

# A Decade of Exploration of Transition-Metal-Catalyzed Cross-Coupling Reactions: An Overview

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X = H, Halogen, BR<sub>2</sub>, SiR<sub>3</sub>, SO<sub>2</sub>R, NR<sub>2</sub>, COOH etc.

Y = H, NH, OH, SH, PH, CH, RM, BR<sub>2</sub> etc.

R<sup>1</sup> = Alkyl, Aryl, Heteroaryl

R<sup>2</sup> = Alkyl, Aryl, Heteroaryl

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**Abstract** During the previous couple of decades, transition-metal (Fe, Co, Cu, Ni, Ru, Rh, Pd, Ag, Au) catalyzed inter- and intramolecular coupling reactions have attracted huge attention for the construction of C–C and C–heteroatom (like C–N, C–P, C–O, C–S, etc.) bonds to synthesize a diverse range of polymers, fine chemicals, and agrochemicals (mainly fungicides, herbicides, and insecticides), as well as biologically and pharmaceutically important organic molecules. Furthermore, the employment of lower cost and easily available metals such as first-row transition-metal salts or metal complexes of Fe, Co, Cu, Ni as catalysts compared to the precious metals such as Pd, Ag, Au in cross-coupling reactions have led to major advances in applications within the fields of synthesis. A number of cross-coupling reactions catalyzed by transition metals have been explored, including Suzuki, Heck, Sonogashira, Stille, Kumada, Kochi, Murahashi, Corriu, and Negishi reactions, as well as carbonylative, decarboxylative, reactions and  $\alpha$ -arylations. In this review, we offer a comprehensive summary of the cross-coupling reaction catalyzed by different transition metals from the year 2009 to date.

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**Keywords** cross coupling, transition metals, catalysis

## 1 Introduction

Over the past years, the construction of carbon–carbon and carbon–heteroatom bonds via cross-coupling reactions catalyzed by transition metals, such as Suzuki–Miyaura,<sup>1</sup> Heck,<sup>2</sup> Sonogashira,<sup>3</sup> Stille,<sup>4</sup> Negishi,<sup>5</sup> Kumada,<sup>6</sup> and Hiya-ma<sup>7</sup> reactions, have remained the most widely employed synthesis protocols in the chemical industry. These reactions represent the fundamental criteria for a number of basic technologies in modern synthetic organic chemistry and have been widely applied in a variety of academic and industrial process,<sup>8,9</sup> including the synthesis of natural products,<sup>10,11</sup> biologically active small molecule, materials science, medicinal, supramolecular catalysis, and coordination chemistry. In addition, several of these reactions have been commercially employed in the fields of pharmaceuticals, agrochemical conjugated polymers,<sup>12,13</sup> and crystalline liquids,<sup>14–16</sup> in the active components of organic light-emitting diodes (OLEDs),<sup>17,18</sup> and as industrial chemicals<sup>12</sup> etc.

The first breakthrough in the direction of cross-coupling was the copper-catalyzed synthesis of biaryl compounds from aryl halides published by F. Ullmann in 1901.<sup>19</sup> This discovery was not limited to a mere presentation of new synthesis methodology, but rather brought the realization that carbon–carbon bonds can be made in a laboratory synthetically. After a long gap of nearly seven decades, the discovery by Ullmann gained the recognition and a variety

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**Jyoti** received her Bachelor's degree in Chemistry from the University of Delhi and her Master's degree from Maharishi Dayanand University. After receiving the prestigious CSIR-NET Junior Research Fellowship,

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**Saurav Kumar** hails from Uttar Pradesh, India. He completed his B.Sc. (H) Chemistry in 2016 at the University of Delhi. Following that, he pursued his

M.Sc. in Organic Chemistry at CCS University in 2018. In the same year, he was awarded with the CSIR-NET JRF. In 2018, Saurav embarked on his Ph.D. jour-

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**Anil Kumar** is a full professor at the Department of Applied Chemistry, Delhi Technological University (formerly, Delhi College of Engineering), Delhi, India. He received his master's and doctorate degrees in chemistry from University of Roorkee, Roorkee (Now IIT Roorkee) and Indian Institute of Technology,

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him through the path of knowledge. His current research interest is corrole and benziporphodimethene-based coordination chemistry and its applications. Kumar lives in Delhi with his wife (Hemlata) and two children (Sarthak Pal and Tanish Pal).

of modifications and new directions subsequently emerged. In particular, the discovery of Kumada coupling in 1972, in which reactive chemical halides and alkenyl/aryl halides were combined using Ni or Pd catalysts, paved the way for the discovery of modern transition-metal (TM) catalyzed cross-coupling methods.<sup>20,21</sup> These developments were followed by Heck in 1972, where unsaturated halides and olefins were combined with Pd catalysts,<sup>22–24</sup> and Sonogashira in 1975, where terminal alkynes and aryl or vinyl halides were combined with Pd and Cu catalysts.<sup>25,26</sup> In an attempt to extend the outreach of these methodologies, Negishi (1977) used Pd or Ni catalysts to combine organozinc compounds with organic halides or triflates.<sup>27,28</sup> Using a similar strategy, in 1978, Stille coupled organotin compounds with a variety of organic electrophiles using Pd,<sup>29,30</sup> Suzuki, in 1979, presented the coupling of boric acid and organohalogen compounds using Pd,<sup>31–33</sup> Hiyama, in 1988, used organosilanes and organic halides with Pd,<sup>34–36</sup> Buchwald–Hartwig, 1994, coupled amines with aryl halides using Pd,<sup>37</sup> and other cross-couplings have been described.<sup>38–40</sup>

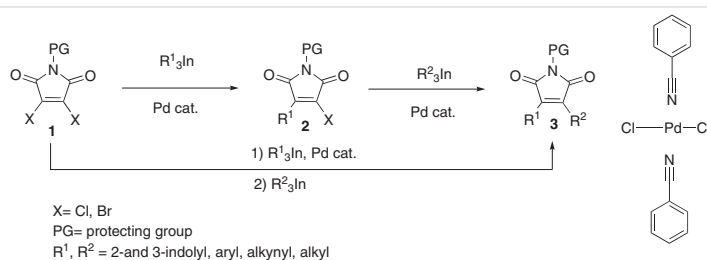
The importance of these palladium-catalyzed cross-couplings was finally recognized when the Nobel Prize in Chemistry in 2010 was jointly awarded to A. Suzuki, R. Heck, and E. Negishi.<sup>41–43</sup> Since the early developments in the dynamic area of cross-coupling reactions nearly fifty years ago, the diversity, scope, reactivity, value effectiveness, toxicity, required synthetic skill, and number of workable applications and limitations of TMs such as palladium,<sup>44–48</sup> iron,<sup>38,49–52</sup> cobalt,<sup>53–56</sup> nickel,<sup>57–61</sup> copper,<sup>62–64</sup> rhodium,<sup>65–69</sup> ruthenium,<sup>70,71</sup> and iridium,<sup>72</sup> has led to thousands of publications in this field, and many reviews and books have cataloged the advancements. With all this, bottlenecks in cross-coupling reactions have encouraged scientists and researchers to formulate novel catalysts primarily based on naturally abundant and environmentally benign elements. Therefore, compared to the widespread applications of late and noble transition-metals in TM-catalyzed cross-couplings, much attention is paid to the first-native transition metals such as Fe, Co, Ni, and Cu due to their obvious advantages, such as high earth abundance, low cost, reduced toxicity, higher nucleophilicity, unique catalytic properties, and environmental friendliness.<sup>73–75</sup>

In particular, Pd-catalyzed coupling appears to be one of the most commonly used reactions for producing good quality chemical compounds on a good scale and it represents one of the most powerful and diverse techniques available to synthetic organic chemists.<sup>76,77</sup> In fact, extensive research has confirmed that nickel-based catalysts are more potent and flexible catalysts for C–C,<sup>78</sup> C–O,<sup>78</sup> C–P,<sup>79</sup> and C–N<sup>80</sup> bond construction.

Moreover, the past 20 years have witnessed an impressive expansion in interest in the advancement of iron-based cross-coupling responses.<sup>38,81,82</sup> Developed by Kharasch and Field in 1941, iron-catalyzed cross-coupling reactions were first detailed in which Grignard reagents were combined with aryl halides under the influence of FeCl<sub>3</sub>.<sup>83</sup> It is intriguing to note here that it required an additional 30 years for a subsequent report to be published that sped up progress in this field; Kochi clarified the cross-coupling of Grignard reagents with alkenyl halides catalyzed by FeCl<sub>3</sub>.

Following Kochi's report, simultaneous work<sup>84</sup> led by the groups of Julia,<sup>85</sup> Molander,<sup>86</sup> Cahiez,<sup>87</sup> and Fürstner,<sup>88</sup> in addition to considerable contributions from the groups of Hayashi,<sup>89</sup> Nakamura,<sup>90</sup> and Itami,<sup>91</sup> Bedford,<sup>92</sup> Knochel,<sup>93</sup> and Shi<sup>94</sup> during the 1990s and early 2000s, dynamically marked the resurgence of Fe-catalyzed reactions. From that point forward, various new iron-catalyzed cross-coupling responses have been discovered that are highly appealing to research in organic synthesis.<sup>81</sup> Nevertheless, the developments towards a viable and economical protocol for iron-mediated cross-coupling catalysis is sluggish in comparison to analogous palladium and nickel-primarily based catalysis.

Given the growing recognition of the importance of cross-coupling chemistry, this review offers a complete overview of the successful applications of numerous transition-metals in cross-coupling strategies that have been carried out as key steps, including Suzuki, Heck, Sonogashira, Stille, Kumada, Kochi, Murahashi, Corriu, and Negishi reactions, in addition to carbonylative, decarboxylative, C–N cross-coupling reactions and  $\alpha$ -arylation reactions, to synthesize heterocycles, organic materials, natural products, and medicinally relevant compounds. The practical challenges and perspectives for these TM-catalyzed coupling protocols for the discovery of polymers, natural products,



**Scheme 1** Pd-catalyzed direct and sequential cross-coupling reaction of triorganoindium reagents and 3,4-dihalomaleimides<sup>95</sup>

agrochemicals, and biologically active compounds are briefly discussed in the final section. This work includes references published from the year 2011 to date that cover the most important developments in this rapidly progressing field. The content of this review is categorized into various transition-metal-catalyzed reactions such as Pd-mediated reactions.

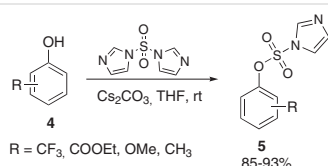
## 2 Pd-Catalyzed Reactions

The discussion in this section is bounded to the use of palladium catalysis in various cross-coupling reactions and is generally presented in chronological order.

### 2.1 C–C Cross-Coupling Reaction

In 2009, Bouissane and co-workers<sup>95</sup> discovered a palladium-mediated sequential or stepwise one-pot cross-coupling reaction with various triorganoindium reagents (40–50 mol%) with 3,4-dihalomaleimides **1** to afford a variety of aryl, heteroaryl, alkyl, alkynyl, 2- and 3-indolyl 3,4-disubstituted maleimides with satisfactory yields with high selectivity and atom economy (Scheme 1).

At the same time, Raju and co-workers first synthesized aryl imidazolylsulfonates **5** as a cost-effective alternative to triflates, which was shown to participate as a fully competent electrophilic coupling partner in palladium-catalyzed cross-coupling Negishi and Suzuki–Miyaura reactions in excellent yields (Scheme 2, Scheme 3, and Scheme 4).<sup>96</sup>

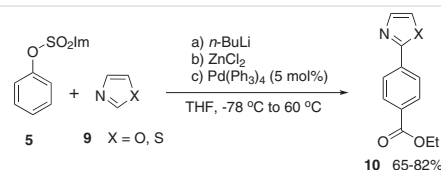


**Scheme 2** Synthesis of imidazolylsulfonates<sup>96</sup>

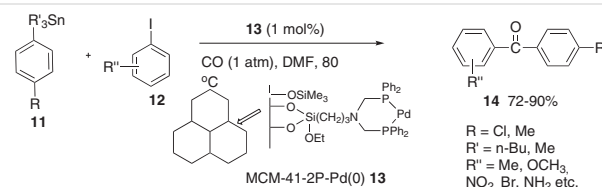
The first successful heterogeneous carbonylative Stille cross-coupling reaction of organostannanes **11** with aryl iodides **12** was demonstrated in 2009 by Cai et al.<sup>97</sup> in the presence of a catalytic amount of an MCM-41-supported bidentate phosphine palladium(0) complex [MCM-41-2P-Pd(0)] (**13**) (Scheme 5). The reaction was carried out at 80

°C under carbon monoxide atmosphere in the presence of DMF, producing a variety of unsymmetrical ketones **14** in high reaction yields.

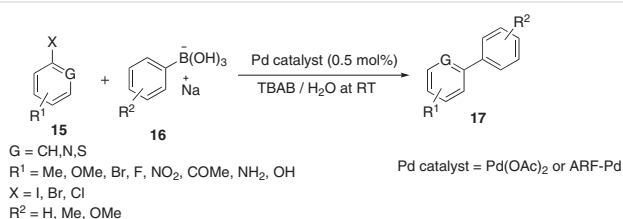
In 2010, Basu and co-workers<sup>98</sup> deciphered the ligand-free, on-water, Pd-catalyzed Suzuki–Miyaura (SM) coupling of the easily accessible sodium salt of aryl trihydroxyborate (**16**) with a variety of aryl halides (**15**) under aerobic conditions. The protocol was also applicable to very challenging substrates like aryl chlorides bearing electron-withdrawing groups, in good to excellent yields. Further, the authors demonstrated that this protocol was effective with heterogeneous palladium-catalysts and also exhibited the synthesis of pharmaceutically important benzotriazole **20** and benzimidazole-based biphenyl scaffolds **19** (Scheme 6 and Scheme 7).



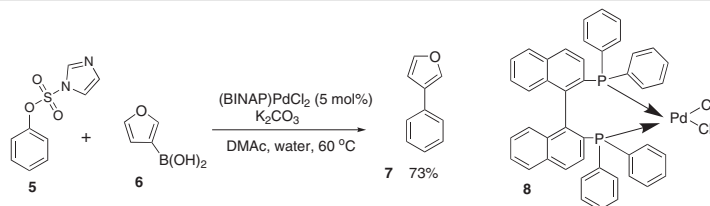
**Scheme 4** Aryl imidazolylsulfonates as coupling partner in Pd-catalyzed Negishi cross-coupling reaction<sup>96</sup>



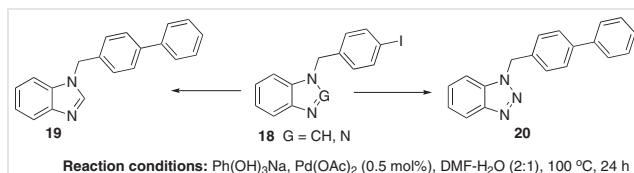
**Scheme 5** Heterogeneous carbonylative Stille cross-coupling reaction of organostannanes<sup>97</sup>



**Scheme 6** Suzuki–Miyaura cross-coupling using palladium acetate<sup>98</sup>



**Scheme 3** Aryl imidazolylsulfonates as coupling partner in Pd-catalyzed Suzuki–Miyaura cross-coupling reaction<sup>96</sup>

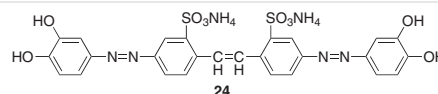


**Scheme 7** Synthesis of benzotriazole and benzimidazole-based biphenyl scaffolds<sup>98</sup>

Lee and co-workers<sup>99</sup> described the synthesis of heterogeneous silica gel-supported  $\beta$ -ketoiminatophosphane-Pd complex ( $\text{Pd@SiO}_2$ ) (**21**) and examined its catalytic activity for Sonogashira, Suzuki, and Stille coupling reactions of a broad range of heteroaryl chlorides with different nucleophilic partners such as aryl boronic acids, organostannanes, and alkynes, providing yields up to 96, 94 and 96%, respectively (Scheme 8). The reaction was carried out in an aqueous medium with 0.5 mol% catalyst loading, as mild conditions.

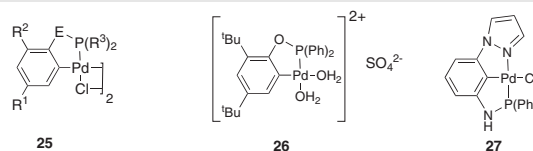
Milton and his research group<sup>100</sup> presented a microwave-accelerated synthesis of the  $[\text{PdCl}_2(\text{L})]$  pre-catalysts synthesized from  $\text{Na}_2\text{PdCl}_4$  and studied the reactivity of the Grignard cross-coupling by screening various ferrocene ligands such as dppf, dippf, dtbpf, and dtbdppf in a new solvent (Scheme 9). The solvent Me-THF has been gaining attention as a greener substitute to THF with no added reaction solvents. The authors performed the cross-coupling of Grignard reagents at 5 molar concentration in Me-THF with the correct matching of catalyst to substrate, and achieved good conversions in short times. This method significantly reduced the amount of solvent in both the Grignard synthesis and Grignard cross-coupling reactions as compared to other typical procedures based on THF. The reaction was found to be strongly dependent on the ligand structure, where 1,1-bis-diphenylphosphino-ferrocene and 1-di-*tert*-butyl-1-diphenylphosphino-ferrocene seemed to be the suitable ligands.

Peng et al.<sup>101</sup> disclosed stilbazole (stilbene-4,4-bis[(1-azo)-3,4-dihydroxybenzene]-2,2-disulfonic acid diammonium salt) (**24**) promoted, ligand-free Suzuki–Miyaura reaction in the presence of palladium catalyst in water at room temperature, which tolerated functional groups well and proceeded with high efficiency (Figure 1).



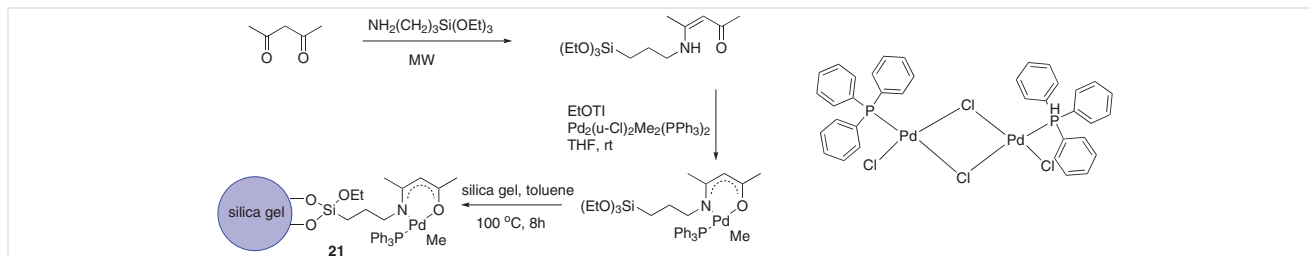
**Figure 1** Stilbazole promoted Suzuki–Miyaura reaction<sup>101</sup>

Marziale and co-workers<sup>102</sup> tested various new palladacyclic catalysts (**25–27**) in aqueous Suzuki–Miyaura coupling conditions and concluded that catalyst **25** displayed high activities at room temperature for a broad range of products and afforded high yields (Figure 2). The isolated products were of high purity and could be separated by simple filtration.

