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Review article

The electrochemical coupling reactions of organic halides compound in a valuable and practical manner for C—C and C–heteroatom formation: An overview



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ABSTRACT

Owing to the environmental and energy problems nowadays, one of the enormous challenges is expanding clean, renewable energy to reduce the destructive ecological effects of chemical industries. Compared with other traditional processes, the electrochemical method has some benefits, such as being selective, causing minor waste, and working under mild conditions with no external oxidizing or reducing reagents, making this approach more economical and eco-friendly. Electrochemistry represents a powerful tool within synthetic organic chemistry. The development part of chemistry intends the performance of organic reactions employing electrons, including adding or removing electrons. Using electric current as a reagent has some advantages, such as simplicity of reactions, accessibility of materials, replacing toxic oxidizing or reducing reagents, and applying an eco-friendly environment. During the last decades, there has been much effort to decrease the usage of fossil fuels, and electricity has emerged as a common energy source. The conversion of electricity energy into chemical energy leads to new synthetic paths, and this energy is naturally safe and environmentally friendly. Developing electrochemistry approaches for performing high-performance organic reactions is essential for chemical industries. The electrochemical reaction is a green strategy because of the utilization of electric current instead of stoichiometric oxidants or reductants. Due to its helpful and environmentally friendly ability to produce reactive intermediates, organic electrochemistry has advanced considerably in oxidative hydrogen evolution coupling and sacrificial anode electroreduction. New developments in organic electrochemistry focus on developing new electrolytic catalysts, photoelectrocatalysis, bioelectrosynthesis, optimizing electrode materials, paired electrolysis, and artificial intelligence-assisted electrosynthesis. Thus, organic electrochemistry is expanding daily because of the significant number of construction projects and the possibilities of applying organic electrochemistry. Electrochemical methods for constructing organic compounds have tolerated renewal for the past decades. Organic electrochemistry has a wealthy background in organic synthesis. We hope this review helps to attract more attention to organic electrochemistry from researchers by using electrochemical processes in the laboratory and the industrial centers, which decrease pollution and create an eco-friendly. In this review, the

Abbreviations: ERCC, Cyclization–carboxylation sequence; [Oct^{V2+}][Tf₂N]₂, 1,10-Dioctyl-4,40-bipyridinium bis(trifluoromethanesulfonate); Zn, Zinc; SmI₂, Samarium(II) iodide; Bu₃SnH, Tributyltin hydride; Mg, Magnesium; Co, Cobalt; NiBr₂bpy, (2,2′-Bipyridine)nickel(II) dibromide; dmbp, 4,4′-Dimethoxybenzophenone; DMF, Dimethylformamide; RTILs, Room temperature ionic liquids; Al, Aluminium; [octyl-mim][BF₄], Octyl-methylimidazoliumtetrafluoroborate; Pd-PDR, Palladium-pyridyl aldehyde complex; TBABF₄, Tetrabutylammonium tetrafluoroborate; Fe, Iron; NaI, Sodium iodide; NiBr₂, Nickel(II) bromide; Pd, Palladium; THF, Tetrahydrofuran; PdCl₂(PPh₃)₂, Bis(triphenylphosphine)palladium chloride; Pt, Platinum; Viologen, (C₅H₄NR)²ⁿ⁺; RT, room temperature; CH₃CN, Acetonitrile; CoCl₂, Cobalt(II) chloride; Py, Pyridine; CoBr₂, Cobalt(II) bromide; MET, Mediated electron transfer; PDIs, Perylene diimides; DMSO, Dimethyl sulfoxide; SET, Single electron transfer; Na⁺OBu, Sodium *tert*-butoxide; Pd(OAc)₂, Palladium(II) acetate; NH₄Br, Ammonium bromide; Cat, Cathode; Cu(OAc)₂, Copper(II) acetate; RVC, Reticulated vitreous carbon; DMA, Dimethylacetamide; NiCl₂ dme, Nickel(II) chloride ethylene glycol dimethyl ether complex; dtbbpy, 4,4′-Di-*tert*-butyl-2,2′-dipyridyl; mA, Milliampere; MgBr₂, Magnesium bromide; bpy, 2,2′-Bipyridine; Olefin, Alkene; NEt₃, Triethylamine; Fe(CO)₅, Iron pentacarbonyl; H₂SO₄, Sulfuric acid; TEAP, Tetraethylammonium perchlorate; C₆H₅Cl, Chlorobenzene; C₆H₅CO₂H, Benzoic acid; TEACl, Tetraethylammonium chloride; BMIMBF₄, 1-Butyl-3-methylimidazolium tetrafluoroborate; NSAIDs, Nonsteroidal anti-inflammatory drugs; CV, Cyclic voltammetry; CH₃I, Iodomethane; TBAI, Tetra-n-butylammonium iodide; LiBr, Lithium bromide; HBpin, Pinacolborane; TBAB, Tetrabutylammonium bromide; (CF₃SO₂)₂NLi, Lithium bis(trifluoromethanesulfonyl)-amide; [DEME][TFSA], *N,N*-Diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis-(tri-fluoromethanesulfonyl)amide; sCO₂, Supercritical CO₂; IL, Ionic liquid; [DEME][TFSI], Diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide; B₂Cat₂, Bis(catecholato)diborane; NLO, Nonlinear optics; Cyclam, 1,4,8,11-Tetraazacyclotetradecane.

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electrochemical coupling reaction of organohalides for synthesizing various coupling products has been summarized and discussed since 2000.

1. Introduction

During the past few decades, efforts to design greener synthetic strategies in chemical procedures have significantly increased. Developing chemical approaches that remove the usage of catalysts is a critical and more attractive method that is proper for all chemistry facets. Organic compounds' electrosynthesis is highly selective compared to the typical chemical reaction. In recent years, electrosynthesis has been a vital research hotspot in organic synthesis transformation. For the electrosynthesis reaction, intermediates exist evenly scattered in the reaction media. The service of electrochemistry persists these days and constructs tons of invaluable chemicals. Electrochemistry is part of chemistry that investigates the interconnection of chemical and electrical impacts. Studying chemical changes that influence the passing electric current is the most crucial section of this field. The principal forces in chemistry-electrochemistry are the electrostatic attractions between electrons and nuclei. Overcoming the kinetic limitations even at low temperatures by utilization of potential and their chemical and stereochemical specific properties make electrochemical reactions beneficial in chemical synthesis (Francke and Little, 2014; Suprun et al., 2014; Suprun et al., 2020; Muster et al., 2011; Rapino et al., 2015; Guan et al., 2023).

Recently, electroorganic conversions have become known as a robust and efficient tool for cross-coupling reactions. Electrochemistry supplies a new area in manufacturing carbon-heteroatom and carbon-carbon bonds and describes probable mechanistic. Organic electrochemistry has a wealthy background in organic synthesis. The construction of new bonds is very crucial in chemical synthesis. Chemistry scientists have developed cross-coupling reactions as an efficient method for carbon-carbon bond generation. The carbon-heteroatom bond formation leads to products that draw considerable interest owing to their role as structural units in enormous synthetic methods for bioactive and natural compounds. Various helpful pharmaceutical agents and materials with various functionalities have been synthesized by constructing carbon-carbon or carbon-heteroatom bonds. Biaryl is a potential structural unit with many applications in natural products, synthetic bioactive compounds, and pharmaceuticals. The compounds in which carbon-nitrogen, carbon-oxygen, or carbon-sulfur bonds exist in the ring structure are seen in many chemistry and biology applications (Hartwig, 2008; Bringmann et al., 1990; Bhunia et al., 2012; Kerru et al., 2019).

Organic electrochemistry explains the oxidation and reduction of

organic molecules at the electrodes. Electrochemical reactions are a kind of electron transition that occurs on the surface of electrodes. The reduction occurs on the cathode electrode, and the oxidation happens on the anode electrode; the reductant is the electron receptor, and the oxidant is the electron donor species. The electron transition process is performed between the electrode surface's and the electro-activated species' energy levels (Alvarado et al., 2022; Rein et al., 2022; Park et al., 2021; Zhu et al., 2021; Liu et al., 2023).

Studies were performed in the nineteenth century led to the emergence of electrochemistry of organic compounds in the twentieth century. In 1800, Volta Pile invented the electric battery for the first time (Volta and Nat, 1800). In 1807, Davy started to survey the chemical effects of electricity on electrolyzing the alkalis, which led to the discovery of potassium and sodium through the electrolysis of metal hydroxides (Davy, 1808). Faraday was the first one to introduce the terms electrolysis, anode, cathode, and ion; he also expressed in his two laws of electrolysis in 1830 (Faraday, 1834). Electrolysis of carboxylic acids to access alkyl radicals was carried on by Kolbe in 1847 (Kolbe, 1847).

Table 1

Historical advancement of the electrochemistry field.

Entry	Discovery	Explorer	Time	References
1	Built the first electric battery	Volta Pile	1800	Volta and Nat, 1800
2	Survey the chemical effects of electricity on electrolyzing the alkalis	Davy	1807	Davy, 1808
3	Introduce the terms electrolysis, anode, cathode, and ion	Faraday	1830	Faraday, 1834
4	Electrolysis of carboxylic acids to access alkyl radicals	Kolbe	1847	Kolbe, 1847
5	Hydrocarbon preparation, achieved from the cathodic reduction	Tafel	1907	Tafel et al., 1907
6	Designed potentiostat conditions	Hickling	1942	Hickling, 1942
7	Anodic oxidation pathways of aromatic amines studies	Eddie T. Seo et al.	1966	Seo et al., 1966
8	Nitroxyl-mediated electrooxidation of alcohols to aldehydes and ketones	M. F. Semmelhack et al.	1983	Semmelhack et al., 1983

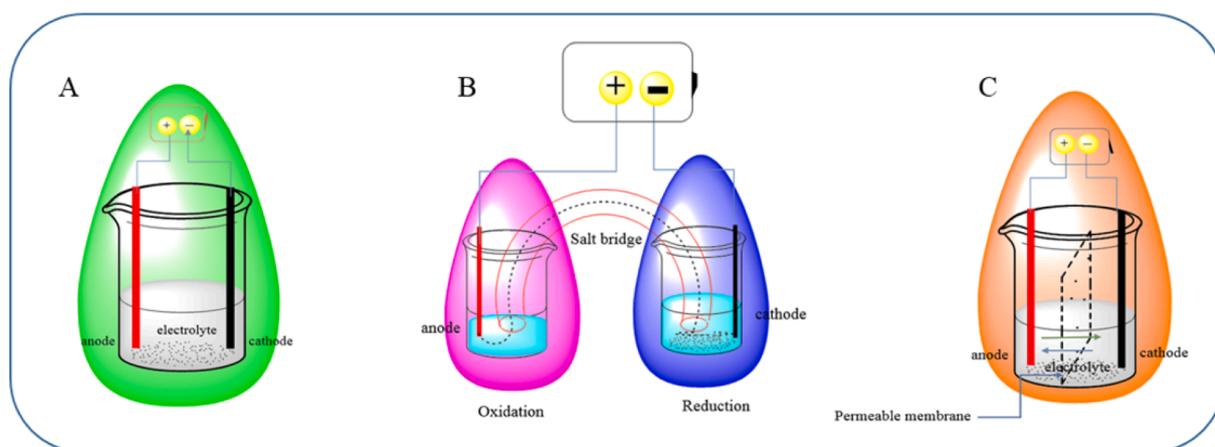
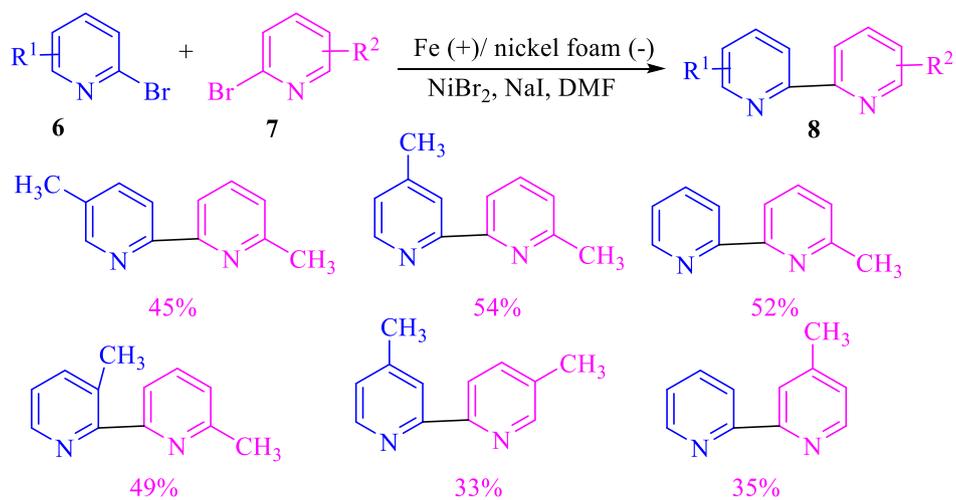
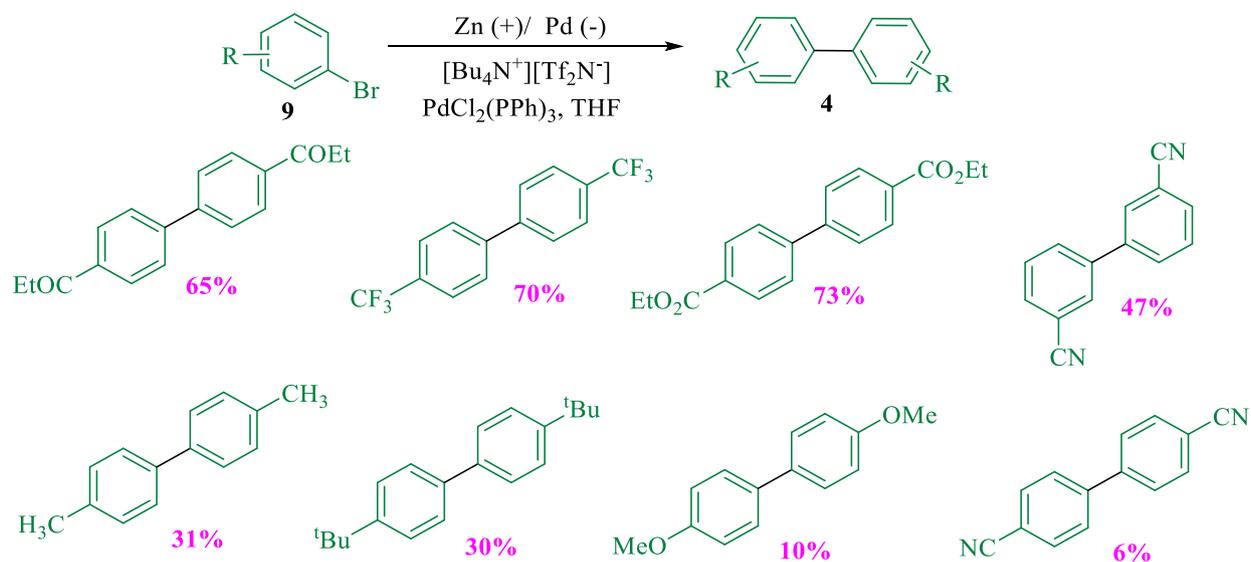


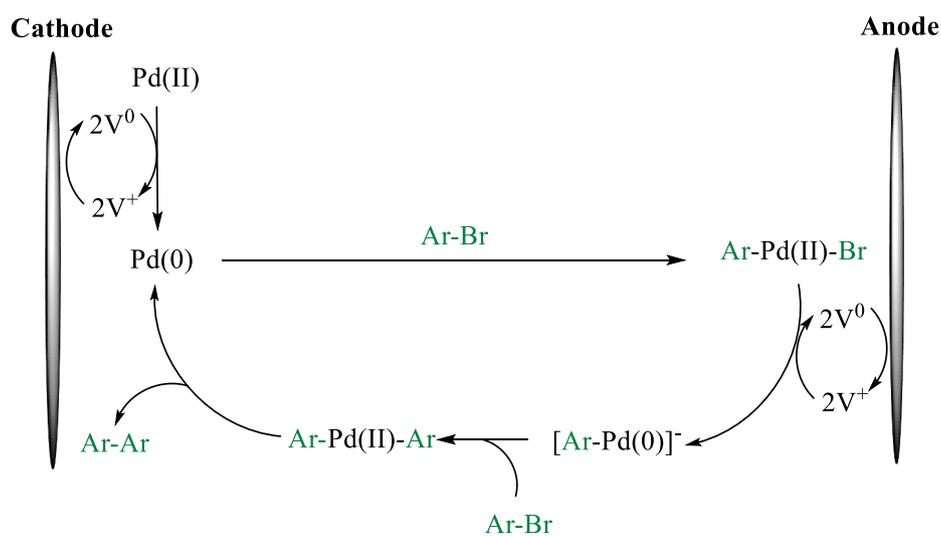
Fig. 1. Undivided cell (A), divided cell, cathode, anode, and electrodes are connected with a salt bridge (B), and split cell, anode, and cathode electrodes are associated with a penetrable membrane (C).



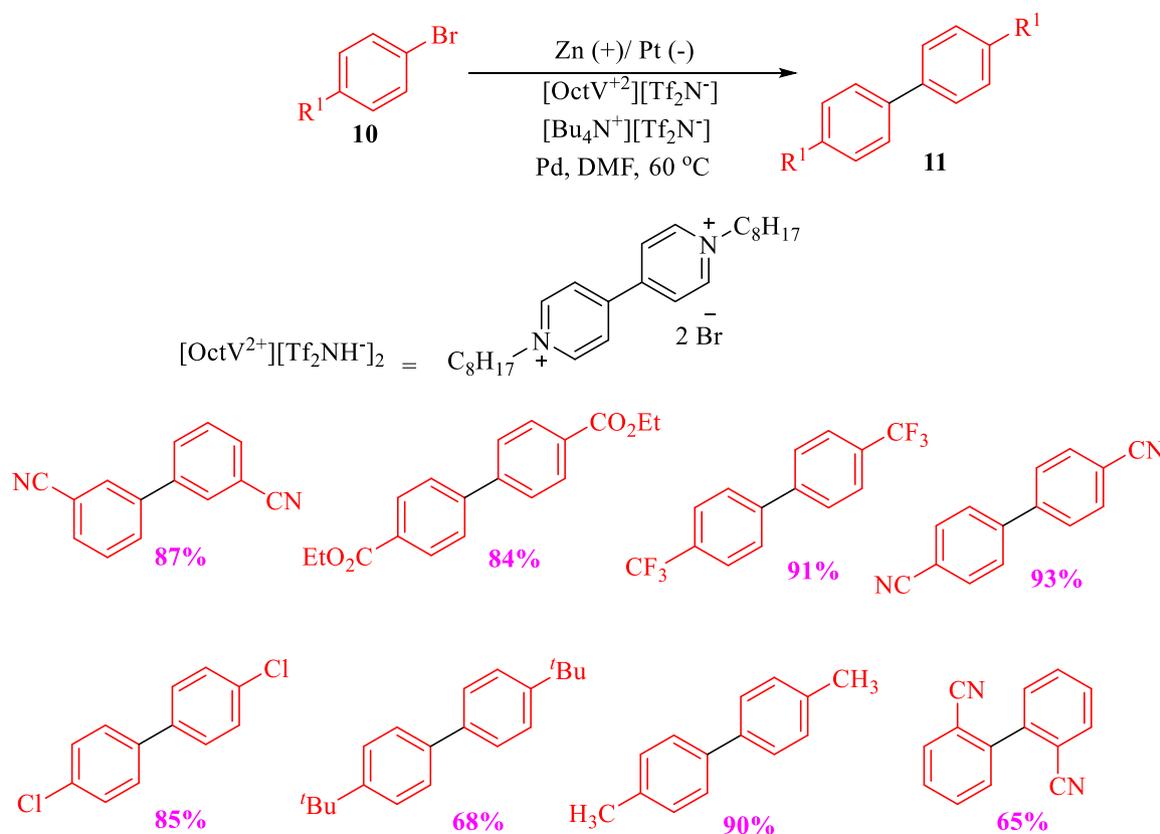
Scheme 4. Heterocoupling of 2-bromopyridines with 2-bromomethylpyridines.



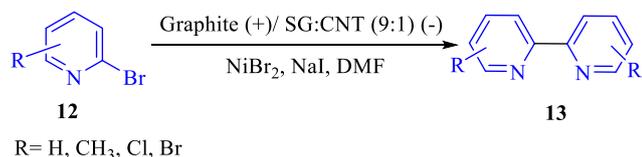
Scheme 5. Electroreductive homocoupling of various aryl halides with Pt (cathode) and Zn (anode).



Scheme 6. Mechanistic pathway representing the reductive coupling.



Scheme 7. Electroreductive homocoupling of aryl halides.



Scheme 8. Electrocatalytic homocoupling of 2-halopyridines.

chamber, it is called an undivided cell (Fig. 1A).

The drawback of this setup is that high energy intermediates produced on the working electrode rapidly reduced in the counter electrode (vice versa), so scientists suggested a divided cell. In this cell, the cathode and anode are placed in independent cells and joined with a salt bridge or in a chamber segregated with a permeable membrane (Fig. 1B and 1C, respectively).

Heyrovsky's pioneering effort in polarography, using dropping mercury electrodes, led to today's cyclic voltammetry, where the current and voltage are associated (Heyrovsky, 1922; Heyrovsky, 1923). In 1942, Hickling opened a new approach to electrochemical synthesis. Before his invention, all electrochemistry was carried out under a galvanostatic condition, where the current was constant and potential increased over time. Hickling designed potentiostat conditions that are currently reduced in constant potential (Hickling, 1942; Lingane et al., 1943). Undivided galvanostatic setups are operationally simple, making them practical despite all the benefits of divided cells and potentiostat setups.

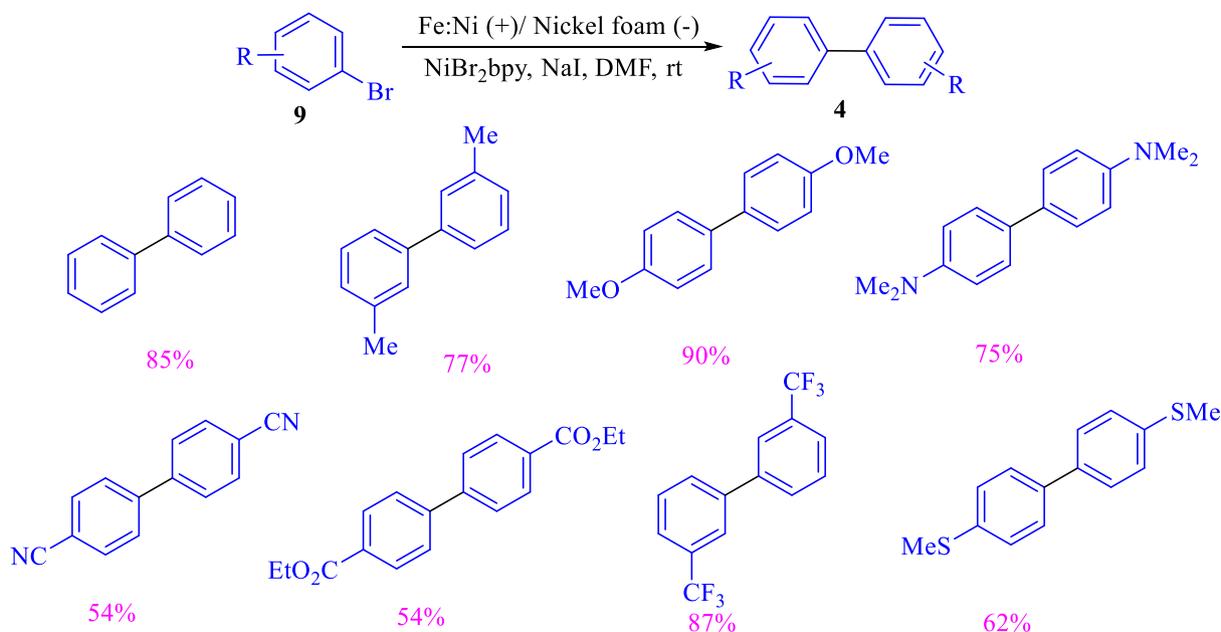
In electrochemical reactions, there are two types of interactions for the transition of electrons between electrode and substrate. In type I, electrons transform from the surface of the electrode to substrate molecules directly. The disadvantage of this type is the high kinetic barrier that interacts between the ions/molecules in the solution and the electrode surface, producing high-energy species like radical anions and

cations accumulated in the area close to the electrode superficial (double layer) (Perry and Wright, 2006). Created reactive species cause some problems in the system, and to avoid this, a mediator (or catalyst) is needed to facilitate the transition of electrons (type II).

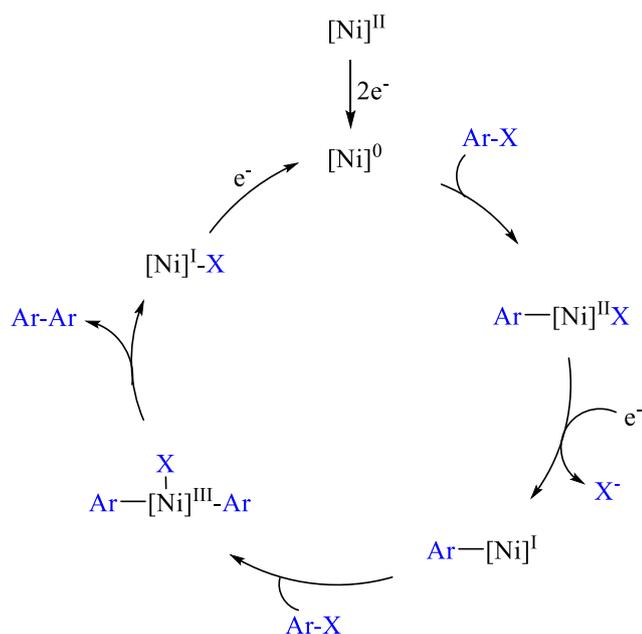
Nitroxyl radicals (Semmelhack et al., 1983), triarylamines (Seo et al., 1966), transition metal complexes, and ionic halides are important category mediators with many applications in indirect oxidation and reduction Table 1. From the green chemistry point of view, organic electrochemical processes are precious because of their high selectivity for functional groups, scalability, and the requirement to moderate reactivity (low temperature, applied accurate of potential, adopted economical solvents), low waste and environment-friendly (Horn et al., 2016) so displays a remarkable role in enormous research, practical field, and industrial applications (Surucu and Abaci, 2017) Organic electrochemistry is a stepping stone to replace with general greenness chemical reaction. The building of carbon-carbon and carbon-heteroatom bonds is a critical key for assembling a compound for connection to material science, agriculture, and medical chemistry Fig. 2 (Roughley and Jordan, 2011; Alvarez-Builla et al., 2011; Boström et al., 2018).

Recently, several groups have given special attention to this field and published several reviews. Lei and colleagues illustrated the recent progress of electrochemical oxidative cross-coupling with iodine-mediated in 2018 (Liu et al., 2018). Waldvogel and coworkers explained electrochemical arylation reactions and recent developments in electrochemical synthesis (Wiebe et al., 2018; Waldvogel et al., 2018).

