Review

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Transition Metal-Catalyzed Transformations of Chalcones

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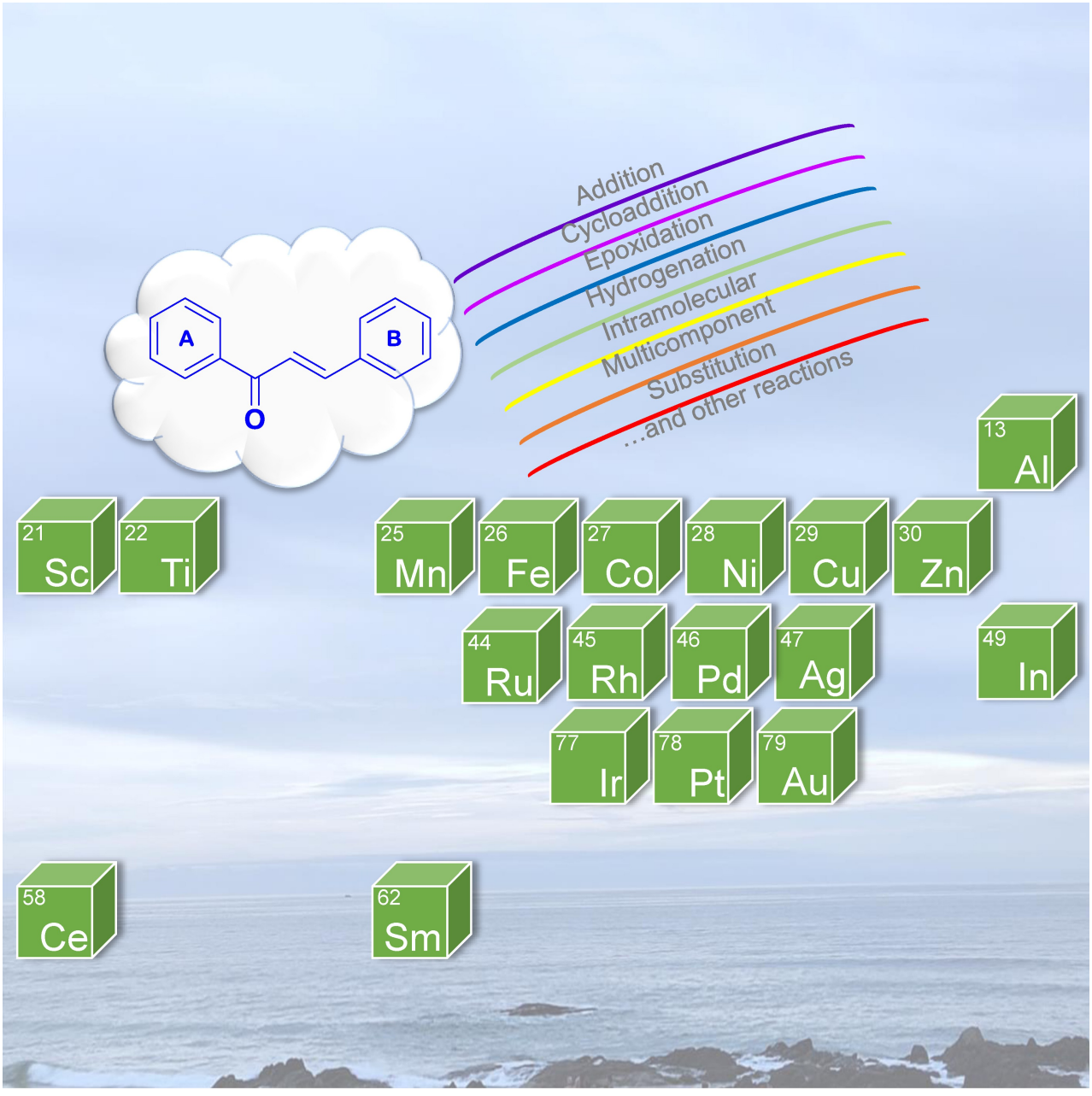

Abstract: Chalcones are a class of naturally occurring flavonoid compounds associated to a variety of biological and pharmacological properties. Several reviews have been published describing the synthesis and biological properties of a vast array of analogues. However, overviews on the reactivity of chalcones has only been explored in a few accounts. To fill this gap, a systematic survey on the most recent developments in the transition metal-catalyzed transformation of chalcones was performed. The chemistry of copper, palladium, zinc, iron, manganese, nickel, ruthenium, cobalt, rhodium, iridium, silver, indium, gold, titanium, platinum, among others, as versatile catalysts will be highlighted, covering the literature from year 2000 to 2023, in more than 380 publications.

