA-OTf (**179**) as a catalyst in oxidative heteroannulations[533-534] and efficient precursor to novel sulfoximidoyl-substituted hypervalent iodine[535] have been recently investigated. Besides, the X-ray crystal structures and the reactions of certain other new pseudocyclic benziodoxole tosylates **180**, analogs of benziodoxole triflate, have also been invetsigated.[536]



Scheme 46 Preparation ofbenziodoxole-based tosylates **181-182** and triflates **183-184**

Further, IBA-tosylate **180a**, was investigated for the synthesis of novel phenol-substituted benziodoxole, namely, 1-(4-hydroxyphenyl)benziodoxole.[444] X-ray structure of tosylate **180b** is given in **Figure 29.** X-ray data revealed a pseudocyclic structure for compound with a secondary bond of 2.362(3) Å between the iodine and carboxylate oxygen. Compound **180b** possesses a tetracoordinated iodine center with a I-C covalent bond (1.926 Å), one I–O covalent bond (1.926 Å), and two iodine–oxygen secondary bonds to carboxylate and tosylate oxygen atoms. This geometry is similar to that of benziodoxole triflate **179**. The iodine center in the cationic fragment of **180b** has a distorted T-shaped geometry typical of hypervalent iodine compounds with as intermolecular distance between iodine and the tosylate oxygen (2.947 Å). Taking into consideration the primary and secondary bonding, the iodine(III) center in **180b** has a pseudo square-planar coordination.

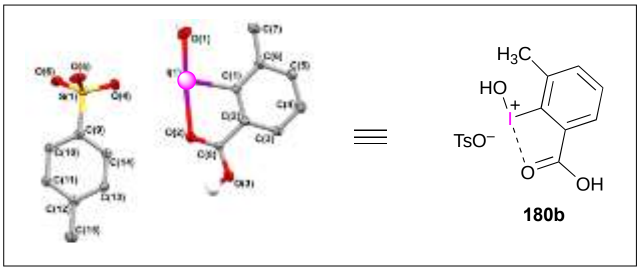
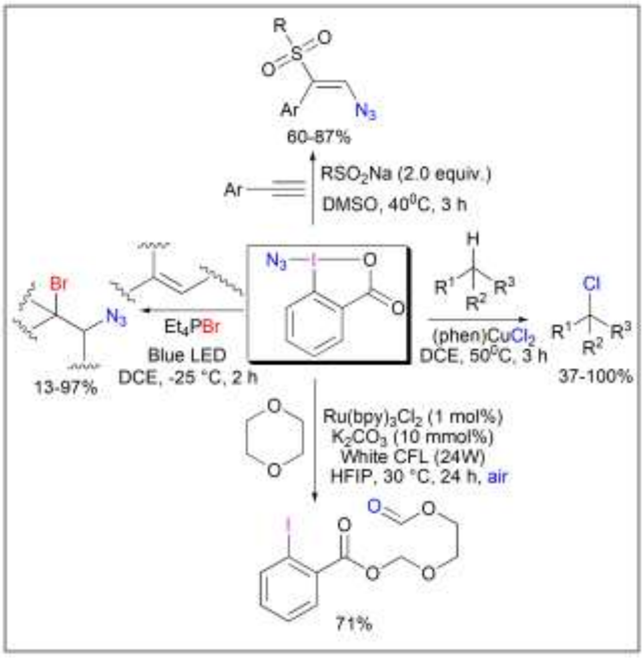


Figure 29 X-ray structure of compound **180b**

Recent progress in the synthetic applications of other classes of benziodoxole reagents, including azido-, amido-, amino-, imino-, cyano-, trifluoromethyl-, trifluoromethylthio-, alkoxy, nitrooxy-, acyloxy- and diazomethyl- has been comprehensively discussed in the 2023 review.[351] Azidobenziodoxoles (**Figure 24**) have been effectively utilized as electrophiles or radical azidation reagents for transferring the azido group to diverse range of substrates.[425-426,444,537-539] These reagents can be prepared by the addition of TMSN$_3$ to the corresponding acetoxybenziodoxoles or the benziodazoles.[540-543] X-ray analysis of these compounds was revealed by Zhdankin and coworkers in 1996 (**Figure 30**).[540] The I-N bond in azidobenziodoxoles has lower bond dissociation energy (BDE) as compared to cyclic hypervalent iodine compounds with any other ligands.[537,544-546] Differential scanning calorimetry results suggested that the azidobenziodoxoles derived from *tert*-butyl substituted benziodoxoles are expected to be safer than the unsubstituted benziodoxles.[547-548] Organic azides can be transformed to the corresponding amines or amides by suitable synthetic methods. On the other hand, amino groups can be directly converted to other organic substrates by utilizing the corresponding benziodoxole derivatives as group transfer reagents, which can be efficiently prepared by ligand exchange reactions of substituted benziodoxoles with the corresponding nitrogen compounds.[535,549-558] Most of these reagents are stable and are easy to handle. Structures of these compounds have been established by X-ray structural analysis.[549-550,552-554,556-558] Certain recently developed synthetic protocols utilizing azidobenziodoxoles such as, azido sulfonylation of terminal alkynes,[559] C(sp^3)-H bond functionalization,[560] bromoazidation of olefins[561] and photocatalytic ring opening of 1,4-dioxane affording the corresponding iodobenzoyloxy derivative,[562] have been summarized in **Scheme 47.**



Scheme 47 Examples for the synthetic utilization of azidobenziodoxoles

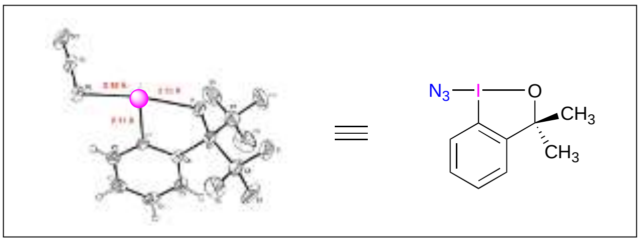
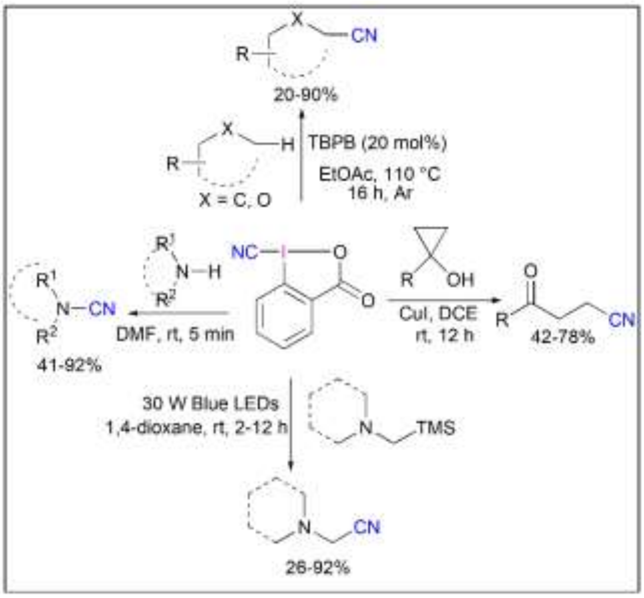


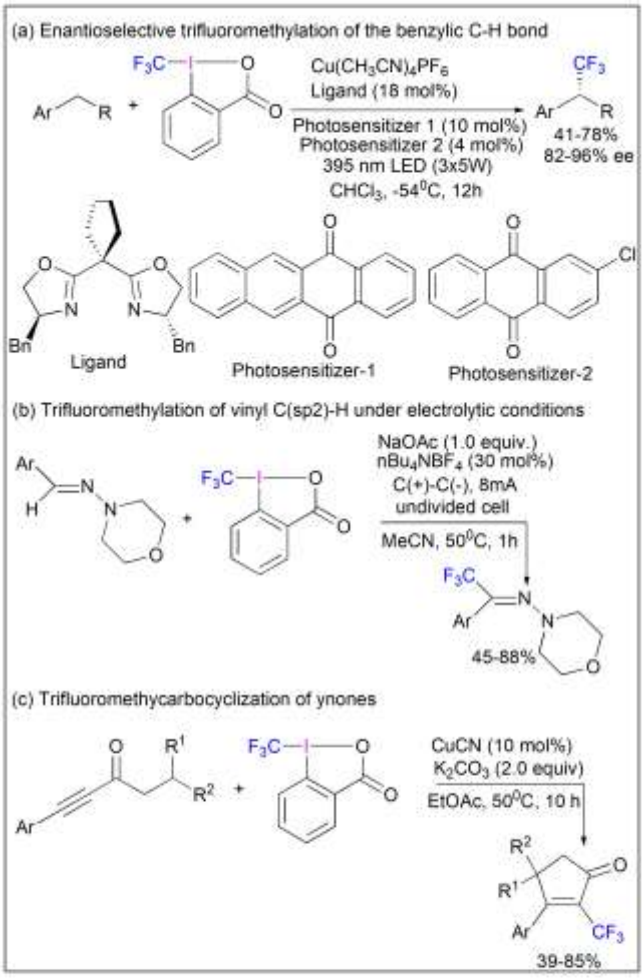
Figure 30 X-ray structure of a stable azidobenziodoxole

In addition to the azidobenziodoxoles, various cyclic cyano-substituted iodanes are known in the literature and have been efficiently used for the transfer of cyano group to the organic substrates.[563-564] Cyclic cyano iodanes were first prepared and investigated more than 25 years ago.[541] Several cyclic cyano iodanes have been synthezied *via* ligand exchange reaction using TMSCN and their structures have been confirmed by X-ray analysis.[542,565-566] Representative recent examples highlighting the use of cyanobenziodoxoles include the following: cyanation of C(sp^3)-H bonds,[567] photo cyanation of tertiary amines,[568] α-cyanation of cyclopropanol,[569] cyanation of primary and secondary amines,[570] etc (**Scheme 48**).



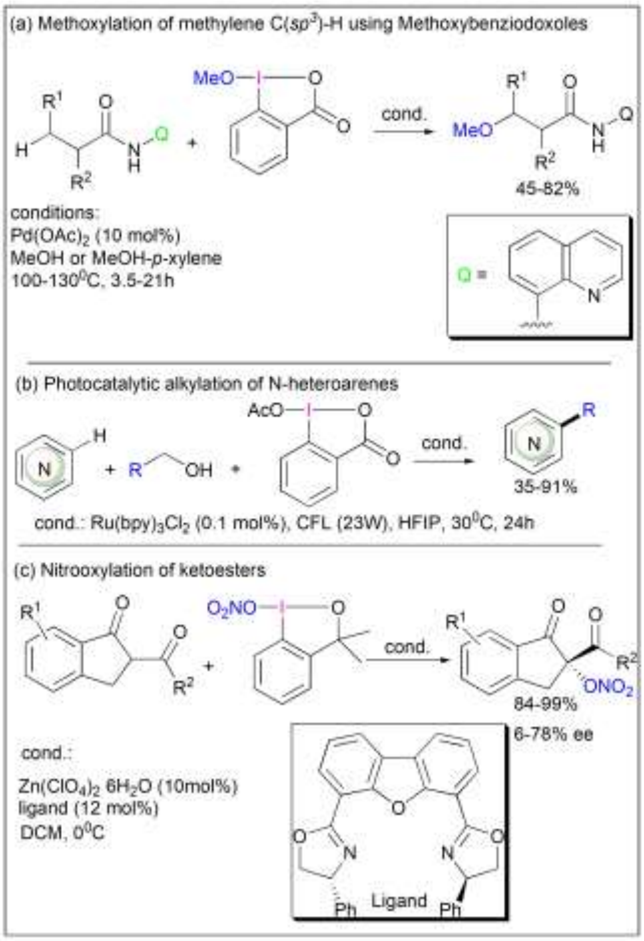
Scheme 48 Examples highlighting the synthetic applications of cyanobenziodoxoles

Benziodoxoles containing trifluoromethyl group (-CF$_3$ group) as a ligand are known as Togni's reagents.[571-574] Trifluoromethylbenziodoxoles can be conveniently prepared from the corresponding acetoxy- or methoxybenziodoxoles by the addition of TMSCF$_3$. These compounds are excellent reagents for selective transfer of -CF$_3$ group to various substrates under metal-free, transition metal-catalyzed, or photocatalyzed conditions. A wide range of cyclic trifluoromethyl-substituted iodanes have been prepared and their structures and reactivity in trifluoromethylation reactions have been reported.[575-581] Cyclic trifluoromethyliodane reagents are comparatively stable and safe to handle as compared to their corresponding acyclic compounds which are, in general, unstable due to the weak C-I bond between the carbon atom of the CF$_3$ group and the hypervalent iodine center. Reactions of these reagents with alkene or alkyne substrates can give the addition of trifluoromethyl groups, as well as trifluoromethylation followed by cyclization.[571-573,582] Other reactions are the insertion of CF$_3$ group into C(sp^3)-H and C(sp^2)-H bonds and trifluoromethylation at heteroatoms.[583-585] Recently reported representative examples include: (i) enantioselective trifluoromethylation of the benzylic C-H bond;[586] (ii) trifluoromethylation of vinyl C(sp^2)-H under electrolytic conditions;[587] (iii) trifluoromethycarbocyclization of ynones[588] as depicted in **Scheme 49**.



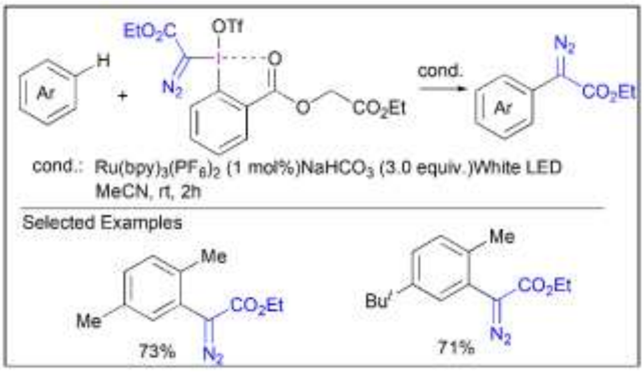
Scheme 49 Synthetic utilization of trifluoromethylbenziodoxoles (Togni's reagents) for diverse trifluoromethylation reactions

Cyclic iodanes bearing alkoxy groups are known for transferring alkoxy groups to appropriate substrates,[589-92] as well as one-electron oxidizing reagents.[593-597] The alkoxybenziodoxoles can be easily accessed by reacting substituted benziodoxoles with alcohols[592,594-595,598] and can be utilized as starting materials for the synthesis of various cyclic hypervalent iodine compounds.[596,599-604] Besides alkoxybenziodoxoles, acyloxybenziodoxoles as well nitrooxybenziodoxoles[605] are also reported in the literature. It is worthwhile to mention here that nitrooxybenziodoxole is shock-insensitive and does not undergo decomposition even stored at room temperature for more than one year.[606] Certain examples of recently reported transformations using these reagents are presented in **Scheme 50**.