Recently, different groups studied the electrochemistry of organic compounds and published many reports (Huang et al., 2022; Liang et al., 2018; Minter and Baran, 2020; Möhle et al., 2018; Novaes et al., 2021; Röckl et al., 2022; Rodrigues et al., 2022; Sauermann et al., 2018; Shi et al., 2020; Wirtanen et al., 2020). Organic electrochemistry possesses a great past in the synthetic organic field. It is a hopeful substitute for



Scheme 9. Electrochemical homocoupling of aryl halides.



Scheme 10. Probable reaction mechanism.

traditional chemical methods because it prevents using stoichiometrically dangerous and venomous reactants. This review highlights the electrochemical methods for carbon-heteroatom and carbon-carbon formation from organohalides since 2000. Herein, we provide a profound summary of the recent advances in electrochemical cross-coupling reactions of organohalides.

2. Electrochemical C—C bond establishment

2.1. Homo-coupling of organic halides

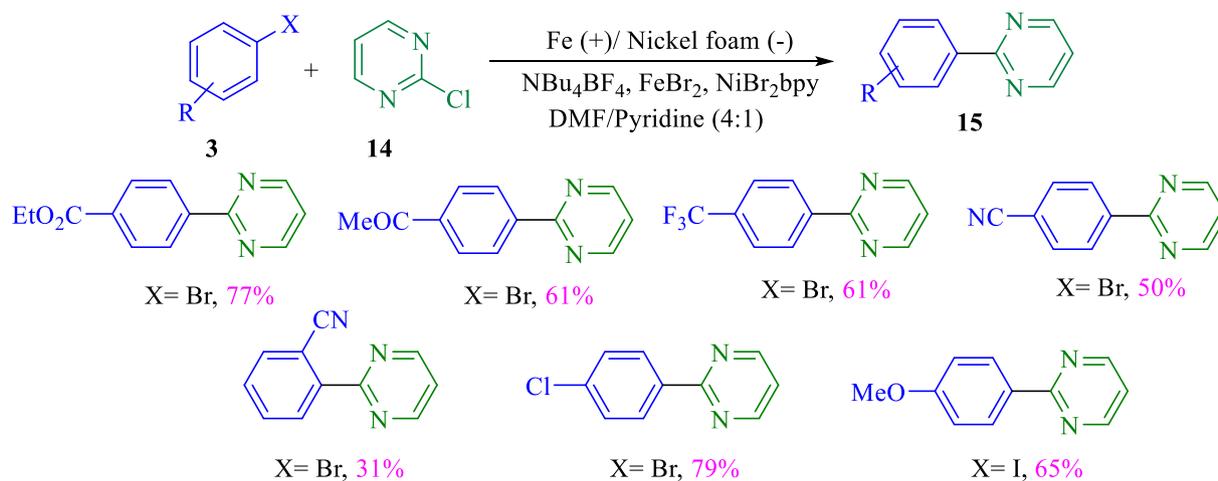
In 2000, Cassol et al. demonstrated the synthesis of 6,6'-dimethyl-2,2'-bipyridine (**2**) using homocoupling of 6-bromopicoline (Scheme 1) (Cassol et al., 2000). They introduced two appropriate and high-yielding methods for the 6,6'-dimethyl-2,2'-bipyridine synthesis (74–67 %). The

first procedure was electroconductive homocoupling of 6-bromopicoline (**1**) by Zinc rod anode, nickel foam cathode was used for electrolysis, and another one was palladium(II) acetate catalyzed coupling of 6-bromopicoline. Either method was straightforward and described a significant advance over the recognized syntheses of disubstituted bipyridine.

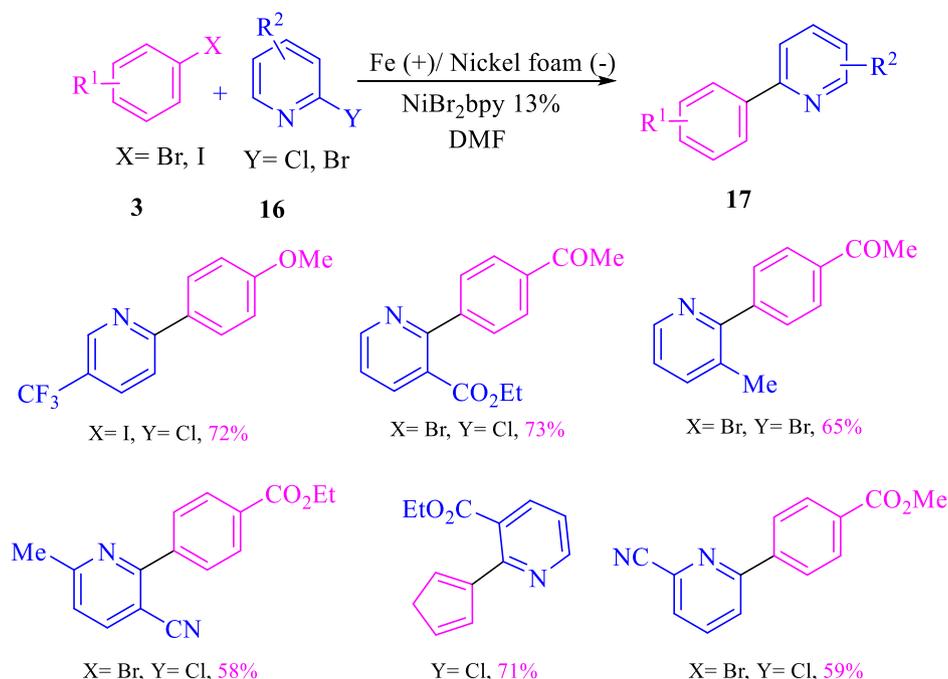
Electrochemical reactions were accomplished in an undivided cell by Zn (anode) and NiBr₂bpy in the role of the catalyst. Various products were obtained in mild status with isolated yields between 58 and 98 %. This report surveyed the effects of methyl groups' position on the ring, temperature, and solvent. The nature of the influence of the methyl and its place on the aromatic ring influenced the dimerization effectiveness. These effects were presumably associated with one or more stage (s) of the catalytic cycle. At ambient temperature, the electric resistance of the media became excessively elevated, and the solubility of the nickel complex was low; also, at 50 °C, no development was reached; therefore, the ambient temperature appeared to be the most suitable.

In 2002, França *et al.* indicated electrochemical homocoupling of 2-bromomethylpyridines and 2-bromopyridine by nickel complexes (De França et al., 2002). Electrochemical reactions were accomplished with Zinc as (anode) and NiBr₂bpy as the catalyst. With mild conditions, divers of products were provided with isolated yields (58–98 %). This report surveyed the effects of the methyl group's position on the ring, temperature, and solvent. The nature of the methyl (Me) group effect and its position on the ring influenced the dimerization efficiency. These effects were presumably associated with one or more stag (s) of the catalytic cycle. Under room temperature, the electric resistance of the medium became too high, and the solubility of the nickel complex was low, also at 50 °C; no development was reached. Therefore, the ambient temperature appeared to be the most suitable. DMF was also better than acetonitrile because the nickel complex solubility in acetonitrile was low.

In 2003, Barhdadi et al. illustrated the direct or nickel-mediated electroconductive homocoupling of organic halides and coupling of them by activated alkenes at room temperature in ionic liquids (RTILs) as a solvent-electrolyte media (Scheme 2) (Barhdadi et al., 2003). They accomplished the electroreductive homocoupling reaction of several alkyl/benzyl halides **3**. The electrolysis was performed by arranging a steady current severity between the Mg or Al bar anode and the nickel grid cathode. Bibenzyl **4** (78–48 %) was achieved from benzyl chloride/bromide in good yields.



Scheme 11. Electrochemical coupling 2-chloropyrimidine and aryl halides.



Scheme 12. Electrosynthesis of functionalized 2-arylpiperidines.

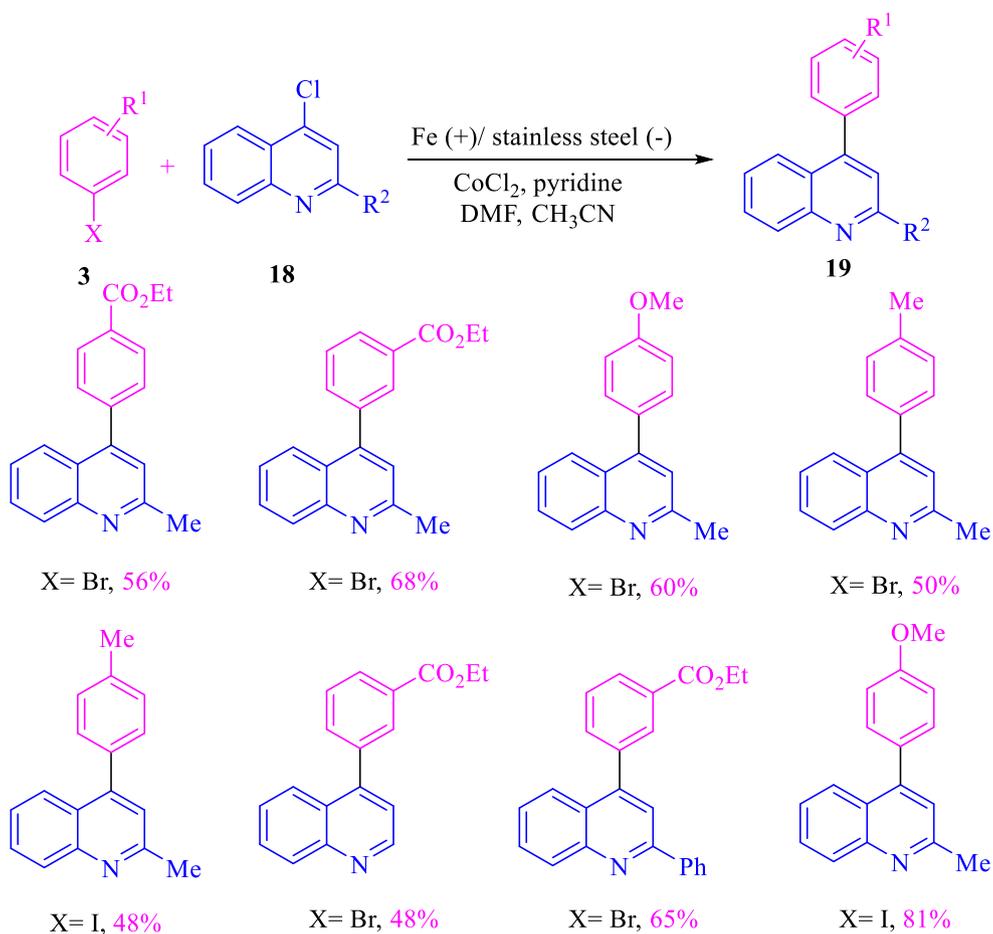
Two years later, Navarro *et al.* studied the supporting electrolyte Zn anode's mixed impact on the homocoupling of 2-bromopyridines (1, Scheme 3) (De França *et al.*, 2005). A spectrum of reactions was conducted with different sorts and concentrations of supporting electrolytes, and it was shown that an essential stage for this procedure was the production of aryl zinc *via* a nickel-zinc transmetalation. Dimerization with ammonium salts was inefficient. In contrast, using sodium iodide (supporting electrolyte) did not inhibit the dimerization, although the organozinc was prepared, and their yields of product 5 were excellent.

Then, the group Navarro reported mono and dihalopyridines (6 and 7) electrochemical coupling for the formation of unsymmetrical 2,2'-bipyridines 8 catalyzed using nickel complex (Scheme 4) (Oliveira *et al.*, 2012). Reactions were applied to an undivided cell enclosed by surrounded by a nickel foam (cathode) and a zinc rod (anode). 2,2'-Bipyridine derivatives 8 were attained in good yields (58–98 %).

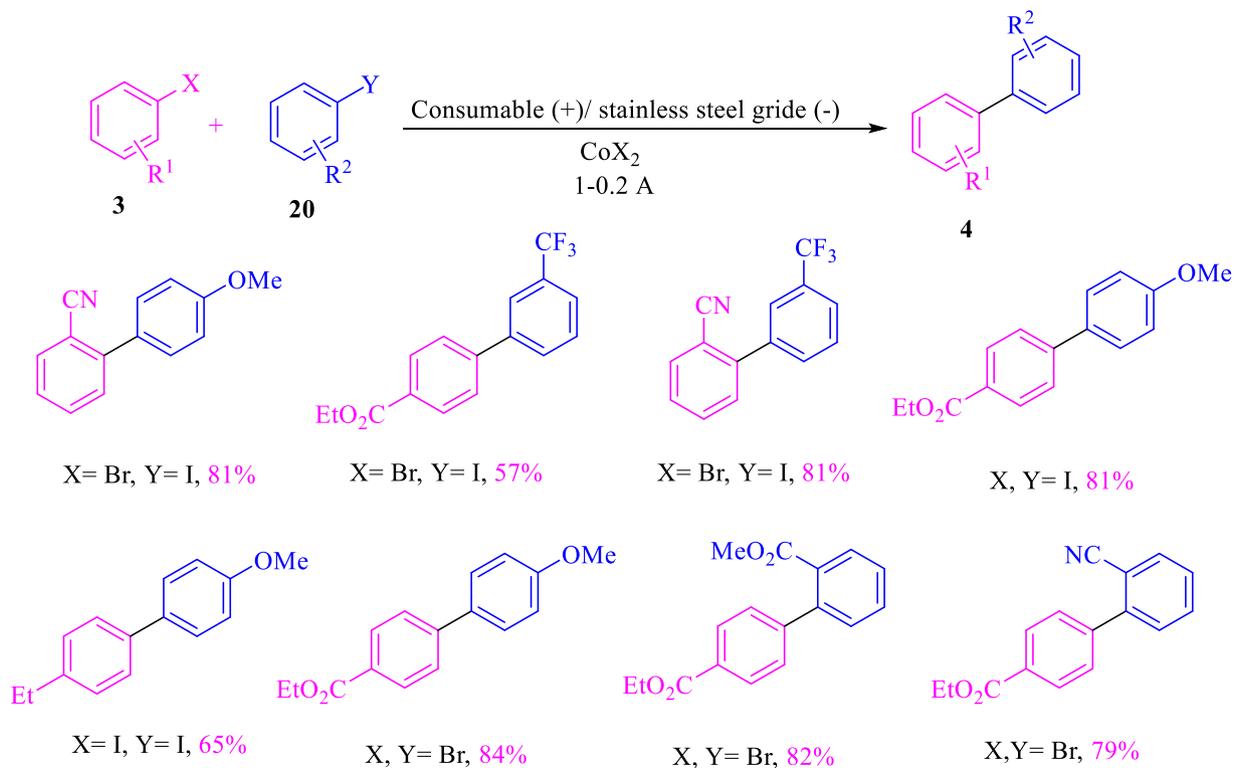
In 2013, the group Tanaka described the electroreductive homocoupling of aryl bromides 9 successfully to prepare the corresponding biaryls 4 (6–73 %) (Scheme 5) (Tanaka *et al.*, 2013). By using a double

mediatory system including *N*-alkyl-4-alkoxycarbonylpyridinium salts and [(C₆H₅)₃P]₂PdCl₂, the electro-reductive coupling was conducted in an undivided cell with a platinum (cathode) and a zinc (anode). The mechanism proposal (Scheme 6) showed that in the cathode, Oct^{V2+} reduced to quinoid Oct^{V0}, which reduces Pd(II) to provide Pd(0) active species together with Oct^{V0+}. Oxidative addition of aryl bromides on the Pd(0) generated Br–Pd(II)–Ar, then this compound was reduced by Oct^{V0} and afforded [Ar–Pd(0)][–]. In the next step, aryl bromide reacted with [Ar–Pd(0)][–] and produced Ar–Pd(II)–Ar, which finally underwent reductive elimination to have biaryls.

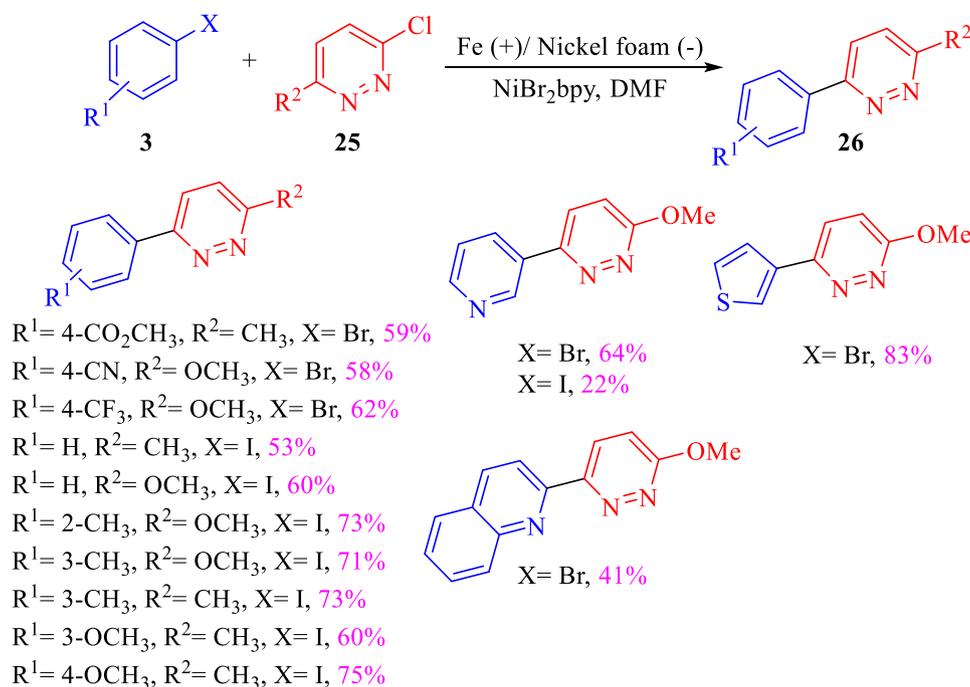
At the same time, this group developed the electrochemical treatment of *N*-alkylpyridinium salts and electro-reductive coupling of aryl bromides 10 in a double mediatory system, including PdCl₂(PPh₃)₂ (catalytic amounts) and *N*-alkylpyridinium salts (Scheme 7) (Kuroboshi *et al.*, 2013). Viologen served as a recyclable organic reductant. Compared with viologen compounds, pyridinium derivatives have complex structures, and their redox potential could be adjusted by introducing substituents. Zinc (anode) and platinum (cathode) were



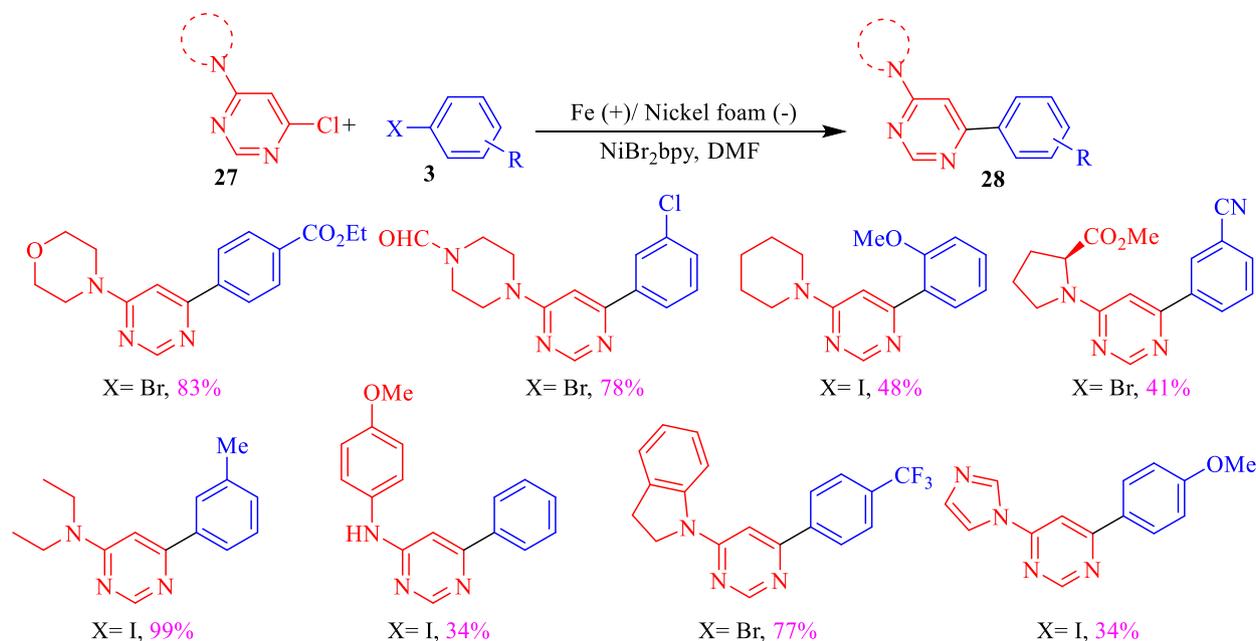
Scheme 13. Electrochemical coupling of 4-chloroquinoline and aryl halides.



Scheme 14. Electrochemical coupling of two various aryl halides.



Scheme 17. Electrochemical synthesis of substituted aryl/hetero arylpyridazines.



Scheme 18. The coupling of aryl halides with 4-amino-6-chloropyrimidines.

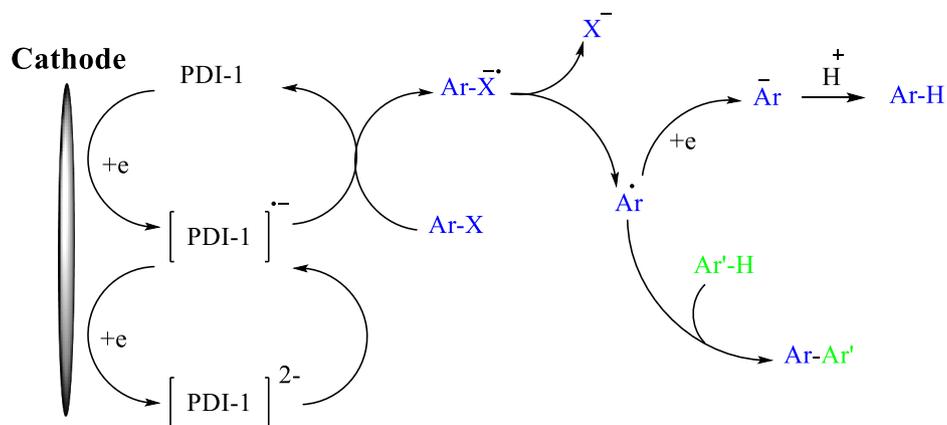
significantly considered, and various research groups have entered this field. In 2000, Gosmini *et al.* reported electrochemical coupling of 2-chloropyridazine/2-chloropyrimidine **14** and functionalized aryl halides **3** catalyzed by 2,2'-bipyridine nickel complex (Scheme 11) (Gosmini *et al.*, 2000a). This reaction was conducted with an iron rod (anode) and a nickel foam (cathode). 2-Aryl pyrimidine/pyridazine derivatives **15** were afforded good yields (31–79 %).

In the same years, this group explained the electrochemical synthesis of 2-arylpyridines **17** from the reaction between aryl halides **3** and 2-halo pyridine **16** (Scheme 12) (Gosmini *et al.*, 2000b). Nickel foam cathode and iron anode were used. Under mild condition derivations, 2-arylpyridines achieved good to high yields (40–76 %).

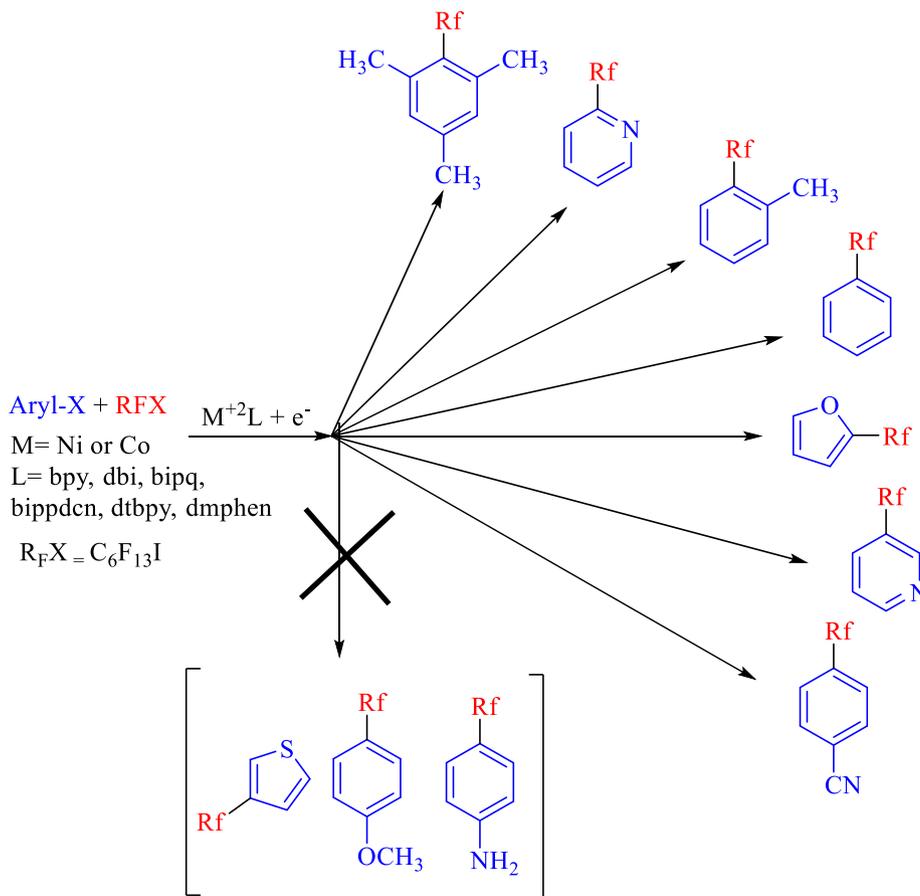
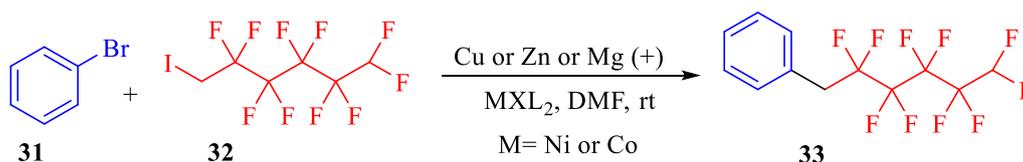
The electrochemical coupling reaction of 4-chloroquinoline **18** and aryl halides **3** by cobalt-catalyzed described by Gosmini's group (Scheme 13) (Le Gall *et al.*, 2001a). By using an iron rod (anode) and a stainless steel grid (cathode), scarcely 4-phenylquinoline derivatives **19** obtained 48–81 % yield.

Both withdrawing and electron-donating groups coupling products achieved acceptable yields. The selection of iron rods was essential for the effectiveness of the electrochemical reaction.

