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Palladium-catalyzed inter- and intramolecular formation of C–O bonds from allenes

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The Pd-catalysed formation of a C–O bond from allenes mainly occurs *via* the inter- or intramolecular reaction with a hydroxyl group belonging to an alcohol, a phenol or an acid. A carbonyl or a carbonate entity can also be involved. In most cases, the formation of the C–O bond is one step of a domino reaction leading also to a C–C or C–N bond, or to another C–O bond. Thus, a wide range of products, in particular highly functionalized heterocycles, have been synthesised. Catalytic cycles have been proposed but the mechanisms often remain speculative.

1. Introduction

The synthesis and transformation of 1,2-dienes involve a variety of procedures.[1] The presence of two contiguous C=C bonds provides a unique reactivity, which has been exploited in synthesis. Although most of the studies on the transition metal-catalysed reactions of unsaturated compounds concern reactions of alkenes, alkynes and arenes, those on allenes have nevertheless led to reviews.[2,3] The purpose of the present review is to highlight the Pd-mediated processes leading to the formation of at least one C–O bond from an inter- or intramolecular reaction with an allenyl unit. That is often only one step of a domino reaction. With the assistance of palladium complexes, allenes are indeed capable of undergoing 1,2-addition with both electrophiles and nucleophiles. In most cases, such three-component reactions lead to the attachment of the electrophile to the central carbon of the allene, whereas the nucleophile is bonded to the 1- or 3-carbon. The order of these steps remains usually determinate,[4] as exemplified in Scheme 1 for reactions between buta-2,3-dien-1-ol and aryl, vinyl or allyl halide using either a Pd^0 or a Pd^{II} catalyst. The attack of the allenyl moiety by the hydroxy group would be an intramolecular Wacker-type reaction requiring the activation of the unsaturated system by a Pd^{II} species, the latter being the PdX_2 catalyst or the RPdX (R = Ar, vinyl, η^1- or η^3-allyl) obtained by insertion of Pd^0 into a C–halide bond. After the formation of the C–O bond from **1A** or **1B**, the resulting intermediate can lead to

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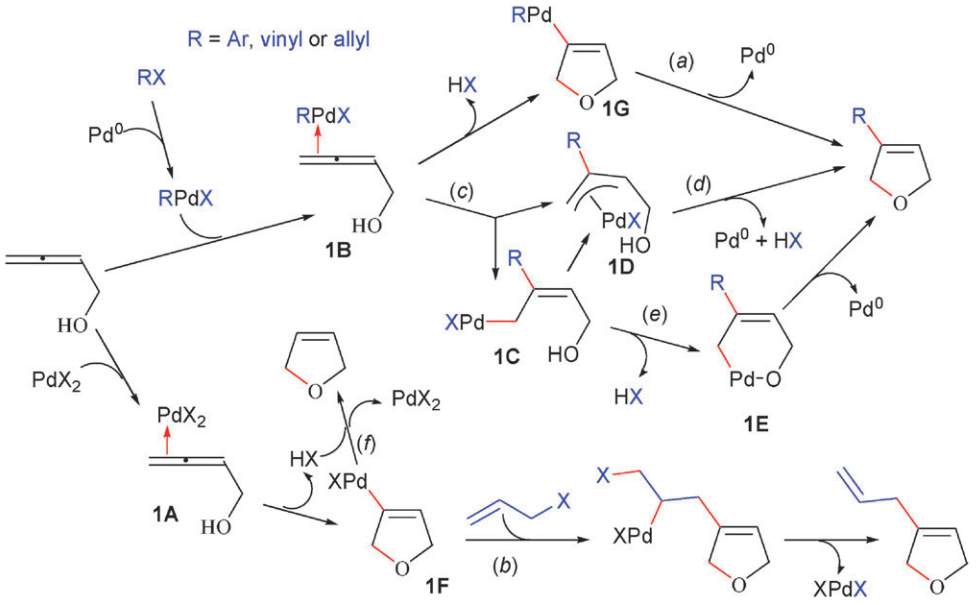
Jean Le Bras

Jean Le Bras obtained his Engineering Diploma from ENSCP-Paris and his MSc degree (DEA) from UPMC. In 1996, he joined the group of Dr Hani Amouri, where he studied iridium mediated functionalization of phenols and obtained his PhD in 1998. He then joined the group of Professor John A. Gladysz in Salt Lake City (USA) and in Erlangen (Germany) and worked on the synthesis of organometallic complexes with polyynediyl chains. In 2000, he became a CNRS fellow at the Université de Reims Champagne Ardenne, and was promoted to Directeur de Recherche in 2013. His current interests are concentrated on oxidative palladium cross-coupling transformations.

Jacques Muzart

Jacques Muzart was born in 1946, in Vienne la Ville, a small village in the Argonne area, 200 km east of Paris. He studied chemistry at the Université de Reims Champagne-Ardenne and received his degrees (Doctorat de 3ème cycle in 1972, Doctorat d'Etat in 1976) for his work with J.-P. Pète on photochemical rearrangements of α,β-epoxyketones and β-diketones. He spent 15 months as a postdoctoral fellow of the National Science Foundation working with Nobel Laureate E. J. Corey at Harvard University on natural product synthesis. He has been the Directeur de Recherche Emérite since 2011, and his research interests concentrate on transition metal-catalysis.



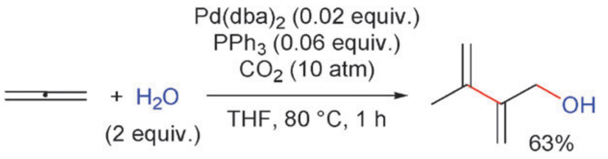
Scheme 1

the formation of the C–C bond with regeneration of the catalyst (paths *a* and *b*). Instead of the Wacker-type reaction, **1B** can evolve *via* the Heck-type addition to afford the allylpalladium complex **1C** or **1D** (path *c*). The formation of the substituted dihydrofuran would then occur from nucleophilic addition to the η^3-allylpalladium complex (path *d*) or *via* the palladacycle **1E** (path *e*). While **1D** is often proposed as an intermediate, it seems that **1E** is never suggested for such domino reactions. A side-reaction from **1F** is the protonolysis leading to 2,5-dihydrofuran (path *f*). Given these different possibilities, the mechanism of these Pd-catalysed cyclisation-coupling reactions remains a matter of debate. It has to be however pointed out that the efficient formation, at room temperature, of η^3-allylpalladium complexes from allenes and alkyl or acyl palladium complexes has been reported.[5]

The oxygen atom of the C–O bond obtained from addition to allenes arises from a hydroxy group (water, alcohol, phenol, acid) or a carbonyl. Moreover, the C–O bond can be formed *via* an inter- or intramolecular reaction. The present review is organised in terms of these different angles.

2. Hydrohydroxylation

Under Pd^0 catalysis, the reaction of allene with water leads to traces of 3-methyl-2-methylene-3-buten-1-ol.[6] Inoue and co-workers discovered that this dimerisation–hydroxylation reaction became efficient under carbon dioxide pressure, especially in THF (eqn (1)).[6] The role of CO_2 has not been determined. An experiment with D_2O has shown that water is the source of the incorporated hydrogen.

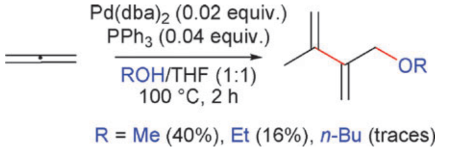


(1)

3. Intermolecular etherification

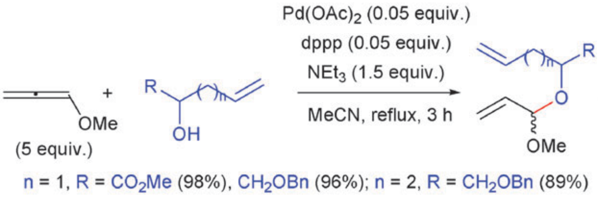
3.1. Hydroalkoxylation

In contrast to the above Pd^0-catalysed water addition–dimerisation of allene, a similar process with methanol occurs with a reasonable yield in the absence of CO_2 (eqn (2)).[6] According to the authors, the efficiency decrease with the size of the alcohol could be due to steric factors.[7]



(2)

Subsequently, the Rutjes team reported the Pd^{II}-catalysed reaction of secondary alcohols with methoxyallene under conditions which did not mediate the dimerisation of the substrate (eqn (3)).[8] Attack of the alcohol onto the complex **2A** formed by the coordination of Pd^{II} with the more electron-rich oxygen-substituted double bond would lead to the vinylpalladium



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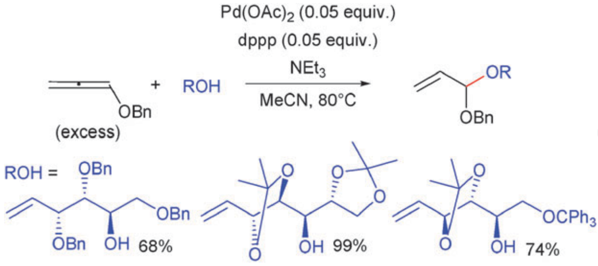

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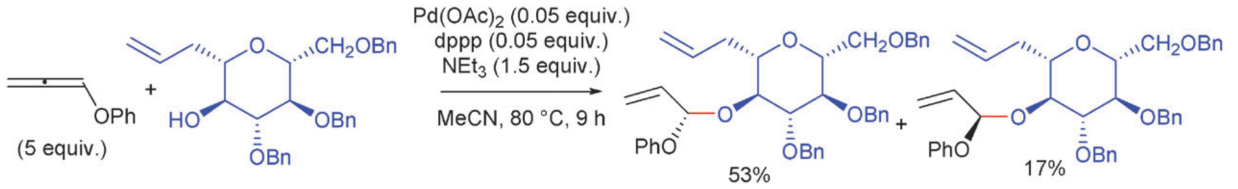
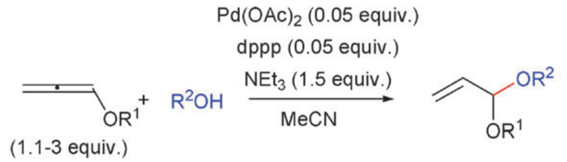


(5)

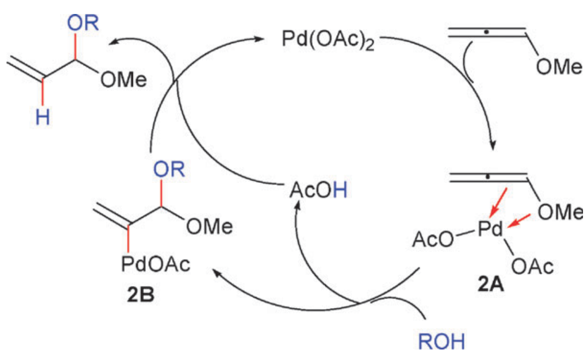
complex **2B**, the protonolysis of which gives the acetal and regenerates the Pd^{II} catalyst (Scheme 2). The Rutjes procedure has been extensively used to obtain acetals from protected propa-1,2-dien-1-ols and a variety of functionalised secondary (eqn (4),[9] (5)[10] and (6)[11])[12] or tertiary (eqn (6)[11]) alcohols.[13]



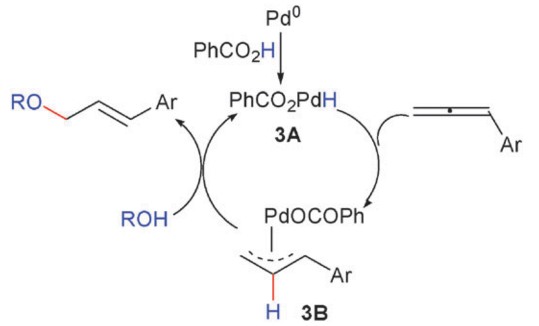
R^1 = Me, R^2OH = $CH_2{=}CHCH_2CH(OH)CO_2Me$, reflux, 3-6 h: 98%
R^1 = Bn, R^2OH = $CH_2{=}CHCH_2CMe(OH)CO_2Me$, rt, 16 h: 97%
R^1 = Me, R^2OH = $Me_3SiC{\equiv}CCH_2CH(OH)CH_2OBn$, reflux, 4 h: 88%

(6)

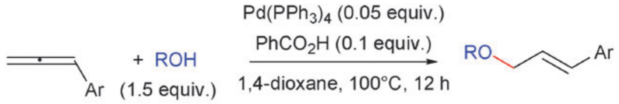
Some years after the above Rutjes report, Yamamoto *et al.* used the $Pd(PPh_3)_4/PhCO_2H$ association to catalyse the hydroalkoxylation of arylallenes by primary and secondary alcohols (eqn (7)).[14] This reaction would involve the oxidative addition of benzoic acid to Pd^0 to provide the hydridopalladium species **3A.** The subsequent hydropalladation of the allene would afford the η^3-allylpalladium complex **3B** (Scheme 3), regioselective addition of the alcohol to the latter delivering the allyl ether.



Scheme 2



Scheme 3

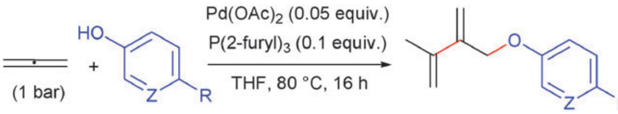


Ar = Ph, R = Bn (71%), *n*-oct. (70%), Cy (71%), Ph_2CH (75%), $Me_2C{=}CHCH_2$ (75%), cyclopropylCH_2 (65%)
Ar = *p*-MeC_6H_4, R = Bn (68%); Ar = *p*-FC_6H_4, R = Bn (72%)

(7)

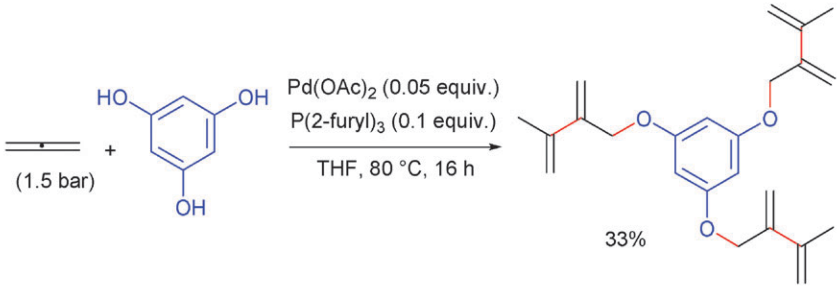
3.2. Hydroaryloxylation

In 1998, Yamaguchi *et al.* observed weak addition of ArOH to the dimer of undeca-1,2-diene obtained under catalysis with the $Pd_2(dba)_3$–ArOH system.[15] Much more efficient conditions have then been disclosed by Grigg's team to synthesise 2-(hetero)aryloxymethyl-3-methyl-1,3-butadienes (eqn (8)).[16]



Z = CH, R = H (67%), OMe (69%), CO_2Me (56%), NO_2 (64%)
Z = N, R = H (34%)

(8)



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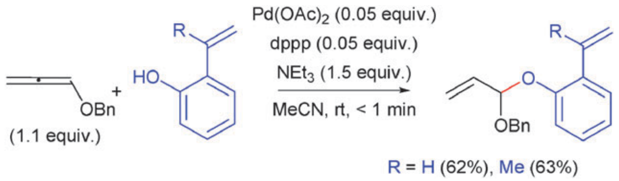


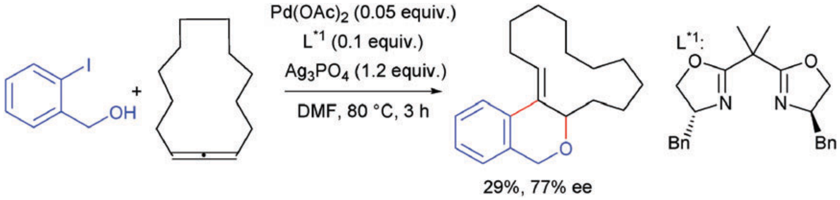
(10)

(11)

Two mechanisms were proposed (Scheme 4, paths *a* and *b*).[16] Path *a* involves the insertion of Pd^0 into the ArO–H bond and the coordination of allene leading to **4A**; the subsequent hydropalladation gives **4B** which reacts with another molecule of allene to provide **4C**. From **4C**, the product would be obtained either *via* the reductive elimination of Pd^0, or *via* a η^3-allylpalladium intermediate and its attack by phenolate occurring externally or by transfer. Path *b* involves the addition of ArOH to the palladacycle **4D** to afford the Pd^{IV} intermediate **4E**, which also leads to **4C**. Whole etherification of 1,3,5-trihydroxybenzene has also been carried out (eqn (9)).[16]With the Rutjes procedure, the hydroaryloxylation of benzyloxyallene effectively happens in a few seconds at room temperature (eqn (10)),[11,17] while that of methoxyallene requires reflux and results in low yields.[17] The reason for this remarkable difference was unexplained.[17]

3.3. Alkoxyarylation

In 1991, Larock *et al.* disclosed the Pd^0-catalysed synthesis of the 4-methyleneisochroman derivative shown in eqn (11).[18] The mechanism proposed by them involves the arylation of the central atom of the 1,2-diene followed by regioselective nucleophilic addition of the alcoholate to the more substituted extremity of the η^3-allylpalladium intermediate (see Scheme 1, path *d*). (2-Iodo(or bromo)phenyl)methanol has also been used for enantioselective annelations (eqn (12))[19,20] and for the coupling with heterosubstituted allenes (eqn (13)[21] and (14)).[22]With *o*-iodobenzaldehyde and 2,3-allenols, Ma and co-workers reported a domino reaction providing oxa-bridged benzocycloheptanes (eqn (15)).[23] These syntheses would imply the η^3-allylpalladium intermediate **5A** (Scheme 5). The base mediates the formation of the alcoholate to perform the intramolecular addition to the aldehyde, resulting in the



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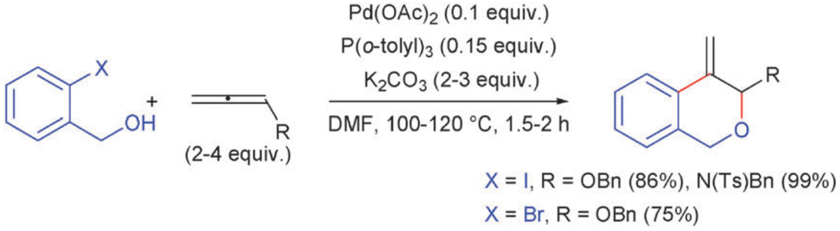

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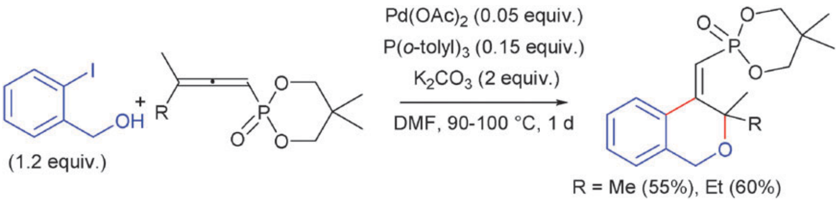

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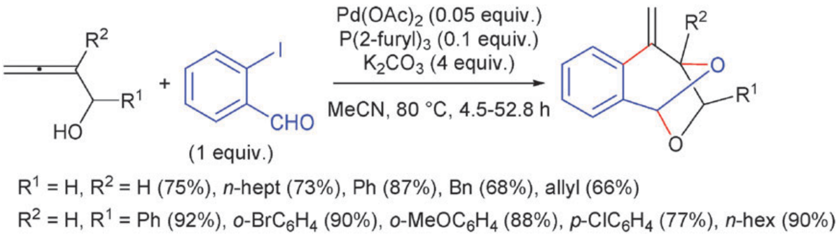

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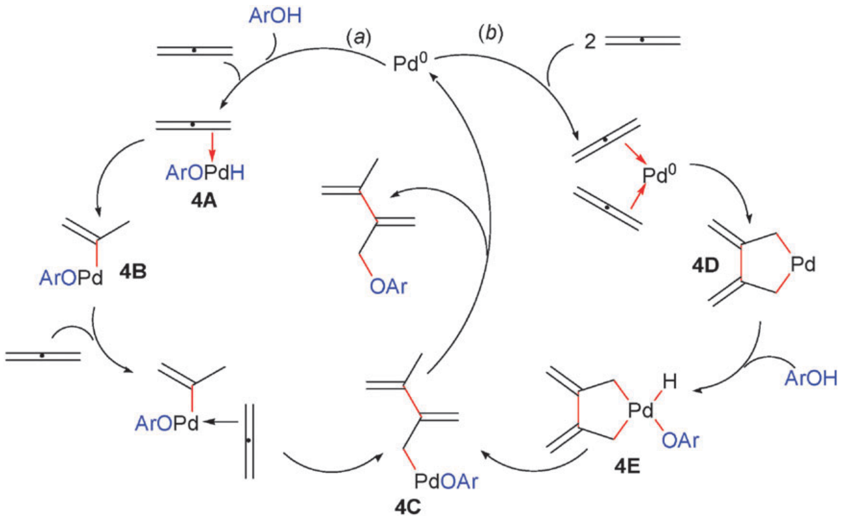
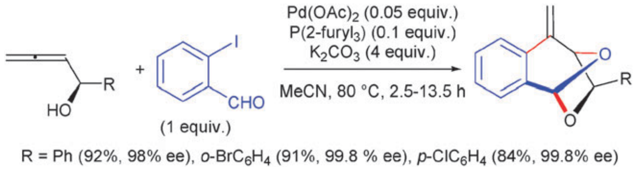


Scheme 4

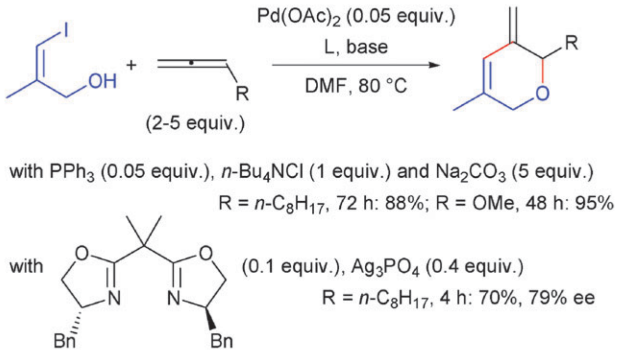
subsequent addition to the η^3-allylpalladium moiety. This high diastereoselectivity observed from optically active 2,3-allenols (eqn (16)) supports the proposed catalytic cycle.