Scheme 50 (a) Methoxylation of methylene C (sp^3)-H using methoxybenziodoxoles; (b) Photocatalytic alkylation of N-heteroarenes; (c) Nitroxylation of ketoesters

Further, in the area of cyclic hypervalent iodine compounds, Suero and coworkers developed the cyclic or pseudocyclic hypervalent iodine reagents with diazomethyl groups and reported their structures and reactivity pattern.[607] These compounds are bench stable and substituted diazomethyl radicals can be generated from these compounds under photocatalytic conditions.[334,607] An interesting example of C-H diazomethylation of arenes using pseudocyclic diazomethylbenziodoxole is outlined in **Scheme 51**. In addition to this, significant transfromations utilizing Rh-carbenoid species generated from pseudocyclicdiazomethylbenziodoxoles and dinuclear rhodium complexes have been reported in the literature.[608-610]



Scheme 51 C-H diazomethylation of arenes using pseudocyclic diazomethylbenziodoxole

In recent years, numereous cyclic and pseudocyclic heterocycle-substituted iodanes have been developed; selected examples of these λ^3-iodanes **185-191** have been presented here (**Figure 31**) and related λ^5-iodanes have been discussed in the next section. Recently, Nachtsheim, Postnikov and coworkers presented a systematic investigation on the thermal stability of these iodanes. [611]

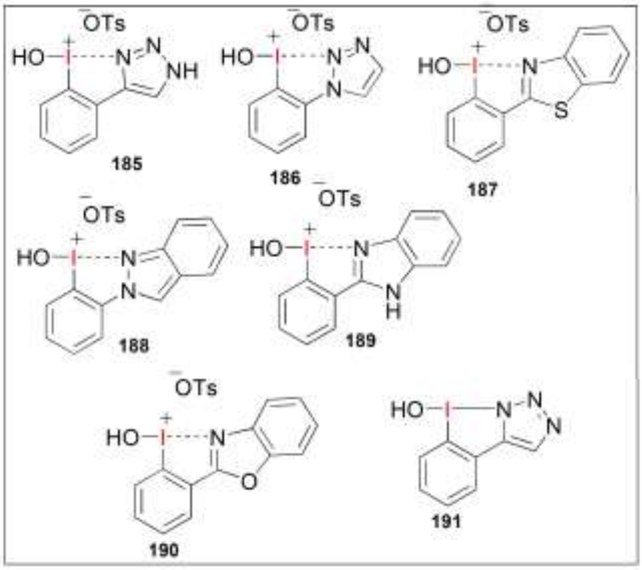


Figure 31 Examples of cyclic and pseudocyclic heterocycle-substituted λ^3-iodanes **185-191**

In addition, various chiral cyclic and pseudocyclic hypervalent iodine(III) derivatives are described in the literature.[349,399-400] These compounds have been reported to play an important role in asymmetric synthesis, and various oxidative transformations have been achieved in excellent yield and enantioselectivitiy using these reagents. Examples of cyclic and pseudocyclic hypervalent λ^3-iodanes **192-205** are given in **Figure 32**.

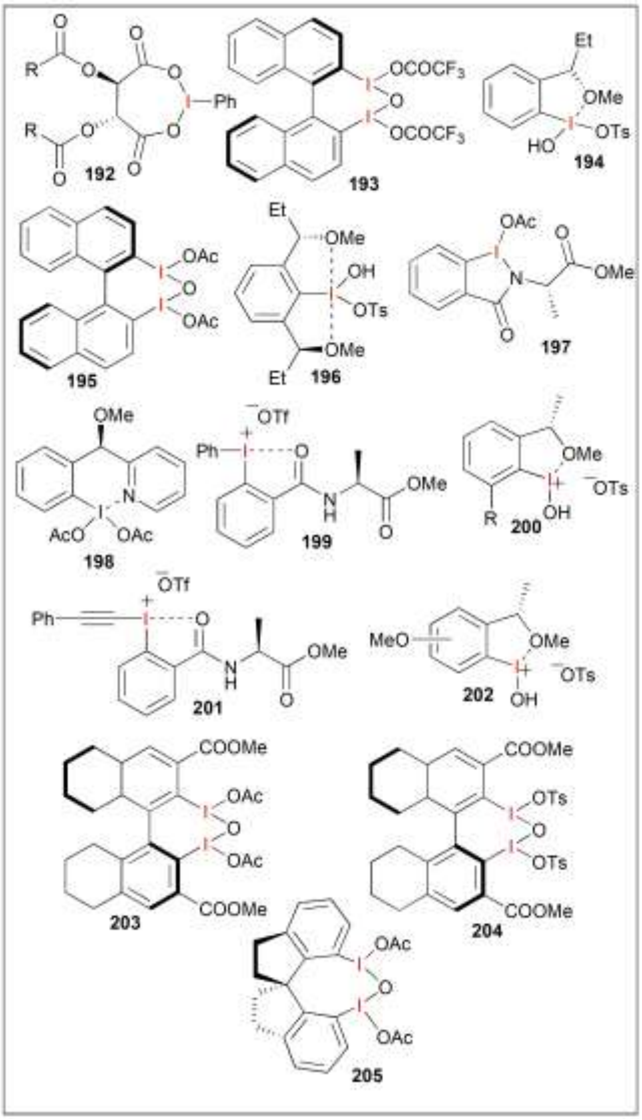


Figure 32 Examples of chiral λ^3-iodanes **192-205**

7.4. Hypervalent Heterocyclic Compounds of Iodine (V)

The chemistry of hypervalent iodine (V) compounds has witnessed remarkable expansion in recent years.[333,612-614] Organoiodine(V) heterocycles are represented by several typical classes **206-222** shown in **Figure 33**. One of the main representatives of these compounds, 2-iodoxybenzoic acid (IBX, **206**), was first synthesized in 1893 by Hartman and Meyer.[615] Later, Mullin and coworkers reported the synthesis of IBX through the oxidation of 2-iodobenzoic acid using potassium bromate under acidic conditions.[616] However, the existence of bromate impurities imparted explosive nature to IBX at elevated temperature; so IBX could not be developed as a potential oxidant, especially for many years until the synthetic method given by Frigerio et al.[617] Since then, IBX have been utilized in a plethora of oxidative transformations, involving oxidation of alcohols, amines, benzylic carbon and, phenols[333,612-614] and oxidative cyclization to diverse heterocyclic rings has been well-documented.[618] A. R. Katritzky and coworkers confirmed the cyclic structure of IBX derivatives by X-ray crystallographic study.[619] Martin and coworkers reported the synthesis, structure, and properties of several cyclic λ^5-iodanes in the 1980s-1990s.[620-623]

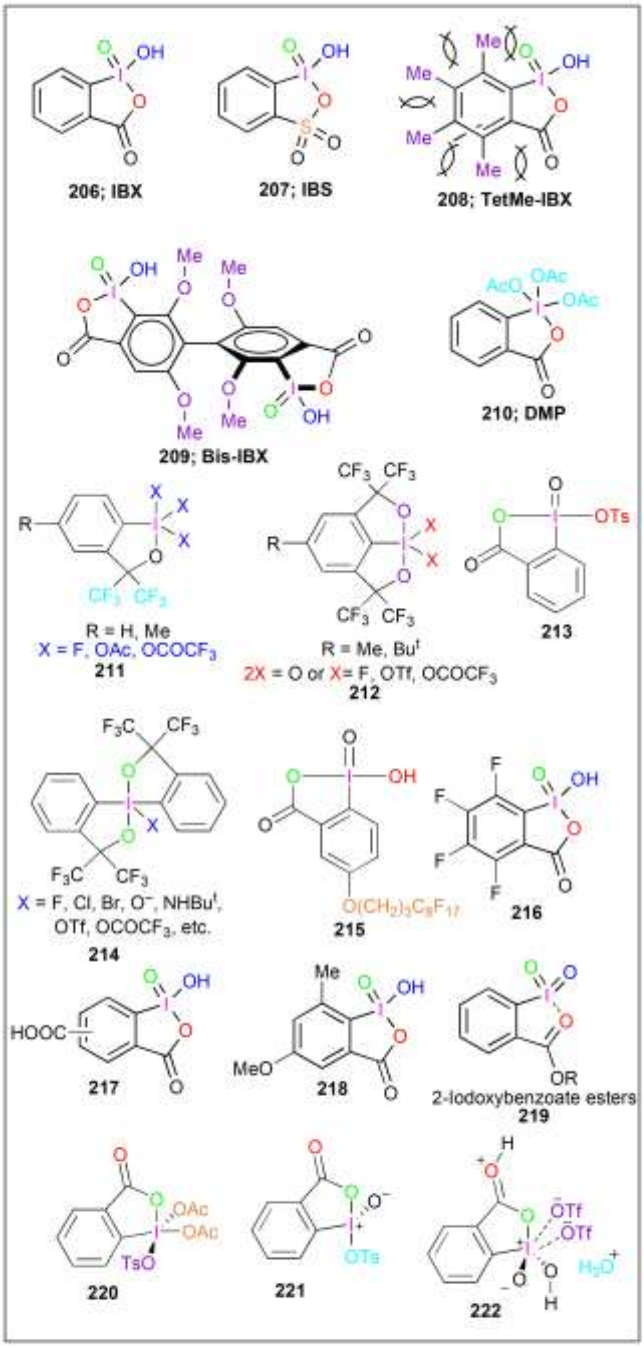


Figure 33 Examples of cyclic hypervalent iodine(V) compounds **206-222**

Iodine(V) heterocycles have found broad practical application as mild and selective reagents for the oxidation of alcohols and some other useful oxidative transformations. Numerous reviews on the chemistry and synthetic applications of IBX (**206**) and related iodine(V) heterocycles have been published previously.[624-626] Recently, synthetic applications of iodine(V)-based oxidants in numerous oxidation reactions have been systematically reviewed.[613-

[614] Further developments in this area include the preparation of safer hypervalent iodine(V) variants with enhanced solubility in common solvents and greater thermal stability. Certain structural analogs of IBX have been synthesized in order to solve the solubility challenges of IBX.[623,627-633] Besides, pseudocyclic iodine(V) compounds, 2-iodoxybenzoate esters (**219**) (**Figure 33**) are also imperative oxidants possessing the intramolecular secondary I----O interactions between the iodine and oxygen atom present in the *ortho*-substituent.[634-635]

Another important λ5-iodane is triacetoxybenziodoxolone, known as Dess-Martin periodinane (DMP) (**210**).[620] DMP was prepared by heating IBX with acetic anhydride and has emerged as the one of the preferred reagents for the oxidation of alcohols to the respective carbonyl compounds. Synthetic applications of DMP as oxidation reagents have been recently reviewed by Kupwade[636] and in the total synthesis by Heravi and coworkers.[637] Moorthy and coworkers reported the synthesis of a highly reactive iodine(V) oxidant, tetramethyl-IBX (TetMe-IBX, **208**). TetMe-IBX is capable of oxidizing alcohols in common organic solvents even at room temperature due to hypervalent 'twisting-promoted' rate enhancement.[640] In another report, Moorthy and coworkers designed and synthesized the twisted 3,3'-diiodo-2,2',6,6'-tetramethoxybiphenyl-4,4'-dicarboxylic acid (**DIDA**) another modified IBX-precatalyst for the *in-situ* generation of Bis-IBX.[641] Bis-IBX, containing perpendicular aromatic planes, presumably undergoes insufficient aggregation that results in good solubility and enhanced reactivity. Bis-IBX oxidizes the primary alcohols to either corresponding carboxylic acid or aldehydes depending upon the solvent system used.

Tosylate derivative of 2-iodoxybenzoic acid (IBX-tosylate, **213**), can be prepared by the reaction of IBX with *p*-toluenesulfonic acid in acetic anhydride.[642] 2-Iodoxybenzenesulfonic acid (IBS, **175**), a thia-analog of IBX and a powerful oxidizing reagent, exists in a cyclic tautomeric form of 1-hydroxy-1*H*-1,2,3-benziodoxothiole 1,3,3-trioxide.[630] Ishihara and coworkers have established that the thia analog is the most powerful catalyst in the iodine(V)-catalyzed oxidation of alcohols using Oxone as a terminal oxidant. Recently, Zhdankin and coworkers reported the preparation and reactivity of the strongest iodine(V) oxidant, 2-iodoxybenzoic acid ditriflate (**222, Figure 33**).[643] Performing X-ray structural studies of compound **222** has been reported to be an extremely challenging task due to its exceptional oxidizing properties. X-ray analysis demonstrated a very complex solid-state assembly formed by primary bonds and various intermolecular secondary interactions.[643] The hypervalent iodine atom in molecule **222** has short primary bonds to carbon and three oxygen atoms and secondary contacts to the oxygen atoms (2.985 Å and 2.820 Å), having significant ionic character (**Figure 34**). The set of four primary and three secondary contacts are indicative of the pseudopentagonal bipyramidal geometry at the hypervalent iodine center. The considerable ionic character of the compound **222** can be a probable reason for the exceptionally high electrophilicity as well as the oxidizing reactivity.

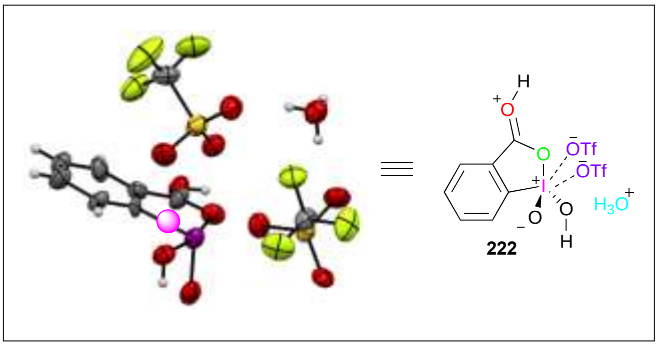


Figure 34 X-ray structure of compound **222**

2-Iodoxybenzoic acid (IBX) and Dess-Martin periodinane (DMP) are examples of frequently used stoichiometric hypervalent iodine(V) reagents, although the recovery of these reagents from the reaction mixture is low yielding. To overcome this, numerous recyclable (polymeric as well as non-polymeric) cyclic hypervalent iodine(V) compounds have also been developed and utilized in diverse organic transformations.[644]

Moreover, Zhdankin and coworkers reported the first chiral cyclic hypervalent λ5-iodanes (**223**).[645] (**Figure 35**) These amino-acid-derived benzioazole oxides (**223**) were prepared by the oxidation of 2-iodobenzamides, obtained from 2-iodobenzoyl chloride with amino acids or their methyl exters, with potassium bromate. Later, the group reported the synthesis of chiral IBX amides (**224**) by the dioxirane oxidation of 2-iodobenzamides[646] and pseudo-benziodoxazines (**225**)[647] (**Figure 35**).

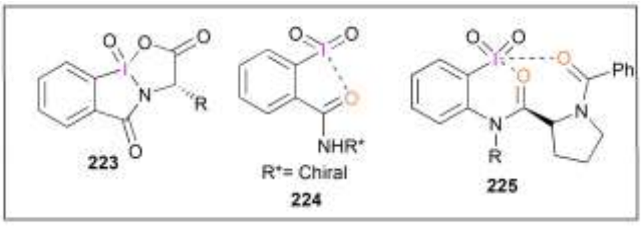


Figure 35 Examples of chiral λ5-iodanes **223-225**

Conclusions

In conclusion, this review demonstrates significant current interest in the chemistry of heterocyclic compounds incorporating an atom of a hypervalent main-group element. Hypervalent heterocycles possess significantly higher thermal stability compared to their acyclic analogs, which adds special features to their chemistry. Increased stability of the cyclic derivatives is especially important for hypervalent bromine and iodine allowing the preparation and broad synthetic application of numerous valuable reagents. In particular, benziodoxole-based hypervalent iodine heterocycles are used as reagents for transferring the substituent on iodine to the organic substrateorasversatile oxidants. We expect that the interest in synthetic applications of hypervalent heterocyclic compounds as versatile reagents for organic synthesis will continue to grow in the future.

Author Contributions

Conflicts of interest

“There are no conflicts to declare”.

Acknowledgements

R.K. gratefully acknowledges the Department of Science and Technology, India for DST-PURSE grant (SR/PURSE/2022/126) and Haryana State Council for Science Innovation and Technology (HSCSIT) DST Haryana for R&D grant (HSCSIT/R&D/163). V.V.Z. is thankful to the National Science Foundation (CHE-2243793) for support of his research program on hypervalent iodine chemistry at University of Minnesota Duluth. T.D. acknowledge support from JSPS KAKENHI grant number 19K05466 (T.D.), JST CREST grant number JPMJCR20R1, and the Ritsumeikan Global Innovation Research Organization (R-GIRO) project. R.K., T.D. and V.V.Z. are grateful to the referees and editors for helpful comments and discussion.

