Chapter 5
Carbonylative Sonogashira Reactions

The Sonogashira reaction is generally known as a coupling reaction of terminal alkynes with aryl or vinyl halides. This reaction was first reported by Sonogashira and Hagihara in 1975 (Scheme 5.1) [1]. Today the Sonogashira coupling reaction is one of most powerful processes for C–C bond formation, especially for the synthesis of substituted alkynes [2–4]. From the reaction mechanism aspect, a transmetalation step was included between the palladium center and the in situ-formed organocopper intermediate.

If the Sonogashira reaction is carried out in a CO atmosphere, the reactions are called Carbonylative Sonogashira Reactions, which will give alkynone as an interesting structural motif found in numerous biologically active molecules [5–7]. Notably, this class of compounds plays a crucial role in the synthesis of natural products [8–12] and as key intermediates for the efficient formation of several heterocycles [13–15]. Traditionally, alkynones have been synthesized by transition metal catalyzed cross-coupling reactions of acid chlorides and terminal alkynes (Scheme 5.2) [16–24]. However, the stability of the respective acid chlorides is limited and a lack of functional tolerance is another problem of this methodology. Without a doubt, carbonylative Sonogashira coupling of corresponding terminal alkynes and aryl halides represents the most straightforward way to set up alkynones.

The first palladium-catalyzed carbonylative Sonogashira coupling was reported in 1981 by Kobayashi and Tanaka [25]. Aryl, heterocyclic, and vinylic halides reacted with CO and terminal acetylenes at 120 °C and 80 bar in the presence of NEt_3 and a catalytic amount of a palladium(II) complex to form alkynones in a 46–93 % yield (Scheme 5.3). Remarkably, aryl bromides and aliphatic alkynes were also included in the range of substrates. But NEt_3 was used as a solvent for this transformation and a relatively high pressure of CO was needed.

Interestingly, in 1991 Alper and Huang described another type of palladium-catalyzed carbonylative Sonogashira coupling of aryl iodides with benzyl acetylenes. Here, furanones were isolated as the terminal products and not the predicted alkynones [26]. In the presence of $Pd(OAc)_2/PPh_3$, aryl iodides and benzyl acetylenes were transformed into furanones in 33–88 % yields (Scheme 5.4). Palladium-catalyzed carbonylative Sonogashira coupling reactions of iodobenzene and

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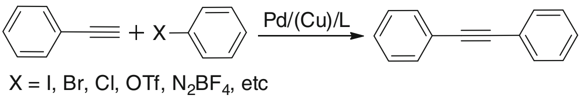
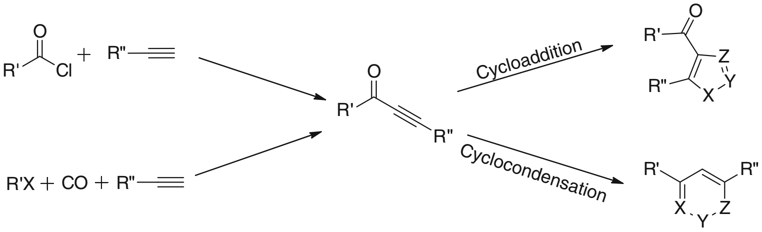
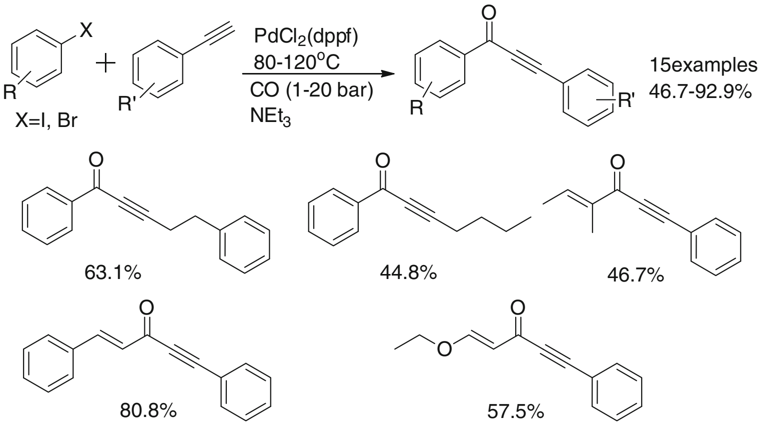


Scheme 5.1 Palladium-catalyzed Sonogashira coupling reaction



Scheme 5.2 Selected synthesis and applications of alkynones

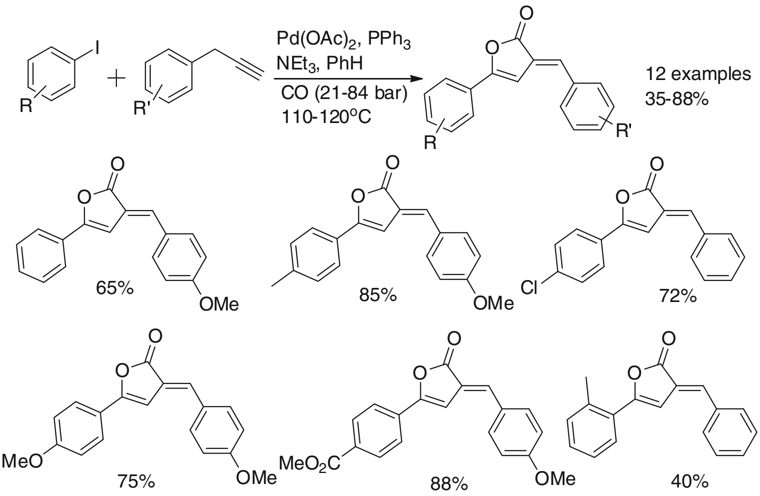


Scheme 5.3 First Pd-catalyzed carbonylative Sonogashira coupling of organic halides

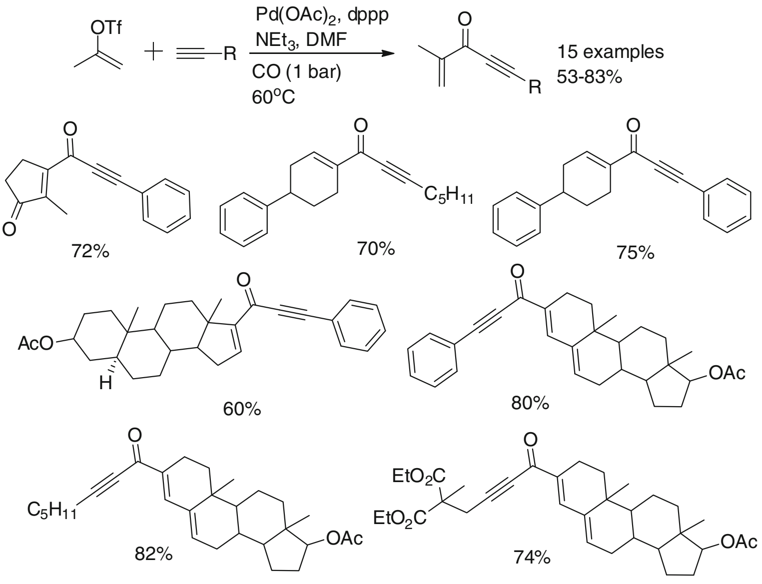
2-methyl-3-butyn-2-ol under biphasic conditions to furanones were also described by Kiji and colleagues [27].