Keywords: cycloaddition, conjugate addition, cross-coupling, hydrogenation, epoxidation

1. Introduction

Chalcones, or 1,3-diarylprop-2-en-1-ones, are open-chain flavonoid-type compounds, comprising a three carbon α,β-unsaturated carbonyl system linked by two aromatic rings A and B (structure type C_6–C_3–C_6). The A-ring is numbered from 1' to 6' and the B-ring from 1 to 6, a unique numbering system in the flavonoid family.[1,2] The configuration of Cα=Cβ double bond can exist as either (*E*)- or (*Z*)-forms, being the former thermodynamically more stable and consequently, most of chalcones are isolated as the (*E*)-isomer. Moreover, the *s-cis* conformation for the O=C–Cα=Cβ system is the adopted by the most stable conformer (Figure 1).[3] For readers convenience, (*E*)-chalcones will be referred solely as chalcones throughout the manuscript; otherwise, it will be mentioned the appropriate stereochemistry. Additionally, for simplicity in the schemes, the numbering system of the substituents refers to the positions in the chalcone starting material and not in the products obtained.

Chalcones are widely spread in nature and a huge variety of derivatives has been isolated from fruits, spices, teas, soy-based foods and various parts of plants such as roots, heartwood, shoots, leaves, flowers, and seeds. In addition, diverse substituents can be found in several positions of the chalcone core, being the hydroxy, methoxy, methyl, isopentenyl and glycosyl groups, the prevailing ones.[1,2]

Natural and synthetic derivatives are known to possess a broad spectrum of biocidal, biological, and pharmacological properties[1,2,4–13] namely as antibacterial,[14–16] anticancer,[17–23] antidiabetic,[24–27] antifungal,[15,16,28–30] anti-inflammatory,[31–33] antioxidant,[34–36] antileishmanial,[37–39] antimalarial,[40–42] antitubercular,[34,43,44] antitumoral,[45] antiviral,[46–48] inhibitor of enzymes like tyrosinase[49] and monoamine oxidase,[50] among others.

Chalcones can be applied as versatile key intermediates in the synthesis and biosynthesis of other flavonoids and diverse heterocyclic compounds. In fact, in the last decades, several reviews have appeared describing an array of methodologies for the synthesis of a wide variety of polyfunctionalized chalcones.[51–54] The synthesis and biological properties of chalcones has also been summarized in several papers.[1,55–65] More dedicated reviews highlight the palladium-catalyzed[66] and metal-catalyzed[67] cross-coupling reactions for the synthesis of chalcone derivatives and palladium-catalyzed coupling reactions in the synthesis of flavonoids, including chalcones.[68] Surprisingly, overviews on the reactivity of chalcones have only been explored in some accounts,[1,61,63–65] including palladium-catalyzed coupling reactions,[68] application of 2'-substituted chalcones in the synthesis of flavanone derivatives,[69] and chalcones as synthons for the synthesis of 5- and 6-membered

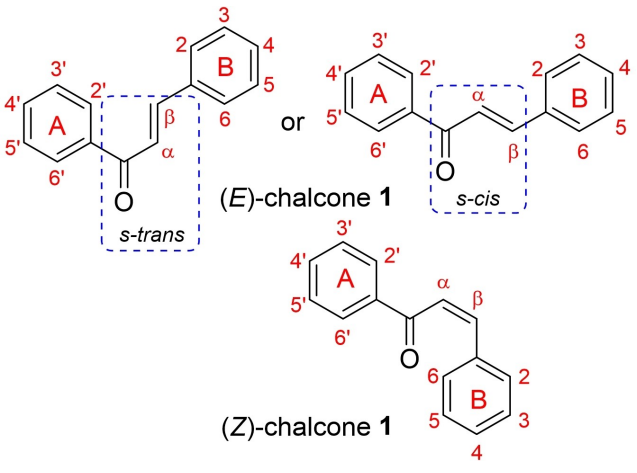

Figure 1. General structure of (*E*)- and (*Z*)-chalcone **1** and numbering system.