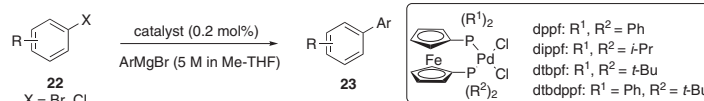


**Figure 2** Palladacyclic catalysts tested in Suzuki–Miyaura coupling<sup>102</sup>

Long and co-workers<sup>103</sup> synthesized monosubstituted ferrocene derivatives **30** by using Suzuki cross-coupling reaction of ferroceneboronic acid (**28**) with a variety of aryl and vinyl triflates **29**. The reaction was carried out in the presence of  $\text{Pd}(\text{PPh}_3)_4$  (0.025 equiv) and  $\text{K}_3\text{PO}_4$  (2 equiv) in refluxing dioxane in excellent yields (Scheme 10). The electronic and steric effects were also observed for *ortho*-, *meta*-, and *para*-substituents of aryl triflates.

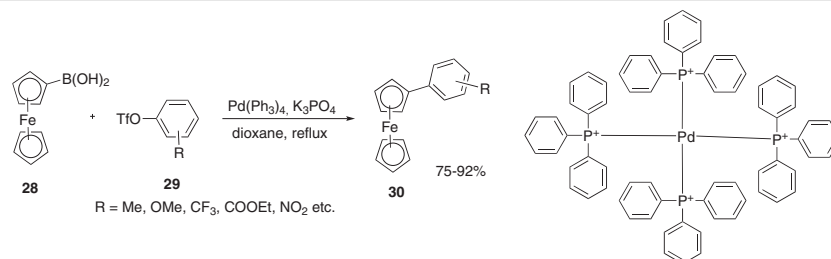


**Scheme 8** Synthesis of silica gel-supported  $\beta$ -ketoiminatophosphane-Pd complex **21**<sup>99</sup>



**Scheme 9** Cross-coupling of Grignard reagent with alkyl halides in Me-THF<sup>100</sup>





**Scheme 10** Pd-catalyzed Suzuki cross-coupling reaction of ferroceneboronic acid<sup>103</sup>

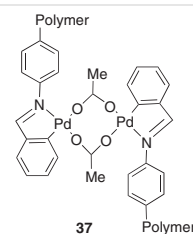
For the first time, Chen and co-workers<sup>104</sup> used oxadisilole (**31**) as a coupling partner in the cross-coupling reaction with aryl halides catalyzed by palladium, affording 2-aryl naphthalenes **33** (Scheme 11). The reaction was carried out in the presence of tetrabutylammonium fluoride and this report offered a new path for the synthesis of functionalized acenes and related structures.

Molander and co-workers<sup>105</sup> devised a new avenue to introduce the amidomethyl functional group into substrates (Scheme 12). The amidomethyltrifluoroborates **35** were first synthesized and applied in the cross-coupling as coupling partners with a number of aryl and heteroaryl chlorides in a one-pot fashion.

In 2011, Liu and co-workers<sup>106</sup> achieved the ligand-free SM reaction of arylboronic acids with aryl bromides or nitrogen-based heteroaryl halides in aqueous DMF with  $K_2CO_3$  and a catalytic amount of  $PdCl_2$  at room temperature in moderate to excellent yields. This mild and simple method tolerated various functional groups and showed that the water/DMF ratio and presence of base are crucial in the reaction.

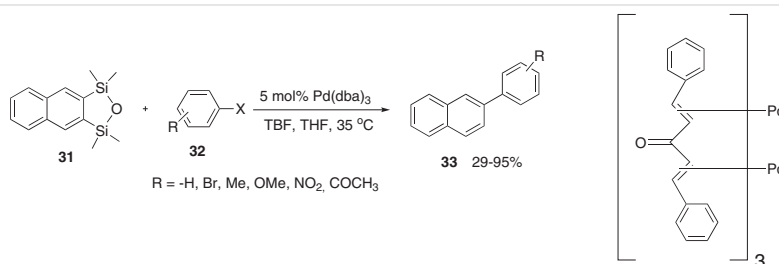
Islam et al.<sup>107</sup> disclosed a synthetic route involving novel polystyrene-assisted palladium(II) complex (PS-[( $C_6H_5CH=N$ )Pd(OAc)]<sub>2</sub>) (**37**) for phosphine-free and cop-

per-free Sonogashira reactions using  $Et_3N$  as a base under aerobic conditions in aqueous (DMF/ $H_2O$ ) medium (Figure 3).

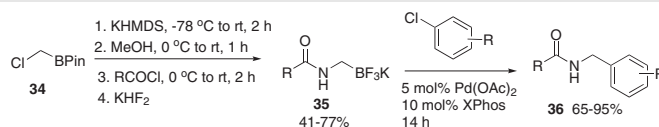


**Figure 3** Polystyrene-supported palladium(II) complex catalyzed copper-free Sonogashira reactions<sup>107</sup>

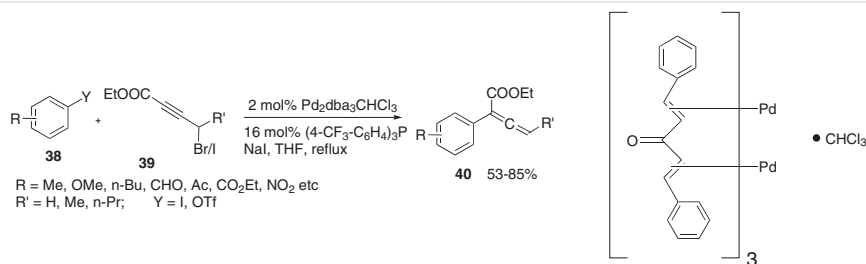
Lee and co-workers<sup>108</sup> published a synthetically valuable process to introduce aryl group to the C2-position of 2,3-alkadienoates **40** via Pd-catalyzed selective allenyl cross-coupling reactions of an electron-withdrawing or electron-donating group containing aromatic iodides with organoindium reagents **39**; i.e., 2-aryl-2,3-alkadienoates and ethyl 4-bromo-2-alkynoates, generated under in situ conditions, with good yield (Scheme 13).



**Scheme 11** Pd-catalyzed cross-coupling of oxadisilole with aryl halides<sup>104</sup>



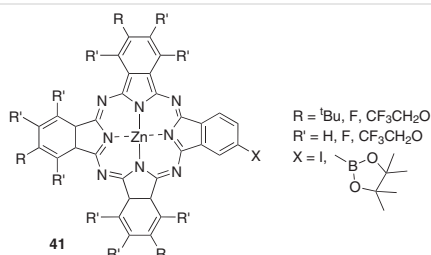
**Scheme 12** Synthesis of amidomethyltrifluoroborates and cross-coupling with aryl chlorides<sup>105</sup>



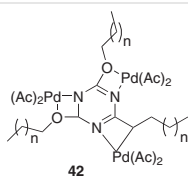
**Scheme 13** Pd-catalyzed allenyl cross-coupling reaction<sup>108</sup>

Ali and co-workers<sup>109</sup> used palladium-catalyzed cross-coupling reactions (Buchwald–Hartwig, Sonogashira, and Suzuki–Miyaura) for the synthesis of a chain of peptides that were mono-functionalized with phthalocyanines (Pc) (**41**) at the N/C-terminal with moderate yields (Figure 4). The authors conjugated Pc with peptide moieties to help establish the selectivity for potential imaging probes for positron emission tomography and fluorescence for applications in the medical field.

A phosphine-free system developed by Modak et al.<sup>110</sup> demonstrated that a new functionalized mesoporous polymer (MPTAT-1) (**42**) developed by radical polymerization of 2,4,6-triallyloxy-1,3,5-triazine (TAT) in an aqueous medium



**Figure 4** Structure of phthalocyanines (Pc) as reaction partner for various cross-coupling reactions<sup>109</sup>

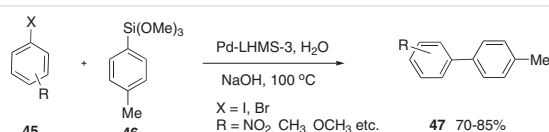


**Figure 5** MPTAT-1 for Suzuki–Miyaura, Mizoroki–Heck, and Sonogashira cross-coupling reactions<sup>110</sup>

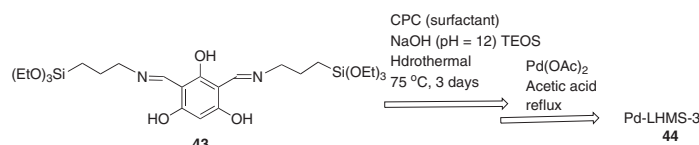
in the presence of an anionic surfactant (sodium dodecyl sulfate) as template, was an effective catalyst for several cross-coupling reactions such as Suzuki–Miyaura, Mizoroki–Heck, and Sonogashira (Figure 5). The template-free MP-TAT-1 provides assistance in immobilizing Pd(II) and appears to be a very good catalytic scheme for eco-friendly conditions such as the use of water as reaction medium.

Later, an additional report was published by the same group<sup>111</sup> in which they prepared a Pd-grafted periodic mesoporous organosilica material (Pd-LHMS-3) (**44**) containing a phloroglucinol-diimine moiety within the pores (Scheme 14). This heterogeneous catalyst was investigated for its catalytic activity in Hiyama and Sonogashira couplings, and in cyanation reactions. The Hiyama cross-couplings executed by this protocol were fluoride-free and performed in water at alkaline pH conditions (Scheme 15). Similarly, copper-free Sonogashira cross-coupling reaction proceeded in water with a base such as hexamine. The catalyst promoted the cyanide-free cyanation of aryl halides with  $\text{K}_4[\text{Fe}(\text{CN})_6]$  as the cyanide source rather than using toxic KCN, NaCN or  $\text{Zn}(\text{CN})_2$ . Excellent yields were presented for the synthesis of unsymmetrical biphenyls, di-substituted alkynes, and substituted benzonitriles under eco-friendly reaction conditions (Scheme 16).

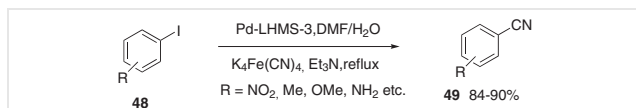
Susanto et al.<sup>112</sup> developed a thermally stable, fluorous oxime-based palladacycle, which promoted various microwave-assisted cross-couplings such as Suzuki–Miyaura, So-



**Scheme 15** Hiyama cross-coupling reaction using Pd-LHMS-3<sup>111</sup>

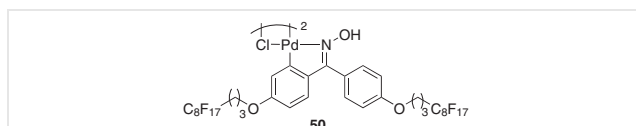


**Scheme 14** Synthetic pathway for the synthesis of Pd-LHMS-3<sup>111</sup>



**Scheme 16** KCN-free cyanation using Pd-LHMS-3<sup>111</sup>

nogashira and Stille reactions in aqueous media (Figure 6). According to this report, Pd leaching was extremely low and **50** was reused five times with no significant loss of activity.

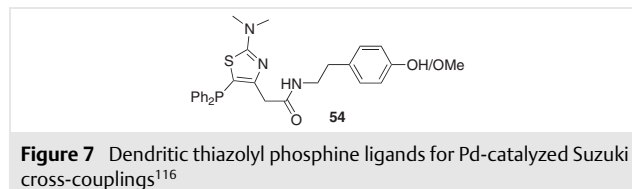


**Figure 6** Fluorous oxime-based palladacycle for Suzuki, Sonogashira and Stille cross-couplings<sup>112</sup>

Mondal et al.<sup>113</sup> produced a catalytic system based on PdCl<sub>2</sub> and sodium sulfate generated in situ for ligand-free cross-coupling reaction in water at room temperature. They also produced a similar catalytic system based on PdCl<sub>2</sub> and sodium chloride or sodium acetate that was found to be equally effective in Suzuki–Miyaura cross-couplings. The Wang group<sup>114</sup> published a report on one-pot tandem Pd(II)-catalyzed Diels–Alder/cross-coupling reactions of 2-boron substituted dienes (Scheme 17). They prepared and characterized several new 2-boron substituted dienes and examined their reactivity in Diels–Alder reactions. The boron substituted cycloadducts thus formed were used in Suzuki cross-couplings.

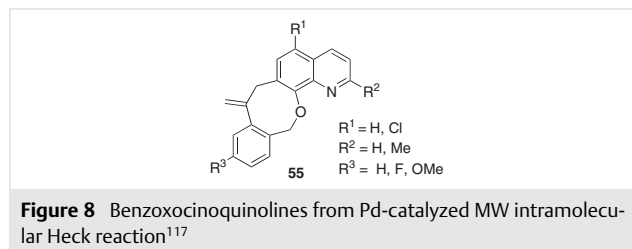
The Liu research group<sup>115</sup> examined Pd(OAc)<sub>2</sub>/(*i*-Pr)<sub>2</sub>NH/H<sub>2</sub>O as a catalytic system for ligand-free and aerobic Suzuki reaction in water in the absence of any additive. It was demonstrated that the protocol tolerated a broad scope of aryl halides with either hydrophobic or hydrophilic groups. Further, the base was found to play a crucial role in this reaction. Keller et al.<sup>116</sup> synthesized a series of novel dendritic thiazolyl phosphine ligands and deployed them in palladium-catalyzed Suzuki couplings using Pd(OAc)<sub>2</sub> (Figure 7). The efficiency of the catalysts were compared with those of the corresponding triphenylphosphines; for example, in

contrast to their triphenylphosphine counterparts, the thiazolyl phosphine-based catalytic arrangements (**54**). The reactions were also conducted either in water/THF mixtures or in pure water in the case of a single substrate.



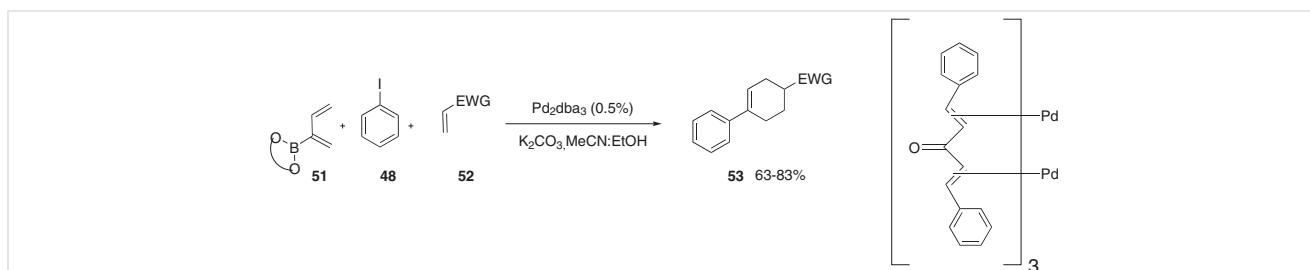
**Figure 7** Dendritic thiazolyl phosphine ligands for Pd-catalyzed Suzuki cross-couplings<sup>116</sup>

Saha and co-workers<sup>117</sup> extended a new protocol for the development of eight-membered benzoxocinoquinoline (**55**) from quinolines by using a basic alumina-supported microwave-assisted intramolecular Heck reaction (Figure 8).



**Figure 8** Benzoxocinoquinolines from Pd-catalyzed MW intramolecular Heck reaction<sup>117</sup>

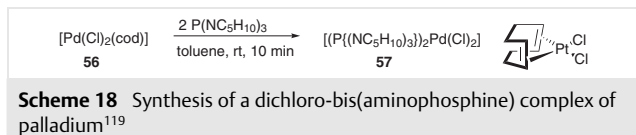
In 2013, the Lu group<sup>118</sup> utilized a nonionic designer amphiphile, (TPGS-750-M) for Pd(P(*t*-Bu)<sub>3</sub>)<sub>2</sub>/DABCO catalyzed Stille couplings between a broad range of substrates (aryl and alkenyl halides) and organostannanes in water at room temperature. Oberholzera and Frech<sup>119</sup> designed a series of highly active, cheap, easily accessible, and air-stable dichloro-bis(aminophosphine) complexes of palladium of general formula [(P((NC<sub>5</sub>H<sub>10</sub>)<sub>3</sub>-*n*-(C<sub>6</sub>H<sub>11</sub>))<sub>2</sub>)PdCl<sub>2</sub>] (**57**) (*n* = 0–3) for Heck cross-coupling reactions with a catalyst loading of 0.05 mol% in DMF at 100 °C using tetrabutylammonium bromide (Scheme 18). The active form of this catalyst was utilized (namely, nanoparticles) in the Heck reaction, which displayed an outstanding functional group tolerance towards aryl bromides containing fluoro, chloro, nitro, nitriles, aldehydes, ketones, esters, ethers, trifluoromethane



**Scheme 17** Tandem Diels–Alder/Suzuki cross-coupling reaction<sup>114</sup>



groups, anilines, amides, phenols, and methylsulfanyl groups, and heterocyclic aryl bromides, such as pyridines and thiophene groups.

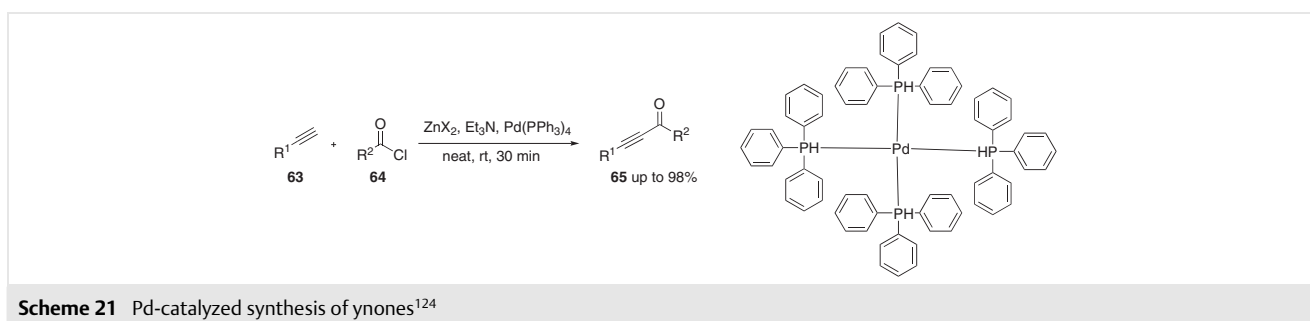
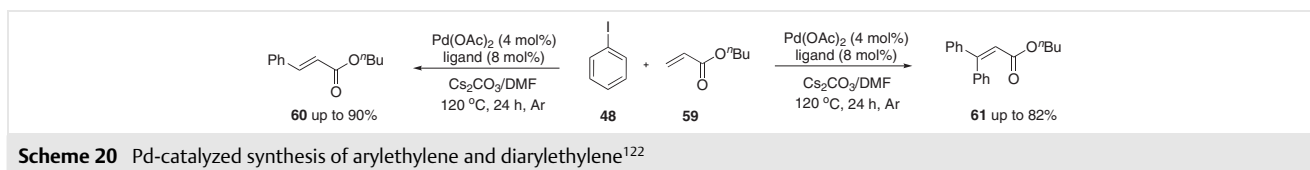
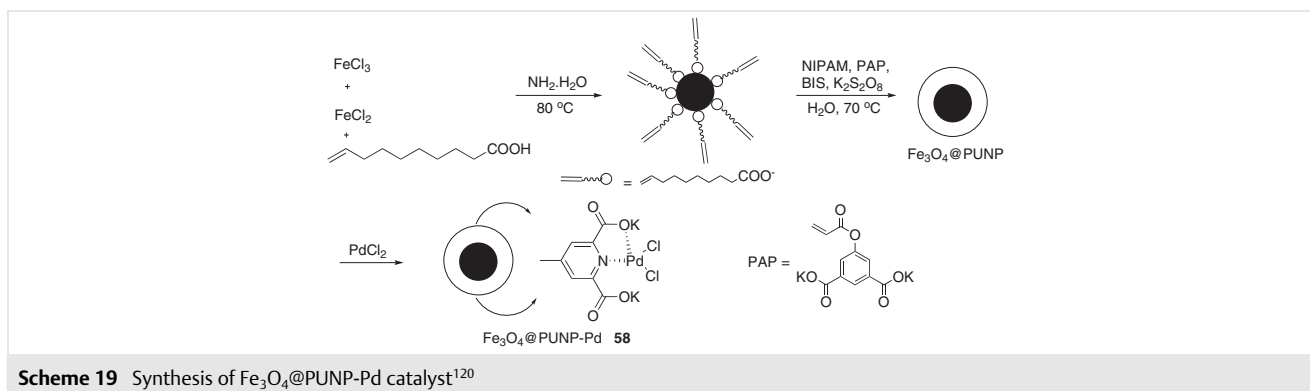
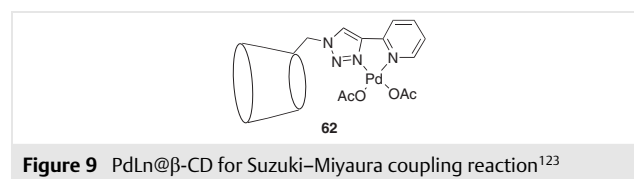


The Yang group<sup>120</sup> developed a novel heterogeneous palladium catalyst by anchoring Pd(II) onto poly(undecylenic acid-co-*N*-isopropylacrylamide-co-potassium 4-acryloylpyridine-2,6-dicarboxylate)-coated Fe<sub>3</sub>O<sub>4</sub> (Fe<sub>3</sub>O<sub>4</sub>@PUNP) magnetic microgel (**58**) (Scheme 19).