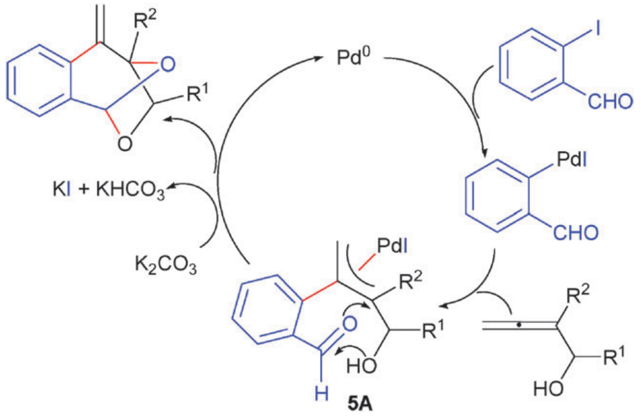
(16)

3.4. Alkoxyvinylation

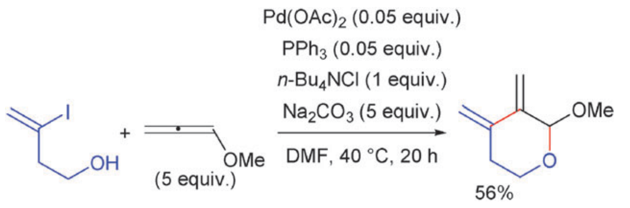
Annelation of allenes with vinylic halides bearing an alcohol group led Larock's team to isolate a variety of heterocycles (eqn (17) to (19)) through, probably, η^3-allylpalladium intermediates, the reaction being enantioselective in using chiral ligands (eqn (17)).[19,20,24] With 2-iodo-3-methylbut-2-en-1-ol, the η^1- or η^3-allylpalladium intermediate inserts a second allene before closing to a seven-membered heterocycle (eqn (19)).[24]



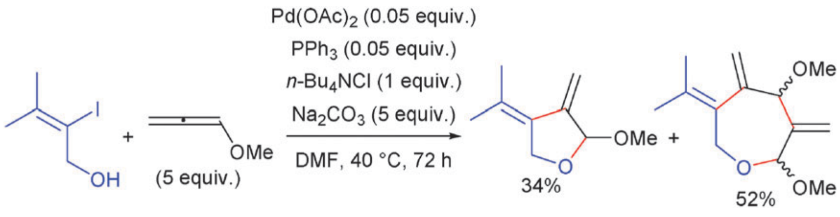
(17)



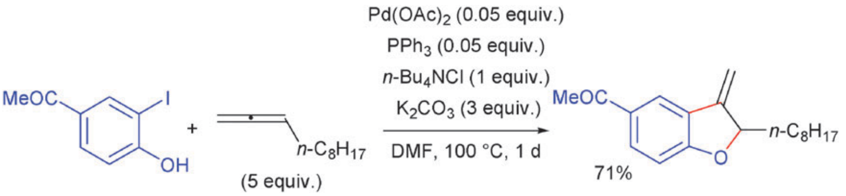
Scheme 5



(18)



(19)



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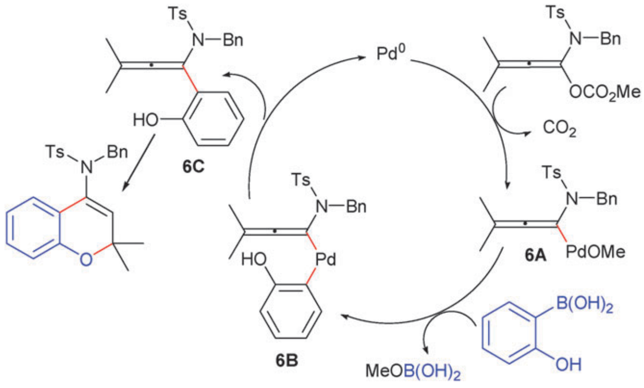
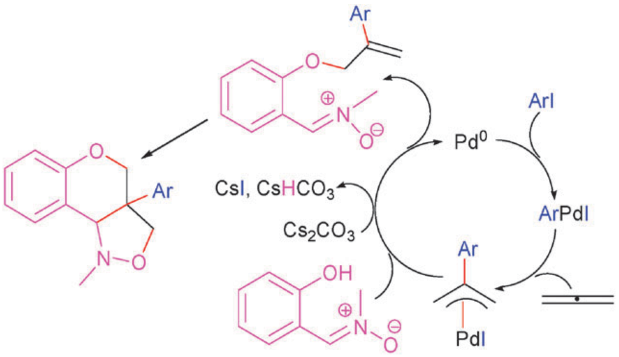


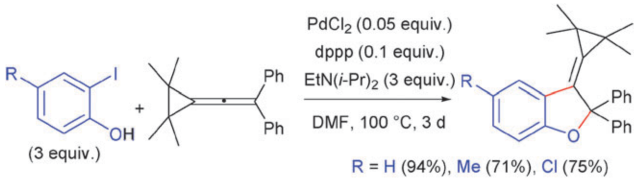
Scheme 6



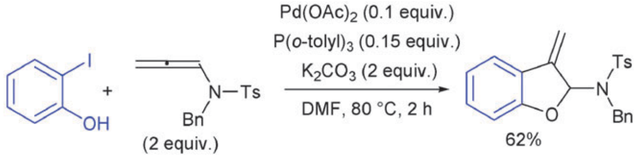
Scheme 7

3.5. Aryloxy-arylation

The annelation of undeca-1,2-diene with *m*-iodo-*p*-hydroxyacetophenone has also been documented by Larock's team (eqn (20)).[18,20] Various examples of a similar domino reaction have then been reported using slightly different experimental conditions (eqn (21),[25] (22),[21] (23)[26] and (24) to (26)[22,27]).



(21)



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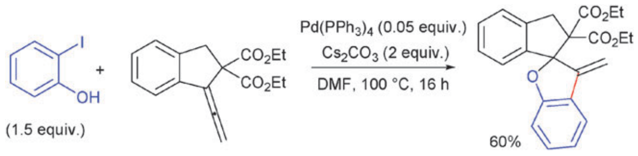

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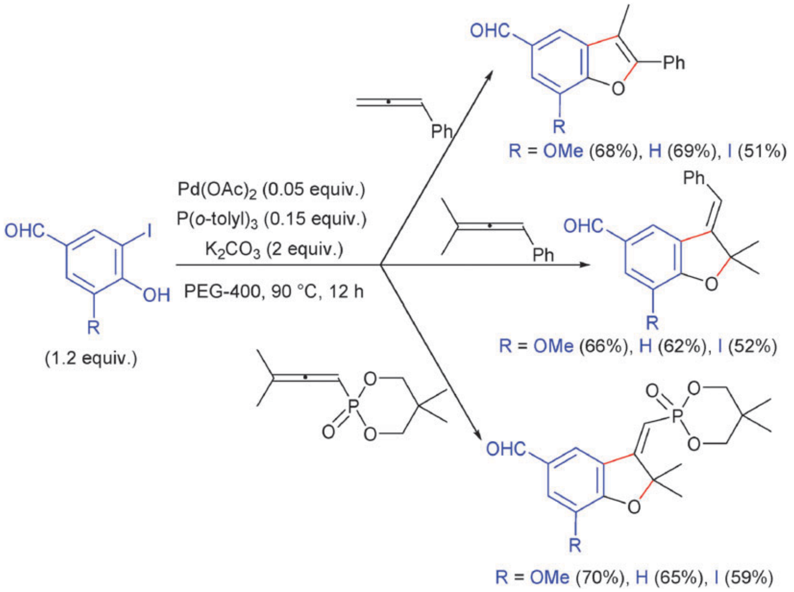
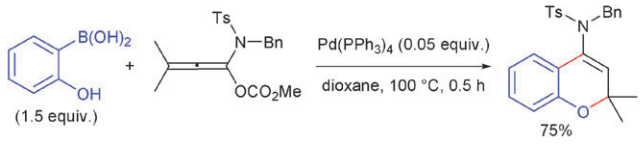


(24)

(25)

(26)

Recently, Cao and co-workers obtained a 4-amino-2*H*-chromene from the addition of 2-hydroxyphenylboronic acid to an 1-alkoxycarbonyloxy allenamide (eqn (27)).[28] The proposed mechanism involves the allenylpalladium intermediate **6A**, which undergoes a transmetalation reaction with the boronic acid to afford **6B** (Scheme 6). Reductive elimination of Pd^0 from the latter provides **6C**. According to the authors, **6C** undergoes spontaneous oxycyclisation leading to the aminochromene. We however suspect that this intramolecular hydroaryloxylation is mediated by the catalyst, as exemplified with the intermolecular reaction depicted in eqn (10).



(27)

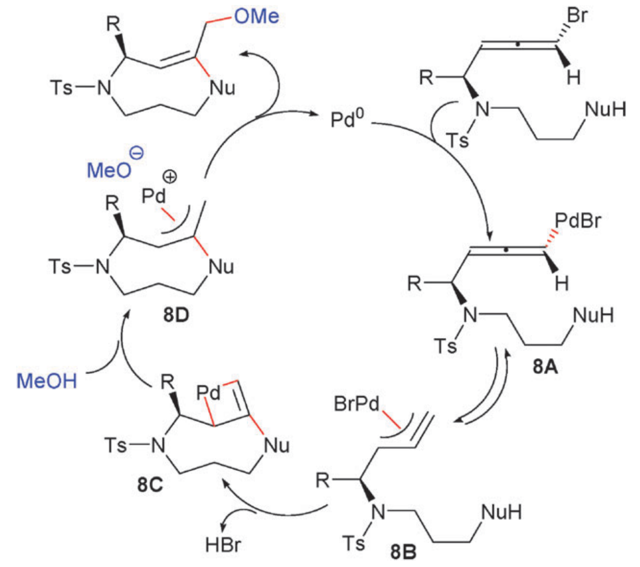
Grigg and co-workers disclosed a three-component reaction leading to isoxazolidines, which involves the successive addition of an aryl iodide and *N*-(2-hydroxybenzylidene)methanamine oxide to allene, followed by 1,3-dipolar cycloaddition of the nitrone to the C═C bond (eqn (28), Scheme 7).[29]

(28)

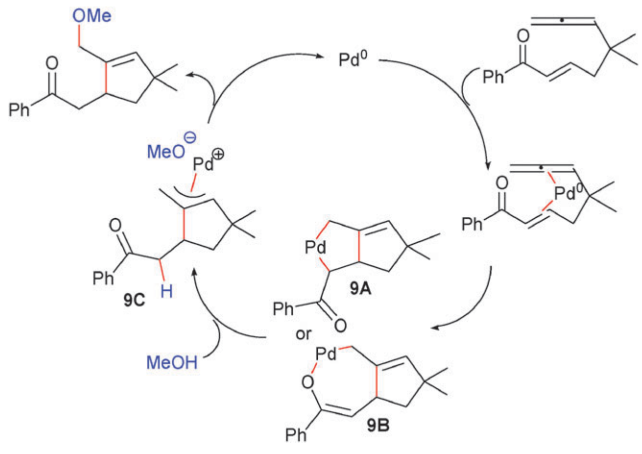
3.6. Other carboalkoxylations

Tanaka *et al.* used the equivalence of 1-bromoallenes to allyl dications to synthesise eight-membered heterocycles from 1-bromoallenes bearing a carbon nucleophilic functionality (eqn (29)).[30] The proposed mechanism implies the insertion of Pd^0 into the C–Br bond (Scheme 8). The resulting η^1-allenylpalladium complex **8A** is in equilibrium with the η^3-propargylpalladium **8B**, intramolecular nucleophilic addition to the central atom of the latter giving the palladocyclobutene **8C**. Protonation of **8C** by methanol generates the η^3-allylpalladium intermediate **8D**, attack of the methoxide to the terminal carbon of which delivers the organic compound and regenerates the catalyst.[30,31]

Pd^0-catalysed annelation of the allenylenone of eqn (30) would occur through the formation of the palladacycle **9A** or **9B** (Scheme 9), their protonation by methanol affording the η^3-allylpalladium complex **9C**, which, as above, is attacked by the methoxide.[32]



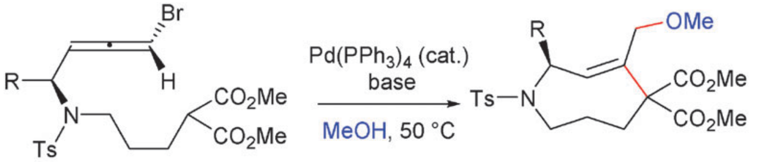
Scheme 8



Scheme 9

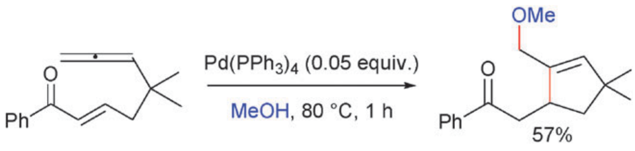
3.7. Aminoalkoxylation

The intramolecular Pd^0-catalysed aminopalladation of 1-bromoallenes 3-substituted with a nucleophilic six- or seven-membered amino-tether can be followed by addition of methoxide (eqn (31) and (32)), *via* a mechanism similar to that of Scheme 8.[30,33,34]

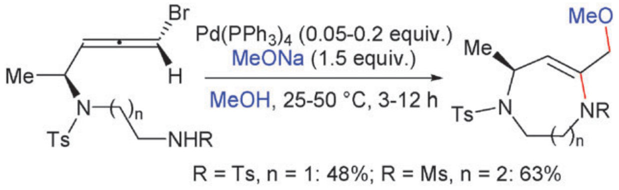


(29)

R = Me, $Pd(PPh_3)_4$ (0.2 equiv.), MeONa (1.5 equiv.), MeOH, 50 °C, 3 h: 56%
R = Bn, $Pd(PPh_3)_4$ (0.1 equiv.), NaH (1.5 equiv.), MeOH/THF (1:1), 50 °C, 4 h: 31%



(30)



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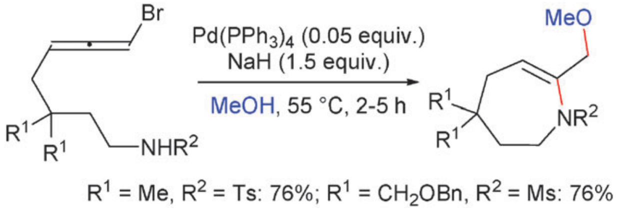
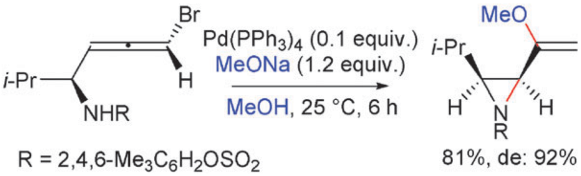


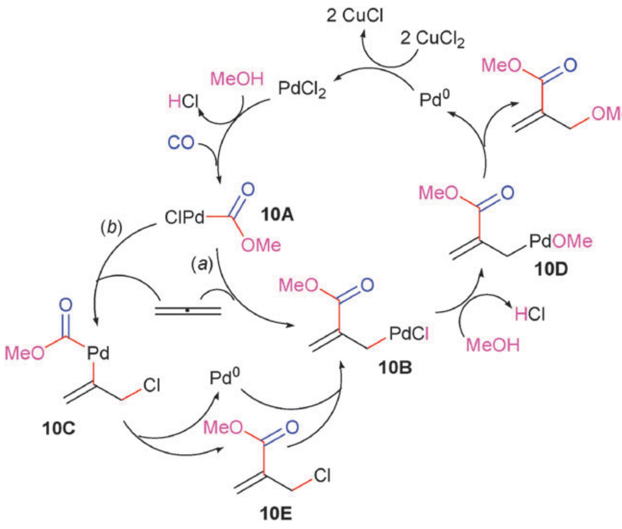
(32)

A different order of the steps would be involved when the nucleophilic amino group is located at the 4-position, the addition of the methylate to the central atom of the allene preceding the cyclisation reaction (eqn (33)).[33]



(33)

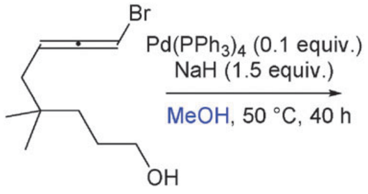
These reactions, which involve the addition of two nucleophilic species, differ from those depicted in Scheme 1 and are due to the bromoallene/allyl dication equivalence.



Scheme 10

3.8. Dialkoxylation

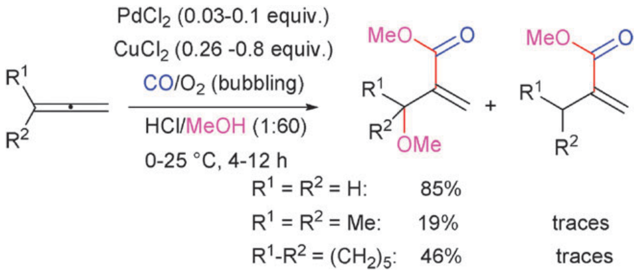
In contrast to the reaction depicted in eqn (29), the Pd^0-catalysed reaction of the hydroxy-tethered 1-bromoallene of eqn (34) with methanol led to the dimethoxylation of the allenyl moiety instead of the eight-membered ring, although the experimental conditions were similar.[30]



(34)

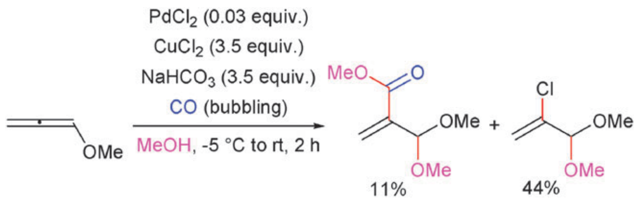
3.9. Alkoxy–alkoxycarbonylation

Alper's team disclosed the effective synthesis of methyl 2-methoxymethylacrylate from allene under Pd^{II}-catalysed carbonylation conditions (eqn (35)).[35] This methoxy–methoxycarbonylation reaction also occurs from 1,l-disubstituted allenes but with lower yields (eqn (35)). Different, but less efficient, experimental conditions have been reported by Trofimov *et al.* (eqn (36)).[36] Various possibilities for the catalytic cycle of the methoxy–methoxycarbonylation can be envisaged from the authors' proposals, all of them involving the methoxycarbonylpalladium chloride **10A** as the key intermediate reacting with the 1,2-diene to afford **10B** or **10C** (Scheme 10).[36b,37] The reaction of **10B** with methanol would lead to the methoxypalladium complex **10D**, which would suffer the reductive elimination of



(35)

(36)



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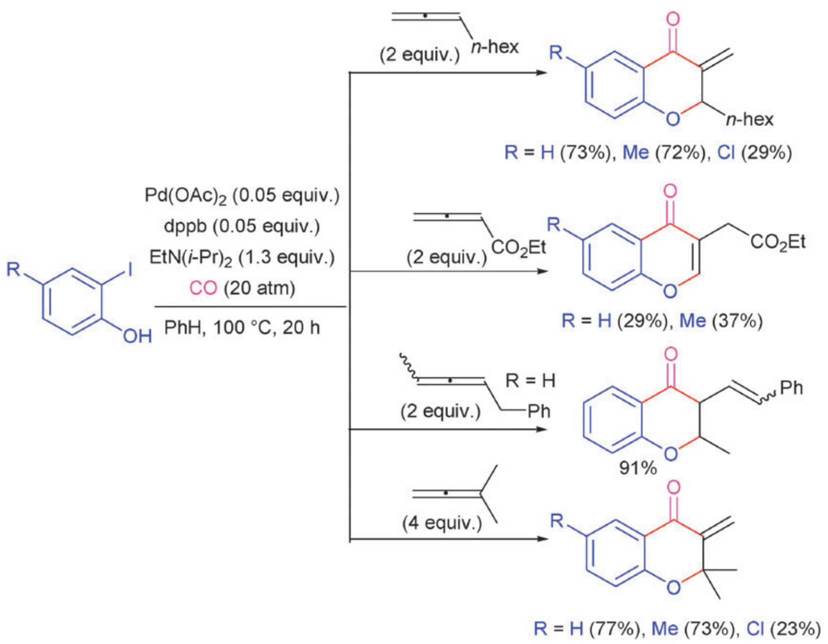


(38)

(39)

(40)

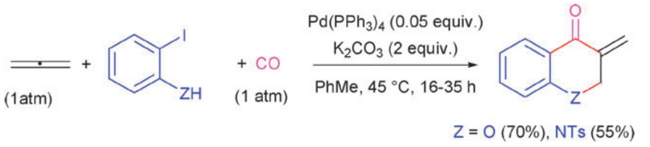
(41)

Pd^0 giving the product. From **10C**, the reductive elimination of Pd^0 leading to the allylic chloride **10E** would be followed by reinsertion of Pd^0 into the C–Cl bond to give **10B.** With methoxyallene as the substrate, Trofimov's procedure affords 2-chloro-3,3-dimethoxyprop-1-ene as the main compound (eqn (37)) through a mechanism which would only involve Cu^{II} catalysis.[37]

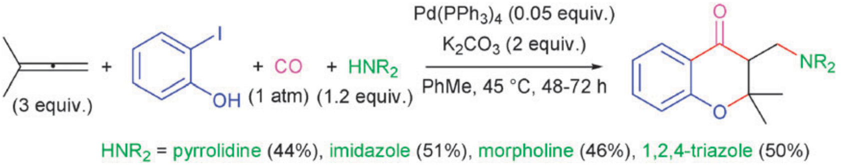
3.10. Aryloxy–aroylation

Q6 Under carbon monoxide pressure and basic conditions, the Pd^0-catalysed reaction of *o*-iodophenols with allenes provides 3-methylene-2,3-dihydro- or 3-vinyl-4*H*-1-benzopyran-4-one derivatives in fair to high yields (eqn (38) to (41)).[38] As a possible mechanism, Alper and Okura suggested the Pd^0-catalysed carbonylation of the iodophenol to afford the corresponding aroylpalladium complex, which undergoes addition to the central atom of the allenyl unit to give a η^3-allylpalladium intermediate. Addition of the phenolate to the latter leads to the annelation product.