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nitrogen heterocycles.[70,71] Inspired by this knowledge, the main goal of this review is to present a systematic survey on the reactivity of chalcones (heterocyclic chalcones were excluded), involving transition metal-catalyzed transformations. These transformations occur not only at the carbonyl group and Cα=Cβ double bond but also, at the substituents attached to the main core, for the synthesis of novel chalcone derivatives and/or structurally diverse heterocyclic compounds. It covers the literature since the beginning of the 21st century until 2023, reported in over 380 papers.

2. Copper-Catalyzed Reactions

2.1. 1,4-Conjugate Additions

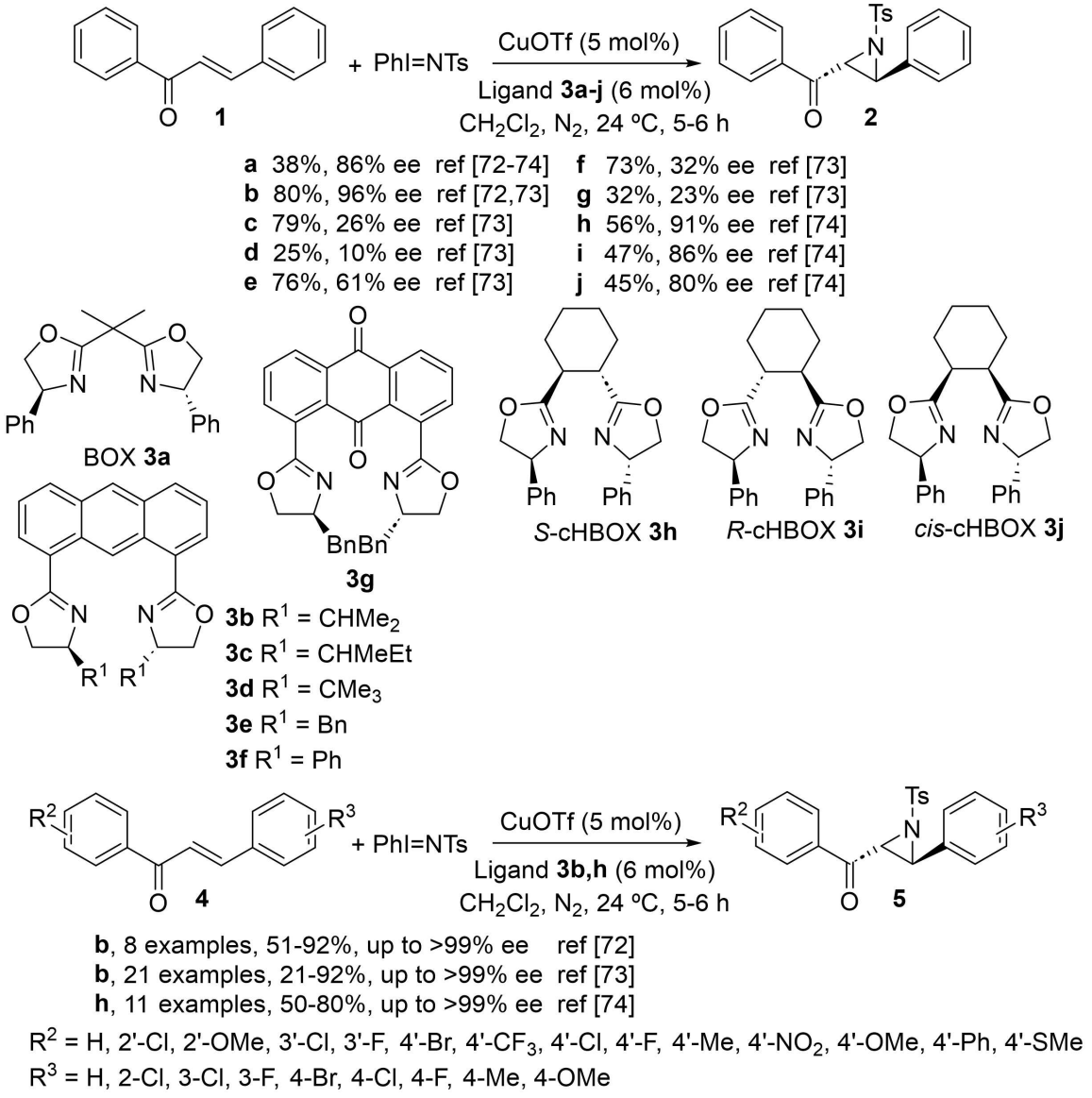
Various chiral C_2-symmetric bis(oxazoline) (BOX) ligands **3a–j** have been designed and applied in the copper(I)-catalyzed asymmetric aziridination of parent chalcone **1** with [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane (PhI=NTs) as the nitrene source (Scheme 1). The reaction occurs in dichloromethane at 24 °C under nitrogen atmosphere and the aziridine **2** is obtained in moderate to good yields and with variable enantioselectivity, according to the ligand used in the reaction.[72–74] The reaction was extended to other substituted chalcones in A- and B-rings **4**, using ligands **3b** and **3h**, to afford the corresponding polysubstituted aziridines **5** (Scheme 1). Other aziridines are enantioselectively prepared from aziridination of chalcones mediated by $(CuOTf)_2 \cdot PhMe$ using *pseudo*-C_3-symmetric tris(oxazoline) ligand in acetonitrile at room temperature for 3 h.[75]