Ding and co-workers<sup>121</sup> fabricated the Pd/bentonite catalyst by a simple impregnation method for Suzuki–Miyaura reaction. Clay is abundant, nontoxic, cheap, and a good support for the preparation of green catalysts. This methodology tolerated aryl bromides and iodides using several EDG and EWG such as -COCH<sub>3</sub>, -OCH<sub>3</sub>, -CH<sub>3</sub>, -F, -NO<sub>2</sub>, -CN, and -Cl

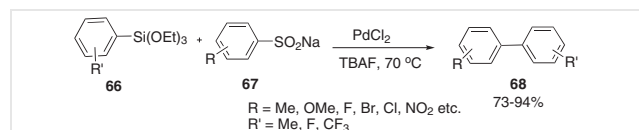
in the coupling reaction with loading of catalyst Pd (0.06 mol%) in very low amount under ambient temperature. Yan and co-workers developed an effective palladium-catalyzed synthesis of aryethylene (mono-substituted alkenes) and diaryethylene (disubstituted alkenes) by coupling various aryl halides with olefins in the presence of easily available ligands (Scheme 20).<sup>122</sup>

Based on functionalized  $\beta$ -cyclodextrin, Zhang and co-workers<sup>123</sup> designed and prepared a novel water-soluble complex PdLn@ $\beta$ -CD (**62**) for Suzuki–Miyaura coupling reactions in aqueous medium (Figure 9). This catalyst was based on click-triazole-functionalized  $\beta$ -cyclodextrin and gave high turnover frequencies and turnover numbers of up to  $4.9 \times 10^8 \text{ h}^{-1}$  and  $9.9 \times 10^8$ , respectively.



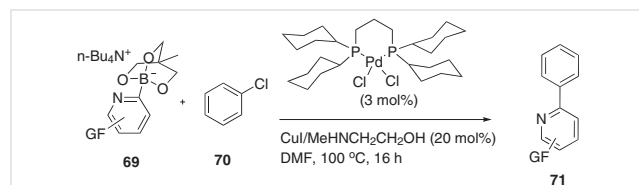
Yuan and co-workers<sup>124</sup> devised a mild and solvent-free procedure for the development of ynones by Pd(PPh<sub>3</sub>)<sub>4</sub> catalyzed cross-coupling of in-situ-generated alkynylzinc derivatives with acyl chlorides in high yields (Scheme 21).

Cheng and co-workers<sup>125</sup> reported Pd-catalyzed Hiyama-type cross-couplings of various organosilanes (**66**) with arenesulfonates (**67**) in good to excellent yields at 70 °C under aerobic conditions (Scheme 22).



**Scheme 22** Pd-catalyzed Hiyama-type cross-coupling of organosilanes with arenesulfonates<sup>125</sup>

Pd-catalyzed Suzuki–Miyura cross-coupling reactions were demonstrated by the Sakashita research group,<sup>126</sup> in which newly synthesized tetrabutylammonium 2-pyridyltriolborate salts **69** were allowed to couple with various challenging aryl/heteroaryl chlorides **70** to produce 2-arylpyridine derivatives **71** in the presence of PdCl<sub>2</sub>dcpf (3 mol%) and CuI/MeNHCH<sub>2</sub>CH<sub>2</sub>OH (20 mol%) without using bases, with excellent yields (Scheme 23). These tetrabutylammonium salts showed better reactivity than the correspondent lithium salts.



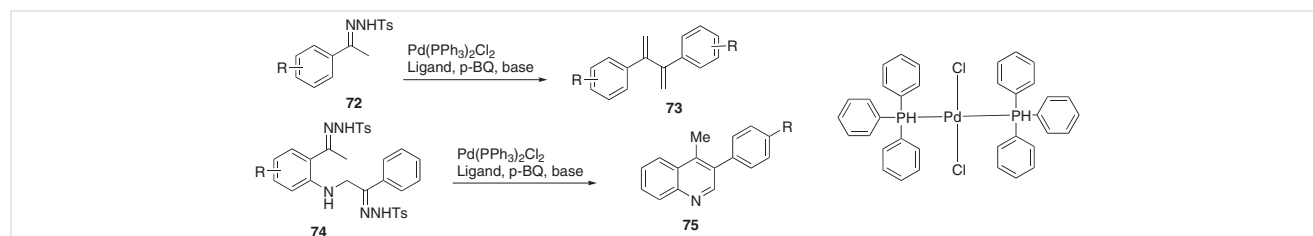
**Scheme 23** Pd-catalyzed SM cross-coupling reactions of tetrabutylammonium 2-pyridyltriolborate salts as coupling partner<sup>126</sup>

Ojha et al.<sup>127</sup> achieved the challenging task of regioselective formation of highly branched dienes by a novel palladium-catalyzed selective coupling reaction of hydrazones **72** with *t*-BuOLi and *p*-benzoquinone (Scheme 24). They utilized carbene transfer reactions in the Pd(II) catalyzed coupling of hydrazones under oxidative conditions, which led to the formation of a Pd-bis-carbene complex with  $\alpha$ -hydrogens finally affording branched dienes **73**. The reaction was versatile and compatible with a range of functional groups to open new avenues for synthesizing useful heterocyclic molecules **75**.

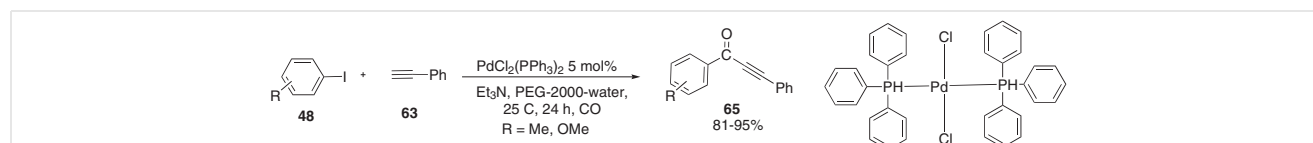
In 2014, the Liu research team<sup>128</sup> envisioned an efficient, recyclable, green and ligand-free method for the Suzuki coupling of aryl or heteroaryl halides in the presence of potassium aryltrifluoroborates with water, in air, using a Pd(OAc)<sub>2</sub>-H<sub>2</sub>O-PEG system to give the desired products in high reaction yields. The catalytic system was recycled eight times without appreciable loss in activity. Similarly, the water and PEG-2000 solvent mixture was utilized by the Zhao research group<sup>129</sup> in which they described the carbonylative Sonogashira coupling reaction of terminal alkynes with aryl iodides in the presence of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and Et<sub>3</sub>N as a base under an atmospheric pressure of CO at 25 °C, giving a scope of alkynyl ketones with satisfactory yields (Scheme 25). This protocol could be effortlessly extended to the synthesis of 2-substituted flavones from *o*-iodophenol and terminal alkynes.

The Nehra group<sup>130</sup> prepared an efficient ionic-liquid-tagged Schiff base palladium complex (**76**) that was stable in air and was water-soluble (Figure 10). This complex showed catalytic activity and was investigated for Heck and Suzuki cross-coupling reactions in aqueous media. The protocol was found to be very effective for more challenging substrates such as chlorides.

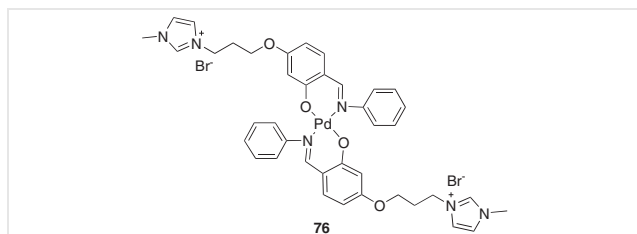
Li et al.<sup>131</sup> reported stereospecific cross-coupling between aryl chlorides and unactivated secondary alkylboron



**Scheme 24** Pd-catalyzed coupling of hydrazones<sup>127</sup>



**Scheme 25** Carbonylative Sonogashira coupling reaction<sup>129</sup>



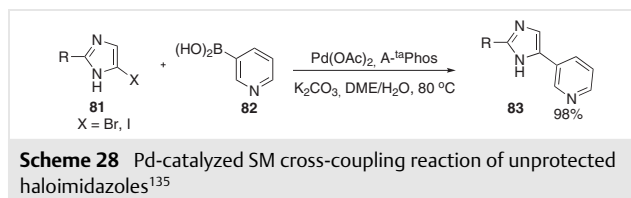
**Figure 10** Ionic-liquid-tagged Schiff base palladium complex<sup>130</sup>

nucleophiles under Pd catalysis. Secondary alkyltrifluoroborates and secondary alkylboronic acids were tolerated in this protocol without noteworthy isomerization of the alkyl nucleophile. In this cross-coupling process, optically active secondary alkyltrifluoroborate reagents underwent stereospecific inversion of configuration. This protocol could be utilized in the construction of optically active drugs from optically active alkylboron compounds. Nadaf et al.<sup>132</sup> described the palladium-catalyzed Suzuki–Miyaura cross-coupling reactions between newly synthesized potassium *N*-methyltrifluoroborate isoindolin-1-one (**77**) and aryl and heteroaryl chlorides to prepare libraries of substituted *N*-benzyl isoindolin-1-ones **78** (Scheme 26).

In cross-coupling reactions, one of the limitations is that azobenzenes act as electrophiles, whereby metalation by halogen-metal exchange causes reduction of the azo group yielding hydrazine derivatives in place of the desired metalated azobenzenes. Strueben<sup>133</sup> provided a solution to this problem by developing a mild method to prepare mono- and distannylated azobenzenes (**79**), which were used as nucleophilic partners in Pd-catalyzed Stille cross-coupling

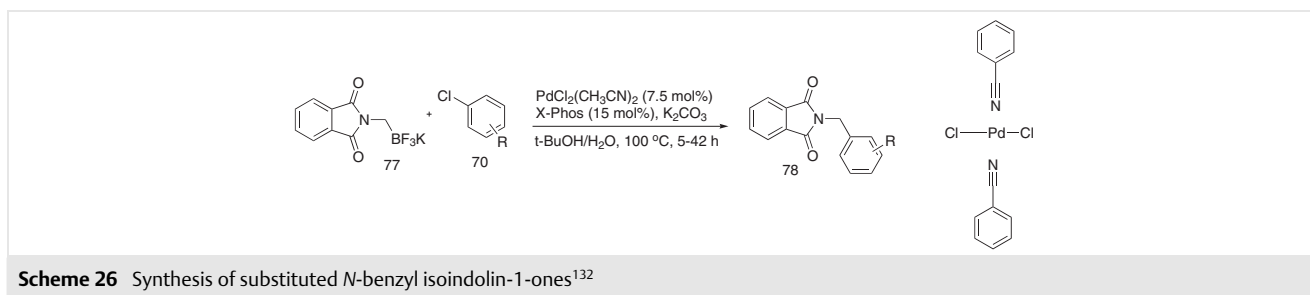
reactions with electron-deficient and electron-rich aryl bromides, resulting in the formation of the cross-coupled products **80** in yields as high as 70 to 93% (Scheme 27).

Sun et al.<sup>134</sup> reported a three-step synthesis of 4,8-azab-oranaphthalene (ABN) on a gram scale and showed that the reaction tolerated a variety of functional groups and cross-coupling partners in various Sonogashira, palladium-catalyzed Suzuki, and Heck cross-coupling reactions. One of the advantages of the coupled product bearing an ABN motif was that it showed a fluorescence response toward Cd(II) and Zn(II) ions. Thus, this protocol is very significant in designing various fluorescent chemosensors. The Tan group<sup>135</sup> published a Suzuki–Miyaura cross-coupling reaction catalyzed by palladium of unprotected haloimidazoles (**81**) with various aryl- and heteroarylboronic acids providing a wide array of functionalized imidazoles (**83**) (Scheme 28). The total synthesis of nortopsentin D was also demonstrated by the group utilizing this method.

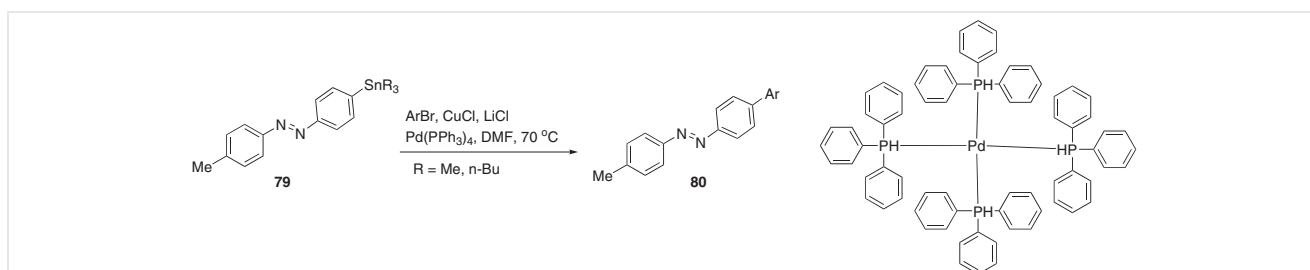


**Scheme 28** Pd-catalyzed SM cross-coupling reaction of unprotected haloimidazoles<sup>135</sup>

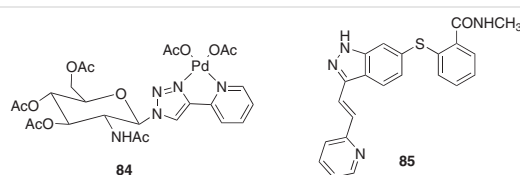
In 2015, Shen et al.<sup>136</sup> synthesized D-glucosamine-derived triazole@palladium catalyst (**84**) via a suitable route in high reaction yields, and its catalytic activity was studied in Heck cross-coupling reactions between olefins (Figure 11). Additionally, the easy synthesis of marketed antitumor drug Axitinib (**85**) was also demonstrated by the group utilizing this protocol.



**Scheme 26** Synthesis of substituted *N*-benzyl isoindolin-1-ones<sup>132</sup>

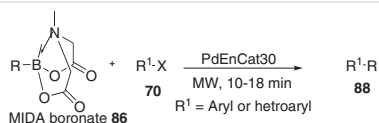


**Scheme 27** Pd-catalyzed Stille cross-coupling reactions of monostannylated azobenzenes<sup>133</sup>



**Figure 11** D-Glucosamine-derived triazole@palladium catalyst **84** and axitinib **85**<sup>136</sup>

An improved and highly efficient procedure was reported by da Silva and co-workers,<sup>137</sup> who described ligand-free microwave-enhanced Suzuki cross-coupling reaction of (het)aryl halides and (hetaryl, allyl)arylboronic acid N-methyl-iminodiacetic acid (MIDA) ester (**86**) for the synthesis of biaryls, bipyrindyls, thienylpyridine, and allylphenols using polyurea microencapsulated Pd catalyst (Pd EnCat 30) in excellent yields in just 10–18 min (Scheme 29). This method did not utilize any phosphine-ligand and was performed in an aqueous medium.

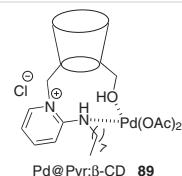


**Scheme 29** MW-assisted SM cross-coupling reaction of (het)aryl halides and MIDA ester<sup>137</sup>

Boruah and co-workers<sup>138</sup> demonstrated a highly efficient, economical alternative and eco-friendly procedure for Suzuki–Miyaura cross-coupling reactions catalyzed by palladium acetate. The reactions were carried out in neat ‘water extract of banana’ at room temperature in the air within 5–90 min in the absence of any ligand, external base, organic medium, and external promoters like additives. Strappaveccia and co-workers<sup>139</sup> investigated the synthesis of stilbines, cinnamate esters and acids by using of GVL in the Pd-catalyzed Heck reaction. Moreover, poly(phenylenevinylene) (PPV) semiconductors were also prepared using this protocol in high yields with very low amount of Pd-content. In a later investigation by this group,<sup>140</sup> they presented  $\gamma$ -valerolactone (GVL) as a non-toxic, biodegradable,

biomass-derived dipolar aprotic solvents like DMF or NMP for the Sonogashira cross-coupling reaction using DABCO as a base, affording the desired products in 62–96% yields. Because of the biomass-derived reactants, this method offers an eco-friendly approach leading to higher sustainability as well as high chemical efficiency.

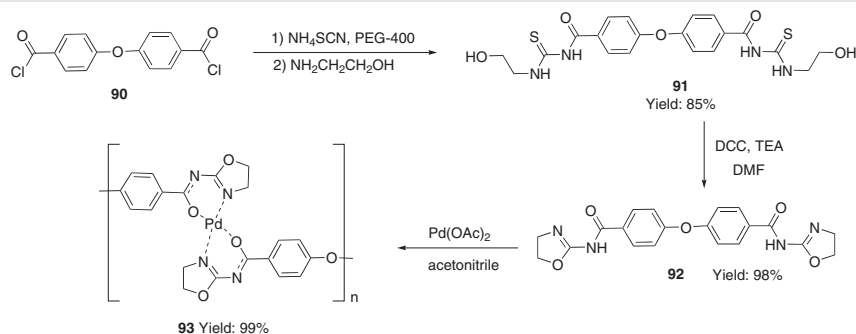
In 2016, Khana et al.<sup>141</sup> prepared an ionic Pd(II) complex stabilized by a water-soluble pyridinium-modified  $\beta$ -cyclodextrin, affording the N-octyl-pyridine-2-amine backbone (Pd(II)@Pyr: $\beta$ -CD) (**89**) and explored the activity of catalyst in Heck cross-coupling and Suzuki–Miyaura coupling reactions in eco-friendly aqueous medium, which provided high yields of the coupled product (Figure 12). Aryl chlorides were also efficiently coupled with phenylboronic acid/styrene using this procedure.



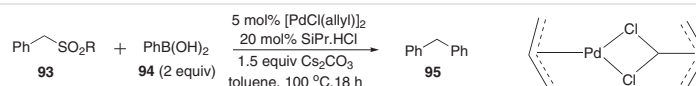
**Figure 12** Pyridinium-modified  $\beta$ -cyclodextrin bearing the N-octylpyridine-2-amine<sup>141</sup>

The Jadhav research group<sup>142</sup> proposed a ligand-free Suzuki–Miyaura reaction and base-free Heck reactions to synthesize a variety of biaryls, acrylates, and prochiral ketones under mild reaction conditions using Pd supported on activated carbon (Pd/C) in an aqueous hydrotropic solution. A hydrotrope was used as a precious, green reaction medium for the first time. Wang and co-workers<sup>143</sup> developed a novel oxazoline-based palladium microsphere complex (**93**) by the self-assembly of the bisoxazoline (**92**) and Pd(OAc)<sub>2</sub> (Scheme 30). This solid microsphere catalyst was explored for phosphine-free Suzuki–Miyaura cross-coupling reactions in aqueous media.