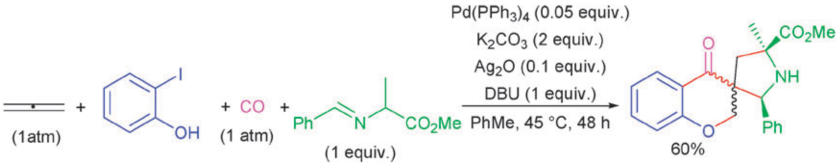
A similar three-component reaction, but employing carbon monoxide at atmospheric pressure, has been reported by Grigg's team to synthesise 3-methylene-4-chromanone and 3-methylene-1-tosyl-2,3-dihydroquinolin-4-one (eqn (42)).[39] Moreover, such domino reactions have also been carried out in the presence of



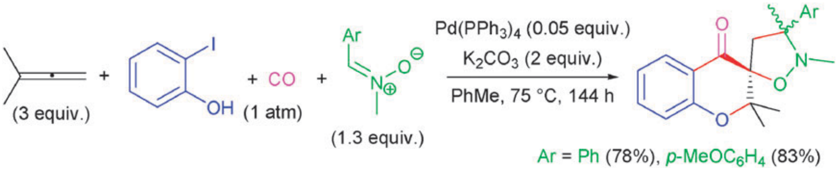
(42)



(43)



(44)



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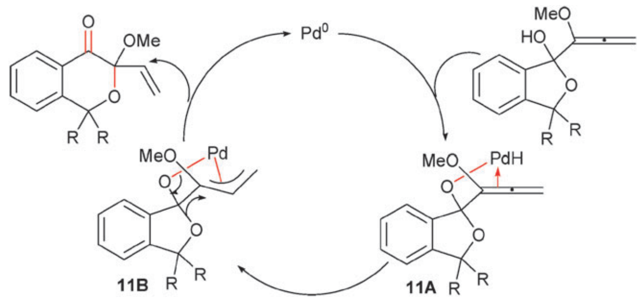
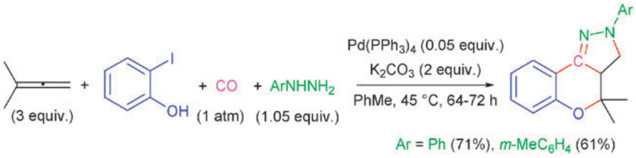


Scheme 11

nucleophilic amines realising an *in situ* Michael addition (eqn (43)),[39] or additives leading to 1,3-dipolar cycloaddition (eqn (44) and (45)) or cyclocondensation products (eqn (46)).[40]

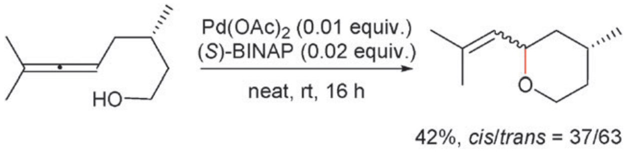


(46)

4. Intramolecular etherification

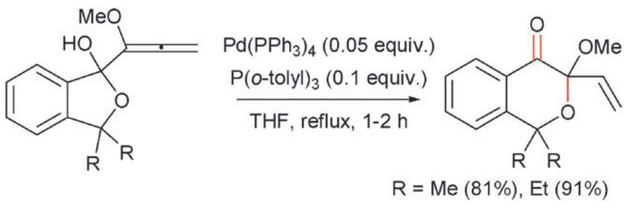
4.1. Hydroalkoxylation

Yamamoto and co-workers synthesised optically active rose oxides *via* the hydroalkoxylation of (3*R*)- and (3*S*)-3,7-dimethyl-6,7-octadien-1-ol catalysed by chiral Pd species (eqn (47)).[41]

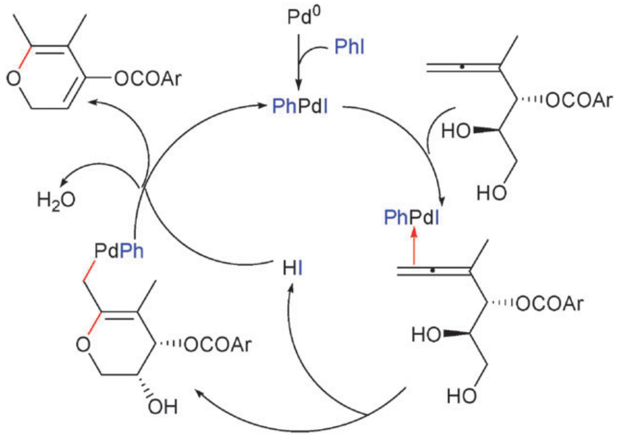


(47)

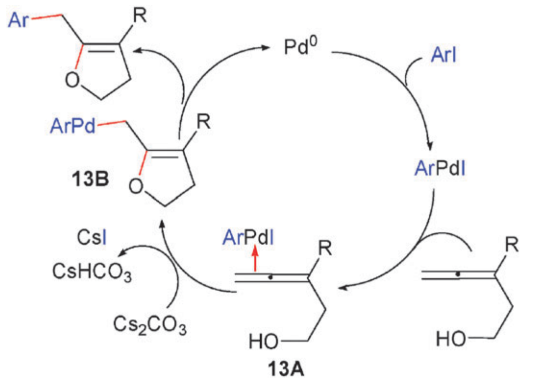
The Pd^0-catalysed ring expansion of hydroxy methoxyallenylphthalans depicted in eqn (48) has been reported by Nagao and co-workers.[42] A likely mechanism implies the hydridopalladium intermediate **11A**, which generates the η^3-allylpalladium complex **11B** (Scheme 11). The rearrangement of the latter affords the one-atom ring expanded product and the starting catalyst.[42]



(48)

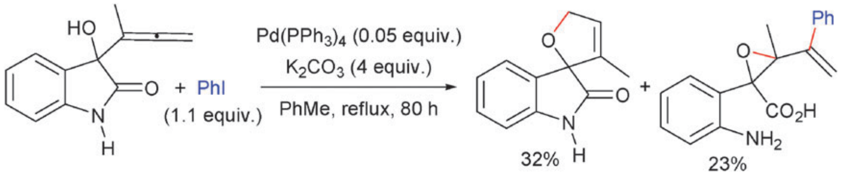


Scheme 12

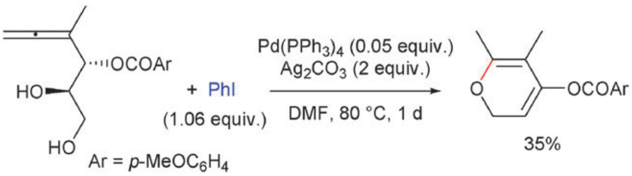


Scheme 13

The Alcaide–Almendros team has observed unexpected hydroalkoxylations when studying the alkoxyarylation of 3-hydroxy-3-(1-methyl-1,2-propadienyl)-2-indolinone (eqn (49))[43] and 1-(1-methyl-1,2-propadienyl)-2,3-dihydroxypropyl *p*-methoxybenzoate (eqn (50)).[44,45] We suspect that PhI plays a role in the formation of the six- and five-membered rings. PhI would react with the Pd^0 catalyst to afford PhPd^{II}I, which promotes the nucleophilic addition of the alcohol in activating the allenyl moiety. This cycloetherification leads to the intermediate corresponding to **1G** (Scheme 1), its subsequent protonolysis liberating the organic compound and PhPd^{II}I. The synthesis of 5,6-dimethyl-2*H*-pyran-4-yl *p*-methoxybenzoate (eqn (50)) arises from the unusual alkoxylation of the central atom of the allene, followed by protonolysis and dehydration (Scheme 12).[44,45]



(49)



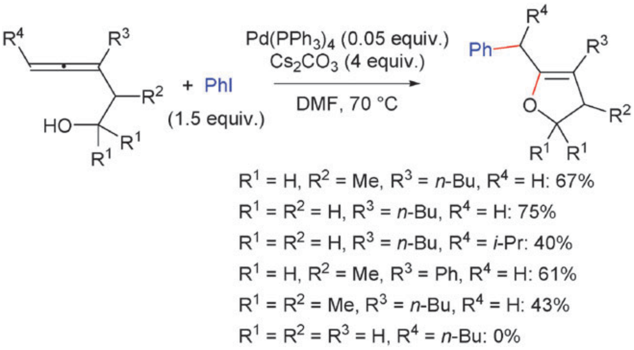
(50)

4.2. Oxyarylation

4.2.1. From allenols. In 1993, Walkup's team disclosed the synthesis of 2-substituted-5-(1-arylvinyl)-tetrahydrofurans from 6-substituted-1,2-dien-6-ols and aryl halides (eqn (51)).[46] The authors proposed that the oxypalladation precedes the formation of the C–Ar bond (as in Scheme 1, path *a*), which contrasts with the proposal from Tsuji[47] and Cazes.[48,49]

(51)

The oxypalladation of 3-substituted-1,2-dien-5-ols with phenyl iodide affords 5-benzyl-2,3-dihydrofurans (eqn (52)) in yields depending on the nature of both the base and the solvent.[50] The cyclisation product was not obtained in the absence of a substituent in C-3 (eqn (52)). The course of these reactions greatly differs from that of the reactions depicted in eqn (51), since the C–Ar bond is formed with the terminal instead of the central carbon of the allene. Ma and Gao proposed the intermediates shown in Scheme 13, the C–O bond formation occurring *via* the 5-*exo-dig* cyclisation of the complex **13A**, and the C–Ar *via* the reductive elimination of Pd^0 from **13B**.



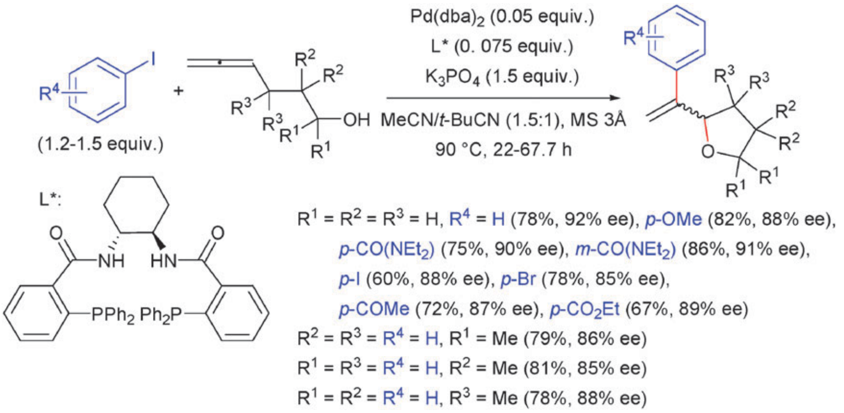
(52)

Recently, Ma and Xie reported the asymmetric coupling-oxycyclisation of γ-allenols with aryliodides with ee up to 92% (eqn (53)).[51] The proposed mechanism implies the arylpalladation of the allenyl group, and the nucleophilic attack of the hydroxyl to the resulting chiral η^3-allylpalladium intermediate.

The unusual regioselectivity of the oxycyclisation–arylation of the above β-hydroxyallenes (eqn (52)) does not seem to arise from the number of carbons between the allene and the hydroxyl groups, because the oxycyclisation–arylation of γ-hydroxyallenes (eqn (51)) and α-hydroxyallenes occurs with the same regioselectivity, giving the corresponding (1-arylvinyl)oxiranes under similar conditions (eqn (54)).[52] Instead of DMF, which, according to Ma's reports,[50,52] would be the optimum organic solvent, Ihara and co-workers used water with a water-soluble ligand and sodium dodecyl sulphate (SDS) (eqn (55)).[53]

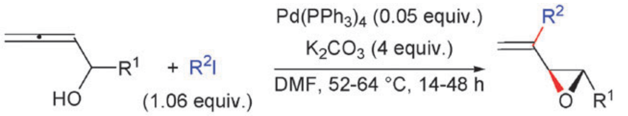
(1-Arylvinyl)oxiranes have also been obtained from α-hydroxyallenes using hypervalent iodonium salts such as diphenyliodonium tetrafluoroborate, instead of aryl iodides (eqn (56)).[54] With such arylating species, Kang's team has also synthesised 2-(1-arylvinyl)-tetrahydrofuran(pyran)s from 1,2-dien-6(or 7)-ols (eqn (57)).[55] Both catalytic cycles, *i.e.* addition of the hydroxy group to a η^3-allylpalladium intermediate or to the Pd-activated allenyl moiety, have been considered as plausible by the authors.[55]

The Alcaide–Almendros team observed the formation of both five- and three-membered rings from the reaction of phenyl iodide with 3-hydroxy-3-(1-methyl-1,2-propadienyl)-2-indolinone (eqn (49))[43] or 3-hydroxy-3-(1-methyl-1,2-propadienyl)-2-azetidinone (eqn (58)).[56] The absence of phenylation of the five-membered ring obtained from the hydroxylindolinone (eqn (49)) is not discussed by the authors. They nevertheless suggested that the cleavage of the β- or γ-lactam



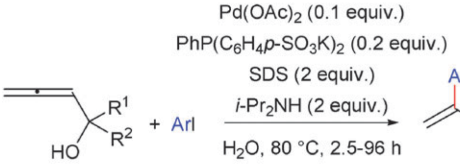
(53)

nucleus concomitant with the formation of the oxirane is probably due to the ring strain of the spirocyclic systems.



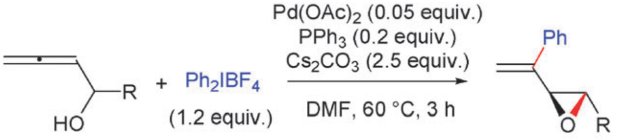
R^1 = n-Bu, R^2 = Ph (71%, dr = 96:4), p-$MeOC_6H_4$ (71%, dr = 97:3),
E-PhCH=CH (65%, dr = 92:8)
R^1 = Ph, R^2 = p-$MeOC_6H_4$ (66%, dr = 92:8), p-MeC_6H_4 (55%, dr = 95:5)
R^1 = n-oct., R^2 = Ph (78%, dr = 98:2), p-BrC_6H_4 (46%, dr = 99:1),
E-1-hexenyl (59%, dr > 99:1)

(54)



Ar = Ph { R^1 = Me, R^2 = Ph (70%); R^1 = R^2 = C_3H_7 (74%); R^1 = R^2 = C_5H_{11} (54%); R^1 = R^2 = Ph (72%)
R^1-R^2 = cyclohexyl { Ar = Ph (83%), p-MeC_6H_4 (33%), p-AcC_6H_4 (69%), p-$NO_2C_6H_4$ (86%), p-$MeOC_6H_4$ (32%)

(55)



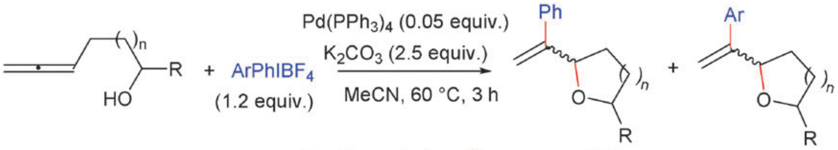
R = Ph (60%), 2-furyl (63%), 2-thienyl (51%),
Cy (62%), i-Pr (59%), n-pent. (65%)

(56)

In contrast to the results depicted in eqn (49) and (58) obtained with phenyl iodide, the arylation of these substrates with arylboronic acids proceeds selectively (eqn (59) and (60)).[57] According to the authors, the Suzuki-type reaction occurs after the heterocyclisation.

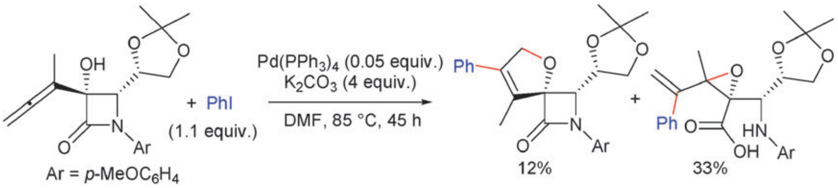
The fully intramolecular oxyarylation shown in eqn (61) has been disclosed by Grigg and co-workers, who proposed a reaction occurring *via* the 6-*exo-dig* carbocyclisation of the ArPdI species onto the allenyl unit, followed by the interception of the resulting η^3-allylpalladium complex by the alcoholate.[58]

4.2.2. From allenyl alkyl ketones. The selectivity of the phenylation of heptadeca-3,4-dien-2-one highly depends on the reaction conditions. In toluene containing triethylamine, $Pd(PPh_3)_4$ catalysis leads to an almost equimolecular mixture of 2-dodecyl-5-methyl-3-phenylfuran and 2-dodecyl-5-methylfuran



(57)

R = H, n = 1, Ar = Ph: 76%
R = Me, n = 1, Ar = Ph: 72%
R = H, n = 2, Ar = Ph: 74%
R = H, n = 1, Ar = p-$MeOC_6H_4$: 35% 44%
R = H, n = 2, Ar = p-$MeOC_6H_4$: 23% 50%



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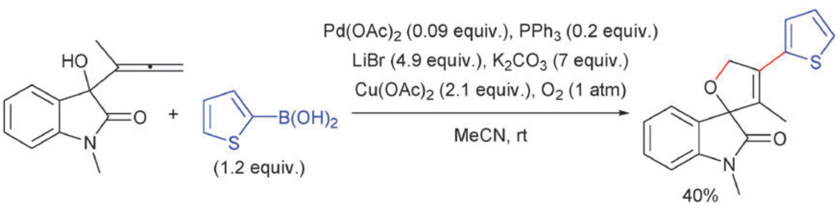

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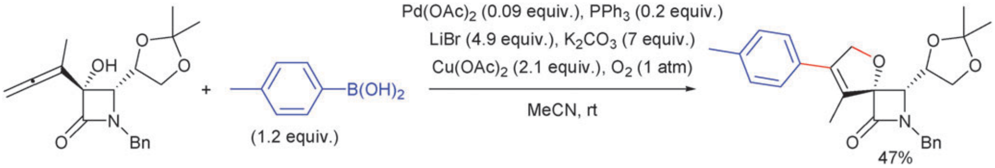
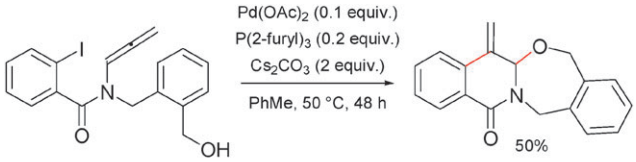
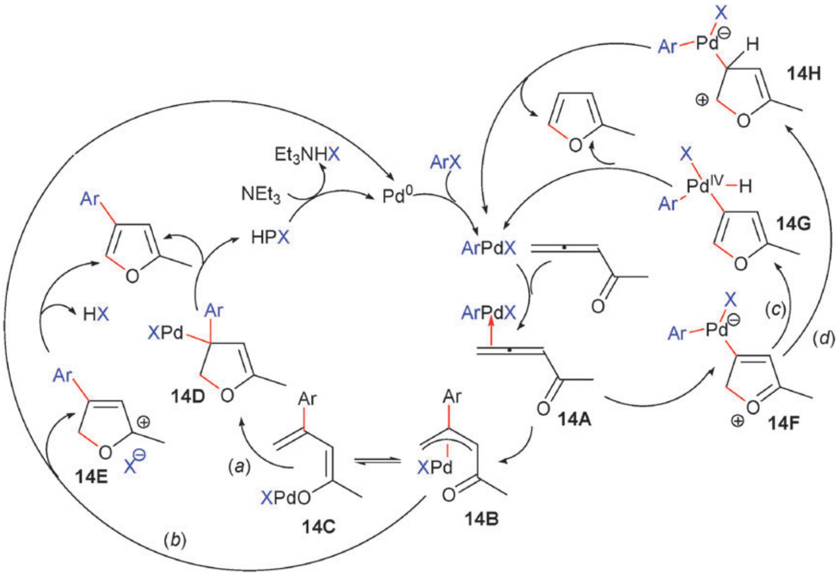


(60)

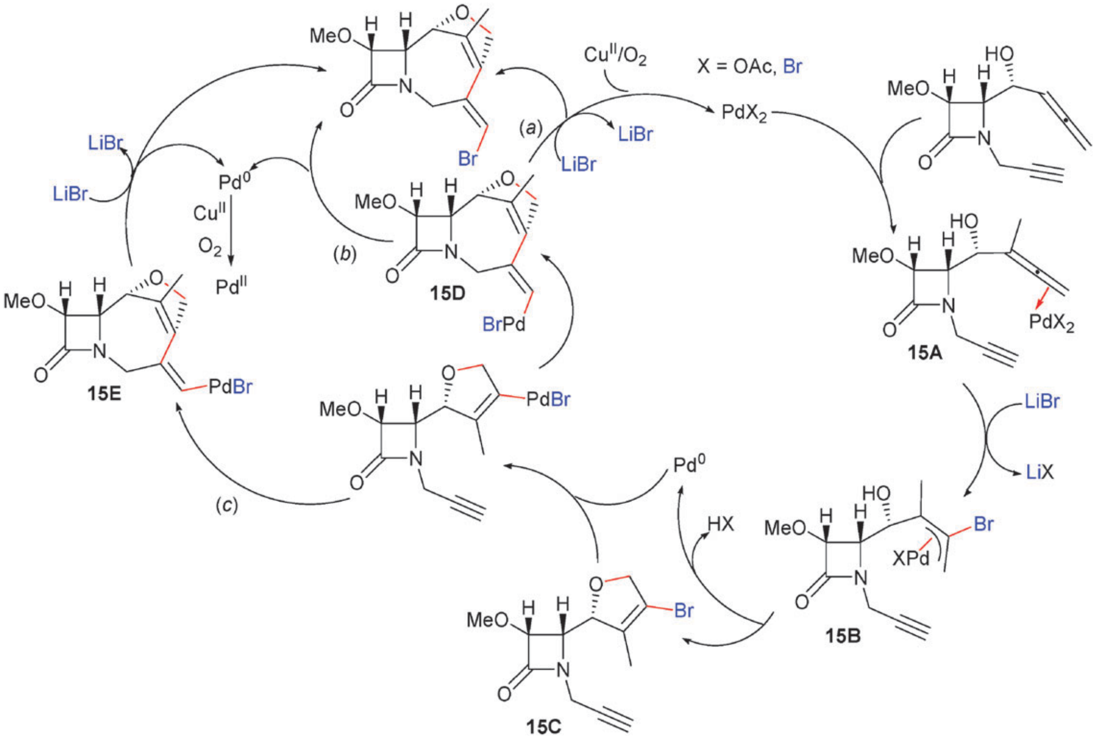


(61)

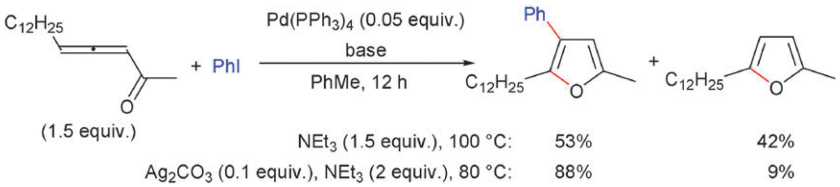
(eqn (62)).[59,60] Co-catalysis with Ag_2CO_3 greatly increased the selectivity towards the cross-coupling adduct (eqn (62)). Thus, this $Pd(PPh_3)_4/Ag_2CO_3$ catalytic system has been used for the synthesis of various trisubstituted (hetero)arylfurans (eqn (63)). In contrast, tetrasubstituted arylfurans were better obtained using catalytic amounts of $Pd(PPh_3)_4$ and n-Bu_4NBr in DMA containing K_2CO_3 (eqn (64)).[60] From control reactions, Ma's team retains two possible catalytic cycles for the synthesis of the cross-coupling compounds (Scheme 14);[60] both involve the coordination of ArPdX to the allene to generate **14A** followed by



Scheme 14



Scheme 15

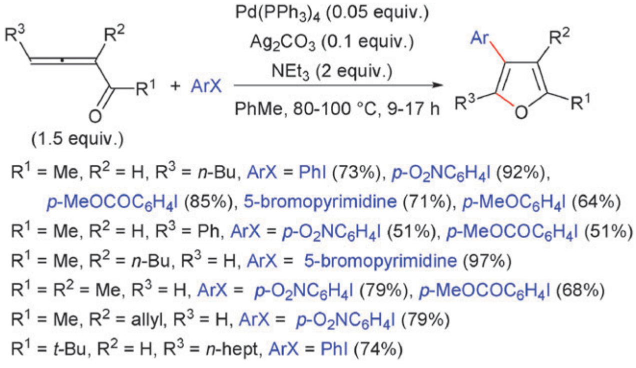


(62)

the insertion reaction leading to the η^3-allypalladium complex **14B**. Equilibrium of the latter with the palladium dienolate **14C** could promote the 5-*endo-trig* heterocyclisation leading to **14D** (path *a*), subsequent β-H elimination liberating the arylfuran. The other possibility is the direct intramolecular nucleophilic attack on **14B** by the carbonyl oxygen atom to afford **14E** and Pd^0 (path *b*). Base-mediated deprotonation of **14E** would yield the arylfuran. As for the non-arylated product, it appears from a cycloisomerisation reaction. Reports from the teams of Marshall[61] and Hashmi[62,63] led us to suggest two catalytic pathways diverging from **14F** for its formation. This mutual intermediate would arise from the oxygen attack on the η^2-palladium complex **14A**. β-H elimination from **14F** would generate the Pd^{IV} intermediate **14G** (path *c*), subsequent reductive elimination giving ArPdX and the furan. This compound could also be obtained from **14H**, the latter resulting from **14F** *via* a 1,2-H-shift (path *d*).