A ligand-free conjugate addition of bis(pinacolato) diboron to chalcones mediated by copper(I) iodide in the presence of potassium carbonate and methanol in anhydrous THF at room temperature provided the 1,4-addition β-B(pin) products, in high yields.[76] An enantioselective version employed copper(II) hydroxide as catalyst, a chiral 2,2'-bipyridine as ligand, acetic acid as additive in water at room temperature to form the 1,4-addition β-B(pin) products which, after treatment with an excess of sodium perborate tetrahydrate, afforded the corresponding chiral 1,3-diaryl-3-hydroxypropan-1-ones, in good to excellent yields.[77] Further derivatives arise from a similar reaction, that proceeded in the presence of methanol as additive and diethyl ether as solvent for the boration step.[78] Mechanistic insights how copper(I) and copper(II) catalysts interact with chalcone in a non-enantioselective and enantioselective manner, respectively, in the boron conjugate addition was studied by density functional theory (DFT) and artificial force induced reaction (AFIR) methods.[79]

A greener strategy for the β-boration of chalcones **4** used recyclable chitosan supported copper catalyst [CS@$Cu(OH)_2$] in the presence of a amide-type pyridine ligand **7** in water to afford the corresponding 1,3-diaryl-3-hydroxypropan-1-ones **6**, in almost quantitative yields (Scheme 2).[80] Moreover, Gandolfi *et al.* developed hybrid catalysts from copper(I) and copper(II) biosorbing bacterial strains for the asymmetric addition of bis(pinacolate)diboron to chalcones and the results showed better conversions using copper(II) complexes.[81]

Dr. Clementina M. M. Santos graduated in Chemistry (1996), obtained her Master in Sciences in Chemistry of Natural Products and Foodstuffs (2000) and received her PhD in Chemistry (2007), all at the University of Aveiro (Portugal). She began her career at Institute Polytechnic of Bragança in 2000 as Assistant and as Assistant Professor in 2010. She has published 39 papers and 19 book chapters. Her research interests' range over the synthesis of heterocyclic compounds and evaluation of their biological properties, especially antioxidant and antidiabetic activity.

Prof. Artur M. S. Silva studied chemistry at the University of Aveiro (Portugal), where he graduated in chemistry physics in 1987. In 1993 he received his PhD in chemistry at Aveiro University. He began his independent career at Aveiro University as an Assistant Professor in 1994. He was appointed to Associate Professor with tenure in 1998 and Full Professor in 2001. He has published over 850 papers (h index of 67) and 57 book chapters. His research interests' range over the chemistry of polyphenolic and nitrogen heterocyclic compounds, with special emphasis on the development of new synthetic routes and also on organocatalytic and metal-catalyzed transformations. A second line of his research is centred on the isolation and structural characterization of natural products from diverse terrestrial and marine sources.