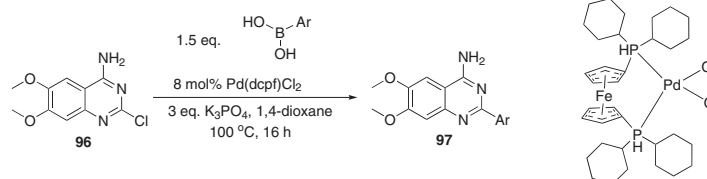
In 2017, Nambo and co-workers<sup>144</sup> described the Pd-catalyzed Suzuki–Miyaura cross-coupling reactions of fluorinated sulfone derivatives as effective electrophiles (Scheme 31). C–SO<sub>2</sub> bonds were activated by introducing an



**Scheme 30** Synthesis of oxazoline-based palladium microsphere complex **93**<sup>143</sup>



**Scheme 31** Pd-catalyzed SM cross-coupling reactions of fluorinated sulfone<sup>144</sup>

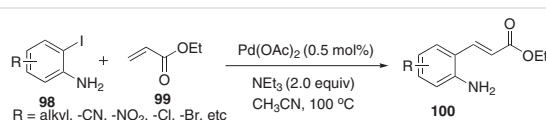


**Scheme 32** Synthesis of 4-aminoquinazoline biaryl compounds<sup>145</sup>

EWG on the aryl ring of the sulfones under Pd-catalysis, leading to a diversity of multiple arylated products in satisfactory yields.

Pulipati and co-workers<sup>145</sup> proposed a vigorous approach for the synthesis of 4-aminoquinazoline biaryl compounds from arylboronic acids and quinazoline containing an unprotected NH<sub>2</sub> group (**96**) via Suzuki–Miyaura coupling reaction using Pd(dcpf)Cl<sub>2</sub> (Scheme 32). The synthesized compounds were also assessed for antimicrobial and antifungal biological activity.

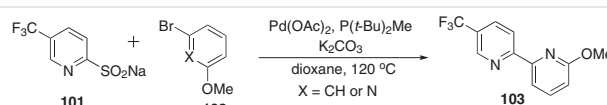
Chen and co-workers<sup>146</sup> developed Pd-catalyzed ligand-free Heck reaction between 2-iodoanilines (**98**) and acrylate (**99**) in CH<sub>3</sub>CN using Pd(OAc)<sub>2</sub> (5.0 mol%) as catalyst and NEt<sub>3</sub> as a base to afford 2-alkenylanilines (**100**) in high yields of up to 93% (Scheme 33).



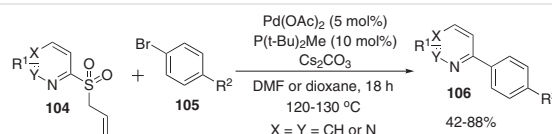
**Scheme 33** Pd-catalyzed ligand-free Heck reaction<sup>146</sup>

Jadhav et al.<sup>147</sup> utilized a Pd(PPh<sub>3</sub>)<sub>4</sub>/Et<sub>3</sub>N/H<sub>2</sub>O/98 °C catalyst system for the Mizoroki–Heck coupling reaction carried out in the absence of any additives under aerobic conditions with TOF of 12 to 14 h<sup>−1</sup> in a very short reaction time. This procedure was applicable for a broad range of electron-donating and electron-withdrawing aryl chlorides and bromides. The Clavé research group<sup>148</sup> developed a bio-based plant-derived EcoPd from the roots of *Eichhornia crassipes* for the Suzuki cross-coupling of heteroaryl compounds for the synthesis of a broad range of heterocyclic–heterocyclic biaryl and heterocyclic biaryl compounds with a small amount of catalyst. The reaction promoted the Suzuki cross-coupling without ligands or additives. In 2018, Markovic et al.<sup>149</sup> described a Pd-catalyzed coupling reaction between heterocyclic sulfinates (**101**) and aryl or heteroaryl halides (**102**), affording high yields of the corresponding biaryls (**103**) (Scheme 34). Furthermore, the heterocyclic allylsulfones (**104**) can function as ideal sulfinate

reagents and, when reacted with aryl halide, deallylation could be restricted, leading to efficient desulfinylative cross-coupling under palladium(0) catalysis (**106**) (Scheme 35). Additionally, the authors also prepared pharmaceutical agents etoricoxib and crizotinib using allyl heteroaryl sulfone coupling partners.

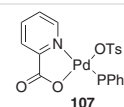


**Scheme 34** Pd-catalyzed cross-coupling reaction of heterocyclic sulfinates<sup>149</sup>



**Scheme 35** Pd-catalyzed desulfinylative cross-coupling reaction<sup>149</sup>

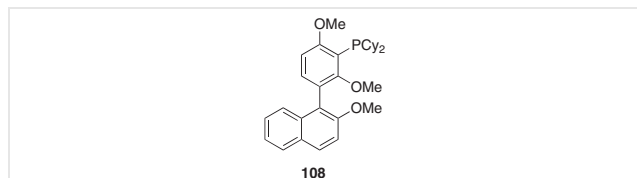
Sharma and co-workers<sup>150</sup> synthesized palladium(II) complex of hemilabile N–O ligand (picolinate) (**107**) for Mizoroki–Heck couplings with high TOF up to >10,000 h<sup>−1</sup> in just 15 min with high selectivity of >99% to the desired products (Figure 13).



**Figure 13** Palladium(II) complex of hemilabile N–O ligand (picolinate)<sup>150</sup>

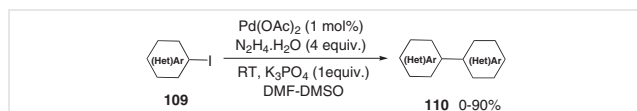
Another exceptional contribution was reported by Landstrom et al.<sup>151</sup> who synthesized a new biaryl phosphine-containing ligand (EvanPhos) (**108**) in only two steps (Figure 14). The complexation was done with either Pd(OAc)<sub>2</sub> or (CH<sub>3</sub>CN)PdCl<sub>2</sub> converting into a highly active Pd(0) species, which served as a precatalyst for Suzuki–

Miyaura cross-couplings of functionalized reaction partners in either water containing nano micelles or uncommon solvent EtOAc. This catalytic system was very effective even at low amounts of 0.05–0.5 mol%. The high rate of reaction was further improved when the reaction was performed in aqueous micellar media instead EtOAc.



**Figure 14** Biaryl phosphine-containing ligand (EvanPhos)<sup>151</sup>

In 2019, Gong and co-workers<sup>152</sup> developed an Ullmann biaryl synthesis using  $\text{Pd}(\text{OAc})_2$  and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  as the reducing reagent for the coupling of both electron-deficient as well as electron-rich aryl or heteroaryl iodides **109** leading to a variety of biaryls **110** at room temperature in good to excellent yields. The *in-situ* generated palladium nanoparticles were found to be active catalysts. The advantages of this protocol were cheap reducing agent, cost-effectiveness, and no need for metal reductants (Scheme 36).

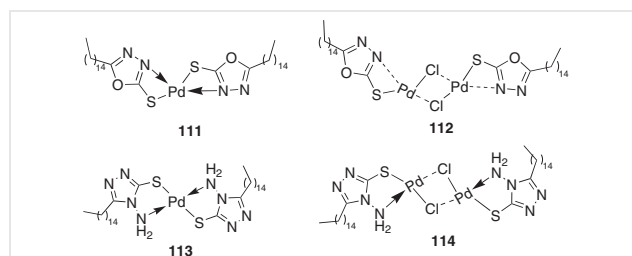


**Scheme 36** Pd-catalyzed Ullmann biaryl synthesis<sup>152</sup>

Chehrouri and co-workers<sup>153</sup> demonstrated the synthesis of palladium complexes derived from 3-pentadecyl-1,3,4-oxadiazole-2(3*H*)-thiones **111**, **112** or 4-amino-3-pentadecyl-3*H*-1,2,4-triazole-3-thiones **113**, **114** (Figure 15). The complexes thus obtained were explored for their catalytic activity in Mizoroki–Heck and Tsuji–Trost reactions, providing very high chemical yield.

The Balfour research group<sup>154</sup> presented the synthesis of a library of 2,6-disubstituted-azaindoles **116**, based on a tandem Sonogashira coupling/5-*endo-dig*/Sonogashira coupling sequence (Scheme 37). This protocol tolerated alkynes containing alcohols, aliphatic chains, and aromatic substituents.

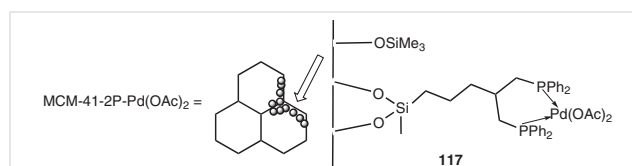
Inspired by advantages of heterogeneous catalysts such as high stability, easy separation from reaction mixture, and good recyclability over homogeneous catalysts Liu et



**Figure 15** Palladium complexes developed by Chehrouri et al.<sup>153</sup>

al.<sup>155</sup> published the synthesis of three pyridine-functionalized *N*-heterocyclic carbene-Pd complexes (HCP-Pd) using a simple external cross-linking reaction. In each complex, Pd was immobilized on the hypercrosslinked polymer (HCP) via the formation of a six-membered ring by pyridine, bidentate ligands of NHC, and  $\text{Pd}^{2+}$ . The newly synthesized catalysts were very effective for the coupling reaction in an aqueous medium under mild conditions. The microporous structure of the support ensured the high dispersion of palladium active sites. Of the three complexes, the recovery and reusability were easier for the HCP-Pd-I catalyst compared to the HCP-Pd-II and III catalysts.

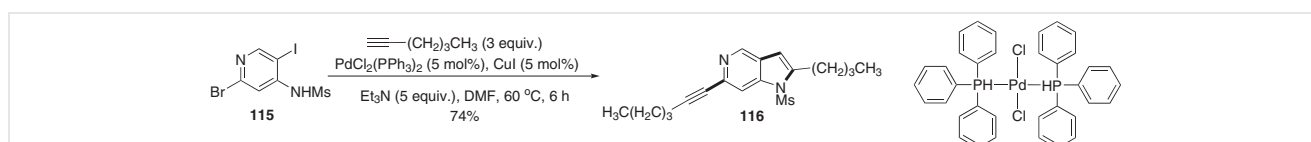
In 2020, Zhou et al.<sup>156</sup> developed a heterogeneous Pd-catalyzed carbonylative Sonogashira coupling by using an MCM-41-2P-Pd( $\text{OAc}$ )<sub>2</sub> (**117**) as a catalyst (Scheme 38). In 2021, Bangar and co-workers<sup>157</sup> used mono- and bidentate chelating oximes as ligands for the Pd catalysis of Suzuki and Heck coupling.



**Scheme 38** Design of MCM-41-2P-Pd( $\text{OAc}$ )<sub>2</sub><sup>156</sup>

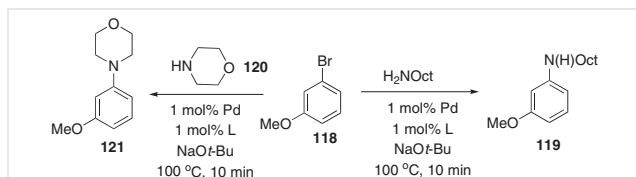
## 2.2 C–N Cross-Coupling Reaction

In 2010, Fors and co-workers<sup>158</sup> disclosed an alternative approach to catalyst advancement, in which they prepared a multiligand-based Pd catalyst (Scheme 39). The designed catalyst was then allowed to catalyze C–N cross-coupling reactions. This catalytic system exhibited the same catalyst activity and substrate scope.

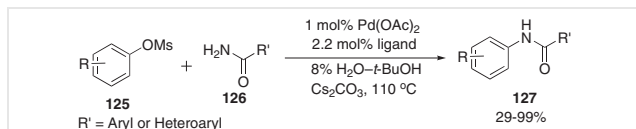


**Scheme 37** Pd-catalyzed tandem Sonogashira coupling/5-*endo-dig*/Sonogashira coupling sequence<sup>154</sup>

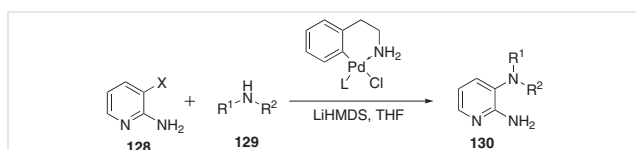




**Scheme 39** C–N cross-coupling reactions using multiligand-based Pd catalyst<sup>158</sup>

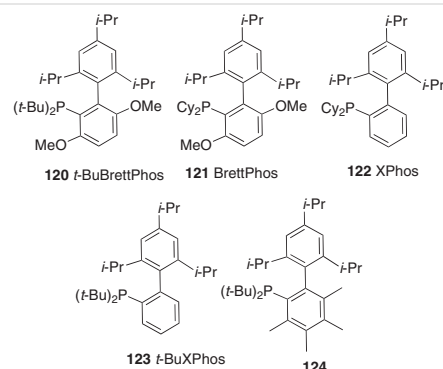


**Scheme 40** Pd-catalyzed coupling of amides and aryl mesylates<sup>159</sup>



**Scheme 41** Pd-catalyzed C–N cross-coupling of unprotected 3-halo-2-aminopyridines<sup>160</sup>

Similar to the Fors report, another group led by Dooleweerd et al.<sup>159</sup> also described a palladium catalyst based on biaryl phosphine ligands (**120–124**) (Figure 16) that allowed the coupling of amides and an array of aryl/heteroaryl mesylates (**125**) (electron-rich, -neutral, and -deficient) to afford the corresponding N-aryl amides **127** in high yields (Scheme 40). Benzamides and aliphatic and heterocyclic amides were also investigated as excellent coupling partners in this protocol.

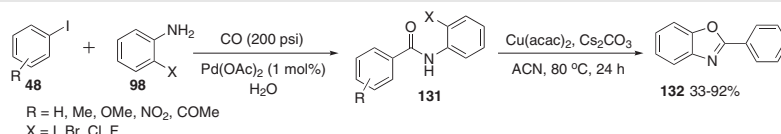


**Figure 16** Biarylphosphine ligands used by Dooleweerd et al.<sup>159</sup>

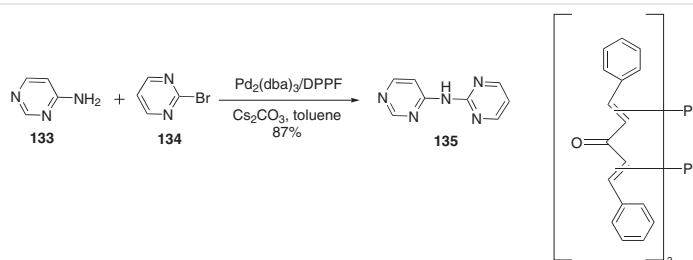
In 2011, Perez and co-workers<sup>160</sup> presented an unprecedented approach to Pd-catalyzed C–N cross-coupling of unprotected 3-halo-2-aminopyridines (**128**) with an array of primary and secondary amines yielding N3-substituted-2,3-diaminopyridines **130** (Scheme 41). The reaction was performed with BrettPhos- and RuPhos-precatalysts in combination with LiHMDS for this C–N cross-coupling reaction.

Tambade et al.<sup>161</sup> disclosed a phosphine-free Pd(OAc)<sub>2</sub> catalyzed procedure for aminocarbonylation or carbonylative cross-coupling that enabled the coupling of a wide range of substituted aryl iodide with *ortho*-haloaniline to form *ortho*-haloanilide (**131**) in water, affording good yields (Scheme 42). Further, *ortho*-haloanilides **131** underwent cyclization for the synthesis of benzoxazoles **132** using Cu(acac)<sub>2</sub> catalyst.

In 2013, Zhang and co-workers<sup>162</sup> devised a Pd-catalyzed method for the cross-coupling of heteroaryl halides and electron-deficient heteroaromatic amines in the presence of Pd<sub>2</sub>(dba)<sub>3</sub> as a catalyst, 1,10-bis(diphenylphosphi-



**Scheme 42** Pd-catalyzed aminocarbonylation cross-coupling<sup>161</sup>



**Scheme 43** Pd-catalyzed C–N cross-coupling<sup>162</sup>

no)ferrocene (DPPF) as ligand, and  $\text{Cs}_2\text{CO}_3$  as a base (Scheme 43). This methodology allowed the coupling of several rarely reported electron-deficient heteroaromatic amines in good yields.

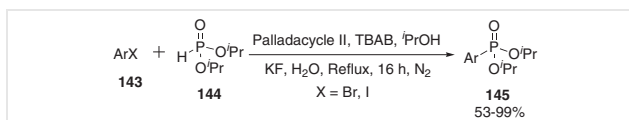
In 2014, Wagner et al.<sup>163</sup> described a versatile green catalytic system ( $[(\text{cinnamyl})\text{PdCl}]_2/t\text{-BuXPhos}$ ) (**123**) for coupling of arylbromides or chlorides with a wide range of amines, carbamates, ureas, and amides under Buchwald–Hartwig cross-coupling reaction conditions in an aqueous micellar medium. The procedure was functional-group tolerant; for example, for esters and halides the reactions were carried out at 30–50 °C providing the target compounds in good to excellent yields (Scheme 44). Compared to the previously reported Takasago's catalyst system (cBRIDP ligand in combination with  $[(\text{allyl})\text{PdCl}]_2$ ), this catalytic system was found to be much more efficient for Buchwald–Hartwig reactions with benzamide derivatives or aliphatic primary amines. No racemization was experienced in this method when a substrate with a chiral center was used. In 2020, Fan et al.<sup>164</sup> described the development of a Pd-catalyzed decarbonylative C–N coupling under a nitrogen atmosphere (Scheme 45).

In 2021, Feng and co-workers<sup>165</sup> achieved the direct cross-coupling of NH-sulfoximines through N-benylation via visible-light photocatalysis. Patel et al.<sup>166</sup> described Pd-

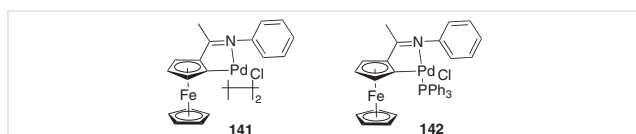
mediated simultaneous CH–CX and CH–NH bond activation followed by intramolecular cyclization reaction to form quinolin-fused benzo[d]azeto[1,2-*a*]benzimidazole analogs.

## 2.3 C–P Cross-Coupling Reaction

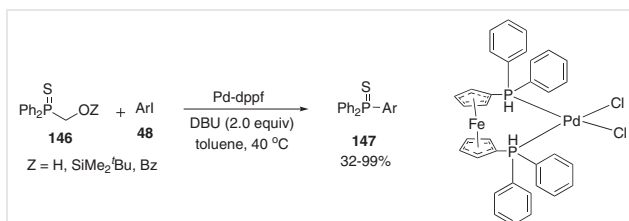
In 2013, Xu and co-workers<sup>167</sup> developed palladacycle-catalyzed phosphonation of aryl halides with diisopropyl H-phosphonate (**144**) using cyclopalladated ferrocenylimines **141**–**142** (Figure 17) with bulky phosphine ligands of X-Phos in water affording the phosphonated products **145** in excellent reaction yields (Scheme 46). The inactive electron-rich and electron-neutral aryl chlorides reacted well in this process. The weak base KF was enough for the activation of C–Cl bond instead of strong bases such as  $\text{NaO}^t\text{Bu}$  or  $\text{KO}^t\text{Bu}$ .