In 1991 Ortar and colleagues published a general procedure for the carbonylative Sonogashira couplings of vinyl triflates with terminal acetylenes [28]. Various alkynyl ketones were produced in moderate to good yields (Scheme 5.5). However, this methodology failed in the case of activated alkynes or aryl triflates.

The catalytic ability of dimeric palladium hydroxide in carbonylative Sonogashira coupling was demonstrated by Alper and his team in 1994 [29]. In this report, terminal alkynes and alkynols were coupled with aryl iodides in the presence of carbon monoxide in moderate to good yields (Scheme 5.6). In 1995 Cacchi and colleagues presented a general methodology for 5-(2-acylethynyl)-

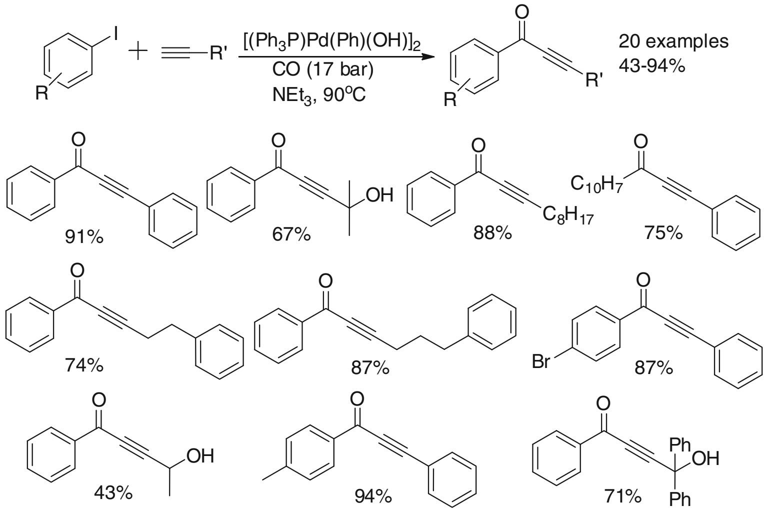


Scheme 5.4 Pd-catalyzed carbonylation of benzyl acetylenes to fuanones



Scheme 5.5 Pd-catalyzed carbonylative Sonogashira coupling of vinyl triflates with 1-alkynes

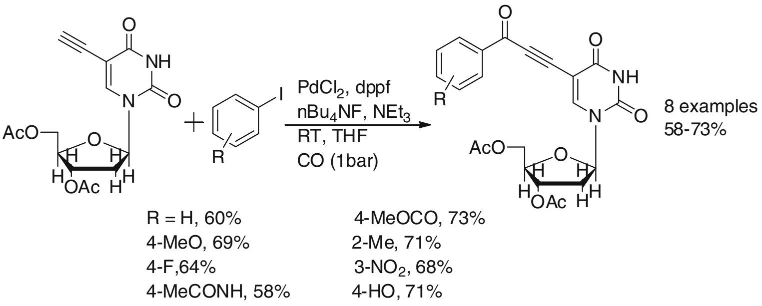
3′,5′-di-*O*-acetyl-2′-deoxyuridines synthesis [30]. In the presence of a palladium-catalyst, the corresponding alkynones were synthesized from aryl iodides and alkynes (Scheme 5.7).



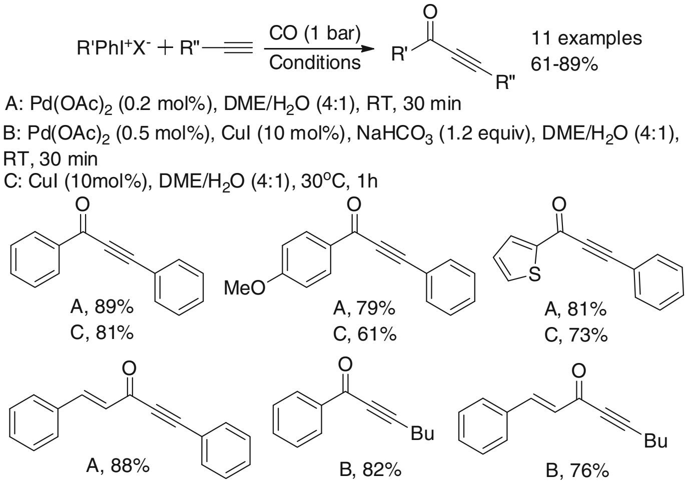
Scheme 5.6 Dimeric palladium hydroxide-catalyzed carbonylative Sonogashira coupling

The carbonylative Sonogashira reaction of iodonium salts with terminal alkynes was described by Kang and colleagues [31]. Both palladium/copper and palladium-catalyst systems alone could be used and various alkynones were synthesized in moderate to good yield in aqueous media (Scheme 5.8). Interestingly, a catalytic amount of CuI could also catalyze the reaction, and gave the corresponding alkynones in good yields.

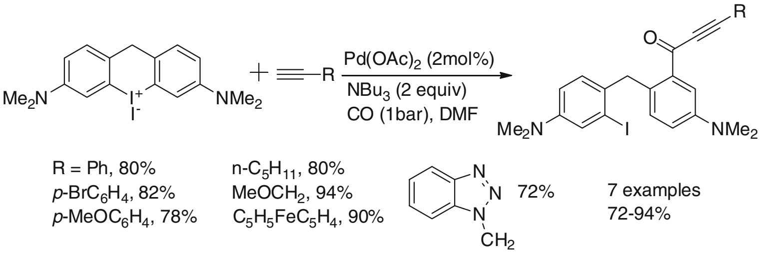
Another example of carbonylative Sonogashira coupling reactions with iodinium iodide and 1-alkynes was published by Ma and colleagues in 2001 [32]. Under mild conditions, iodine-substituted alkynones were produced in good yields (Scheme 5.9). Both aromatic, aliphatic and heterocyclic terminal acetylenes can be applied as their substrates.