4.3. Oxyvinylation

4.3.1. From allenols. The intermolecular reaction of vinylic halides with α- and γ-allenyl alcohols has led to the corresponding epoxides (eqn (54))[52] and tetrahydrofurans (eqn (51))[46] substituted by a 1,3-dienic tether, the oxycyclisation-cross-coupling of an optically active α-allenyl alcohol occurring without loss of chirality (eqn (65)).[52]



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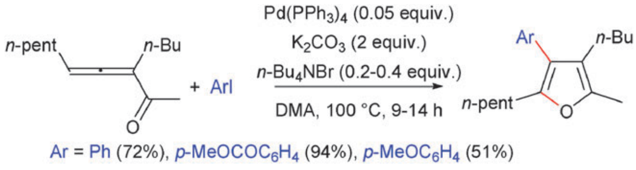
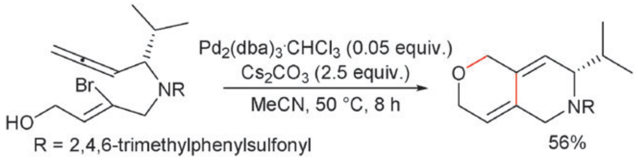


(64)

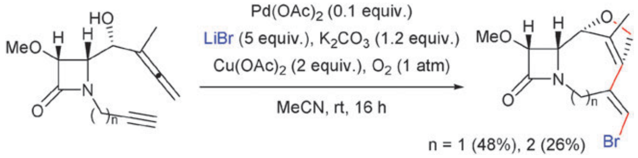
(65)

The Ohno–Fujii team disclosed the intramolecular alkoxyvinylation of a substrate containing three reactive species, that is the allene, the vinylic bromide and the alcohol (eqn (66)).[64] The catalytic cycle would entail the addition of the vinylic palladium bromide to the central allene carbon, followed by intramolecular alcoholate attack of the resulting η^3-allylpalladium complex.[64]



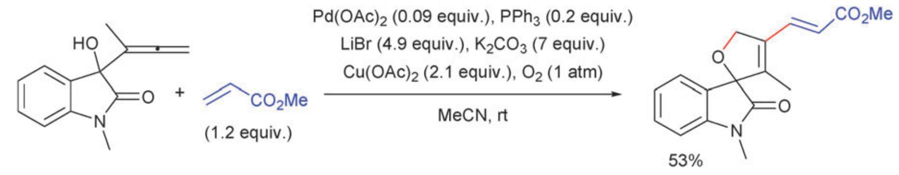
(66)

In the presence of lithium bromide and potassium carbonate, the Pd^{II}-catalysed reaction of acetylene-linked allenyl alcohols can afford bridged tricyclic β-lactams bearing a vinylbromide substituent as shown in eqn (67).[65] Alcaide and coworkers proposed that this domino reaction implies the addition of bromide to the allenepalladium complex **15A** to give the η^3-allylpalladium complex **15B**, which suffers the intramolecular alkoxy addition leading to **15C** (Scheme 15). Insertion of Pd^0 into the C–Br bond of this five-membered intermediate is followed by a Heck-type addition to the C≡C bond giving **15D**. According to the authors, the product is obtained from the trapping of **15D** by the bromide anion (path *a*).[65] In fact, **15D** could liberate the isolated compound through the reductive elimination of Pd^0 (path *b*). We also suspect that the *exo-dig* cyclisation could lead to **15E** rather than to **15D**, its S_N2 by the bromide anion giving the product and Pd^0 (path *c*).

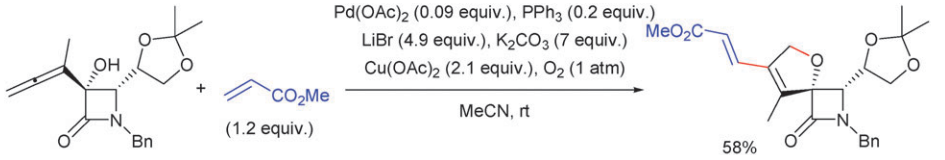


(67)

The vinylation can arise from the reaction with methyl acrylate as reported by the Alcaide–Almendros team in 2005 (eqn (68) and (69)).[57] These syntheses would proceed through

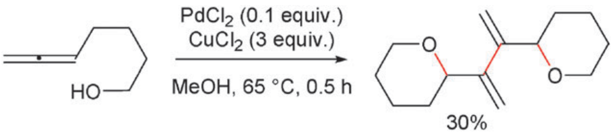


(68)



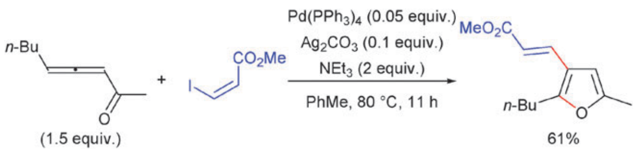
(69)

successive Wacker-type and Heck-type reactions and regeneration with Cu(OAc)$_2$/O$_2$ of the catalyst required for the heterocyclisation. In fact, such an intramolecular oxypalladation followed by addition to methyl acrylate was reported, as early as 1992 by Gallagher *et al.*, using hepta-5,6-dien-1-ol as the substrate but in a low yield and with a stoichiometric amount of PdCl$_2$.[66] Using the same substrate but under catalytic oxidative conditions, Gallagher *et al.* obtained a dimerisation reaction (eqn (70)), which could be considered as the addition of a vinylic system to the oxypalladation intermediate.[66]

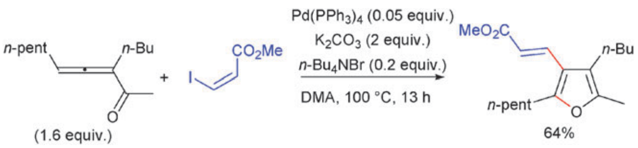


(70)

4.3.2. From allenyl alkyl ketones. The cross-coupling-cyclisation reaction of nona-3,4-dien-2-one with methyl (*Z*)-3-iodoacrylate (eqn (71)) efficiently arises with the Pd(PPh$_3$)$_4$/Ag$_2$CO$_3$ catalytic system already used for the arylation-cyclisation of this substrate (eqn (63)).[59,60] As above (eqn (64)), a modified procedure was favoured when both α- and γ-positions of the allenyl ketone were substituted (eqn (72)).[60]

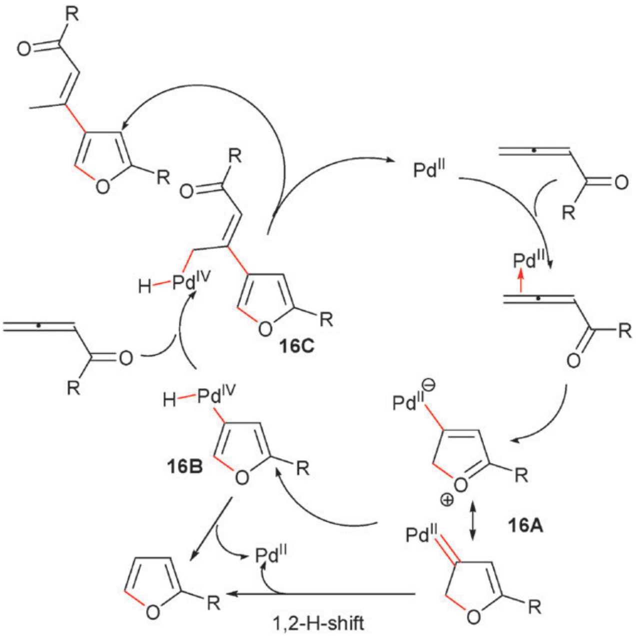


(71)



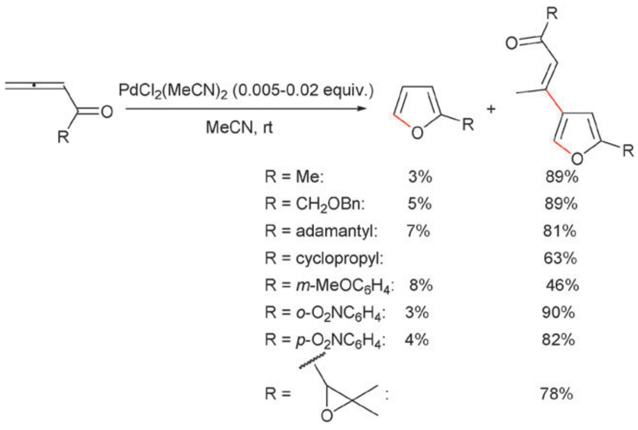
(72)

A vinylic substitution in C-4 of furans can arise from the Pd-catalyzed dimerisation of terminal allenyl ketones disclosed by Hashmi's team. In most cases, these reactions lead to minor amounts of the cycloisomerisation compound (eqn (73)).[63,67,68]



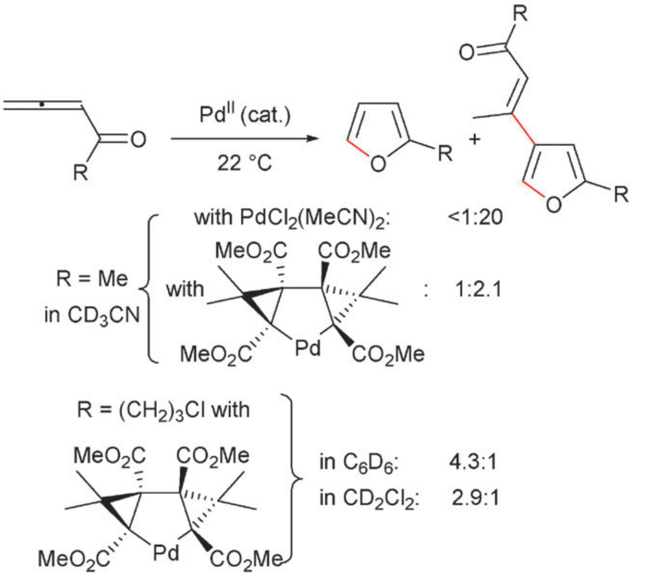
Scheme 16

Nevertheless, the selectivity can greatly depend on the nature of the catalyst, the solvent and the carbonyl substituent as exemplified in eqn (74).[69] Complete inhibition of the dimerisation



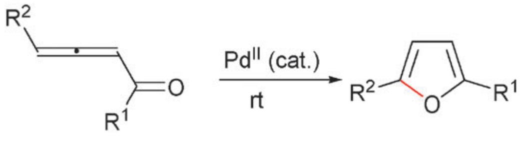
R = Me:	3%	89%
R = CH$_2$OBn:	5%	89%
R = adamantyl:	7%	81%
R = cyclopropyl:		63%
R = m-MeOC$_6$H$_4$:	8%	46%
R = o-O$_2$NC$_6$H$_4$:	3%	90%
R = p-O$_2$NC$_6$H$_4$:	4%	82%
R = :		78%

(73)



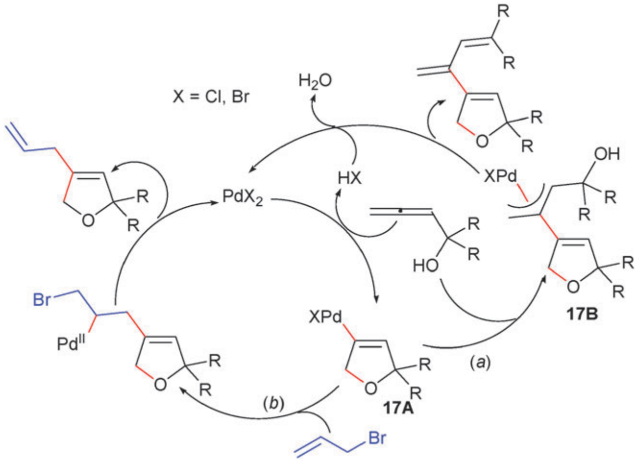
(74)

reaction has been observed from a γ-substituted allenyl ketone[62] or aldehyde[69] (eqn (75)). From the investigation of various plausible reaction pathways, the authors prioritized the catalytic cycle depicted in Scheme 16.[63] The oxypalladation of the allene moiety provides **16A,** which could have the structure of either a σ-Pd complex or a carbene palladium complex. This intermediate could lead to the hydridopalladium^{IV} complex **16B** *via* a β-H elimination, or to the 2-alkylfuran *via* a 1,2-hydrogen-shift. The 2-alkylfuran could also be produced by reductive elimination from **16B**. The latter could also carbonylate the terminal C=C bond of another molecule of the substrate to afford another hydridopalladium^{IV} complex (**16C**), reductive elimination of Pd^{II} giving the dimeric product. The procedure has been, subsequently, used for the synthesis of macrocycles from diallenyldiketones (eqn (76)).[70]



(75)

R^1 = R^2 = Me or R^1 = H, R^2 = *n*-hex

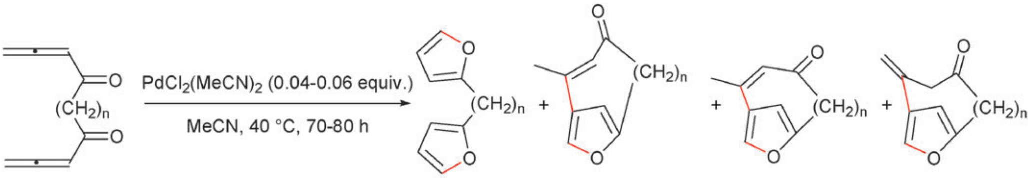


Scheme 17

4.3.3. From monoesters of allenyl phosphonic acids. Ma and co-workers reported the Pd^{II}-catalysed oxycyclisation-Heck reaction of ethyl allenylphosphonic acids with regeneration of the active catalytic species using either benzoquinone or a NaI/O$_2$/CaH$_2$ association (eqn (77)).[71]

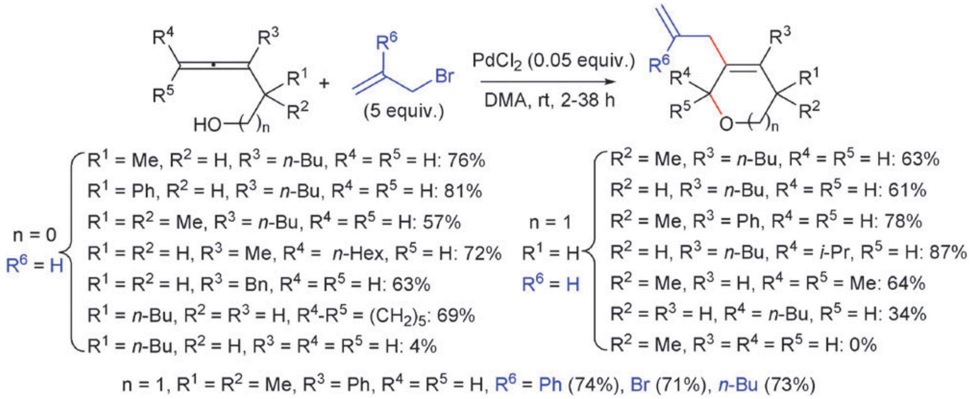
4.4. Oxyallylation

4.4.1. From allenols. To the best of our knowledge, Ma and Gao were the first to disclose the synthesis of 4-(2′-alkenyl)-2,5-dihydrofurans and 3-propenyl-5,6-dihydropyrans from the Pd^{II}-catalysed cyclisative coupling reaction of α- and β-hydroxyallenes with allylic halides (eqn (78) and (79)).[72,73] These domino reactions would proceed as underlined in Scheme 1, path *b*, and preserve the chirality of the substrate (eqn (80)).[74] With allyl bromide, the cyclisation-cross-coupling of 2-methylpenta-3,4-dien-1-ol was however not observed (eqn (78)), whereas that of 1-(propa-1,2-dienyl)cyclohexanol afforded 3-(1-cyclohexylidenemethylvinyl)-1-oxaspiro[4.5]dec-3-ene as the major product (eqn (81)), the palladium intermediate **17A** reacting with the substrate to give **17B** (Scheme 17, path *a*)

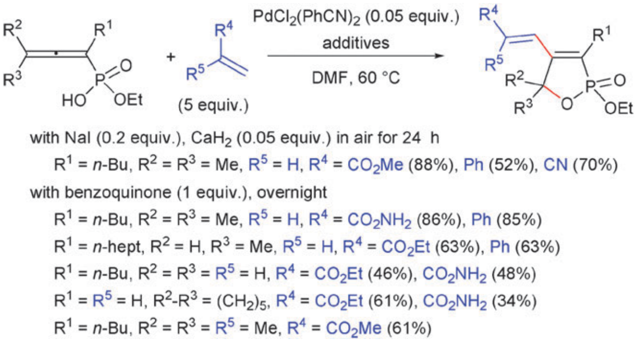


n = 6:	14%	1%	18%	4%
n = 7:	9%	1%	10%	6%
n = 8:	7%	1%	19%	11%
n = 9:	11%	5%	15%	13%
n = 10:	10%	24%	3%	2%
n = 11:	16%	35%	1%	2%
n = 12:	6%	28%		
n = 14:	7%	27%		

(76)

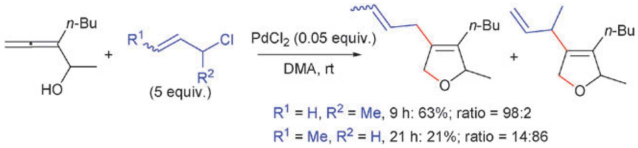


(78)

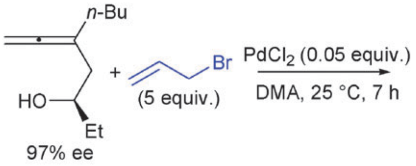


(77)

rather than with allyl bromide (Scheme 17, path *b*).[73] Subsequent β-OH elimination leads to the trienic system. According to the authors, this bimolecular cyclisative coupling is caused by the absence of a substituent on the allenyl moiety, hence its high reactivity. The effect of the substitution was also observed with octa-1,2-dien-4-ol, which gave the allylated heterocycle in only 4% yield (eqn (78)). It has been proposed that the substitution of the 1,2-dienyl unit results in steric hindrance favouring the reaction with allyl bromide at the expense of that with another molecule of allenol. This seems to agree with the results depicted in eqn (79): the Heck-type reaction with 3-chlorobut-1-ene occurs with a fair yield, while that with 1-chlorobut-2-ene is much less efficient.[72,73] Recently, the Ma's protocol, but in DMF instead of DMA, has been used by Bäckvall and Deng to synthesise the bicyclic compound shown in eqn (82).[75]

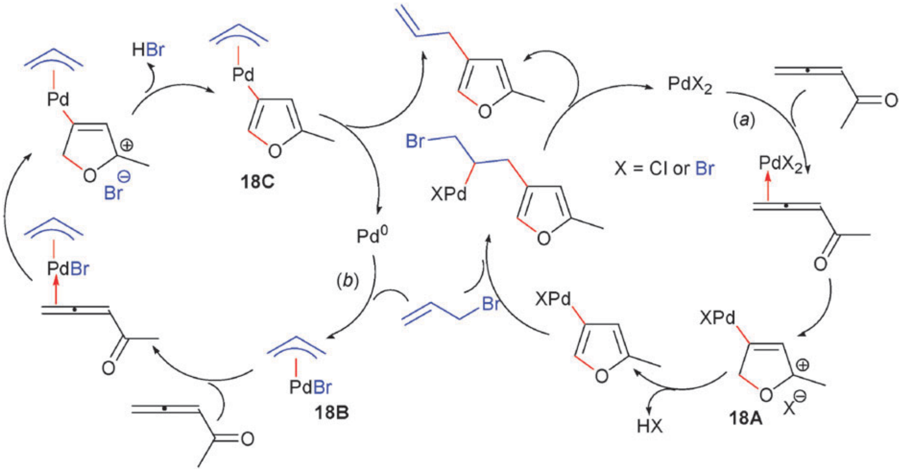


(79)

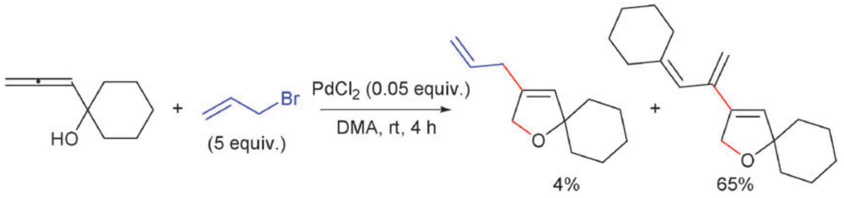


(80)

The Alcaide–Almendros team has generously exploited the above oxycyclisation-Heck addition procedure using, as substrates, lactams substituted by an allenyl alcohol (eqn (83)),[76] or an allenyl unit and either a hydroxy (eqn (84),[56] (85)[77–79] and (86)[43]) or a hydroxylated tether (eqn (87)[44]).

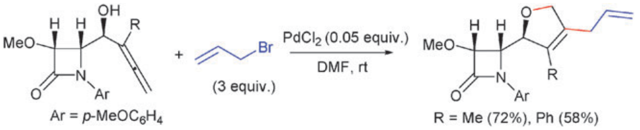


Scheme 18

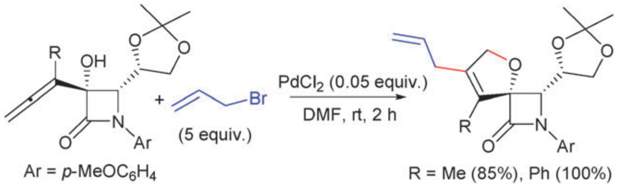


(81)

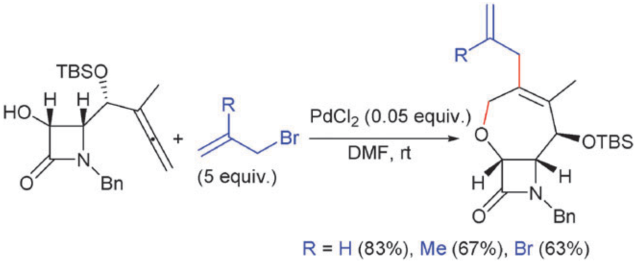
(82)



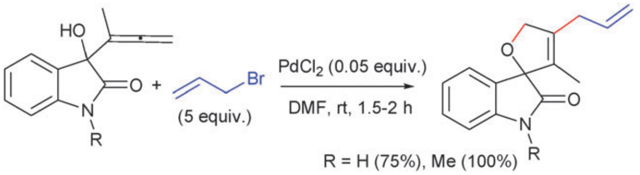
(83)



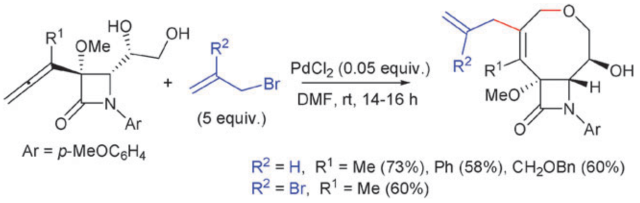
(84)



(85)

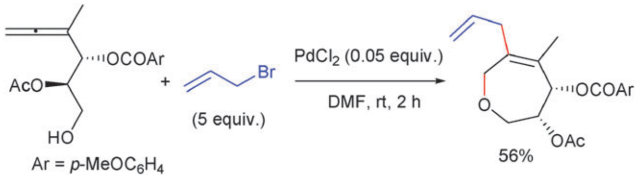


(86)



(87)

Allylated seven-membered heterocycles have been synthesized from a γ-allenol (eqn (88))[80] and a γ,δ-allendiol (eqn (89)).[45] From the comparison of the reactivity of a γ-allenol[80] and different allendiols,[45] we observed that the favoured Pd^{II}-catalysed oxycyclisations with one extremity of the allenyl moiety would be 5-*exo* rather than 6-*exo* or 7(or 8)-*endo* (eqn (90)), 6-*endo* rather than 4(or 5)-*exo* or 7-*endo* (eqn (91)), and 7-*endo* rather than 5(or 6)-*exo* or 8-*endo* (eqn (88) and (89)). It is however required to point out that this classification is made from substrates without substitution of the terminal carbon and with disubstitution of the other extremity of the allenyl unit.