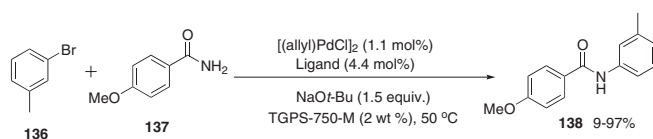
**Scheme 46** Palladacycle-catalyzed phosphonation reaction<sup>167</sup>



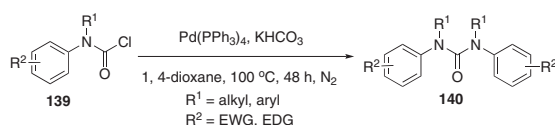
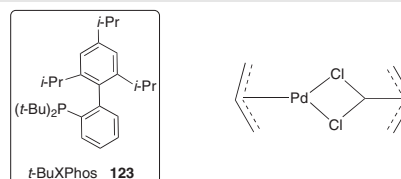
**Figure 17** Cyclopalladated ferrocenylimine ligands<sup>167</sup>



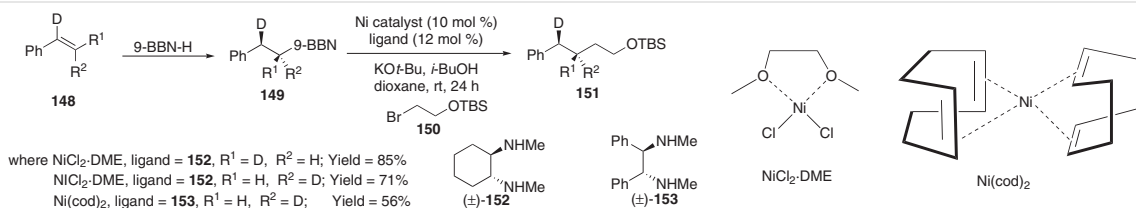
**Scheme 47** Pd-catalyzed deformylative C–P cross-couplings<sup>168</sup>



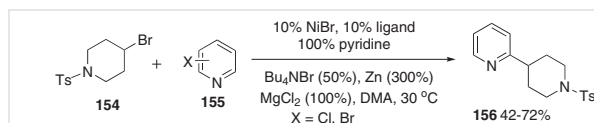
**Scheme 44** Pd-catalyzed Buchwald–Hartwig cross-coupling reaction<sup>163</sup>



**Scheme 45** Pd-catalyzed decarbonylative C–N coupling<sup>164</sup>

Scheme 48 Ni-catalyzed SM cross-coupling reaction<sup>169</sup>

The Hayashi group<sup>168</sup> achieved the syntheses of tertiary phosphine derivatives by Pd-catalyzed deformylative C–P cross-couplings of hydroxymethylphosphine derivatives **146** (Scheme 47). Triarylphosphine synthesis was also achieved by sequential triple couplings using this protocol.

Scheme 49 Ni-catalyzed alkylation of halo-pyridines<sup>170</sup>

### 3 Ni-Catalyzed Cross-Coupling Reactions

We will discuss in this section the use of nickel catalysis in various cross-coupling reactions and is generally presented in chronological order.

#### 3.1 C–C Cross-Coupling Reaction

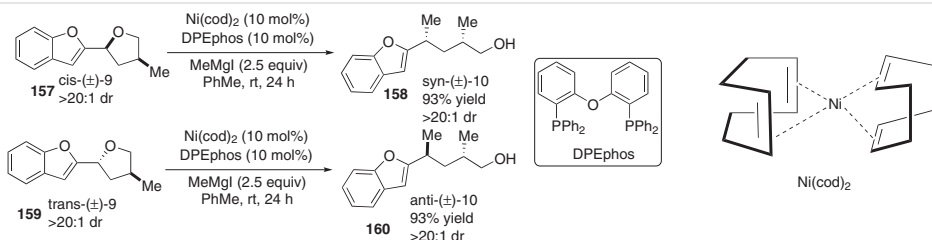
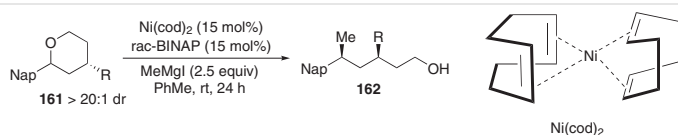
In 2011, the Taylor group<sup>169</sup> introduced deuterium-labeled alkylborane reagents **149**, which were allowed to undergo nickel-catalyzed Suzuki cross-coupling reactions in the presence of diamine ligands **152** and **153** (Scheme 48), resulting in transmetalation from boron to nickel with retention of configuration.

In 2014, Liu et al.<sup>170</sup> disclosed a method for Ni-catalyzed cross-electrophile coupling of secondary alkyl bromides **154** with halogenated pyridines **155** using zinc as a reductant, yielding different alkyl-substituted pyridines **156** in moderate to excellent yields (Scheme 49). This report pro-

vided a solution to the unreported instances in the previous literature on alkylation of halo-pyridines.

Tollefson's research group<sup>171</sup> reported the stereospecific Ni-catalyzed ring-opening cross-couplings of *O*-heterocycles such as aryl-substituted tetrahydropyrans, tetrahydrofurans, and lactones to give acyclic alcohols and carboxylic acids (Scheme 50). This method paved the way for the stereochemical synthesis of acyclic polyketide analogs. The authors showed that Ni-catalyzed Kumada-type coupling of aryl-substituted tetrahydropyrans and tetrahydrofurans proceeded with a variety of Grignard reagents to provide acyclic alcohols with excellent diastereoselectivity (Scheme 51).

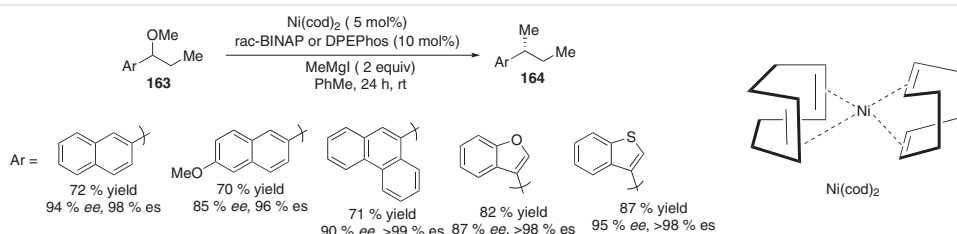
One year later, in 2015, the Tollefson research group<sup>172</sup> presented further research findings on the Ni-catalyzed Kumada, Negishi, and Suzuki cross-coupling reactions of benzylic ethers such as methyl ethers, tetrahydrofurans, tetrahydropyrans, esters, and lactones as one of the reaction

Scheme 50 Ni-catalyzed stereospecific ring-opening cross-couplings of *O*-heterocycles<sup>171</sup>Scheme 51 Ni-catalyzed stereospecific ring-opening cross-couplings of tetrahydropyrans<sup>171</sup>

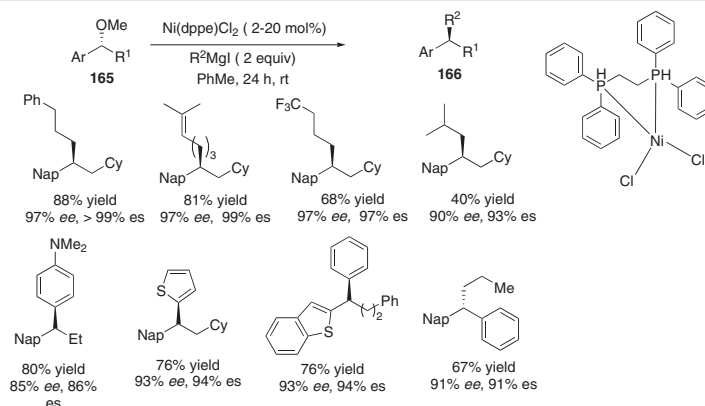
partners (Scheme 52). Several Grignard reagents such as aryl, methyl, and *n*-alkyl Grignard reagents were engaged in Kumada coupling reactions. Specifically, with methylmagnesium iodide as coupling partner, the ligands DPEphos or rac-BINAP afforded the highest reaction yield and stereospecificity (Scheme 53). The functional group tolerance was described in Negishi cross-coupling reactions using dimethylzinc. Similarly, Suzuki reactions using arylboronic esters were also reported, with different stereochemical outcomes employing different achiral ligands giving opposite enantiomers of the product. Using *N*-heterocyclic carbene ligand (SIMes) in Suzuki reaction caused inversion in the product, and use of the electron-rich phosphine PCy<sub>3</sub>

gave retention with stereospecificity (Scheme 54). Various pharmacophores units such as 1,1-diarylalkane and 2-arylalkane have been synthesized by using these cross-coupling reactions.

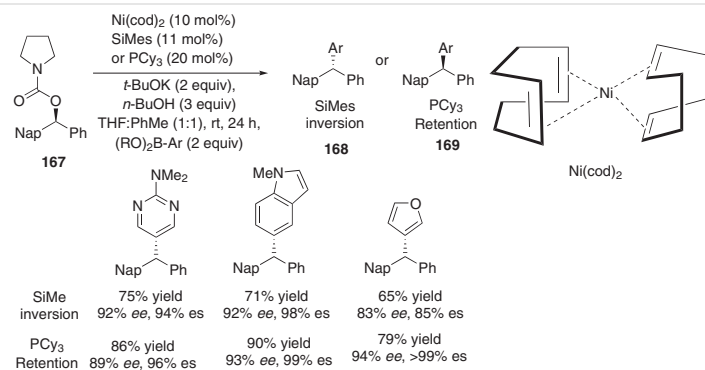
Dawson and Jarvo<sup>173</sup> published a similar kind of approach as previously described by the Tollefson group (in which they also have been the members), whereby they emphasized the development of stereospecific reactions for use in the field of pharmaceutical chemistry (Scheme 55). They reported a highly stereospecific gram-scale Kumada cross-coupling reaction with inversion at the benzylic position using a sustainable and inexpensive nickel catalyst.



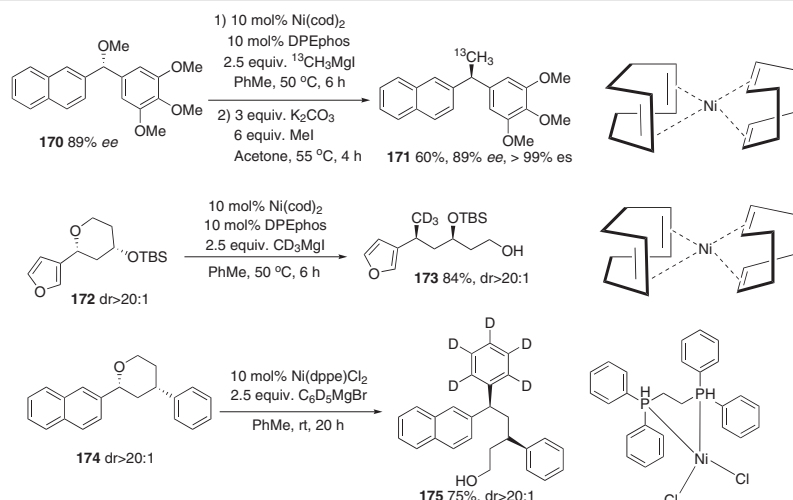
**Scheme 52** Ni-catalyzed Kumada cross-coupling reaction<sup>172</sup>



**Scheme 53** Ni-catalyzed Kumada cross-coupling reaction<sup>172</sup>

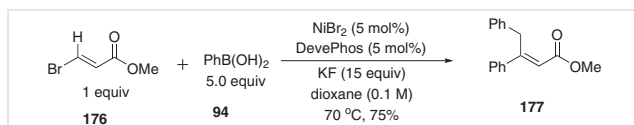


**Scheme 54** Ni-catalyzed Suzuki cross-coupling reaction<sup>172</sup>



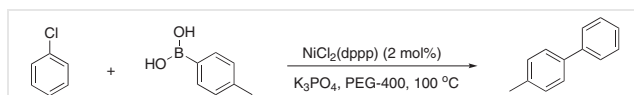
**Scheme 55** Kumada cross-couplings of isotopically labeled Grignard reagents<sup>173</sup>

An unprecedented report was published by the Funicello research group<sup>174</sup> in which they carried out the Ni-catalyzed C–Br/C–H double phenylation of methyl 4-bromocrotonate (**176**) affording a useful bis-arylated synthon through a cross-coupling reaction (Scheme 56).



**Scheme 56** Ni-catalyzed C–Br/C–H double phenylation<sup>174</sup>

In 2019, Liao and co-workers<sup>175</sup> developed a catalytic system consisting of 2 mol% NiCl<sub>2</sub>(dppp) in PEG-400 for Suzuki–Miyaura coupling reaction at 100 °C using a base (i.e. K<sub>3</sub>PO<sub>4</sub>), providing a range of biaryls with high reaction yields (Scheme 57). The NiCl<sub>2</sub>(dppp)/PEG-400 catalytic system could be simply recycled and re-applied up to five times without significant loss of activity. The main advantages of this protocol lie in the fact that it avoids the use of toxic and easily volatile toluene or dioxane as solvent, and solves the critical problem of nickel catalyst reuse.



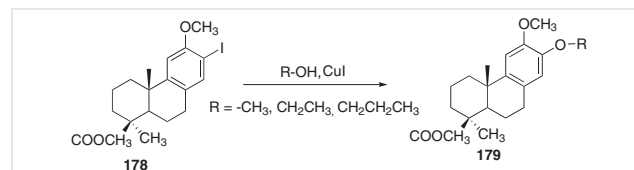
**Scheme 57** Ni-catalyzed Suzuki–Miyaura coupling reaction<sup>175</sup>

## 4 Cu-Catalyzed Cross-Coupling Reactions

We will discuss in this section the use of copper catalysis in various cross-coupling reactions and is generally presented in chronological order.

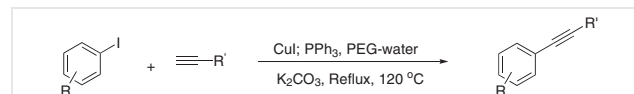
### 4.1 C–C Cross-Coupling Reactions

In 2010, Yalavarty and co-workers<sup>176</sup> found a new copper-catalyzed method of synthesizing podocarpic acid ether derivatives through the one-step cross-coupling reaction of methyl 13-iodo-*O*-methylpodocarpate (**178**) with alcohols in excellent yields (Scheme 58). Copper iodide was utilized as an inexpensive catalyst to achieve this transformation.



**Scheme 58** Cu-catalyzed synthesis of podocarpic acid ether derivatives<sup>176</sup>

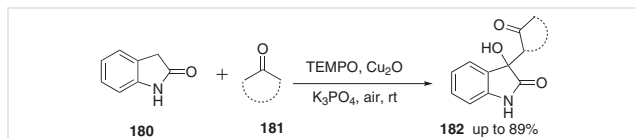
In 2011, the Chen research group<sup>177</sup> established an efficient CuI/PPh<sub>3</sub>/PEG–H<sub>2</sub>O catalytic system for Sonogashira coupling of electron-deficient or electron-rich aryl iodides with terminal acetylenes in water–polyethylene glycol under microwave irradiation or reflux to provide good to excellent yields (Scheme 59).



**Scheme 59** Cu-catalyzed Sonogashira coupling reaction<sup>177</sup>

In 2015, Wang et al.<sup>178</sup> developed easy and efficient protocol that allowed the synthesis of a variety of 3-(2-oxalkyl)-3-hydroxyoxindoles **182** through tandem oxidative cross-couplings of oxindoles (**180**) with ketones by using

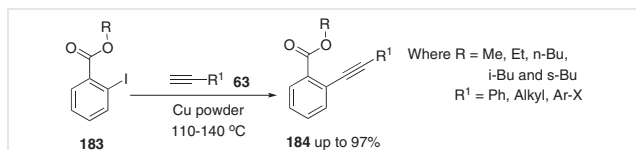
Cu<sub>2</sub>O as a catalyst and 2,2,6,6-tetramethylpiperidine N-oxyl (TEMPO) in the air with high reaction yields (Scheme 60). This methodology offers a possible approach through the generation of all-carbon quaternary centers at the C3 position of oxindoles with outstanding regioselectivity under mild conditions.



**Scheme 60** Cu-catalyzed tandem oxidative cross-couplings of oxindoles<sup>178</sup>

In 2016, Sagadevan and co-workers<sup>179</sup> devised a novel visible-light-initiated Cu-catalyzed process for the cross-coupling reaction of terminal alkynes to furnish bio-active 1,3-unsymmetrical conjugated diynes at room temperature. This method did not require pre-functionalized substrates, ligands, bases, additives, or costly palladium/gold catalysts.

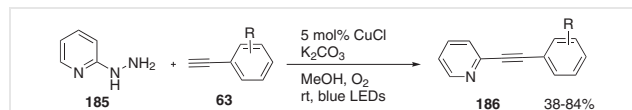
In 2017, Ali and co-workers<sup>180</sup> presented a Cu-catalyzed Sonogashira reaction of alkyl-2-iodobenzoates **183** with alkynes under solvent-, co-catalyst-, and base-free conditions providing coupling product yields up to 97% (Scheme 61). According to the authors, the reported compounds may act as anti-fobic and anti-cizmatic agents and also have the potential to control diseases such as Alzheimer's and schizophrenia.



**Scheme 61** Cu-catalyzed Sonogashira reaction of alkyl-2-iodobenzoates<sup>180</sup>

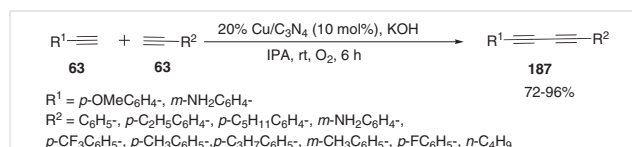
In another report in 2018 by Charpe et al.,<sup>181</sup> in which Sagadevan was co-worker, described the first report on visible-light initiated Cu-catalyzed denitrogenative oxidative coupling of 2-hydrazinopyridines (**185**) with terminal alkynes to provide 2-(alkyl/arylethynyl) pyridines **186** at room temperature with N<sub>2</sub> and water as the only byproducts (Scheme 62). The reaction proceeded by formation of copper(II) superoxo/peroxo complex *in situ*. This method

offered the green synthesis of 2-methyl-6-(phenylethynyl)pyridine (MPEP), mGluR5 receptor antagonists, and 2-((3-methoxyphenyl)ethynyl)-6-methylpyridine (M-MPEP).



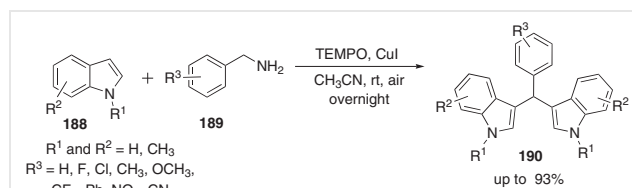
**Scheme 62** Visible-light-initiated Cu-catalyzed denitrogenative oxidative coupling<sup>181</sup>

Xu and co-workers<sup>182</sup> prepared an environmentally friendly Cu/C<sub>3</sub>N<sub>4</sub> composite and examined it as a highly effective catalyst for the homo- and cross-coupling reaction of terminal alkynes affording symmetrical and unsymmetrical 1,3-diynes **187** in good yields (Scheme 63). The reaction was performed with oxygen as an oxidant in an isopropanol solution with excellent functional group tolerance under ambient conditions.