Scheme 5.7 Pd-catalyzed carbonylative Sonogashira coupling of aryl iodides



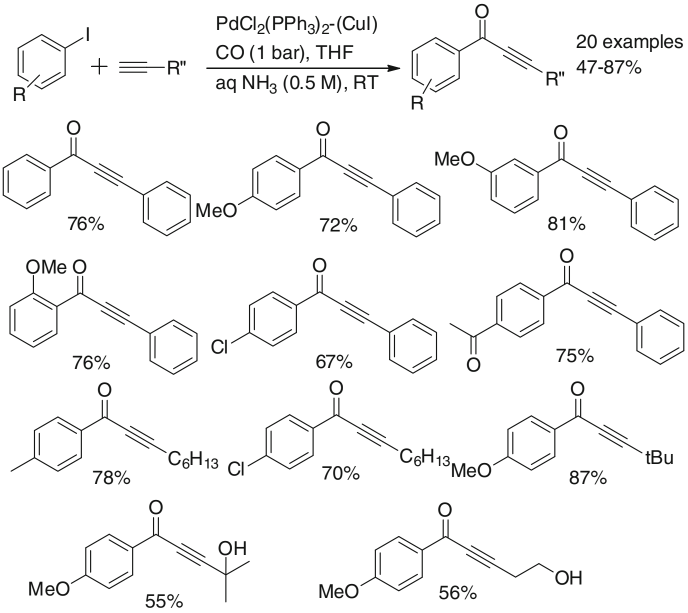
Scheme 5.8 Pd-catalyzed carbonylative Sonogashira coupling of iodonium salts with and without Cu co-catalysts



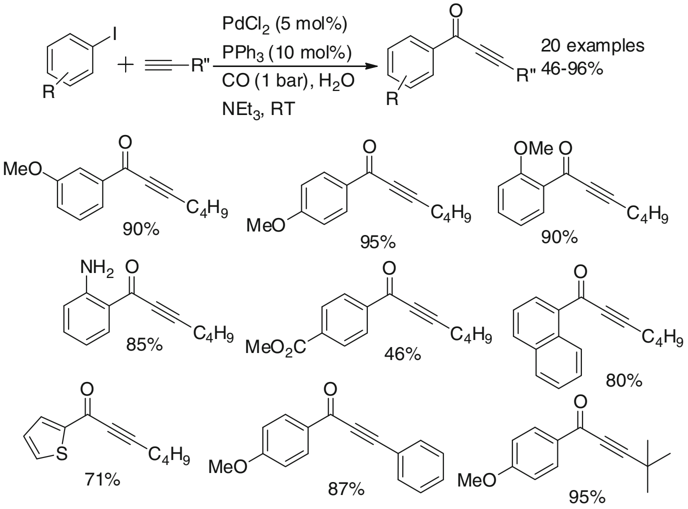
Scheme 5.9 Pd-catalyzed carbonylative Sonogashira coupling of iodinium iodide

An interesting room temperature carbonylation using a palladium/copper-catalyst system was published by Mori and Ahmed in 2003 [33–35]. As shown in Scheme 5.10, various aromatic alkynones were produced in moderate to good yields using aqueous ammonia as a base. Surprisingly, no competitive amination reaction occurred. This methodology was further exploited by Bishop's group to generate pyrazoles [35].

Water as a green solvent has been successfully applied as a reaction medium for palladium-catalyzed carbonylative Sonogashira reactions (Scheme 5.11) [36]. Instead of using alkynes, activated acetylenes stibanes can also be applied as coupling partners in carbonylations. An example is the palladium-catalyzed carbonylative Sonogashira coupling of alkynyl stibanes with aryl iodides that was published by Kakusawa and Kurita in 2006 [37]. The reaction was carried out under 1 bar of CO in DMAc using 5 mol% of $Pd(OAc)_2$ and 20 mol% of PPh_3.

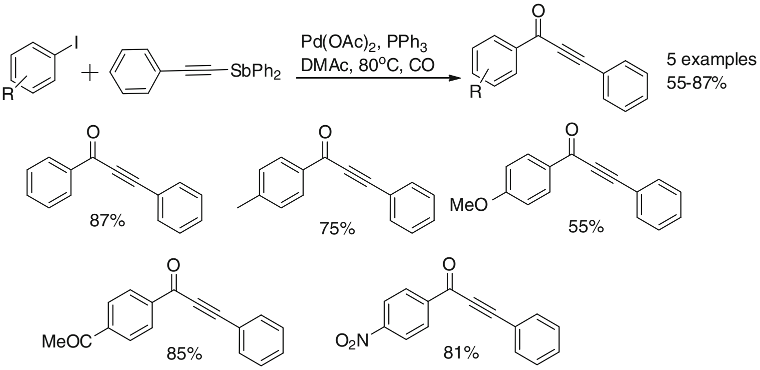


Scheme 5.10 Carbonylative room temperature Sonogashira reaction in aqueous ammonia



Scheme 5.11 Pd-catalyzed carbonylative Sonogashira coupling in water

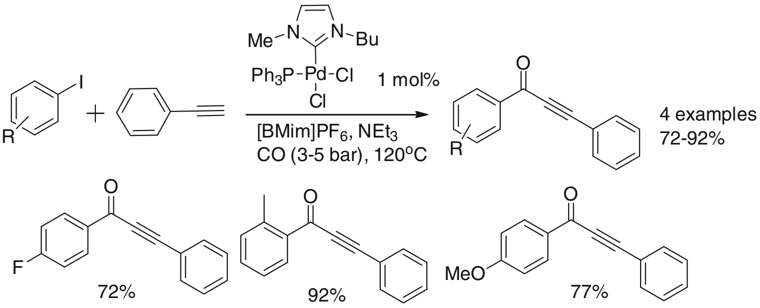
Alkynones were obtained in good yields along with a small amount of non-carbonylative coupling products (Scheme 5.12). However, this side reaction can be completely suppressed by increasing the CO pressure to 20 bar.



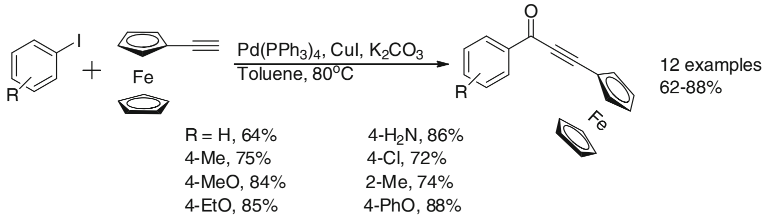
Scheme 5.12 Pd-catalyzed carbonylative Sonogashira coupling of ethynyl stibane with aryl iodides

The use of ionic liquids and flow chemistry technologies attract increasing attention. Consequently, these novel tools have also been successfully used in carbonylative Sonogashira reactions by Ryu and colleagues [38, 39]. Various alkynones were synthesized in moderate to good yields at a low pressure of CO in *n*-butyl methyl imidazolium hexafluorophosphate. The microreactor-based flow system was compared with typical batch conditions, and higher yields could be achieved with flow system (Scheme 5.13).

In 2006 Chen and his colleagues described a convenient, effective method for the carbonylative Sonogashira coupling of aryl iodides with ethynyl ferrocene under one atmosphere of CO [40]. Various aryl ferrocenylethynyl ketones have been synthesized in a 62–88 % yield (Scheme 5.14). Unexpectedly, strongly activated aryl iodides (4-Ac, 4-NO_2) and iodopyridine gave no desired carbonylation product. However, this methodology was also applied to a two-step synthesis of ferrocenyl pyrazole and pyrimidine derivatives by Skoda–Foldes and co-worker [41]. In 2009, this group reported on another protocol for the synthesis of ferrocenylethynyl ketones in water [42].