Notes and references

1 J. C. Martin, *Science,* 1983, **221**, 509–514.
2 K. Akiba, *Heteroat. Chem.*, 2011, **22**, 207–274.
3 J. I. Musher, *Angew.Chem. Int. Ed.*, 1969, **8**, 54–68.
4 W. B. Jensen, *J. Chem. Educ.*, 2006, **83**, 1751–1752.
5 K. Y. Akiba, *Chemistry of Hypervalent Compounds*, John Wiley & Sons, 1998.
6 C. A. Ramsden, *Chem. Soc. Rev.*, 1994, **23**, 111–118.
7 C. A. Ramsden, *Arkivoc*, 2014, (**i**), 109–126.
8 S. Sugden, The Parachor and Valency; Knopf: New York, NY, 1930; Chapter 6.
9 G. C. Pimentel, *J. Chem. Phys.*, 1951, **19**, 446–448.
10 R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, 1951, **73**, 4321–4324.
11 M. L. H. Green and G. Parkin, *Dalton Trans.*, 2016, **45**, 18784–18795.
12 A. Grohmann, J. Riede and H. Schmidbaur, *Nature*, 1990, **345**, 140–142.
13 G. A. Olah, A. M. White and D. H. O’Brien, *Chem. Rev.*, 1970, **70**, 561–591.
14 G. A. Olah and G. Rasul, *Acc. Chem. Res.*, 1997, **30**, 245–250.
15 P. v. R. Schleyer, E. U. Wuerthwein, E. Kaufmann, T. Clark and J. A. Pople, *J. Am. Chem. Soc.*, 1983, **105**, 5930–5932.
16 H. Kudo, *Nature*, 1992, **355**, 432–434.
17 P. v. R. Schleyer, B. Tidor, E. D. Jemmis, J. Chandrasekhar, E. U. Wuerthwein, A. J. Kos, B. T. Luke and J. A. Pople, *J. Am. Chem. Soc.*, 1983, **105**, 484–488.
18 Z. Varga, *Struct. Chem.*, 2017, **28**, 297–301
19 W. Zhizhong, Z. Xiange and T. Auchin, *J. Mol. Struct. (Theochem)*, 1998, **453**, 225–231.
20 R. D. Harcourt, *J. Organomet. Chem.*, 1994, **478**, 131–140.
21 B. Braïda, P. C. Hiberty, *Nat. Chem.*, 2013, **5**, 417–422.
22 R. H. Crabtree, *Chem. Soc. Rev.*, 2017, **46**, 1720–1729.
23 A. S. Ivanov, I. A. Popov, A. I. Boldyrev and V. V. Zhdankin, *Angew.Chem. Int. Ed.*, 2014, **53**, 9617–9621.
24 E. F. Perozzi, R. S. Michalak, G. D. Figuly, W.H. Stevenson III, D. B. Dess, M. R. Ross and J. C. Martin, *J. Org. Chem.*, 1979, **44**, 1779 and references cited therein.
25 G. F. Koser, The Chemistry of Functional Groups, Suppl. D, (Eds.) S. Patai and Z. Rappoport, (Wiley-Interscience, Chichester) **1983**, Chap. 18, pp. 721-811.
26 M. Ochiai, Y. Masaki and M. Shiro, *J. Org. Chem*. 1991, **56**, 5511
27 V. V. Zhdankin, *Adv. Heterocycl. Chem.*, 2016, **119**, 57–79.
28 C. W. Perkins, J. C. Martin, A. J. Arduengo, W. Lau, A. Alegria and J. K. Kochi, *J. Am. Chem. Soc.*, 1980, **102**, 7753–7759.
29 E. E. Coyle and C. J. O’Brien, *Nat. Chem.*, 2012, **4**, 779–780.
30 M. Driess, N. Muresan, K. Merz and M. Päch, *Angew.Chem. Int. Ed.*, 2005, **44**, 6734–6737.
31 S. A. Culley and A. J. Arduengo, *J. Am. Chem. Soc.*, 1984, **106**, 1164–1165.
32 A. J. Arduengo, C. A. Stewart, F. Davidson, D. A. Dixon, J. Y. Becker, S. A. Culley and M. B. Mizen, *J. Am. Chem. Soc.*, 1987, **109**, 627–647.
33 A. J. Arduengo and C. A. Stewart, *Chem. Rev.*, 1994, **94**, 1215–1237.
34 N. L. Dunn, M. Ha and A. T. Radosevich, *J. Am. Chem. Soc.*, 2012, **134**, 11330–11333.
35 T. P. Robinson, D. M. DeRosa, S. Aldridge and J. M. Goicoechea, *Angew.Chem. Int. Ed.*, 2015, **54**, 13758–13763.
36 W. Zhao, S. M. McCarthy, T. Y. Lai, H. P. Yennawar and A. T. Radosevich, *J. Am. Chem. Soc.*, 2014, **136**, 17634–17644.
37 H. Kameo and H. Nakazawa, *Chem. Rec.*, 2017, **17**, 268–286.
38 J. M. Bayne and D. W. Stephan, *Chem. Soc. Rev.*, 2016, **45**, 765–774.
39 D. W. Stephan, *Angew.Chem. Int. Ed.*, 2017, **56**, 5984–5992.
40 D. You and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2017, **139**, 6843–6846.
41 N. Tan, Y. Chen, S. Yin, R. Qiu, Y. Zhou and C. T. Au, *Curr. Org. Chem.*, 2012, **16**, 2462–2481.
42 J. S. Jones, C. R. Wade, M. Yang and F. P. Gabbaï, *Dalton Trans.*, 2017, **46**, 5598–5604.
43 J. S. Jones and F. P. Gabbai, *Chem. Eur. J.*, 2017, **23**, 1136–1144.
44 J. S. Jones and F. P. Gabbaï, *Acc. Chem. Res.*, 2016, **49**, 857–867.
45 W. H. Powell, *Pure Appl. Chem.*, 1984, **56**, 769–778.
46 A. E. Reed and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1990, **112**, 1434–1445.
47 J. A. Dobado, H. Martínez-García, Molina and M. R. Sundberg, *J. Am. Chem. Soc.*, 1998, **120**, 8461–8471.
48 R. Gillespie, *Coord. Chem. Rev.*, 2002, **233–234**, 53–62.
49 X. Sun, *Chem. Educator*, 2002, **7**, 261–264.
50 S. Noury, B. Silvi and R. J. Gillespie, *Inorg. Chem.*, 2002, **41**,2164–2172.
51 S. C. A. H. Pierrefixe, C. F. Guerra and F. M. Bickelhaupt, *Chem. Eur. J.*, 2008, **14**, 819–828.
52 P. G. Nelson, *Chem. Educ. Res. Pract.*, 2001, **2**, 67–72.
53 A. Kalemos, *J. Phys. Chem. A*, 2018, **122**, 2178–2183.
54 M. C. Durrant, *Chem. Sci.*, 2015, **6**, 6614–6623.

55 R. D. Harcourt and T. M. Klapötke, *Chem. Sci.*, 2016, **7**, 3443–3447.

56 M. C. Durrant, *Chem. Sci.*, 2016, **7**, 3448–3449.

57 S. C. A. H. Pierrefixe, S. J. M. v. Stralen, J. N. P. v. Stralen, C. F. Guerra and F. M. Bickelhaupt, *Angew.Chem. Int. Ed.*, 2009, **48**, 6469–6471.

58 V. P. Oliveira, E. Kraka and F. B. C. Machado, *Inorg. Chem.*, 2019, **58**, 14777-14789

59 T. R. Forbus and J. C. Martin, *J. Am. Chem. Soc.*, 1979, **101**, 5057–5059.

60 D. Y. Lee and J. C. Martin, *J. Am. Chem. Soc.*,1984, **106**, 5745–5746.

61 T. R. Forbus and J. C. Martin, *Heteroat. Chem*, 1993, **4**, 129–136.

62 M.Hojo, T. Ichi and K. Shibato, *J Org Chem*, 1985, **50**, 1478–1482.

63 H. W. Roesky, M. G. Walawalkar and R. Murugavel, *Acc. Chem. Res.*, 2001, **34**, 201–211.

64 W. Neugebauer, A. J. Kos and P. v. R. Schleyer, *J.Organomet. Chem.*, 1982, **228**, 107–118.

65 M. Yamashita, Y. Yamamoto, K. Y. Akiba and S. Nagase, *Angew. Chem. Intl. Ed.*, 2000, **39**, 4055–4058.

66 M. Yamashita, Y. Yamamoto, K. Akiba, D. Hashizume, F. Iwasaki, N. Takagi and S. Nagase, *J. Am. Chem. Soc.*, 2005, **127**, 4354–4371.

67 T. Yano, T. Yamaguchi and Y. Yamamoto, *Chem. Lett.*, 2009, **38**, 794–795.

68 J.-Y. Nakatsuji, Y. Moriyama, S. Matsukawa, Y. Yamamoto and K.-Y. Akiba, *Main Group Chem.*, 2006, **5**, 277–285.

69 Y. Hirano, S. Kojima and Y. Yamamoto, *J. Org. Chem.*, 2011, **76**, 2123–2131.

70 G. P. McGovern, D. Zhu, A. J. A. Aquino, D. Vidović and M. Findlater, *Inorg. Chem.*, 2013, **52**, 13865–13868.

71 C. Dou, S. Saito and S. Yamaguchi, *J. Am. Chem. Soc.*, 2013, **135**, 9346-9349

72 V. Ya. Lee, H. Sugasawa, O. A. Gapurenko, R. M. Minyaev, V. I. Minkin, H. Gornitzka and A. Sekiguchi, *J. Am. Chem. Soc.*,2018, **140**, 6053–6056.

73 T. W. Myers and L. A. Berben, *Organometallics*, 2013, **32**, 6647–6649.

74 I.-C. Chen, S.-M. Ho, Y.-C. Chen, C.-Y. Lin, C.-H. Hu, C.-Y. Tu, A. Datta, J.-H. Huang and C.-H. Lin, *Dalton Trans.*, 2009, 8631.

75 A. Khan and D. Foucher, *Coord. Chem. Rev.*, 2016, **312**, 41–66.

76 M. J. Janseen, J. G. A. Lujiten and G. J. M. v.Kerk, *J. Organomet. Chem.*, 1964, 286–291.

77 I. R. Beattie and T. Gilson, *J. Chem. Soc.*, 1961, 2585–2586

78 R. Hulme, *J. Chem. Soc.*, 1963, 1524–1527.

79 T. R. Forbus Jr, *Hypervalent Trigonal Bipyramidal Carbon*, University of Illinois at Urbana-Champaign, 1981.

80 T. R. Forbus and J. C. Martin, *Heteroat. Chem.*, 1993, **4**, 113–128.

81 T. R. Forbus, J. L. Kahl, L. R. Faulkner and J. C. Martin, *Heteroat. Chem.*, 1993, **4**, 137–143.

82 K.-Y. Akiba, M. Yamashita, Y. Yamamoto and S. Nagase, *J. Am. Chem. Soc.*, 1999, **121**, 10644–10645.

83 M. Yamashita, Y. Mita, Y. Yamamoto and K.-Y. Akiba, *Chem. Eur. J*, 2003, **9**, 3655–3659.

84 K.-Y. Akiba, Y. Moriyama, M. Mizozoe, H. Inohara, T. Nishii, Y. Yamamoto, M. Minoura, D. Hashizume, F. Iwasaki, N. Takagi, K. Ishimura and S. Nagase, *J. Am. Chem. Soc.*, 2005, **127**, 5893–5901.

85 Y. Yamamoto and K.-Y. Akiba, *J. Synth. Org. Chem.,*2004, **62**, 1128–1137.

86 T. Yamaguchi, Y. Yamamoto, D. Kinoshita, K.-Y. Akiba, Y. Zhang, C. A. Reed, D. Hashizume and F. Iwasaki, *J. Am. Chem. Soc.*, 2008, **130**, 6894–6895.

87 T. Yamaguchi and Y. Yamamoto, *Pure Appl. Chem*, 2013, **85**, 671–682.

88 Y. Yamamoto, Y. Shi, T. Masui, D. Saito, T. Inoue, H. Sato, C. Dohi, E. Muneta, R. Shang and M. Nakamoto, *Eur. J. Chem.*, 2023, **29**, e202203162.

89 E. F. Perozzi and J. C. Martin, *J. Am. Chem. Soc.*, 1979, **101**, 1591–1593.

90 E. F. Perozzi, R. S. Michalak, G. D. Figuly, W. H. Stevenson, D. Dess, M. R. Ross and J. C. Martin, *J. Org. Chem.*, 1981, **46**, 1049–1053.

91 E. L. Muetterties and R. A. Schunn, *Q. Rev. Chem. Soc.*, 1966, **20**, 245.

92 R. Hoffmann, J. M. Howell and E. L. Muetterties, *J. Am. Chem. Soc.*, 1972, **94**, 3047–3058.

93 J. C. Martin and E. F. Perozzi, *J. Am. Chem. Soc.*, 1974, **96**, 3155–3168.

94 R. M. Beesley, C. K. Ingold and J. F. Thorpe, *J. Chem. Soc., Trans.*, 1915, **107**, 1080–1106.

95 C. K. Ingold, *ibid*, 1921, **119**, 305–329.

96 M. E. Jung, G. Pizzi, *Chem. Rev.*, 2005, **105**, 1735–1766

97 H. Lenormand, V. Corcé, G. Sorin, C. Chhun, L.-M. Chamoreau, L. Krim, E.-L. Zins, J.-P. Goddard and L. Fensterbank, *J. Org. Chem.*, 2015, **80**, 3280–3288.

98 S. E. Denmark and S. K. Ghosh, *Angew.Chem. Int. Ed.*, 2001, **40**, 4759–4762.

99 J. Chen, B. Captain and N. Takenaka, *Org. Lett.*, 2011, **13**, 1654–1657.

100 H. Ikeda and S. Inagaki, *J. Phys. Chem. A*, 2001, **105**, 10711–10718.

101 M. G. Voronkov, V. V. Belyaeva and K. A. Abzaeva *Chem. Heterocycl. Comp.* 2012, **47**, 1330-1338 and references therein

102 J. K. Puri, R. Singh and V. K. Chahal, *Chem. Soc. Rev*. 2011, **40**, 1791-1840

103 J. K. Verkade, *Coord. Chem. Rev* 1994, **137**, 233-295

104 C. Chuit, R. J. P. Corriu, C. Reye and J. C. Young, *Chem. Rev.*, 1993, **93**, 1371-1448

105 M. G. Voronkov, O. M. Trofimova, Y. I. Bolgova and N. F. Chernov. *Chem. Rev.* 2007, **76**, 825

106 M. G. Voronkov, V. M. Dyakov and S. V. Kirpichenko, *J. Organomet. Chem.*, 1982, **233**, 1-147

107 J. E. Boggs, C. Peng, V. A. Pestunovich and V. F. Sidorkin, *J. Mol. Struct.* 1995, **357**, 67-73

108 V. F. Sidorkin, V. A. Pestunovich and M.G. Voronkov, Dokl. Akad. Nauk SSSR **1977**, *235*, 1363–1366

109 M. G. Voronkov, O. M. Trofimova, Y. I. Bolgova and N. F. Chernov, *Russ. Chem. Rev.*, 2007, **76**, 825-845.

110 G. J. Csonka and P. Hencsei, *J. Comput. Chem.,* 1994, **15**, 385-394

111 S. Patai and Z. Rappoport, *The Chemistry of Organic Germanium, Tin, and Lead Compounds*, Wiley, 2002, **vol. 2**.

112 D. Barreca, F. Benetollo, S. Garon, E. Tondello and P. Zanella, *Acta Crystallogr.C,* 2000, **56**, e290–e291.

113 H. Reuter and D. Schröder, *J. Organomet. Chem.*, 1993, **455**, 83–87.

114 Y. Yamamoto, A. Sakaguchi, N. Ohashi and K.-Y. Akiba, *J. Organomet. Chem.*, 1996, **506**, 259–263.

115 S. W. Ng, V. G. K. Das, G. Yap and A. L. Rheingold, *Acta Crystallogr. C*, 1996, **52**, 1369–1371.

116 Z. H. Chohan, P. J. Cox and J. L. Wardell, *J. Chem. Crystallogr.*, 1997, **27**, 137–140.

117 J. F. Vollano, R. O. Day and R. R. Holmes, *Organometallics*, 1984, **3**, 750–755.

118 V. Chandrasekhar, A. Chandrasekaran, R. O. Day, J. M. Holmes and R. R. Holmes, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 1996, **115**, 125–139.

119 H. C. Chiang, S. F. Hwang and C. H. Ueng, *Acta Crystallogr. C*, 1995, **51**, 1258–1260.

120 K. Jurkschat, F. Hesselbarth, M. Dargatz, J. Lehmann, E. Kleinpeter, A. Tzschach and J. Meunier-Piret, *J. Organomet. Chem.*, 1990, **388**, 259–271.

