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REVIEW

Diaryliodonium(III) Salts in One-Pot Double Functionalization of C–I^{III} and *ortho* C–H Bonds

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Since the 1950s, diaryliodonium(III) salts have been demonstrated to participate in various arylation reactions, forming aryl–heteroatom and aryl–carbon bonds. Incorporating the arylation step into sequential transformations would provide access to complex molecules in short steps. This focus review summarizes the double functionalization of carbon–iodine(III) and *ortho* carbon–hydrogen bonds using diaryliodonium(III) salts. This involves arylation/intramolecular rearrangement, arylation followed by electrophilic aromatic substitution, three-component [2 + 2 + 2] cascade annulation, sequential metal-catalyzed arylations, and double functionalization via aryne formation.

1. Introduction

1-1. General properties of diaryliodonium(III) salts

Diaryliodonium salts ($Ar^1Ar^2I^+X^-$, diaryl-λ^3-iodanes) are hypervalent iodine(III) compounds, which are generally air- and moisture-stable salts that have been employed as arylating agents in organic synthesis.[1,2] Various aryl–heteroatom and aryl–carbon bonds can be constructed via transition-metal-free and -catalyzed transformations of diaryliodonium salts.

The structures of these compounds have a trigonal bipyramidal geometry and exhibit a T-shape, wherein two aryl groups are arranged on each of the equatorial and apical positions (Figure 1a). The iodine(III) centre shares a hypervalent three-centre-four-electron bond with the counter anion and one aryl group on each of the apical positions. The nonbonding HOMO of the hypervalent bond contains a node at the central iodine atom (Figure 1b); therefore, the iodine centre of diaryliodonium salts have electrophilic properties.

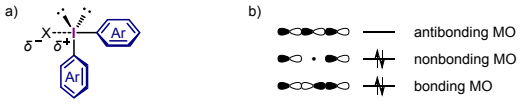

Figure 1. General structure of diaryliodonium salts

Various synthetic methods have been developed to obtain diaryliodonium salts. Some of typical preparation methods for diaryliodonium salts constitute dehydrative condensation of electron-rich arenes with hypervalent iodine(III) species, such as (diacetoxyiodo)arenes, [hydroxy(tosyloxy)iodo]arenes, and iodosoarenes.[1a,3] Metal–iodine(III) exchange is also effective approach to the synthesis of various diaryliodonium salts, wherein organometallic aryl species, including aryllithium, arylsilane, arylstannane, arylboronic acid, and arylboronate are employed.[4] The combination with iodine(III) transfer reagents provides useful access to symmetrical diaryliodonium salts bearing the same aryl groups.[5] Based on these aryl–iodine(III) bond formations, one-pot methods for the preparation of diaryliodonium salts have been well developed, which are recognized as robust methods. These involve the oxidation of aryl iodides with appropriate oxidants followed by introduction of arenes.[6,7] The combination of arenes with elemental iodine has also been employed for one-pot synthesis.[8]

1-2. Utilization of diaryliodonium salts to arylation reactions

The diaryliodonium salts react with nucleophiles to generate the Nu–I^{III} intermediate via ligand exchange with the counter anion (Scheme 1a). Subsequent ligand coupling of the nucleophiles with the aryl group at the equatorial position affords the corresponding arylation products **1**, owing to the high leaving group ability of aryliodide. Beringer and co-workers performed the reactions of diphenyliodonium salts with various nucleophiles in the 1950s.[1b] After their pioneering work, several groups have developed arylation reactions of a wide range of nucleophiles with diaryliodonium salts under transition-metal-free conditions. Functionalized arenes, such as aryl ethers,[9] esters,[9b,10] amines,[11] amides,[12] azides,[13] and fluorides[14] are synthesized using diaryliodonium salts via ligand exchange followed by ligand coupling. Carbon nucleophiles, such as ketones, esters, and nitroalkanes, can be employed for C–C bond formations.[15] Biaryls are also synthesized in the absence

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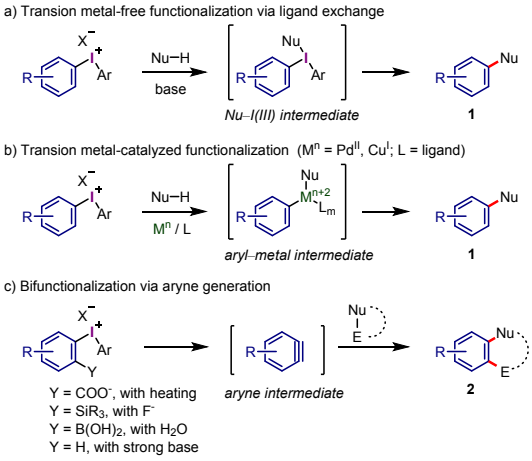


Scheme 1. Various transformations of diaryliodonium salts

of transition metals via single electron transfer (SET) or nucleophilic substitution reactions.[16]

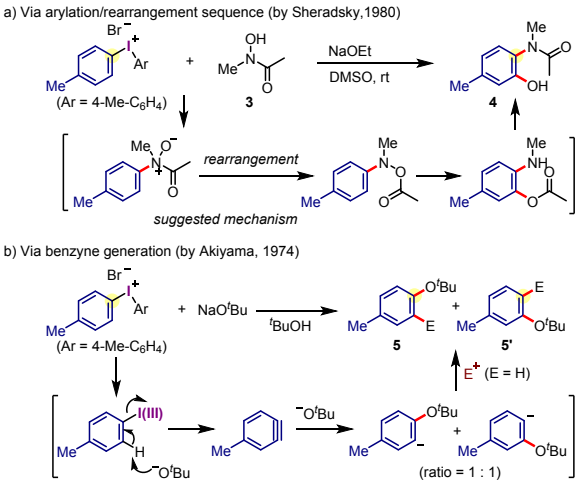
Since the mid-2000s, biaryl synthesis enabling C–C bond formation has been developed by the Sanford and Gaunt groups using palladium and copper catalysts, respectively (Scheme 1b).[17,18] In these reactions, the generation of high valent metal species, such as aryl–palladium(IV) and aryl–copper(III), via the oxidation of palladium(II) or copper(I) by diaryliodonium salts have been proposed. The high-valent aryl–metal intermediates undergo reductive elimination to afford the desired biarly products **1**. On the other hand, the C–N bond formation of diaryliodonium salts with *N*-heterocyclic arenes was achieved via a transition-metal-catalyzed coupling reaction.[19]

In addition, diaryliodonium salts serve as aryne precursors when an appropriate activating group is attached at the *ortho* position of the iodonium(III) group (Scheme 1c).[20,21–23] Various combinations of aryne generation methods have been reported, such as the application of carboxylate with heating,[21] silyl groups in conjunction with fluoride anions,[22] and boronic acids in the presence of water.[23] Diaryliodonium salts without activating groups at the *ortho* position also serve as aryne precursors when subjected to *ortho*-deprotonation by a strong base.[24–26] Thus generated aryne intermediates would react with various trapping reagents to afford the corresponding *ortho*-bifunctionalized arenes **2**.

The above-mentioned synthetic methods provide access to various diaryliodonium salts ($Ar^1Ar^2I^+X^-$). However, symmetrical diaryliodonium salts ($Ar^1 = Ar^2$) containing the extremely electron-rich, -poor, or sterically hindered aromatic rings are difficult to prepare. In contrast, unsymmetrical diaryliodonium salts ($Ar^1 \neq Ar^2$) bearing these aryl groups are relatively accessible. The chemoselectivity of the arylation strongly depend on the nature of introduced aryl groups, including electron inductive and steric effects.[27] To control the reactivity and unified chemoselectivity of the arylation, auxiliary aryl groups, such as thienyl,[28] anisyl,[29] trimethoxyphenyl (TMP),[30] and mesityl (Mes) groups[31] have been employed as aryl groups in diaryliodonium salts. These aryl groups serve as inert dummy ligands during the arylation reaction, and bond formation proceeds with the opposite aryl groups.

1-3. Double functionalization of C–I^{III} and *ortho* C–H bonds

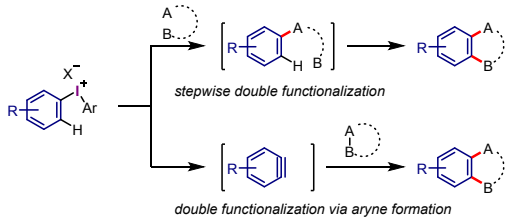
Diaryliodonium salts serve as electrophiles in the arylation reactions of various nucleophiles. Sequential transformations after the arylations produce highly functionalized aryl compounds. For example, Sheradsky et al. reported in 1980 that a diaryliodonium salt reacted with *N*-hydroxy-*N*-methylacetamide (**3**) to afford *N*-(2-hydroxyphenyl)-*N*-methyl-acetamide (**4**) instead of *N*-phenoxy-*N*-methylacetamide, which was unexpected (Scheme 2a).[32] In this reaction, the authors suggested that *N*-arylation occurred initially followed by rearrangement to afford the final product, although the other mechanisms involving radical or aryne formations can be also acceptable. The nucleophiles are designed such that they provide a double functionalization system through an arylation–rearrangement sequence with simple diaryliodonium salts.



Scheme 2. Early examples for *ortho* C-H bond functionalization of diaryliodonium salt

Arylation using diaryliodonium salts typically produces regioismers (**5** and **5'**) in the presence of a strong base, wherein the aryne generation competes with direct arylation (Scheme 2b).[24] In this reaction, the aryne intermediate is generated via *ortho* C–H deprotonation despite the absence of an activating group at the *ortho* position of the iodonium group. Controlling aryne generation in the presence of an appropriate trapping reagent would produce double-functionalized arenes.