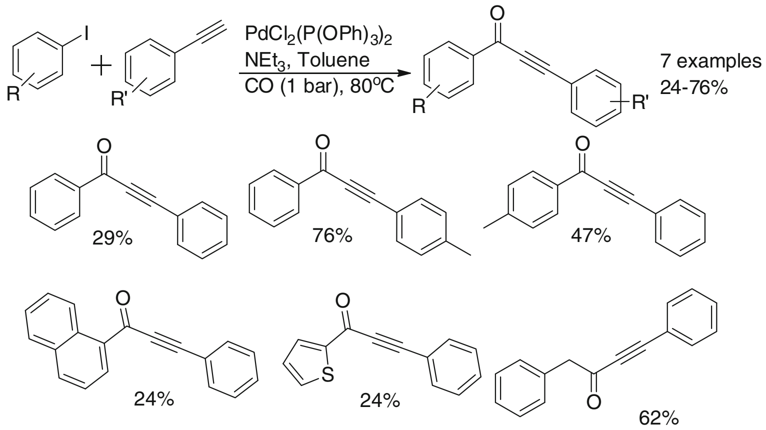
Scheme 5.13 Pd-catalyzed carbonylative Sonogashira reaction in ionic liquids



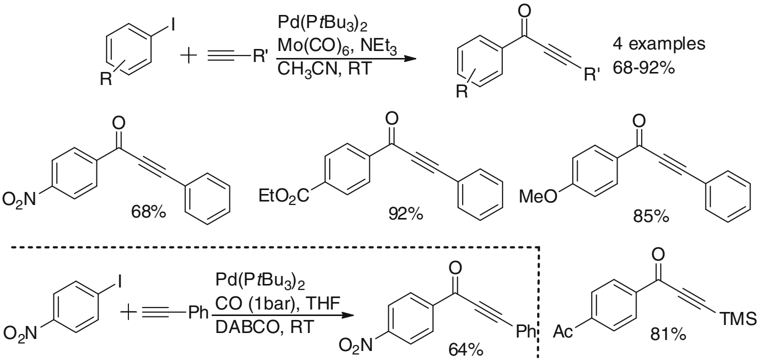
Scheme 5.14 Pd-catalyzed carbonylative Sonogashira coupling of ethynyl ferrocene with aryl iodides

The use of phosphites, e.g., $P(OPh)_3$ as a ligand in palladium-catalyzed carbonylative Sonogashira coupling, was first reported by Trzeciak and colleagues [43]. Using the defined complex $PdCl_2[P(OPh)_3]_2$ as a catalyst, alkynones were produced in low to moderate yields at 1 bar of CO (Scheme 5.15). When the reaction was conducted in an ionic liquid, the catalyst could be reused in four consecutive catalytic runs with high activity. Notably, benzyl bromide was reported as a substrate for the first time, but 2 equivalents of acetylenes were required for this system.

Kondo and Iizuka presented a palladium-catalyzed "CO-free" method for alkynone synthesis, which applies stoichiometric amounts of $Mo(CO)_6$ as a CO source [44]. The reaction was carried out at room temperature, and P*t*Bu_3 was found to be an essential ligand under these conditions. When strong electron-withdrawing substituted aryl iodides were used as substrates in this protocol, the corresponding alkynones were produced in good to excellent yields (Scheme 5.16). Again, a one-pot synthesis of pyrazoles via condensation of corresponding alkynones with hydrazine



Scheme 5.15 $PdCl_2[P(OPh)_3]_2$-catalyzed carbonylative Sonogashira coupling of aryl iodides with alkynes

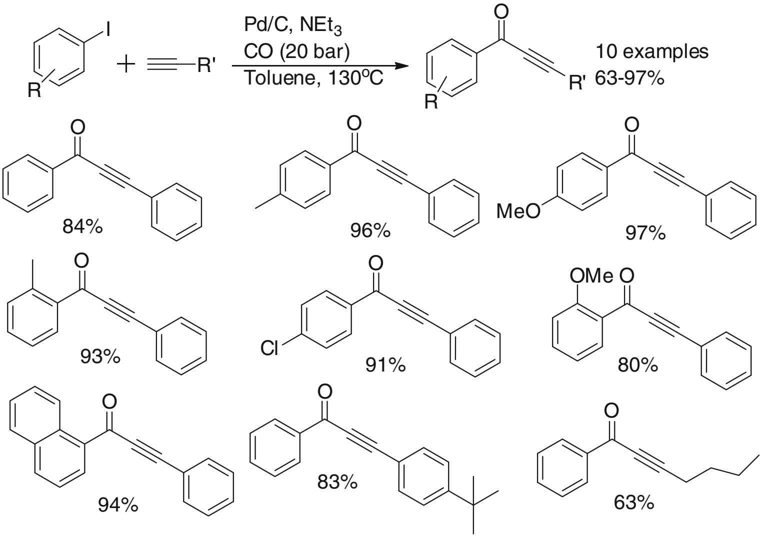


Scheme 5.16 Pd-catalyzed carbonylative Sonogashira coupling reaction with $Mo(CO)_6$ as a CO source

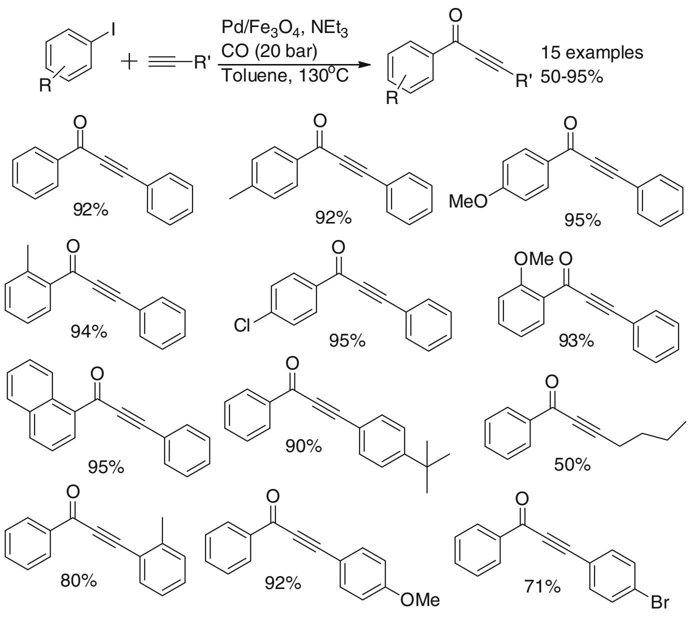
was also conducted and the corresponding products were obtained in good yields at room temperature.