121 T. K. Gar, N. A. Viktorov and V. F. Mironov, *Zh. Obshch. Khim.*, 1982, **52**, 1593–1599.

122 A. A. Macharashvili, Yu. I. Baukov, E. P. Kramarova, G. I. Oleneva, V. A. Pestunovich, Yu. T. Struchkov and V. E. Shklover, *Zh. Strukt. Khim.*, 1987, **28**, 114–119.

123 T. K. Gar, N. A. Viktorov, V. F. Mironov, S. N. Gurkova, A. I. Gusev, D. A. Ivashchenko, V. S. Nikitin, N. V. Alekseev and V. P. Feshin, Zh. Obshch. Khim., 1982, 52, 1593.

124 A. Jain, S. Saxena and A. K. Rai, *Main Group Metal Chemistry*, *Main Group Met. Chem.*, 1999, **22**, 553–555.

125 J. T. B. H. Jastrzebski, E. Wehman, J. Boersma, G. v. Koten, K. Goubitz and D. Heijdenrijk, *J. Organomet. Chem.*, 1991, **409**, 157–162.

126 D. Dakternieks, K. Dunn, C. H. Schiesser and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.*, 2000, 3693–3698.

127 K. M. Lo, S. Selvaratnam, S. W. Ng, C. Wei and V. G. K. Das, *J. Organomet. Chem.*, 1992, **430**, 149–166.

128 J. T. B. H. Jastrzebski, P. A. Van der Schaaf, J. Boersma, G. Van Koten, M. C. Zoutberg and D. Heijdenrijk, *Organometallics*, 1989, **8**, 1373–1375.

129 G. van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, A. L. Spek and J. C. Schoone, *J. Organomet. Chem.*, 1978, **148**, 233–245.

130 V. A. Benin, J. C. Martin and M. R. Willcott, *Tetrahedron*, 1997, **53**, 10133–10154.

131 S. W. Ng, V. G. K. Das, M. Gielen and E. R. T. Tiekink, *Appl.Organomet. Chem.*, 1992, **6**, 19–25.

132 S. A. Artamkin, V. N. Sergeev, Y. I. Baukov, A. O. Mozzhukin, M. Y. Antipin and Y. T. Struchkov, *Organomet. Chem. USSR (Engl. Transl.)*, 1991, **4**, 1238.

133 R. H. P. Francisco, M. T. d. P. Gambardella, G. F. d. Sousa and A. Abras, *Acta Crystallogr. C*, 2000, **56**, 187–189.

134 M. Carcelli, D. Delledonne, A. Fochi, G. Pelizzi, M. C. R.-Argüelles and U. Russo, *J. Organomet. Chem.*, 1997, **544**, 29–35.

135 C. Pettinari, M. Pellei, A. Cingolani, D. Martini, A. Drozdov, S. Troyanov, W. Panzeri and A. Mele, *Inorg. Chem.*, 1999, **38**, 5777–5787.

136 E. K. Lermontova, M. Huan, A. V. Churakov, J. A. K. Howard, M. V. Zabalov, S. S. Karlov and G. S. Zaitseva, *Dalton Trans.*, 2009, 4695–4702.

137 M. Saito, S. Imaizumi, T. Tajima, K. Ishimura and S. Nagase, *J. Am. Chem. Soc.*, 2007, **129**, 10974–10975.

138 R. R. Maar, S. D. Catingan, V. N. Staroverov and J. B. Gilroy, *Angew.Chem. Int. Ed.*, 2018, **57**, 9870–9874.

139 K. Tanimura, M. Gon and K. Tanaka, *Inorg. Chem.*, 2023, **62**, 4590–4597.

140 S. L. Benjamin and G. Reid, *Coord. Chem. Rev.*, 2015, **297–298**, 168–180.

141 A. Gagnon, J. Dansereau and A. L.Roch, *Synthesis*, 2017, **49**, 1707–1745.

142 H. Staudinger and J. Meyer, *Helv.Chim. Acta*, 1919, **2**, 608–611.

143 H. Staudinger and J. Meyer, *Helv.Chim. Acta*, 1919, **2**, 619–635.

144 W. Schlenk and J. Holtz, *Ber. Dtsch. Chem. Ges.*, 1916, **49**, 603–608.

145 W. Schlenk and J. Holtz, *Ber. Dtsch. Chem. Ges.*, 1917, **50**, 274–275.

146 D. Hellwinkel and H. Seifert, *Justus Liebigs Ann. Chem.*, 1972, **762**, 29–54.

147 G. Wittig and M.-H. Wetterling, *Justus Liebigs Ann. Chem*., 1947, **557**, 193–201.

148 K. O. Christe, W. W. Wilson, G. J. Schrobilgen, R. V. Chirakal and G. A. Olah, *Inorg. Chem.*, 1988, **27**, 789–790.

149 R. W. Johnson and E. R. Holm, *J. Am. Chem. Soc.*, 1977, **99**, 8077–8078.

150 G. A. Olah, D. J. Donovan, J. Shen and G. Klopman, *J. Am. Chem. Soc.*, 1975, **97**, 3559–3561.

151 H. F. Bettinger, P. v. R. Schleyer and H. F. Schaefer, *J. Am. Chem. Soc.*, 1998, **120**, 11439–11448.

152 C. S. Ewig and J. R. Van Wazer, *J. Am. Chem. Soc.*, 1990, **112**, 109–114.

153 C. S. Ewig and J. R. Van Wazer, *J. Am. Chem. Soc.*, 1989, **111**, 4172–4178.

154 H. H. Michels and J. A. Montgomery, *J. Chem. Phys.*, 1990, **93**, 1805–1813.

155 I. V. Getmanskii and R. M. Minyaev, *J. Struct. Chem.*, 2008, **49**, 973–978.

156 D. Kurzydłowski and P. Z.-Ejgierd, *Sci. Rep.*, 2016, **6**, 36049.

157 A. R. Miller, R. R. Tsukimura and R. Velten, *Science*, 1967, **155**, 688–688.

158 I. J. Solomon, J. N. Keith. And A. Snelson, *J. Fluor. Chem.*, 1972, **2**, 129–136.

159 A. Hasegawa, R. L. Hudson, O. Kikuchi, K. Nishikida and F. Williams, *J. Am. Chem. Soc.*, 1981, **103**, 3436–3440.

160 K. Nishikida and F. Williams, *J. Am. Chem. Soc.*, 1975, **97**, 7166–7168.

161 S. A. Shaffer, M. Sadílek and F. Tureček, *J. Org. Chem.*, 1996, **61**, 5234–5245.

162 K. Fuke and R. Takasu, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 3309–3318.

163 V. Q. Nguyen, M. Sadilek, J. Ferrier, A. J. Frank and F. Tureček, *J. Phys. Chem. A*, 1997, **101**, 3789–3799.

164 R. W. Alder, A. G. Orpen and J. M. White, *J. Chem. Soc. Chem. Commun.*, 1985, 949–951.

165 F. Gerson, G. Gescheidt, U. Buser, E. Vogel, J. Lex, M. Zehnder and A. Riesen, *Angew.Chem. Int. Ed.*, 1989, **28**, 902–904.

166 F. Gerson, J. Knoebel, U.Buser, E. Vogel and M. Zehnder, *J. Am. Chem. Soc.*, 1986, **108**, 3781–3783.

167 C. Yan, M. Takeshita, J. Nakatsuji, A. Kurosaki, K. Sato, R. Shang, M. Nakamoto, Y. Yamamoto, Y. Adachi, K. Furukawa, R. Kishi and M. Nakano, *Chem. Sci.*, 2020, **11**, 5082–5088.

168 D. Schomburg, W. Strozer, R. Bohlen, W. Kuhn and G. Röschenthaler, *Chem. Ber.*, 1983, **116**, 3301–3308.

169 D. Hellwinkel, *Chem. Ber.*, 1966, **99**, 3642–3659.

170 D. Hellwinkel, *Chem. Ber.*, 1965, **98**, 576–587.

171 P. B. Kisanga and J. G. Verkade, *Tetrahedron*, 2001, **57**, 467–475.

172 A. N. Kornev, V. V. Sushev, Y. S. Panova, N. V. Zolotareva, E. V. Baranov, G. K. Fukin and G. A. Abakumov, *Eur. J. Inorg. Chem.*, 2015, 2057–2066.

173 X.-D. Jiang, S. Matsukawa, K. Kakuda, Y. Fukuzaki, W.-L. Zhao, L.-S. Li, H.-B. Shen, S. Kojima and Y. Yamamoto, *Dalton Trans.*, 2010, **39**, 9823–9829.

174 X.-D. Jiang, S. Matsukawa, S. Kojima and Y. Yamamoto, *Inorg. Chem.*, 2012, **51**, 10996–11006.

175 X.-D. Jiang, S. Matsukawa, H. Yamamichi and Y. Yamamoto, *Inorg. Chem.*, 2007, **46**, 5480–5482.

176 X.-D. Jiang, K.-i. Kakuda, S. Matsukawa, H. Yamamichi, S. Kojima and Y. Yamamoto, *Chem.-Asian J.*, 2007, **2**, 314–323.

177 X.-D. Jiang, Y. Toya, S. Matsukawa, S. Kojima, J. O. C. J.-Halla, R. Shang, M. Nakamoto and Y. Yamamoto, *Chem. Sci.*, 2019, **10**, 3466–3472.

178 V. D. Romanenko, J.-M. Sotiropoulos, *Comprehensive Hetero. Chem.*, 2022, 14, 877–895.

179 L. Engman, *Acc. Chem. Res.*, 1985, **18**, 274–279.

180 G. Zeni, D. S. Lüdtke, R. B. Panatieri and A. L. Braga, *Chem. Rev.*, 2006, **106**, 1032–1076.

181 F. V. Singh and T. Wirth, *Org. Lett.*, 2011, **13**, 6504–6507.

182 S. Saba, J. Rafique and A. L. Braga, *Adv Synth Catal*, 2015, **357**, 1446–1452.

183 F. V. Singh and T. Wirth, *Phy. Sci. Rev.*, 2019, **4**, 20170131

184 X. Xiong, F. Tan and Y.-Y. Yeung, *Org. Lett.*, 2017, **19**, 4243–4246.

185 F. Shibahara, T. Fukunaga, S. Kubota, A. Yoshida and T. Murai, *Org. Lett.*, 2018, **20**, 5826–5830.

186 T. Prochnow, A. Maroneze, D. F. Back and G. Zeni, *J. Org. Chem.*, 2019, **84**, 2891–2900.

187 Q. Jiang, Y. Liang, Y. Zhang and X. Zhao, *Org. Lett.*, 2020, **22**, 7581–7587.

188 T. A. C. Goulart, D. F. Back, S. Moura E. Silva and G. Zeni, *J. Org. Chem.*, 2022, **87**, 3341–3351.

189 M. Jiang, J. Guo, B. Liu, Q. Tan and B. Xu, *Org. Lett.*, 2019, **21**, 8328–8333.

190 C. W. Nogueira, G. Zeni and J. B. T. Rocha, *Chem. Rev.*, 2004, **104**, 6255–6286.

191 C. H. Schiesser, *Chem.Commun.*, 2006, 4055–4065.

192 T. Wirth, *Angew.Chem. Int. Ed.*, 2015, **54**, 10074–10076.

193 K. Arai, T. Takei, M. Okumura, S. Watanabe, Y. Amagai, Y. Asahina, L. Moroder, H. Hojo, K. Inaba and M. Iwaoka, *Angew.Chem. Int. Ed.*, 2017, **56**, 5522–5526.

194 E. L. Borges, M. T. Ignasiak, Y. Velichenko, G. Perin, C. A. Hutton, M. J. Davies and C. H. Schiesser, *Chem. Commun.*, 2018, **54**, 2990–2993.

195 K. Arai, Y. Sato, I. Nakajima, M. Saito, M. Sasaki, A. Kanamori and M. Iwaoka, *Bioorg. Med. Chem.*, 2021, **29**, 115866.

196 P. H. W. Lau and J. C. Martin, *J. Am. Chem. Soc.*, 1978, **100**, 7077–7079.

197 W. Y. Lam, E. N. Duesler and J. C. Martin, *J. Am. Chem. Soc.*, 1981, **103**, 127–135.

198 S. Ogawa, Y. Matsunaga, S. Sato, I. Iida and N. Furukawa, *J. Chem. Soc. Chem. Commun.*, 1992, 1141–1142.

199 P. H. W. Lau and J. C. Martin, *J. Am. Chem. Soc.*, 1977, **99**, 5490–5491.

200 C. W. Perkins and J. C. Martin, *J. Am. Chem. Soc.*, 1983, **105**, 1377–1379.

201 R. S. Michalak and J. C. Martin, *J. Am. Chem. Soc.*, 1982, **104**, 1683–1692.

202 T. Kawashima, *Phosphorus Sulfur Silicon Relat. Elem.*, 2011, **186**, 1046–1054.

203 Y. Imada, H. Nakano, K. Furukawa, R. Kishi, M. Nakano, H. Maruyama, M. Nakamoto, A. Sekiguchi, M. Ogawa, T. Ohta and Y. Yamamoto, *J. Am. Chem. Soc.*,2016, **138**, 479–482.

204 S. Bezzi, M. Mammi and C. Garbuglio, *Nature*, 1958, **182**, 247–248.

205 N. Matsumura, R. Hirase, S. Kamitani, Y. Okumura and K. Mizuno, *J. Heterocycl. Chem.*, 2005, **42**, 1175–1180.

206 N. Matsumura, T. Konishi, H. Hayashi, K. Mizuno, M. Yasui and F. Iwasaki, *J. Heterocycl. Chem.*, 2002, **39**, 189–202.

207 R. Gleiter and R. Gygax, *in Bonding Structure*, Springer-Verlag, Berlin/Heidelberg, 1976, vol. **63**, pp. 49–88.

208 K. B. Andersen, J. Abildgaard, J. G. Radziszewski and J. S.-Larsen, *J. Phys. Chem. A*, 1997, **101**, 4475–4480.

209 J. Fabian, K. Gloe, M. Wüst, T. K.-rambusch, O. Rademacher and H. Graubaum, *PhosphorusSulfur Silicon Relat. Elem.*, 1998, **140**, 35–52.

210 W. D. Ollis, S. P. Stanforth and C. A. Ramsden, *Tetrahedron*, 1985, **41**, 2239–2329.

211 A. R. Katritzky, C. A. Ramsden, J. A. Joule and V. V. Zhdankin, *Handbook of Heterocyclic Chemistry: Edition 3*, Elsevier, 2010.

212 H. J. Shine and D. R. Thompson, *Tetrahedron Lett.*, 1966, **7**, 1591–1597.

213 Y. Murata and H. J. Shine, *J. Org. Chem.*, 1969, **34**, 3368–3372.

214 H. J. Shine and Y. Murata, *J. Am. Chem. Soc.*, 1969, **91**, 1872–1874.

215 J. J. Silber and H. J. Shine, *J. Org. Chem*., 1971, **36**, 2923–2926.

216 H. J. Shine and L. Piette, *J. Am. Chem. Soc*., 1962, **84**, 4798–4806.

217 K. Kim, V. J. Hull and H. J. Shine, *J. Org. Chem*., 1974, **39**, 2534–2537.

218 H. J. Shine, P. Rangappa, J. N. Maxr, D. C. Shelly, T. Ould-Ely and K. H. Whitmire, *J. Org. Chem*., 2005, **70**, 3877–3883.

219 P. Rangappa, H. J. Shine, J. N. Maxr, T. Ould-Ely, A. T. Kelly and K. H. Whitmire, *J. Org. Chem*., 2005, **70**, 9764–9770.

220 B.-J. Zhao, D. H. Evans, N. A. Mac´ıas-Ruvalcaba and H. J. Shine, *J. Org. Chem*., 2006, **71**, 3737–3742.

221 B.-J. Zhao, H. J. Shine, J. N. Marx, C. Hofmann and K. H. Whitmire, *J. Org. Chem*., 2007, **72**, 6154–6161.

222 X.-Y. Chen, Y. Wu and P. Wang, *Synthesis*, 2022, **54**, 3928–3940.

223 P. S. Engl, A. P. H¨aring, F. Berger, G. Berger, A. P´erez-Bitri´an and T. Ritter, *J. Am. Chem. Soc*., 2019, **141**, 13346–13351.

224 F. Juli´a, Q. Shao, M. Duan, M. B. Plutschack, F. Berger, J. Mateos, C. Lu, X.-S. Xue, K. N. Houk and T. Ritter, *J. Am. Chem. Soc.*, 2021, **143**, 16041–16054.