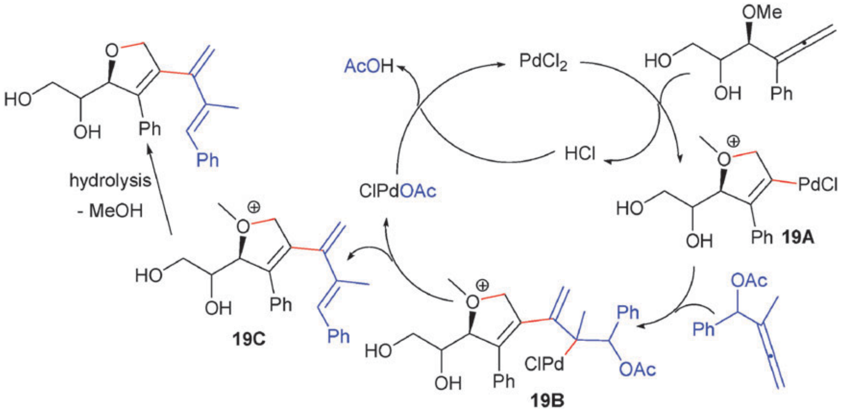
(88)

(89)

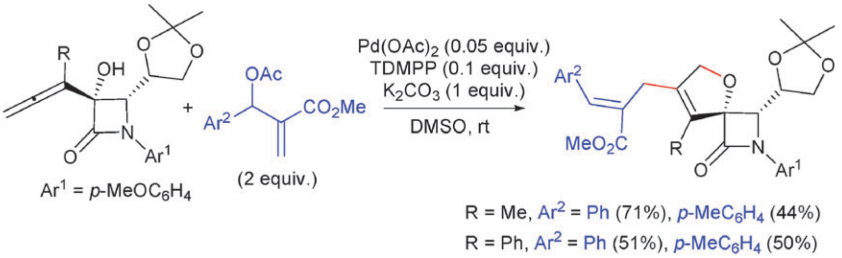
(90)

(91)

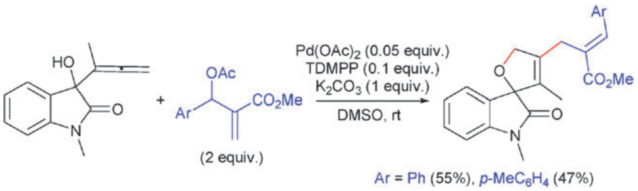
The Spanish team has also used Baylis–Hilman acetates instead of allyl halides to obtain spirocyclic lactams (eqn (92) and (93)).[81]



Scheme 19

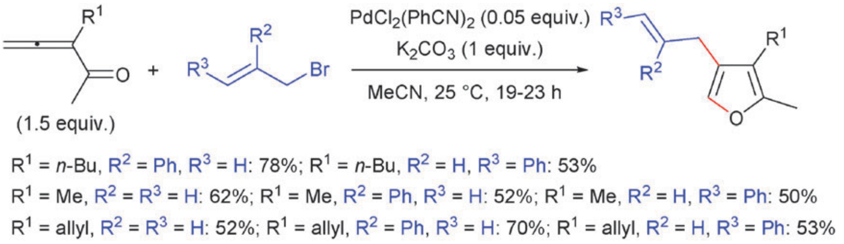


(92)

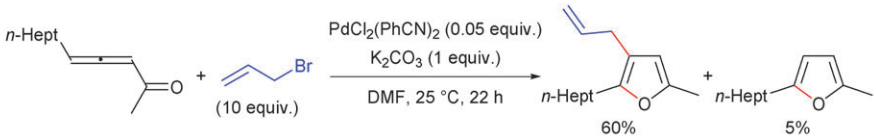


(93)

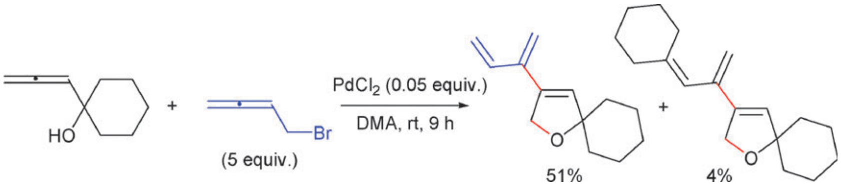
4.4.2. From allenyl alkyl ketones. Experiments under various conditions led Ma and Li to finalize the selective coupling-cyclisation reaction of 1-substituted 1,2-allenyl ketones with allylic bromides (eqn (94)).[82] The proposed procedure was less selective with a 3-substituted-1,2-dienyl ketone. Using a large excess of allyl bromide in DMF instead of MeCN, the expected product was nevertheless obtained in a fair yield (eqn (95)). These reactions, performed with a Pd^{II} catalyst, could happen as shown in Scheme 18, path *a*. Oxypalladation, mediated by



(94)



(95)



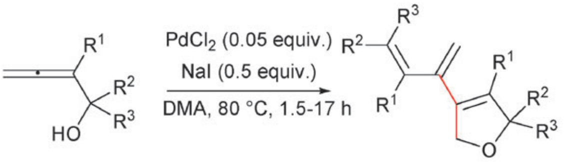
(96)

coordination of PdX$_2$ to the allene, would afford **18A**, elimination of HX followed by a Heck-type reaction giving the product.[60,82] Having also observed the reaction under Pd$_2$(dba)$_3$·CHCl$_3$ catalysis,[83] the authors proposed another plausible catalytic cycle (path *b*), which involves the activation of the allene by the η^3-allylpalladium **18B**. This would allow the oxypalladation reaction leading, after removal of HBr, to **18C**. This complex would undergo a reductive elimination to afford the product.

4.5. Oxydienylation

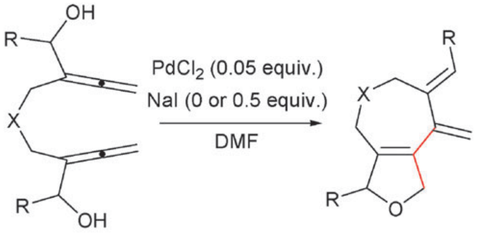
The cycloetherification-dienylation of allenols has been documented above with the bimolecular cyclisative coupling of 3-(1-cyclohexylidenemethylvinyl)-1-oxaspiro[4.5]dec-3-ene reported by Ma and Gao (eqn (81)). In the presence of 4-bromobuta-1,2-diene, the dienylation mainly occurs with this additive (eqn (96)).[73] This reaction occurs following a mechanism similar to the one depicted in Scheme 17, path *a*, the elimination involving the bromide atom instead of the hydroxyl group.

Ma and co-workers observed that the homodimeric coupling-cyclisation of 2,3-allenols easily occurs, even with a bulky substituent in C-2 (eqn (97)), and without racemisation of optically active substrates when PdCl$_2$ is associated to NaI as catalyst.[84] The authors proposed the *in situ* formation of PdI$_2$ to mediate the reaction. The PdCl$_2$/NaI catalytic system has then been used for the synthesis of 2,5-dihydrofuran-fused bicyclic skeletons from bisallenols, the addition of NaI being however not required when the allenol moieties are connected by a CH$_2$NTsCH$_2$ tether (eqn (98)).[85] Such a reaction also occurs when one hydroxyl group is protected as the acetate (eqn (99)).[85] This Chinese team used PdI$_2$ with a stoichiometric amount of BF$_3$·Et$_2$O in DMSO for the coupling–cyclisation of two different 2,3-allenols (eqn (100)).[86]



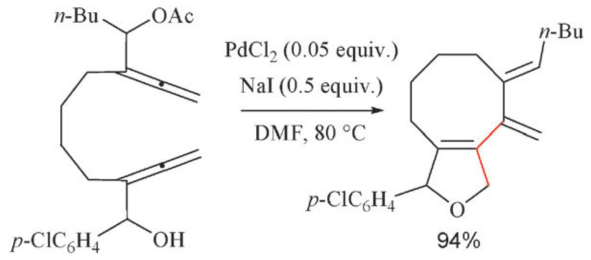
R^1 = H, R^2-R^3 = (CH$_2$)$_5$: 86%; R^1 = H, R^2 = R^3 = *n*-Bu: 92%
R^1 = H, R^2 = R^3 = Me: 66%; R^1 = *n*-Bu, R^2 = R^3 = H: 84%
R^1 = *n*-Bu, R^2 = Me, R^3 = H: 83%; R^1 = Ph, R^2 = *n*-Bu, R^3 = H: 75%
R^1 = CO$_2$Me, R^2 = Et, R^3 = H: 58%; R^1 = allyl, R^2 = Me, R^3 = H: 61%

(97)

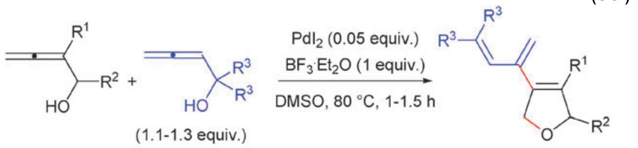


(98)

using PdCl$_2$ at 25 °C for 4 h
R = Et, X = NTs (62%), CH$_2$ (0%)
using PdCl$_2$ and NaI at 80 °C for 1-2 h
R = Et, X = CH$_2$ (58%), O (57%), SO$_2$ (81%)
R = *n*-Bu, X = CH$_2$CH$_2$ (68%)



(99)



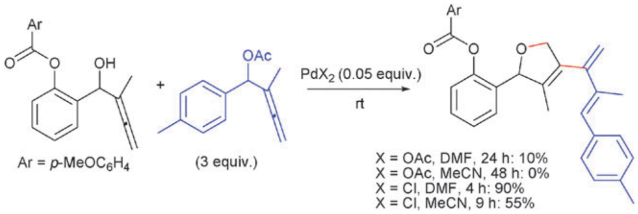
R^1 = *n*-Bu, R^2 = Et, R^3 = H: 57%; R^1 = *n*-Bu, R^2 = Ph, R^3 = H: 78%
R^1 = Ph, R^2 = *n*-Bu, R^3 = H: 70%; R^1 = allyl, R^2 = Me, R^3 = H: 49%
R^1 = CO$_2$Me, R^2 = *p*-MeC$_6$H$_4$, R^3 = H: 55%; R^1 = *n*-Bu, R^2 = *p*-O$_2$NC$_6$H$_4$, R^3 = Et: 50%

(100)

As for the Alcaide–Almendros team, it obtained various functionalized buta-1,3-dienyl dihydrofurans from the intramolecular oxypalladation of α-allenols followed by coupling with α-allenic esters (eqn (101) and (102)), the efficiency depending on the nature of both the Pd$^{\text{II}}$ catalyst and the solvent (eqn (102)).[87,88]

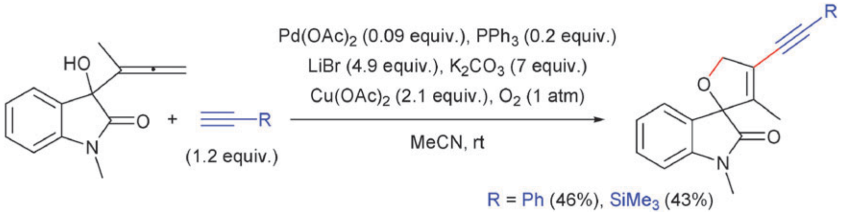
R^1 = *p*-MeOC$_6$H$_4$, R^2 = MeO, R^3 = Me, Ar = *p*-tolyl: 75%
R^1 = Bn, R^2 = *p*-MeOC$_6$H$_4$CO$_2$, R^3 = Me, Ar = Ph: 67%
R^1 = Bn, R^2 = *p*-MeOC$_6$H$_4$CO$_2$, R^3 = Ph, Ar = *p*-tolyl: 54%

(101)

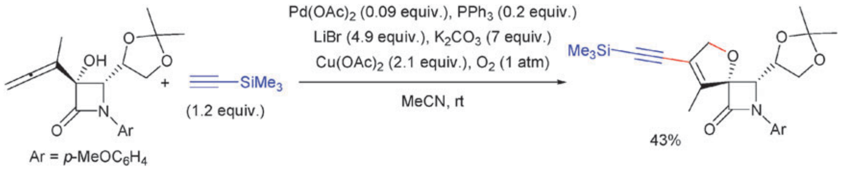


(102)

Use of β,γ-allenols instead of α-allenols provided access to functionalized buta-1,3-dienyl dihydropyrans through a chemo- and regioselective heterocyclisation-coupling reaction (eqn (103)).[89] This domino process is sensitive to the steric properties of the allendiol, a complex mixture being obtained when the C3 position bears a phenyl substituent (eqn (103)). Surprisingly, a trisubstituted dihydrofuran was isolated from the reaction of 3-methoxy-4-phenylhexa-4,5-diene-1,2-diol with 2-methyl-1-phenylbuta-2,3-dienyl acetate (eqn (104)).[89] The mechanism proposed by the Alcaide–Almendros team involves the intramolecular oxypalladation of the α-methoxy allenyl ether (Scheme 19). The cross-coupling reaction of the resulting palladium intermediate **19A** with the α-allenic acetate provides **19B**. The subsequent deacetoxypalladation[90] leads to **19C**,

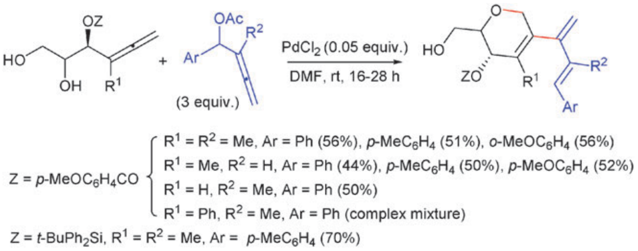


(105)

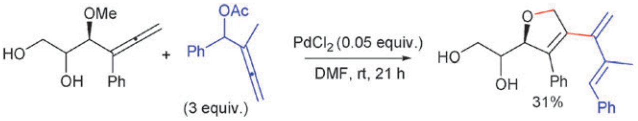


(106)

hydrolysis of the latter giving the isolated dihydrofuran.



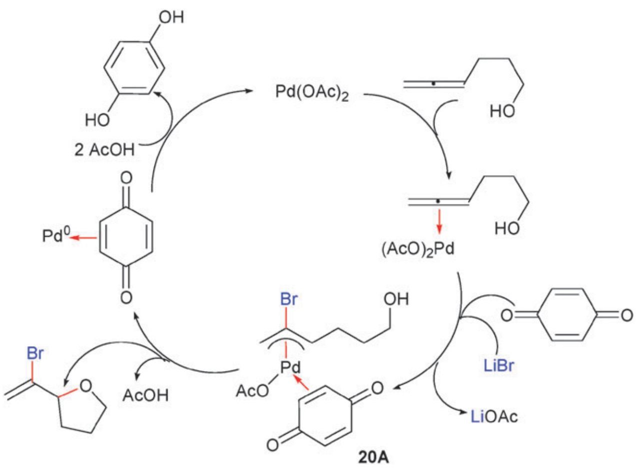
(103)



(104)

4.6. Oxycyclisation-Sonogashira reaction

The palladium intermediate arising from the oxypalladation of α-allenols can participate in a Sonogashira reaction (eqn (105) and (106)).[57]

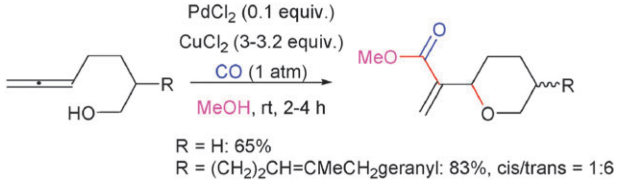


Scheme 20

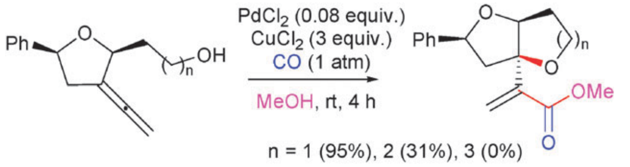
4.7. Oxy–alkoxycarbonylation

4.7.1. From a hydroxyallene. In 1987, Walkup and Park disclosed the Pd^{II}-catalysed synthesis of methyl 2-(tetrahydrofuran-2-yl)acrylates from γ-allenols, carbon monoxide and methanol (eqn (107)).[91–93] The authors considered that the cyclisation precedes the carbonylation reaction. The procedure has been used to prepare methyl 2-(tetrahydropyran-2-yl)acrylates (eqn (108))[66,94] and bicyclic heterocycles (eqn (109)).[95]

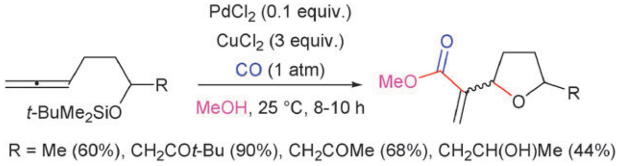
(107)



(108)



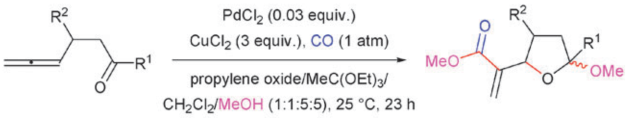
(109)



(110)

4.7.2. From a γ-silyloxy allene. The above protocol led also to methyl 2-(tetrahydrofuran-2-yl)acrylates from γ-silyloxy allenes (eqn (110)).[91,93] Apparently, the experimental conditions mediate the cleavage of the O–Si bond before the interaction with the allenyl group.[93]

4.7.3. From a γ-oxoallene. The treatment of 4,5-dienals under the experimental conditions of eqn (110) led to complex mixtures, but addition of propylene oxide and triethyl orthoacetate as acid and water traps, respectively, provided the corresponding methyl 2-(5-methoxytetrahydrofuran-2-yl)acrylates in good crude yields. Unfortunately, these furanosides are unstable under chromatographic conditions, hence the relatively low yields of pure products (eqn (111)).[96,97] The same procedure is inefficient from β-allenylketones (eqn (111)).[97]

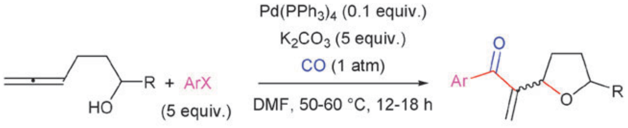


R^1 = H R^2 = H (44%), OSiMe$_2$*t*-Bu (37%), OSiPh$_2$*t*-Bu (36%)
R^2 = H R^1 = Me (trace), Et (7%)

(111)

4.8. Oxyaroylation

The cyclisation–arylation of γ-hydroxyallenes has been documented in Section 4.2.1 by Walkup's team. The authors observed the same reaction under a CO atmosphere at 70–80 °C, whereas the selective cyclisation–aroylation occurred at 55–60 °C (eqn (112)).[46,98,99]

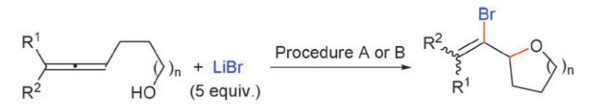


ArX = PhI, R = Me (63%), Et (84%), *i*-Pr (72%)
ArX = *p*-MeOC$_6$H$_5$I, R = Me (52%), Et (87%)
ArX = *p*-MeCOC$_6$H$_5$Br, R = Me (52%), Et (42%), *i*-Pr (50%)
ArX = *p*-O$_2$NC$_6$H$_5$Br, R = Me (51%), Et (66%)[a], *i*-Pr (43%)
[a]The cyclisation/arylation product was also isolated (19%)

(112)

4.9. Oxybromination

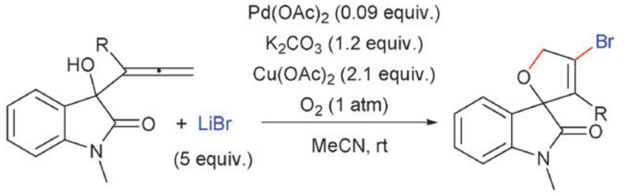
In 2000, Bäckvall and co-workers disclosed two Pd^{II}-catalysed procedures for the cyclisation–bromination of primary γ- and δ-allenic alcohols (eqn (113)).[100] These reactions would imply the addition of bromide to the activated allenyl group to give the corresponding η^3-(2-bromoallyl)palladium complex. In the presence of benzoquinone, the authors assumed that the quinone acts as a ligand,[101] leading to **20A** (Scheme 20). Then, regioselective 5-*exo*-cycloetherification affords the cyclisation product and the Pd^0-benzoquinone complex, which reacts with AcOH to regenerate the Pd^{II} catalyst.