In 2008, Xia and Chen described a recyclable phosphine-free catalyst system for alkynone synthesis [45]. Using palladium on charcoal (Pd/C) and NEt_3, the carbonylative Sonogashira coupling of aryl iodides with alkynes was smoothly carried out and the desired products were isolated in moderate to excellent yields (Scheme 5.17).

Later on, the same group presented an unusual variation of the palladium-catalyzed carbonylative Sonogashira coupling reaction [46]. Here, a magnetically



Scheme 5.17 Pd/C-catalyzed carbonylative Sonogashira reaction of aryl iodides

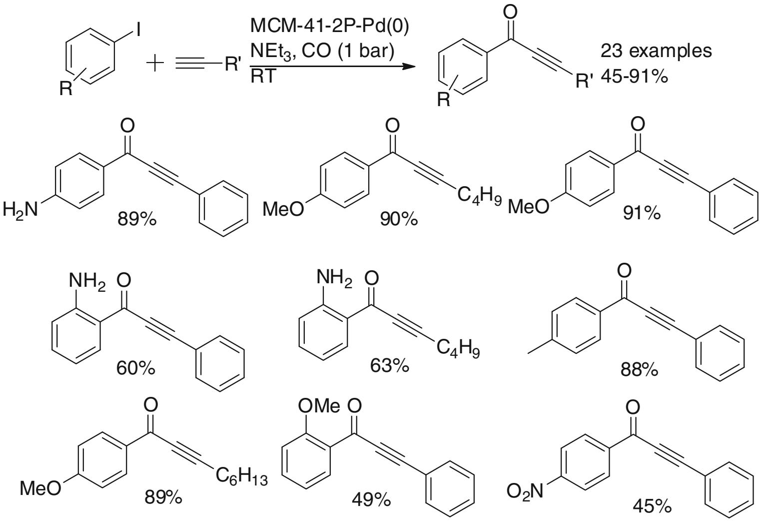


Scheme 5.18 Pd/Fe_3O_4-catalyzed carbonylative Sonogashira coupling of aryl iodides

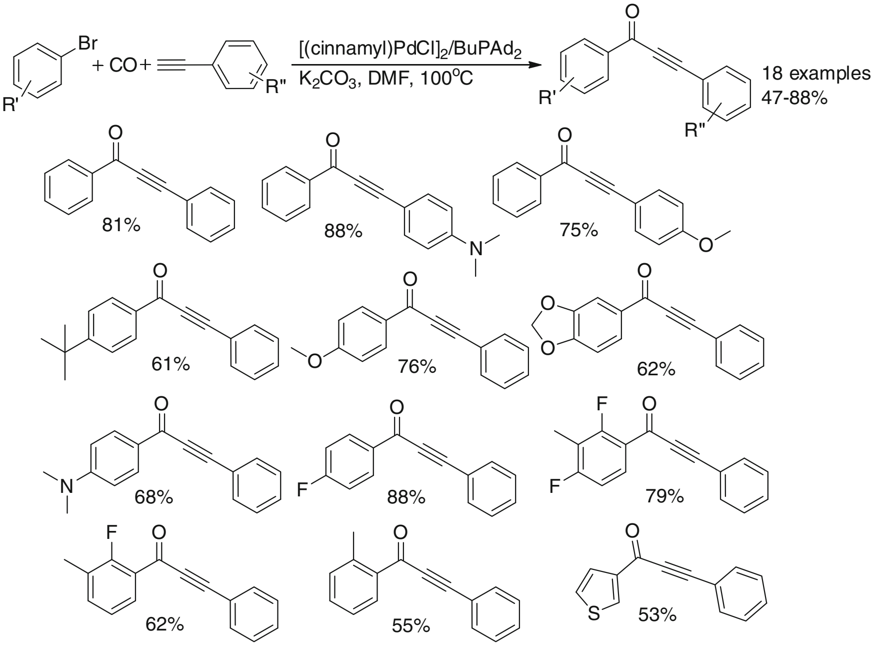
separable palladium-catalyst was synthesized by combining palladium nanoparticles and superparamagnetic Fe_3O_4 nanoparticles in a KBH_4 solution. This catalyst proved to be effective for the carbonylation reaction of aryl iodides with alkynes under phosphine-free conditions. Because of the magnetic behavior of Fe_3O_4, the catalyst could be reused with sustained selectivity and activity. Various alkynones have been synthesized in good to excellent yields (Scheme 5.18).

Another approach applying a heterogeneous palladium-catalyst was recently published by Cai and colleagues. They disclosed the MCM-41-supported bidentate phosphine palladium complex [MCM-41-2p-Pd(0)] as a polymer-supported palladium-catalyst [47]. Terminal alkynes were converted with aryl iodides under 1 bar CO to give alkynones in good to high yields (Scheme 5.19). Noteworthy is the fact that the use of a polymer as support in a Sonogashira coupling reaction was already reported by Takahashi and colleagues in 2008. The products can be released from the polymer by adding acid [48].

So far, basically all methodology developments in this area have focused on the use of expensive and easy-to-activate aryl iodides. Thus it was interesting that in 2010 Beller's group discovered a general and convenient palladium-catalyzed carbonylative Sonogashira coupling of aryl bromides [49]. The key to the success was the application of $BuPAd_2$ as a ligand in the presence of K_2CO_3. Alkynones have been generated in moderate to good yields from the corresponding aryl bromides and terminal alkynes (Scheme 5.20). The one-pot synthesis of isoxazolines and pyrazoles was also successful.



Scheme 5.19 [MCM-41-Pd]-catalyzed carbonylative Sonogashira coupling reaction of aryl iodides