225 H. J. Shine, B.-J. Zhao, J. N. Marx, T. Ould-Ely and K. H. Whitmire, *J. Org. Chem*., 2004, **69**, 9255–9261.

226 J. Chen, J. Li, M. B. Plutschack, F. Berger and T. Ritter, *Angew. Chem. Int. Ed.,* 2020, **59**, 5616–5620

227 H. Meng, M.-S. Liu and W. Shu, *Chem Sci*, 2022, **13**, 13690-13707

228 A. Fava, P. B. Sogo and M. Calvin, *J. Am. Chem. Soc*., 1957, **79**, 1078–1083.

229 E. A. C. Lucken, *J. Chem. Soc*., 1962, 4963–4965.

230 H. J. Shine and C. F. Dais, *J. Org. Chem.,* 1965, **30**, 2145– 2148

231 F. Berger, M. B. Plutschack, J. Riegger, W. Yu, S. Speicher, M. Ho, N. Frank and T. Ritter, *Nature*, 2019, **567**, 223-228

232 J. Wu, Z. Wang, X.-Y. Chen, Y. Wu, D. Wang, Q. Peng and P. Wang, *Sci. China Chem*., 2020, **63**, 336–340.

233 R. Xie, J. Zhu and Y. Huang, *Org. Chem. Front*., 2021, **8**, 5699–5704.

234 D. E. Holst, D. J. Wang, M. J. Kim, I. A. Guzei and Z. K. Wickens, *Nature*, 2021, **596**, 74–79.

235 H. Jia, A. P. Häring, F. Berger, L. Zhang and T. Ritter, *J. Am. Chem. Soc.*, 2021, **143**, 7623–7628.

236 B. Liu and H. J. Shine, J. Phys. Org. Chem., 2001, 14, 81–89.

237 C. Chen, M. Wang, H. Lu, B. Zhao and Z. Shi, *Angew. Chem., Int. Ed.*, 2021, **60**, 21756–21760

238 E. M. Alvarez, M. B. Plutschack, F. Berger and T. Ritter, *Org. Lett.*, 2021, **22**, 4593–4596.

239 X.-Y. Chen, X.-X. Nie, Y. Wu and P. Wang, *Chem. Commun*., 2020, **56**, 5058–5061.

240 Y. Wu, Y.-H. Huang, X.-Y. Chen and P. Wang, *Org. Lett*., 2020, **22**, 6657–6661.

241 X.-X. Nie, Y.-H. Huang and P. Wang, *Org. Lett*., 2020, **22**, 7716–7720

242 B. Lansbergen, P. Granatino and T. Ritter, *J. Am. Chem. Soc*., 2021, **143**, 7909–7914

243 D. Zhao, R. Petzold, J. Yan, D. Muri and T. Ritter, *Nature*, 2021, **600**, 444–449.

244 Y. Ye, J. Zhu and Y. Huang, *Org. Lett*., 2021, **23**, 2386–2391.

245 M. Wang, X. Zhang, M. Ma and B. Zhao, *Org. Lett*., 2022, **24**, 6031–6036.

246 B. Zhao, Q. Wang, T. Zhu, B. Feng and M. Ma, *Org. Lett*., 2022, **24**, 5608–5613

247 S. Tang, X. Zhao, L. Yang, B. Li, B. Wang, *Angew. Chem. Intl. Ed.*, 2022, **61**, e202212975

248 S. Ni, J. Yan, S. Tewari, E. J. Reijerse, T. Ritter and J. Cornella, *J. Am. Chem. Soc.,* 2023, **145**, 9988-9993

248 F. Ye, F. Berger, H. Jia, J. Ford, A. Wortman, J. Borgel, C. Genicot and T. Ritter, *Angew. Chem. Intl. Ed.*, 2019, **58**, 14615-14619

250 R. Sang, S. E. Korkis, W. Su, F. Ye, P. S. Engl, F. Berger and T. Ritter, *Angew. Chem., Int. Ed*., 2019, **58**, 16161–16166.

251 J. Li, J. Chen, R. Sang, W.-S. Ham, M. B. Plutschack, F. Berger, S. Chabbra, A. Schnegg, C. Genicot and T. Ritter, *Nat. Chem*., 2020, **12**, 56–62.

252 X.-Y. Chen, Y.-H. Huang, J. Zhou and P. Wang, *Chin. J. Chem*., 2020, **38**, 1269–1272.

253 L. Liang, H.-Y. Niu, R.-L. Li, Y.-F. Wang, J.-K. Yan, C.-G. Li and H.-M. Guo, *Org. Lett.*, 2020, **22**, 6842–6846.

254 E. M. Alvarez, T. Karl, F. Berger, L. Torkowski and T. Ritter, *Angew. Chem. Int. Ed*., 2021, **60**, 13609–13613.

255 Y. Zhao, C. Yu, W. Liang and F. W. Patureau, *Org. Lett*., 2021, **23**, 6232–6236.

256 Y.-L. Zhang, G.-H. Wang, Y. Wu, C.-Y. Zhu and P. Wang, *Org. Lett.*, 2021, **23**, 8522–8526.

257 M. J. Cabrera-Afonso, A. Granados and G. A. Molander, *Angew. Chem. Int. Ed*., 2022, **61**, e202202706.

258 A. Granados, M. J. Cabrera-Afonso, M. Escolano, S. O. Badir and G. A. Molander, *Chem. Catal*., 2022, **2**, 898–907.

259 F.-S. He, P. Bao, Z. Tang, F. Yu, W.-P. Deng and J. Wu, *Org. Lett.*, 2022, **24**, 2955–2960.

260 K. Sun, A. Shi, Y. Liu, X. Chen, P. Xiang, X. Wang, L. Qu and B. Yu, *Chem. Sci*., 2022, **13**, 5659–5666.

261 Q. Li, J. Huang, Z. Cao, J. Zhang and J. Wu, Org. Chem. Front., 2022, 9, 3781–3785.

262 L. Shan, Z. Ma, C. Ou, Y. Cai, Y. Ma, Y. Guo, X. Ma and C. Liu, *Synth Commun*, 2023, 1784-1978

263 H. Xu, X. Li, J. Ma, J. Zuo, X. Song, J. Lv and D. Yang, *Chin Chem Lett*, 2023, **34**, 108403

264 X. Kong, Y. Chen, Q. Liu, WJ Wang, S. Zhang, Q. Zhang, X. Chen, Y.-Q. Xu and Z.-Y. Cao, *Org. lett*., 2023, 25, 581-586

265 J. Zhu, Y. Ye and Y. Huang, *Organometallics*, 2022, **41**, 2342–2348.

266 F. Juli´a, J. Yan, F. Paulus and T. Ritter, *J. Am. Chem. Soc.*, 2021, **143**, 12992–12998.

267 M.-S. Liu, H.-W. Du and W. Shu, *Chem. Sci*., 2022, **13**, 1003–1008.

268 D. J. Wang, K. Targos and Z. K. Wickens, *J. Am. Chem. Soc*., 2021, **143**, 21503–21510.

269 M. S. Liu, H.-W. Du and W. Shu, *Angew. Chem. Int. Ed*., 2022, **61**, e202209929.

270 H. Jia and T. Ritter, *Angew. Chem. Int. Ed*., 2022, **61**, e202208978

271 C. Chen, Z.-J. Wang, H. Lu, Y. Zhao and Z. Shi, *Nat. Commun*., 2021, **12**, 4526.

272 X. Li, W. Si, Z. Liu, H. Qian, T. Wang, S. Leng, J. Sun, Y. Jiao and X. Zhang, *Org. Lett.*, 2022, **24**, 4070–4074

273 H. Fujihara, H. Mima and N. Furukawa, *J. Am. Chem. Soc.*, 1995, **117**, 10153–10154.

274 D. Hellwinkel and G. Fahrbach, *Justus Liebigs Ann. Chem.*, 1968, **715**, 68–73.

275 D. Hellwinkel and G. Fahrbach, *Justus Liebigs Ann. Chem.*, 1968, **712**, 1–20.

276 R. S. Michalak, S. R. Wilson and J. C. Martin, *J. Am. Chem. Soc.*, 1984, **106**, 7529–7539.

277 J. Młochowski, K. Kloc, R. Lisiak, P. Potaczek and H. Wójtowicz, *Arkivoc*, 2007, **vi**, 14-46.

278 M. Batabyal, S. Jain, A. Upadhyay, S. Raju and S. Kumar, *Chem. Commun.*, 2022, **58**, 7050–7053.

279 N. Kurose, T. Takahashi and T. Koizumi, *J. Org. Chem.*, 1996, **61**, 2932–2933.

280 N. Kurose, T. Takahashi and T. Koizumi, *J. Org. Chem.*, 1997, **62**, 4562–4563.

281 T. Shimizu and N. Kamigata, *Org. Prep. Proced. Int.*, 1997, **29**, 603–629.

282 K. Venkateshwaran, R. Deka, S. Raju, H. B. Singh and R. J. Butcher, *Acta Crystallogr. C*, 2019, **75**, 70–76.

283 B. Olofsson, Ilan Marek and ZviRappoport., *The Chemistry of Hypervalent Halogen Compounds*, John Wiley & Sons, 2019, vol. **2**.

284 C. Willgerodt, *J. Prakt. Chem.*, 1885, **33**, 154–160.

285 R. B. Sandin and A. S. Hay, *J. Am. Chem. Soc.*, 1952, **74**, 274–275.

286 O. Ruff and H. Krug, *Z. Anorg.Allg. Chem.*, 1930, **190**, 270–276.

287 K. Miyamoto and M. Uchiyama, *Chem. Lett.*, 2021, **50**, 832–838.

288 A. N. Nesmeyanov, L. G. Makarova and T. P. Tolstaya, *Tetrahedron*, 1957, **1**, 145–157.

289 G. A. Olah and Y. Yamada, *J. Org. Chem.*, 1975, **40**, 1107–1110.

290 A. N. Nesmeyanov, T. P. Tolstaya and L. S. Isaeva, *Dokl. Akad. Nauk. SSSR*, 1955, **104**, 872–875.

291 G. A. Olah, T. Sakakibara and G. Asensio, *J. Org. Chem.*, 1978, **43**, 463–468.

292 N. E. Shchepina, V. D. Nefedov, M. A. Toropova, V. V. Avrorin, S. B. Lewis and B. Mattson, *Tetrahedron Lett.*, 2000, **41**, 25–27.

293 N. E. Shchepina, G. A. Badun, V. D. Nefedov, M. A. Toropova, V. M. Fedoseev, V. V. Avrorin and S. B. Lewis, *Tetrahedron Lett.*, 2002, **43**, 4123–4124.

294 I. M. Riddlestone, A. Kraft, J. Schaefer and I. Krossing, *Angew.Chem. Int. Ed.*, 2018, **57**, 13982–14024.

295 Y. Shoji, N. Tanaka, K. Mikami, M. Uchiyama and T. Fukushima, *Nat. Chem.*, 2014, **6**, 498–503.

296 M. Lanzi, T. Rogge, T. S. Truong, K. N. Houk and J. Wencel-Delord, *J. Am. Chem. Soc.*, 2023, **145**, 345–358.

297 G. Prakash and P. v. R. Schleyer, *Stable CcarbocationChemistry*, John Wiley & Sons, 1996.

298 G. A. Olah, K. K. Laali, Q. Wang and G. K. S. Prakash, *Onium Ions*, John Wiley & Sons Inc.: New York, 1998.

299 G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, 1967, **89**, 4744–4752.

300 G. A. Olah, P. Schilling, P. W. Westerman and H. C. Lin, *J. Am. Chem. Soc.*, 1974, **96**, 3581–3589.

301 W. A. Nugent, *J. Org. Chem.*, 1980, **45**, 4533–4534.

302 G. A. Olah and P. E. Peterson, *J. Am. Chem. Soc.*, 1968, **90**, 4675–4678.

303 M. Ochiai, N. Tada, T. Okada, A. Sota and K. Miyamoto, *J. Am. Chem. Soc.*, 2008, **130**, 2118–2119.

304 M. Ochiai, A. Yoshimura, K. Miyamoto, S. Hayashi and W. Nakanishi, *J. Am. Chem. Soc.*, 2010, **132**, 9236–9239.

305 B. Winterson, T. Patra and T. Wirth, *Synthesis*, 2022, **54**, 1261–1271.

306 M. Ochiai, A. Yoshimura, T. Mori, Y. Nishi and M. Hirobe, *J. Am. Chem. Soc.*, 2008, **130**, 3742–3743.

307 M. Lanzi, Q. Dherbassy and J. W.-Delord, *Angew.Chem. Int. Ed.*, 2021, **60**, 14852–14857.

308 M. Ochiai, K. Miyamoto, T. Kaneaki, S. Hayashi and W. Nakanishi, *Science*, 2011, **332**, 448–451.

309 I. Sokolovs, N. Mohebbati, R. Francke and E. Suna, *Angew.Chem. Int. Ed.*, 2021, **60**, 15832–15837.

310 A. N. Nesmeyanov, I. N. Lisichkina and T. P. Tolstaya, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1973, **22**, 2123–2123.

311 Z. J. Hou, Y. Zhu and Q. Wang, *Sci. China, Ser. B: Chem.*, 1996, **39**, 260–268.

312 Y. Yoshida, S. Ishikawa, T. Mino and M. Sakamoto, *Chem. Commun.*, 2021, **57**, 2519–2522.

313 G. Cavallo, J. S. Murray, P. Politzer, T. Pilati, M. Ursini and G. Resnati, *IUCrJ*, 2017, **4**, 411–419.

314 H. H. Wenk, M. Winkler and W. Sander, *Angew.Chem. Int. Ed.*, 2003, **42**, 502–528.

315 S. S. Bhojgude, A. Bhunia and A. T. Biju, *Acc. Chem. Res.*, 2016, **49**, 1658–1670.

316 P. M. Tadross and B. M. Stoltz, *Chem. Rev.*, 2012, **112**, 3550–3577.

317 H. Takikawa, A. Nishii, T. Sakai and K. Suzuki, *Chem. Soc. Rev.*, 2018, **47**, 8030–8056.

318 Y. Chen ; R. C. Larock,(Ed. L. Ackermann) *Modern Arylation Methods*, Wiley-VCH Verlag Gmbh& Co., Germany, 2009.

319 J.-A. G.-López and M. F. Greaney, *Chem. Soc. Rev.*, 2016, **45**, 6766–6798.

320 Y. Yoshida, T. Mino and M. Sakamoto, *ACS Catal.*, 2021, **11**, 13028–13033.

321 Y. Yoshida, T. Ao, T. Mino and M. Sakamoto, *Molecules*, 2023, **28**, 384.

322 G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, 1968, **90**, 947–953.

323 H. S.-Tilk, R. G. Ball and R. S. Brown, *J. Am. Chem. Soc.*, 1985, **107**, 4504–4508.

324 T. T. Nguyen and J. C. Martin, *J. Am. Chem. Soc.*, 1980, **102**, 7382–7383.

325 K. Miyamoto, M. Saito, S. Tsuji, T. Takagi, M. Shiro, M. Uchiyama and M. Ochiai, *J. Am. Chem. Soc.*, 2021, **143**, 9327–9331.

326 I. Sokolovs and E. Suna, *Org. Lett.*, 2023, **25**, 2047-2052.

327 P. J. Stang, *J. Org. Chem.*, 2003, **68**, 2997–3008.

328 V. V. Zhdankin and P. Stang, *Chem. Rev.*, 2002, **102**, 2523–2584.

329 P. J. Stang and V. V Zhdankin, *Chem. Rev.*, 1996, 96, 1123–1178.

330 K. Muniz and K. Ishihara, *Iodine Catalysis in Organic Synthesis*, 2022.

331 A. Yoshimura and V. V. Zhdankin, *Chem. Rev.*, 2016, **116**, 3328–3435.

332 V. V. Zhdankin and P. J. Stang, *Chem. Rev.*, 2008, **108**, 5299–5358.

333 V. V. Zhdankin, *J. Org. Chem.*, 2011, **76**, 1185–1197.

334 R. Zhao and L. Shi, *Angew.Chem. Int. Ed.*, 2020, **59**, 12282–12292.

335 X.-G. Yang, K. Zheng and C. Zhang, *Org. Lett.*, 2020, **22**, 2026–2031.

336 T. Wirth, *Angew.Chem. Int. Ed.*, 2005, **44**, 3656–3665.

337 R. M. Moriarty, *J. Org. Chem.*, 2005, **70**, 2893–2903.

338 V. V. Zhdankin, *Arkivoc*, 2020, 1–11.

339 X.-G. Yang, Z.-N. Hu, M.-C. Jia, F.-H. Du and C. Zhang, *Synlett*, 2021, **32**, 1289–1296.

340 T. Dohi and Y. Kita, *Hypervalent Iodine-Induced Oxidative Couplings (New Metal-Free Coupling Advances and Their Applications in Natural Product Syntheses)*, 2016.