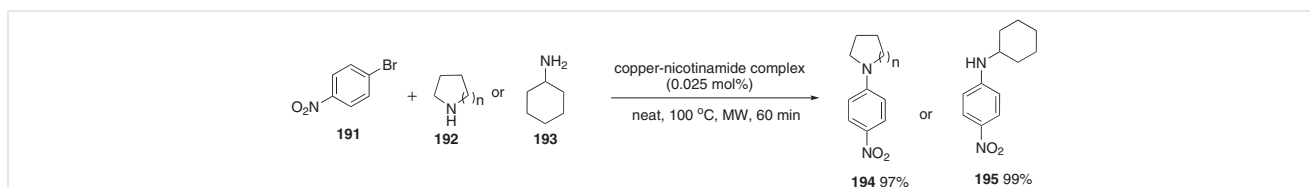
**Scheme 63** Cu/C<sub>3</sub>N<sub>4</sub> composite-catalyzed coupling of terminal alkynes<sup>182</sup>

Liao et al.<sup>183</sup> found TEMPO/CuI to be an effective catalyst for the cross-coupling of benzylic amines **189** with indoles **188**, generating the corresponding bis(indolyl)phenylmethanes **190** under air at room temperature in high yields (Scheme 64).



**Scheme 64** TEMPO/CuI-catalyzed cross-coupling of benzylic amines with indoles<sup>183</sup>

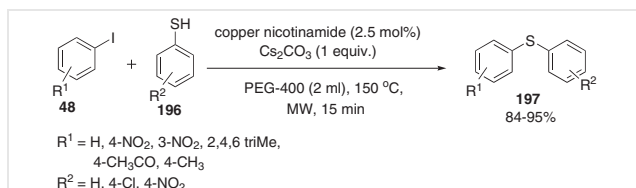
A mixed example of a Cu-catalyzed coupling reaction was described by Baig and co-workers,<sup>184</sup> who synthesized a versatile crystalline copper(II)-nicotinamide complex that



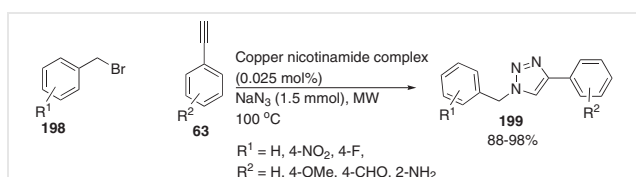
**Scheme 65** Copper(II)-nicotinamide complex-catalyzed MW-enhanced C–N coupling reaction<sup>184</sup>



efficiently catalyzed the MW-accelerated C–N, C–S bond-forming and cycloaddition reactions (Scheme 65, Scheme 66, and Scheme 67).



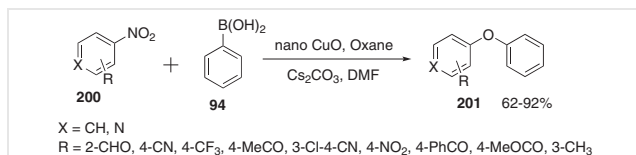
**Scheme 66** Copper(II)-nicotinamide complex-catalyzed MW-enhanced C–S coupling reaction<sup>184</sup>



**Scheme 67** Copper(II)-nicotinamide complex-catalyzed MW-enhanced cycloaddition reaction<sup>184</sup>

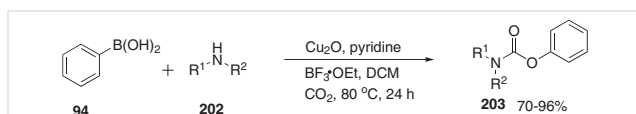
## 4.2 C–O Cross-Coupling Reaction

In 2012, Zhang and co-workers<sup>185</sup> developed the first example of a Cu-catalyzed coupling of nitroarenes with arylboronic acid, providing diaryl ethers **201** in moderate to excellent yields (Scheme 68). The reaction did not involve any ligand, and deuterium labeling in mechanistic studies showed that water was essential for this transformation.



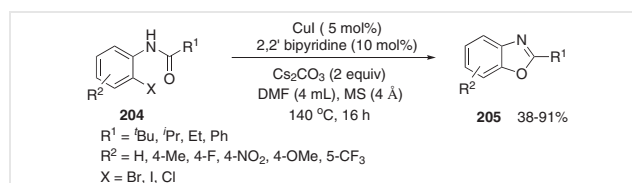
**Scheme 68** Cu-catalyzed coupling of nitroarenes with arylboronic acid<sup>185</sup>

In 2017, Xiong and co-workers<sup>186</sup> described the first report on the Cu-catalyzed oxidative coupling reaction of carbon dioxide, amines, and arylboronic acids to synthesize various *O*-aryl carbamates **203** using BF<sub>3</sub>·OEt<sub>2</sub> (Scheme 69). A wide functional group tolerance could be seen in this transformation.



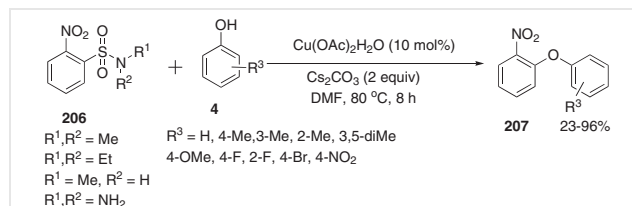
**Scheme 69** Cu-catalyzed oxidative coupling reaction<sup>186</sup>

In 2019, a new method for the synthesis of bioactive 2-substituted benzoxazoles **205** was developed by the Saranya research group<sup>187</sup> via Cu-catalyzed intramolecular C–O cross-coupling of 2-haloanilides **204** in moderate to good yields (Scheme 70). This transformation occurred by employing CuI (5 mol%)/2,2'-bipyridine (10 mol%) as a catalytic system, Cs<sub>2</sub>CO<sub>3</sub> (2 equiv) as base, and DMF solvent with 4 Å molecular sieves at 140 °C. The reaction was observed to be influenced by the amide and aromatic substituents of 2-haloanilides.



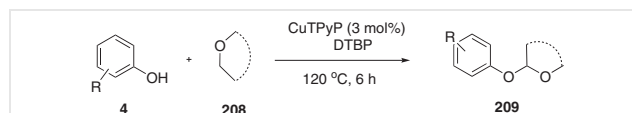
**Scheme 70** Cu-catalyzed intramolecular C–O cross-coupling reaction<sup>187</sup>

Chen et al.<sup>188</sup> observed an unprecedented ligand-free Cu-catalyzed *O*-arylation of arenesulfonamides **206** with phenols generating a range of unsymmetric biaryl ethers **207** in excellent yields (Scheme 71). The reaction involved cleavage of C–S bond with excellent regioselectivity and good functional groups tolerance on phenols.

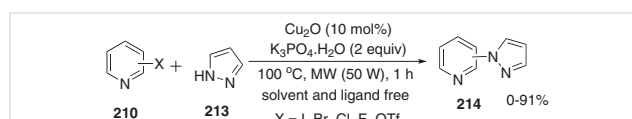


**Scheme 71** Cu-catalyzed *O*-arylation of arenesulfonamides<sup>188</sup>

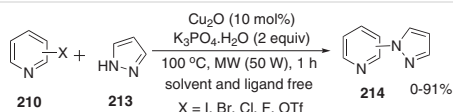
Recently, the Wang group<sup>189</sup> investigated the cross-dehydrogenative coupling (CDC) reaction between the C(sp<sup>3</sup>)–H bond and the hydroxyl group of phenol substrates (Scheme 72).



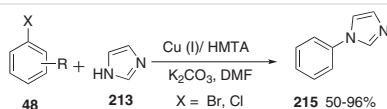
**Scheme 72** Cu-catalyzed cross-dehydrogenative coupling (CDC) reaction<sup>189</sup>



**Scheme 73** Cu-catalyzed N-arylation of nitrogen-containing heterocycles<sup>190</sup>



**Scheme 74** MW-promoted Cu-catalyzed amination of halopyridines<sup>191</sup>



**Scheme 75** Cu(I)/HMTA-catalyzed C–N cross-coupling of imidazole and aryl halides<sup>192</sup>

### 4.3 C–N Cross-Coupling Reaction

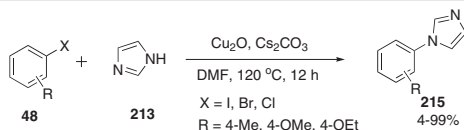
In 2010, the Li group<sup>190</sup> developed a simple Cu-catalyzed method for N-arylations of nitrogen-containing heterocycles and aliphatic amines in water as a solvent and (1*E*,2*E*)-oxalaldehyde dioxime (**211**) as a ligand at 100 °C (Scheme 73).

In 2011, Liu and co-workers<sup>191</sup> described a microwave-promoted solvent- and ligand-free Cu-catalyzed amination of several halopyridines **210** with various nitrogen nucleophiles **213**, giving corresponding N-heteroarylated products **214** in good yields (Scheme 74).

In 2012, Cao and co-workers<sup>192</sup> reported an efficient C–N cross-coupling reaction that allowed the coupling of imidazole (**213**) with aryl chlorides or bromides by employing



**Scheme 76** Cu-catalyzed direct oxidative C–N coupling reaction<sup>193</sup>



**Scheme 77** Cu-catalyzed Ullmann-type N-arylation<sup>195</sup>

an inexpensive catalytic system Cu(I)/HMTA, providing products in moderate to good yields. Moreover, the presence of electron-withdrawing or electron-donating groups in the aryl halides had no adverse effect on the outcome of the reaction (Scheme 75).

In 2015, Sagadevan and co-workers<sup>193</sup> reported a copper(I) chloride catalyzed green process for direct oxidative C<sub>sp</sub>–N coupling reactions of anilines and alkynes affording biologically important  $\alpha$ -ketoamides **217** under visible-light irradiation at room temperature without the need for a base, ligands, or an external oxidant (Scheme 76).

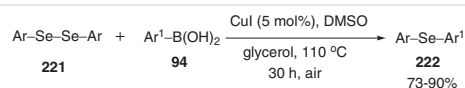
In 2017, Wang et al.<sup>194</sup> established a new Cu-catalyzed ligand-free method for Ullmann-type N-arylation of N-containing heterocycles **213** with aryl **48** or heteroaryl bromides or iodides without the protection of an inert gas, affording the desired products with high reaction yields (Scheme 77). In 2021, Bai et al.<sup>195</sup> reported a simple strategy for the C–N cross-coupling of indazole with a modification of substituted aryl bromides under ligand-free conditions.

### 4.4 C–P Cross-Coupling Reaction

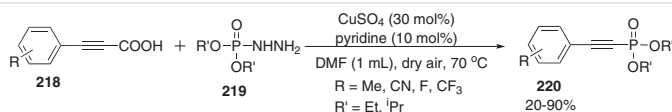
In 2016, the first attractive synthetic tool was provided by the Chen research group<sup>196</sup> for the synthesis of valuable alkynylphosphonates **220**, which involved Cu-catalyzed decarboxylative coupling of various arylpropionic acids **218** with readily available dialkyl hydrazinylphosphonates **219** giving up to 90% yield (Scheme 78).

### 4.5 C–Se Cross-Coupling Reaction

In 2012, Ricordi and co-workers<sup>197</sup> described the Cu-catalyzed cross-coupling reaction of diaryl diselenides **221** including arylboronic acids with CuI and DMSO as additive and glycerol as a recyclable solvent, affording the corresponding diaryl selenides **222** in high reaction yields (Scheme 79). The reaction was performed under an open atmosphere at 110 °C.



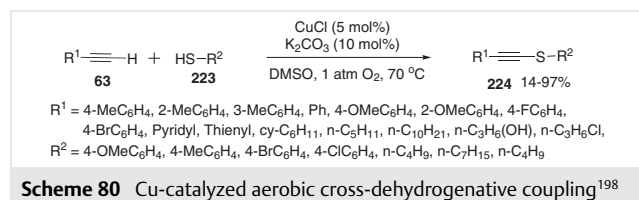
**Scheme 79** Cu-catalyzed cross-coupling reaction of diaryl diselenides<sup>197</sup>



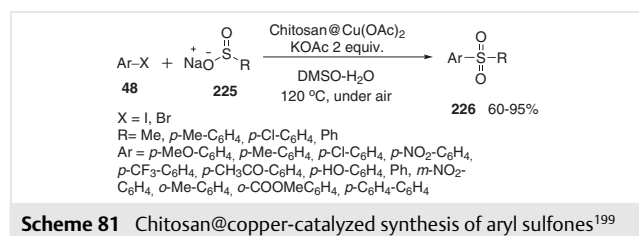
**Scheme 78** Cu-catalyzed decarboxylative coupling reaction<sup>196</sup>

## 4.6 C–S Cross-Coupling Reaction

In 2013, Yang et al.<sup>198</sup> demonstrated a Cu-catalyzed aerobic cross-dehydrogenative coupling reaction for the synthesis of alkynyl sulfides **224** from terminal alkynes with thiols using K<sub>2</sub>CO<sub>3</sub> and molecular O<sub>2</sub> as the oxidant under mild reaction conditions (Scheme 80).

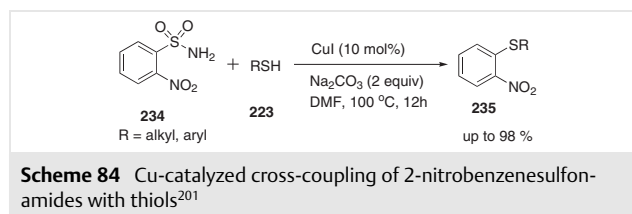
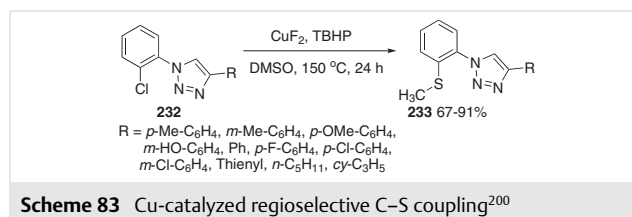


In 2014, Shen and co-workers<sup>199</sup> utilized chitosan@copper as a recoverable catalyst for the synthesis of aryl sulfones **226** from aryl halide and sodium sulfinates through cross-coupling reactions with high reaction yields (Scheme 81). Interestingly, the antiulcer drug zolimidine (**231**) could easily be synthesized by employing this protocol (Scheme 82).

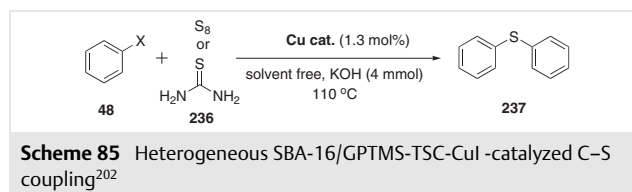


In 2018, Yu and co-workers<sup>200</sup> demonstrated the regioselective C–S coupling of 1,4-disubstituted 1,2,3-triazole halides (**232**) mediated by CuF<sub>2</sub> using DMSO as a methylthiolation source, in which the *ortho*-C–X bond in the N(1) aryl group was selectively cross-coupled without affecting other C–X bonds (Scheme 83).

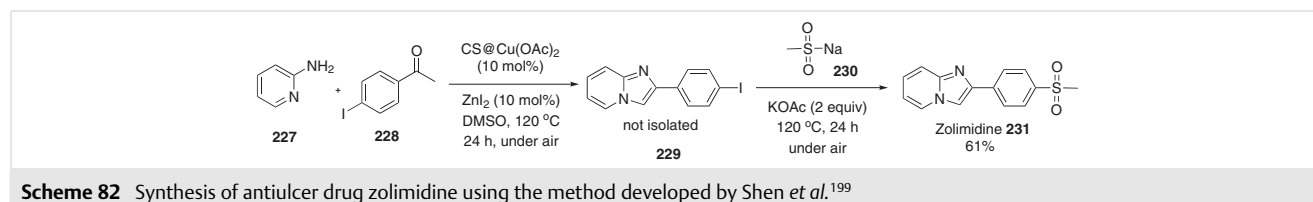
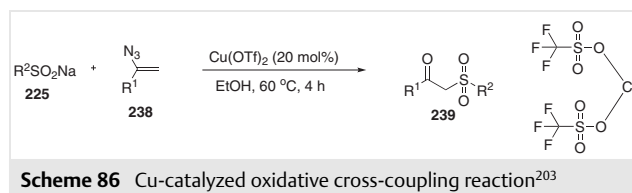
Chen et al.<sup>201</sup> presented a novel Cu(I)-catalyzed method for the cross-coupling of 2-nitro benzenesulfonamides (**234**) with thiols generating unsymmetrical sulfides (**235**) in high to excellent yields by using CuI in DMF as solvent at 100 °C (Scheme 84). This method offered **234** as a new coupling partner for the first time and occurred through cleavage of the Ar–SO<sub>2</sub>NH<sub>2</sub> bond without cleavage of the C–NO<sub>2</sub> bond.

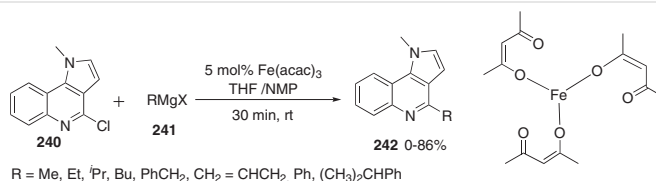


In 2019, Ghodsinia and co-workers<sup>202</sup> synthesized a recyclable heterogeneous SBA-16/GPTMS-TSC-CuI catalytic system in which CuI was anchored onto a mesoporous material (SBA-16) functionalized by aminated 3-glycidyloxypropyltrimethoxysilane (GPTMS) with thiosemicarbazide (TSC). This novel mesostructured catalyst was investigated for the C–S coupling products of aryl halides with S8/thiourea under solvent-free conditions in high reaction yields (Scheme 85). The reaction was performed in notably reduced reaction times in comparison to the earlier reports.



In 2021, the Ning group<sup>203</sup> developed an oxidative cross-coupling reaction between sodium sulfinates **225** and vinyl azides **238** to form β-ketosulfones **239** (Scheme 86).





**Scheme 87** Fe-catalyzed Kumada cross-coupling of 4-chloropyrrolo[3,2-*c*]quinoline<sup>204</sup>

## 5 Fe-Catalyzed Reactions

We will discuss in this section the use of iron catalysis in various cross-coupling reactions and is generally presented in chronological order.

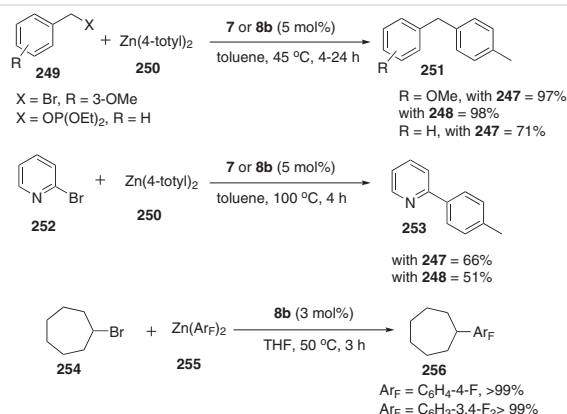
### 5.1 C–C Cross-Coupling Reaction

In 2009, Colacino and co-workers<sup>204</sup> developed Fe-catalyzed cross-coupling reaction of 4-chloropyrrolo[3,2-*c*]quinoline (**240**) with aryl or alkyl magnesium halides in the presence of Fe(acac)<sub>3</sub> (Scheme 87). The reaction was performed in a mixture of THF and NMP in just 30 min. The coupled products are useful scaffolds for medicinal chemistry and were obtained moderate to excellent yields of 52–94%.

In 2012, Liu et al.<sup>205</sup> discovered a Fe-catalyzed arylation of benzoazoles **243** with aromatic aldehydes with oxygen as an oxidant in good to excellent yields under base-free conditions (Scheme 88). The reaction was achieved by using a mixture of water/diglyme instead of organic solvents and better yields were obtained when benzothiazoles were employed as substrates.