In 2002, this group showed the electrochemical coupling of diverse aryl halides (chlorides, bromides, and iodides) **3** and **20** for synthesizing unsymmetrical biaryls **4** (Scheme 14) (Gomes *et al.*, 2002a). A stainless steel grid (cathode) and an iron rod (anode) were used. The coupling



Scheme 21. Proposal catalytic cycle.

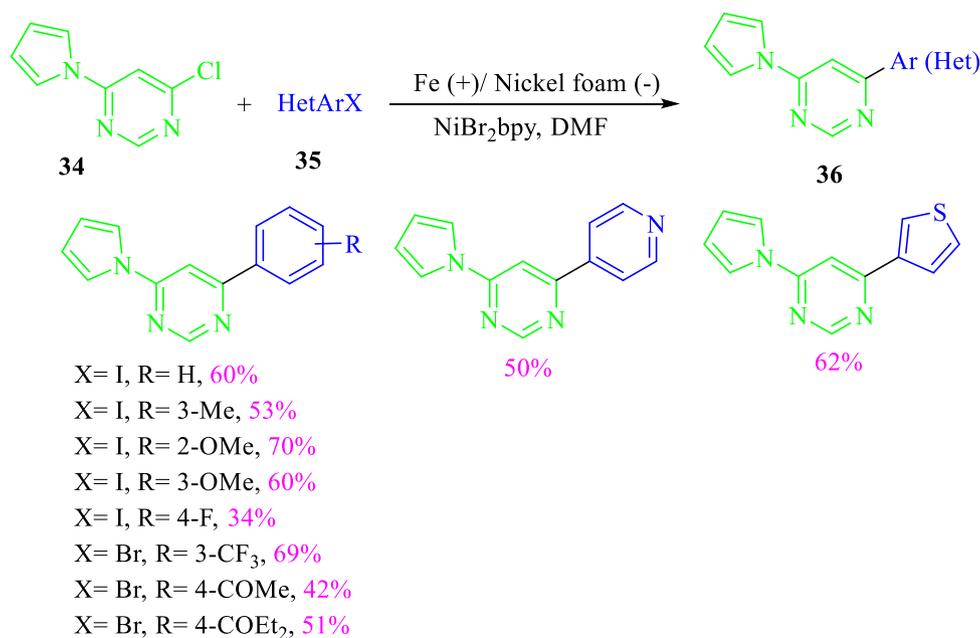


Scheme 22. The electrocatalytic cross-coupling of organic halides by nickel and cobalt complexes catalyst.

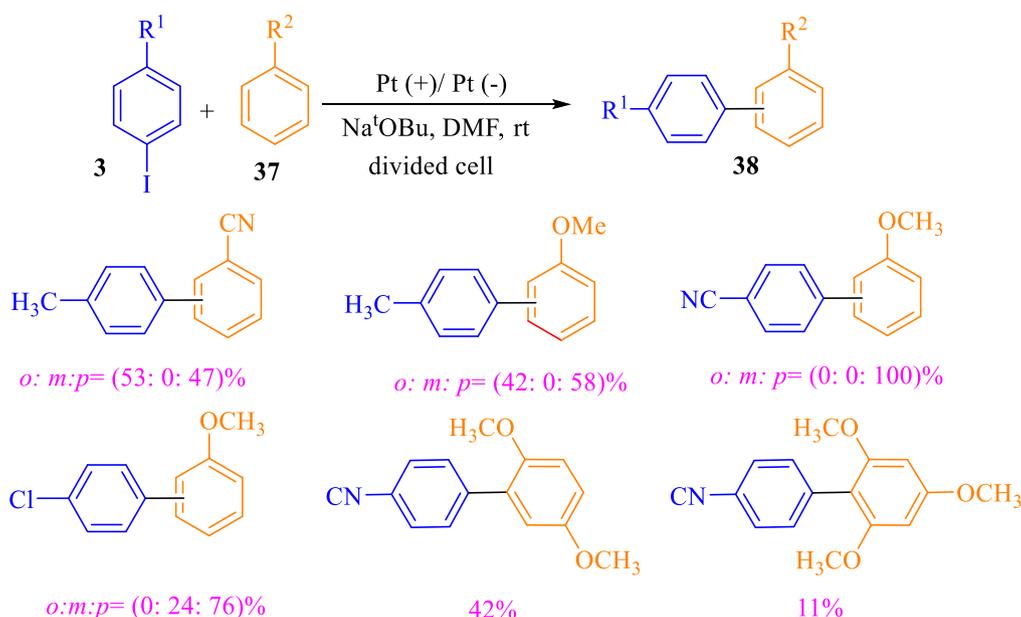
aryl halides **3** with vinylic acetates **23** using cobalt as a catalyst in an undivided cell with a stainless steel grid (cathode) and a consumable iron (anode) (Scheme 16) (Gomes et al., 2003b) This simple electrochemical procedure is a mild and helpful method for synthesizing different vinyl-aryl compounds. Styrene derivatives **24** were obtained with good yields (20–92 %). Cobalt associated with bi-pyridine

appeared more efficient for this reaction than palladium complexes.

In 2007, Leonel *et al.* exhibited a proper electrochemical procedure for the syntheses of aryl/hetero aryl pyridazine **26** from the reaction of 3-chloro-6-aryl pyridazine **25** and phenyl halides **3** using Ni-catalyzed (Scheme 17) (Sengmany et al., 2007). An iron rod (anode) covered by a nickel foam (cathode) was applied. Under the standard condition, the



Scheme 23. Electrochemical cross-couplings aryl/hetero halides and 4-chloro-6-pyrrolylpyrimidine.



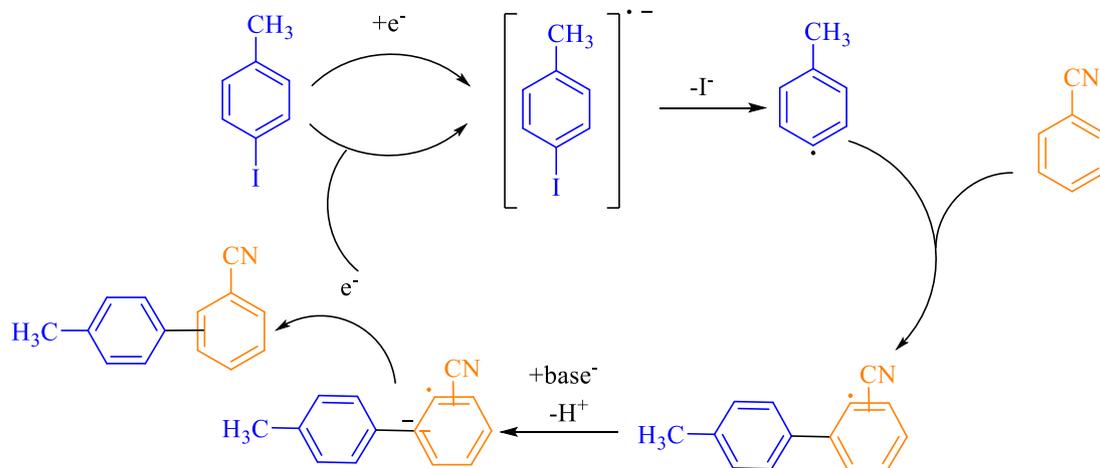
Scheme 24. The cathodic coupling reaction of arenes with aryl halides.

differences substituted aryl/hetero arylpyridazines obtained moderate to good yields (22–83 %).

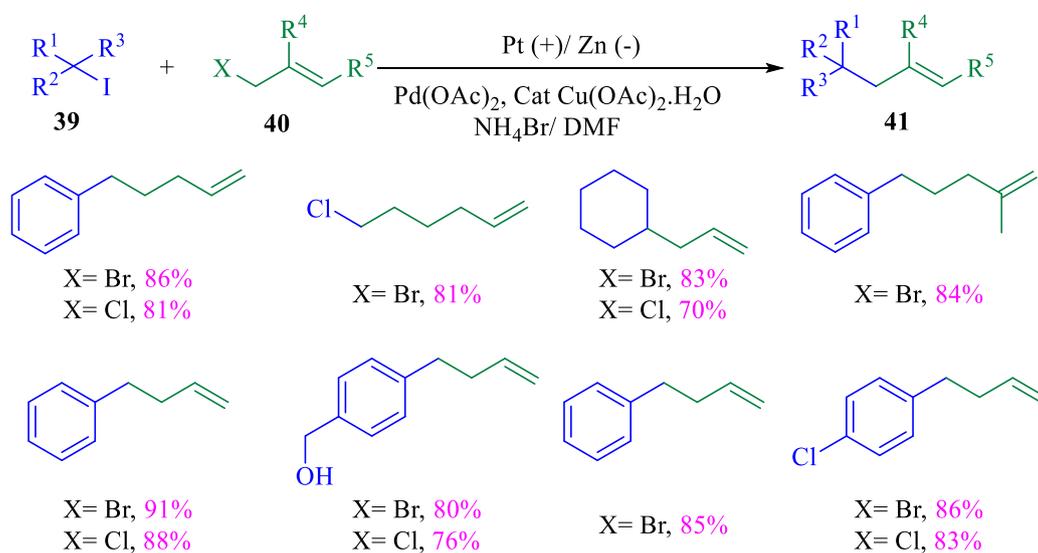
In 2011, Léonel *et al.* displayed an electrochemical reductive coupling aryl halides **3** and 4-amino-6-chloropyrimidines **27** for the synthesis of scope of 4-amino-6-arylpyrimidines **28** (Scheme 18) (Sengmany *et al.*, 2011). Using an iron rod (anode) and a nickel foam (cathode) several 4-amino-6-arylpyrimidines were provided with moderate to excellent yields (34–99 %). The putative mechanism showed that, firstly, Ni(II) was redacted into Ni(0) (Scheme 19). In this step, the oxidative addition of Ni(0) into the carbon-halide bond of either aryl halide or chloropyrimidine occurred, leading to the generation of HetArNi(II)Cl. The monoelectronic reduction of the complex provided a HetArNiI that was affected in another oxidative addition onto the aryl halide, providing a HetArNi(III)(Ar)X complex. Reductive elimination in the final step

produced the desired coupling product.

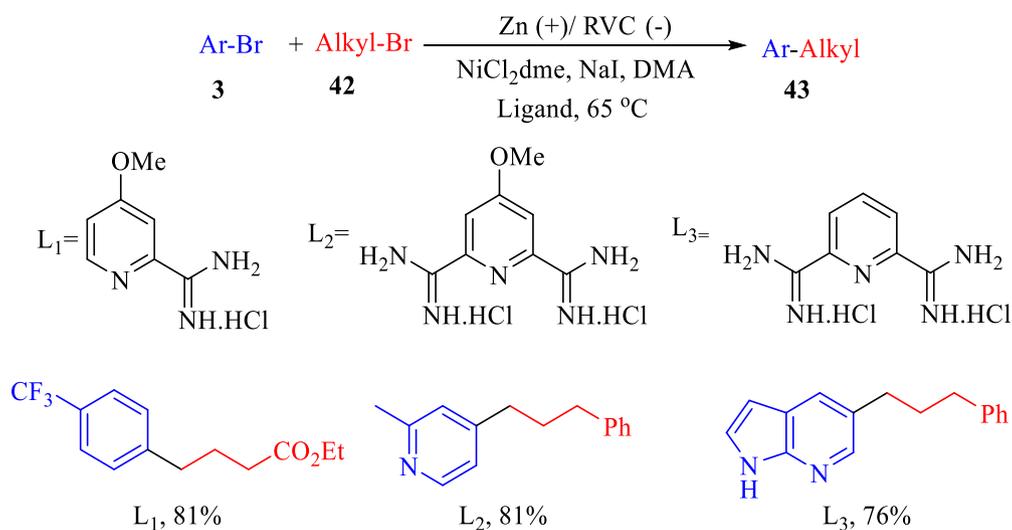
The indirect electroreductive coupling of pyrroles **29** and aryl halides **3** employing perylene bisimide (as an electron-transfer mediator) was offered (Scheme 20) (Sun *et al.*, 2016). For the first time, this group introduced perylene bisimides as an indirect electroreductive mediator. The extraordinary electron transfer capabilities and outstanding stabilities of perylene bisimides, with their flexibility for structural modification, make them encouraging nominees as indirect electroconductive mediators. The electrochemical reaction was performed with no utilization of a metal catalyst and the addition of a base using a sacrificial zinc anode. Under mild status, pyrrole compounds **30** were provided with an average to good yield (50–71 %). A proposal mechanism depicted those radical anions deriving from the cathodic reduction reduced aryl halides to aryl radicals, which underwent other reactions

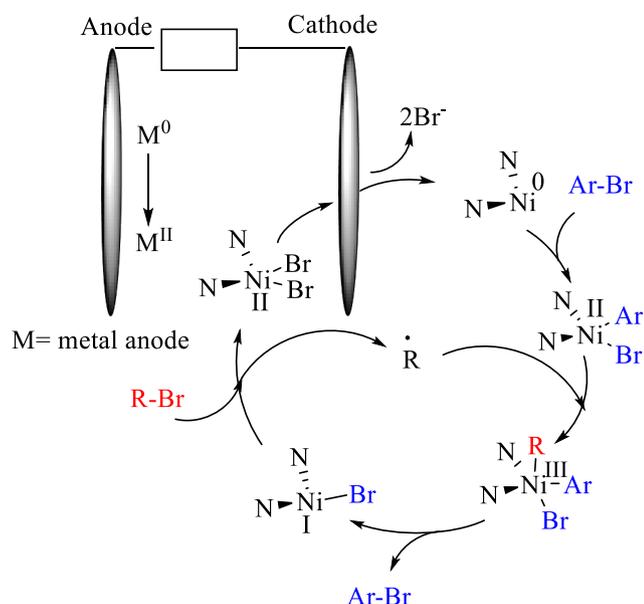


Scheme 25. The suitable mechanism for the cathodic reaction.



Scheme 26. Electrochemical allylic alkylation between allylic and alkyl halides.

Scheme 27. Electrochemical for sp^3 - sp^2 cross-electrophile coupling of unactivated alkyl halides.



Scheme 28. The mechanism that explains the electrochemical cross-electrophile coupling.

by pyrroles generating coupling products. (Scheme 21).

During the same time, Khrizanforov et al. presented a novel approach to single-step preparation of perfluoro alkylated arenes **33** through cross-coupling of bromo/chloro arenes or hetero arenes (aryl, furan, and pyridine) **31** and organic perfluoro alkyl halides **32** (Scheme 22) (Khrizanforov et al., 2016). Perfluoroalkylated compounds were achieved in good yields. They chose several complexes, including nitrogen ligands that stabilize the low-oxidation-state metals, for instance, α -diimine compound (dtbpy, tpy, bpy, and dmphen). These reactions used a complex of cobalt and nickel in various ligand environments. The more negative the reduction potential is, the more efficient the catalyst is.

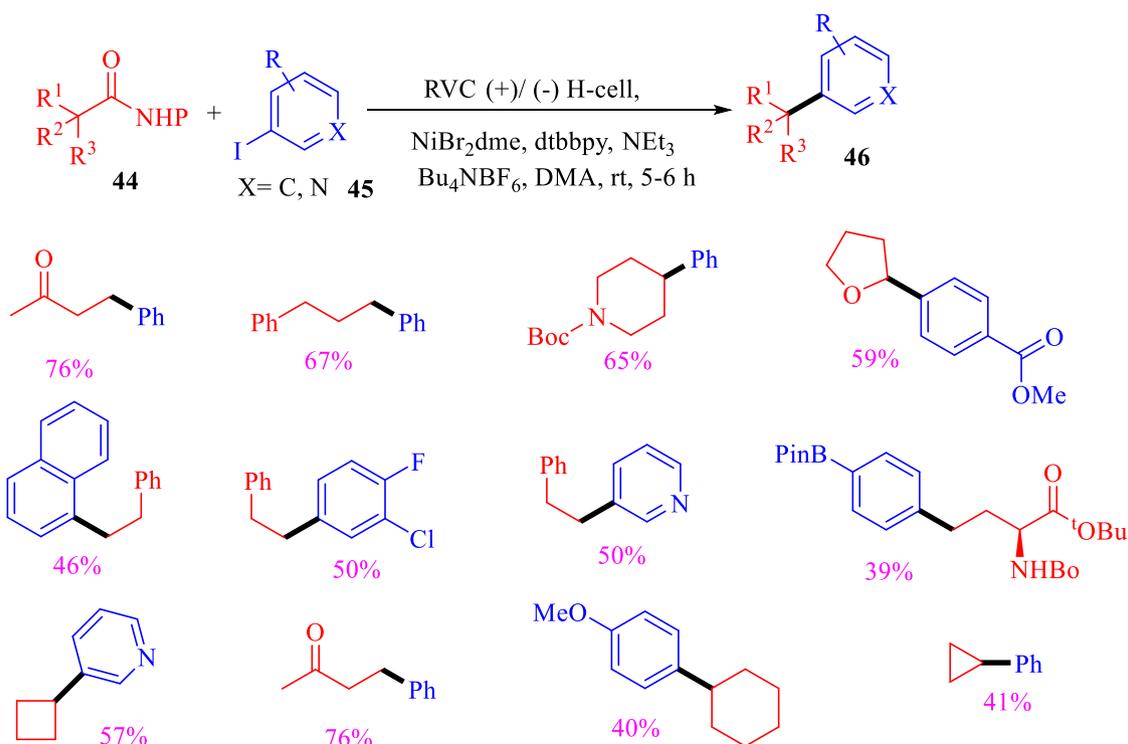
Also in 2016, Leonel's group demonstrated the synthesis of the 4-aryl/hetero-6-pyrrolyl pyrimidines **36** (34–70 %) by electroreductive nickel catalyzed from cross-coupling chloro pyrimidines **34** and aryl halides **35** (Scheme 23) (Sengmany et al., 2016). This reaction was a catalyst in an undivided cell wrapped by nickel foam (cathode), iron (anode), and $NiBr_2bpy$. They revealed that the scarcely described aryl/hetero aryl pyrrolyl pyrimidines, potentially attractive novel structures for the transition-metal ligands or pharmaceutical industry, could be easily provided by reductive and electrochemical cross-coupling.

In 2017, Atobe et al. designed a new cathodic coupling reaction of arenes **37** with aryl halides **3** (Scheme 24) (Qu et al., 2017). Using the cathodic SET mechanism for the activation of aryl halides allows the coupling reaction (31–76 %) to continue with no the requirement for any transition metal catalysts and single electron donors in a moderate status. Mechanism studies reveal that the SET from a cathode starts a radical chain by producing an anion radical of the aryl halide (Scheme 25). Platinum plates were utilized both for the cathode and anode.

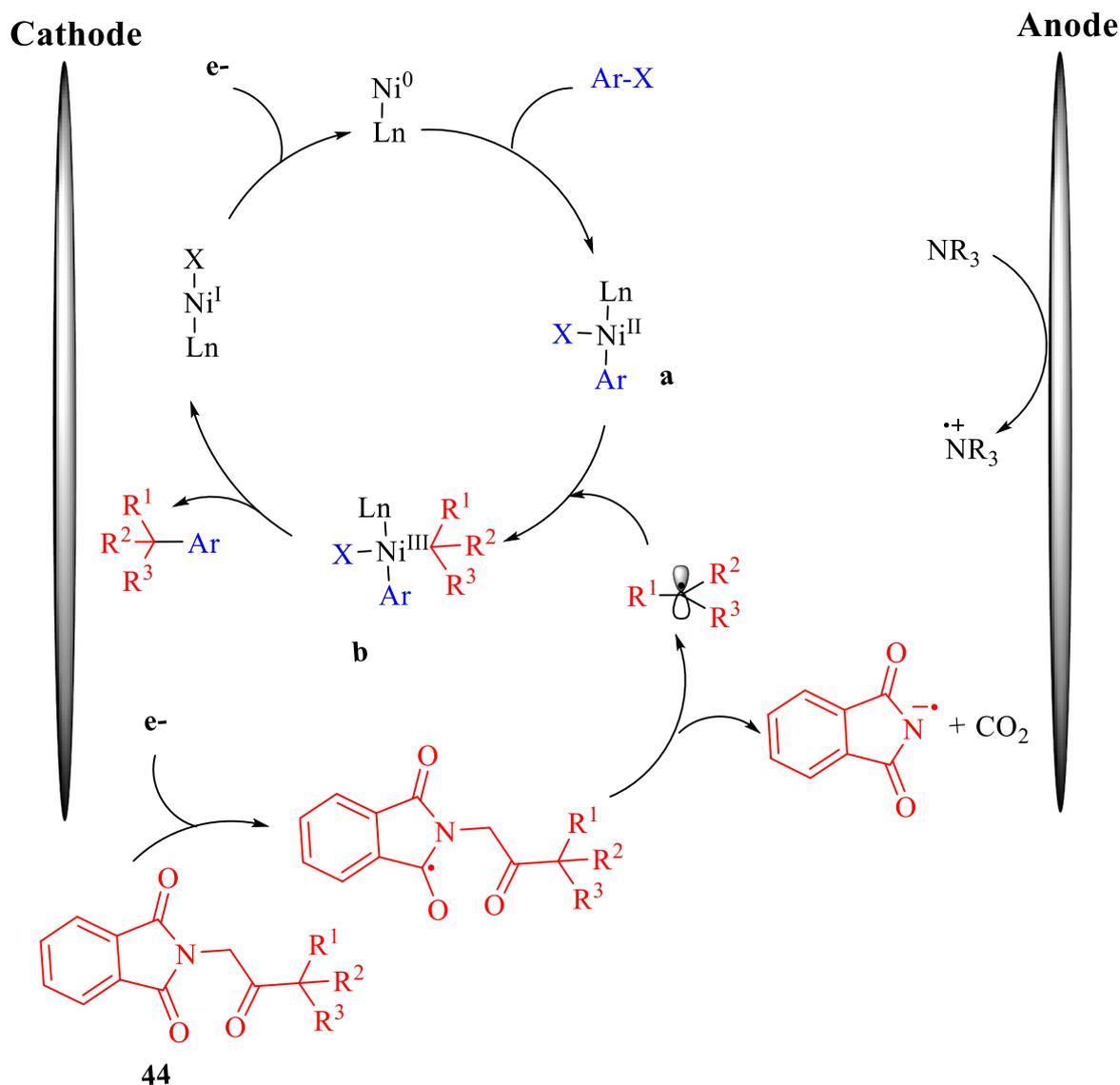
The Huang group created a novel pathway for directly coupling allylic/alkyl halides utilizing an electrochemical approach (Scheme 26) (Lai and Huang, 2017). This reaction was performed in an undivided cell with zinc foil (cathode) and a platinum wire (anode) in an aqueous medium by catalyzed palladium(II) acetate. This method was helpful for the coupling reaction (76–91 %) of alkyl halides **39** with allylic halides **40**, such as tertiary, secondary, and inactivated primary halides, as well as activated halides.

This year, Hansen et al. declared the electrochemical procedure for nickel-catalyzed reductive sp^3 - sp^2 couplings alkyl **42** and aryl bromides **3** (Scheme 27) (Perkins et al., 2017). A Reticulated Vitreous Carbon (RVC) foam (cathode) and zinc rod (anode) were used for electrolysis. RVC was selected as the cathode substance for its chemical inertness and high surface area. The yields of product **43** were attained at 51–86 %. The mechanism offered by Weix et al. for metal powder reductive coupling (Biswas and Weix, 2013), where $Ni(0)$ enters the catalytic cycle through the reduction of $Ni(II)$ at the cathode (Scheme 28).

In 2018, Li et al. indicated nickel-catalyzed reductive coupling of *N*-hydroxy phthalimide esters **44** and aryl halide derivatives **45** (Scheme



Scheme 29. Electrochemical decarboxylative arylations.



Scheme 30. Proposed mechanism of electrochemical-driven decarboxylative arylation by nickel-catalyzed.

29) (Li et al., 2018). This report provides a new and practical approach to using carboxylic acids as precursors to carbon–carbon bond-making. The reaction proceeded with mild status in a divided cell and employed triethylamine (as the reductant). This decarboxylative C(sp²)-C(sp³) bond-making showed great substrate functional group adaptability 46 (39–76 %). They proposed to utilize electron-rich amines as sacrificial reductants, which readily underwent anodic oxidation and donated electrons to the system.

Mechanism determination revealed that cathodic reduction of the redox-active NHP ester 44 appeared in a decarboxylative fragmentation, resulting in the production of the C(sp³) radical (a) (Scheme 30). Afterward, alkyl radical (a) is intercepted by a homogeneous nickel catalyst, which could be either Ni(II) or Ni(0) created from the oxidative addition of aryl halides. Upon production of Ni(III) species (b), the aryl/alkyl groups were expected to undergo reductive elimination to afford the C(sp²)-C(sp³) coupling product.

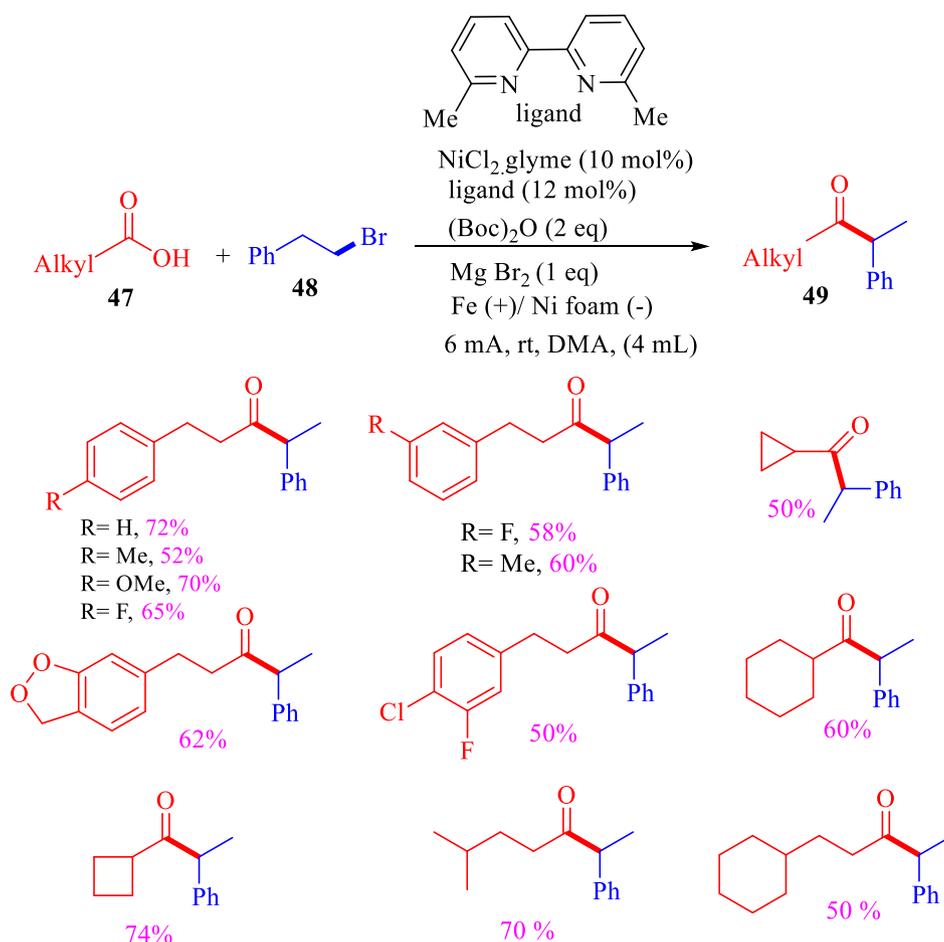
In 2021, Jiao et al. reported a simple synthesis of 1,1-dialkyl ketones 49 via a nickel catalyst electrochemical reductive cross-coupling of alkyl bromides 48 with alkyl acids 47 in an undivided cell. Alkyl bromides having various functional groups like ether, fluoro, chloro trifluoromethoxy, trifluoromethyl, and OTIPS were used and obtained products in good yields in contrary alkyl bromide with polysubstituted

aryl rings did not went well and provided low results (Scheme 31) (Jiao et al., 2021).