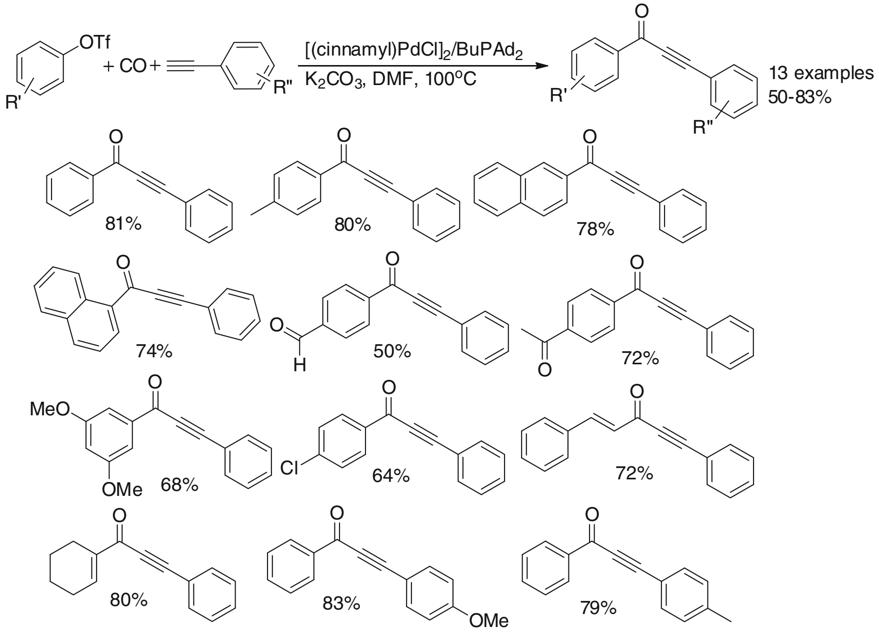


Scheme 5.20 Pd-catalyzed carbonylative Sonogashira coupling of aryl bromides

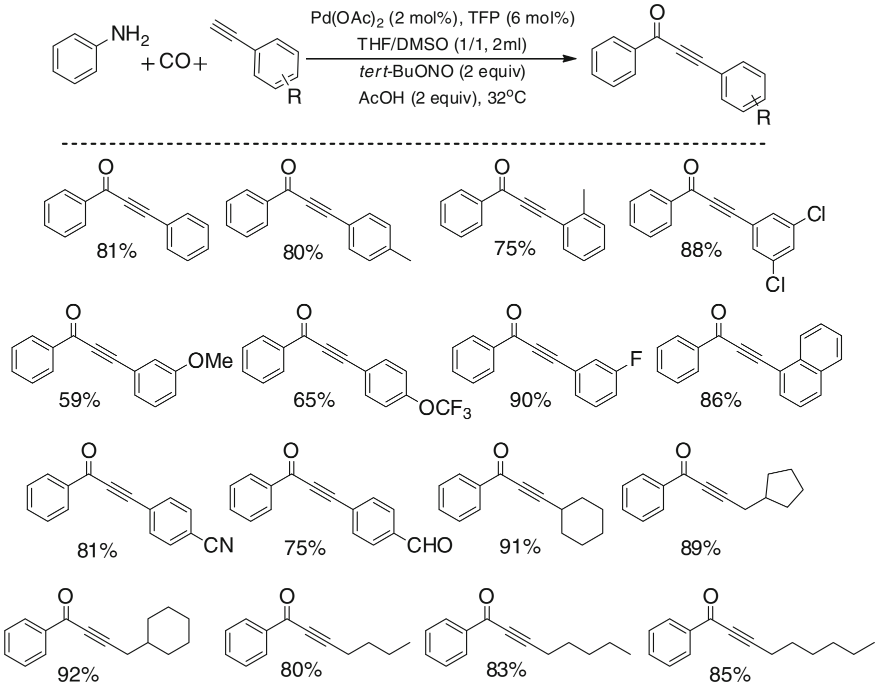
Since aryl triflates can easily be generated from corresponding phenols, Beller also developed a palladium-catalyzed carbonylative Sonogashira coupling of aryl triflates in 2010 [50]. This is the first carbonylative Sonogashira protocol that can apply aryl triflates as substrates. Various alkynones were produced in moderate to good yields under low pressure of CO (Scheme 5.21). A one-pot synthesis of enaminones was also achieved by running the reaction in the presence of primary amines.

Taking the advantages of anilines, Beller and his colleagues developed the first general and efficient methodology for carbonylative Sonogashira reaction of anilines [51]. This transformation proceeded under mild reaction conditions, and no base was needed. Both aromatic and aliphatic alkynes are suitable starting materials, and 30 different kinds of alkynones were produced in moderate to excellent yields (Scheme 5.22).

They also extended their methodologies to benzyl chlorides [52]. Applying an unusual $Pd(PPh_3)_2Cl_2/P(OPh)_3$ catalyst system, eight different alkynones are produced in moderate to good yields (45–80 %) by the carbonylation of benzyl chlorides and alkynes. Benzyl acetylene gave the corresponding furanones in moderate a yield (45–68 %) via palladium-catalyzed domino double carbonylation reactions. Based on this work, the carbonylative synthesis of furanones from aryl bromides and aryl triflates were developed as well [53]. The generality of this methodology was proved by more than 30 examples that proceeded good yields



Scheme 5.21 Pd-catalyzed carbonylative Sonogashira coupling of aryl triflates



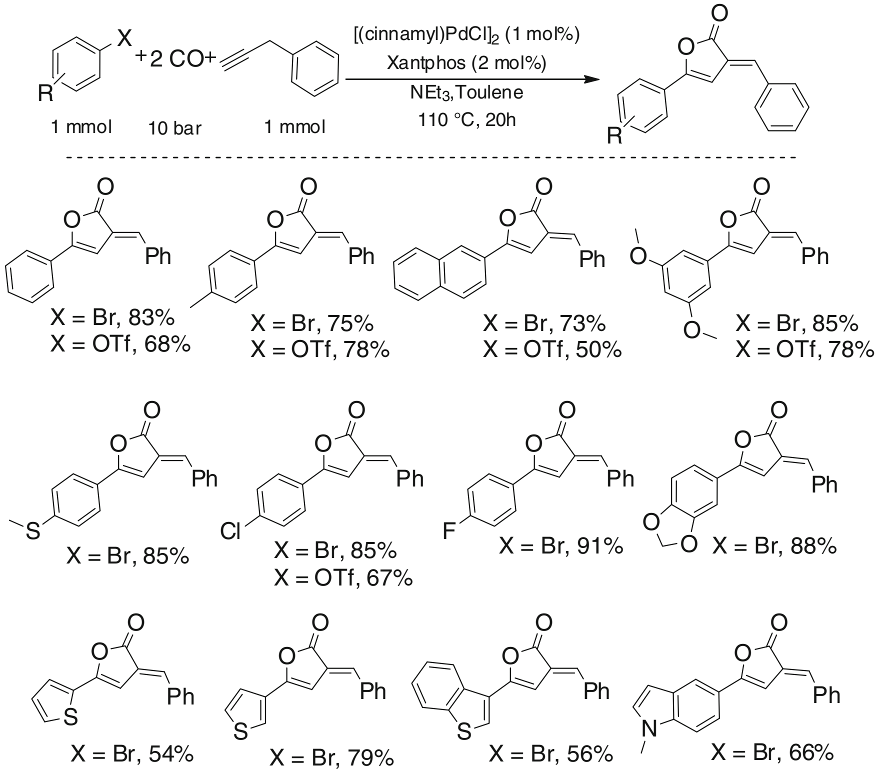
Scheme 5.22 Palladium-catalyzed Sonogashira carbonylation of anilines

(Scheme 5.23). Notably, the straightforward synthesis of permethylated BE-23372M, a kinase inhibitor, was achieved. Later on, they found that the carbonylation of aryl iodides with benzylacetylenes could even be carried out at room temperature under 1 bar of CO [54].

Ryu and colleagues described the synthesis of alkyl alkynyl ketones via the Pd/light-induced carbonylative Sonogashira coupling of iodoalkanes with terminal alkynes [55]. Using xenon light, in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$ and NEt_3, alkynones were produced in good yields (Scheme 5.24). This represents the first examples for Sonogashira carbonylations of alkyl iodides [56].