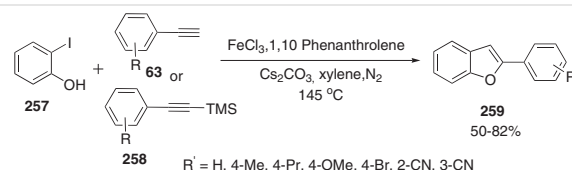
Adams and co-workers<sup>206</sup> demonstrated the synthesis of Fe(I) complexes, [FeX<sub>2</sub>(dpbz)<sub>2</sub>] [X = 4-tolyl, Cl, Br, dpbz = 1,2-bis(diphenylphosphino)benzene] (Scheme 89) and in-

vestigated their catalytic efficiency in Negishi cross-coupling reactions with arylzinc reagents (Scheme 90).

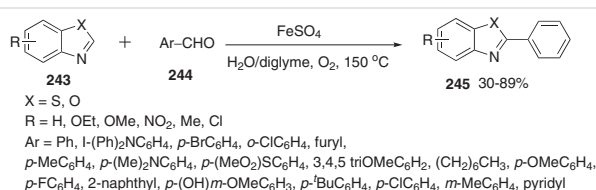


**Scheme 90** Fe(I) complex-catalyzed Negishi cross-coupling reactions<sup>206</sup>

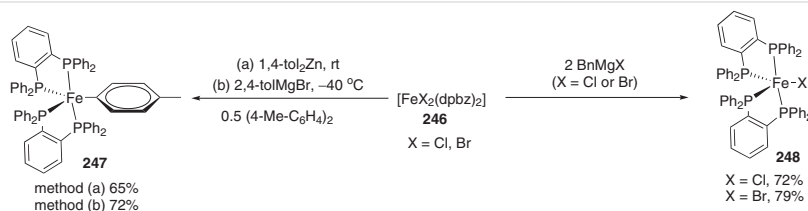
In 2013, Yang and co-workers<sup>207</sup> discovered a Fe-catalyzed method to achieve both the intramolecular O-arylation of *o*-iodophenols and Sonogashira cross-coupling and aryl acetylenes/1-substituted-2-trimethylsilyl acetylenes to afford the corresponding 2-arylbenzo[*b*]furans (**259**) in good reaction yields (Scheme 91). The procedure utilized 5% FeCl<sub>3</sub> and 10% 1,10-phenanthroline as a catalytic system.



**Scheme 91** Fe-catalyzed Sonogashira cross-coupling and intramolecular O-arylation<sup>207</sup>

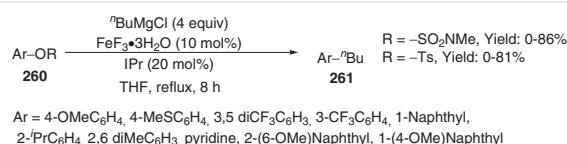


**Scheme 88** Fe-catalyzed arylation of benzoazoles<sup>205</sup>



**Scheme 89** Synthesis of Fe(I) complexes [FeX-(dpbz)<sub>2</sub>]<sup>206</sup>

Agrawal et al.<sup>208</sup> achieved the Fe-catalyzed cross-coupling of alkyl Grignard reagents using aryl sulfamates or tosylates **260** in quantitative yields (Scheme 92).

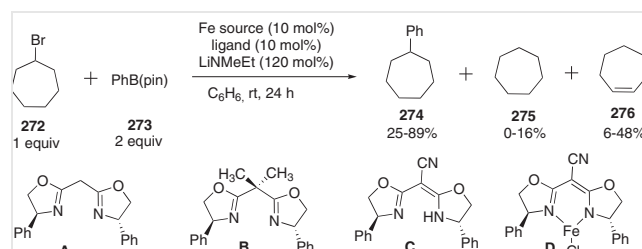


**Scheme 92** Fe-catalyzed cross-coupling of aryl sulfamates or tosylates with alkyl Grignard reagents<sup>208</sup>

Hajipour and co-workers<sup>209</sup> prepared heterogeneous Fe-based catalyst supported on acac-functionalized silica, which was employed as a catalyst in Mizoroki–Heck reaction of aryl iodides and olefins in poly(ethylene glycol) as a green solvent (Scheme 93). Interestingly, this protocol allowed selective coupling reaction of aryl iodides in the presence of bromides. The catalyst could be recovered well from the reaction mixture and recycled up to five times.

In 2017, Bisz and co-workers<sup>210</sup> reported that benign cyclic ureas (DMI, DMPU) are efficient and sustainable ligands instead of hazardous NMP in Fe-catalyzed alkylations of aryl chlorides or tosylates with alkyl Grignard reagents (Scheme 94 and Scheme 95). Moreover, this protocol allowed C(sp<sup>2</sup>)–C(sp<sup>3</sup>) cross-coupling synthesis of a dual NK1/serotonin receptor antagonist.

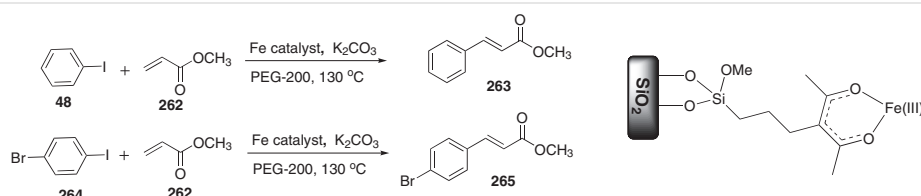
In 2018, Crockett and co-workers<sup>211</sup> discovered a Fe-catalyzed cross-coupling reaction between alkyl halides and arylboronic esters by employing lithium amide bases coupled with Fe complexes containing deprotonated cyano-bis(oxazoline) ligands (A–D) affording up to 89% yields of the coupled products (Scheme 96). Remarkably, the reaction required neither alkyllithium reagents for activation of the boronic ester nor magnesium additives. Moreover, the two-step synthesis of pharmaceutically important Cinacalcet (**281**) was shown by using this protocol (Scheme 97).



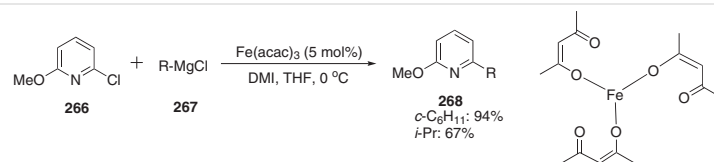
**Scheme 96** Fe-catalyzed cross-coupling reaction between alkyl halides and arylboronic esters<sup>211</sup>

## 5.2 C–S Cross-Coupling Reaction

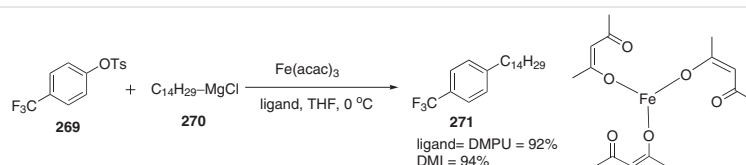
In their study In 2009, Wu and co-workers<sup>212</sup> developed a catalytic system that is greener and used reusable of Fe-Cl<sub>3</sub>·6H<sub>2</sub>O/cationic 2,2'-bipyridyl for the coupling of aryl iodides with thiols to make C–S bond in refluxed water under aerobic conditions (Scheme 98).



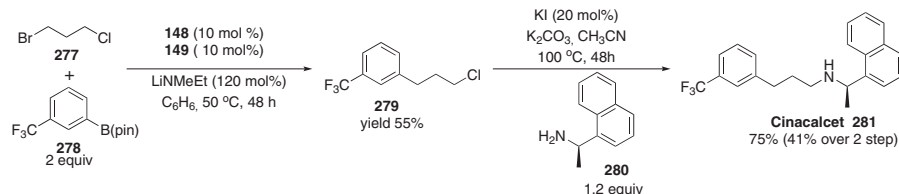
**Scheme 93** Fe-catalyzed selective coupling reaction of aryl iodides<sup>209</sup>



**Scheme 94** Fe-catalyzed alkylation of aryl chlorides<sup>210</sup>



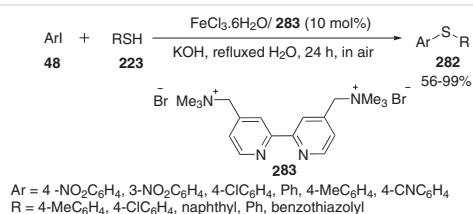
**Scheme 95** Fe-catalyzed alkylation of aryl tosylates<sup>210</sup>



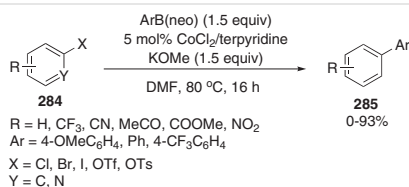
**Scheme 97** Fe-catalyzed synthesis of pharmaceutical compound Cinacalcet<sup>211</sup>

## 6 Co-Catalyzed Reactions

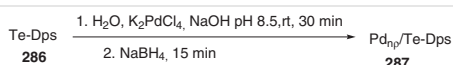
We will discuss in this section the use of cobalt catalysis in various cross-coupling reactions and is generally presented in chronological order.



**Scheme 98** FeCl<sub>3</sub>·6H<sub>2</sub>O/cationic 2,2'-bipyridyl catalytic system for C-S cross-coupling<sup>212</sup>



**Scheme 99** Cobalt(II)/terpyridine-catalyzed SM cross-coupling reaction<sup>213</sup>



**Scheme 100** Synthesis of Pd nanoparticles stabilized within the protein cavity of Dps protein<sup>214</sup>

In 2017, Duong and co-workers<sup>213</sup> described a Co-catalyzed Suzuki–Miyaura cross-coupling reaction of aryl halides and arylboronic esters by employing cobalt(II)/terpyridine catalyst and KOMe, generating the corresponding (hetero)biaryls in moderate to excellent yields (Scheme 99). This procedure tolerated the  $\pi$ -electron-rich and  $\pi$ -electron-deficient heteroaryl halides and electron-deficient aryl halides.

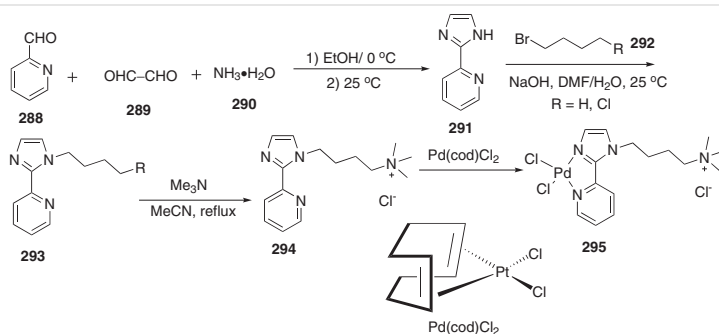
## 7 Transition-Metal Nanoparticle-Promoted Reactions

We will discuss in this section the use of nanoparticle catalysis in various cross-coupling reactions and is generally presented in chronological order.

### 7.1 Pd Nanoparticles

In 2009, Prastaro and co-workers<sup>214</sup> prepared a precatalyst consisting of Pd nanoparticles stabilized within the protein cavity of Dps protein (PdnP/Te-Dps) (**287**) and tested its catalytic ability for Suzuki–Miyaura cross-coupling reactions under phosphine-free, aerobic conditions in water (Scheme 100).

Based on the well-known fact that bacteria can recover Pd(0) in the form of nanoparticles, Søbberg and co-workers<sup>215</sup> decided to investigate the scope of the reactions that could be catalyzed by bio-recovered palladium. They demonstrated that the Mizoroki–Heck and Suzuki–Miyaura reactions were catalyzed by bio-Pd(0) nanoparticles set up



**Scheme 101** Synthesis of water-soluble ammonium-functionalized bidentate nitrogen-containing ligand and its Pd chelating complex<sup>216</sup>



on the surface of Gram-negative bacteria such as *C. necator* and *P. putida*. In 2011, Zhou and co-workers<sup>216</sup> synthesized a water-soluble ammonium-functionalized bidentate nitrogen-containing ligand (**294**) and its Pd chelating complex (**295**) and utilized this for Suzuki–Miyaura cross-coupling reaction in neat water under aerobic conditions (Scheme 101).

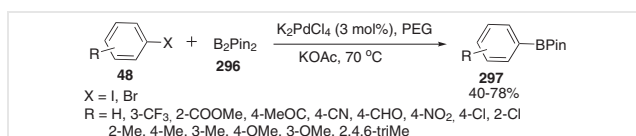
Khalafi-Nezhad and co-workers<sup>217</sup> published a report on the synthesis of a recyclable heterogeneous catalyst system in which they managed to immobilize Pd NPs on a silica-starch substrate (PNP-SSS) and found an effective catalyst in

Heck and copper-free Sonogashira reactions with water as an eco-friendly solvent. The silica-starch substrate effectively stabilized and provided a platform to Pd NPs and prevented their aggregation and separation from the SSS surface. In 2012, Bej and co-workers<sup>218</sup> generated Pd nanoparticles in PEG that catalyzed the reaction of aryl/benzyl halides with bis(pinacolato)diboron to furnish aryl/benzyl boronates in high yield, which, in turn, were used as a reaction partner in the solvent- and ligand-free Suzuki–Miyaura coupling reaction with different aryl/benzyl halides in 53–72% yield (Scheme 102).

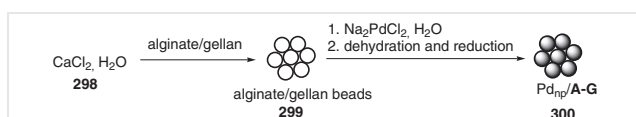
Cacchi and co-workers<sup>219</sup> made Pd nanoparticles stabilized by natural beads of an alginate/gellan mixture for the phosphine- and base-free Suzuki–Miyaura cross-coupling reaction of potassium aryltrifluoroborates and arenediazonium tetrafluoroborates in 1:1 molar ratio with catalyst loading of just 0.01–0.002 mol% under aerobic conditions in water (Scheme 103, Scheme 104).

In 2014, Huang and co-workers<sup>220</sup> reported a synthetic procedure of Pd nanocomposite by depositing palladium nanoparticles in the micropores of the SBA-15 with hydrophobic triphenylsilyl or trimethylsilyl groups grafted on the mesopores. The authors then allowed ligand-free Miyama cross-couplings of aryl halides and various aryltriethoxysilanes at 100 °C in air. Puthiaraja and co-workers<sup>221</sup> synthesized a novel nitrogen-rich functional mesoporous covalent organic polymer (MCOP), which offered excellent support for Pd nanoparticles (Pd@MCOP) by nucleophilic substitution reaction of cyanuric chloride (**304**) and 4,4'-dihydroxybiphenyl (**305**) (Scheme 105).

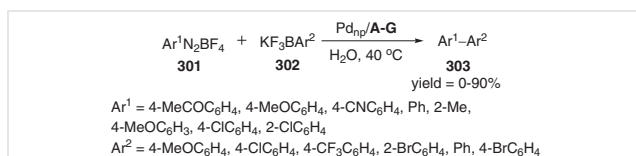
In 2015, Mandegani and co-workers<sup>222</sup> developed the synthesis of a novel nano tetraamine Pd(0) complex (**310**) with the complexation of Pd(OAc)<sub>2</sub> with *N,N*-bisimine li-



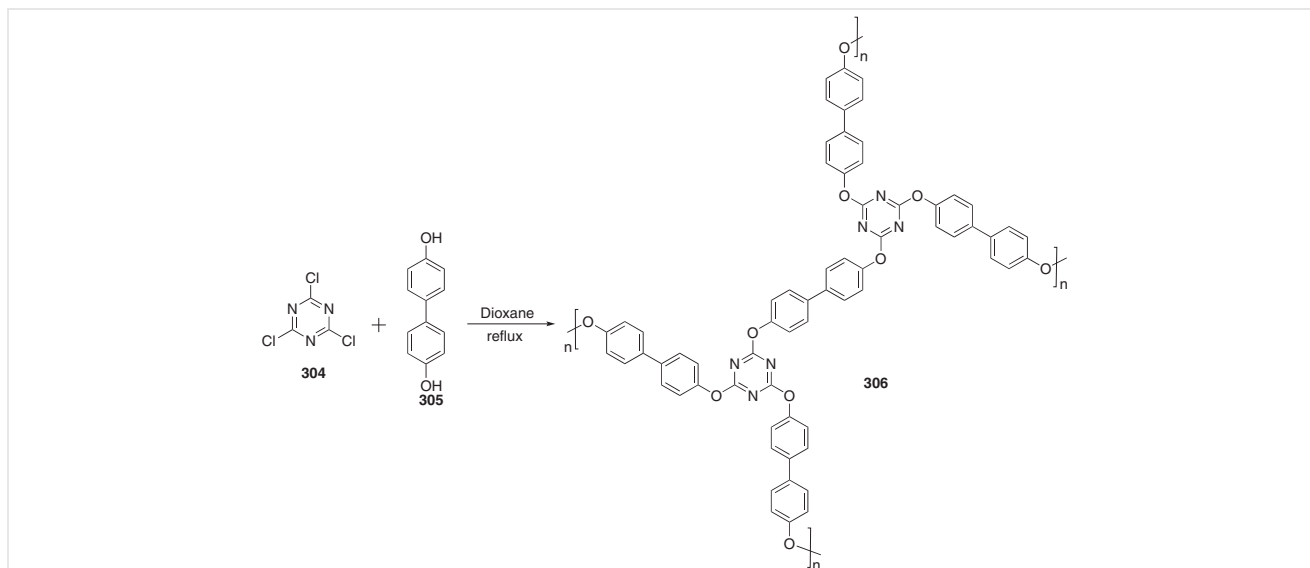
**Scheme 102** Synthesis of aryl boronates<sup>218</sup>



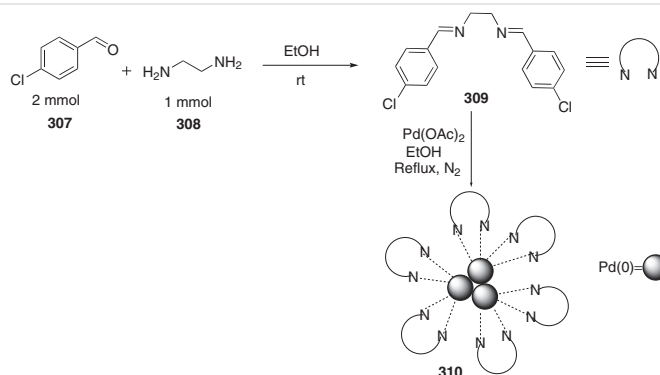
**Scheme 103** Synthesis of Pd nanoparticles stabilized by natural beads of alginate/gellan mixture<sup>219</sup>



**Scheme 104** Pdnp/A-G mediated Suzuki–Miyaura cross-coupling reaction<sup>219</sup>



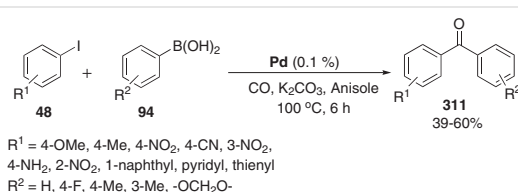
**Scheme 105** Synthesis of functional mesoporous covalent organic polymer (MCOP)<sup>221</sup>



**Scheme 106** Synthesis of a novel nano tetraimine Pd(0) complex<sup>222</sup>

gand (**309**) (Scheme 106). The catalytic efficiency of this heterogeneous nano-complex was investigated towards the Heck–Mizoroki reaction in water. The catalyst could be reusable and recycled without loss in catalytic activity.

In 2016, Gautam and co-workers<sup>223</sup> investigated the efficiency of PdNPs supported on fibrous nanosilica (KCC-1) towards carbonylative Suzuki–Miyaura cross-coupling reaction with a low Pd loading of 0.1% (Scheme 107). This KCC-1-PEI/Pd catalytic system displayed a TON 28-times and TOF 51-times bigger than already reported supported Pd catalyst in the literature for this reaction, probably owing to the fibrous nature of the KCC-1 support and because the PEI functionalization enhanced the stability.