The chemical method for reductive acylation between alkyl bromides and alkyl carboxylic acids by nickel-catalyzed has been reported Wang et al. This approach suffers from a long reaction time (24h) (He et al., 2019). A common limitation is employing stoichiometric amounts of manganese or zinc as reductants. The electrochemical method can be an excellent choice for solving this matter. The mechanism is offered in Scheme 32.

In 2023, Cantillo et al. described the electrochemical coupling of alkyl bromides 42 and alkyl tosylates 50 by nickel catalyzed (Scheme 33) (Ibrahim et al., 2023). The results illustrated that the reaction proceeds high selectivity under a constant current (4 mA) using NaBr as the electrolyte in DMSO. The alkyl–alkyl bond-making reactions (42–78 %) are essential in medicinal chemistry, so electroorganic synthesis of this compound is growing. The mechanistic pathway representing electrochemical cross-coupling was depicted in Scheme 34.

In the same year, Qiu et al. reported NiH-catalyzed electrochemical coupling of alkyl alkenes/halides in an undivided cell with 4.0 mA (constant current) for 12h (Scheme 35) (Li et al., 2023). Alkyl halides perform double roles as coupling substrates and hydrogen sources to cause NiH species to be at electrochemical status. The approach displays



Scheme 31. Electrochemical nickel-catalyzed coupling of alkyl halides with alkyl carboxylic acids .

a broad precursor range and generates good to high yields with up to seventy examples.

2.3. Addition of organic halides to unsaturated groups

Conjugate additions onto activated alkenes are valuable for carbon–carbon bond creation in organic synthesis (Perlmutter, 1992). In 2000, Gosmini and colleagues demonstrated that CoBr_2 was an impressive catalyst for the electrochemical addition of aryl bromides **3** onto activated olefins **54** (Scheme 36) (Gomes et al., 2000). No additional product was acquired for other metals, e.g., Mg, Zn, or Al; nickel foam (cathode) and iron (anode) were used. Electrolysis was conducted at 0.2 A (constant current) in an undivided cell with good yield products **55** (20–70 %). The solvent acetonitrile /pyridine offered advantages over pyridine/DMF, affording slightly better results and avoiding using 2,2'-bipyridine as a ligand.

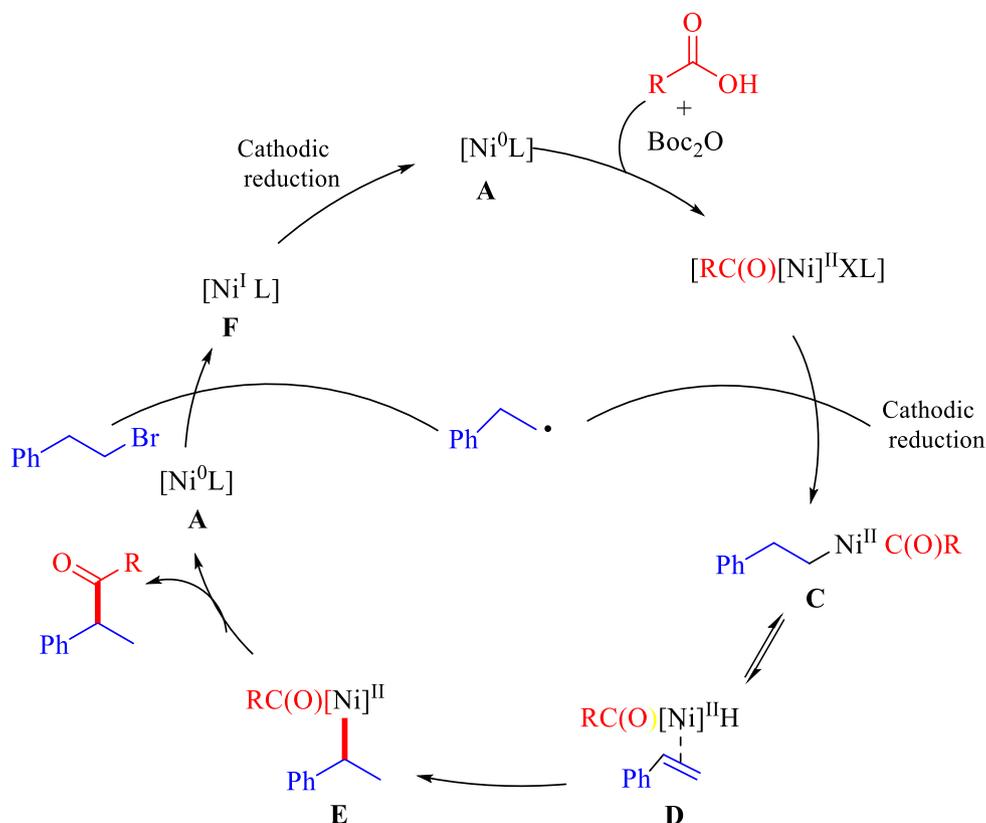
In the same year, Condon *et al.* demonstrated a direct procedure of activation of alkenyl halides, enabling the fabrication of substantial target compounds, including ketones, γ,δ - or β,γ - unsaturated esters, nitriles, or conjugated dienes as well as alkenylated aryl products (Scheme 37) (Cannes et al., 2000). Homo and cross-coupling, including alkenyl halides **56**, were carried out efficiently using electroassisted nickel complex catalysis with (50–77 %) yield. They also exhibited that activating alkenyl chlorides, bromides, or iodides was possible. However, the reaction was born at 50 °C or higher. In cross-coupling reactions, using alkenyl iodides is not beneficial because of the dimerization; this is also observed with bromo styrene.

In 2001, Durandetti *et al.* indicated the electrochemical coupling of aldehydes **58** with organic halide **3** to synthesize arenecarboxaldehydes

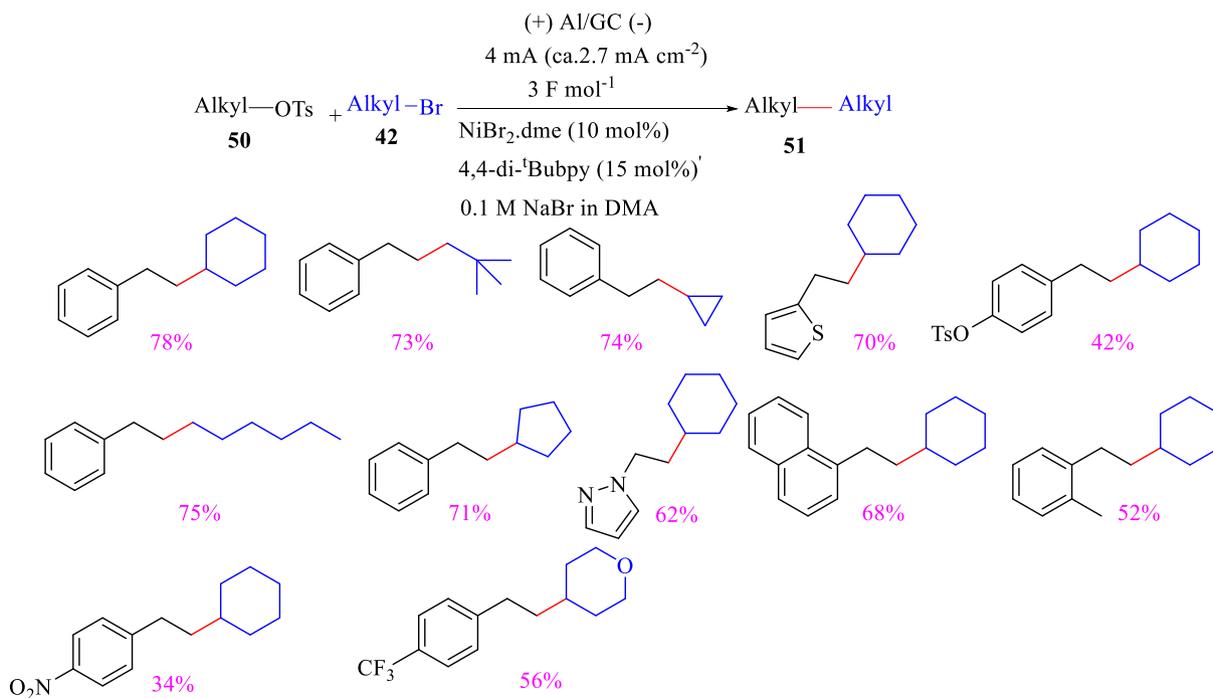
59 (the Nozaki-Hiyama-Kishi reaction) (Scheme 38) (Durandetti et al., 2001). The electrochemical procedure includes a one-compartment cell fitted with a nickel sponge (cathode) and a stainless steel rod (anode) using chromium and nickel catalyst. Secondary alcohols were achieved in the mild to good yields (50–70 %). Different benzhydrol derivatives could be obtained to satisfy outcomes in one stage by a highly facile electrochemical procedure. The reaction was catalytic in chromium salt (7 %/ $\text{C}_6\text{H}_5\text{CHO}$). Also, the process was used to add α -chloroester, allyl acetate, or vinyl halide to aryl aldehydes.

One year later, Condon *et al.* described electrochemical heteroarylation of activated olefins **61** by nickel catalyst (Scheme 39) (Condon et al., 2002). The conjugate addition reaction of hetero/aryl halides **60** to functionalized olefins had been favorably attained with nickel catalysis combined with the consumable anode method and prepared available to diverse functionalized hetero aryl products **62** (5–76 %). The structures of hetero aromatic are critical building blocks for synthesizing biologically active fragments as agrochemicals or pharmaceuticals. The reactions were conducted in an undivided cell flushed with a concentric nickel foam (cathode) and a stainless steel rod or iron (anode) in an argon atmosphere.

The same year, Gosmini *et al.* demonstrated electrochemical vinylation of vinyl/aryl halides **3** with acrylate esters **63** using CoBr_2 (Scheme 40) (Gomes et al., 2002b). A stainless steel grid (cathode) and an iron (anode) were performed. Pyridine/triethylamine/acetonitrile was used as a solvent, and bipyridine was used as a ligand. The CoBr_2 , 2,2'-bipyridine (specifically substituted by an electron-donating group), and acrylate esters with vinyl chlorides were used. This stereoselective reaction generated only *E*-olefins **64** (45–61 %) in all the investigated cases. Aryl bromides (substituted by an electron-donating group) in the



Scheme 32. Plausible catalytic process.

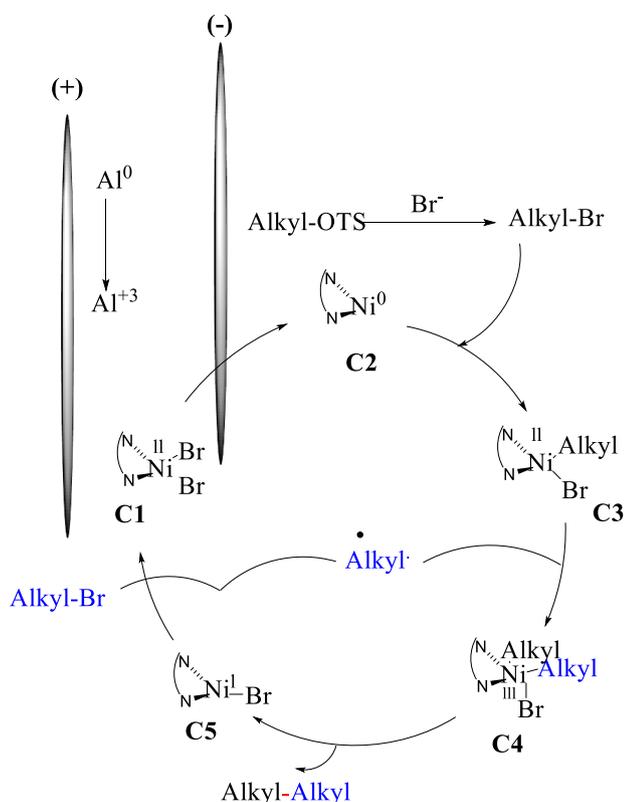


Scheme 33. Electrochemical cross-coupling of alkyl tosylates with alkyl bromides.

para status gave the best results.

In 2002, Nédélec *et al.* revealed two pathways to obtain medium-sized lactones based on the electrochemical arylation of activated olefins **63** catalyzed by a nickel complex (Scheme 41) (De Mendonça Cavalcanti *et al.*, 2002). Preparation of 6-, 7-, and 8- membered lactones

68 was applied through electrochemical arylation of electron-deficient olefins. The electrochemical reaction was done in the undivided cell with an iron rod (anode) and a nickel foam (cathode). This group found an exciting alternative based on the coupling between an α - β -unsaturated ester **63** and an *o*-aryl halide **66** (60–85 %), followed by



Scheme 34. Mechanistic pathway for electrochemical cross-coupling.

lactonization.

Direct electrochemical cross-coupling between a mixture of hetero/aryl chlorides **3** and carbonates or allylic acetates **22** was offered by Gomes *et al.* (Scheme 42) (Gomes *et al.*, 2003a). The electrochemical cell has a stainless steel grid (cathode) and a sacrificial iron (anode). This catalytic reaction is a suitable path for the S_N2 with aryl halides. Various aryl allyl compounds **22** were achieved in good yields (30–81 %).

In 2003, Condon *et al.* illustrated the arylation of organic halides **3** with acrolein diethyl acetal **69** by nickel(II) bromide as a catalyst precursor (Scheme 43) (Condon *et al.*, 2003). (*E*)- and (*Z*)-enol ethers **70** (28–58 %) were obtained by allylic displacement of an alkoxy group. The reactions were carried out using an iron or stainless steel (Fe/Cr/Ni, 72/18/10) anode in steady current intensity at 70 °C, and S_N2 substitution derivatives were not attained. Furthermore, the *Z*-isomer is barely preferred; the isomer ratio was constant in the reaction.

In 2005, Moeller and Tian published the status for electrochemically assisted Heck reactions (Scheme 44) (Tian and Moeller, 2005). This reaction not only notably accelerates the room-temperature Heck reactions without adding ligands but also leads to high product yields **71** (62–89 %). Coupling iodobenzene **3** to electron-rich, electron-poor, and

conjugated olefins series **61** was performed. The reactions were accomplished using a straightforward design utilizing a battery as the energy supply.

2.4. Carboxylation and carbonylation of organic halides

Electrochemical fixation of CO_2 to organic chemicals is a beneficial procedure for synthesizing different carboxylic acids under neutral and moderate status. These electrochemical carboxylations occur efficiently even in the atmospheric pressure of CO_2 ; meanwhile, an active metal, including Al or Mg, is utilized as a sacrificial anode in the electrolysis (Wang *et al.*, 2022; Zhao *et al.*, 2023). CO_2 is a plentiful, cheap, non-toxic, and renewable carbon source; the kinetic and thermodynamic stability of the molecule limits its utilization in the chemical industry for the transformation to helpful chemicals (Costentin *et al.*, 2012; Benson *et al.*, 2009; Kumar *et al.*, 2012).

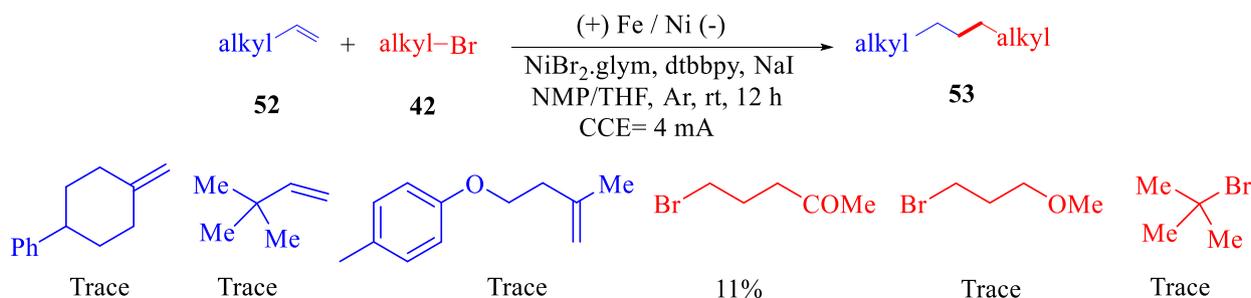
In 2001, Troupel *et al.* reported the fabrication of unsymmetrical carbonyls **73** from aryl iodide **3** and benzylic chlorides **72** employing iron pentacarbonyl like the origin of CO (carbon monoxide) (Scheme 45) (Dolhem *et al.*, 2001). The electrochemical reaction was done in an undivided cell supplied by a sacrificial stainless steel rod (anode) encircled by a cylindrical nickel grid (cathode). Applying carbon monoxide gas in mild status, this procedure provided symmetrical ketones derived with good yields (76–88 %).

Reddy *et al.* declared electrochemical carboxylation of benzyl chlorides **74** catalyzed using Pd(II) complex for synthesizing 2-aryl propionic acids (Scheme 46) (Damodar *et al.*, 2001). This reaction was performed in a cell with an Mg (anode) and Pt (cathode) under atmospheric pressure of carbon dioxide at constant current, producing 2-aryl propionic acids **75** in good yields (74–84 %). Organometallic catalysts did not play any chemical role in the stage of carboxylation but aided in activating the C–X bond, allowing the two-electron reduction of organic halide. Mechanistic research illustrated the reduced Palladium species' cooperative function for carbon dioxide activation.

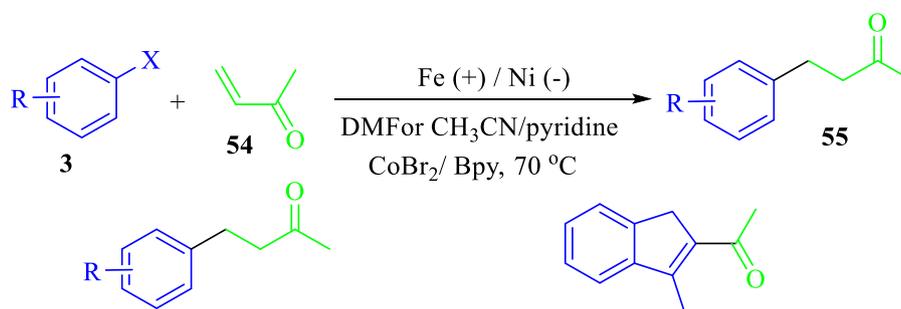
In 2002, Gennaro and Isse explained that electrocarboxylation of benzyl chlorides was performed with no use to homogeneous catalysts (Isse and Gennaro, 2002). This work's most significant advantage is that the silver cathode process occurred at a more optimistic potential than other published catalysts. This method gave carboxylic acids excellent yields. Silver has displayed satisfactory catalytic attributes in the electroreduction of various organic halides.

One year later, Raju and colleagues described the preparation of 6-amino nicotinic acid **78** from 2-amino-5-chloropyridine **76** using H_2SO_4/CO_2 in a cathode surface (Scheme 47) (Raju *et al.*, 2003). Electrochemical carboxylation was executed at an undivided cell by platinum (cathode) and magnesium (anode).

This new procedure involved the combination of electrochemical carboxylation and hydrogenation for the synthesis of 6-amino nicotinic acid. Scheme 48 offers a proposed mechanistic rationalization for reductive carboxylation. The two-electron reduction of 2-amino-5-chloropyridine generates an intermediate carbanion, which attacks CO_2 to generate CO_2^- . The catch of the anion by metal ions afforded by the



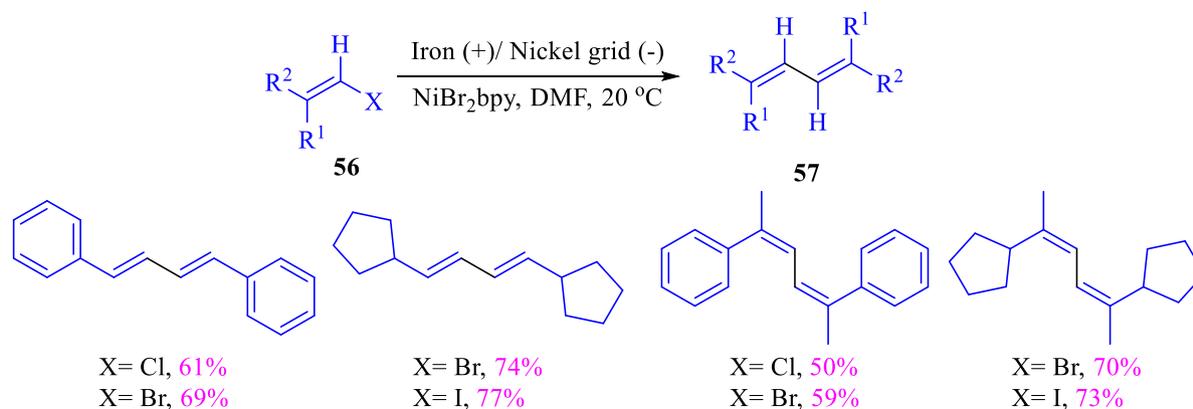
Scheme 35. Electrochemical coupling of unactivated alkenes and alkyl bromide.



R= 4-COOEt, X= Br, Solvent: DMF, 64%
 R= 4-COMe, X= Br, Solvent: DMF, 56%
 R= 4-CF₃, X= Br, Solvent: DMF, 45%
 R= 4-CN, X= Br, Solvent: DMF, 55%
 R= 4-CHO, X= Br, Solvent: DMF, 30%
 R= H, X=Br, Solvent: DMF, 33%
 R= 4-OMe, X= I, Solvent: DMF, 22%
 R= 2-COMe, X= Br, Solvent: DMF, 45%
 R= 4-COOEt, X= Br, Solvent: CH₃CN, 70%
 R= 4-COMe, X= Br, Solvent: CH₃CN, 55%
 R= 4-CN, X= Br, Solvent: CH₃CN, 70%
 R= 4-COMe, X= Cl, Solvent: CH₃CN, 20%

X= Br, Solvent= DMF, 45%

Scheme 36. Electrochemical addition of aryl halides onto activated alkenes.



Scheme 37. Electrochemical couplings of vinyl halides.

dissolution of the anodic metal provided a metal carboxylate. Lastly, treating the metal carboxylate with acid furnished the desired product (60–84 %).

In 2004, Gennaro *et al.* demonstrated a novel method for preparing 6-amino nicotinic acid with the electrocatalytic reduction of 2-amino-5-bromopyridine at silver cathodes (Gennaro *et al.*, 2004). They discovered that the procedure required just the stoichiometric charge at Ag cathodes. They gave good yields of 6-amino nicotinic acid, while in DMF/CH₃CN, reduction of the halide compounds in the typically employed electrodes, including Pt, Hg, and GC, required negative potentials, including Pt, Hg, and GC, required very negative possibilities, which were only slightly more positive than that of carbon dioxide.

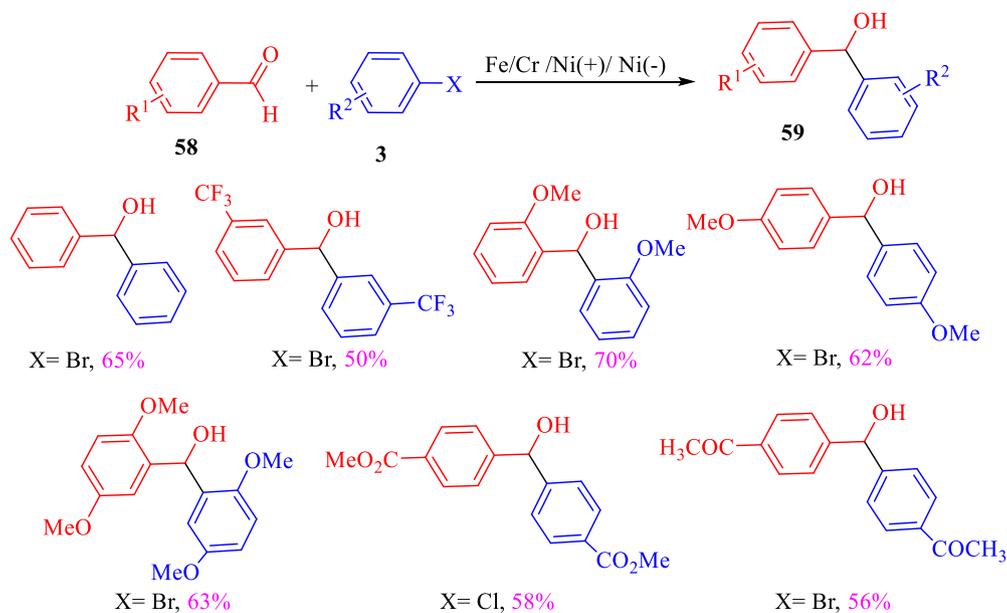
In 2005, Isse *et al.* surveyed the electrochemical reduction of some aryl ethyl chlorides by silver and glassy carbon electrodes in dimethylformamide /acetonitrile (Isse *et al.*, 2005). In these two solvents, silver showed a significant catalytic influence. Better results were obtained at lower temperatures. The acid product yields were 70–81 % and 61–73 % at 273.15 K and 298.15, respectively.