Despite all the synthetic developments, relatively little detailed mechanistic work has been performed on Sonogashira carbonylations until the present. The generally accepted mechanism is shown in Scheme 5.25. The typical reaction begins with the oxidative addition of ArX to a palladium(0) complex to form an aryl palladium(II) intermediate. The subsequent insertion of CO leads to the respective palladium acyl complex. Transmetallation, and finally reductive elimination, releases the product and a new catalytic cycle can be started. Notably, all species passing through the cycle are believed to be in a reversible equilibrium.

Besides the intermolecular Sonogashira carbonylation reactions, intramolecular Sonogashira carbonylations offer various possibilities for the preparation of interesting heterocycles. Typically, in these reactions 2-halophenols and

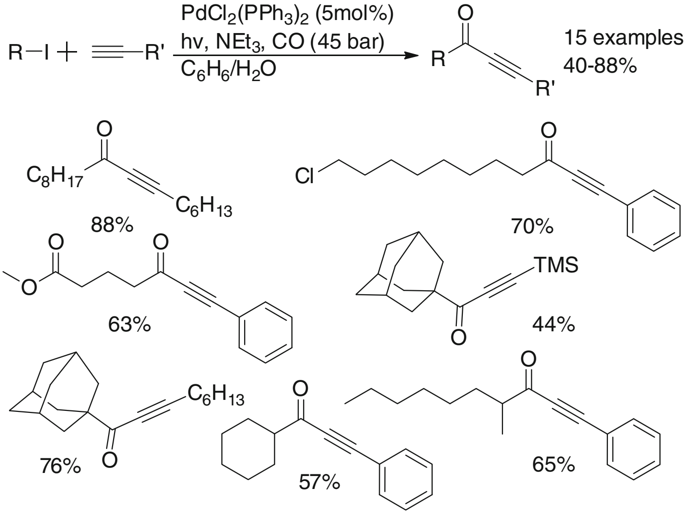


Scheme 5.23 Palladium-catalyzed furanones synthesis

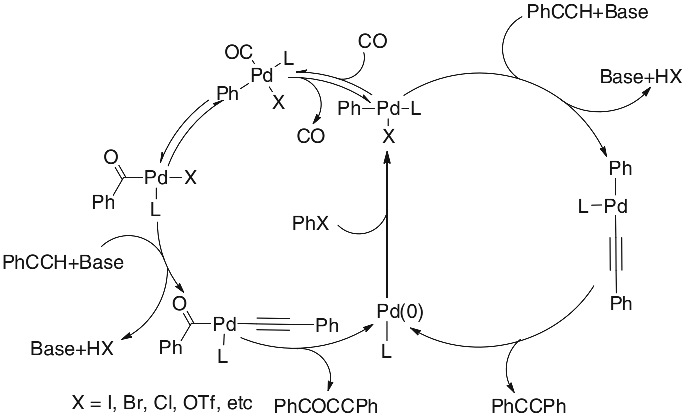
2-haloanilines or their derivatives are used with terminal alkynes. As early as 1990, Chiusoli and colleagues reported on the palladium-catalyzed synthesis of indoxyl derivatives (Scheme 5.26) [57].

Shortly afterwards, Torii and co-worker reported a novel methodology for the synthesis of quinolines [58, 59]. Here, quinolines were produced in good yields via palladium-catalyzed carbonylation of 2-haloaniline with terminal alkynes in the presence of CO (Scheme 5.27).

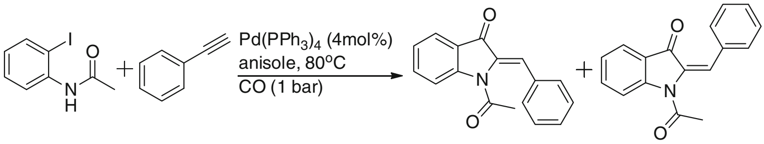
When the amino group of the 2-haloaniline substrate is primary, the cyclization proceeded without problem. But using alkylated anilines under the same conditions, the yield of the corresponding cyclization product decreased dramatically. A similar methodology was reported by Kalinin and colleagues in 1992, using PdCl$_2$(dppf) as a palladium precursor [60]. This cyclization was applied to synthesize the quinolone substructure of BILN 2061, a serin protease inhibitor [61, 62]. That same year, Chiusoli and colleagues published an interesting methodology for indenone synthesis [63]. The sequential oxidative addition of *ortho*-alkoxycarbonylmethylene or alkylamido-methylene-substituted aryl iodides, CO insertion, reductive coupling with terminal alkynes, nucleophilic attack by the activated methylene group, and



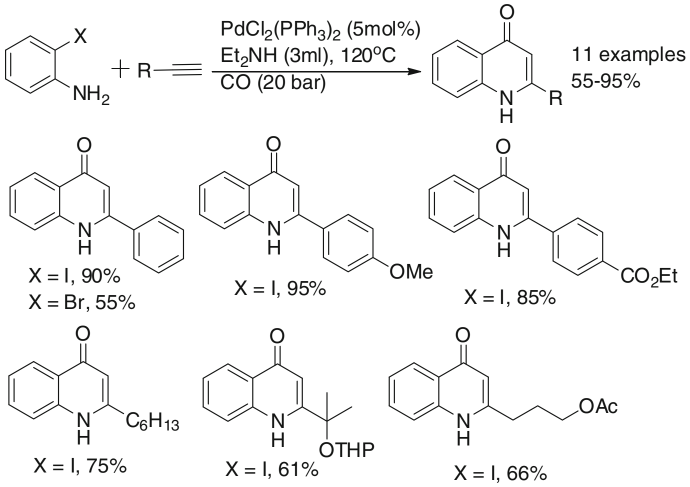
Scheme 5.24 Pd-catalyzed carbonylative Sonogashira coupling of iodoalkanes using xenon light



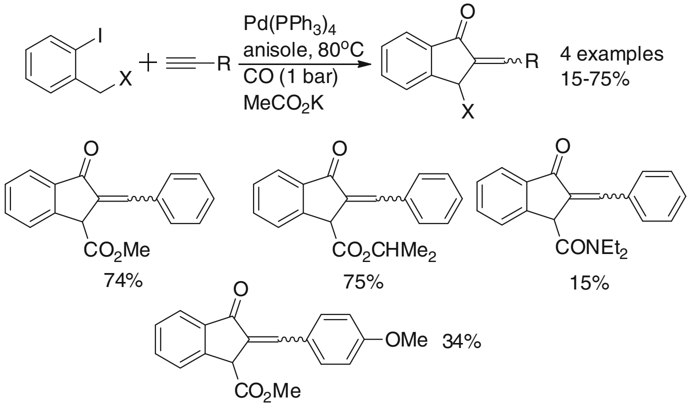
Scheme 5.25 Proposed reaction mechanism for carbonylation Sonogashira reaction