In this focus review, we summarize various double functionalization systems using diaryliodonium salts, wherein the C–I^{III} and *ortho* C–H bonds are converted to C–C or C–heteroatom bonds (Scheme 3). These transformations construct highly functionalized arenes from relatively simple diaryliodonium salts, which can contribute to the synthesis of organic functional materials and natural products bearing complicated skeletons.



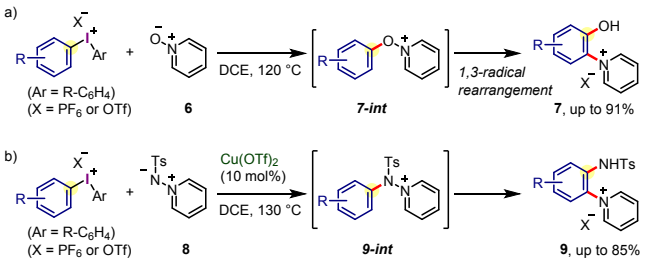
Scheme 3. Double functionalization of C-I^{III} and/or *ortho* C-H bonds

2. Stepwise double functionalization

2-1. Arylation/rearrangement sequence

As shown in Scheme 2a, the reaction of diaryliodonium salts with hydroxylamine affords double-functionalized products through nucleophilic substitution followed by rearrangement. Various hydroxylamines have been employed to obtain the corresponding double functionalization products via a similar reaction pathway.

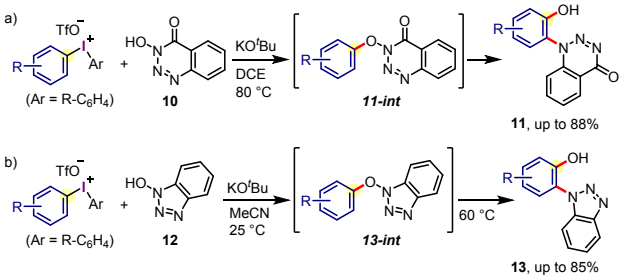
Pyridine *N*-oxides (**6**) were employed as hydroxylamines to achieve double functionalization (Scheme 4a).[33] Heating a mixture of diphenyliodonium hexafluorophosphate and pyridine *N*-oxide at 120 °C afforded 2-pyridinium phenol hexafluorophosphate (**7**), which was converted to a stable betaine upon treatment with K_2CO_3. The crystal structure, confirmed by X-ray diffraction, showed that the N–O bond was cleaved with the insertion of a phenylene group. According to the mechanism proposed by the authors, the reaction proceeds via arylation followed by a 1,3-radical rearrangement. After the *O*-arylation, the N–O bond of ***7-int*** was homolytically cleaved under heating conditions to afford a pyridine cationic radical along with a phenoxy radical. Rearrangement of the radical at the *ortho* carbon atom followed by bond formation with the pyridine cationic radical furnishes the double-functionalized products. The authors also performed density functional theory (DFT) calculations to confirm the proposed mechanism.



Scheme 4. Arylation followed by [1,3]-rearrangement sequence

The pyridine *N*-amidate (**8**) also underwent a similar reaction at 120 °C, which led to the formation of the 2-pyridinium aniline derivative (**9**) (Scheme 4b).[34] The corresponding arylation intermediate ***9-int*** was isolated by performing the reaction at a lower temperature of 80 °C in the presence of a copper catalyst. Treatment of the intermediate at 130 °C furnished the rearranged product. The authors demonstrated the reactions of various combinations of diaryliodonium salts and pyridinium *N*-amidate in the presence of a copper catalyst to afford 2-pyridinium aniline derivatives.

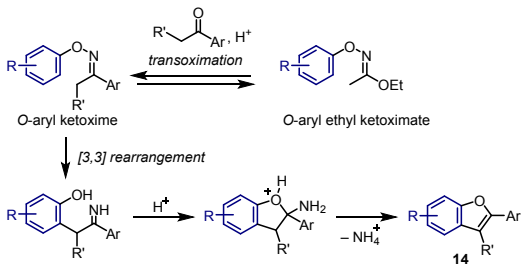
The Su and Mo group employed *N*-hydroxybenzotriazinone and *N*-hydroxybenzotriazole as hydroxylamines, which undergo the arylation of the hydroxy group followed by [3,3]-rearrangement to afford double functionalization products.[35] *N*-Hydroxybenzo[1,2,3]triazin-4(3*H*)-one (**10**) reacted with diaryliodonium triflate at 80 °C in the presence of KO^{t}Bu to produce *N*-aryl benzo[1,2,3]-triazin-4(1*H*)-one (**11**) (Scheme 5a).[35a] The reaction when performed at a lower temperature of 50 °C, generated the *O*-arylation product ***11-int***, which was converted to phenol derivatives **11** by treatment at 80 °C. The authors also performed mechanistic studies. The reaction proceeds even in the presence of radical trap TEMPO, which suggests that a radical process is not involved. The crossover reaction indicates that N–O bond cleavage occurs via an intramolecular [3,3]-rearrangement.



Scheme 5. Arylation followed by [3,3]-rearrangement sequence

In the case of *N*-hydroxybenzotriazole (**12**), the arylation of the hydroxy group proceeded smoothly even at room temperature (Scheme 5b).[35b] The *O*-arylation product ***13-int*** was converted to *N*-(2-hydroxyaryl)-benzotriazoles (**13**) via a [3,3]-rearrangement at 60 °C. In this reaction, [1,3]-rearrangement products were also generated as side products. The authors also demonstrated a one-pot reaction for sequential *O*-arylation and [3,3]-rearrangement.

O-Arylketoximes equipped with α-hydrogen atoms also lead to [3,3]-rearrangement, which generates the corresponding ketoimine bearing a 2-phenol moiety at the α-position, which then converts readily to benzofuran derivatives **14** via subsequential cyclization in the presence of an acid (Scheme 6).

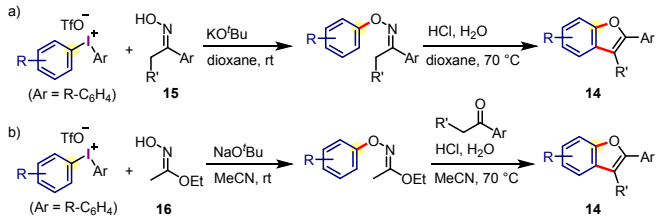


Scheme 6. Benzofuran synthesis via [3,3]-rearrangement/ cyclization sequence

The starting *O*-arylketoximes can be prepared via the *O*-arylation of ketoximes. Ethyl hydroxamate also provides *O*-arylketoxime species via *O*-arylation of ethyl acetohydroxamate, followed by transoximation with ketones in

the presence of an acid. The Kürti,[36] Togo,[37] and Olofsson groups[38] independently reported the transition-metal-free synthesis of benzofuran, which involves the [3,3]-rearrangement/cyclization of *O*-arylketoximes generated via *O*-arylation of oxime derivatives with diaryliodonium salts.

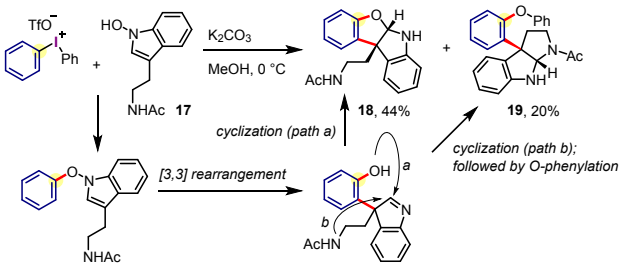
Kürti and coworkers demonstrated the *O*-arylation of ketoxime **15** or ethyl acetohydroxamate **16** with various diaryliodonium salts in the presence of KO^{t}Bu (Scheme 7).[36] The resulting arylation products were transformed to the corresponding benzofurans **14** via a [3,3]-rearrangement/cyclization process in the presence of HCl. In this study, the authors applied the one-pot synthesis of benzofuran derivatives via *O*-arylation of ketoximes.



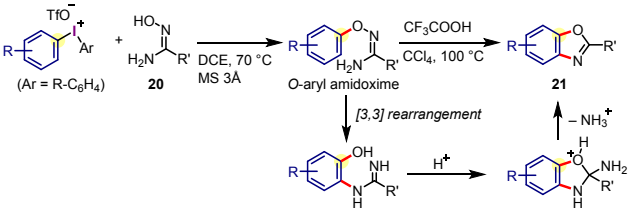
Scheme 7. Benzofuran synthesis induced by *O*-arylation of oxime derivatives (two-step procedure)

Diaryliodonium triflate reacted with ketoxime in the presence of KO^{t}Bu at room temperature to generate an *O*-aryl ketoxime, which underwent a [3,3]-rearrangement/cyclization sequence in the presence of HCl at 70 °C to afford the final products. The Togo group focused on the one-pot synthesis of benzofuran derivatives **14** using ketoximes **15** as the nucleophiles (Scheme 7a).[37] The authors synthesized various 2-arylbenzofurans via *O*-arylation of a ketoxime **15** with diaryliodonium triflate, followed by treatment with HCl at 70 °C in a one-pot sequential procedure. On the other hand, the Olofsson group employed ethyl acetohydroxamate **16** as a starting material for the one-pot synthesis of benzofuran **14** (Scheme 7b).[38] After the reaction of diaryliodonium salts with ethyl acetohydroxamate **16** in the presence of NaO^{t}Bu at room temperature for 0.5 h, the reaction mixture was treated with ketones in the presence of HCl at 70 °C to afford the corresponding benzofurans.