In 2007, Aishah *et al.* explained the electrosynthesis of benzoic acid

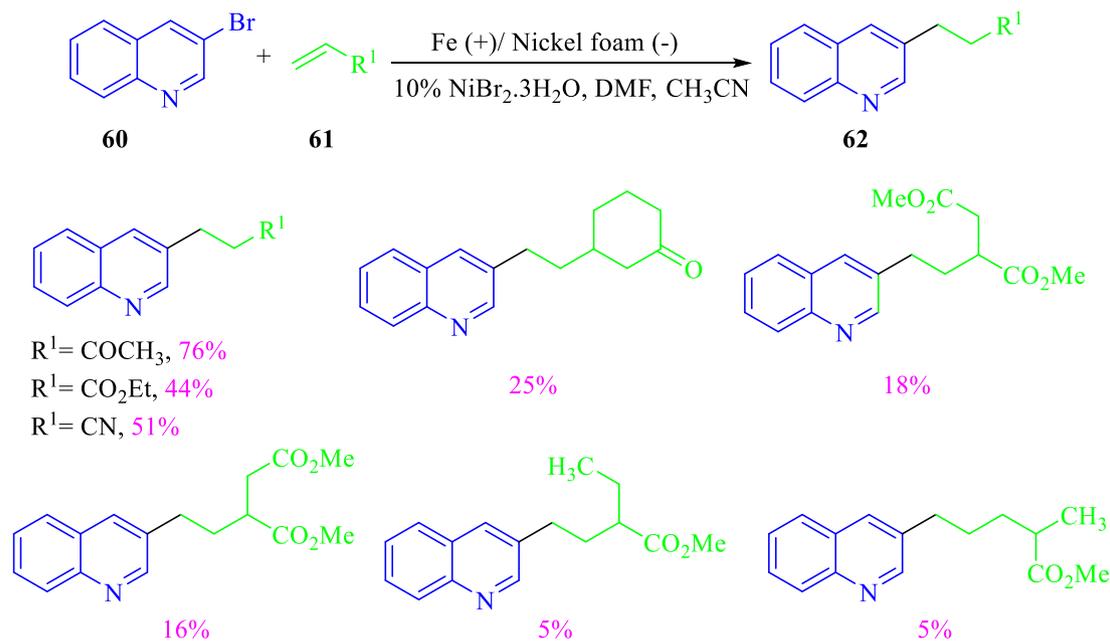
80 from chlorobenzene **79** by CO₂ fixation procedure (Scheme 49) (Aishah *et al.*, 2007). The electrolysis was conducted at a one-compartment cell provided by palladium (cathode) and aluminium (anode) under the optimum status of electrocarboxylation, which showed a 72 % yield of C₆H₅CO₂H from C₆H₅Cl. In addition, these statuses were employed in 1,2- and 1,3- dichlorobenzene to transform them into their desired benzoic acids.

At the same time, Yamauchi *et al.* indicated the electrochemical carboxylation of α,α -difluorotoluene derivatives **81**, and **84** by the electrochemical reduction using carbon dioxide in an undivided cell with a magnesium rod (anode) and platinum plate (cathode). (Scheme 50) (Yamauchi *et al.*, 2008). They illustrated that this procedure is highly effective for synthesizing α -fluorinated nonsteroidal and 2-fluoro-2-arylpropanoic acids **82**, **83**, and **85**. In an efficient carbon dioxide fixation, the related α -fluorophenylacetic acids were achieved in high yields (40–74 %).

In 2008, Niu *et al.* demonstrated an efficient and easy electrocarboxylation reaction of aliphatic halides **86** (Scheme 51) (Niu *et al.*, 2008). They showed that diverse status, including the supporting



Scheme 38. Electroreductive cross-coupling between aryl halides and benzaldehydes.



Scheme 39. Reaction of activated olefins with 3-bromoquinoline.

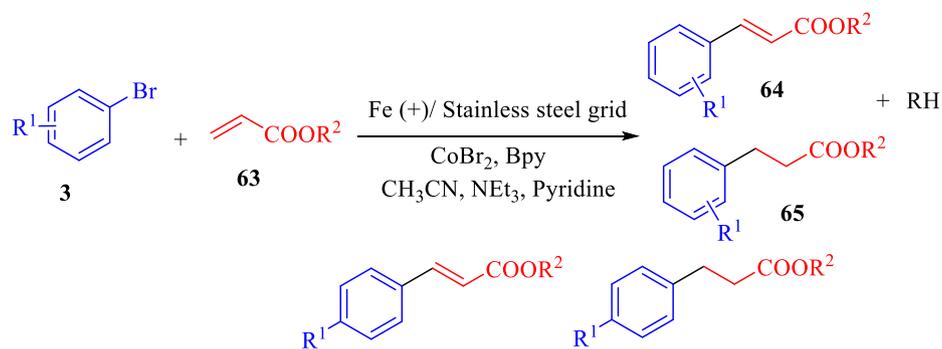
electrolyte, temperature, and the nature of the electrode, could affect $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ yield. Under the standard reaction status, medium to high yields (22–89 %) were achieved to form corresponding carboxylic acids **87**.

For the first time, the electrocarboxylation of benzyl chloride was surveyed at the silver cathode in CO_2 -saturated ambient temperature ionic liquid (BMIMBF₄) solution by Jiaying *et al.* in 2009 (Niu *et al.*, 2009). The electrochemical treatment was investigated at various electrodes by cyclic voltammetry, which exhibited the remarkable electrocatalytic impact of the silver electrode in the reduction of benzyl chloride. The most elevated yield of phenylacetic acid (45 %) was acquired under optimization status. The ionic liquid was recovered after four cycles of minimal efficiency loss.

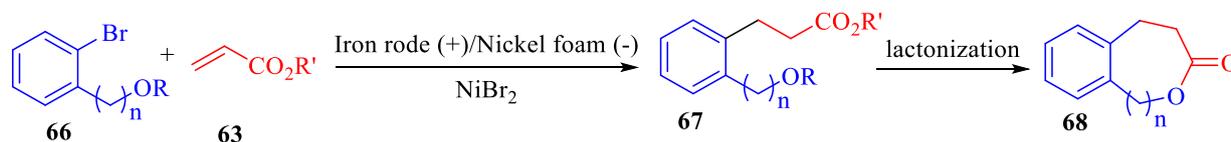
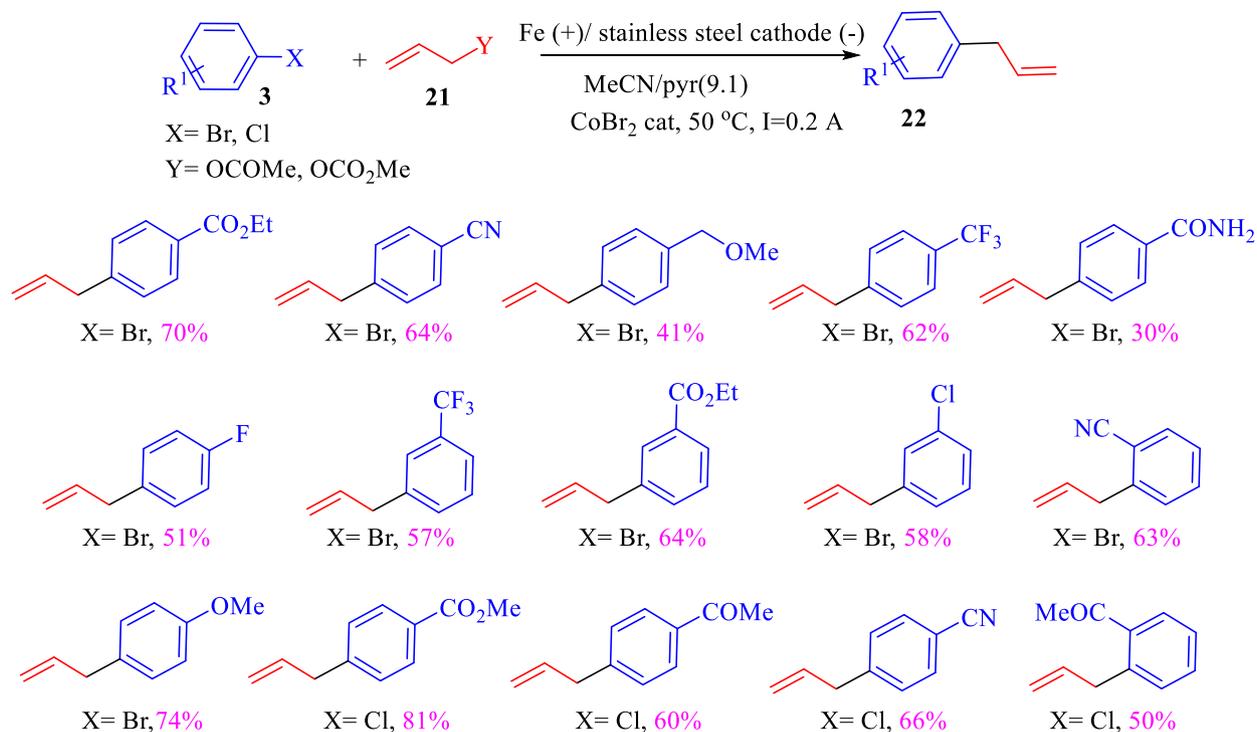
In 2010, Yamauchi *et al.* illustrated the electrochemical reduction of 1-bromo-2,2,2-trifluoroethyl benzene (**88**) to synthesize 2-aryl-3,3,3-

trifluoropropanoic acid (**89**) using CO_2 in an undivided cell fitted by a zinc plate (anode) and a Pt plate (cathode) (Scheme 52) (Yamauchi *et al.*, 2010). The desired products with good yields (23–70 %). Also, this current reaction was effectively employed to synthesize β,β,β -trifluorinated non-steroidal anti-inflammatory medicines (NSAIDs).

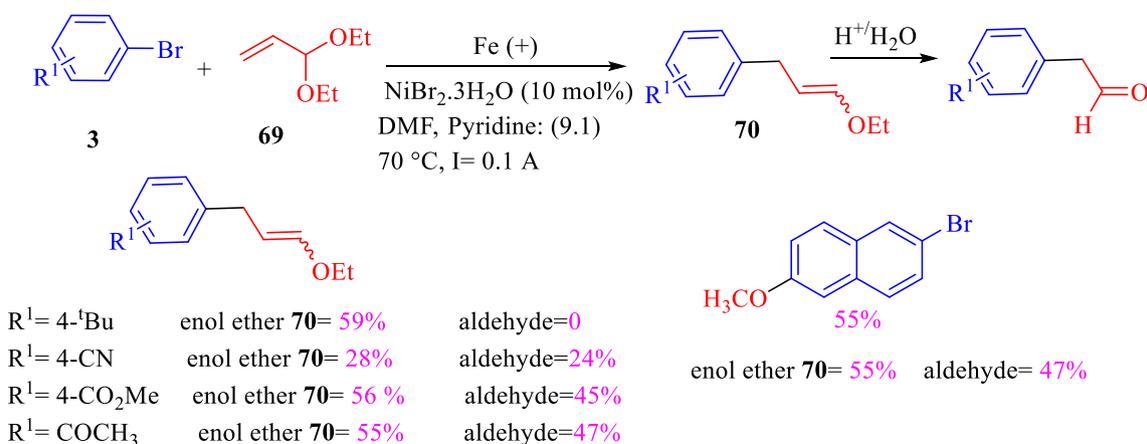
In 2010, Hiejima *et al.* studied the electrochemical carboxylation of α -chloroethyl benzene **90** with CO_2 in ionic liquids compressed (Scheme 53) (Hiejima *et al.*, 2010). The current efficiency increased with pressure and temperature. The influence of carbon dioxide pressure on the present efficiency of the carboxylation reaction was surveyed. The sacrificial magnesium is satisfactorily utilized in TFSA-DEME compressed with carbon dioxide, allowing it to handle the auxiliary oxidation in the counter electrode and enhance the existing carboxylation efficiency (32–60 %).



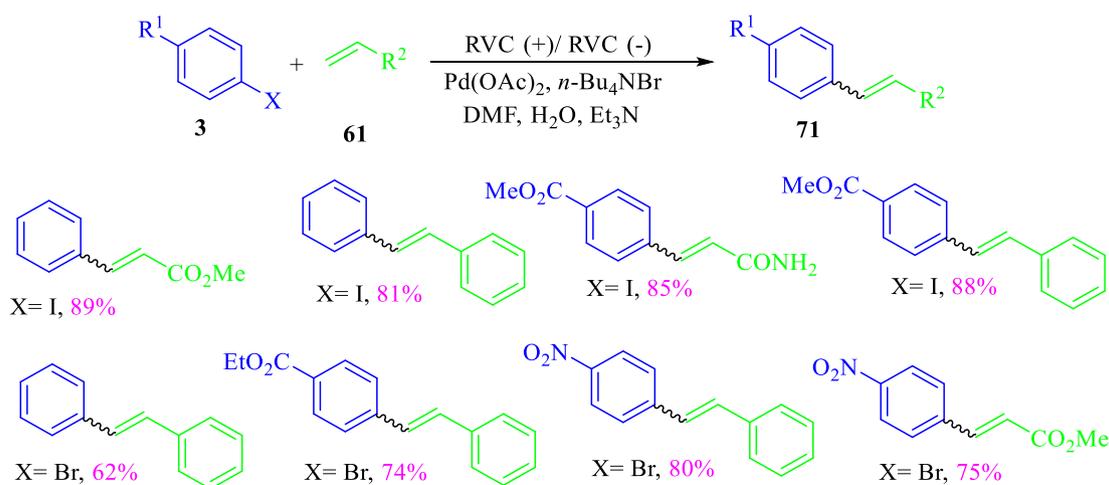
$\text{R}^1 = \text{H}, \text{R}^2 = \text{Et}$	56%	22%
$\text{R}^1 = \text{CH}_3, \text{R}^2 = \text{Et}$	54%	25%
$\text{R}^1 = \text{C}(\text{CH}_3)_2, \text{R}^2 = \text{Et}$	61%	29%
$\text{R}^1 = \text{OCH}_3, \text{R}^2 = \text{Et}$	57%	24%
$\text{R}^1 = \text{N}(\text{CH}_3)_2, \text{R}^2 = \text{Et}$	58%	18%
$\text{R}^1 = \text{SCH}_3, \text{R}^2 = \text{Et}$	47%	35%
$\text{R}^1 = \text{CO}_2\text{Et}, \text{R}^2 = \text{Et}$	45%	31%
$\text{R}^1 = \text{OCH}_3, \text{R}^2 = \text{Bu}$	55%	21%

Scheme 40. Coupling of acrylate esters with vinyl/aryl halides using CoBr_2 .Scheme 41. Bimolecular coupling between esters of acrylic acid and *o*-aryl halides.

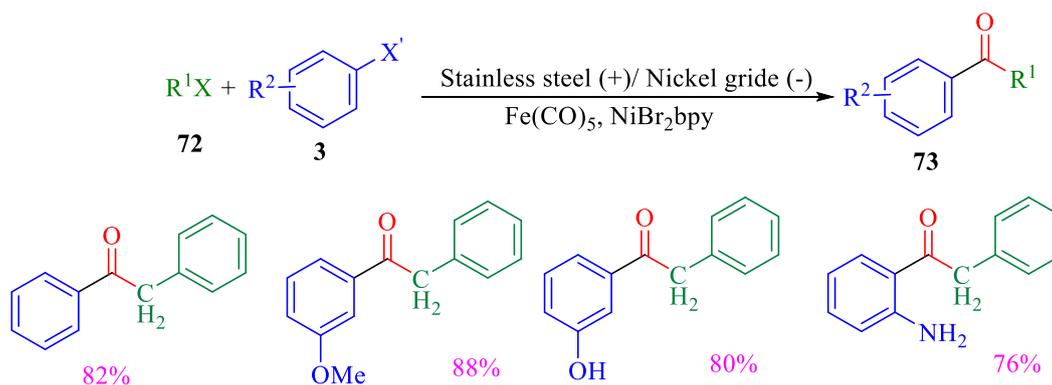
Scheme 42. Coupling reaction between allyl acetate and aryl halides.



Scheme 43. Arylation of acrolein diethyl acetal using nickel catalyzed.



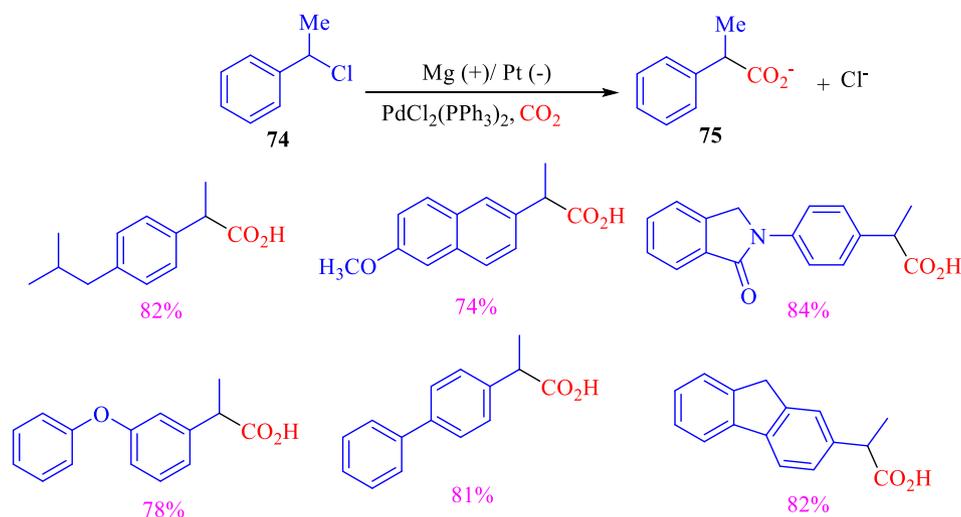
Scheme 44. Coupling bromo/iodobenzene to different olefin series.



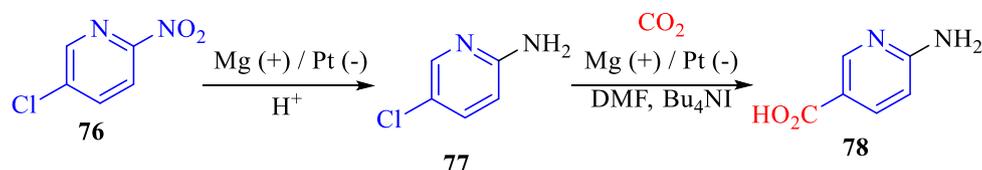
Scheme 45. Electrosynthesis of various ketones from different aryl halides.

A novel electrochemical method for the electrocatalytic carboxylation of 2-amino-5-bromopyridine and CO₂ in BMIMBF₄ (ionic liquid) to 6-amino nicotinic acid was surveyed in 2010 by Feng *et al.* (Feng *et al.*, 2010). The reactions were completed in three electrodes undivided cells without catalysts or toxic and volatile solvents under mild status. Cyclic voltammetry shows that BMIMBF₄ could serve as a medium for 2-amino-5-bromopyridine reduction and the effect of working potential, temperature, passed charge, and concentrations. Under optimized conditions, 6-amino nicotinic acid can be obtained in 75 % yield with excellent selectivity. In addition, the ionic liquid was recycled.

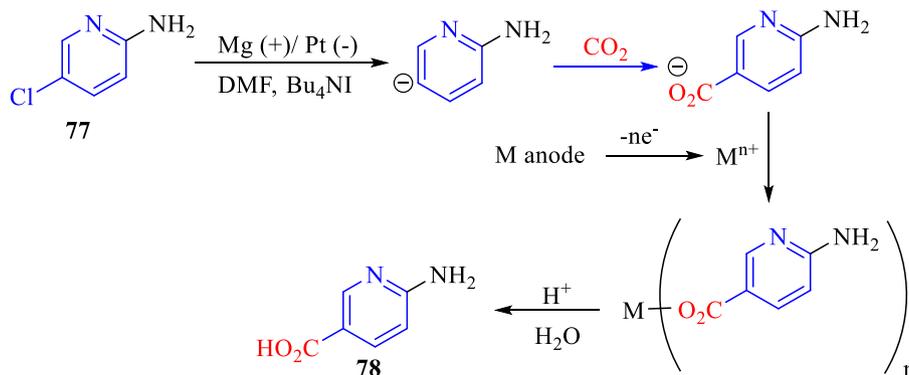
In 2010, Yuan *et al.* indicated that the electrochemical pathway with nickel cathode was efficient for the electrocarboxylation of polycyclic aryl hydrocarbons **92** with carbon dioxide without additional catalysts under mild status (Scheme 54) (Yuan *et al.*, 2010). Nickel cathode catalyzed in reducing polycyclic aryl hydrocarbons or carbon dioxide. The work provided an efficient and convenient method for synthesizing dicarboxylic acids from CO₂ and polycyclic aryl hydrocarbons. The formation of *trans*-dicarboxylic acids during electrolyzes is due to electrostatic repel and the steric hindrance effect between two CO₂ groups in the products. The related *trans*-dicarboxylic acids **93** were found in



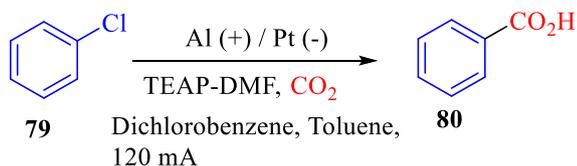
Scheme 46. Electrochemical preparation of 2-aryl propionic acids.



Scheme 47. The carboxylation of 2-amino-5-chloropyridine by electrochemical reaction.



Scheme 48. Proposed mechanism of reductive-carboxylation.

Scheme 49. Electrosynthesis of C₆H₅CO₂H from C₆H₅Cl.

62–90 % yields.

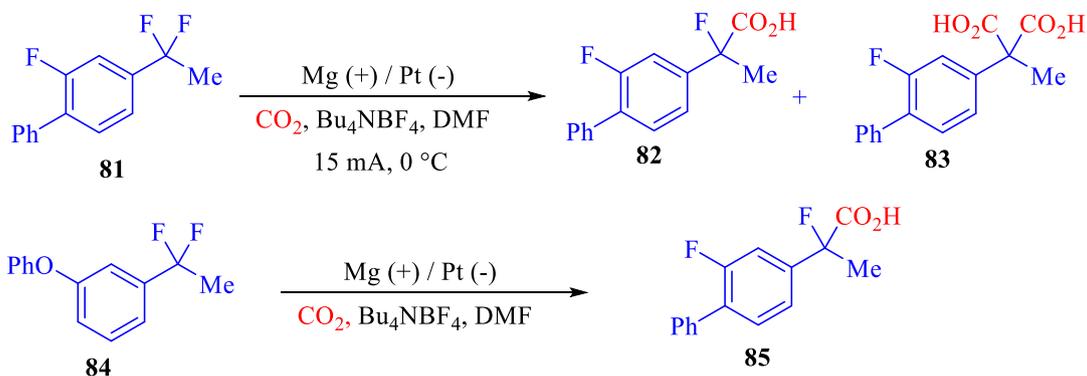
An efficient and straightforward electrocatalytic carboxylation of aryl bromides **3** was extended by Lu *et al.* in 2011. Magnesium as an anode and silver as a cathode were used (Scheme 55) (Zhang *et al.*, 2011). The influences of fundamental factors (including temperature, the current density, and the nature of the cathode material) on this reaction were examined. The desired carboxylic acids **94** were achieved in 30–78 % yields. The electrochemical treatment was checked in various electrodes (Ni, Ti, Cu, and Ag) by cyclic voltammetry, which exhibited

the notable electrocatalytic effect of the silver electrode in the reductive carboxylation of aryl bromides.

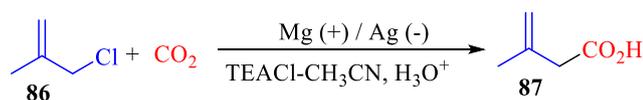
The same group presented the electrochemical reduction of di-bromobenzenes **95** using carbon dioxide (Scheme 56) (Lan *et al.*, 2012). Diverse selectivity of individual isomers determined by cyclic voltammetry. Several cathode materials were surveyed, including titanium, copper, silver, and nickel. The most satisfactory results were achieved with silver as a cathode material owing to the less harmful reduction potential. By using *o*-di-bromobenzene, a transformation of just 49 % could be observed.

Conversely, an average conversion of 71 and 68 % was found in *p*- and *m*- di-bromobenzene, respectively. These conversions were not selective. *O*-di-bromobenzene was mainly monocarboxylate, which could be explained by a significantly more significant reduction potential of both reduction events in 1.61 V.

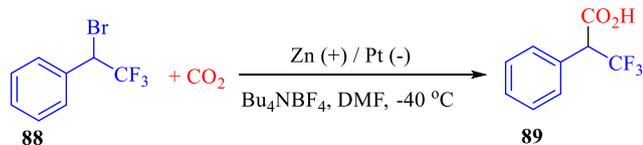
In 2013, Senboku *et al.* surveyed the electrochemical carboxylation of hexafluorobenzene **99** (Scheme 57) (Senboku *et al.*, 2013). The electrolysis was stereo- and regio- selective, and polyfluorobenzoic acids



Scheme 50. The carboxylation of α,α -difluorotoluene compound by electrochemical method.



Scheme 51. Electrochemical carboxylation of 3-chloro-2-methylpropene.



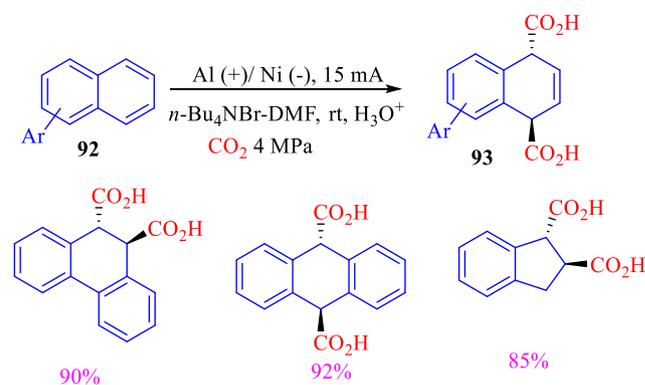
Scheme 52. Electrochemical carboxylation of 1-bromo-2,2,2-trifluorobenzene.

100 were attained in medium to superb yields (44–84 %).

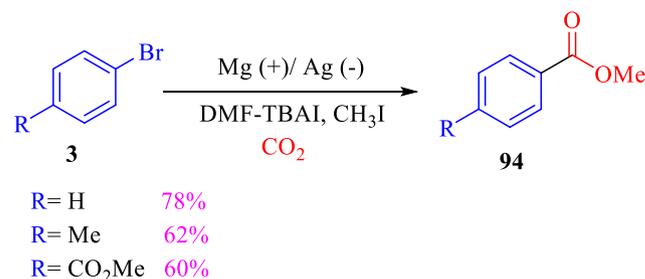
In 2014, Chen *et al.* reported the asymmetric electrocarboxylation of 1-phenylethylchloride **90** with carbon oxide using a chiral [Co^I(salen)]-complex catalyst (Scheme 58) (Chen *et al.*, 2014). This process was accomplished in an undivided glass cell by GC (cathode) and magnesium (anode). Although the yield (13–66 %) and the enantiomeric excess values are moderate, this elegant study rendered an alternative method for synthesizing optically active carboxylic acids **101**.