341 R. Oishi, K. Segi, H. Hamamoto, A. Nakamura, T. Maegawa and Y. Miki, *Synlett*, 2018, **29**, 1465–1468.

342 M. Uyanik and K. Ishihara, *Chem. Commun.*, 2009, 2086–2099.

343 S. E. Shetgaonkar and F. V. Singh, *Arkivoc*, 2021, **iv**, 86–161.

344 Y. Li, D. P. Hari, M. V. Vita and J. Waser, *Angew.Chem. Int. Ed.*, 2016, **55**, 4436–4454.

345 J. H. Lee, S. Choi and K. B. Hong, *Molecules*, 2019, **24**, 2634.

346 Y. He, L. Huang, L. Xie, P. Liu, Q. Wei, F. Mao, X. Zhang, J. Huang, S. Chen and C. Huang, *J. Org. Chem.*, 2019, **84**, 10088–10101.

347 F. V. Singh and T. Wirth, *Arkivoc*, 2021, 12–47.

348 E. Merritt and B. Olofsson, *Synthesis*, 2011, 517–538.

349 F. V. Singh, S. E. Shetgaonkar, M. Krishnan and T. Wirth, *Chem. Soc. Rev.*, 2022, **51**, 8102–8139.

350 V. V. Zhdankin, *Adv.Heterocycl. Chem.*, 2015, 1–91.

351 A. Yoshimura, A. Saito and V. V. Zhdankin, *Adv.Synth.Catal.*, 2023, **365**, 2653–2675.

352 X. Peng, A. Rahim, W. Peng, F. Jiang, Z. Gu and S. Wen, *Chem. Rev.*, 2023, **123**, 1364–1416.

353 D. Zhu, Q. Liu, B. Luo, M. Chen, R. Pi, P. Huang and S. Wen, *Adv. Synth. Catal.*, 2013, **355**, 2172–2178.

354 M. Matsumoto, K. Wada, K. Urakawa and H. Ishikawa, *Org. Lett.*, 2020, **22**, 781–785.

355 H. Xie, S. Yang, C. Zhang, M. Ding, M. Liu, J. Guo and F. Zhang, *J. Org. Chem.*, 2017, **82**, 5250–5262.

356 X. Peng, Z. Sun, P. Kuang, L. Li, J. Chen and J. Chen, *Org. Lett.*, 2020, **22**, 5789–5795.

357 T. Hu, Z. Ye, K. Zhu, K. Xu, Y. Wu and F. Zhang, *Org. Lett.*, 2020, **22**, 505–509.

358 Z. Liu, D. Zhu, B. Luo, N. Zhang, Q. Liu, Y. Hu, R. Pi, P. Huang and S. Wen, *Org. Lett.*, 2014, **16**, 5600–5603.

359 B. Li, Z. Chao, C. Li and Z. Gu, *J. Am. Chem. Soc.*, 2018, **140**, 9400–9403.

360 M. Wang, Q. Fan and X. Jiang, *Org. Lett.*, 2018, **20**, 216–219

361 M. Saito, K. Miyamato and M. Ochiai, *Chem. Commun.,* 2011, **47,** 3410-3412

362 D. Zhu, M. Chen, M. Li, B. Luo, Y. Zhao, P. Huang, F. Xue, S. Rapposelli, R. Pi and S. Wen, *Eur. J. Med. Chem.*, 2013, **68**, 81–88.

363 D. Zhu, Y. Wu, B. Wu, B. Luo, A. Ganesan, F.-H. Wu, R. Pi, P. Huang and S. Wen, *Org. Lett.*, 2014, **16**, 2350–2353.

364 V. V. Grushin, *Chem. Soc. Rev.*, 2000, **29**, 315–324.

365 V. V. Grushin, *Acc. Chem. Res.*, 1992, **25**, 529–536.

366 Y. Wang, G. An, L. Wang and J. Han, *Curr. Org. Chem.*, 2020, **24**, 2070–2105.

367 D. Wang, Q. Li, M. Li, Z. Du and Y. Fu, *Curr. Org. Chem.*, 2021, **25**, 1298–1320.

368 N. Chatterjee and A. Goswami, *Eur. J. Org. Chem.*, 2017, **2017**, 3023–3032.

369 M. Wang, S. Chen and X. Jiang, *Chem. Asian. J*, 2018, **13**, 2195–2207.

370 L. Mascarelli and G. Benati, *Gazz. Chim. Ital.*, 1909, **38**, 619–629.

371 H. Heaney and P. Lees, *Tetrahedron*, 1968, **24**, 3717–3723.

372 J. Collette, D. McGreer, R. Crawford, F. Chubb and R. B. Sandin, *J. Am. Chem. Soc.*, 1956, **78**, 3819–3820.

373 T. Sato, K. Shimizu and H. Moriya, *J. Chem. Soc. Perkin Trans 1*, 1974, 1537–1539.

374 A. N. Vanchikov, M. S. Bobyleva, E. E. Komissarova, N. S. Kulikov and T. P. Tolstaya, *Chem.Heterocycl. Compd. (NY)*, 1998, **34**, 371–377.

375 K. B. Geahigan, R. J. Taintor, B. M. George, D. A. Meagher and T. W. Nalli, *J. Org. Chem.*, 1998, **63**, 6141–6145.

376 Y. V. Razskazovskii, M. J. Raiti and M. D. Sevilla, *J. Phys. Chem. A*, 1999, **103**, 6351–6359.

377 W. Lesueur, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1997, **36**, 3354–3362.

378 T. P. Tolstaya, L. I. Sukhomlinova, A. N. Vanchikov and N. A. Bumagin, *Chem.Heterocycl. Compd. (NY)*, 1999, **35**, 106–111.

379 T. P. Tolstaya, A. N. Vanchikov, E. V. Vinnik and L. D. Asulyan, *Chem. Heterocycl. Compd.*, 1999, **35**, 978–983.

380 M. Ochiai, Y. Kitagawa, N. Takayama, Y. Takaoka and M. Shiro, *J. Am. Chem. Soc.*, 1999, **121**, 9233–9234.

381 B. Ma, X. Nie, Z. Tan and W. Huang, *Chem. Abstract*, 1985, **102**, 6426.

382 G. F. Koser, R. H. Wettach and C. S. Smith, *J. Org. Chem.*, 1980, **45**, 1543–1544.

383 P. S. Postnikov, O. A. Guselnikova, M. S. Yusubov, A. Yoshimura, V. N. Nemykin and V. V. Zhdankin, *J. Org. Chem.*, 2015, **80**, 5783–5788.

384 B. Zu, J. Ke, Y. Guo and C. He, *Chin. J. Chem.*, 2021, **39**, 627–632.

385 M. Elsherbini and W. J. Moran, *Org.Biomol. Chem.*, 2021, **19**, 4706–4711.

386 L. D. Caspers, J. Spils, M. Damrath, E. Lork and B. J. Nachtsheim, *J. Org. Chem.*, 2020, **85**, 9161–9178.

387 M. Damrath, L. D. Caspers, D. Duvinage and B. J. Nachtsheim, *Org. Lett.*, 2022, **24**, 2562–2566.

388 D. Zhu, Z. Wu, B. Luo, Y. Du, P. Liu, Y. Chen, Y. Hu, P. Huang and S. Wen, *Org Lett*, 2018, **20**, 4815–4818.

389 A. Boelke, T. J. Kuczmera, L. D. Caspers, E. Lork and B. J. Nachtsheim, *Org. Lett.*, 2020, **22**, 7261–7266.

390 N. S. Antonkin, Y. A. Vlasenko, A. Yoshimura, V. I. Smirnov, T. N. Borodina, V. V. Zhdankin, M. S. Yusubov, A. Shafir and P. S. Postnikov, *J. Org. Chem.*, 2021, **86**, 7163–7178.

391 Y. A. Vlasenko, P. S. Postnikov, M. E. Trusova, A. Shafir, V. V. Zhdankin, A. Yoshimura and M. S. Yusubov, *J. Org. Chem.*, 2018, **83**, 12056–12070.

392 A. Boelke, S. Sadat, E. Lork and B. J. Nachtsheim, *Chem. Commun.*, 2021, **57**, 7434–7437.

393 K. Kepski, C. R. Rice and W. J. Moran, *Org. Lett.*, 2019, **21**, 6936–6939.

394 H. Wang, L. Liang, Z. Guo, H. Peng, S. Qiao, N. Saha, D. Zhu, W. Zeng, Y. Chen, P. Huang and S. Wen, *iScience*, 2020, **23**, 101307.

395 P. J. Stang and V. V. Zhdankin, *J. Am. Chem. Soc.*, 1993, **115**, 9808–9809.

396 U. Radhakrishnan and P. J. Stang, *J. Org. Chem.*, 2003, **68**, 9209–9213.

397 G. Li, R. Smith, M. Gembicky, A. L. Rheingold and J. D. Protasiewicz, *Chem. Commun.*, 2022, **58**, 1159–1162.

398 Q. Tan, D. Zhou, T. Zhang, B. Liu and B. Xu, *Chem. Commun.*, 2017, **53**, 10279–10282.

399 A. Parra, *Chem. Rev.*, 2019, **119**, 12033–12088.

400 R. Kumar and T. Wirth, *Top. Curr. Chem*. 2016, **373**, 243–261.

401 Y. Yoshida, T. Fujimura, T. Mino and M. Sakamoto, *Adv. Synth. Catal.*, 2022, **364**, 1091–1098.

402 W. Liang, Y. Yang, M. Yang, M. Zhang, C. Li, Y. Ran, J. Lan, Z. Bin and J. You, *Angew.Chem. Int. Ed.*, 2021, **60**, 3493–3497.

403 M. Wang, M. Zhang, Y. Luo, Z. Liu, C. Yang, J. Lan, D. Wu and J. You, *Org. Lett.*, 2020, **22**, 135–139.

404 J. Li, Q.-N. Xu, Z.-B. Wang, Y. Li and L. Liu, *ACS Omega*, 2018, **3**, 12923–12929.

405 H. Xie, M. Ding, M. Liu, T. Hu and F. Zhang, *Org. Lett.*, 2017, **19**, 2600–2603.

406 Z. Ye, Y. Li, K. Xu, N. Chen and F. Zhang, *Org. Lett.*, 2019, **21**, 9869–9873.

407 M. Wang, J. Wei, Q. Fan and X. Jiang, *Chem. Commun.*, 2017, **53**, 2918–2921.

408 Y. Wu, F. Wu, D. Zhu, B. Luo, H. Wang, Y. Hu, S. Wen and P. Huang, *Org.Biomol. Chem.*, 2015, **13**, 10386–10391.

409 M. Wang, S. Chen and X. Jiang, *Org. Lett.*, 2017, **19**, 4916–4919.

410 D. Zhu, P. Liu, W. Lu, H. Wang, B. Luo, Y. Hu, P. Huang and S. Wen, *Eur. J. Chem.*, 2015, **21**, 18915–18920.

411 K. H. Vase, A. H. Holm, K. Norrman, S. U. Pedersen and K. Daasbjerg, *Langmuir*, 2007, **23**, 3786–3793.

412 N. Purkait, G. Kervefors, E. Linde and B. Olofsson, *Angew. Chem.*, 2018, **130**, 11597–11601.

413 Q. Li, M. Zhang, S. Zhan and Z. Gu, *Org. Lett.*, 2019, **21**, 6374–6377.

414 X. Peng, L. Li, Y. Ren, H. Xue, J. Liu, S. Wen and J. Chen, *Adv. Synth. Catal.*, 2020, **362**, 2030–2038.

415 D. Zhu, M. Li, Z. Wu, Y. Du, B. Luo, P. Huang and S. Wen, *Eur. J. Org. Chem.*, 2019, **2019**, 4566–4571.

416 S. Yang, F. Wang, Y. Wu, W. Hua and F. Zhang, *Org. Lett.*, 2018, **20**, 1491–1495.

417 J. Luo, T. Zhang, L. Wang, G. Liao, Q. Yao, Y. Wu, B. Zhan, Y. Lan, X. Lin and B. Shi, *Angew.Chem. Int. Ed.*, 2019, **58**, 6708–6712.

418 Z. Gao, J. Qian, H. Yang, X.-C. Hang, J. Zhang and G. Jiang, *Chem. Commun.*, 2020, **56**, 7265–7268.

419 A. J. Fugard, A. S. K. Lahdenperä, J. S. J. Tan, A. Mekareeya, R. S. Paton and M. D. Smith, *Angew. Chem. Int. Ed.*, 2019, **58**, 2795–2798.

420 X. Bao, J. Rodriguez and D. Bonne, *Angew. Chem. Int. Ed.*, 2020, **59**, 12623–12634.

421 C. G. Newton, E. Braconi, J. Kuziola, M. D. Wodrich and N. Cramer, *Angew. Chem. Int. Ed.*, 2018, **57**, 11040–11044.

422 M. Saito, Y. Kobayashi, S. Tsuzuki and Y. Takemoto, *Angew. Chem. Int. Ed.*, 2017, **56**, 7653–7657.

423 A. Labattut, P.-L. Tremblay, O. Moutounet and C. Y. Legault, *J. Org. Chem.*, 2017, **82**, 11891–11896.

424 V. Meyer and W. Wachter, *Ber. Dtsch. Chem. Ges.*, 1892, **25**, 2632–2635.

425 I. A. Mironova, S. F. Kirsch, V. V. Zhdankin, A. Yoshimura and M. S. Yusubov, *Eur. J. Org. Chem.*, 2022, e202200754

426 D. P. Hari, P. Caramenti and J. Waser, *Acc. Chem. Res.*, 2018, **51**, 3212–3225.

427 N. Declas, G. Pisella and J. Waser, *Helv.Chim. Acta.*, 2020, **103**, e2000191

428 I. F. D. Hyatt, L. Dave, N. David, K. Kaur, M. Medard and C. Mowdawalla, *Org.Biomol. Chem.*, 2019, **17**, 7822–7848.

429 I. A. Mironova, D. M. Noskov, A. Yoshimura, M. S. Yusubov and V. V. Zhdankin, *Molecules*, 2023, **28**, 2136.

430 E. Le Du and J. Waser, *Chem. Commun.*, 2023, **59**, 1589–1604.

431 F. M. Beringer and I. Lillien, *J. Am. Chem. Soc.*, 1960, **82**, 725–731.

432 F. M. Beringer and S. J. Huang, *J. Org. Chem.*, 1964, **29**, 445–448.

433 J. B. S. Bonilha, N. Petragnani and V. G. Toscano, *Chem. Ber.*, 1978, **111**, 2510–2516.

434 R. D. Miller, L. Franz and G. N. Fickes, *J. Org. Chem.*, 1985, **50**, 3200–3203.

435 E. A. Merritt and B. Olofsson, *Eur. J. Org. Chem.*, 2011, **2011**, 3690–3694.

436 M. S. Yusubov, R. Y. Yusubova, V. N. Nemykin and V. V. Zhdankin, *J. Org. Chem.*, 2013, **78**, 3767–3773.

437 M. S. Yusubov, N. S. Soldatova, P. S. Postnikov, R. R. Valiev, D. Y. Svitich, R. Y. Yusubova, A. Yoshimura, T. Wirth and V. V. Zhdankin, *Eur. J. Org. Chem.*, 2018, **2018**, 640–647.