Scheme 5.26 Pd-catalyzed carbonylative synthesis of indoxyls



Scheme 5.27 Pd-catalyzed carbonylative synthesis of quinolines

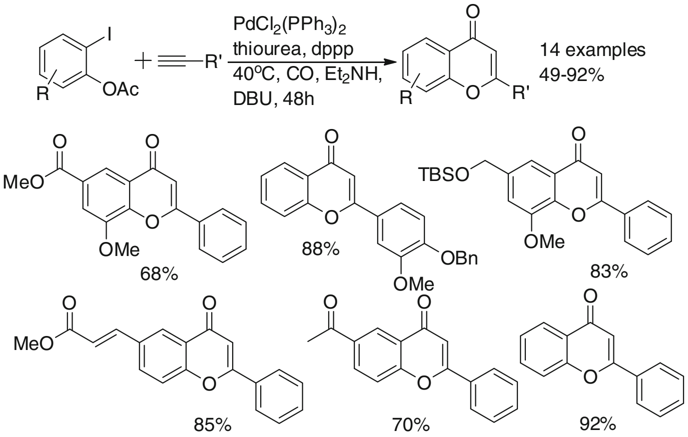


Scheme 5.28 Pd-catalyzed carbonylative synthesis of indenones

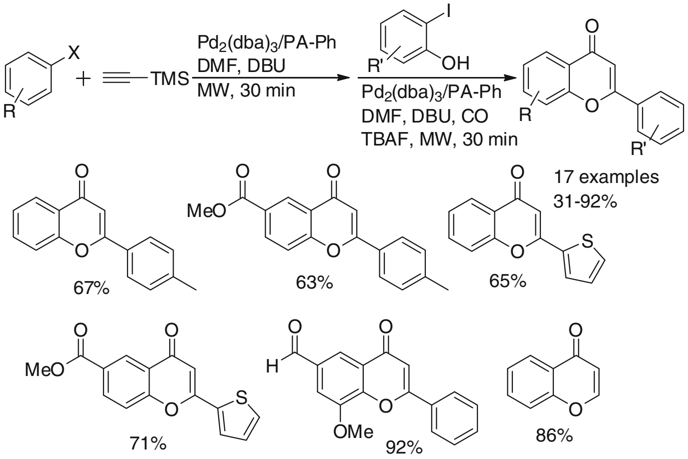
protonation with metal elimination, afford the indenones high yields in a one-pot process (Scheme 5.28).

In 2000 Yang and Miao reported a novel method for the preparation of flavones [64]. Various flavones are easily synthesized via palladium-catalyzed carbonylative annulation of iodophenol acetates with terminal acetylenes in high yields (Scheme 5.29). This novel reaction provides the possibility of a combinatorial synthesis of flavones on solid supports.

More recently, Capretta and Awuah described a microwave-assisted, one-pot palladium-catalyzed carbonylative Sonogashira annulation reaction [65]. Various flavones have been produced in moderate to good yields (Scheme 5.30). Alper and



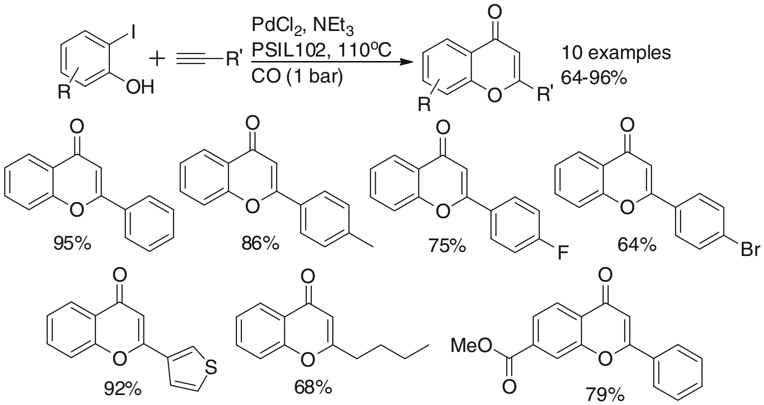
Scheme 5.29 Pd-catalyzed carbonylative synthesis of flavones



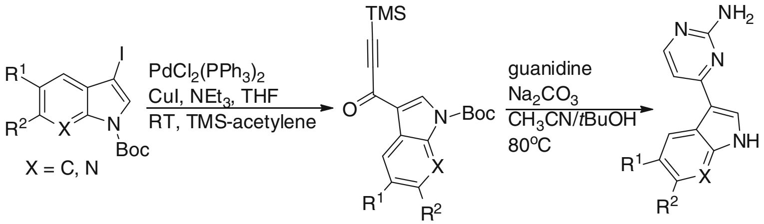
Scheme 5.30 Pd-catalyzed carbonylative synthesis of flavones

Yang reported another example of carbonylations of *o*-iodophenols with terminal acetylenes to obtain flavones. Their reaction proceeded under 1 bar of CO in ionic liquids based on phosphonium salt (PSIL102, $C_{14}H_{29}(C_6H_{13})_3)P^+Br^-$) [66]. It should be noted that by using PSIL102 as an ionic liquid, no phosphine ligand was required (Scheme 5.31).

Elegant synthetic applications of carbonylative Sonogashira reactions were described by Müller and his group. For example, in 2005 they succeeded in producing palladium-catalyzed one-pot, four-component carbonylations for the



Scheme 5.31 Pd-catalyzed carbonylative synthesis of flavones in PSIL102



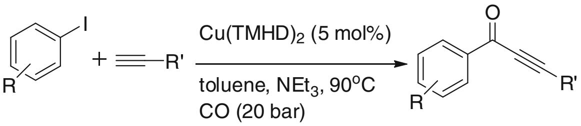
Scheme 5.32 Pd-catalyzed carbonylative synthesis of meridianins

synthesis of meridianins [67], which are natural and biologically activated compounds (Scheme 5.32).

In 2008 Bhanage's team reported on a copper-catalyzed carbonylative Sonogashira reaction of aryl iodides [68]. In this procedure, copper bis(2,2,6,6-tetramethyl-3,5-heptanedionate) [Cu(TMHD)$_2$] was used as the catalyst for this transformation and using NEt$_3$ as a base. Alkynones were produced in good yields (Scheme 5.33). A nickel-catalyzed carbonylation of allyl halides and acetylenes was reported on by Moretó and colleagues [69]. Cyclopentane skeletons were produced in high yields and with controlled stereochemistry.

In this chapter, we have discussed the carbonylative Sonogashira reaction of organohalides and their synthetic applications. Palladium-catalysts are still the main catalysts in this area. From the mechanism point of view, the same as the

Scheme 5.33 Copper-catalyzed carbonylative Sonogashira reaction



contents of Chap. 4, transmetalation is involved in the case of in situ formation of alkynylcopper intermediate. But the mechanism is different if a palladium-catalyst is the sole catalyst, which should be similar to the contents that will be discussed in the next chapter.

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