N-Hydroxyindoles **17** can also participate in *O*-arylation with diaryliodonium salts, which induces the following [3,3]-rearrangement/cyclization sequence to afford benzofuro-indolines **18** (Scheme 8).[39] Vincent and coworkers. demonstrated that diaryliodonoum triflate reacted with *N*-hydroxyindole in the presence of K_2CO_3 to produce the corresponding benzofuro-indolines **18** (*path a*). In this reaction, pyrroloindolines **19** were also formed via side-chain attacks during cyclization (*path b*) followed by *O*-phenylation. When an amidoxime **20** is used as an oxime, the corresponding benzoxazoles **21** can be obtained via similar sequential reactions, involving C–N bond formation induced by [3,3]-rearrangement (Scheme 9).[40] Mo and coworkers reported that amidoximes **20** reacted with diaryliodonium triflates to generate *O*-arylation products at 70 °C even under base-free conditions. The obtained *O*-aryl amidoximes were treated with



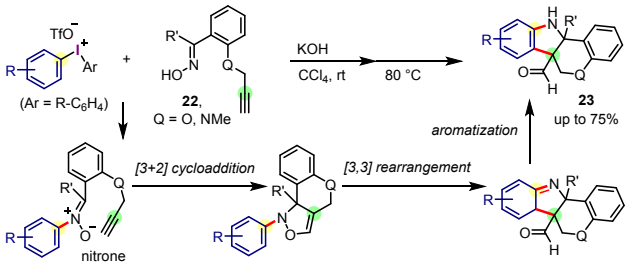
Scheme 8. Benzofuroindoline synthesis induced by *O*-arylation of *N*-hydroxyindole



Scheme 9. Benzoxazole synthesis induced by *O*-arylation of oxime derivatives (two-step procedure)

trifluoroacetic acid to transform them to benzoxazoles **21** through [3,3]-rearrangement/cyclization. In this study, however, the one-pot synthesis of benzoxazoles was not demonstrated.

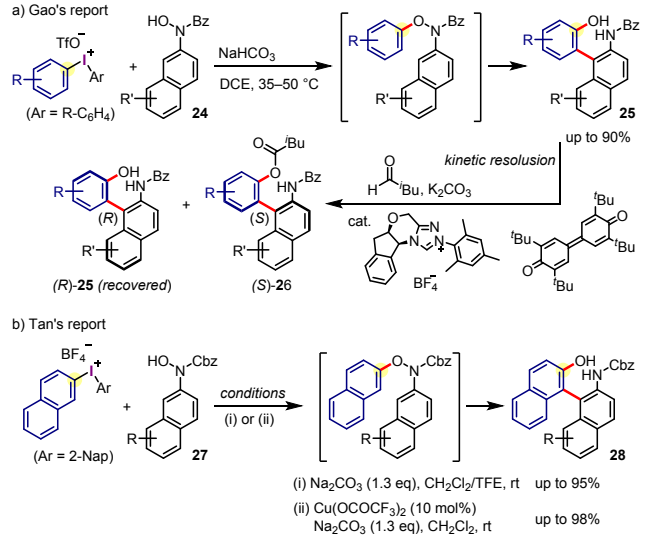
The Su and Mo group demonstrated the construction of 2,3-quaternary fused indolines containing a tetracyclic skeleton **23**, which involves sequential reactions triggered by the arylation of the ketoxime (**22**) (Scheme 10).[41] The authors prepared alkynyl-tethered oximes **22** as starting materials and subsequently treated them with diphenyliodonium triflate in the presence of KOH. In this case, arylation occurred at the nitrogen atom to generate a nitrone, accompanied by 2,3-fused indoline. After optimizing the reaction conditions, they found that the two-step procedure improved the reaction yield: an alkynyl-tethered oxime was treated with KOH in CCl_4 at room temperature and then heated at 80 °C. In this reaction, an alkynyl-tethered nitrone was initially generated by *N*-arylation, which underwent [3 + 2] cycloaddition followed by [3,3]-rearrangement followed by rearomatization to furnish the final products **23**. Various 2,3-quaternary fused indolines can be synthesized via such elegant sequential reactions.



Scheme 10. Construction of 2,3-quaternary fused indolines via *O*-arylation of oxime derivatives

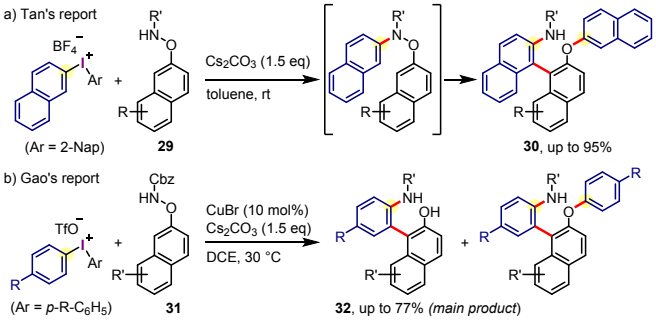
O-Arylation of *N*-hydroxyaniline (**24** and **27**) proceeds with diaryliodonium salt to generate *N*,*O*-diarylhydroxylamine, which undergoes [3,3]-rearrangement to afford a highly functionalized biphenyl with both hydroxy and amino groups on each phenyl ring (**25** and **28**) (Scheme 11).[42,43] This transformation can be applied to the transition-metal-free synthesis of 2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN)-type ligands as described below.

Gao and coworkers performed the reaction of *N*-hydroxynaphthylamine **24** with diaryliodonium salts in the presence of $NaHCO_3$ at 35–50 °C to afford the corresponding biaryls **25**, including NOBIN-type ligands (Scheme 11a).[42] In this case, the [3,3]-rearrangement occurred smoothly under mild conditions. The obtained racemic biaryls **25** were successfully resolved by NHC-catalyzed kinetic resolution with isovaleraldehyde to obtain enantioenriched NOBIN-type biaryls. The authors synthesized various NOBIN-type biaryls using this sequential protocol. The resulting chiral biaryls were further transformed into various biaryl derivatives, which can be used as chiral ligands. In the same year, the Tan and Li group reported the construction of NOBIN-type biaryls involving *O*-arylation and [3,3]-rearrangement under similar conditions (Scheme 11b).[43a] The authors found that the combination of diaryliodonium tetrafluoroborate, Na_2CO_3, and a mixed solvent of dichloromethane and trifluoroethanol (5:1) improved the reaction yield. The preparation of enantioenriched NOBIN was also performed via NHC-catalyzed kinetic resolution or in the presence of a chiral auxiliary, albeit with one example. Furthermore, the addition of a copper catalyst was effective for the arylation step, accelerating the sequential reaction.[43b]

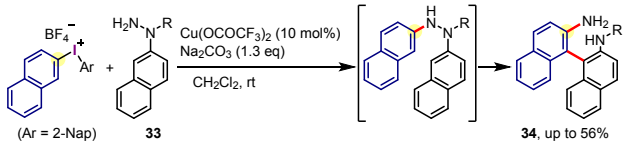


Scheme 11. Synthesis of NOBIN-type biaryls induced by *O*-arylation of *N*-hydroxy-2-aminonaphthol

The reaction of *O*-naphthylhydroxylamines (**29** and **31**) with diaryliodonium salts also produces NOBIN-type biaryls via *N*-arylation followed by [3,3]-rearrangement (Scheme 12).[43a] In this reaction, the hydroxy groups in the generated biaryls were arylated again to afford a NOBIN-type ligand bearing naphthyl ether **30** (Scheme 12a). On the other hand, Gao reported that the second arylation was partially suppressed by the addition of a copper catalyst to afford a NOBIN-type ligand bearing free hydroxy group **32** (Scheme 12b).[44] In a similar manner, 1,1′-binaphthyl-2,2′-diamine (BINAM)-type ligands **34** were successfully synthesized using *N*-naphthylhydrazines (**33**) as nucleophiles via an *N*-arylation/[3,3]-rearrangement sequence, which was performed by Tan and Xiang's group (Scheme 13).[43b]



Scheme 12. Synthesis of NOBIN-type biaryls induced by *N*-arylation of *O*-arylhydroxylamine

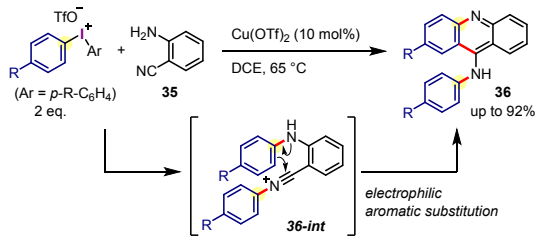


Scheme 13. Synthesis of BINAM-type biaryls induced by *N*-arylation of *N*-arylhydrazine

2-2. Arylation followed by electrophilic aromatic substitution

Electrophilic aromatic substitution can also be a key reaction for the second step in the double functionalization of the C–I/*ortho* C–H bonds of diaryliodonium salts. In this section, the transformation of diaryliodonium salts via arylation followed by intramolecular electrophilic aromatic substitution is discussed. Electrophilic substitution to afford the corresponding cyclization product occurs after the ligand coupling when the electrophilic moiety is attached to the appropriate position.