Procedure A: Pd(OAc)$_2$ (0.05 equiv.), benzoquinone (2.5 equiv.), AcOH, 40 °C, 8 h
n = 1, R^1 = R^2 = Me (70%)
n = 1, R^2 = H, R^1 = *n*-C$_5$H$_{11}$ (75%), *i*-Pr (70%), *n*-BuCHEt (62%)
Procedure B: Pd(OAc)$_2$ (0.1 equiv.), Cu(OAc)$_2$·H$_2$O (2.1 equiv.), K$_2$CO$_3$ (1.2 equiv.), O$_2$ (1 atm), MeCN, rt, 2.5-4 h
n = 1, R^1 = R^2 = Me (71%); n = 1, R^2= H, R^1 = *n*-C$_5$H$_{11}$ (46%)
n = 2, R^2 = H, R^1 = *n*-C$_5$H$_{11}$ (78%), *i*-Pr (70%)

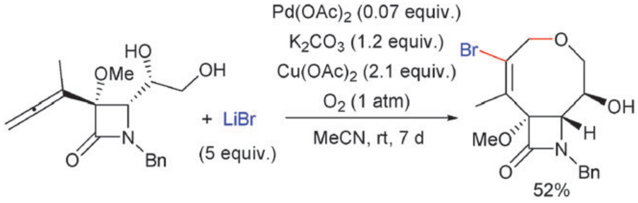
(113)

The Alcaide–Almendros team has subsequently carried out the synthesis of varied bromoheterocycles from primary, secondary and tertiary allenic alcohols (eqn (114)[43,57] (115),[44] (116)[44,45] and (117)[45,80]) through the regio- and, often, chemioselective 5-, 6- 7- or 8-*endo*-cycloetherification. The reactions depicted in eqn (116) and (118)[44,45] show that the regioselectivity can, however, depend on the substitution of the allenic group. According to the authors, this difference could result from ''the electron-withdrawing capacities of the phenyl substituent relative to the electron-donating methyl group''. The strengthening of the electrophilicity of the benzylic carbon atom by the phenyl substituent would favor the 5-*exo* cyclization of the primary hydroxy group over the 6-*endo* cyclization of the secondary hydroxy group.[45]

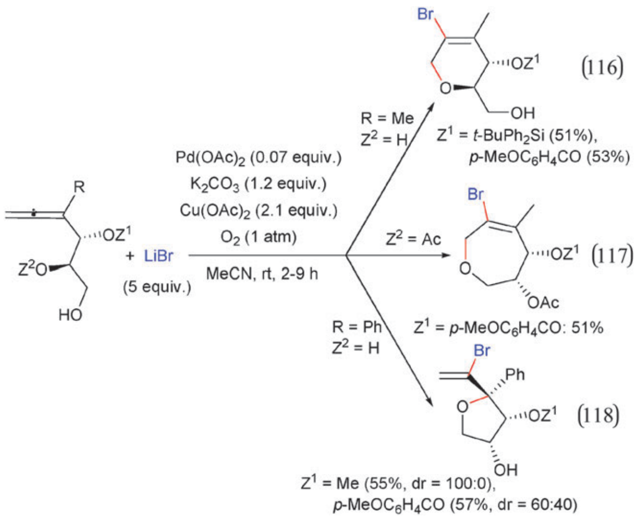


R = Me (20 h: 52%), Ph (120 h: 38%)

(114)



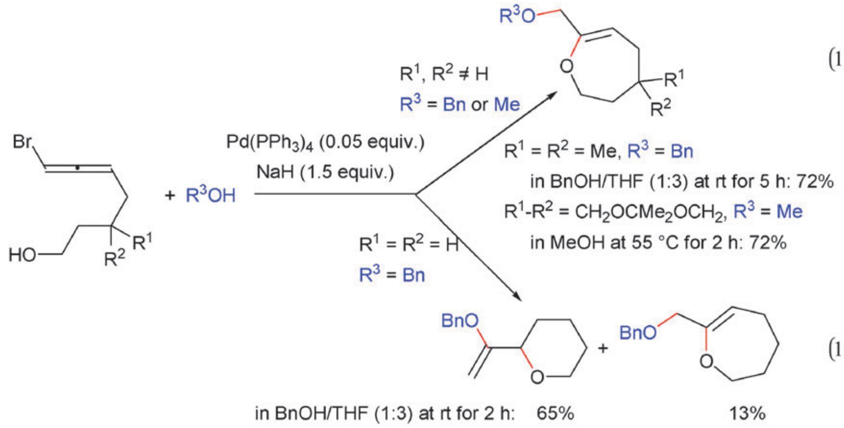
(115)



Z^1 = *t*-BuPh$_2$Si (51%), *p*-MeOC$_6$H$_4$CO (53%)

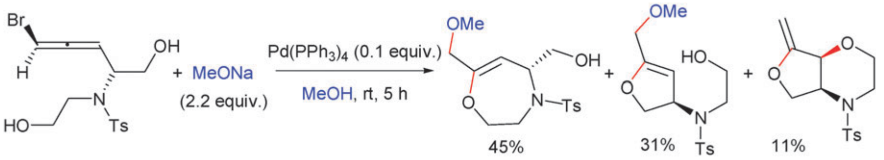
Z^1 = *p*-MeOC$_6$H$_4$CO: 51%

Z^1 = Me (55%, dr = 100:0), *p*-MeOC$_6$H$_4$CO (57%, dr = 60:40)



(121)

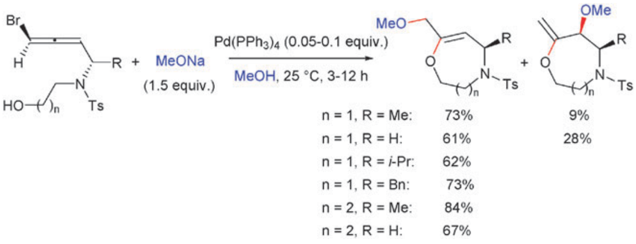
(122)



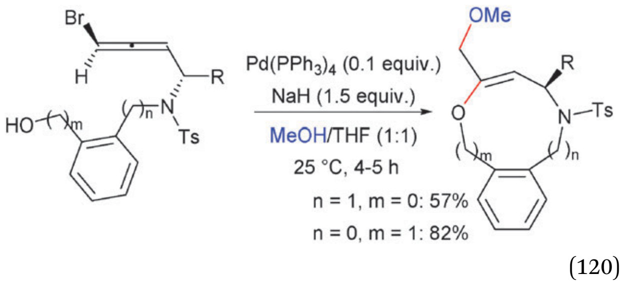
(123)

4.10. Oxyalkoxylation

Bromoallenes, substituted by a heteroatomic or substituted carbon tether terminated by a hydroxyl, have been used in an alcohol under basic conditions and Pd^0 catalysis to obtain seven- and eight-membered unsaturated rings possessing one or two heteroatoms and an alkoxy or methylalkoxy substituent (eqn (119) to (121)).[30,33,34] According to Tanaka and co-workers, these reactions would occur *via* the intramolecular hydroxyl addition to a η^1-allenylpalladium complex followed by the intermolecular addition of the alcohol to the resulting η^3-allylpalladium complex. The selectivity however greatly depends on the substitution of the tether as shown with the reaction of 7-bromohepta-5,6-dien-1-ol, which mainly affords the six-membered ring (eqn (122)).[30] This tetrahydropyran would be obtained *via* intermolecular alcoholate addition to the η^1-allenylpalladium complex and subsequent cycloetherification proceeding at the level of the η^3-allylpalladium complex.[30]

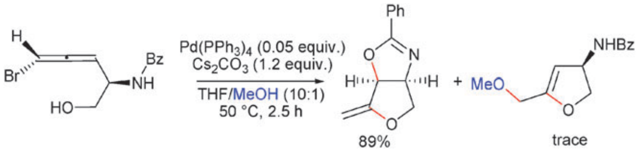


(119)



(120)

When the tether possesses two oxygen functionalities susceptible to undergo cycloetherification leading to five- and seven-membered rings, a mixture of these two heterocycles and a bicyclic compound resulting from two intermolecular etherifications has been obtained (eqn (123)).[33] The biscyclisation was the main domino reaction from a bromoallene bearing a tether possessing both hydroxy and benzamide groups as depicted in eqn (124).[102,103]



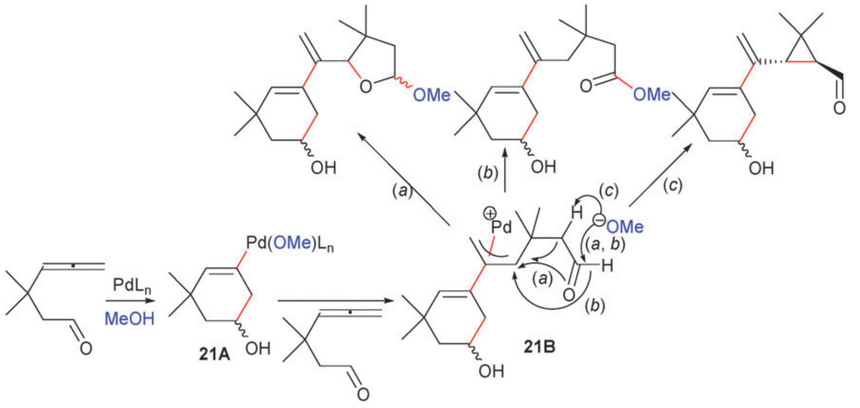
(124)

The Pd^0-catalysed reaction of 3,3-dimethylhexa-4,5-dienal in MeOH led to 3-(1-(5-methoxy-3,3-dimethyl-tetrahydrofuran-2-yl)vinyl)-5,5-dimethylcyclohex-3-enol as the main product (eqn (125)).[104] According to Tsukamoto *et al.*, the reaction implies the alkenylpalladium complex **21A** formed *via* an anti-Wacker-type addition (Scheme 21). This intermediate would undergo the carbopalladation of the allene to afford the η^3-allylpalladium species **21B**. Reaction of the latter with MeOH would produce the three isolated products.

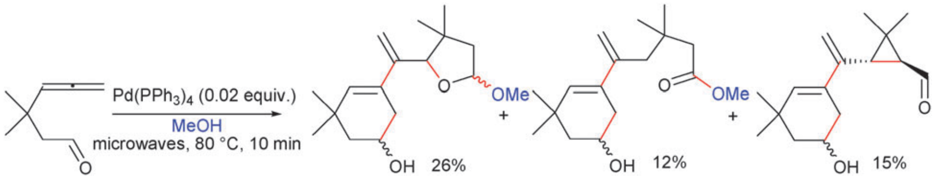
5. Intermolecular acyloxylation

5.1. Hydroacyloxylation

In 1967, Shier reported the Pd-catalysed reaction of allene in AcOH containing AcONa.[105] A small amount of allyl acetate was isolated, the favoured pathway being the formation of dimer derivatives, mainly 3-methyl-2-methylenebut-3-enyl acetate

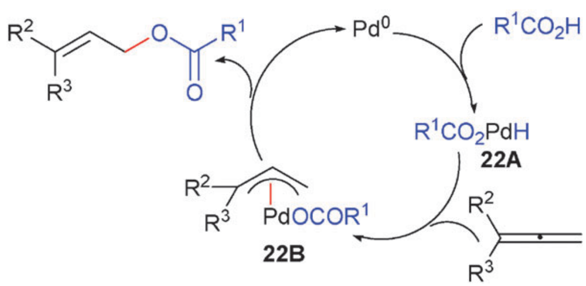


Scheme 21

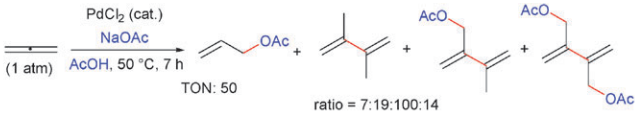


(125)

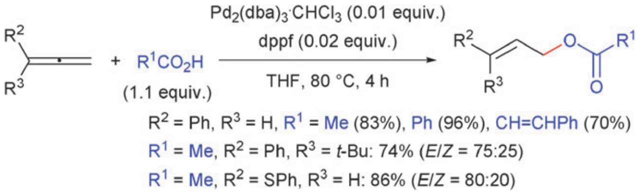
(eqn (126)). Thirty years later, Yamamoto and Al-Masum disclosed an effective procedure to selectively obtain allyl esters from arylallenes or phenylthioallene and carboxylic acids (eqn (127)).[106] These hydroacyloxylations would proceed by oxidative insertion of Pd^0 into the RCO_2–H bond to afford the hydridopalladium species **22A** (Scheme 22). Addition of **22A** to the allene leads to the η^3-allylpalladium complex **22B**, reductive elimination of Pd^0 from the latter liberating the allylcarboxylate.[106] Such a mechanism agrees with the formation of buta-1,3-dienylbenzene from 1-phenyl-3-methylallene, the β-H elimination being the favoured reaction pathway from the η^3-allylpalladium intermediate (eqn (128)).[106]



Scheme 22



(126)



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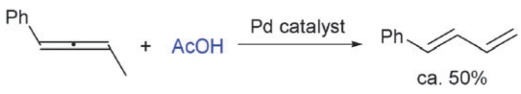

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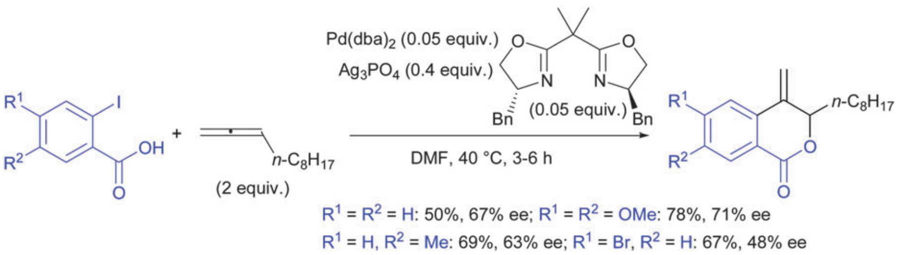

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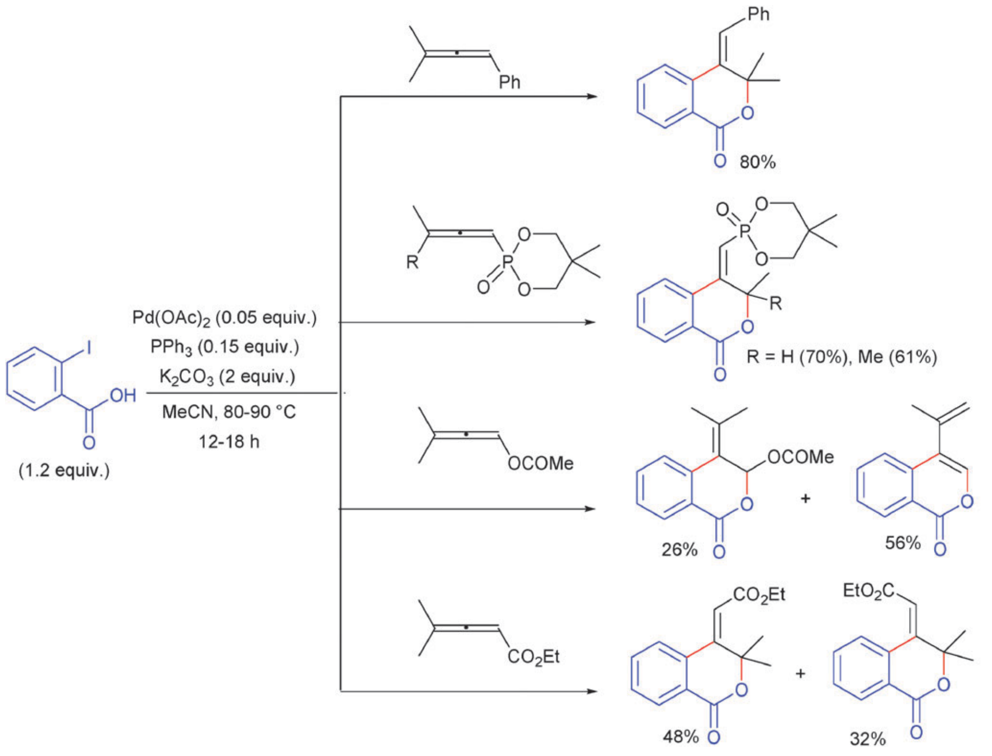
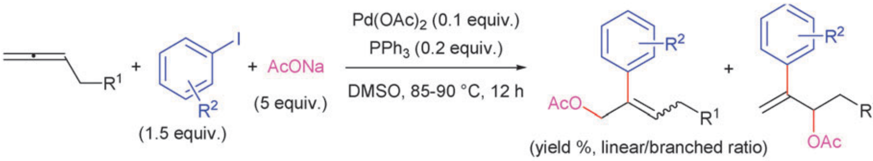


(130)

(131)

(132)

(133)



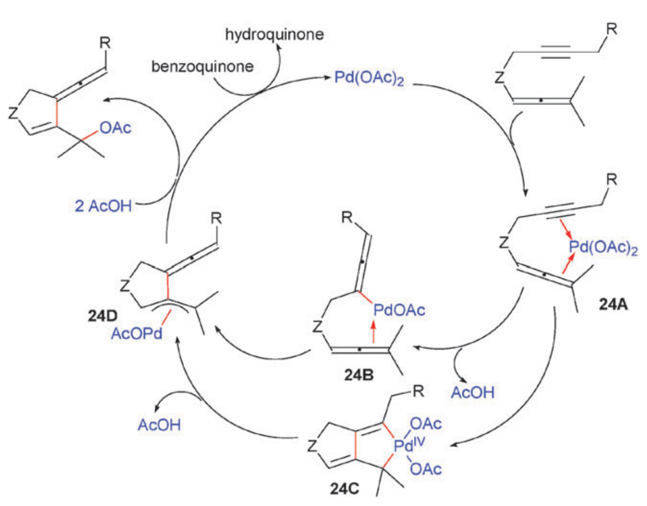
(134)

R^1 = BnO, R^2 = H (64, 3:1), *p*-Me (64, 2.6:1), *m*-OMe (63, 1.4:1), *m*-NO$_2$ (50, 5.2:1), *p*-COMe (31, 2.7:1)
R^1 = (*p*-MeC$_6$H$_4$SO$_2$)NBn, R^2 = H (63, 1:0), *p*-Me (64, 1:0), *p*-OMe (68, 1:0)

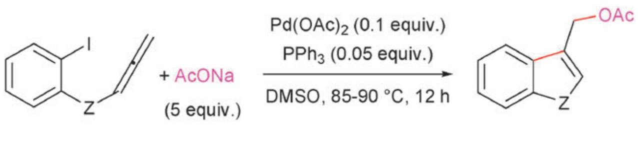
5.2. Arylaroyloxylation

In 1984, Larock and co-workers disclosed the formation of isocoumarins from the Pd^{II}-mediated coupling of *o*-thallated benzoic acids with allenes followed by a basic treatment.[107] As organothallium compounds are toxic, the subsequent synthesis of these heterocycles using allenes, *o*-iodo benzoic acids and Pd^0 catalysis was of interest. Moreover, optically active compounds were obtained in the presence of chiral ligands (eqn (129)).[19,20] More recently, Kumara Swamy and co-workers carried out such domino reactions using phenylallenes, allenyl phosphonates, acetates or esters (eqn (130) to (133)).[22,27,108]

Savic's team has synthesised various arylated allylic acetates from the reaction of both aryl iodides and sodium acetate with buta-2,3-dienyl benzyl ether or *N*-benzyl-*N*-(buta-2,3-dienyl)-4-toluenesulfonamide (eqn (134)).[109,110] This team has also carried out the synthesis of heterocyclic systems using aryl iodides *o*-substituted with an allenic hetero-tether (eqn (135)).[110]

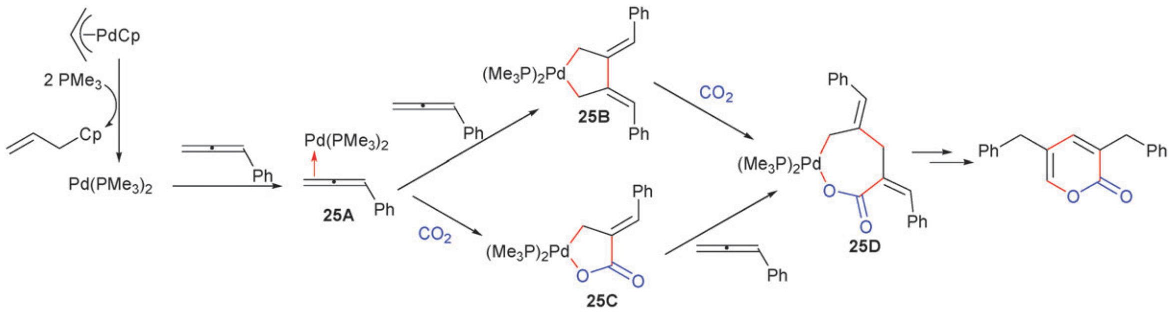


Scheme 23

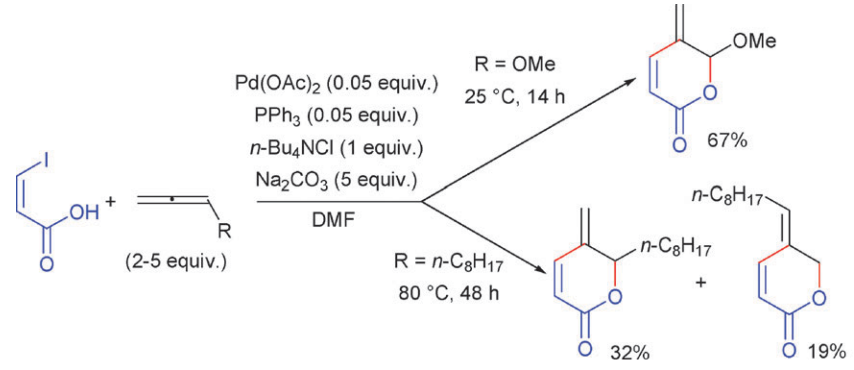


Z = NTs (52%), NTs-CH$_2$ (48%), O (47%), CO-NMe (46%)

(135)

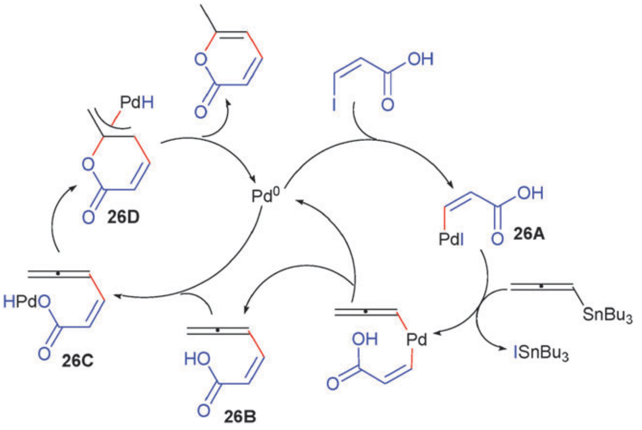


Scheme 24



(136)

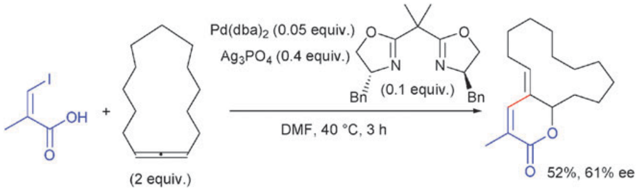
(137)



Scheme 25

5.3. Vinylalkenoyloxylation

Allenes and (*Z*)-β-iodo-α,β-unsaturated acids have been used, under Pd^0 catalysis, to obtain various 5-methylene-5,6-dihydropyran-2-one derivatives (eqn (136), (137)[24] and (138)[19,20]). The vinylalkenoyloxylation has also been reported from a three-component reaction (eqn (139)).[110]

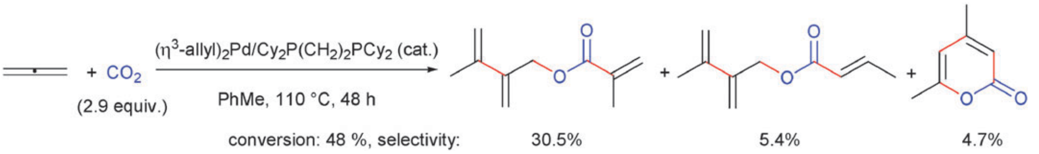


(138)

5.4. Carboacyloxylation

Bäckvall and Deng synthesised acyloxylated vinylallenes from allenynes and acetic acid (eqn (140) and (141)).[75] The coordination of the substrate to $Pd(OAc)_2$ would lead to the chelate **24A** (Scheme 23). A rearrangement of the latter arising through the cleavage of a propargylic C–H bond would afford **24B**. Another possibility is the formation of the Pd^{IV} intermediate **24C**. Both **24B** and **24C** could evolve towards the η^3-allylpalladium complex **24D**. Intra- or intermolecular attack of the allyl moiety by AcO^- would yield the isolated compound, the regeneration of the catalyst being assumed by benzoquinone and AcOH.