**Scheme 107** PdNPs/KCC-1 mediated carbonylative SM cross-coupling reaction<sup>223</sup>

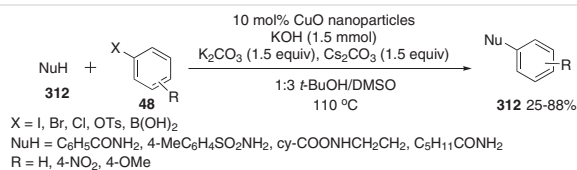
In 2019, Yamada and co-workers<sup>224</sup> investigated the effect of a co-existing metal in the ligand-free Suzuki–Miyaura coupling reaction of an aryl chloride under continuous irradiation microwave and a PdNPs catalyst (SGIPd), and established that the co-existing metal such as aluminum foil is involved in this reaction due to its microwave absorption ability in the reaction system. Mohazzab and co-workers<sup>225</sup> synthesized reusable mesh-GO/Pd catalyst by immobilization of Pd NPs on stainless-steel mesh. Dhara and co-workers<sup>226</sup> prepared glucose-stabilized palladium nanoparticles with recycling and reusing capability up to four times and explored its catalytic potential for both Suzuki and Heck reactions in aqueous medium supported by microwave irra-

diation. This procedure allowed the coupling of various electron-rich and electron-deficient aryl halides in high reaction yields.

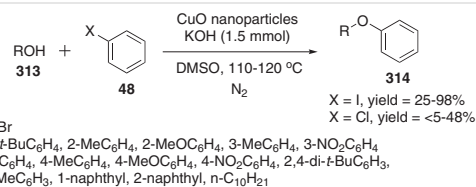
Blanco and co-workers<sup>227</sup> impregnated graphene acid (GA) with Pd(OAc)<sub>2</sub> yielding GA-Pd nanohybrids with a size ranging from 1 nm up to 9 nm and applied the material in the Suzuki–Miyaura cross-coupling reaction.

## 7.2 Cu Nanoparticles

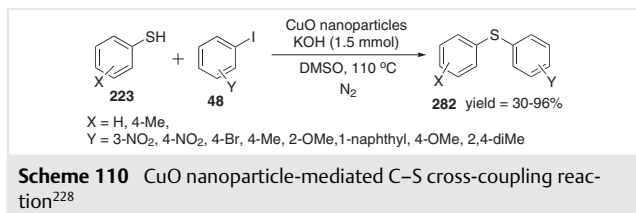
In 2009, Jammi and co-workers<sup>228</sup> studied the catalytic behavior of CuO nanoparticles for C–S, C–O, and C–N bond formations through ligand-free cross-coupling reactions of different nucleophiles such as imidazoles, amides, amines, alcohols, thiols, and phenols with aryl halides by using a base (i.e., KOH, K<sub>2</sub>CO<sub>3</sub>, and Cs<sub>2</sub>CO<sub>3</sub>) at moderate temperature to afford the cross-coupled products in high yield (Scheme 108, Scheme 109, and Scheme 110).



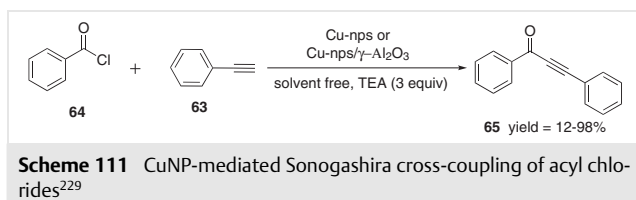
**Scheme 108** CuO nanoparticle-mediated C–N cross-coupling reaction<sup>228</sup>



**Scheme 109** CuO nanoparticle-mediated C–O cross-coupling reaction<sup>228</sup>



In 2013, Sun and co-workers<sup>229</sup> utilized supported copper NPs for the first time in Pd-, ligand-, and solvent-free coupling reactions of acyl chlorides with terminal alkynes to generate corresponding ynones in 12–98% yield (Scheme 111).

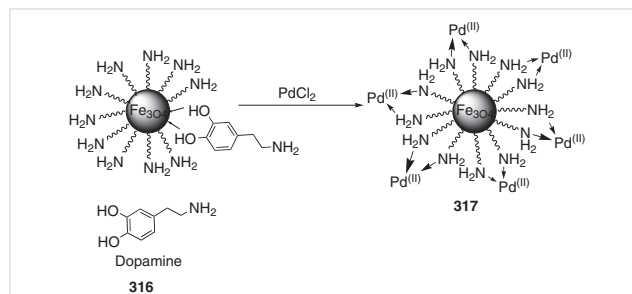


In 2017, a similar report for the synthesis of ynones via solvent-free Sonogashira reactions was disclosed by Wang and co-workers<sup>230</sup> by employing mesoporous phenol-formaldehyde resin-supported copper nanoparticles catalyst (Cu NPs@MP) having wide surface areas and narrow pore-size distributions. The catalyst was synthesized by the melt infiltration of copper nitrate hydrates and subsequent *in-situ* reduction of Cu(II) by template pyrolysis. This catalyst displayed higher catalytic efficiency than copper powder and mesoporous silica SBA-15-supported Cu NPs.

## 8 Miscellaneous Reactions

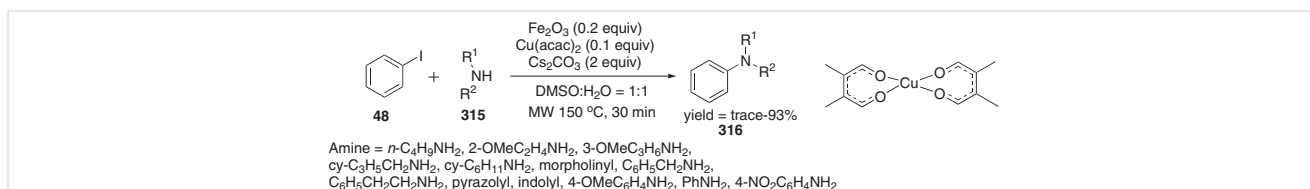
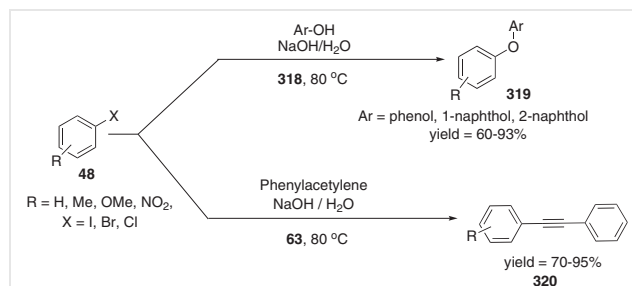
In 2010, Guo and co-workers<sup>231</sup> reported a ligand-free iron/copper co-catalyzed amination of aryl halides affording the corresponding products under microwave irradiation in good yields (Scheme 112).

In 2012, Vaddula and co-workers<sup>232</sup> discovered a magnetically recoverable heterogenized Pd catalyst (**317**) for the Heck-type arylation of alkenes with diaryliodonium salts in aqueous polyethylene glycol using ultrasonication within 1–5 min (Scheme 113). The protocol was equally well suited for unactivated alkenes such as styrene, allyl alcohol, and allyl acetate.

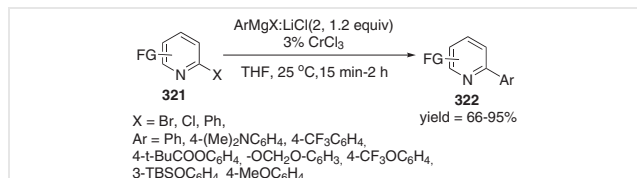


In 2013, Al-Amin and co-workers<sup>233</sup> utilized sulfur-modified gold-supported palladium material (SAPd) and two categories of microwave approaches, single- and multi-mode in conjunction with Suzuki–Miyaura cross-coupling reactions. The catalyst had very low leaching properties. In 2017, Akiyama and co-workers<sup>234</sup> described novel sulfur modified gold-supported ruthenium nanoparticles (SARu) via a three-step process involving immobilization of ruthenium using Ru(acac)<sub>3</sub> and 4-methoxybenzyl alcohol as a reductant via *in-situ* metal nanoparticle and nano space organization without requiring any preformed template to immobilize and stabilize metal nanoparticles. The catalyst was evaluated for ligand-free Suzuki–Miyaura coupling of arylboronic acids and aryl halides including aryl chlorides with low Ru leaching. In 2013, Zolfigol and co-workers<sup>235</sup> prepared a stable magnetically divisible Pd nanocatalyst [Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PPh<sub>2</sub>@Pd(0)] and explored in Sonogashira cross-coupling reactions and O-arylation of phenols using NaOH as a base in water (Scheme 114).

Steib and co-workers<sup>236</sup> disclosed ligand-free Cr-catalyzed cross-couplings of *N*-heterocyclic halides, alkenyl io-



dides, aromatic halogenated ketones, or imines with various (hetero)arylmagnesium reagents by employing 3% of chromium(II) chloride at 25 °C (Scheme 115). This method produces lower amounts of homo-coupled products in comparison to the corresponding manganese, iron, or cobalt cross-couplings.



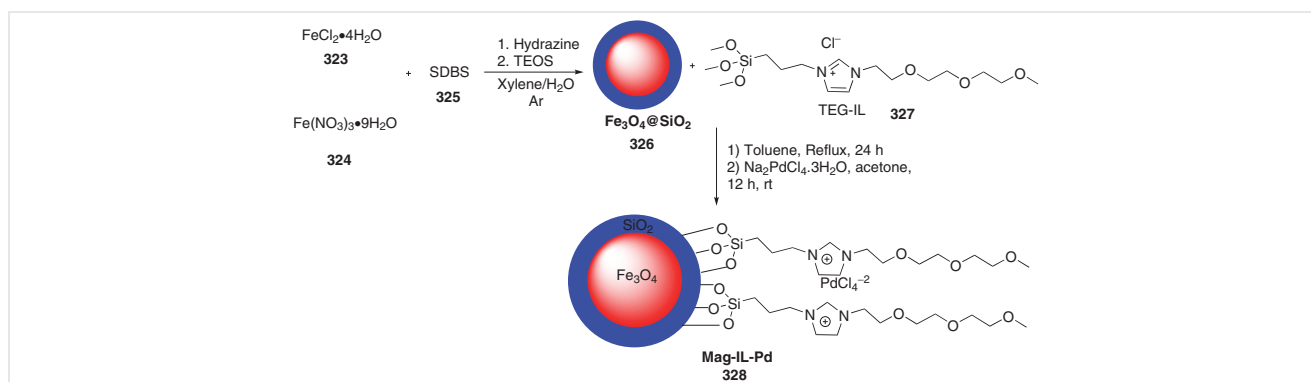
**Scheme 115** Cr-catalyzed cross-couplings of *N*-heterocyclic halides<sup>236</sup>

In 2014, Karimi and co-workers<sup>237</sup> prepared a novel magnetically recoverable Pd catalyst (Mag-IL-Pd) (**328**) by anchoring an imidazolium ionic liquid in front of triethylene glycol motifs on the surface of silica-coated iron oxide nanoparticles (Scheme 116). This nanocomposite exhibited notable activity for the Suzuki–Miyaura coupling reaction in water. The protocol allowed the coupling of challenging substrates such as heteroaryl/*ortho*-substituted aryl halides and aryl chlorides efficiently in excellent yields.

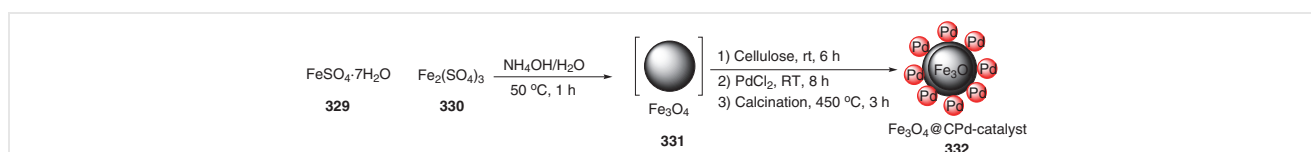
Baig and co-workers<sup>238</sup> synthesized a magnetically recoverable carbon-supported Pd catalyst (**332**) via *in-situ* generation of nano ferrites and fusion of carbon from naturally abundant biopolymer cellulose via calcinations (Scheme 117). The catalytic efficiency of this catalyst was investigated for various reactions such as oxidation of alcohols, arylation of aryl halides, and amination reactions.

In 2016, Rathi and co-workers<sup>239</sup> prepared a nanocatalyst made up of ultra-small Pd/PdO nanoparticles supported on maghemite via co-precipitation using inexpensive raw materials and was employed efficiently in various cross-coupling reactions such as Suzuki and Heck–Mizoroki reaction and the allylic oxidation of alkenes. In 2017, Mohammadinezhad and co-workers<sup>240</sup> reported the synthesis of a heterogeneous magnetically separable core-shell-like Fe<sub>3</sub>O<sub>4</sub>@Boehmite–NH<sub>2</sub>–CoII NPs (**342**) of 13–54 nm size as an eco-friendly catalyst and explored its catalytic efficiency for the Suzuki and Heck cross-coupling reactions in water (Scheme 118). Moreover, the catalyst can be reused at least seven times without a significant and decrease in the catalytic activity.

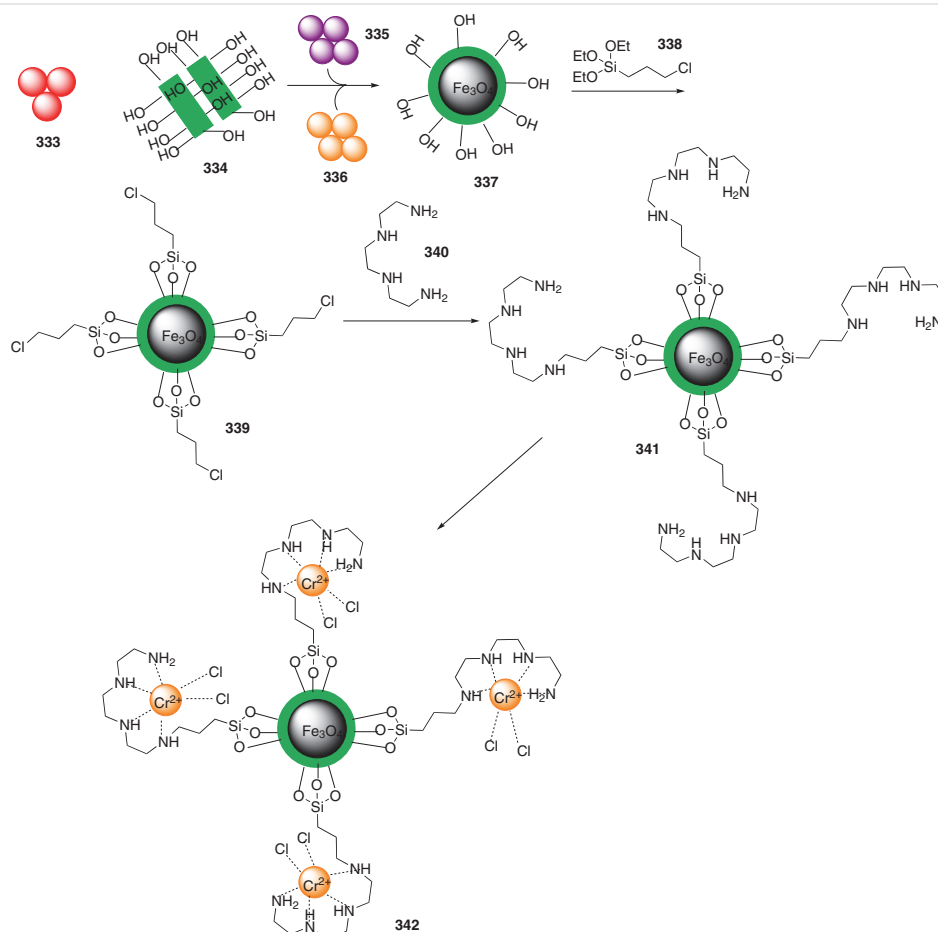
In 2018, Kaur and co-workers<sup>241</sup> presented a green catalytic approach involving zero-valent Pd–Ni alloy NPs using microwaves as an energy source and ethanol/water as a solvent system. Metallosurfactants were synthesized that capped the Pd–Ni alloy NPs. The synthesized NPs exhibited catalytic efficiency for the Heck coupling reaction. The main attributes of the protocol include short reaction time, wide substrate scope, mild reaction conditions, avoiding the use of toxic organic solvents, and reusability of the catalyst. In 2019, Kazemnejadi and co-workers<sup>242</sup> prepared a magnetically recoverable, heterogeneous Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Im[Cl]Co(III)–melamine nanocomposite and investigated its efficiency for Sonogashira and Heck cross-coupling reactions. The coupling reaction was phosphine-, base-, and ligand-free, used ethanol as solvent and proceeded with high to excellent yields.



**Scheme 116** Synthesis of Pd catalyst (Mag-IL-Pd)<sup>237</sup>



**Scheme 117** Synthesis of carbon-supported Pd catalyst<sup>238</sup>



**Scheme 118** Synthesis of  $\text{Fe}_3\text{O}_4\text{@Boehmite-NH}_2\text{-Coll NPs}$ <sup>240</sup>

## 9 Perspectives and Future Directions

This review included information and examples of an impressive and appealing range of past and recent developments of the various approaches to transition-metal-catalyzed cross-coupling reactions such as Suzuki, Heck, Sonogashira, Stille, Kumada, Kochi, Murahashi, Corriu, Hiyama, and Negishi reactions, as well as decarboxylative, carbonylative, and  $\alpha$ -arylation, C–O, C–N, C–S bond-forming reactions for the synthesis of natural products and agrochemicals. The past more than 45 years have seen continuous growth in cross-coupling protocols, and plenty of new tools for cross-coupling have been reported by researchers. In the last twelve years especially, we have observed an explosive development of this chemistry. Modern synthetic organic chemistry has seen a marvelous advancement after the dawn of Pd and later by other transition metals (copper, iron, nickel, cobalt or Zr) catalyzed cross-coupling reactions for C–C and C–heteroatom bond formation. As reflected in this chapter, copper, in some cases, can replace the more traditional palladium systems because of some obvious rea-

sons of being cheaper, readily available, and more efficient, using mild reaction conditions, offering high functional group tolerance, and involving less toxic oxygen or nitrogen ligands for selective C–O or C–N bond formation. Similarly, Ni has proved to be an amazingly versatile catalyst for such transformations in large-scale processes compared to the corresponding palladium catalysts, because of its lower cost, greater reactivity toward halocarbon electrophiles such as C–Cl and even inert C–F bonds, C–O-derived electrophiles such as less reactive mesylates and tosylates, phosphates, sulfamates, carbamates, phosphoramides, carbonates, certain esters, activated ethers, and phenols. Apart from the several interesting reports mentioned in this chapter, the field of cobalt and iron-catalyzed cross-coupling reactions is still immature. Since the renaissance of the field of iron-catalyzed cross-coupling in the early 2000s the metal has presented itself as a useful alternative to palladium-catalyzed cross-coupling reactions despite the significant challenges. Finally, it is expected that the recently developed early-transition-metal-catalyzed cross-coupling reactions will serve as an impetus for chemists to address



longstanding challenges in this field in the forthcoming years to enlarge the armory of tools available to them. Hence, the profound interest in early-transition-metals Cu, Ni, Fe, Zr in cross-coupling reactions for C–C and C–heteroatom bond formation and the significant collaborations between organic and inorganic chemists have emerged only in recent years and it will be exciting to see its full potential unlocked soon.

## Conflict of Interest

The authors declare no conflict of interest.

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