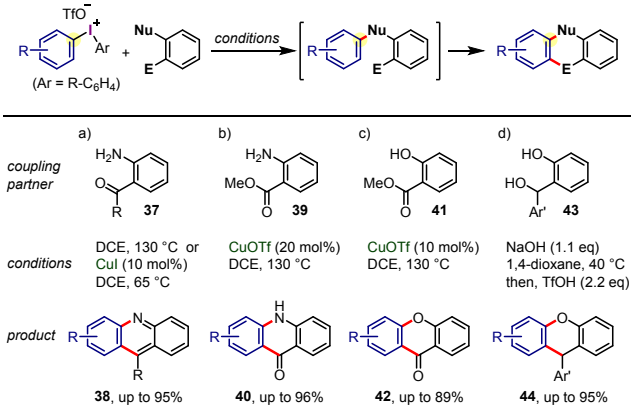
Chen and coworkers reported that the reaction of 2-cyanoaniline (**35**) with 2 equivalents of diarylidonium triflate in the presence of a $Cu(OTf)_2$ catalyst produced 9-aminoacridine derivatives **36** at 65 °C (Scheme 14).[45] Both the amino and nitrile



Scheme 14. Synthesis of 9-aminoacridine via amination/ electrophilic substitution sequence

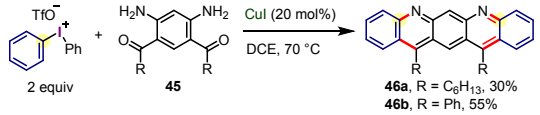
nitrogen atoms of 2-cyanoaniline are initially arylated in the presence of a copper catalyst to generate ***36-int***, and then intramolecular electrophilic substitution with the generated nitrilium cation proceeds to afford the cyclized product **36**. When the reaction was performed using 2 equivalents of 2-cyanoaniline, the corresponding quinazoline derivative was obtained.

2-Acylanilines, such as 2-aminophenyl ketones **37** and 2-aminobenzoates **39**, undergo a similar annulation via nucleophilic amination followed by intramolecular electrophilic substitution to generate acridine **38** (Scheme 15a) or 9-acridinone derivatives **40** (Scheme 15b), respectively.[46] The former reaction proceeded at 130 °C in the absence of a copper catalyst, whereas the addition of a CuI catalyst enhanced the reactivity to furnish the products even at 65 °C. On the other hand, the efficient preparation of 9-acridinones **40** requires both a copper catalyst and a high temperature of 130 °C. Xanthone derivatives **42** were also synthesized via nucleophilic etherification followed by electrophilic substitution in the presence of a copper catalyst (Scheme 15c).[47] Wang and coworkers reported the synthesis of xanthene derivatives **44** employing 2-hydroxybenzylalcohol **43** and diaryliodonium triflate via sequential nucleophilic and electrophilic substitutions (Scheme 15d).[48] In this reaction, the phenolic hydroxy group is arylated by diaryliodonium triflate in the presence of NaOH to afford the corresponding diarylmethanol derivative. Treatment of the reaction mixture with triflic acid afforded the corresponding xanthene derivative **44** via intramolecular electrophilic substitution under a one-pot sequential conditions.



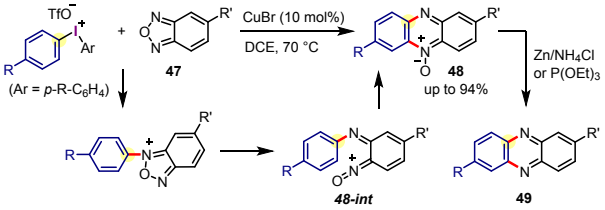
Scheme 15. Synthesis of acridine and xanthene derivatives

Utilizing the reaction of diaryliodonium salts and 2-aminophenyl ketones **45**, the Grimsdale group synthesized diazapentacene derivatives **46**, which have potential applications in organic electronics (Scheme 16).[49] Diaminodiketones **45** were reacted with 2 equivalents of diphenyliodonium triflate at 70 °C in the presence of a CuI catalyst to afford 5,7-diazapentacenes bearing hexyl (**46a**) or phenyl groups (**46b**) at positions 12 and 14.



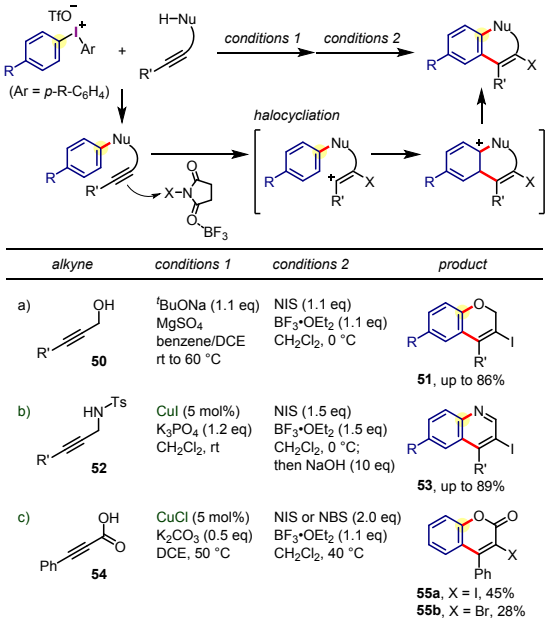
Scheme 16. Synthesis of 5,7-diazapentacene derivatives

Copper-catalyzed *N*-arylation followed by electrophilic substitution can enable the construction of phenazine derivatives **49** from benzoxadiazoles **47** (Scheme 17).[50] Benzoxadiazole **47** reacted with diaryliodonium triflate in the presence of a CuBr catalyst at 70 °C to afford phenazine *N*-oxide **48**. In the first step, one nitrogen atom of benzoxadiazole **47** is selectively arylated to generate a nitrogen cation intermediate ***48-int*** via isomerization with N–O bond cleavage. Sequential electrophilic substitution formed a phenazine skeleton **48**. The reduction of the resulting phenazine *N*-oxides **48** using Zn/NH_4Cl or $P(OEt)_3$ produces the corresponding phenazine derivatives **49**.



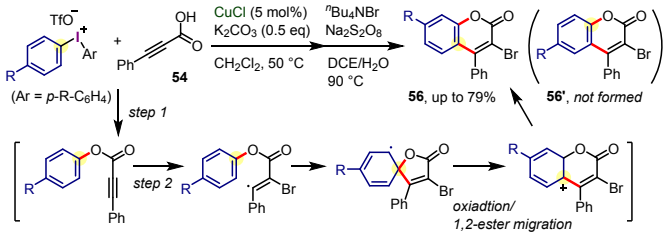
Scheme 17. Synthesis of phenazine derivative

The Togo group employed halocyclization as the second step in the double functionalization of diaryliodonium salts (Scheme 18).[51] The alkynyl moiety is introduced to the aryl group by ligand coupling, and then the resulting alkyne bearing an aryl group is converted to the cyclization product in the presence of a halogen source via halogenative electrophilic substitution.



Scheme 18. Ligand coupling/halocyclization sequence (two-step procedure)

The reaction of propargyl alcohol **50** with diaryliodonium triflate proceeded in the presence of NaO^{t}Bu to generate the corresponding aryl ether, which underwent iodocyclization upon treatment with *N*-iodosuccinimide and boron trifluoride to afford 3-iodochromene **51** (Scheme 18a).[51a] This sequential reaction can be applied in a one-pot reaction. Various chromene derivatives were synthesized based on C–I bond functionalization. In the case of propargyl amine **52**, a copper catalyst is required in the first step (Scheme 18b).[51b] The obtained phenylpropargylamine was transformed into a 3-iodoquinoline derivative **53** via iodocyclization in the presence of *N*-iodosuccinimide and boron trifluoride, followed by treatment with NaOH. The use of *N*-bromosuccinimide or *N*-chlorosuccinimide produced the corresponding bromo- and chloroquinolines. The authors also performed a one-pot transformation and further functionalization of 3-iodoquinolines. Propynoic acid **54** can also be employed for the ligand coupling, followed by halocyclization using *N*-iodosuccinimide or *N*-bromo-succinimide to afford the corresponding halocoumarins **55** (Scheme 18c).[51c] When the combination of tetrabutylammonium bromide and $Na_2S_2O_8$ was used in the bromocyclization step, the reaction proceeded via radical-mediated spirocyclization followed by 1,2-ester migration to generate **56** (Scheme 19).[52]

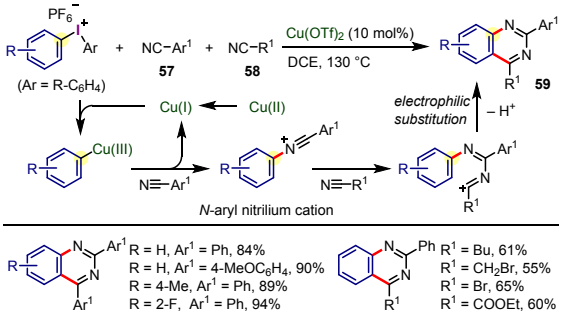


Scheme 19. Ligand coupling/halocyclization sequence via 1,2-ester migration (two-step procedure)

2-3. [2 + 2 + 2] Cascade annulation via copper-catalyzed aryl C–N bond formation

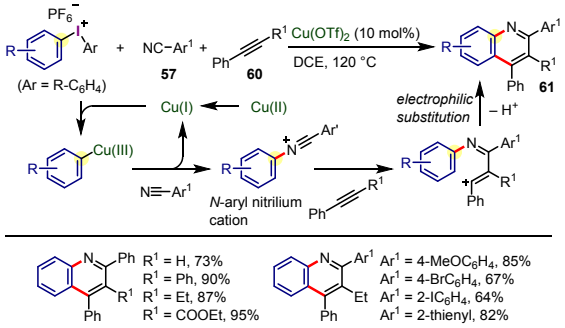
As described in the introduction section, diaryliodonium salts serve as an aryl source for hypervalent metal–aryl species, such as aryl–copper(III) intermediates, which have high electrophilicity and react with various nucleophiles. The combination of diaryliodonium salts with nitrile derivatives can generate *N*-aryl nitrilium cations in the presence of copper(II). The cationic species can be converted to cyclization products via reactions with nucleophiles, followed by intramolecular electrophilic substitution. This [2 + 2 + 2] cascade annulation using diaryliodoniumsalts with nitriles has been well investigated especially by Chen's group since 2013.