The electrochemical virtues of ionic liquid and CO₂ systems were surveyed as new reaction media by Tateno *et al.* in 2015 (Scheme 59) (Tateno *et al.*, 2015). The Electrochemical reaction in ionic liquid and supercritical CO₂ to diverse organohalide compounds **90** illustrated appropriate yields (22–59 %). The obtained consequences exhibit that this system is a valuable medium for electrochemical carboxylation reactions. The chemical fixation of carbon dioxide as a raw material is usually challenging owing to its high stability. Therefore, Grignard and organolithium reagents generally react directly with carbon dioxide (Cai

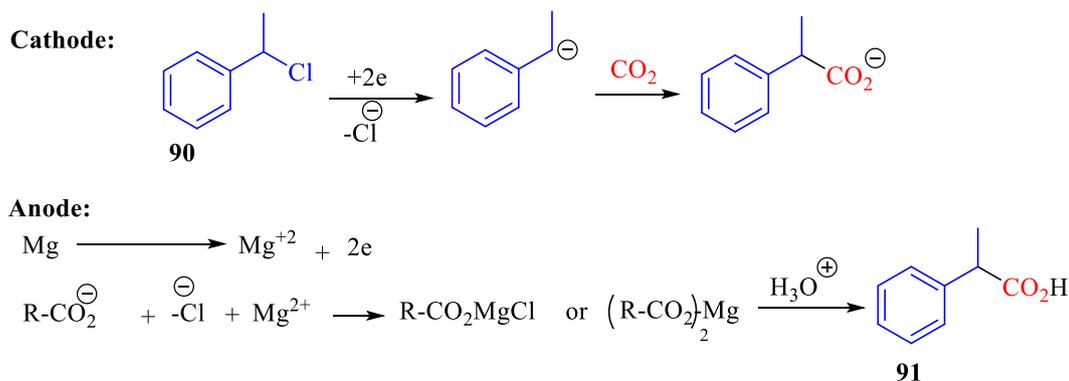
and Xie, 2013). The drawbacks of these approaches are the problem of handling and using costly and toxic reagents and the production of enormous amounts of reagent waste. The electrochemical fixation of



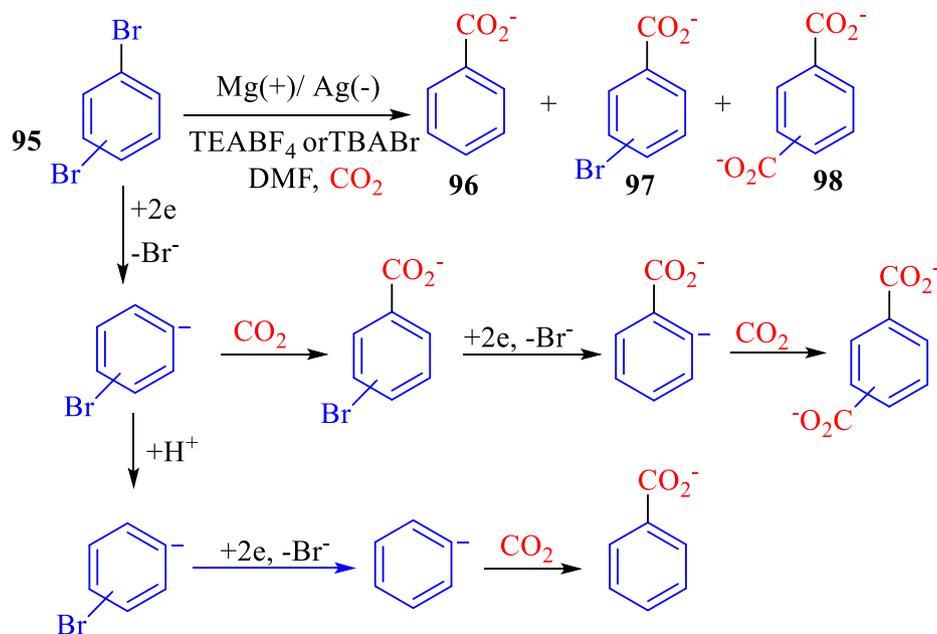
Scheme 54. Electrochemical dicarboxylation of naphthalene with CO₂.



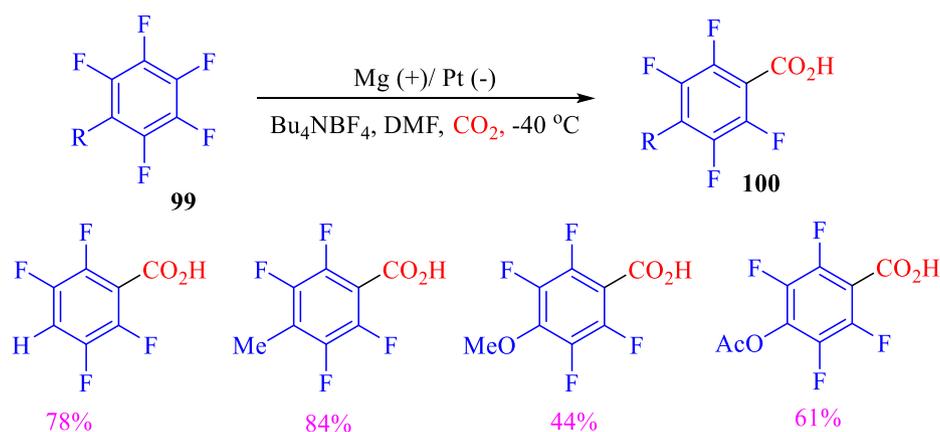
Scheme 55. Electrocatalytic carboxylation of aryl bromides.



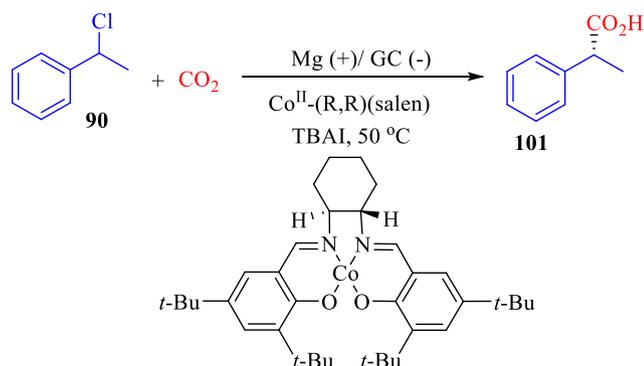
Scheme 53. Electrochemical carboxylation of α -chloroethylbenzene.



Scheme 56. The electrochemical carboxylation of di-bromobenzenes compounds.



Scheme 57. Electrochemical carboxylation of polyfluoroarenes.



Scheme 58. The asymmetric carboxylation of achiral 1-phenylethyl chloride.

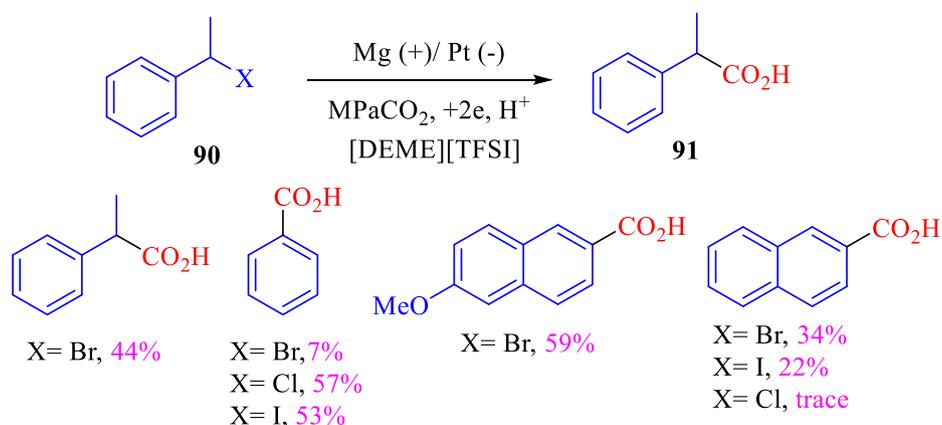
carbon dioxide to organic compounds is an attractive alternative to traditional chemical procedures (Senboku, 2021).

3. Electrochemical Hetero-Coupling of organic halides

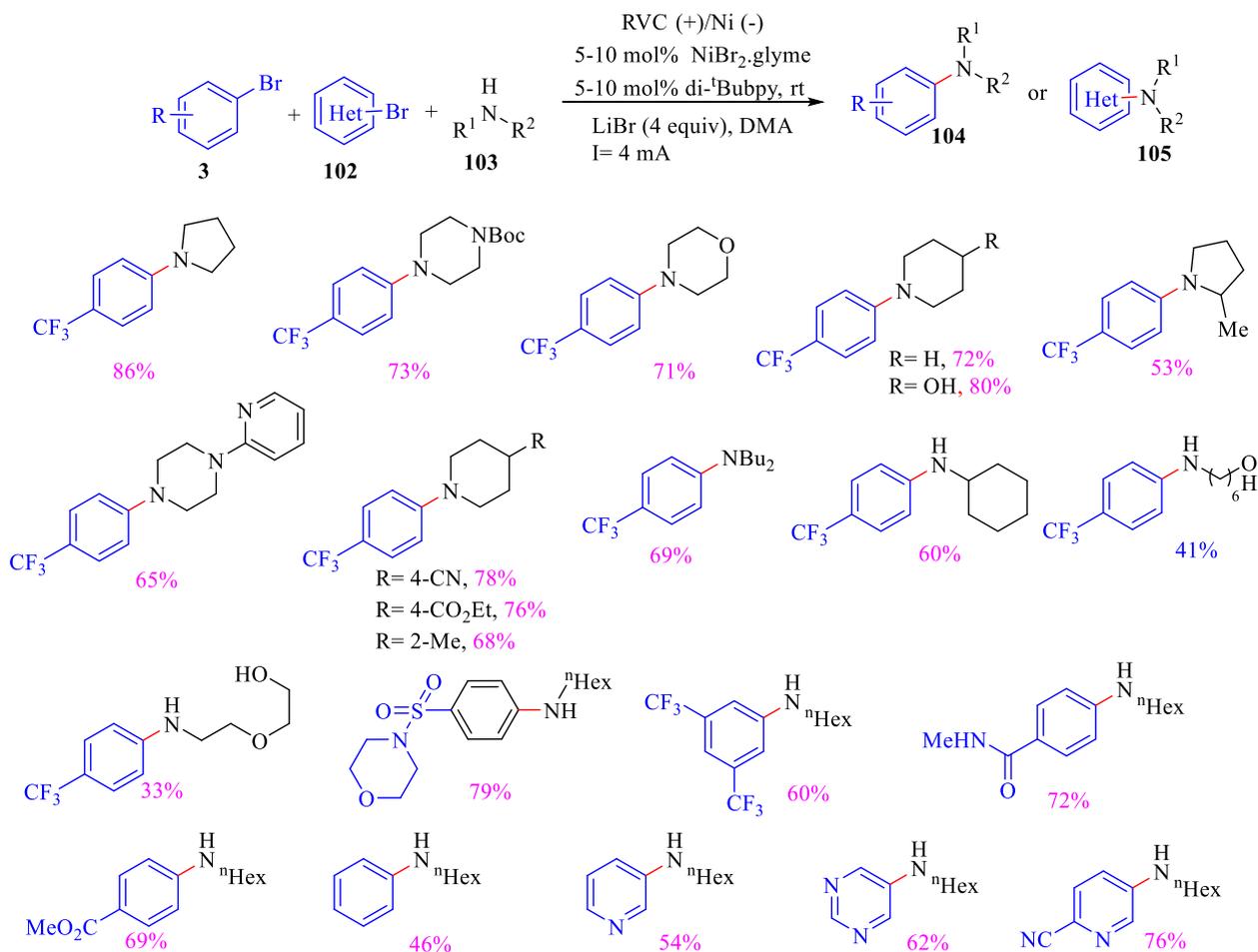
3.1. C–N bond formation reaction

Carbon-nitrogen cross-coupling is one of the most widespread and valuable transforms in organic synthesis fields. C–N cross-coupling reactions are vital for providing N-containing compounds with numerous applications in synthetic, biological, pharmaceutical, and materials science (Kafi-Ahmadi et al., 2021; Parsa Habashi and Poursattar Marjani, 2022; Payamifar et al., 2024a; Payamifar and Poursattar Marjani, 2023a, 2023b, 2024b, Poursattar Marjani et al., 2017, 2019b, 2019a; Schlummer and Scholz, 2004).

In 2017, Baran et al. introduced an electrochemical procedure to attain the cross-coupling between aliphatic amines **103** and aryl halides **3** and **102** (Scheme 60) (Li et al., 2017). The range of the electrolytic protocol comprises aryl chlorides, bromides, iodides, and triflates. Additionally, amides and alcohols could be used as nucleophiles. Electrochemical reactions were performed in an undivided cell by RVC (anode) and nickel (cathode) without an external base. Under milder



Scheme 59. Electrochemical carboxylation of diverse organohalide compounds using [DEME][TFSI].



Scheme 60. Electrochemical amination of aryl halides by nickel-catalyzed.

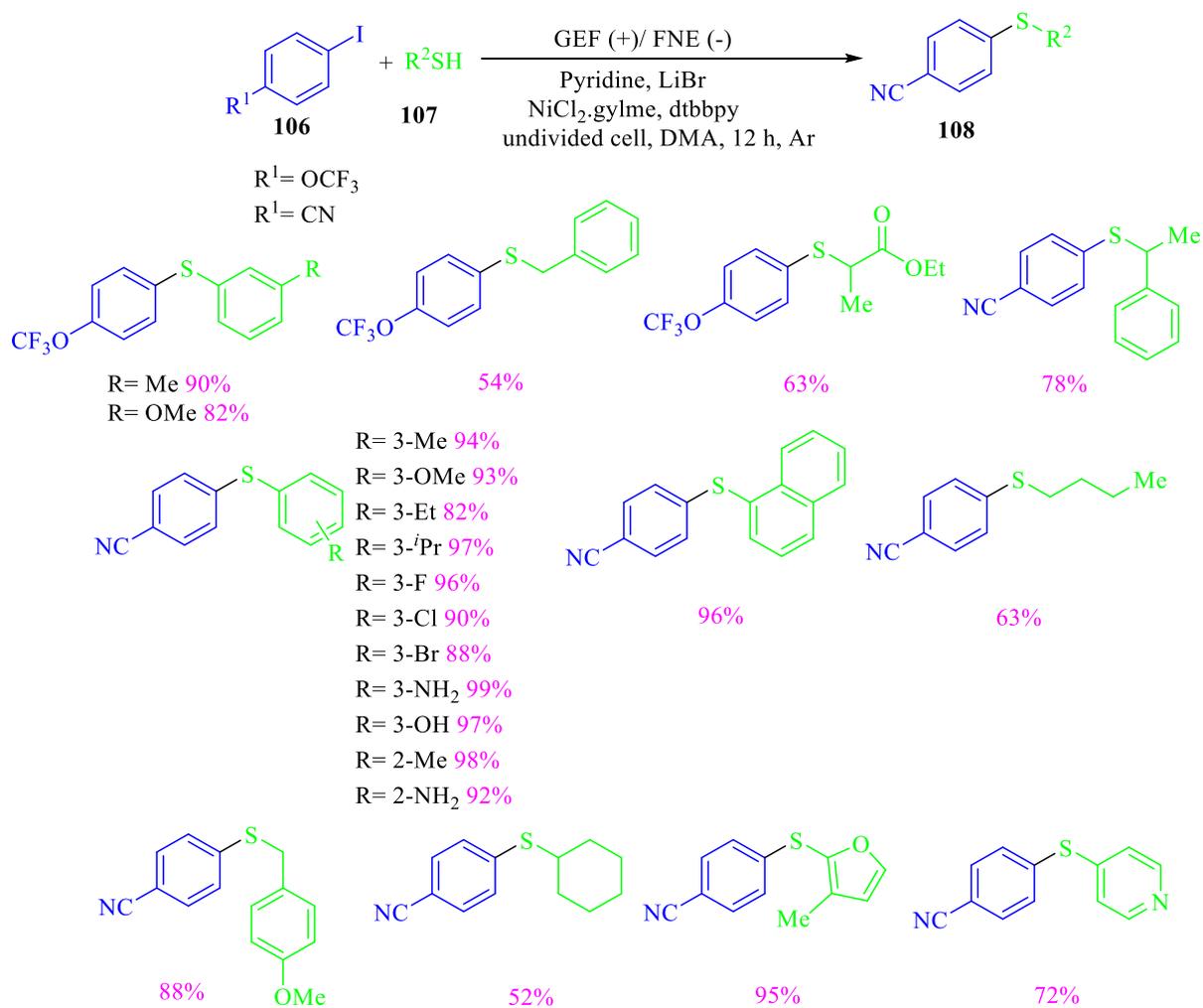
conditions, various aryl donors (Ar–OTf, Ar–I, Ar–Br, and Ar–Cl) and secondary and primary amines with functional group tolerance are viable electrophiles in this reaction. This work displayed using an inexpensive nickel catalyst to enable carbon–nitrogen bond formation and exhibited a rare instance of anodic and cathodic processes adapted to synergistic produce reactive catalyst species in various oxidation states; therefore, a sacrificial electrode was not included. There are many previous reports on the formation of aryl carbon–nitrogen bonds between aryl halides and amines (Lavoie et al., 2016; Park et al., 2014; Ge et al., 2014; Fine Nathel et al., 2014; Manolikakes et al., 2008). The harsh reaction conditions prevented them from being extended. In this

electrochemical method, cross-coupling between aryl halides and alkyl amines was performed without an external base at room temperature.

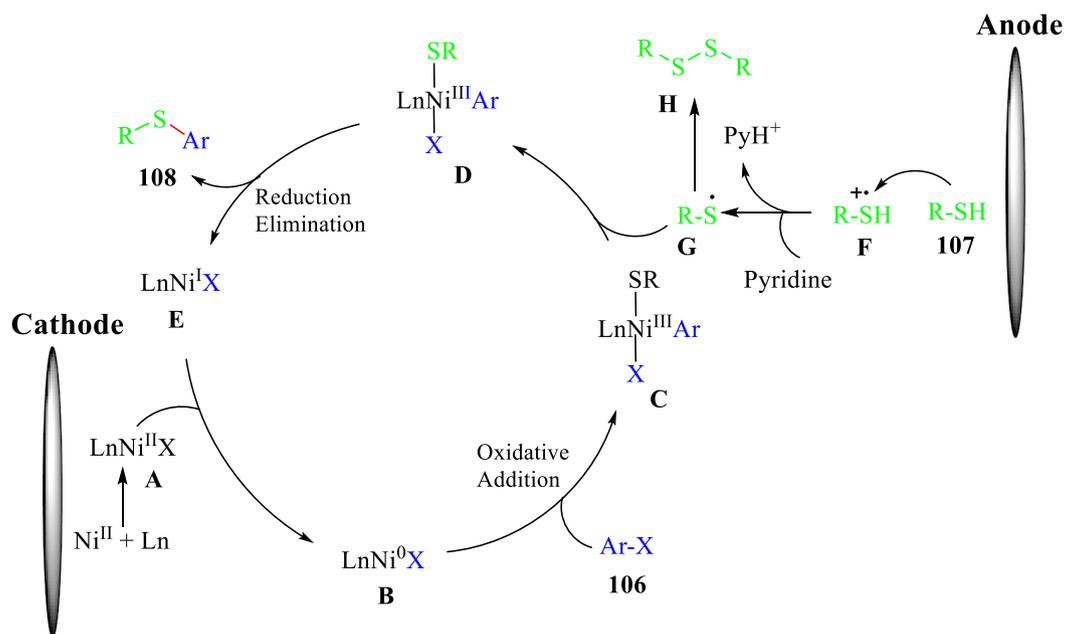
3.2. C–S bond formation reaction

The C–S bond generation reactions are used as powerful means in synthetic organic chemistry for the synthesis of different pharmaceutical, biological, and molecule materials (Feng et al., 2016; Boyd, 2016; Evano et al., 2013).

Recently, Wang et al. revealed electrochemical thiolation of aryl iodides **106** for carbon–sulfur bond formation by nickel-catalyzed



Scheme 61. Electrochemical cross-coupling thiols and aryl halides.



Scheme 62. The proposed mechanism reaction.

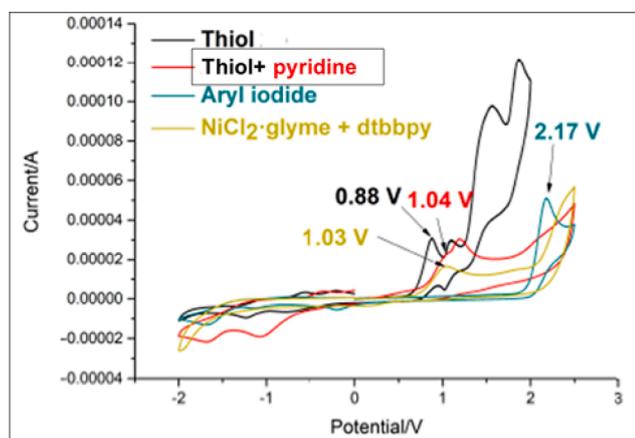


Fig. 3. The cyclic voltammetry study Wang et al., 2019.

(Scheme 61) (Wang et al., 2019). The reaction was attained in an undivided cell by graphene/nickel foam electrodes, which were chosen to enhance the charge exchange. The electrochemical reaction was performed under moderate electrochemical status and provided alkyl and aryl sulfides **108** in superb yields (54–99 %). In an undivided cell unit, radical-mediated nickel species of various oxidation states, the cathodic and anodic processes synergistically harness. Manuel reported that the palladium-catalyzed coupling of aryl halides with thiols was used using the chemical method (Fernández-Rodríguez et al., 2006). This reaction was performed in DME as the solvent and DME as the base at 110 °C. This reaction needs a high mole percent palladium catalyst at high temperatures to afford sulfide derivatives.

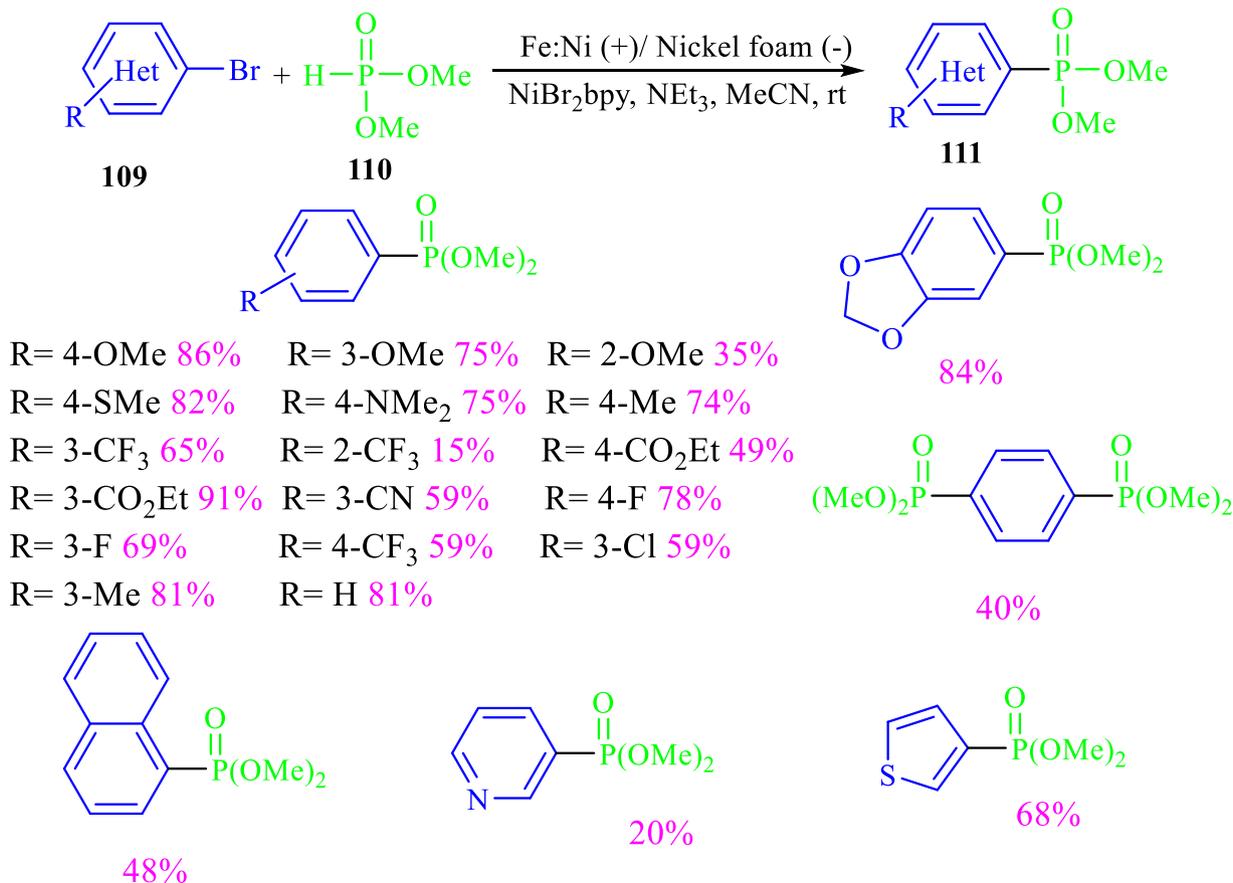
The proposal mechanism (Scheme 62) showed that the anodic

oxidation of thiol **107** caused cation radical F. Hydrogen abstraction from cation radical by pyridine generated the thiol radical G with aryl sulfide H. Meanwhile, $\text{Ni}^{(0)}\text{-X}$ B was produced from a cathodic reduction of $\text{NiCl}_2\text{-dtbbpy}$ A. Oxidative addition B with aryl halide **106** generated $\text{X-Ni}^{(III)}\text{-Ar}$ species C, which trapped the thiol radical G to deliver a $\text{Ni}^{(III)}$ -complex D. Lastly, reductive elimination of D furnished the coupling product **108** and $\text{Ni}^{(I)}\text{-X}$ complex E observed with the cathodic reduction to regenerate $\text{Ni}^{(0)}\text{-X}$ B.

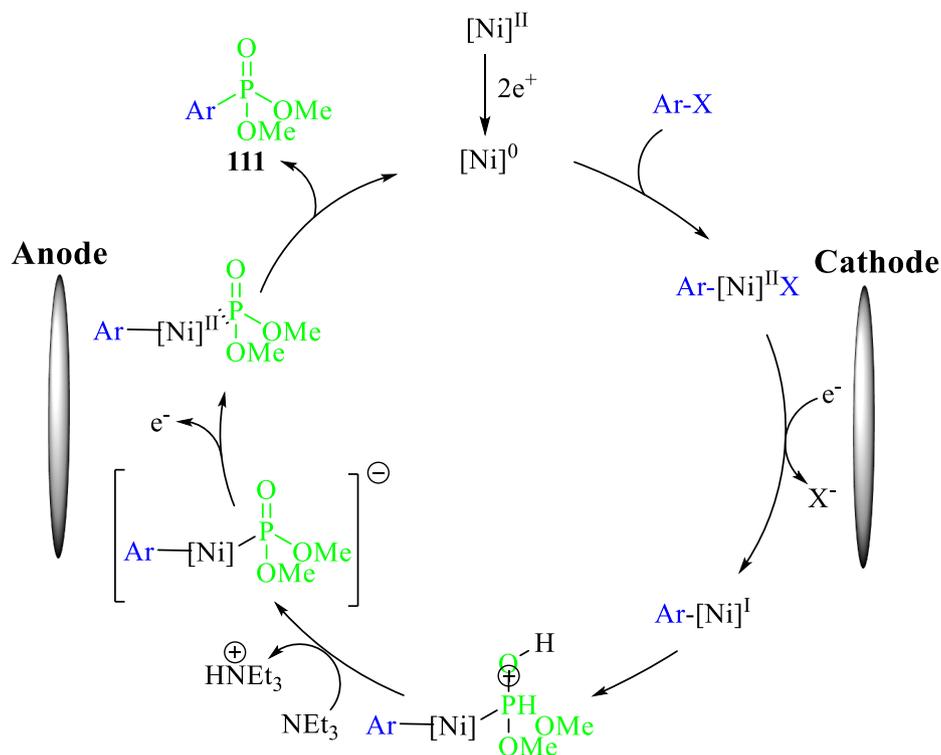
The cyclic voltammetry studies were performed, as shown in Fig. 3. According to this data, aryl iodide and nickel (II) catalysts exhibited relatively high oxidative potentials (2.17 and 1.03 V vs SCE, respectively). Thiol indicated multiple irreversible oxidative waves from 0.88 V vs SCE. By adding pyridine to thiol, only one oxidative wave showed at 1.04 V, demonstrating that pyridine could stabilize the oxidation process of thiols. These anodic events substantiated that the initiation of the catalytic cycle was more likely to be the oxidation of thiol to its radical R–S radical.