438 G. F. Morrison and J. Hooz, *J. Org. Chem.*, 1970, **35**, 1196–1198.

439 L. F. Fieser and M. J. Haddadin, *Org. Synth.*, 1966, **46**, 107–112.

440 B. Wu, J. Wu and N. Yoshikai, *Chem. Asian. J.*, 2017, **12**, 3123–3127.

441 W. Ding, C. Wang, J. R. Tan, C. C. Ho, F. León, F. García and N. Yoshikai, *Chem. Sci.*, 2020, **11**, 7356–7361.

442 A. Yoshimura, S. M. Larson, G. B. Frahm, C. D. Huss, G. T. Rohde, V. N. Nemykin, M. S. Yusubov, A. Saito and V. V. Zhdankin, *Arkivoc*, 2020, **2020**, 35–49.

443 R. J. Batchelor, T. Birchall and J. F. Sawyer, *Inorg. Chem.*, 1986, **25**, 1415–1420.

444 A. Yoshimura, M. T. Shea, O. Guselnikova, P. S. Postnikov, G. T. Rohde, A. Saito, M. S. Yusubov, V. N. Nemykin and V. V. Zhdankin, *Chem. Commun.*, 2018, **54**, 10363–10366.

445 A. A. Almasalma and E. Mejía, *Eur. J. Org. Chem.*, 2018, **2018**, 188–195.

446 A. Yoshimura, M. S. Yusubov and V. V. Zhdankin, *Org.Biomol. Chem.*, 2016, **14**, 4771–4781.

447 A. Y. Koposov, V. N. Nemykin and V. V. Zhdankin, *New J. Chem.*, 2005, **29**, 998.

448 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441–451.

449 A. Yoshimura, A. Saito and V. V. Zhdankin, *Chem. Eur. J.*, 2018, **24**, 15156–15166.

450 R. A. Scherrer and H. R. Beatty, *J. Org. Chem.*, 1980, **45**, 2127–2131.

451 A. V. Ozerskaya, M. S. Larkina, E. V. Podrezova, D. Y. Svitich, R. Y. Yusubova, V. V. Zhdankin and M. S. Yusubov, *Arkivoc*, 2022, **vii**, 108–125.

452 S. Preshlock, M. Tredwell and V. Gouverneur, *Chem. Rev.*, 2016, **116**, 719–766.

453 M. S. Yusubov, D. Y. Svitich, M. S. Larkina and V. V. Zhdankin, *ARKIVOC*, 2013, **i**, 364–395.

454 P. Caramenti, S. Nicolai and J. Waser, *Chem. Eur. J.*, 2017, **23**, 14702–14706.

455 S. Banerjee, V. W. Bhoyare and N. T. Patil, *Chem. Commun.*, 2020, **56**, 2677–2690.

456 C. Chen, X. Wang and T. Yang, *Front. Chem.*, 2020, **8**, 551159

457 J. P. Brand and J. Waser, *Chem. Soc. Rev.*, 2012, **41**, 4165–4179.

458 F. Le Vaillant and J. Waser, *Chem. Sci.*, 2019, **10**, 8909–8923.

459 N. Yoshikai, *J. Syn. Org. Chem.*, 2022, **80**, 1011–1018.

460 J. Kaschel and D. B. Werz, *Angew.Chem. Int. Ed.*, 2015, **54**, 8876–8878.

461 M. Ochiai, Y. Masaki and M. Shiro, *J. Org. Chem.*, 1991, **56**, 5511–5513.

462 J. P. Brand, C. Chevalley, R. Scopelliti and J. Waser, *Chem. Eur. J.*, 2012, **18**, 5655–5666.

463 G. L. Tolnai, S. Ganss, J. P. Brand, J. Waser, *Org. Lett.*, 2013, **15**, 112–115

464 J. P. Brand, J. Charpentier and J. Waser, *Angew. Chem. Int. Ed.*, 2009, **48**, 9346–9349.

465 Y. Yang, P. Antoni, M. Zimmer, K. Sekine, F. F. Mulks, L. Hu, L. Zhang, M. Rudolph, F. Rominger and A. S. K. Hashmi, *Angew. Chem. Int. Ed.*, 2019, **58**, 5129–5133.

466 S. Banerjee, S. B. Ambegave, R. D. Mule, B. Senthilkumar and N. T. Patil, *Org. Lett.*, 2020, **22**, 4792–4796.

467 Z. Wang, X. Li and Y. Huang, *Angew. Chem. Int. Ed.*, 2013, **52**, 14219–14223.

468 Z. Wang, L. Li and Y. Huang, *J. Am. Chem. Soc.*, 2014, **136**, 12233–12236.

469 Y. Liu, M. C. Dietl, C. Han, M. Rudolph, F. Rominger, P. Krämer and A. S. K. Hashmi, *Org. Lett.*, 2022, **24**, 7101–7106.

470 S. Banerjee, B. Senthilkumar and N. T. Patil, *Org. Lett.*, 2019, **21**, 180–184.

471 D. P. Hari and J. Waser, *J. Am. Chem. Soc.*, 2016, **138**, 2190–2193.

472 D. P. Hari and J. Waser, *J. Am. Chem. Soc.*, 2017, **139**, 8420–8423.

473 J. Borrel, G. Pisella and J. Waser, *Org. Lett.*, 2020, **22**, 422–427.

474 G. Pisella, A. Gagnebin and J. Waser, *Chem. Eur. J.*, 2020, **26**, 10199–10204.

475 N. P. Ramirez, G. Pisella and J. Waser, *J. Org. Chem.*, 2021, **86**, 10928–10938.

476 Y. Tokimizu, S. Oishi, N. Fujii and H. Ohno, *Org. Lett.*, 2014, **16**, 3138–3141.

477 R. Takai, D. Shimbo, N. Tada and A. Itoh, *J. Org. Chem.*, 2021, **86**, 4699–4713.

478 R. Kawakami, S. Usui, N. Tada and A. Itoh, *Chem. Commun.*, 2023, **59**, 450–453.

479 S. Nicolai, S. Erard, D. F. González and J. Waser, *Org. Lett.*, 2010, **12**, 384–387.

480 B. Lu, J. Wu and N. Yoshikai, *J. Am. Chem. Soc.*, 2014, **136**, 11598–11601.

481 J. Wu and N. Yoshikai, *Angew.Chem. Int. Ed.*, 2015, **54**, 11107–11111.

482 A. Ariafard, *Organometallics*, 2014, **33**, 7318–7324.

483 X. Li, P. Chen and G. Liu, *Chem. Commun.*, 2022, **58**, 2544–2547.

484 Y. Pan, K. Jia, Y. Chen and Y. Chen, *BeilsteinJ. Org. Chem.*, 2018, **14**, 1215–1221.

485 Q.-Q. Zhou, W. Guo, W. Ding, X. Wu, X. Chen, L.-Q. Lu and W.-J. Xiao, *Angew.Chem. Int. Ed.*, 2015, **54**, 11196–11199.

486 F. LeVaillant, T. Courant and J. Waser, *Angew. Chem. Int. Ed.*, 2015, **54**, 11200–11204.

487 S. Mukherjee, R. A. Garza-Sanchez, A. Tlahuext-Aca and F. Glorius, *Angew.Chem. Int. Ed.*, 2017, **56**, 14723–14726.

488 X. Liu, L. Yu, M. Luo, J. Zhu and W. Wei, *Chem. Eur. J.*, 2015, **21**, 8745–8749.

489 H. Tan, H. Li, W. Ji and L. Wang, *Angew.Chem. Int. Ed.*, 2015, **54**, 8374–8377.

490 H. Wang, L. Guo, S. Wang and X.-H. Duan, *Org. Lett.*, 2015, **17**, 3054–3057.

491 B. Liu, C.-H. Lim and G. M. Miyake, *J. Am. Chem. Soc.*, 2018, **140**, 12829–12835.

492 R.-Y. Zhang, L.-Y. Xi, L. Zhang, S.-Y. Chen and X.-Q. Yu, *Tetrahedron*, 2015, **71**, 6176–6182.

493 S. He, X. Guo, J. Li, Y. Zhang, L. Chen and T. Kang, *Eur. J. Org. Chem.*, 2022, e202200516.

494 E. Voutyritsa, M. Garreau, M. G. Kokotou, I. Triandafillidi, J. Waser and C. G. Kokotos, *Chem. Eur. J.*, 2020, **26**, 14453–14460.

495 S. G. E. Amos, S. Nicolai and J. Waser, *Chem. Sci.*, 2020, **11**, 11274–11279.

496 J.-Y. Shou, X.-H. Xu and F.-L. Qing, *J. Fluor. Chem.*, 2022, **261–262**, 110018.

497 D. Abegg, R. Frei, L. Cerato, D. Prasad Hari, C. Wang, J. Waser and A. Adibekian, *Angew.Chem. Int. Ed.*, 2015, **54**, 10852–10857.

498 S. R. Adusumalli and G. J. L. Bernardes, *Chem.*, 2019, **5**, 1932–1934.

499 R. Tessier, J. Ceballos, N. Guidotti, R. Simonet-Davin, B. Fierz and J. Waser, *Chem.*, 2019, **5**, 2243–2263.

500 B. Liu, J. V. Alegre-Requena, R. S. Paton and G. M. Miyake, *Eur. J. Chem.*, 2020, **26**, 2386–2394.

501 M. Li, J.-H. Wang, W. Li and L.-R. Wen, *Org. Lett.*, 2018, **20**, 7694–7698.

502 M. Li, W. Li, C.-D. Lin, J.-H. Wang and L.-R. Wen, *J. Org. Chem.*, 2019, **84**, 6904–6915.

503 A. Shimizu, A. Shibata, T. Kano, Y. Kumai, R. Kawakami, H. Esaki, K. Fukushima, N. Tada and A. Itoh, *Org. Lett.*, 2022, **24**, 8859–8863.

504 A. Roy, M. K. Das, S. Chaudhuri and A. Bisai, *J. Org. Chem.*, 2018, **83**, 403–421.

505 Z.-C. Chen, P. Chen, Z. Chen, Q. Ouyang, H.-P. Liang, W. Du and Y.-C. Chen, *Org. Lett.*, 2018, **20**, 6279–6283.

506 B. Meng, Q. Shi, Y. Meng, J. Chen, W. Cao and X. Wu, *Org.Biomol. Chem.*, 2021, **19**, 5087–5092.

507 L.-F. Chu, Y. Yao and C.-D. Lu, *Org. Lett.*, 2022, **24**, 9135–9140.

508 T. Kitamura, T. Fukuoka and Y. Fujiwara, *Synlett*, 1996, **1996**, 659–660.

509 J. Wu, X. Deng, H. Hirao and N. Yoshikai, *J. Am. Chem. Soc.*, 2016, **138**, 9105–9108.

510 R. Frei, M. D. Wodrich, D. P. Hari, P.-A. Borin, C. Chauvier and J. Waser, *J. Am. Chem. Soc.*, 2014, **136**, 16563–16573.

511 E. Stridfeldt, A. Seemann, M. J. Bouma, C. Dey, A. Ertan and B. Olofsson, *Chem. Eur. J.*, 2016, **22**, 16066–16070.

512 A. Boelke, L. D. Caspers and B. J. Nachtsheim, *Org. Lett.*, 2017, **19**, 5344–5347.

513 G. Pisella, A. Gagnebin and J. Waser, *Org. Lett.*, 2020, **22**, 3884–3889.

514 L. Castoldi, E. M. Di Tommaso, M. Reitti, B. Gräfen and B. Olofsson, *Angew.Chem. Int. Ed.*, 2020, **59**, 15512–15516.

515 R. A. Laskar, W. Ding and N. Yoshikai, *Org. Lett.*, 2021, **23**, 1113–1117.

516 P. Caramenti, N. Declas, R. Tessier, M. D. Wodrich and J. Waser, *Chem. Sci.*, 2019, **10**, 3223–3230.

517 D. Shimbo, T. Maruyama, N. Tada and A. Itoh, *Org.Biomol. Chem.*, 2021, **19**, 2442–2447.

518 T. Ura, D. Shimbo, M. Yudasaka, N. Tada and A. Itoh, *Chem. Asian J.*, 2020, **15**, 4000–4004.

519 J. Wu, X. Deng and N. Yoshikai, *Chem. Eur. J.*, 2019, **25**, 7839–7842.

520 J. Chai, W. Ding, J. Wu and N. Yoshikai, *Chem. Asian J.*, 2020, **15**, 2166–2169.

521 W. Ding, J. Chai, C. Wang, J. Wu and N. Yoshikai, *J. Am. Chem. Soc.*, 2020, **142**, 8619–8624.

522 J. Chai, W. Ding, C. Wang, S. Ito, J. Wu and N. Yoshikai, *Chem. Sci.*, 2021, **12**, 15128–15133.

523 J. Kikuchi, K. Maesaki, S. Sasaki, W. Wang, S. Ito and N. Yoshikai, *Org. Lett.*, 2022, **24**, 6914–6918.

524 C.-S. Wang, P. S. L. Tan, W. Ding, S. Ito and N. Yoshikai, *Org. Lett.*, 2022, **24**, 430–434.

525 L. I. Dixon, M. A. Carroll, T. J. Gregson, G. J. Ellames, R. W. Harrington and W. Clegg, *Org.Biomol. Chem.*, 2013, **11**, 5877.

526 M. S. Yusubov, P. Postnikov, A. Yoshimura and V. V. Zhdankin, *Synlett*, 2020, **31**, 315–326.

527 V. V. Zhdankin, C. J. Kuehl, J. T. Bolz, M. S. Formaneck and A. J. Simonsen, *Tetrahedron Lett.*, 1994, **35**, 7323–7326.

528 V. V. Zhdankin, C. J. Kuehl, A. P. Krasutsky, J. T. Bolz and A. J. Simonsen, *J. Org. Chem.*, 1996, **61**, 6547–6551.

529 C. A. Panetta, S. M. Garlick, H. D. Durst, F. R. Longo and J. R. Ward, *J. Org. Chem.*, 1990, **55**, 5202–5205.

530 G. C. Geary, E. G. Hope, K. Singh and A. M. Stuart, *Chem. Commun.*, 2013, **49**, 9263.

531 A. Yoshimura, K. C. Nguyen, S. C. Klasen, A. Saito, V. N. Nemykin and V. V. Zhdankin, *Chem. Commun.*, 2015, **51**, 7835–7838.

532 A. Yoshimura and V. V. Zhdankin, *Arkivoc*, 2017, **iii**, 32–40.

533 A. Yoshimura, K. C. Nguyen, S. C. Klasen, P. S. Postnikov, M. S. Yusubov, A. Saito, V. N. Nemykin and V. V. Zhdankin, *Asian J. Org. Chem.*, 2016, **5**, 1128–1133.

534 A. Yoshimura, K. C. Nguyen, G. T. Rohde, A. Saito, M. S. Yusubov and V. V. Zhdankin, *Adv. Synth. Catal.*, 2016, **358**, 2340–2344.

535 H. Wang, D. Zhang, H. Sheng and C. Bolm, *J. Org. Chem.*, 2017, **82**, 11854–11858.

536 A. Yoshimura, S. C. Klasen, M. T. Shea, K. C. Nguyen, G. T. Rohde, A. Saito, P. S. Postnikov, M. S. Yusubov, V. N. Nemykin and V. V. Zhdankin, *Chem. Eur. J.*, 2017, **23**, 691–695.

537 M. Shee and N. D. P. Singh, *Chem. Soc. Rev.*, 2022, **51**, 2255–2312.

538 X. Wang and A. Studer, *Acc. Chem. Res.*, 2017, **50**, 1712–1724.

539 R. Simonet-Davin and J. Waser, *Synthesis*, 2023, **55**, 1652–1661.

540 V. V. Zhdankin, A. P. Krasutsky, C. J. Kuehl, A. J. Simonsen, J. K. Woodward, B. Mismash and J. T. Bolz, *J. Am. Chem. Soc.*, 1996, **118**, 5192–5197.

541 V. V. Zhdankin, C. J. Kuehl, A. P. Krasutsky, M. S. Formaneck and J. T. Bolz, *Tetrahedron Lett.*, 1994, **35**, 9677–9680.