The reaction of diphenyliodonium hexafluorophosphate with 3 equivalents of benzonitrile (**57**, Ar^1 = Ph) in the presence of a catalytic amount of $Cu(OTf)_2$ afforded the corresponding quinazoline derivative, wherein two benzonitrile moieties were incorporated into the product **59** (Scheme 20).[53] Various diaryliodonium salts, aryl nitriles **57**, or aliphatic nitriles **58** have been employed. Furthermore, the authors performed a three-component reaction using two different nitriles. Diaryliodonium hexafluorophosphate and aryl nitrile **57** were stirred at 120 °C for 0.5 h, and then the reaction mixture was treated with a second nitrile **58** at 120 °C to furnish the corresponding products **59**.



Scheme 20. Quinazoline synthesis induced by [2 + 2 + 2] annulation

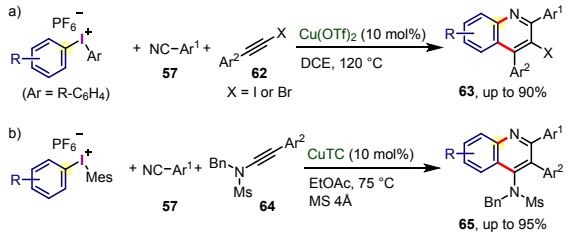
The three-component annulation reaction using diaryliodonium salts with nitriles leads to the regioselective synthesis of quinoline derivatives **61** in the presence of alkynes (Scheme 21).[54] A mixture of diphenyliodonium hexafluorophosphate, aryl nitrile **57**, phenyl acetylene **60**, and $Cu(OTf)_2$ as a catalyst at 120 °C produced 2,4-diphenylquinoline **61** in a high yield. Various diaryliodonium salts, terminal or internal alkynes, and nitriles were employed for this transformation, and highly substituted quinoline derivatives were synthesized. In this reaction, the diaryliodonium salt reacts with the nitrile in the presence of a copper catalyst to generate the *N*-aryl nitrilium cation, which is attacked by an alkyne to afford an alkenyl cation and subsequently electrophilic substitution occurs to furnish the annulation product **61**.



Scheme 21. Quinazoline synthesis induced by [2 + 2 + 2] annulation

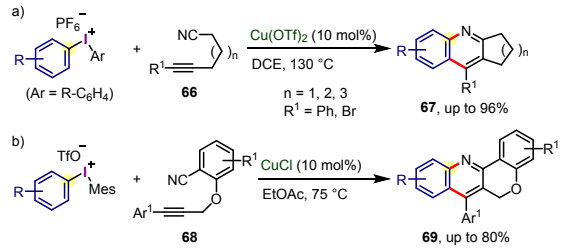
The other two groups applied the three-component [2 + 2 + 2] annulation to the synthesis of functionalized quinolines bearing halogen **63** or nitrogen substituents **65** (Scheme 22). Wang and Hu's group employed 1-halogeneted alkynes **62** to prepare 3-halogenated quinolines **63**, which can be derivatized to C-3 substituted quinolines via further transformations, such as catalytic coupling reactions (Scheme 22a).[55] Park and coworkers synthesized 4-aminoquinolines **65** using ynamides **64** as the alkyne components in the presence of a CuTC catalyst at 75 °C (Scheme 22b).[56] Furthermore, the obtained **65** were converted

to the corresponding quinolinylmethanesulfonamides via [1,3]-rearrangement.



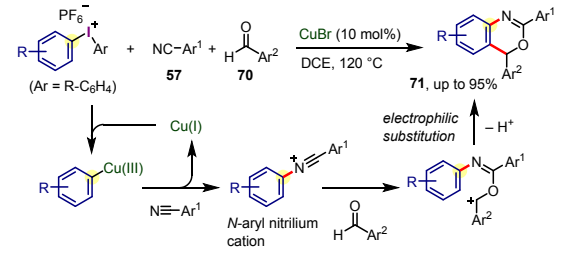
Scheme 22. Application to haloquinoline and aminoquinoline syntheses

When a diaryliodonium salt reacted with a nitrile tethered to an alkyne moiety **66**, [2 + 2 + 2] annulation proceeded to afford polycyclic quinolines **67** (Scheme 23a).[57] A substrate bearing a cyano group, 1-bromoalkyne also participates in the cascade annulation to afford the corresponding bromoquinoline, which can be further transformed into various polycyclic quinoline derivatives. On the other hand, Novák and coworkers applied the [2 + 2 + 2] annulation to chromenoquinoline synthesis (**69**) using arylpropynyloxybenzonitriles **68**, which were prepared from hydroxybenzonitrile and propargyl bromide (Scheme 23b).[58] The reaction proceeded smoothly at 75 °C in the presence of a CuCl catalyst to afford the corresponding products **69**. Various aryl groups bearing functional groups can be incorporated into chromenoquinoline derivatives.



Scheme 23. Application to polycyclic quinoline syntheses

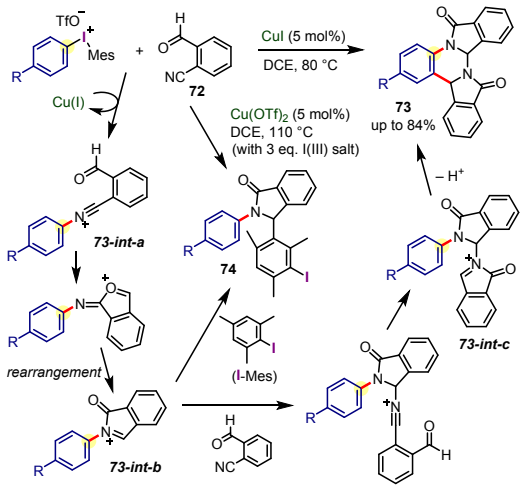
The combination of a diaryliodonium salt, aryl nitrile **57**, and aryl aldehyde **70** to produce benzo[1,3]oxazine **71** via a similar three-component [2 + 2 + 2] annulation was also reported (Scheme 24).[59] This reaction was catalyzed by CuBr at 120 °C to afford 2,4-diaryl-4*H*-benzo[*d*][1,3]oxazine derivatives **71**. *N*-Aryl nitrilium cations generated in situ react with benzaldehyde to generate benzyl cations, which undergo electrophilic substitution to accomplish the cyclization.



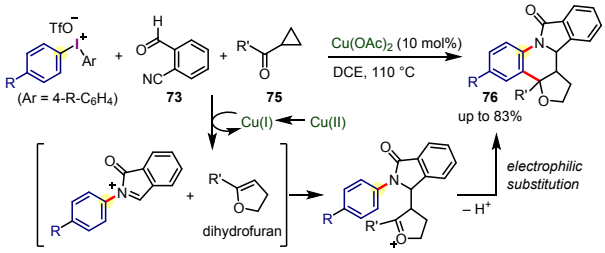
Scheme 24. Benzo[1,3]oxazine synthesis induced by [2 + 2 + 2] annulation

When 2-formylbenzonitrile **72** is employed for the reaction with diaryliodonium salts, *N*-aryl nitrilium cations are trapped intramolecularly with the formyl group to generate a cyclic cation intermediate (Scheme 25). The Miao and Li group constructed *N*-aryl isoindolinone derivatives **73** utilizing these cyclization events.[60] The reaction of diaryliodonium triflate and 2-formylbenzonitrile **72** in the presence of the CuI catalyst at 80 °C afforded the isoindolinone derivatives **73** incorporated with two folds of 2-formylbenzonitriles. The nitrilium cation ***73-int-a*** is initially generated via arylation, which undergoes intramolecular cyclization followed by rearrangement to afford the cyclic nitrogen cation species ***73-int-b***, and then the second formylbenzonitrile attacks the cation intermediate. Similarly, the sequential cyclization/rearrangement proceeds again to generate ***73-int-c***. In the final step, electrophilic substitution proceeded to afford bis(isoindolinone) derivatives **73**. When the reaction was conducted in the presence of excess diaryliodonium salt in the presence of $Cu(OTf)_2$ at 110 °C, different isoindolinone derivatives **74** were obtained, wherein the cation intermediate ***73-int-b*** was trapped by the generated iodomesitylene.

The above-mentioned cyclic nitrogen cation species could also be trapped by dihydrofuran derivatives, which are generated from cyclopropyl ketones **75** in the presence of copper catalyst (Scheme 26).[61] A three-component reaction consisting of a diaryliodonium salt, 2-formylbenzonitrile **73**, and cyclopropyl



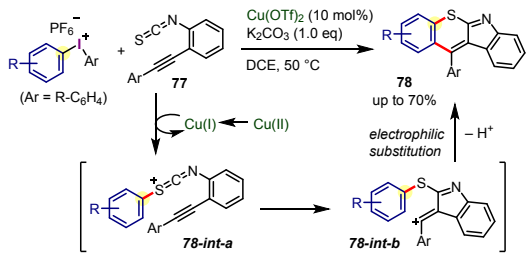
Scheme 25. Reaction of aryl(mesityl)iodonium salt with 2-formylbenzonitrile



Scheme 26. Three component annulation with dihydrofuran generated in situ

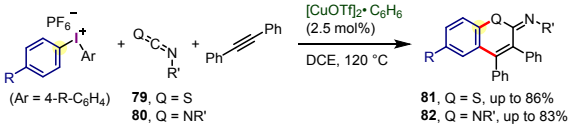
ketone **75**, proceeds in the presence of a $Cu(OAc)_2$ catalyst to afford the pentacyclic isoindolinone derivatives **76**.