3.3. C–P bond formation reaction

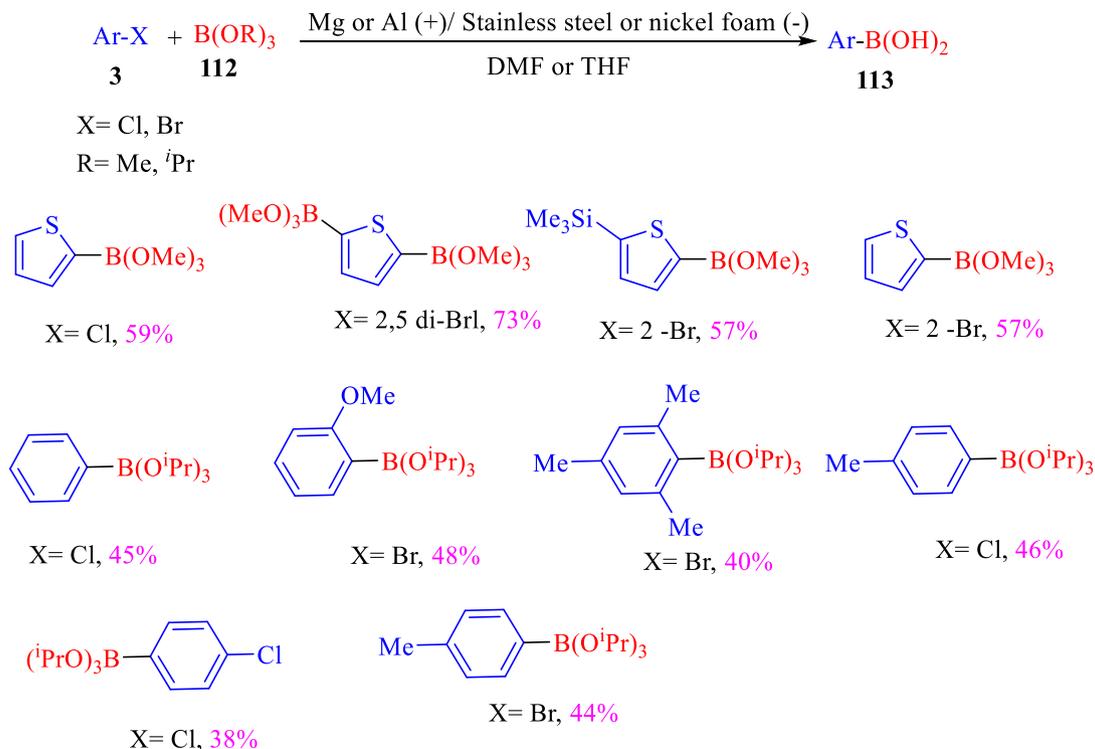
Organophosphorus is a beneficial reagent in catalysis, organic synthesis, coordination chemistry, and medicinal chemistry (Montchamp, 2014; Tang and Zhang, 2003). An appropriate procedure for their preparation commonly comprises carbon-phosphorus coupling between nucleophilic phosphorus-containing compounds and aryl halides (Tappe et al., 2010; Demmer et al., 2011). The electrochemical synthesis of aryl/hetero phosphonates from di-methyl phosphite and aryl/hetero halides for the first time was published by the group's Léonel in 2018 (Scheme 63) (Sengmany et al., 2018). These reactions were accomplished in the galvanostatic mode in an undivided cell with an iron/nickel rod anode enclosed by a Ni foam cathode. NiBr_2bpy was applied



Scheme 63. Electrochemical cross-coupling of aryl halides and di-methyl phosphite.



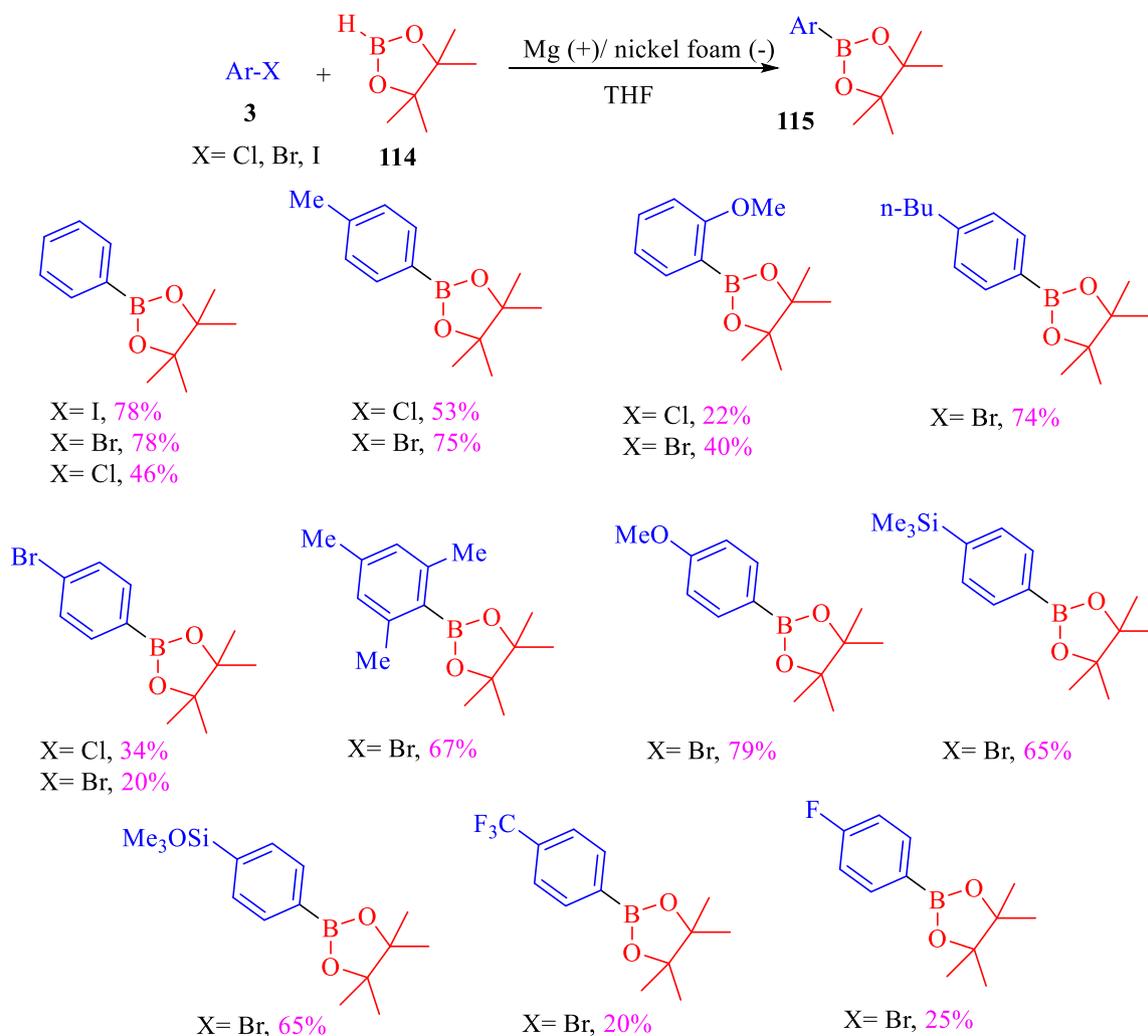
Scheme 64. The suggested mechanism of electrochemical carbon-phosphorus bond fabrication.



Scheme 65. Electrosynthesis of aryl boronic acids with B(Oⁱpr)₃ or B(OMe)₃.

as the comfortably available pre-catalyst, TBAB (Supporting electrolyte), and trimethylamine as a base. Both aryl iodides and bromides could be utilized **109**, providing the related hetero/aryl phosphonates **111** with good yields. Electron-rich and electron-deficient aryl bromides coupling with di-methyl phosphite **110** produce products in excellent yields (40–86 %). The other di-alkyl phosphites were used in this

process. In the chemical method, Yamaguchi reported the synthesis of arylphosphinates by zinc-mediated nickel-catalyzed coupling of aryl halides and H-phosphinate (Kinbara et al., 2015). This reaction needs long reaction times at high temperatures to afford phosphorus derivatives. The electrochemical method has some advantages, such as a short-time reaction and high yield at room temperature.



Scheme 66. Electrosynthesis of aryl boronic pinacol esters from pinacol borane and aryl halides.

The admissible mechanism showed that an initial cathodic reduction of the nickel^(II) pre-catalyst led to the Ni⁽⁰⁾ species, pursued by oxidative addition of the halide and reductive electron transfer to produce Ni^(I) species (Scheme 64). Di-methyl phosphite was then added to create a Ni-phosphorus ylide. Proton abstraction on the hydroxyl of by Et₃N led to the critical complex, which would be oxidized to generate Ar–Ni(II)P(O)(OMe)₂. Reductive elimination afforded the target compound **111** and the catalyst of the process Ni⁽⁰⁾.

3.4. C–B bond fabrication reactions

The electrochemical methodology suggests an appealing alternative to the classical preparation of organoboronic derivatives. In unique boronic acids and esters, boronic derivatives constitute highly valuable intermediates for their broad applications in the agrochemical and pharmaceutical areas and polymer and material chemistry (Silva et al., 2020). However, the chief interest of esters and boronic acids is their usage as intermediates in coupling reactions. Coupling reactions permit the creation of new carbon–carbon bonds to form novel and complex molecules exhibiting particular features.

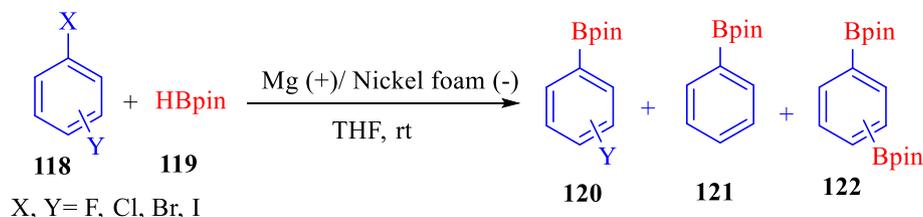
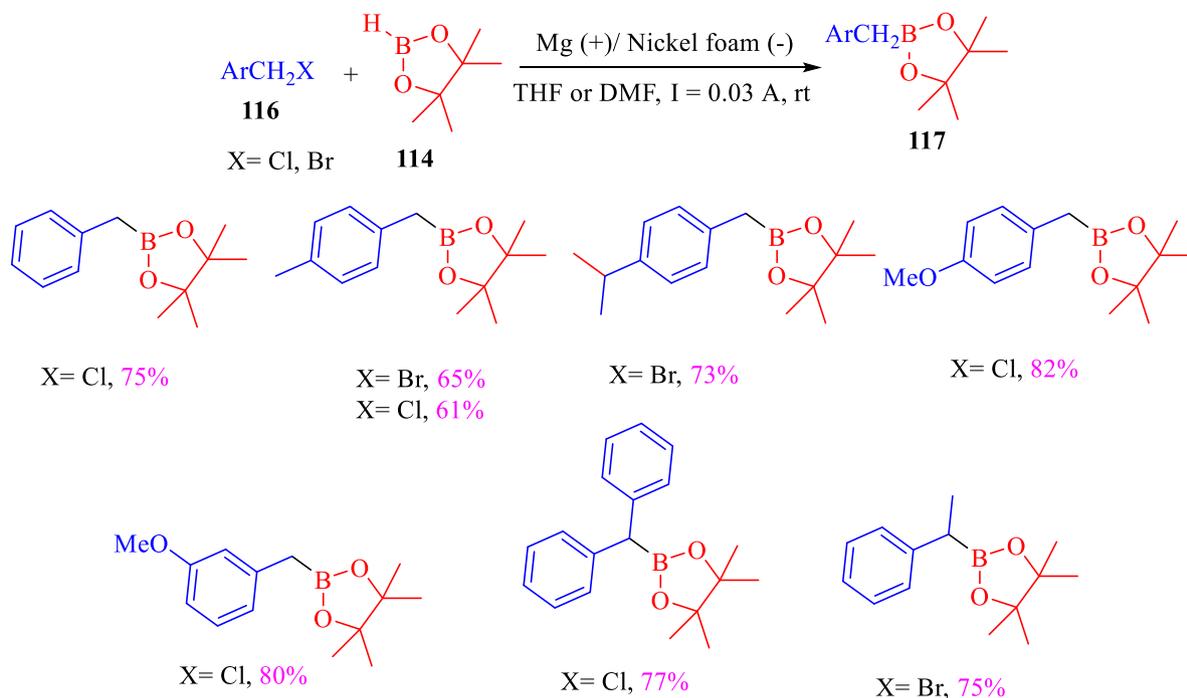
In 2002, Dunach *et al.* reported electrochemical coupling of aromatic or heteroaromatic halides **3** and a trialkyl borate including B(OⁱPr)₃ or B(OMe)₃ **112** for the obtaining of aryl/hetero boronic acids **113** (Scheme 65) (Laza et al., 2002). The selectivities of aryl boronic acids were in the scope of 32–73 %. The reactions were employed in a single-compartment cell with a magnesium or aluminum (anode) and

stainless steel or nickel foam (cathode).

One year later, the same group represented a novel electrochemical synthesis of aryl boronic esters **115** from pinacolborane **114** and aryl halides **3** (Scheme 66) (Laza and Dunach, 2003). They used pinacolborane (HBpin) as a suitable substance for the functionalization of aryl halide. In this case, aryl boronic esters yielded up to 95 %. The electrochemical reaction was conducted in a single-compartment cell fitted with a nickel foam (cathode) and a consumable magnesium (anode). The nature of the electrodes ultimately affected the results. A magnesium anode was shown to be more efficient than aluminium or zinc. This electrochemical method exhibited several advantages compared to the classical boration of aryl halides. The boration occurred in one-pot without the requirement to prepare the Grignard reagent or its Li equivalent.

In 2004, the group Dunach demonstrated the electrochemical procedure, including the straightforward coupling of pinacolborane **114** and benzylic halides **116** for synthesizing benzyl boronic pinacol esters **117** (Scheme 67) (Pintaric et al., 2004). Under mild status, the reaction was conducted in a single-compartment cell with a magnesium (anode) and a nickel (cathode). Benzyl boronic pinacol esters were attained in 61–82 % yields.

The electrochemical reduction of aryl halide compounds **118** using pinacolborane (**119**) as Dunach's group had reported the electrophile to obtain aryl boronic acids selectively that still bear halogen substituents for further functionalization (Scheme 68) (Laza et al., 2005). Reactions were acted in a single cell compartment using a magnesium (anode) and a nickel foam (cathode) in tetrahydrofuran. The relative nature and



place of the halogen substituents affect the boration outcomes. Some halogenated aryl boronic esters **120–122** achieved satisfactory yields at unfinished transformations.

By control of the electrolysis conditions, *p*-F, *p*-Cl, *p*-Br, and *m*-Br phenyl pinacol boronic esters were obtained in 45, 75, 67, and 60 % yields, respectively. Also, *m*-phenyl-di-boronic ester yields 57 % after 4F/mol electrolysis of *m*-di-bromobenzene.

Electrosynthesis of allyl boronic pinacol esters from the electrochemical boration of pinacolborane **124** with various allyl halides **123** illustrated by the group of Dunach in 2009 (Table 2) (Godeau et al., 2009). The electro-synthesis was done in a single-compartment cell with a nickel foam (cathode) and a consumable Al (anode) in a tetrahydrofuran solution comprising (CF₃SO₂)₂NLi. The allyl boronic **125** and **126** derivatives were acquired in 60–86 % yields, generally as mixtures of linear and branched isomers, with the linear isomers usually being the significant compounds. The process is simple and does not require organometallic catalysis, and the reaction takes one step. The terminal borated substance having the less hindered achieved preferential with 68–91 % selectivities. The *E*-derivative was the principal or particular stereoisomer.

In 2023, for the first time, Wang et al. declared electrochemical borylation of alkyl boronic esters to unactivated alkyl halides **127** at high current (Scheme 69) (Wang et al., 2021). The tertiary, secondary, primary, and alkyl boronic esters provide good to superb yields **129** (70 examples). Mechanistic investigations revealed that B₂cat₂ **128** acts as both a cathodic mediator and a reagent, which could electro reduction at a low potential of about alkyl bromides or chlorides difficult-to-reduce.

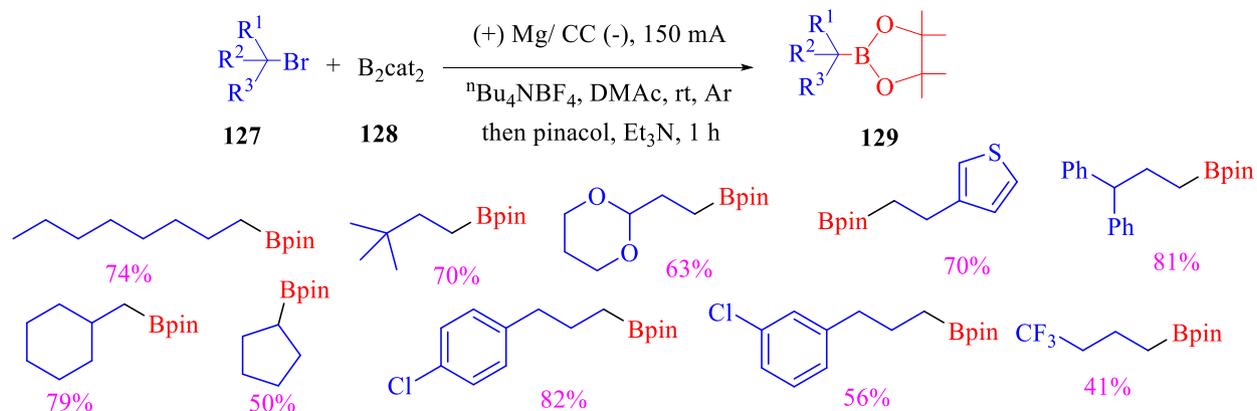
Recently, transition-metal catalyzed borylation of alkyl halides has developed as a valuable strategy for synthesizing alkylboron compounds. Regardless, these methods depend mainly on transition-metal catalysts, long reaction times, and stoichiometric quantities of activators (Yang et al., 2012; Yi et al., 2012; Wang et al., 2021; Ito and Kubota, 2012). The Electrochemical approach is milder, safer, simpler, and environmentally efficient for synthesizing alkyl boron compounds. The cyclic voltammetry (CV) experiments are shown in Fig. 4. The mechanism for the reaction can be explained using cyclic voltammetry data.

3.5. C–Si bond formation reaction

In 2001, Moreau et al. illustrated the electrochemical synthesis of functional aryl/hetero arylchlorosilanes **132** (Scheme 70) (Moreau et al., 2001). An efficient and selective procedure for synthesizing functionalized di- and mono-chlorosilanes as an essential intermediate for polarized organosilicons that are fascinating for NLO applications was described. This reaction was done in an undivided cell with an aluminium or magnesium (anode), a concentric stainless steel grid, or carbon (cathode). Due to its versatility and selectivity, the electro-synthesis pathway is especially beneficial for constructing new organosilicon models. Electrochemical reduction of aryl halides, halopyridines, halofurans, and halothiophenes **130** for synthesizing various functional aryl/hetero arylchlorosilanes (43–88 %).

Table 2
Electrosynthesis of allyl boronic pinacol esters from pinacolborane and allyl halides.

Entry	Substrate	Products ratio	E/Z ratio of 125	Boration yield
1		90:10	70/30	81 %
2		91:9	74/26	86 %
3		84:16	96/4	70 %
4		7:90	–	7 %
5		79:21	–	76 %
6		–	–	65 %
7		83:17	100/-	74 %
8		68:32	100/-	64 %



Scheme 69. Electrochemical borylation of alkyl halides for synthesizing alkyl boronic esters.

4. Electrochemical cyclizations of organic halides

Employing the electron as a reagent usually provides inexpensive and actively suitable reactions in organic electrochemistry. In the many synthetic strategies, radical cyclizations include a primary process for

forming diverse cyclic and natural products comprising heterocyclic rings (Giese, 1986; Giese et al., 1996; Ezzati et al., 2017; Poursattar Marjani et al., 2018; Khalafy et al., 2014; Poursattar Marjani et al., 2019). Radical cyclization methods show benefits over other techniques, which may need the laborious multi-step alternative synthesis.

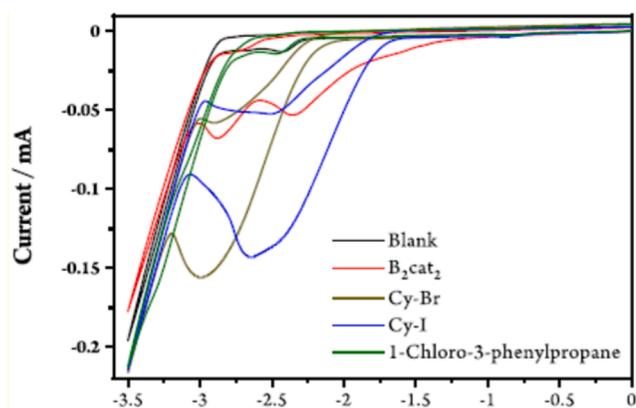


Fig. 4. The cyclic voltammetry data Wang et al., 2021.

The electrochemical nickel catalyst was offered for the impressive fabrication of benzolactones using carbon dioxide for disubstituted epoxides **133** by Dunach and Tascadda in 2000 (Scheme 71) (Tascadda and Duñach, 2000). This reaction suggested that the first reductive carboxylation was pursued with the oxirane ring-opening and cyclization. For terminal epoxides, a cyclic carbonate was established from the straight placing CO₂ into the epoxide. Six-membered ring isocoumarins **134** and **135** (48–88 %) were achieved using 2,2'-bipyridine, whereas five-membered ring benzolactones were selectively formed with cyclam as the ligand.

The synthesis of benzothiophenes **137** through the cyclization of *o*-halo allyl/aryl thioethers **136** had been described using nickel (catalyst) by Dunach et al. in 2004 (Scheme 72) (Pelletier et al., 2004). This electrochemical process had an effortless setup and equipped a carbon fiber cathode and an Mg anode. Dihydrobenzo[*b*]thiophenes were obtained in superb yields (59–95 %). The procedure was highly reliant on the type of ligand related to the metal center. Ni(II) complexes associated with tetra aza macrocyclic ligands, including cyclam, could catalyze intramolecular cyclization efficiently.

Senboku et al. (2011) offered facile preparation of 2,3-dihydrobenzofuran-3-ylacetic acids **139** (33–85 %). Corresponding analogs were attained using a new electrochemical aryl radical cyclization–carboxylation sequence of 2-allyloxy-2-bromobenzenes **138** by applying methyl 4-*tert*-butylbenzoate (electron-transfer mediator) (Scheme 73) (Senboku et al., 2011). The outcomes indicated that the current became a vital instrument for synthesizing (2,3-dihydrobenzofuran-3-yl)acetic acids and desired analogs utilizing carbon dioxide with no metal substance, including SmI₂ and Bu₃SnH.

Scheme 74 offers a suggested mechanistic rationalization using ERCC. A one-electron reduction of aryl halide selectively occurred by a radical anion of the mediator to produce aryl radical. Without a mediator, two-electron reduction of aryl halide competitively occurred to create the related aryl anion furnishing immediately carboxylated benzoic acid. Dissolving the Mg (anode) as magnesium ion prevents any species from oxidizing at the anode.

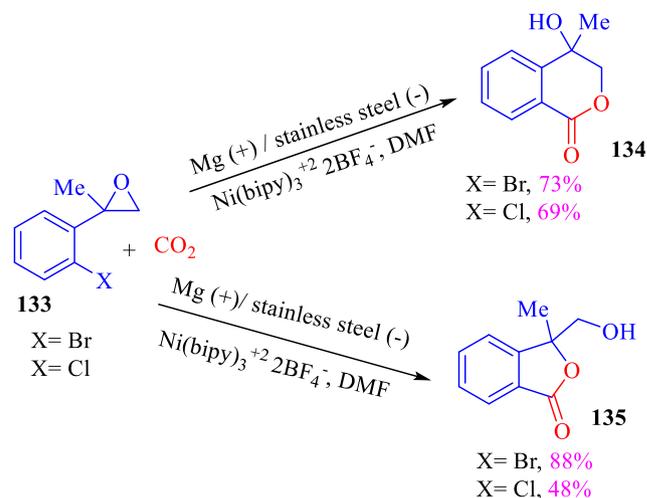
In 2016, Senboku et al. designed a sequential carboxylation aryl radical cyclization with alkyne using electrolysis of 2-(2-propargyloxy) bromobenzenes (Scheme 75) (Katayama et al., 2016). The electrochemical reaction was done in an undivided cell with a platinum

(cathode) and magnesium (anode) using CO₂ and methyl 4-*tert*-butyl benzoate as an electron transfer mediator. Aryl radical cyclization, dihydro benzofuran, indoline, indane, and dihydro benzothiophene, also tetrahydropyran framework **140**, could be created effectively, and following tandem carboxylation produced the desired derivatives of 2,2-ring-fused succinic acid **141** in excellent yields (38–71 %).

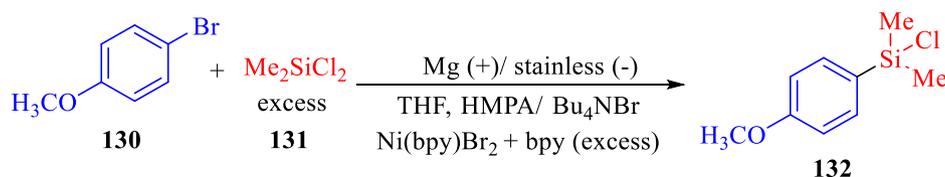
Mechanism studies revealed that one-electron reduction of methyl *p*-(*tert*-butyl)benzoate at the cathode utilized as an electron transfer mediator produced the respective radical anion (Scheme 76). One-electron reduction of aryl bromide **140** using the methyl *p*-(*tert*-butyl) benzoate radical anion (**II**) produced the anion radical (**I**), resulting in the break of the C–Br bond, yielding the aryl radical **A**₁. Without electron transfer mediator (**II**), two-electron reduction of aryl bromide **140** at the cathode forms the desired aryl anion species that straight provides carboxylated benzoic acid. The construction of cyclized vinyl radical **B**₁ results from the intramolecular 5-exo cyclization of a C–C triple bond with aryl radical **A**₁. Moreover, one-electron reduction formed the vinyl anion **C**₁, CO₂ reacted, creating the α,β-unsaturated carboxylate ion **D**, which had a cinnamic acid part.