542 Y. Kita, S. Akai, T. Okuno, M. Egi, T. Takada and H. Tohma, *Heterocycles*, 1996, **42**, 47.

543 M. V. Vita and J. Waser, *Org. Lett.*, 2013, **15**, 3246–3249.

544 X. Huang and J. T. Groves, *ACS Catal.*, 2016, **6**, 751–759.

545 K. Matsumoto, M. Nakajima and T. Nemoto, *J. Phys. Org. Chem.*, 2019, **32**, e3961

546 J.-D. Yang, M. Li and X.-S. Xue, *Chin. J. Chem.*, 2019, **37**, 359–363.

547 S. Alazet, J. Preindl, R. Simonet-Davin, S. Nicolai, A. Nanchen, T. Meyer and J. Waser, *J. Org. Chem.*, 2018, **83**, 12334–12356.

548 S. P. Green, K. M. Wheelhouse, A. D. Payne, J. P. Hallett, P. W. Miller and J. A. Bull, *Angew. Chem. Int. Ed.*, 2020, **59**, 15798–15802.

549 K. Kiyokawa, T. Kosaka, T. Kojima and S. Minakata, *Angew. Chem. Int. Ed.*, 2015, **54**, 13719–13723.

550 A. Yoshimura, S. R. Koski, J. M. Fuchs, A. Saito, V. N. Nemykin and V. V. Zhdankin, *Chem. Eur. J.*, 2015, **21**, 5328–5331.

551 X.-H. Hu, X.-F. Yang and T.-P. Loh, *ACS Catal.*, 2016, **6**, 5930–5934.

552 N. Lucchetti, A. Tkacheva, S. Fantasia and K. Muñiz, *Adv. Synth. Catal.*, 2018, **360**, 3889–3893.

553 K. Kiyokawa, D. Okumatsu and S. Minakata, *Angew.Chem. Int. Ed.*, 2019, **58**, 8907–8911.

554 T. Lan, H. Qin, W. Chen, W. Liu and C. Chen, *Chin. Chem. Lett.*, 2020, **31**, 357–360.

555 Y. Hu, S. Zheng, W. Fan and W. Yuan, *Adv. Synth. Catal.*, 2021, **363**, 4701–4707.

556 Y. Zhang, J. Lu, T. Lan, S. Cheng, W. Liu and C. Chen, *Eur. J. Org. Chem.*, 2021, **2021**, 436–442.

557 D. L. Poeira, A. C. R. Negrão, H. Faustino, J. A. S. Coelho, C. S. B. Gomes, P. M. P. Gois and M. M. B. Marques, *Org. Lett.*, 2022, **24**, 776–781.

558 D. Okumatsu, K. Kawanaka, S. Kainuma, K. Kiyokawa and S. Minakata, *Chem. Eur. J.*, 2023, 29, e202203722.

559 L. Zheng, Z. Wang, C. Li, Y. Wu, Z. Liu and Y. Ning, *Chem. Commun.*, 2021, **57**, 9874–9877.

560 A. Fawcett, M. J. Keller, Z. Herrera and J. F. Hartwig, *Angew.Chem. Int. Ed.*, 2021, **60**, 8276–8283.

561 G. Schulz, V. George, D. Taser and A. Kirschning, *J. Org. Chem.*, 2023, **88**, 3781–3786.

562 Y. Wang, Q. He, Z. Cao, P. Wang, G. Chen and M. Beller, *Org. Chem. Front.*, 2022, **9**, 5592–5598.

563 F. Le Vaillant and J. Waser, *Chimia (Aarau)*, 2017, **71**, 226.

564 T. Govender, P. I. Arvidsson, G. E. M. Maguire, H. G. Kruger and T. Naicker, *Chem. Rev.*, 2016, **116**, 9375–9437.

565 V. V. Zhdankin, C. J. Kuehl, A. M. Arif and P. J. Stang, *Mendeleev Commun.*, 1996, **2**, 50–51.

566 V. V. Zhdankin, C. J. Kuehl, A. P. Krasutsky, J. T. Bolz, B. Mismash, J. K. Woodward and A. J. Simonsen, *Tetrahedron Lett.*, 1995, **36**, 7975–7978.

567 M.-X. Sun, Y.-F. Wang, B.-H. Xu, X.-Q. Ma and S.-J. Zhang, *Org Biomol Chem*, 2018, **16**, 1971–1975.

568 Z. Chen, S. Zheng, Z. Wang, Z. Liao and W. Yuan, *ChemPhotoChem*, 2021, **5**, 906–910.

569 Y.-S. Feng, Y.-J. Shu, P. Cao, T. Xu and H.-J. Xu, *Org. Biomol. Chem.,* 2017, **15**, 3590–3593.

570 Z. Chen and W. Yuan, *Chem. Eur. J.*, 2021, **27**, 14836–14840.

571 J. Charpentier, N. Früh and A. Togni, *Chem. Rev.*, 2015, **115**, 650–682.

572 T. Koike and M. Akita, *Acc. Chem. Res.*, 2016, **49**, 1937–1945.

573 R. Mamgain, R. Nagarkar and F. V. Singh, *Arkivoc*, 2022, **2022**, 57–107.

574 J.-Y. Chen, J. Huang, K. Sun and W.-M. He, *Org. Chem. Front.*, 2022, **9**, 1152–1164.

575 J. Kalim, T. Duhail, T.-N. Le, N. Vanthuyne, E. Anselmi, A. Togni and E. Magnier, *Chem. Sci.*, 2019, **10**, 10516–10523.

576 H. Jiang, T.-Y. Sun, Y. Chen, X. Zhang, Y.-D. Wu, Y. Xie and H. F. Schaefer, *Chem. Commun.*, 2019, **55**, 5667–5670.

577 R. Wang, I. Kalf and U. Englert, *RSC Adv.*, 2018, **8**, 34287–34290.

578 V. Matoušek, J. Václavík, P. Hájek, J. Charpentier, Z. E. Blastik, E. Pietrasiak, A. Budinská, A. Togni and P. Beier, *Chem. Eur. J.*, 2016, **22**, 417–424.

579 N. Santschi, C. Matthey, R. Schwenk, E. Otth and A. Togni, *Eur. J. Org. Chem.*, 2015, **2015**, 1925–1931.

580 K. Niedermann, J. M. Welch, R. Koller, J. Cvengroš, N. Santschi, P. Battaglia and A. Togni, *Tetrahedron*, 2010, **66**, 5753–5761.

581 N. Santschi, R. C. Sarott, E. Otth, R. Kissner and A. Togni, *Beil.J. Org. Chem.*, 2014, **10**, 1–6.

582 H. Egami, *Chem. Pharm. Bull.*, 2020, **68**, 491–511.

583 A. Tlili, F. Toulgoat and T. Billard, *Angew.Chem. Int. Ed.*, 2016, **55**, 11726–11735.

584 A. Prieto, O. Baudoin, D. Bouyssi and N. Monteiro, *Chem. Commun.*, 2016, **52**, 869–881.

585 X. Liu, C. Xu, M. Wang and Q. Liu, *Chem. Rev.*, 2015, **115**, 683–730.

586 R. Muta, T. Torigoe and Y. Kuninobu, *Org. Lett.*, 2022, **24**, 8218–8222.

587 Y. Shi, K. Wang, Y. Ding and Y. Xie, *Org.Biomol. Chem.*, 2022, **20**, 9362–9367.

588 S. Le, Y. Bai, J. Qiu, Z. Zhang, H. Zheng and G. Zhu, *Org. Chem. Front.*, 2022, **9**, 4670–4675.

589 Y. Zong and Y. Rao, *Org. Lett.*, 2014, **16**, 5278–5281.

590 X. Yang, T.-Y. Sun and Y. Rao, *Chem. Eur. J.*, 2016, **22**, 3273–3277.

591 P. Abdolalian, S. K. Tizhoush, K. Farshadfar and A. Ariafard, *Chem. Sci.*, 2021, **12**, 7185–7195.

592 G. Shan, X. Yang, Y. Zong and Y. Rao, *Angew.Chem. Int. Ed.*, 2013, **52**, 13606–13610.

593 E. Ito, T. Fukushima, T. Kawakami, K. Murakami and K. Itami, *Chem.*, 2017, **2**, 383–392.

594 X. Hu, G.-X. Li, G. He and G. Chen, *Org. Chem. Front.*, 2019, **6**, 3205–3209.

595 A. R. Rivero, P. Fodran, A. Ondrejková and C.-J. Wallentin, *Org. Lett.*, 2020, **22**, 8436–8440.

596 S. K. Ghosh, M. Hu and R. J. Comito, *Chem. Eur. J.*, 2021, **27**, 17601–17608.

597 Y. Sakakibara, K. Murakami and K. Itami, *Org. Lett.*, 2022, **24**, 602–607.

598 M. Liu, H. Huang and Y. Chen, *Chin. J. Chem.*, 2018, **36**, 1209–1212.

599 Y. Sakakibara, P. Cooper, K. Murakami and K. Itami, *Chem. Asian J.*, 2018, **13**, 2410–2413.

600 Y. Sakakibara, E. Ito, T. Fukushima, K. Murakami and K. Itami, *Chem. Eur. J.*, 2018, **24**, 9254–9258.

601 J. Hu, T. Lan, Y. Sun, H. Chen, J. Yao and Y. Rao, *Chem. Commun.*, 2015, **51**, 14929–14932.

602 X. Sun, X. Yao, C. Zhang and Y. Rao, *Chem. Commun.*, 2015, **51**, 10014–10017.

603 B. Yang, X.-H. Xu and F.-L. Qing, *Org. Lett.*, 2016, **18**, 5956–5959.

604 Y. Ge, Y. Shao, S. Wu, P. Liu, J. Li, H. Qin, Y. Zhang, X. Xue and Y. Chen, *ACS Catal.*, 2023, **13**, 3749–3756.

605 B. Li, X. Cheng, Z.-Y. Guan, S.-Y. Li, T. Huo, G. Cheng, Y.-H. Fan, F.-S. Zhou and Q.-H. Deng, *Org. Chem. Front.*, 2020, **7**, 3509–3514.

606 R. Calvo, A. Le Tellier, T. Nauser, D. Rombach, D. Nater and D. Katayev, *Angew.Chem. Int. Ed.*, 2020, **59**, 17162–17168.

607 Z. Wang, A. G. Herraiz, A. M. d. Hoyo and M. G. Suero, *Nature*, 2018, **554**, 86–91.

608 Z. Wang, L. Jiang, P. Sarró and M. G. Suero, *J. Am. Chem. Soc.*, 2019, **141**, 15509–15514.

609 L. Jiang, P. Sarró, W. J. Teo, J. Llop and M. G. Suero, *Chem Sci*, 2022, **13**, 4327–4333.

610 H.-F. Tu, A. Jeandin and M. G. Suero, *J. Am. Chem. Soc.*, 2022, **144**, 16737–16743

611 A. Boele, Y. A. Vlasenko, M. S. Yusubov, B. J. Nachtsheim and P. S. Postnikov, *Beil. J. Org. Chem.*, 2019, **15**, 2311-2318.

612 U. Ladziata and V. V Zhdankin, *Arkivoc*, 2006, **ix**, 26–58.

613 S. Soni, Rimi, V. Kumar, K. Kikushima, T. Dohi, V. V. Zhdankin and R. Kumar, *Arkivoc*, 2022, **vii**, 27–56.

614 S. E. Shetgaonkar, S. Jothish, T. Dohi and F. V. Singh, *Molecules*, 2023, **28**, 5250.

615 C. Hartmann and V. Meyer, *Ber. Dtsch. Chem. Ges.*, 1893, **26**, 1727–1732.

616 R. K. Boeckman, P. Shao and J. Mullins, *Org. Synth.*, 2000, **77**, 141.

617 M. Frigerio, M. Santagostino and S. Sputore, *J. Org. Chem.*, 1999, **64**, 4537–4538.

618 Y. Venkata Durga Nageswar, K. Ramesh and K. Rakhi, *Front. Chem.*, 2022, **10**, 841751.

619 A. R. Katritzky, G. P. Savage, G. J. Palenik, K. Qian, Z. Zhang and H. D. Durst, *J. Chem. Soc., Perkin Trans 2*, 1990, 1657.

620 D. B. Dess and J. C. Martin, *J. Org. Chem.*, 1983, **48**, 4155–4156.

621 L. Weclas-Henderson, T. T. Nguyen, R. A. Hayes and J. C. Martin, *J. Org. Chem.*, 1991, **56**, 6565–6573.

622 D. B. Dess, S. R. Wilson and J. C. Martin, *J. Am. Chem. Soc.*, 1993, **115**, 2488–2495.

623 D. B. Dess and J. C. Martin, *J. Am. Chem. Soc.*, 1991, **113**, 7277–7287.

624 V. Satam, A. Harad, R. Rajule and H. Pati, *Tetrahedron*, 2010, **66**, 7659–7706.

625 A. Duschek and S. F. Kirsch, *Angew.Chem. Int. Ed.*, 2011, **50**, 1524–1552.

626 T. Wirth, *Angew. Chem. Int. Ed.*, 2001, **40**, 2812–2814.

627 A. P. Thottumkara and T. K. Vinod, *Tetrahedron Lett.*, 2002, **43**, 569–572.

628 A. Kommreddy, M. S. Bowsher, M. R. Gunna, K. Botha and T. K. Vinod, *Tetrahedron Lett.*, 2008, **49**, 4378–4382.

629 R. D. Richardson, J. M. Zayed, S. Altermann, D. Smith and T. Wirth, *Angew.Chem. Int. Ed.*, 2007, **46**, 6529–6532.

630 A. Y. Koposov, D. N. Litvinov, V. V. Zhdankin, M. J. Ferguson, R. McDonald and R. R. Tykwinski, *Eur. J. Org. Chem.*, 2006, **2006**, 4791–4795.

631 M. Uyanik, M. Akakura and K. Ishihara, *J. Am. Chem. Soc.*, 2009, **131**, 251–262.

632 S. De Munari, M. Frigerio and M. Santagostino, *J Org Chem*, 1996, **61**, 9272–9279.

633 J. J. Parlow, B. L. Case and M. S. South, *Tetrahedron*, 1999, **55**, 6785–6796.

634 V. V. Zhdankin, D. N. Litvinov, A. Y. Koposov, T. Luu, M. J. Ferguson, R. McDonald and R. R. Tykwinski, *Chem Comm*, 2004, 106.

635 V. V. Zhdankin, A. Y. Koposov, D. N. Litvinov, M. J. Ferguson, R. McDonald, T. Luu and R. R. Tykwinski, *J. Org. Chem.*, 2005, **70**, 6484–6491.

636 R. V. Kupwade, *Mini Rev. Org. Chem.*, 2020, **17**, 946–957.

637 M. M. Heravi, T. Momeni, V. Zadsirjan and L. Mohammadi, *Curr. Org. Synth.*, 2021, **18**, 125–196.

638 J. N. Moorthy, K. Senapati, K. N. Parida, S. Jhulki, K. Sooraj and N. N. Nair, *J. Org. Chem.*, 2011, **76**, 9593–9601.

639 J. N. Moorthy and K. N. Parida, *J. Org. Chem.*, 2014, **79**, 11431–11439.

640 J. T. Su and W. A. Goddard, *J. Am. Chem. Soc.*, 2005, **127**, 14146–14147.

641 S. Seth, S. Jhulki and J. N. Moorthy, *Eur. J. Org. Chem.*, 2013, **2013**, 2445–2452.

642 M. S. Yusubov, D. Yu. Svitich, A. Yoshimura, V. N. Nemykin and V. V. Zhdankin, *Chem. Commun.*, 2013, **49**, 11269.

643 M. S. Yusubov, N. S. Soldatova, P. S. Postnikov, R. R. Valiev, A. Yoshimura, T. Wirth, V. N. Nemykin and V. V. Zhdankin, *Chem. Commun.*, 2019, **55**, 7760–7763.

644 R. Rimi, S. Soni, B. Uttam, H. China, T. Dohi, V. V. Zhdankin and R. Kumar, *Synthesis*, 2022, **54**, 2731–2748.

645 V. V. Zhdankin, J. T. Smart, P. Zhao and P. Kiprof, *Tetrahedron Lett*. 2000, **41**, 5299-5302

646 V. V. Zhdankin, A. Y. Koposov, B. C. Netzel, N. V. Yashin, B. P. Rempel, M. J. Ferguson and R. R. Tykwinski, *Angew. Chem. Intl. Ed.*, 2003, **42**, 2194-2196.

647 U. Ladziata, J. Carlson, V. V. Zhdankin, *Tetrahedron Lett*. 2006, **47**, 6301−6304.