In addition to the nitrile derivatives, isothiocyanate and carbodiimide participate in the copper-catalyzed [2 + 2 + 2] annulation with diaryliodonium salts and alkynes to produce the corresponding fused heterocycles (Schemes 27 and 28). The Guo and Li group synthesized tetracyclic thiochromenoindole **78** using isothiocyanate tethered with an alkynyl moiety **77** (Schemes 27).[62] The reaction proceeded at 50 °C in the presence of the $Cu(OTf)_2$ catalyst and K_2CO_3. Isothiocyanate **77** is initially arylated by the diaryliodonium salt in the presence of a copper catalyst to generate the cation intermediate ***78-int-a***, which undergoes intramolecular cyclization with an alkyne moiety to generate ***78-int-b*** via the 5-endo-trig mode rather than 6-endo-trig cyclization. Electrophilic substitution furnishes the corresponding thiochromenoindoles **78**.



Scheme 27. Thiochromenoindole synthesis induced by [2 + 2 + 2] annulation

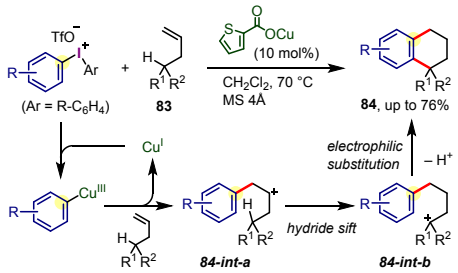
The Zhang group demonstrated a three-component [2 + 2 + 2] annulation using isothiocyanate **79** or carbodiimide **80** combined with a diaryliodonium salt and alkyne to afford **81** and **82**, respectively (Scheme 28).[63] The mixture of diaryliodonium salt, carbodiimide **80**, and alkyne was treated at 120 °C in the presence of a copper catalyst to afford the corresponding iminoquinoline **82**. Copper-catalyzed arylation initially generates an aza-allenyl cation intermediate, which reacts with the internal alkyne to afford an alkenyl cation species stabilized by the aryl ring. In the final step, electrophilic substitution proceeds to accomplish cyclization.



Scheme 28. Three component annulation with isothiocyanate or carbodiimide

2-4. Sequential metal-catalyzed arylation reactions

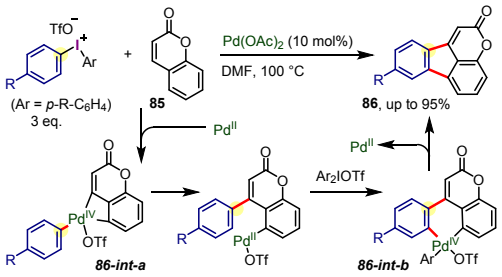
Aryl–copper(III) species generated from diaryliodonium salts and copper catalysts also participate in C–C bond formation. Gaunt has developed the catalytic carbofunctionalization of alkenes and alkynes using diaryliodonium salts, wherein the aryl–copper(III) species served as a carbon electrophile to generate key carbocation intermediates.[18c,d,e] The authors reported that the reaction of diaryliodonium triflate and terminal alkenes **83** in the presence of a copper catalyst afforded a tetralin derivative **84** via double functionalization of diaryliodonium salts (Scheme 29).[64] The copper-catalyzed arylation of the alkene moiety initially occurs to generate the carbocation intermediate ***84-int-a***, which undergoes hydride shift to transfer the cation centre generating ***84-int-b***. Finally, the electrophilic substitution reaction furnished the tetraline derivative. Overall, carbocyclization via double C–C bond formation was achieved by using diaryliodonium salt and an alkene in the presence of a copper catalyst.



Scheme 29. Copper-catalyzed carbocyclization using alkene and diaryliodonium salt

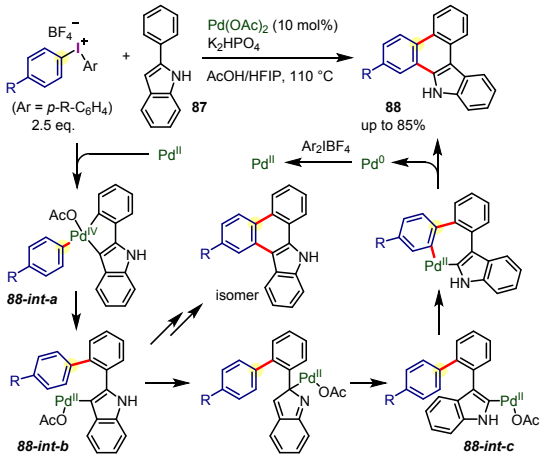
As discussed in the introduction section, the combination of a diaryliodonium salt with a palladium catalyst generates an organometallic aryl–palladium(IV) intermediate, which undergoes an arylation reaction via reductive elimination. Sequential arylation via organometallic species enables the double functionalization of the C–I/*ortho* C–H bonds of the diaryliodonium salts.

The Wang and Han group reported the reaction of coumarin **85** and 3 equivalents of diaryliodonium triflate in the presence of a palladium catalyst, which afforded the fused tetracyclic compound, 4,5-benzocoumarin **86** (Scheme 30).[65] The authors proposed that the in situ generated aryl palladium species attacks the C4 position of the coumarin with a synergetic C–H activation to afford a cyclic aryl–palladium(IV) ***86-int-a***, which undergoes reductive elimination to form an aryl–aryl bond. Sequential oxidative C–H bond activation assisted by diaryliodonium triflate generates a cyclic palladium(IV) species ***87-int-b***, which undergoes reductive elimination to furnish the double-functionalization product **87**. In the cyclization step, a palladium(0/II) catalytic cycle via C–H bond insertion can be also acceptable mechanism.



Scheme 30. Synthesis of 4,5-benzocoumarin via palladium-catalyzed C–H bond arylation

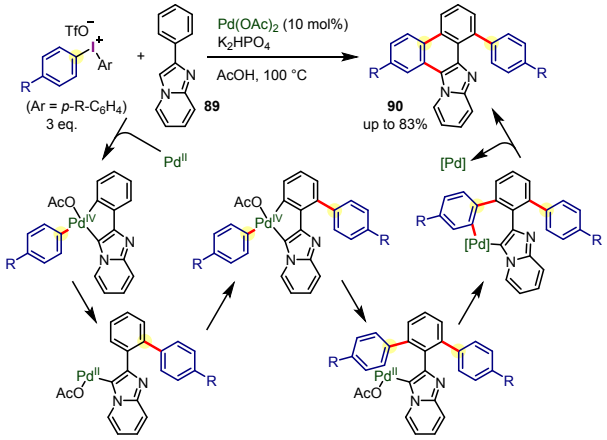
Introduction of an indole moiety enables electrophilic palladation to generate σ-indole–palladium(II) species, which undergo subsequent oxidative arylation with diaryliodonium salts via the palladium(II/IV) cycle.[17b] Jana and coworkers demonstrated the palladium-catalyzed coupling reaction of 2-phenylindole **87** and diaryliodonium triflate to achieve sequential arylation/cyclization affording pentacyclic arenes **88** (Scheme 31).[66] After electrophilic palladation, C–H bond activation occurs at the phenyl group in the presence of the diaryliodonium salt to generate a cyclic aryl–palladium(IV) intermediate ***89-int-a***, which underwent reductive elimination to introduce the aryl group. The generated organometallic palladium(II) species ***89-int-b*** undergoes sequential rearrangement to furnish ***89-int-c***. The authors suggested that subsequent C–H bond insertion generate a cyclic palladium(II) intermediate ***89-int-d***, and then reductive cyclization proceeds to form the corresponding product **89**. When the second palladacycle generation occurs faster than the rearrangement, a regioisomeric product is obtained. It is also possible that the final cyclization proceeds through a palladium(II/IV) catalytic cycle promoted with the aid of diaryliodonium salt.



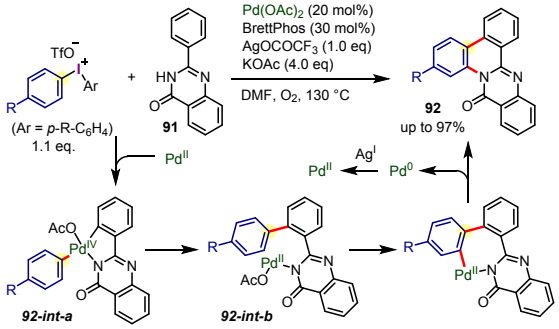
Scheme 31. Sequential C–H bond arylation/cyclization using indole derivative

In the case of imidazopyridine **89**, two aryl groups were introduced before the cyclization to achieve sequential triple C–C bond formation, which was performed by Han and Wang's group (Scheme 32).[67] Similar to the report of Jana, double arylation initially occurs via sequential electrophilic palladation, oxidative cyclopalladation, and reductive elimination. Subsequently, dehydrogenative cyclization via C–H bond activation leads to the final product **90**.

Park and Hong employed a 4-quinazolinone derivative **91** as a directing group to induce C–H bond palladation (Scheme 33).[68] The electrophilic palladation of the nitrogen atom followed by oxidative C–H bond activation generates the palladacyclic intermediate ***92-int-a***. Reductive elimination of the palladium(IV) species leads to aryl–aryl bond formation generating ***92-int-b***. The authors proposed that subsequent cyclization proceeds via a palladium(0/II) catalytic cycle to afford the π-extended product **92**, although cyclization via a palladium(II/IV) catalytic cycle combined with a silver oxidant cannot be ruled out.