(139)



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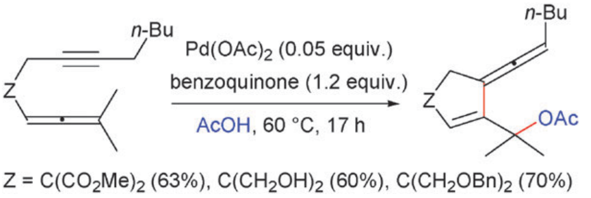
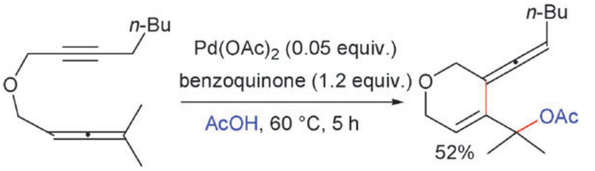
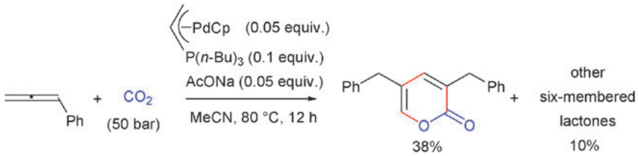


(140)



(141)

The carboacyloxylation can also occur in the course of the dimerisation of allene as depicted in eqn (126)[105] and (142).[111] The 3,5-dimethylpyranone is obtained from the coupling of two molecules of allene with one molecule of carbon dioxide, while one more molecule of allene is implied in the formation of 3-methyl-2-methylenebut-3-enyl methacrylate and 3-methyl-2-methylenebut-3-enyl but-2-enoate (eqn (142)). The synthesis of these two esters requires two supplementary hydrogens per molecule through an indeterminate mechanism. Six-membered lactones can be obtained in better yields using methoxyallene[112] or phenylallene (eqn (143)).[113] The Choi/Sakakura team has recently proposed two likely pathways for formation of 3,5-dibenzylpyranone mediated by the (η^3-allyl)PdCp/PMe$_3$ association (Scheme 24).[113] The Pd^0 complex **25A** would react with either another molecule of allene or carbon dioxide to afford the five-membered heterocycles **25B** or **25C**, respectively. The reaction of either allene or carbon dioxide with these species would lead to the seven-membered palladalactone **25D**, which would evolve towards the disubstituted pyranone.

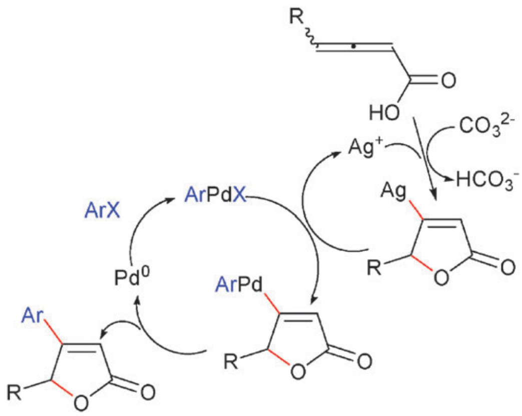


(143)

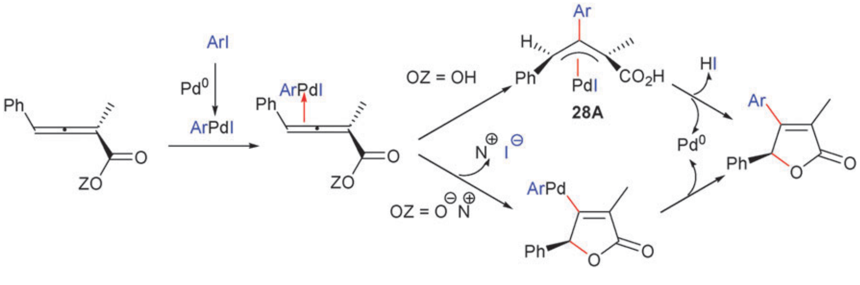
6. Intramolecular acyloxylation or alkenoyloxylation

6.1. Hydrolactonisation

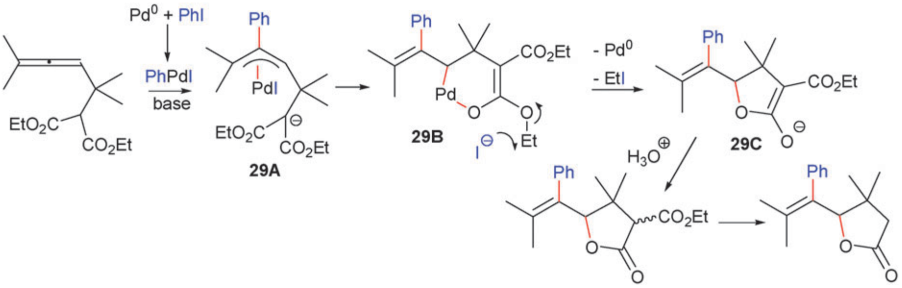
Duchêne, Parrain and co-workers obtained pyranones from allenyl stannanes, β-iodo vinylic acids and catalytic amounts of Pd^0 (eqn (144)).[114] In fact, these syntheses involve two reactions in one pot. Firstly, the Stille reaction of the allenyltin with the vinylpalladium complex **26A** affords the allenic acid **26B** and Pd^0 (Scheme 25). Then, the intramolecular reaction of



Scheme 26

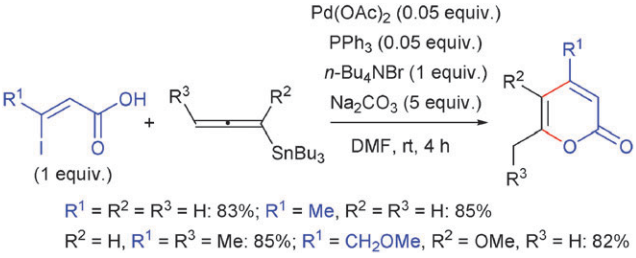


Scheme 27



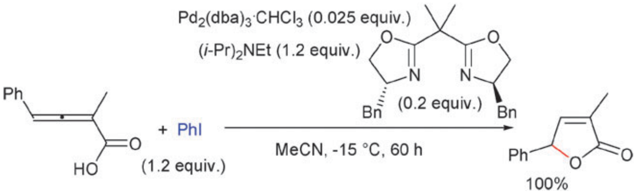
Scheme 28

the palladium carboxylate **26C** provides the hydrido-(η^3-allyl)-palladium complex **26D**. Reductive elimination of Pd^0 from the latter yields the pyranone.



(144)

When Ma and co-workers tested the asymmetric lactonisation-arylation of 2-methyl-4-phenyl-2,3-butadienoic acid, the expected arylation did not occur: 4-phenyl-2-methyl-2-butenolide was the only product (eqn (145)).[115] Given the results below reported in eqn (149),[115] we suspect that it is due to the 2-methyl substituent, which would hamper the approach of the allene moiety by the arylating species. Subsequently, Ma's team observed the hydrolactonisation of 2-propyl-4-phenyl-2,3-butadienoic acid under different experimental conditions (eqn (146)).[116]



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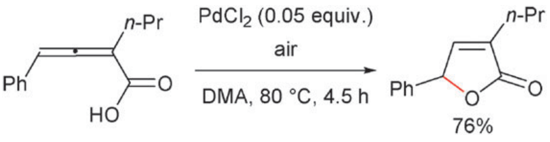
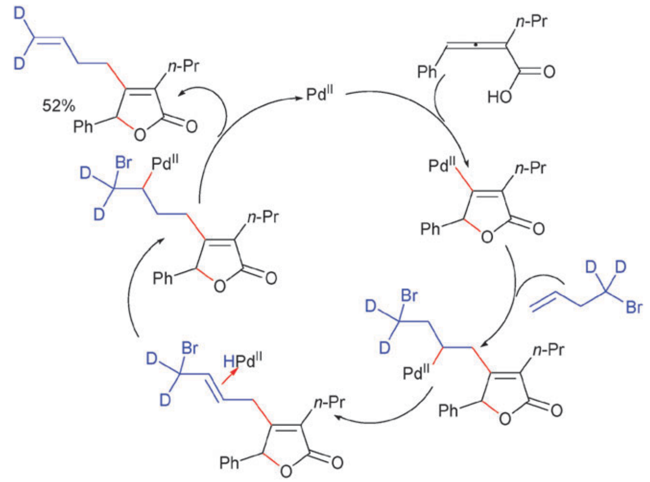


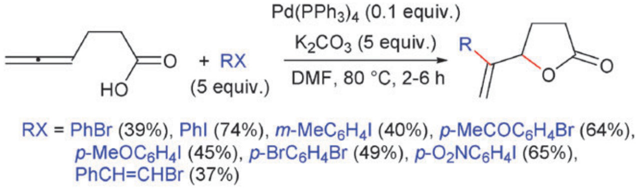
(146)

6.2. Lactonisation-arylation

In 1993, Walkup and co-workers disclosed the Pd^0-catalysed synthesis of 5-(1-arylvinyl)-dihydrofuran-2(3*H*)-ones from 4,5-hexadienoic acid and aryl halides (eqn (147)).[46] The authors suspected that the cyclisation precedes the arylation. For the lactonisation-arylation of α-allenic acids (eqn (148)), Ma and Shi reported, in 1998, the increase of the yields by co-catalysis with silver carbonate.[117,118] They proposed a catalytic cycle involving firstly the arylation when the reaction was performed in the absence of Ag_2CO_3 (as in Scheme 1, paths *c* and *d*), whereas, under Pd/Ag catalysis, they suspected a Ag-mediated cyclisation followed by *trans*-metalation with ArPdX of the resulting 3-silver-2-butenolide intermediate (Scheme 26).



Scheme 29



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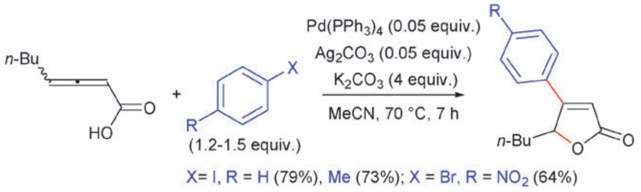
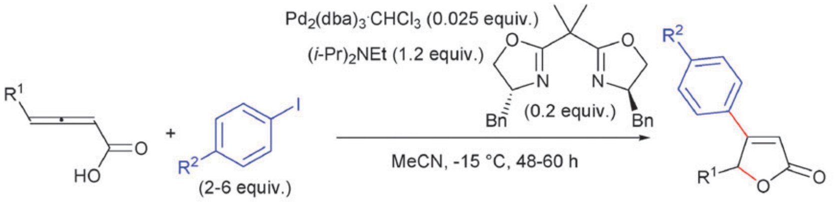


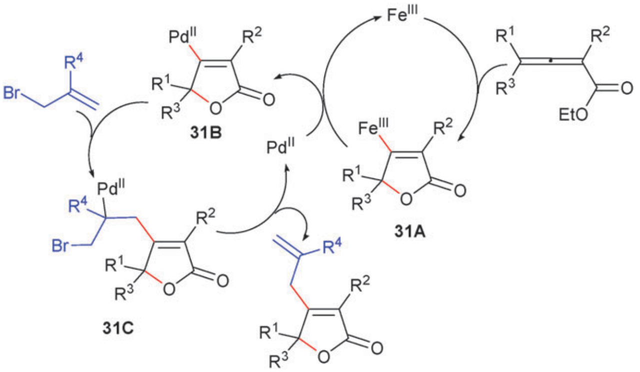
(148)



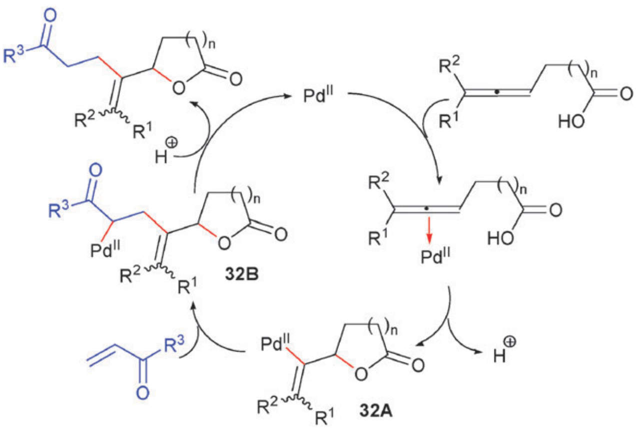
R^1 = n-hept, R^2 = H (52%, 52% ee), Me (51%, 43% ee), MeOCO (52%, 49% ee), MeO (53%, 47% ee)
R^1 = n-Bu, R^2 = H (47%, 50% ee), Me (44%, 53% ee), MeOCO (53%, 53% ee), MeO (51%, 46% ee)
R^1 = Cy, R^2 = H (36%, 0% ee)

(149)

The use of the Pd/Ag procedure in the presence of chiral ligands led to 3-aryl-2-butenolides with low ee's. This would be due to the Ag-mediated cyclisation (Scheme 26), which would occur without participation of the chiral ligand, hence the enantioselective synthesis of such compounds using a silver-free method with, after some investigation, the chiral ligand (eqn (149))[115] already used by Larock (see eqn (129) and (138)). The success of these domino reactions highly depends on the substituent of the allene group. Indeed, a low ee was observed with 4-cyclohexylbuta-2,3-dienoic acid as the substrate (eqn (149)), whereas the arylation of 2-methyl-4-phenyl-2,3-butadienoic acid did not occur (eqn (145)).

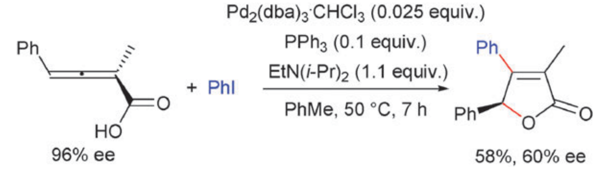


Scheme 30

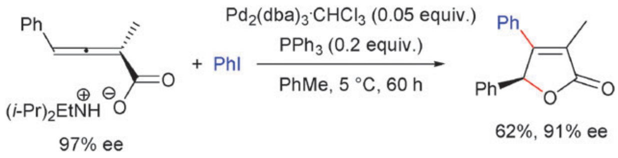


Scheme 31

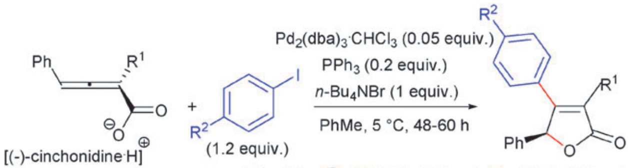
Subsequently, Ma and Shi carried out these syntheses using chiral acids (eqn (150)) or their salts (eqn (151) and (152)).[119] According to the authors, the dependence of the enantioselectivities on the nature, acid or acid salt, of the substrate is due to a mechanism switch: formation firstly of the Ar–C bond from the acid leading to some loss of the chirality at the level of the η^3-allylpalladium complex **28A**, and of the O–C bond from the acid salt (Scheme 27).



(150)



(151)



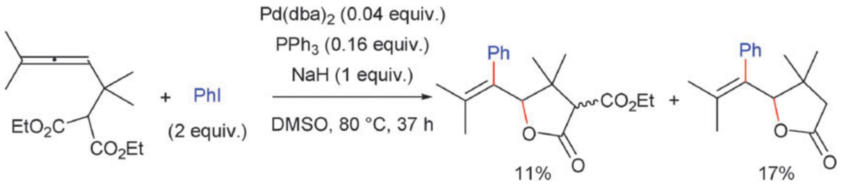
R^1 = Me, R^2 = H (90%, 91% ee), Me (66%, 92% ee)
R^1 = n-Pr, R^2 = H (72%, 91% ee), Me (75%, 91% ee)

(152)

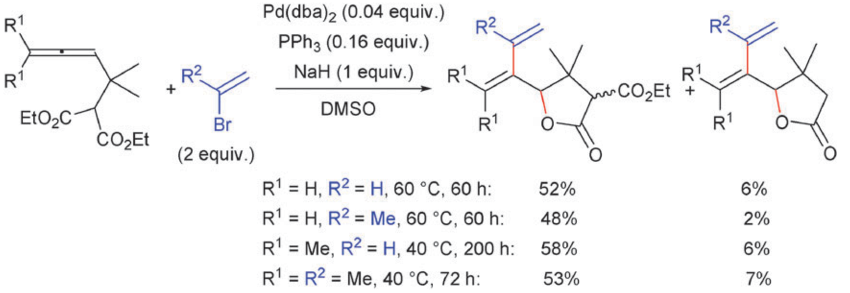
Bi- and tricyclic lactones have been synthesized using the Walkup[46]-Gallagher[120] experimental conditions (eqn (153) and (154)).[95]

n = 1 (32%), 2 (20%), 3 (0%)

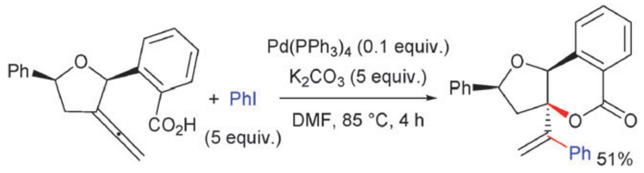
(153)



(156)

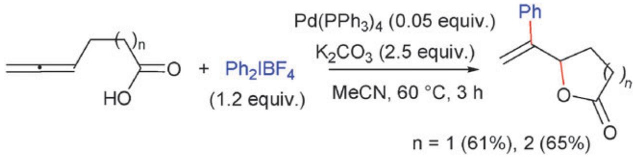


(157)



(154)

The Pd^0-catalysed lactonisation-arylation has also been carried out using either α-allenic acids and aryl iodides anchored to Merrifield resin to afford polymer-supported butenolides,[121] or a γ(or δ)-allenic acid and diphenyliodonium tetrafluoroborate to provide the corresponding lactone (eqn (155)).[55]



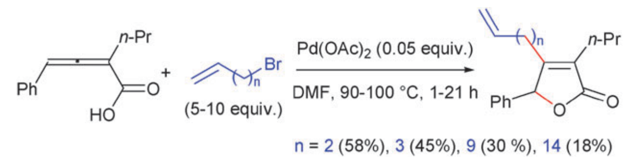
(155)

Cazes and co-workers isolated the substituted γ-lactones shown in eqn (156) from the Pd^0-catalysed reaction of diethyl 2-(2,5-dimethylhexa-3,4-dien-2-yl)malonate with phenyl iodide under basic conditions.[122] According to the authors, the anionic η^3-allylpalladium species **29A** obtained from the addition of the arylating species to the substrate evolves into the six-membered palladacycle **29B** (Scheme 28). The transformation of the latter to **29C** will be mediated by the iodide anion, subsequent hydrolysis leading to the substituted lactone.

6.3. Lactonisation-alkenylation

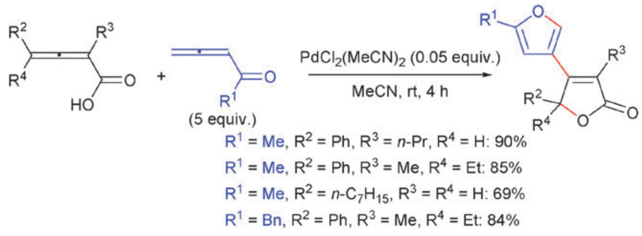
The Walkup procedure is also effective for the cyclisation-vinylation of 4,5-hexadienoic acid (eqn (147)).[46] The synthesis, under Cazes conditions, of substituted γ-lactones from allenyl malonates led to higher yields when using vinylic bromides (eqn (157)) instead of phenyl iodide (eqn (156)).[122]

Ma and Yu obtained butenolides β-substituted with a terminal-unsaturated tether having up to 16 carbons from the reaction of 2,3-allenoic acids with 1-alkenyl bromides (eqn (158)).[123] An experiment using a deuterated homoallylic bromide demonstrated a reaction occurring through successive oxycyclisation, Heck reaction, hydropalladation and debromopalladation (Scheme 29). It is remarkable that the dehydropalladation–hydropalladation sequence can travel through a chain of 14 carbon atoms.

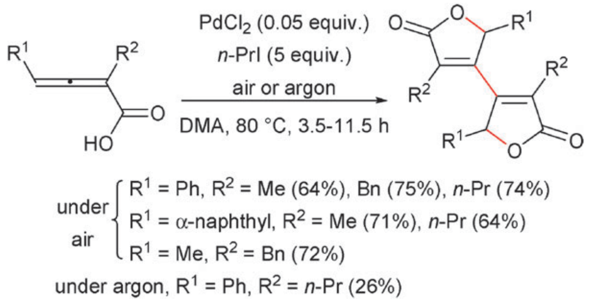


(158)

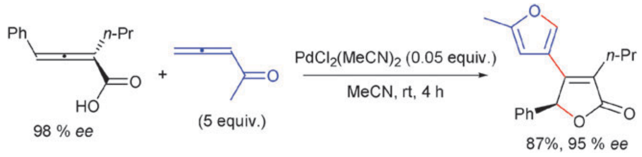
Ma and co-workers have also reported the synthesis of butenolides β-substituted with a furanyl or butenolide group. These compounds were obtained from the cyclisation of 2,3-allenoic acids followed by carbopalladation of either a 2,3-allenoic ketone (eqn (159))[124,125] or another molecule of the substrate (eqn (160)).[116,126] For the latter reaction, the catalyst was regenerated with alkyl iodide and oxygen, the use of only the alkyl iodide being less efficient (eqn (160)). Nevertheless, most of the alkyl iodide was not consumed in the course of the process (recovery of 94% of (3-iodopropyl)benzene for example). Subsequently, the authors observed that iodo salts or benzoquinone can be effectively used instead of the alkyl iodide.[126] The above couplings using optically active substrates have been realised with excellent diastereoselectivities (eqn (161)[125] and (162)[126]).



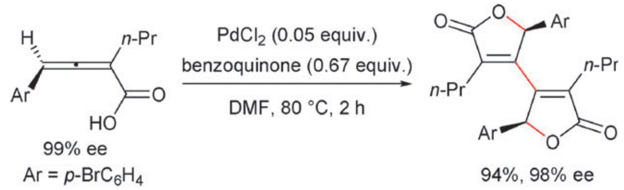
(159)



(160)

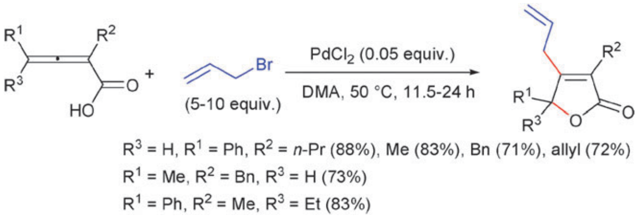


(161)



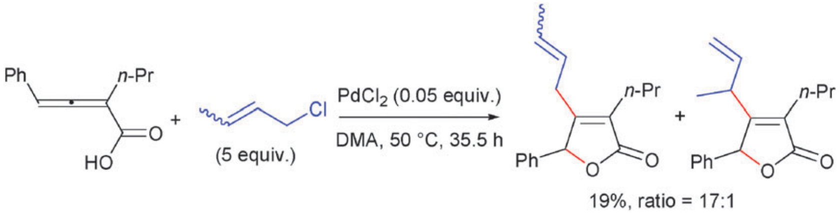
(162)

The Pd^{II}-catalysed reaction of 2,3-allenoic acids with allyl bromide affords the expected β-allenic butenolides (eqn (163)), whereas the use of 1-chloro-2-butene leads to two regioisomers (eqn (164)).[127] After analysis of different hypotheses, Ma and Zu concluded that this mixture results from an equilibrium of 1-chloro-3-butene with 3-chloro-1-butene under the reaction conditions. Thus, the formation of these β-allenic butenolides involves an oxycyclisation followed by Heck-type reaction and elimination of palladium halide.