Consequently, reducing one more electron of α,β-unsaturated carboxylate ion **D**₁ may rapidly produce the radical anion **E**₁. Resonance of the radical anion **E**₂ to stable enol form, followed by the reduction of one-electron, had the anion **F**₁. Selective insertion of CO₂ at the benzylic position gave intermediate **G**₁ and created an acid environment, further obtaining the desired product.

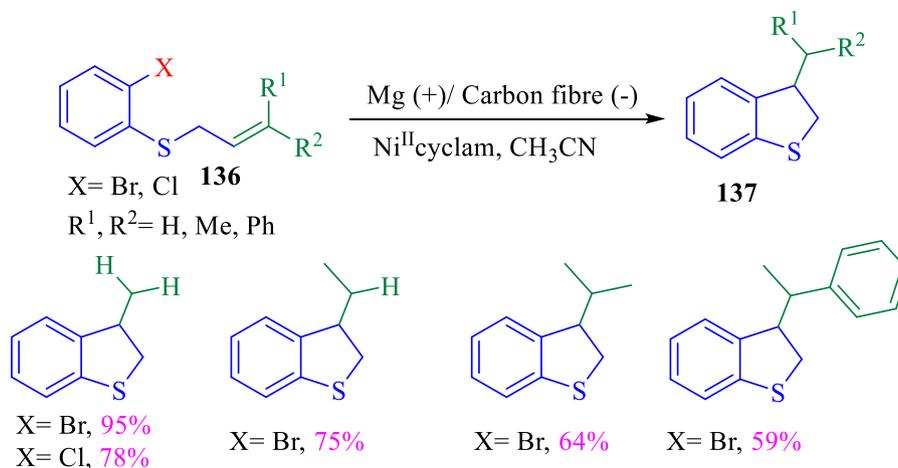
In the same year, Senboku and Katayama offered an electrochemical reduction of vinyl bromide **142** using carbon dioxide that produced vinyl radical **143**, **144**, and **145** utilizing methyl *p*-(*tert*-butyl)benzoate as an electron transfer mediator (Scheme 77) (Katayama and Senboku, 2016). Cyclization accompanied by carbon dioxide insertion with a carbon–carbon bond creation produced γ,δ-unsaturated carbo- and heterocycle carboxylic acids in excellent outcomes (39–71 %). Electrochemical reactions were conducted in an undivided cell using a Mg rod (anode) and a platinum plate (cathode). Cyclic voltammetry was used to determine the role of methyl 4-*tert*-butylbenzoate, as displayed in Fig. 1.



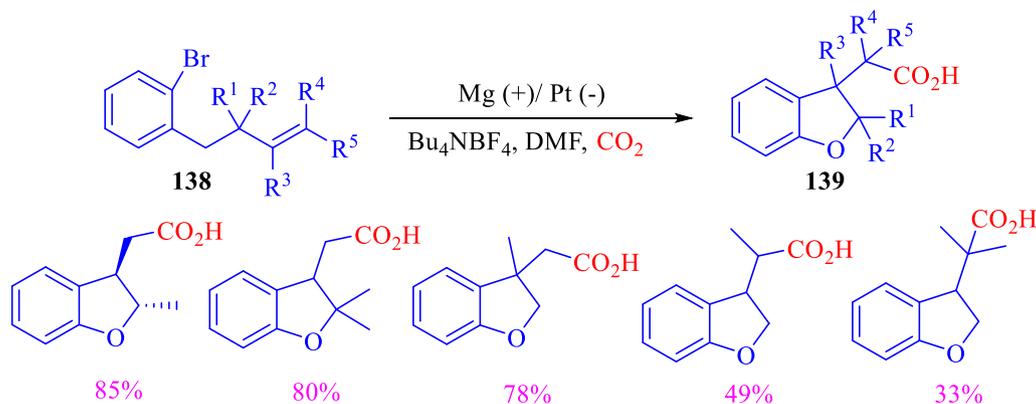
Scheme 71. Electrosynthesis of cyclic carbonates and benzolactones from epoxide-aryl halides.



Scheme 70. Ni-catalyzed electrochemical synthesis of *p*-methoxyphenyldimethylchlorosilane.



Scheme 72. The cyclization of *o*-halo allyl/aryl thioethers using nickel(II)-catalyst.



Scheme 73. Formation of (2,3-dihydrobenzohuran-3-yl)acetic acids using ERCC.

A proposal mechanism exhibited that at the cathode, one-electron reduction of methyl *p*-(*tert*-butyl)benzoate, utilized as an electron transfer intermediate, took place to afford the related radical anion (Scheme 78).

5. Electrochemical preparation of organo-metal compounds from organic halides

Organozinc materials have earned a remarkably substantial role in advancing novel approaches in the organic synthesis field (Knochel and Singer, 1993).

In 2000, Gosmini *et al.* explained the synthesis of aryl zinc compounds **146** from the electroreduction of aryl bromides/chlorides **3** using a cobalt catalyst (Scheme 79) (Gosmini *et al.*, 2000c). An electrochemical cell was equipped with a consumable nickel or stainless steel (cathode) and zinc (anode) using cobalt chloride with pyridine as a ligand. Formation of aryl zinc halides achieved excellent yields, and this procedure is especially effective on aryl halides containing an electron-withdrawing group.

One year later, this group demonstrated electroreduction of diverse aryl organozinc derivatives **147** and their coupling with pyridine using the cobalt catalyzed (Scheme 80) (Le Gall *et al.*, 2001b). Normal protocols, including halogenated compounds and nickel catalysts, were ineffective. This procedure's significant privilege relies on using mild and straightforward reaction status. A stainless steel grid (cathode) and a zinc rod (anode) were used. 4-aryl-pyridines **150** were attained in high yields (54–85 %).

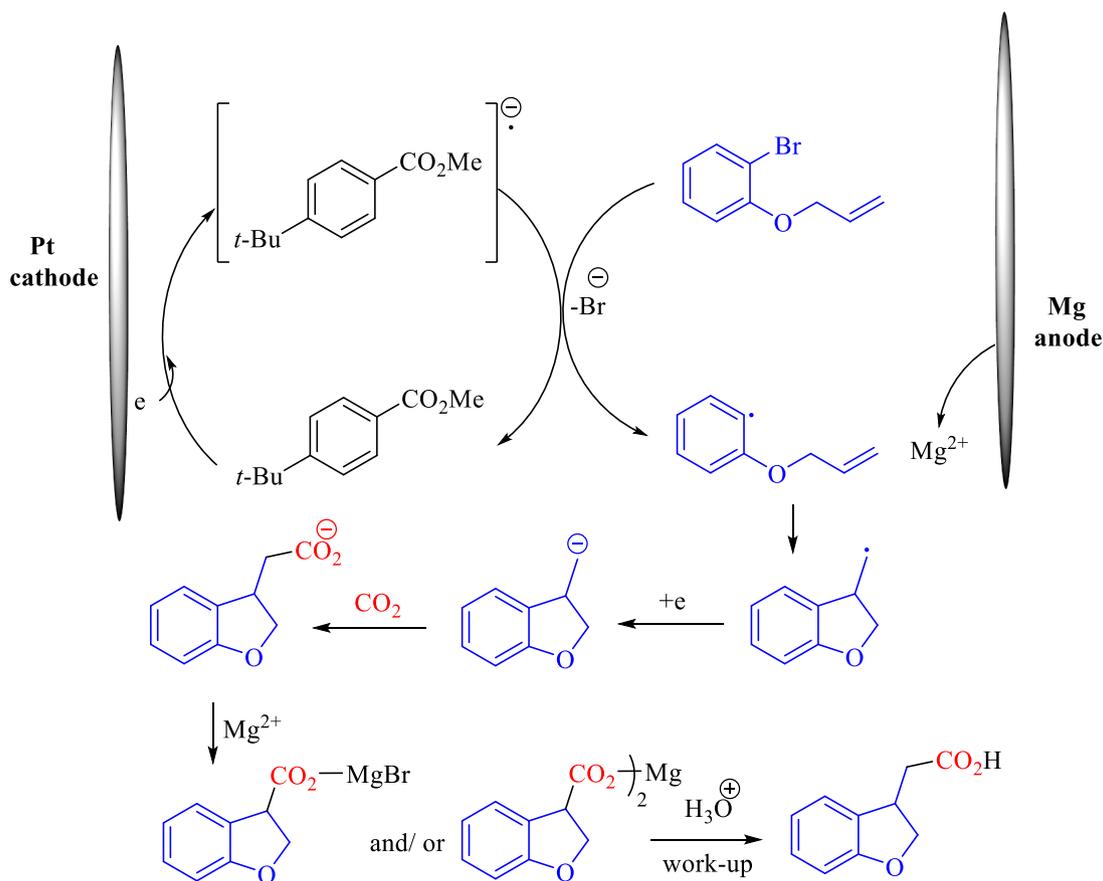
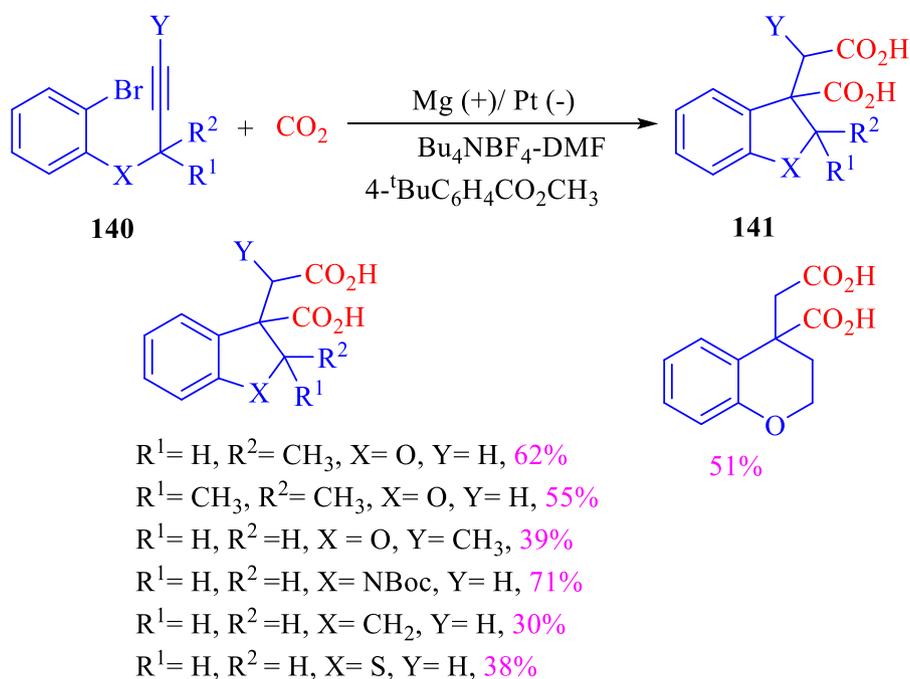
The establishment of 3-substituted monothienylzinc species was

attained using electrochemical procedures and a selective and original bromination method by Mellah *et al.*, as reported in 2001 (Scheme 81) (Mellah *et al.*, 2001). Electrolysis is arranged into an undivided cell by a sacrificial Zn (anode) utilizing NiBr₂bpy (amount catalyst) for the construction of monothienylzinc **152** and **153** archived in moderate to excellent yields (20–100 %).

The electroreduction of di- and mono- Zn species using dibromo benzenes or activated dichloro benzene by the group of Gosmini was explained in the same year (Fillon *et al.*, 2001). at a one-compartment cell by a nickel foam (cathode) and a consumable Zn (anode). Diorganozinc compounds were synthesized using cobalt catalysis with good to superior. The di- and mono- Zn products were provided concurrently at 2F/mol, excluding bromochloro benzene, where just the mono-Zn species is noticed. In 4F/mol, the di-Zn species is exclusively provided from di-bromobenzenes. On the contrary, di-chlorobenzene reagents combine di- and mono- Zn materials. In *o*-dibromobenzene, the yield is decreased.

6. Conclusion

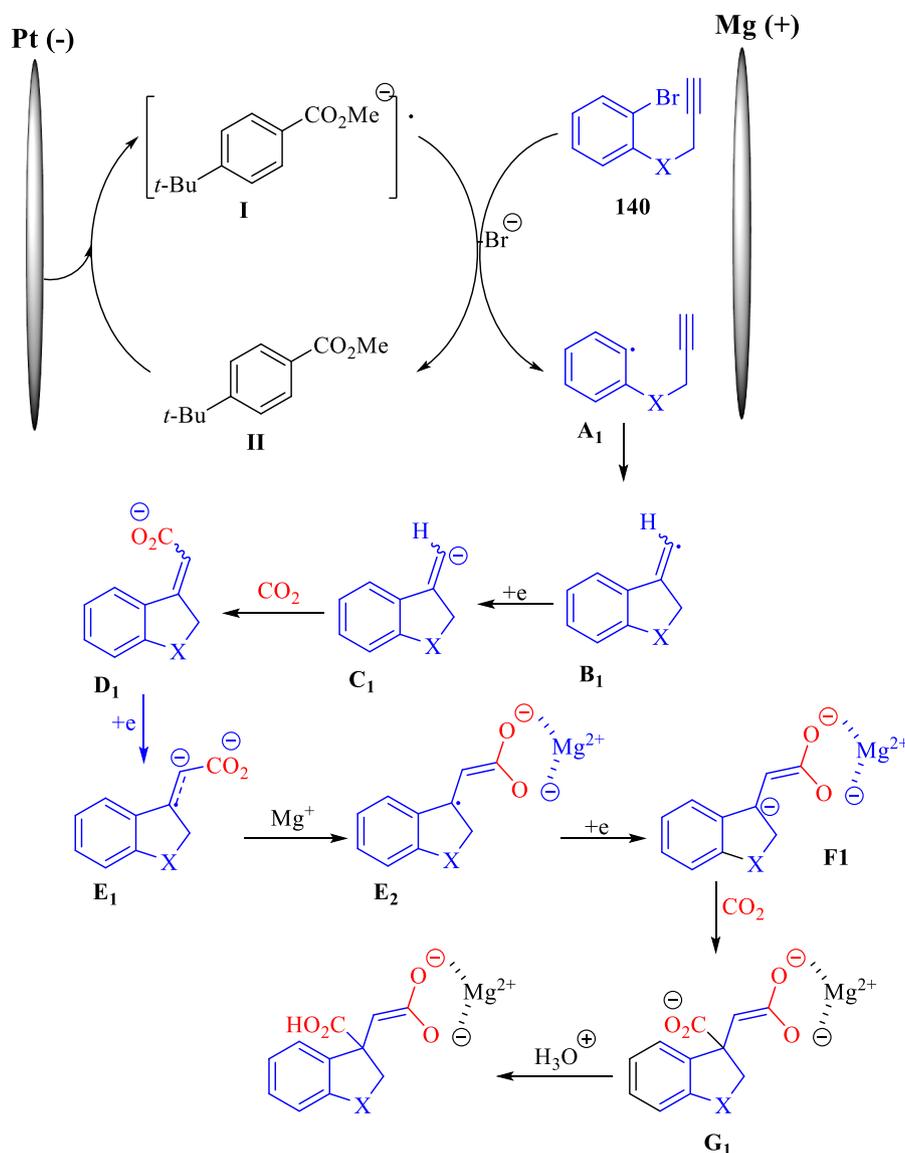
The synthesis of organic compounds requires various methods, and lately, scientists have developed new synthetic methods adaptable to green chemistry aims. One of the most promising ways is electroreduction, which has attained notable attraction in the academic community and industrial field. Electroreduction is a valuable and practical technique in organic transformation. The application of this powerful method in organic conversion is fascinating and impressive. Photochemistry and electrochemistry are two powerful tools in organic synthesis, and merging both is a highly advantageous approach to fulfilling

Scheme 74. The stepwise reaction of methyl 4-*tert*-butylbenzoate.

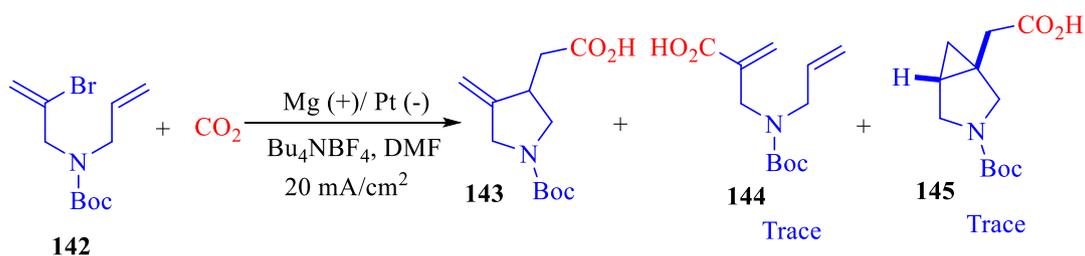
Scheme 75. Electrochemical aryl radical cyclization with alkyne.

modern organic synthesis's green and sustainable needs. Also, it can develop a system in which each technique's defects can be wholly compensated for by their respective benefits, thus creating probable novel reaction paths that are unachievable with individual procedures.

Indeed, more developments and applications of this merging will persist and be used in the future in the organic synthesis field (Wu et al., 2022). Organic photoelectrochemistry is a growing field with notable attention due to its potential for renewable energy transformation and storage



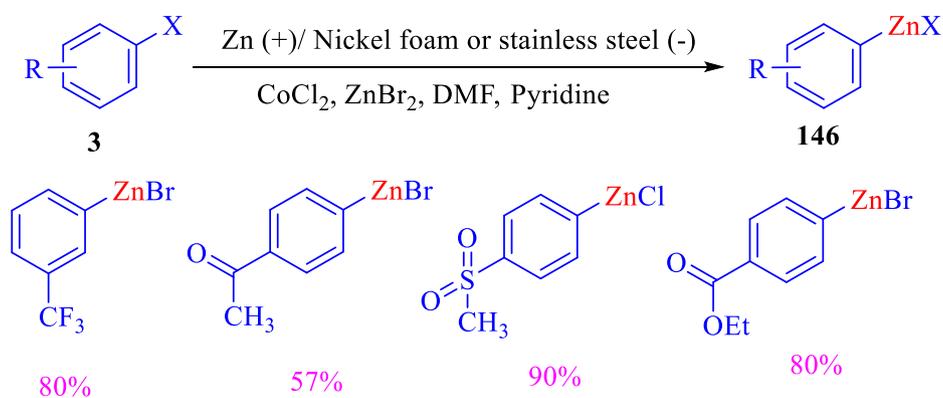
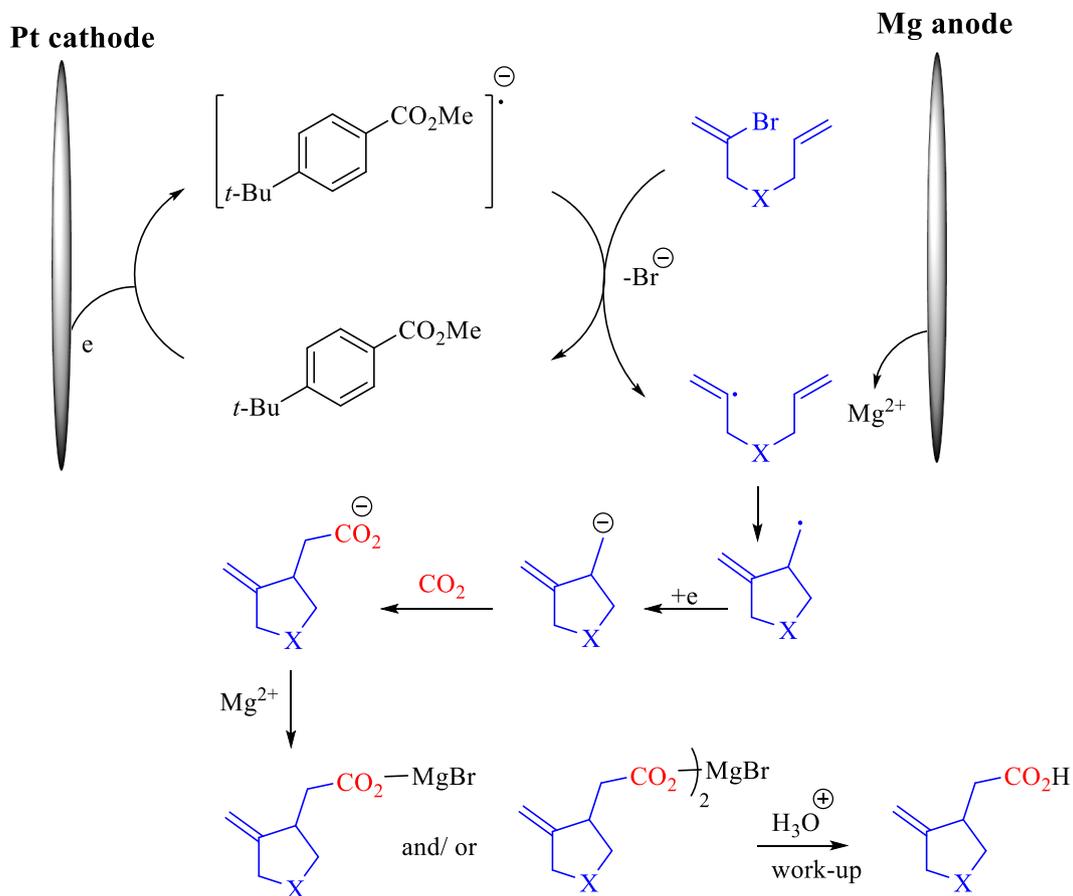
Scheme 76. The acceptable mechanism of the radical cyclization.

Scheme 77. Electrochemical reduction of vinyl radical cyclization-fixation of CO₂.

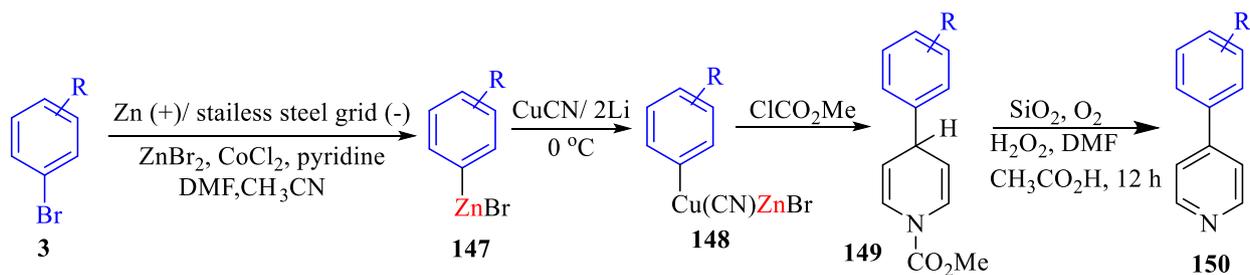
uses.

Further, reactions in photoelectrochemistry and flow chemistry are two hopeful electrochemistry strategies, and their combination offers excellent potential for use in solar energy and energy conversion technologies. These combination systems can perform more eco-friendly and energy-saving with high atom and step economies (Murtaza et al., 2023). Photoelectrochemical catalysis can present more efficient, better, cheaper, environmentally safer, and greener replacement reaction methodologies in organic transformations (Hardwick and Ahmed, 2021; Hardwick et al., 2020).

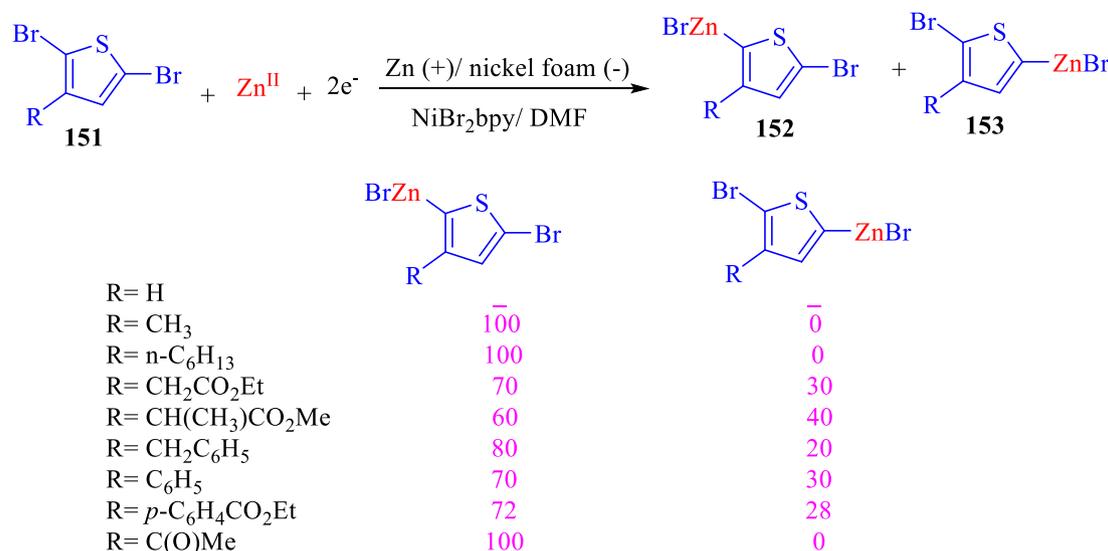
In the current work, we have offered recent expansions for electrochemical coupling reactions of organohalides to create carbon-carbon and carbon-heteroatom bonds. Electrochemistry has some natural benefits involving reaction tenability, recyclable and cheap electrodes, and scalability. Although electro-organic synthesis has been well-known for over 150 years, notable growth has been made in recent decades. Using the electrochemical approach in drug discovery and investigation of physiological activity is considerable for many chemists. The utilization of electrochemical methodologies in organic synthesis is earning notable consideration because transformations can frequently be accomplished



Scheme 79. Preparation of aryl zinc compounds from aryl halides using CoCl_2 .



Scheme 80. Electrosynthesis of organozinc reagents for functionalized 4-phenyl-pyridines.



Scheme 81. The electrochemical synthesis of thienyl Zn species.

more efficiently, and electrochemical methods can reduce contamination and make the chemistry environmentally friendly; hence, more research groups are focusing on these topics. Electrochemical cross-coupling reactions provide a new opportunity for synthesizing green organic carbon-carbon and carbon-heteroatom bonds. Our aim in this study is to exhibit an overall outlook of electrochemical coupling reaction aryl halides as an old tool in the organic reaction. We hope our review will attract enthusiasts and pioneers in the coupling field toward clean, readily available, and inexpensive electrochemical methods. Hence, more attention must be given to organic electrochemistry, and this review will, without a doubt, encourage chemists to develop more future studies in the electrochemistry field and make it a common approach in the modern organic chemistry world shortly.

CRedit authorship contribution statement

Sara Payamifar: Investigation, Writing – original draft. **Leila Behrouzi:** Investigation, Writing – original draft. **Ahmad Poursattar Marjani:** Investigation, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data have been given in the article.

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