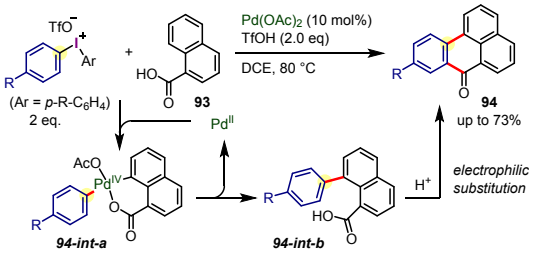


Scheme 32. Sequential double C–H bond arylation/cyclization using indole derivative



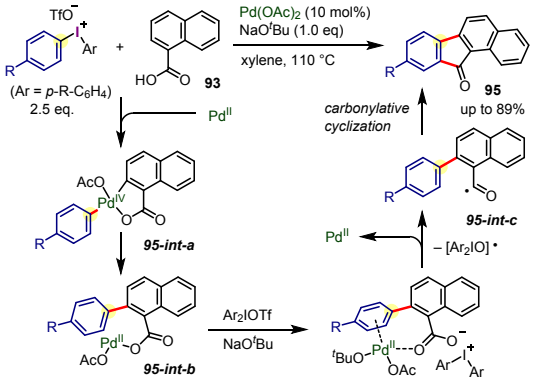
Scheme 33. Sequential C–H bond arylation/cyclization using 4-quinazolinone derivative

Carboxylic acid also serves as a directing group for the C–H palladation step (Schemes 34 and 35).[69,70] Han and coworkers reported the reaction of diaryliodonium triflate and 1-naphthoic acid **93** producing benzanthrone derivatives **94** in the presence of a palladium catalyst and triflic acid (Scheme 35).[69] In this reaction, C–H bond palladation occurs at the C8 position rather than at the C2 position to generate a cyclic palladium(IV) species ***94-int-a***. The second C–C bond formation proceeds through intramolecular electrophilic substitution of ***94-int-b*** induced by triflic acid.



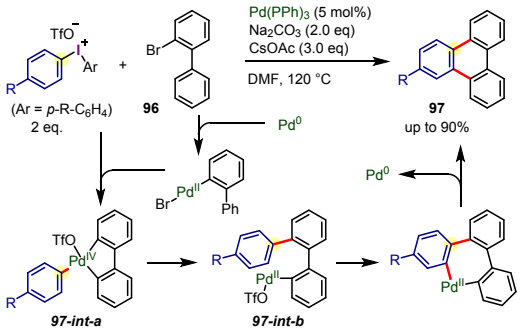
Scheme 34. Sequential C–H bond arylation/cyclization using naphthoic acid via electrophilic substitution

Under basic conditions, C–H bond palladation occurs at relatively inert C2 position of 1-naphthoic acid. The use of NaO^{t}Bu instead of triflic acid afforded fluorenone derivatives **95** (Scheme 35).[70] The authors proposed that an acyl radical (***95-int-c***) is the reaction intermediate, which is generated via ***95-int-b*** assisted by NaO^{t}Bu and diaryliodonium triflate. Sequential carbonylative cyclization furnishes the final product **95**.



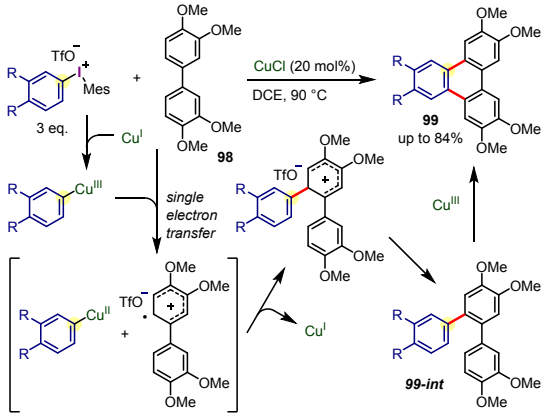
Scheme 35. Sequential C–H bond arylation/cyclization using naphthoic acid via acyl radical

The oxidative addition of aryl bromide also induces palladacycle formation even in the absence of directing groups (Scheme 36). The combination of diaryliodonium triflate and 2-bromobiphenyl **96** afforded triphenylene **97** in the presence of a Pd(PPh$_3$)$_4$ catalyst.[71] The cyclic palladium(IV) intermediate ***97-int-a*** is generated via oxidative addition, followed by oxidative C–H bond activation by a diaryliodonium salt, which undergoes reductive elimination to generate ***97-int-b***. Subsequently, dehydrogenative cyclization via palladium-catalyzed C–H bond activation proceeds to generate the final product **97**. In this reaction, the authors propose that the sequential C–C bond formation involves the palladium(0/II/IV) catalytic cycle.



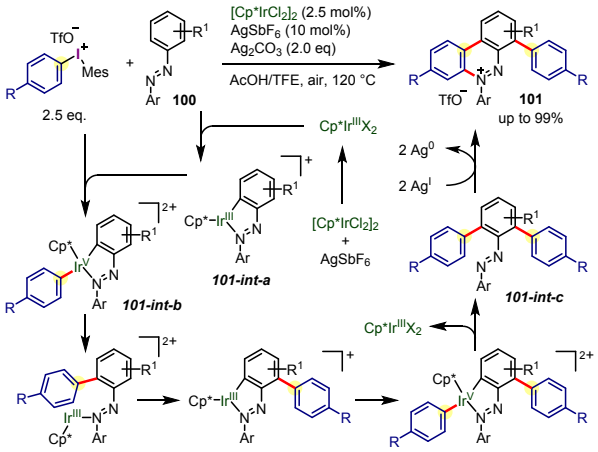
Scheme 36. Synthesis of triphenylene via sequential palladium-catalyzed arylations

The Xiang and Feng group also achieved triphenylene synthesis via the double functionalization of diaryliodonium salt using a copper catalyst, wherein electron-rich biphenyls **98** were employed as coupling partners (Scheme 37).[72] The authors proposed that the reaction proceeds via a SET mechanism: the copper(I) catalyst is oxidized by the diaryliodonium salt to generate a copper(III) intermediate, which serves as the oxidant for the electron-rich biaryl **98** to induce the first C–H bond arylation. The formed terphenyl ***99-int*** is further oxidized by the copper(III) intermediate to convert it into the final triphenylene product **99**.



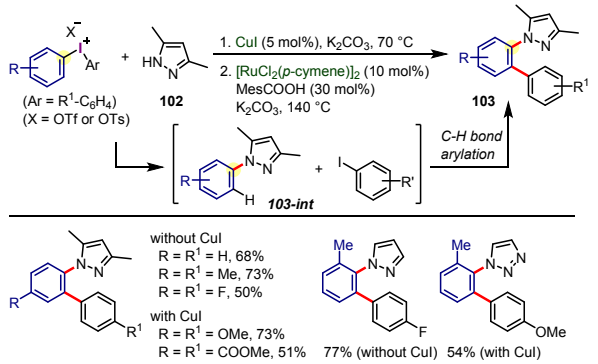
Scheme 37. Synthesis of triphenylene via sequential copper-catalyzed arylations

The You group employed an iridium catalyst for the double functionalization of C–I and C–H bonds of diaryliodonium triflate using azobenzene **100** as the coupling partner in the presence of a silver oxidant (Scheme 38).[73] The azo group serves as a directing group for C–H metalation to generate a cyclic iridium(III) intermediate ***101-int-a***[74] from azoarene **100** with iridium(III) species formed in situ. The diaryliodonium salt oxidizes the iridium(III) species to afford cyclic iridium(V) intermediates ***101-int-b***, which undergo reductive elimination to form aryl–aryl bonds. Likewise, the second arylation proceeds via the iridium(III/V) catalytic cycle. In the final step, oxidative cyclization of ***101-int-c*** is induced by silver carbonate to afford the corresponding 5,6-phenanthrolinium **101**, which can be applied to mitochondria-targeted fluorescent probes.



Scheme 38. Synthesis of 5,6-phenanthrolinium via iridium-catalyzed arylation/cyclization sequence

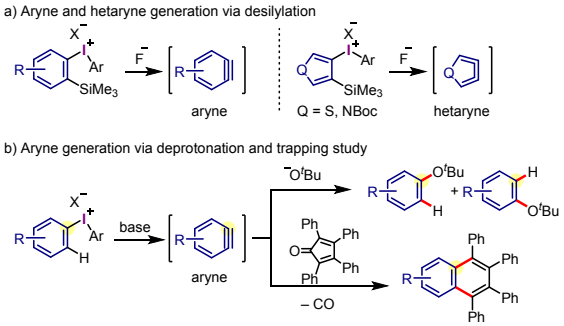
As shown in the above examples, directing groups are required to promote C–H bond metalation to induce the following arylation reaction in almost all cases. Greaney and coworkers demonstrated a sequential functionalization strategy consisting of the introduction of a directing group via *N*-arylation followed by ruthenium-catalyzed C–H bond arylation induced by the introduced directing group (Scheme 39).[75] The reaction of pyrazole **102** and diaryliodonium triflate proceeded with or without a copper catalyst to generate the corresponding *N*-aryl pyrazole ***103-int*** and iodoarene. Treatment of the reaction mixture with a catalytic amount of ruthenium salt at 140 °C led to the C–H bond arylation with the generated iodoarene to afford the coupling product **103**. The introduced pyrazole serves as a directing group for C–H bond activation to induce the next coupling reaction. Specific mesityliodonium salts and/or 1,2,3-triazoles can also be employed for sequential *N*-arylation/C–H bond arylation strategies accompanying selective aryl transfer.