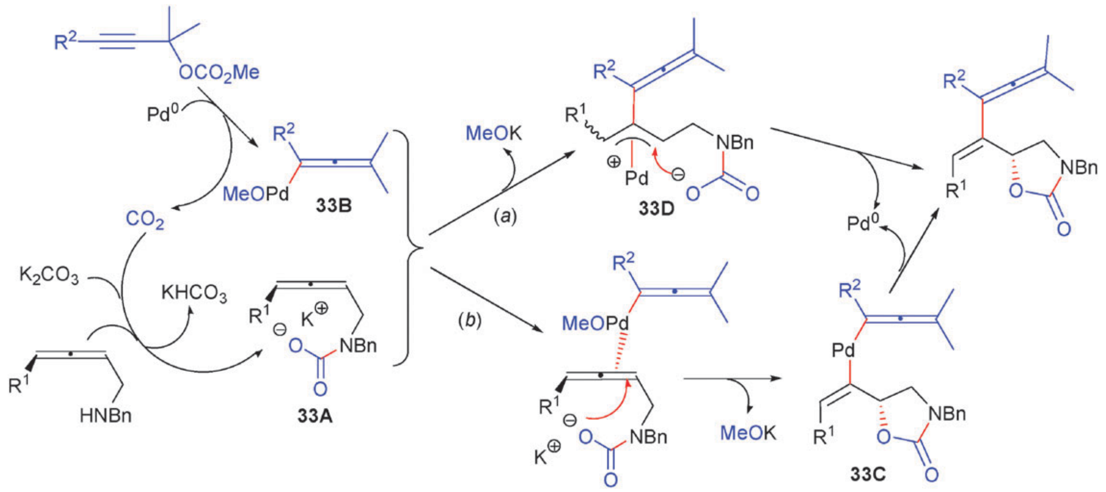


(163)

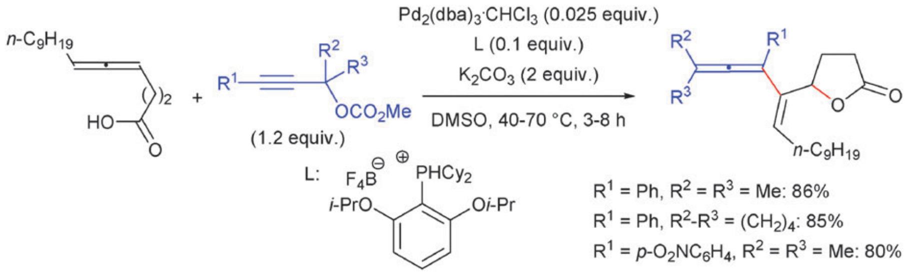
Subsequently, Ma and Chen carried out the synthesis of β-allenic butenolides using allenyl esters instead of allenyl acids (eqn (165)).[128] The reaction requires the addition of catalytic amounts of a Lewis acid, in particular $FeCl_3$, which mediates the oxycyclisation to afford the furanonyl iron species **31A** (Scheme 30). Subsequent *trans*-metalation with $PdCl_2$ gives **31B**, regenerating Fe^{III} species. Heck reaction of **31B** with the allylic bromide leads to **31C**, the subsequent β-Br elimination delivering the product and regenerating the Pd^{II} catalyst.



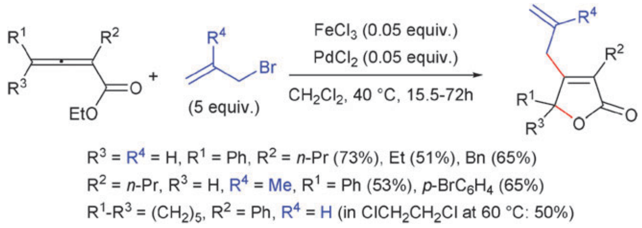
(164)



Scheme 32



(166)



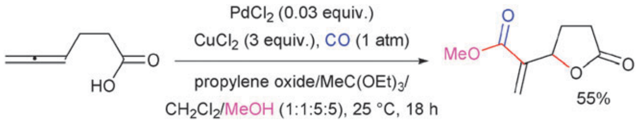
(165)

6.4. Lactonisation-allenylation

Recently, Ma and co-workers reported the stereoselective synthesis of (*Z*)-5-(1,3,4-alkatrien-2-yl)-4,5-dihydro-2-(3*H*)-furanones from 6-monosubstituted 4,5-allenoic acids and propargylic carbonates (eqn (166)).[129]

6.5. Lactonisation-carbonylation

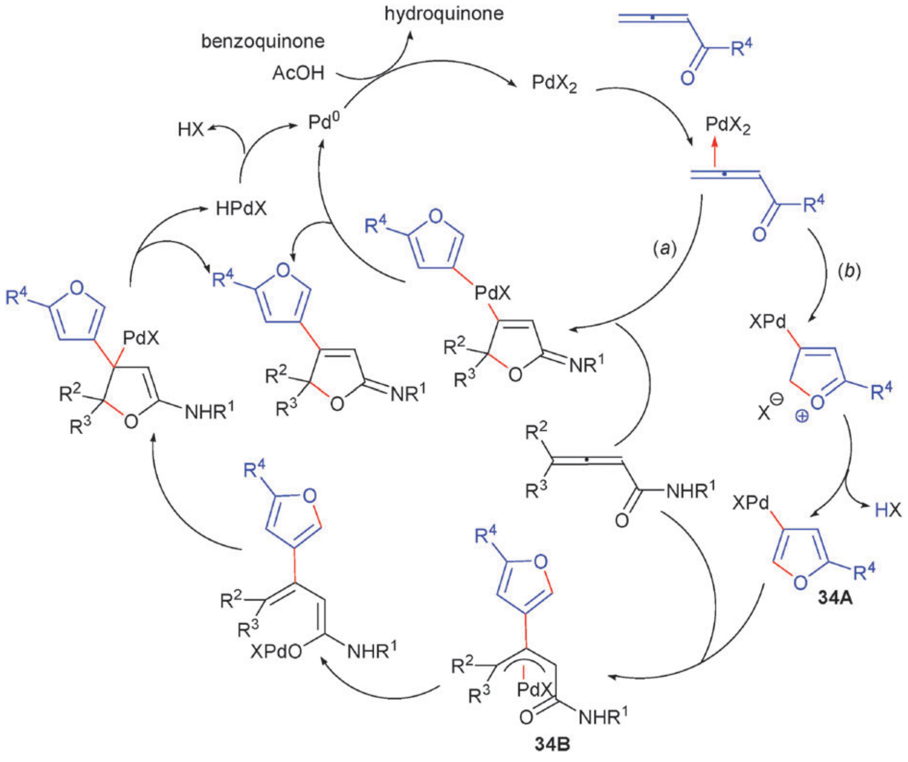
Under the experimental conditions they used for the cyclisation–carbonylation of 4,5-dienals (eqn (111)), Walkup and Mosher synthesised the furanone shown in eqn (167) from 4,5-hexadienoic acid.[96]



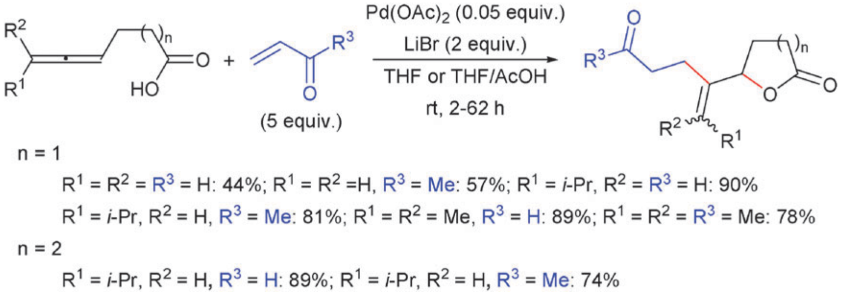
(167)

6.6. Bromination-lactonisation

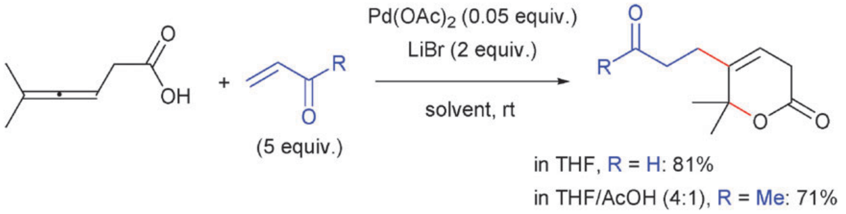
In 1998, Bäckvall and Jonasson disclosed the synthesis of the bromolactones shown in eqn (168) from the Pd^{II}-catalysed



Scheme 33

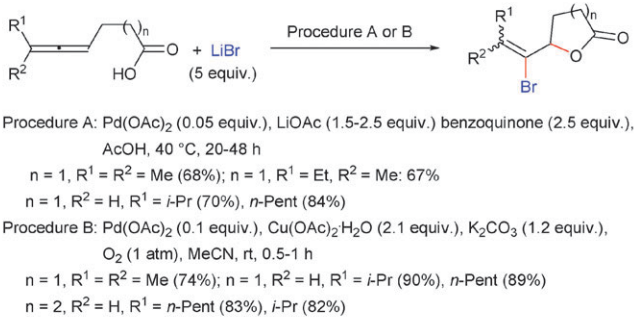


(169)



(170)

reaction of 4,5- and 5,6-hexadienoic acids with lithium bromide.[100,130] The mechanism is likely similar to the one proposed for the oxybromination of allenic alcohols (Scheme 20), the bromination preceding the cyclisation and the regeneration of the catalyst being also assumed by benzoquinone or Cu^{II}/O$_2$.[100,130]



(168)

6.7. Lactonisation/Michael-type addition

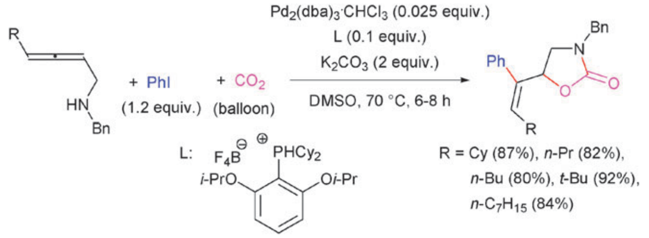
In 2003, Lu and Liu reported the Pd^{II}-catalysed intramolecular cyclisation of 4,5- and 5,6-hexadienoic acids with conjugate addition to α,β-unsaturated carbonyl compounds (eqn (169)).[131] Although the reactions were carried out in the presence of an excess of lithium bromide, as under the above previous Bäckvall experimental conditions summarised in eqn (168), the formation of bromolactones was not observed. The mechanism suggested for these domino cyclisation-conjugate additions involves the 5- or 6-*exo-trig* addition of the carboxylate to the Pd^{II}-coordinated allenyl moiety to afford the vinyl palladium intermediate **32A** (Scheme 31). Addition of the latter to the α,β-unsaturated carbonyl compound provides **32B**, which suffers protonolysis. The role of LiBr would be to inhibit the β-H elimination from **32B**;[131] its coordination to Pd would lead to the absence of a vacant coordination position, which is a prerequisite for the PdH elimination.[132] In contrast, the absence of a bromide addition to the allenyl moiety remains unexplained.

In contrast to the *exo-trig* cyclisation of 4,5- and 5,6-hexadienoic acids (eqn (169)), the reaction of 5-methylhexa-3,4-dienoic acid under Lu's conditions led to dihydropyranones stemming from a 6-*endo-trig* cyclisation (eqn (170)).[131]

7. Oxazolidinonisation

7.1. Oxazolidinonisation-arylation

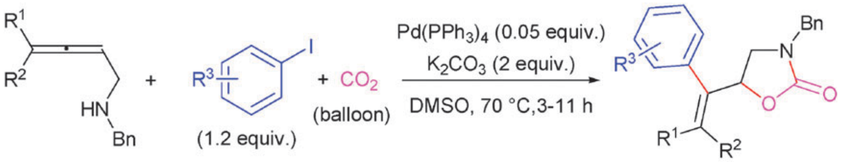
Under basic conditions, Ma's team carried out the stereoselective synthesis of the 5-alkenyloxazolidin-2-ones shown in eqn (171) from the Pd-catalysed reaction of 4-monosubstituted 2,3-allenyl amines with carbon dioxide and then phenyl iodide.[129] Subsequently, these domino reactions have been reported using *N*-benzylbuta-2,3-dien-1-amine and 4,4-disubstituted 2,3-allenyl amines (eqn (172)).[133]



(171)

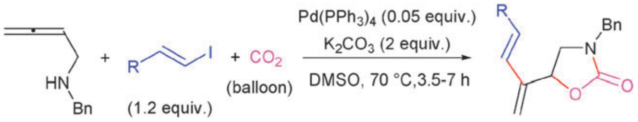
7.2. Oxazolidinonisation-alkenylation

The 5-*exo-trig* cyclisation of *N*-benzylbuta-2,3-dien-1-amine can be also followed by cross-coupling with 1-hexenyl iodide or (2-iodovinyl)benzene (eqn (173)).[133]



$R^1 = R^2 = H$, $R^3 = H$ (91%), p-Me (92%), m-Me (81%), p-OMe (93%), p-Ac (82%), p-F (91%), p-CF_3 (85%), p-CO_2Et (86%), p-NO_2 (72%), p-OH (73%)
$R^1 = R^2 =$ Me, $R^3 = H$ (76%); R^1-$R^2 = (CH_2)_5$, $R^3 = H$ (74%)

(172)



R = $Me(CH_2)_3$ (82%), Ph (83%)

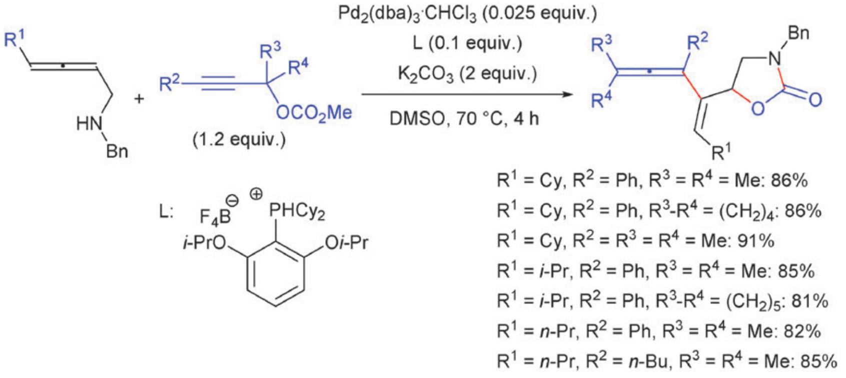
(173)

7.3. Oxazolidinonisation-allenylation

A reaction rather similar to that depicted in eqn (166) has been obtained using 4-monosubstituted 2,3-allenyl amines instead of the 4,5-allenoic acids (eqn (174)).[129] In adjusting the reaction temperature, an efficient transfer of chirality was observed from enantioenriched 2,3-allenyl amines (eqn (175)). Two plausible reaction pathways have been proposed (Scheme 32).[129] Path *a* involves the carbopalladation of the substrate derivative **33A** by the allenylpalladium complex **33B** obtained from the propargylic carbonate. The intramolecular nucleophilic addition to the resulting η^3-allylpalladium unit provides the product. Path *b* occurs *via anti*-oxypalladation of **33A** by **33B** to afford **33C**, the subsequent reductive elimination of Pd^0 giving the product. The transfer of axial chirality from enantioenriched 2,3-allenyl amines (eqn (175)) led Ma and co-workers to be in favor of path *b*, since racemization may occur from the η^3-allylpalladium intermediate **33D** through a σ–π–σ process.

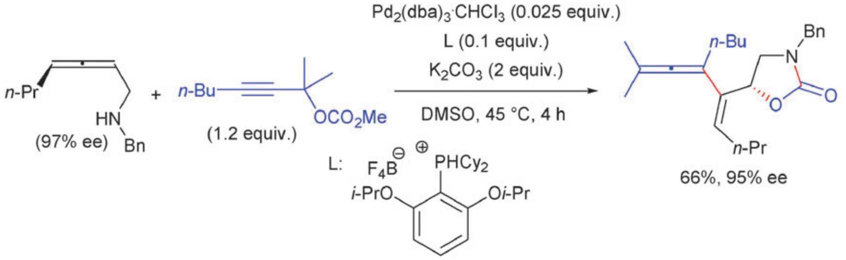
8. Carboiminolactonisation or carbolactamisation

The Pd^0-catalysed reaction of 4,4-disubstituted 2,3-allenamides with aryl iodides affords arylated iminolactones in high yields (eqn (176)).[134] The domino reaction arises also effectively with vinyl iodides, and, moreover, occurs with preservation of the configuration of the C=C bond (eqn (176)). Instead of such a reaction, 4-monosubstituted 2,3-allenamides provided γ-hydroxy-γ-lactams (eqn (177)).[134] These reactions would proceed *via* carbopalladation of the allenyl unit to give a η^3-allypalladium complex. The intermolecular *N*- or *O*-attack of the latter would depend on the steric hindrance at the 4-position. The *N*-attack will be followed by oxidation of the lactam.[134]



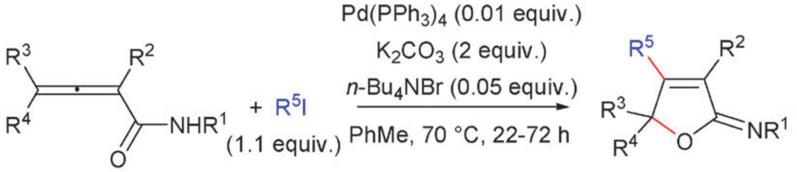
R^1 = Cy, R^2 = Ph, $R^3 = R^4$ = Me: 86%
R^1 = Cy, R^2 = Ph, R^3-$R^4 = (CH_2)_4$: 86%
R^1 = Cy, $R^2 = R^3 = R^4$ = Me: 91%
R^1 = i-Pr, R^2 = Ph, $R^3 = R^4$ = Me: 85%
R^1 = i-Pr, R^2 = Ph, R^3-$R^4 = (CH_2)_5$: 81%
R^1 = n-Pr, R^2 = Ph, $R^3 = R^4$ = Me: 82%
R^1 = n-Pr, R^2 = n-Bu, $R^3 = R^4$ = Me: 85%

(174)



66%, 95% ee

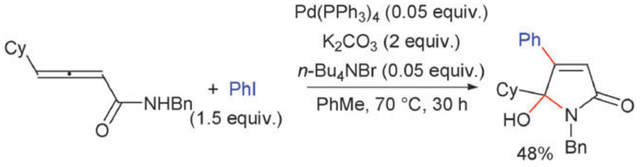
(175)



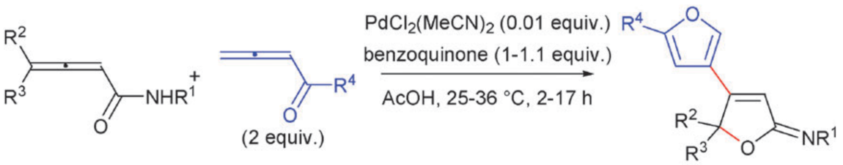
R^1 = Bn, R^2 = n-Pr, R^3-R^4 = (CH$_2$)$_5$, R^5 = Ph (95%), p-MeC$_6$H$_4$ (95%),
p-MeOC$_6$H$_4$ (95%), p-O$_2$NC$_6$H$_4$ (94%), p-MeO$_2$CC$_6$H$_4$ (100%)
R^1 = R^2 = Bn, R^3 = R^4 = Me, R^5 = Ph (96%), p-MeC$_6$H$_4$ (92%),
p-MeOC$_6$H$_4$ (93%), p-O$_2$NC$_6$H$_4$ (94%), p-MeO$_2$CC$_6$H$_4$ (96%)
R^1 = R^2 = H, R^3 = R^4 = Me, R^5 = p-MeC$_6$H$_4$ (94%), p-MeOC$_6$H$_4$ (93%),
p-MeO$_2$CC$_6$H$_4$ (90%)
R^1 = Bn, R^2 = R^3 = R^4 = Me, R^5 = (E)-1-hexenyl (75%), (Z)-MeO$_2$CCH=CH (99%),
(E)-MeO$_2$CCH=CH (99%)

(176)

From 4,4-disubstituted 2,3-allenamides, a similar process was obtained using 1,2-allenyl ketones instead of organic iodides (eqn (178)).[135] The catalytic cycle presented by Ma's team (Scheme 33, path *a*) is oversimplified. We suspect the carbopalladation of the allenyl ketone leading to **34A**. The reaction of **34A** with the allenamide would give the η^3-allylpalladium complex **34B**, which could evolve as proposed in Scheme 14, path *a*.



(177)

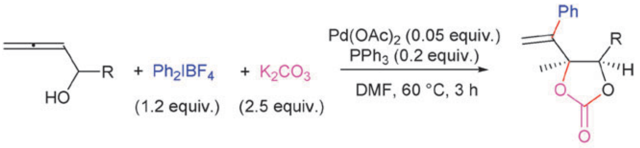


(178)

R^1 = Bn, R^2 = R^3 = Me, R^4 = Me (86%), Ph (56%), Bn (81%), n-Bu (76%), n-hept (64%)
R^1 = H, R^2 = R^3 = Me, R^4 = Me (81%), Ph (55%), n-Bu (76%), n-hept (59%)
R^1 = H, R^2-R^3 = (CH$_2$)$_5$, R^4 = Me (80%), n-Bu (70%)

9. Carbocarbonatation

With potassium carbonate instead of cesium carbonate, Kang and co-workers have, in some cases, obtained (1-phenylvinyl)-dioxolanones (eqn (179)) rather than (1-arylvinyl)oxiranes (eqn (56)) from α-hydroxyallenes and diphenyliodonium tetrafluoroborate.[54] In these reactions, potassium carbonate has a dual role: base and source of carbon dioxide.



R = n-pent (76%), i-Pr (73%), Cy (68%)

(179)

(180)

R^{5}X = PhI
n = 0
R^1 = R^2 = R^3 = R^4 = H: 52%; R^1 = R^2 = R^3, R^4 = Me: 99%;
R^1 = Me, R^2 = R^3 = H, R^4 = Me: 82%; R^1 = Ph, R^2 = R^3 = H, R^4 = Me: 72%;
R^1 = R^2 = Me, R^3 = H, R^4 = Me: 72%; R^1 = R^2 = H, R^3 = R^4 = Me: 93%
n = 1
R^1 = R^2 = R^3 = H, R^4 = Me: 70%
R^1 = R^2 = R^3 = R^4 = H (at 50 °C for 40 h): 27%

n = 0, R^1 = R^2 = R^3 = H, R^4 = Me
R^{5}X = CH$_2$=CBrPh: 80%
R^{5}X = PhCH=CHBr: 55%

Cyclic carbonates have also been obtained from α-, β- and γ-hydroxyallenes by Uemura's team using Pd^0 catalysis, an aryl or styryl halide and both potassium carbonate and carbon dioxide pressure (eqn (180)).[136] The η^3-allylpalladium obtained from the Pd^0-mediated addition of the organic halide to the allenyl moiety was presumed as an intermediate.

10. Conclusions

Even if this review is limited to the Pd-catalysed formation of C–O bonds from reactions with carbons of allenes, the diversity of the possibilities presented above highlights the interest of these substrates in organic chemistry, especially for the synthesis of heterocycles. While some efficient diastereoselective reactions have been disclosed, only a few examples of enantioselective processes have been reported and, in most cases, better ligand-mediated chirality would be highly desirable. Most of the above methods involve domino reactions, but the order of the successive steps often remains a matter of debate. Given the number of related reports in the last few years, we anticipate that further applications and new valuable developments are bound to unfold.

Abbreviations

BINAP	2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl
cat.	Catalytic
Cp	η^5-C_5H_5
Cy	Cyclohexyl
dba	Dibenzylidene acetone
dppb	1,4-Bis(diphenylphosphino)butane
dppp	1,3-Bis(diphenylphosphino)propane
ee	Enantiomeric excess
equiv.	Equivalent
rt	Room temperature
TDMPP	Tris(2,6-dimethoxyphenyl)phosphine

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