Scheme 39. Introduction of directing group followed by C–H bond arylation

3. Double functionalization via aryne generation

As described in the introduction, diaryliodonium salts provide the aryne intermediates when aryl group has an appropriate activating substituent, such as carboxylate,[21] silyl group,[22] and boronic acid,[23] at the *ortho* position. Among them, the silylated diaryliodonium salts developed by Kitamura have been widely employed and expanded to the generation of hetaryne including 3,4-didehydrothiophene and 3,4-didehydropyrroles (Scheme 40a).[76] On the other hand, aryne generation induced by *ortho*-deprotonation of diaryliodonoum salts without activating groups at the *ortho* position was already reported in the 1970s (Scheme 40b).[24,25]



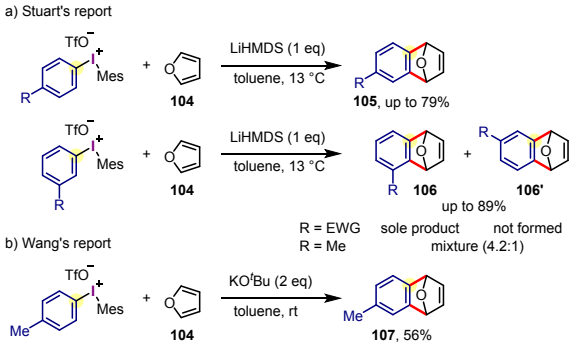
Scheme 40. Early studies for aryne generation from diaryliodonium salts

According to Akiyama, the reaction of bis(4-tolyl)iodonium bromide with NaO^{t}Bu generated a mixture of 3- and 4-*tert*-buthoxytolunene via an aryne intermediate.[24] Cadogan et al. employed tetraphenylcyclopentadienone as a trapping reagent for aryne intermediates generated via the thermal decomposition of diaryliodonium chloride in the presence of sodium acetate, albeit in low yields.[25] These early studies suggest that controlling the *ortho*-deprotonation to generate aryne leads to the double functionalization of diaryliodonium salts.

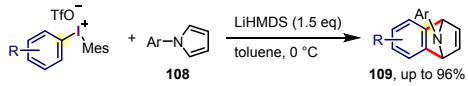
The Stuart group developed an efficient method for the generation of an aryne intermediate via *ortho* C–H deprotonation of a diaryliodonium salt, which was subjected to cycloaddition to achieve the double functionalization of C–I and C–H bonds (Scheme 41a).[77] The reaction of aryl(mesityl)-iodonium tosylates with furan **104** in the presence of LiHMDS afforded the corresponding oxabicyclic products, **105** and **106**. In this reaction, the iodomesitylene moiety served as the effective leaving group. When the aryl group has an electron-withdrawing substituent at the *meta*-position, deprotonation occurs selectively at the 2-position. However, the reaction using (3-tolyl)(mesityl)iodonium salt generates a mixture of regioisomeric cycloaddition products, **106** and **106'**. Contemporaneous with the reports published by the Stuart reports, Wang et al. demonstrated aryne generation using KO^{t}Bu salts and applied it to the *N*-arylation of amides.[78] In this report, the authors performed a cycloaddition reaction with furan **104** to prove the aryne formation. However, the corresponding oxyabicyclic compound **107** was obtained in a moderate yield, and only one example was reported (Scheme 41b).

N-Arylpyrroles **108** can also participate in cycloaddition reactions via aryne intermediates from aryl(mesityl)iodonium salts, as reported by Han and Wang (Scheme 42).[79] The reaction proceeds in the presence of LiHMDS to afford the corresponding bridge-ring arylamines **109**, which are further

transformed into diarylamines via acid-catalyzed ring-opening reactions.

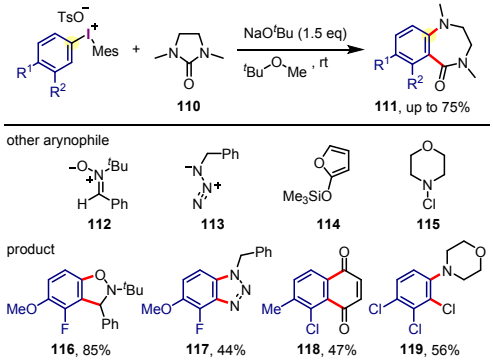


Scheme 41. Aryne formation followed by cycloaddition with furan



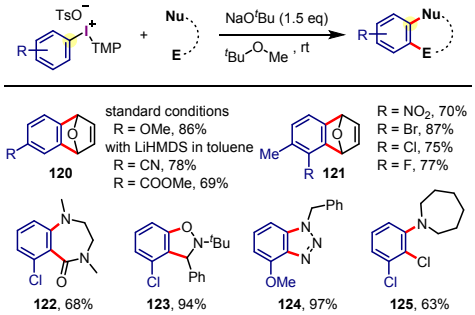
Scheme 42. Aryne formation followed by cycloaddition with pyrroles

The double functionalization strategy via the aryne intermediate provides access to multi-substituted benzene derivatives, which are found in naturally occurring compounds and pharmaceuticals. Stuart and Cheong's group achieved the regioselective synthesis of 1,2,3,4-tetrasubstituted benzene by double functionalization via aryne formation (Scheme 43).[80] Aryl(mesityl)iodonium salts bearing multi substituents reacted with *N*,*N*-dimethylimidazolidinone **110** in the presence of NaO^{t}Bu to afford the corresponding bicyclic product containing a 1,2,3,4-tetrasubstituted benzene moiety **111**. Various aryl(mesityl)iodonium salts and arynophiles, **112–115**, are amenable to selective transformation leading to the corresponding 1,2,3,4-tetrasubstituted benzenes, **116–119**. The authors also performed computational studies including DFT calculations to examine the regioselectivity of aryne formation, wherein both substituents on the aryl group contributed the selectivity.



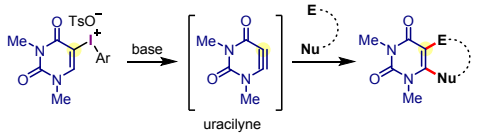
Scheme 43. Synthesis of 1,2,3,4-tetrasubstituted benzenes via aryne formation

Furthermore, Stuart and coworkers demonstrated aryne generation using TMP-iodonium salts as aryne precursors, which addresses the limitations of aryl(mesityl)-iodonium salts, such as narrow aryl scopes and competing substitution reactions (Scheme 44).[81] As described in the introduction section, TMP group also serves as an inert dummy ligand. Similar to the above-mentioned examples, various combinations of TMP-iodonium salts with arynophiles can be employed for double functionalization to afford multi-substituted benzene derivatives, **120–125**.

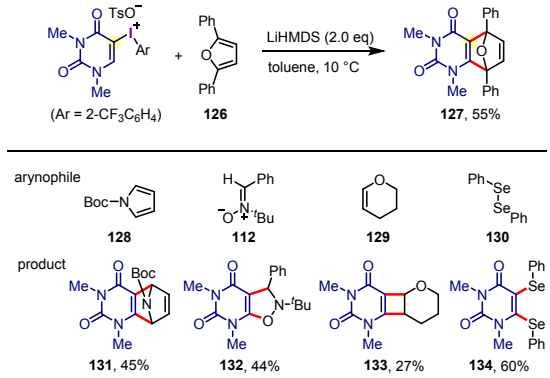


Scheme 44. Double functionalization of TMP-iodonium salt via aryne formation

Hetaryne was also successfully generated by the C–H deprotonation of a diaryliodonium salt, leading to subsequent cycloaddition.[82] Dohi and Takenaga et al. reported the first generation of uracilyne (a heteroaryne analog of uracil) via the deprotonation of uracil-iodonium tosylate (Scheme 45), which can be prepared from uracil via a simple condensation with a Koser-type reagent. Optimization of the reaction conditions indicated that the *ortho*-trifluoromethyl phenyl group was the most appropriate dummy aryl ligand for this transformation. The combination of uracil-iodonium tosylate and furan **126** in the presence of LiHMDS afforded the corresponding oxyabicyclic product **127**. Pyrroles **128** also serve as trapping reagents to afford bridge-ring amines **131**. Furthermore, various arynophiles, such as nitrones **112**, pyrans **129**, and diselenides **130** have been employed for the double functionalization of C–I and C–H bonds to generate uracil derivatives, **132–134** (Scheme 46).



Scheme 45. Uracilyne generation for double functionalization



Scheme 46. Uracilyne formation followed by trapping with various arynophiles

Conclusions

A variety of double functionalization procedures applied to C–I and *ortho* C–H bonds induces multiple bond formations using diaryliodonium salts in a one-pot procedure. There are two approaches to achieve double functionalization: stepwise bond formation via sequential arylations and aryne generation. Owing to recent developments in synthetic methods employing diaryliodonium salts, various bond formation strategies have been developed to produce arylated compounds. In the stepwise bond formation approach, the first bond formation was induced by transition-metal-free or transition-metal-catalyzed reactions. Sequential intramolecular rearrangements or electrophilic aromatic substitution reactions in the second step form aryl–carbon or aryl–heteroatom bonds. In the case of the three-component [2 + 2 + 2] annulation, several nucleophilic attacks induce stepwise multi-bond formation. Furthermore, double functionalization via sequential transition-metal-catalyzed arylation was introduced, wherein the single metal catalyst induced both the first and second bond formations. In the double functionalization via aryne generation, diaryliodonium salts are employed as aryne precursors in the presence of a strong base.

These double functionalization strategies for diaryliodonium salts enable the construction of highly functionalized molecules, which are applicable for short-step access to structurally complex molecules, such as pharmaceutical products and organic functional materials. We believe that further investigation of the synthetic utility of diaryliodonium salts and the associated double functionalization strategies can contribute to the development of step-economical synthetic methods and green sustainable chemistry.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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