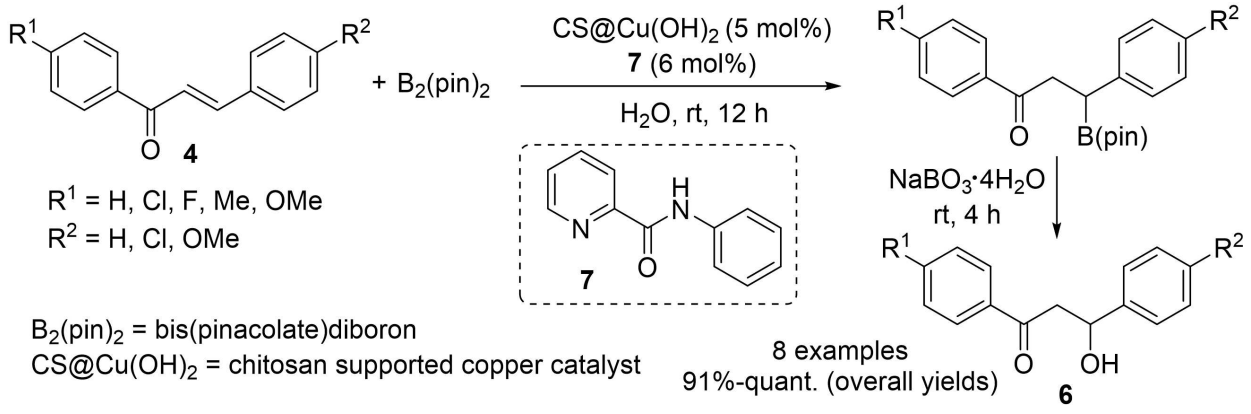


Scheme 1. Copper(I)-catalyzed asymmetric aziridination of chalcones **1** and **4**.

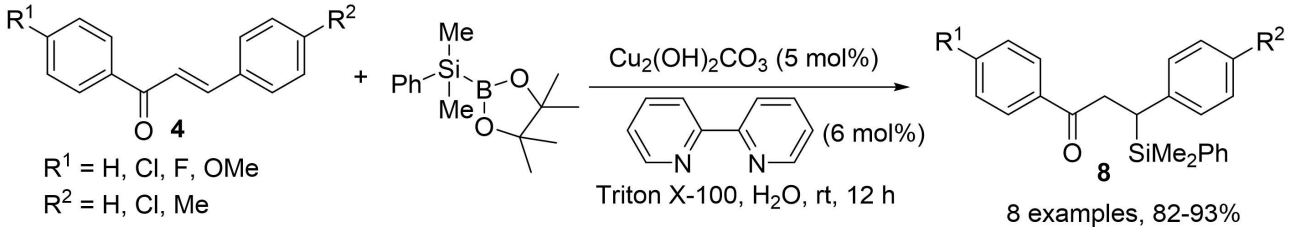
Kitanosono *et al.* reported the asymmetric silyl conjugate addition of dimethylphenylsilyl pinacolatoboronate [$PhMe_2SiB(pin)$] to chalcones promoted by copper(II) acetylacetonate [$Cu(acac)_2$] and a chiral 2,2'-bipyridine ligand in water at room temperature to deliver a series of chiral 1,3-diaryl-3-(dimethylphenylsilyl)propan-1-ones, in high yields and enantioselectivity.[82] A non-asymmetric protocol used basic copper(II) carbonate as catalyst, 2,2'-bipyridine as ligand and Triton X-100 in water at room temperature to obtain the desired 1,4-addition products **8** (Scheme 3).[83]

Copper(II) tetrafluoroborate in methanol at room temperature efficiently catalyzes Michael addition of aliphatic and aromatic thiols to parent chalcone to give 3-(alkyl/aryl)thio-1,3-diphenylpropan-1-ones.[84] On the other hand, few 4-acetyl-1,3-diarylhexane-1,5-diones were synthesized in modest yields via copper(II) triflate-catalyzed Michael addition reaction of acetyl acetone to chalcones in the presence of a biphenyl-based bis-Schiff ligand in 1,2-DCE at room temperature, after 6 days of reaction.[85]

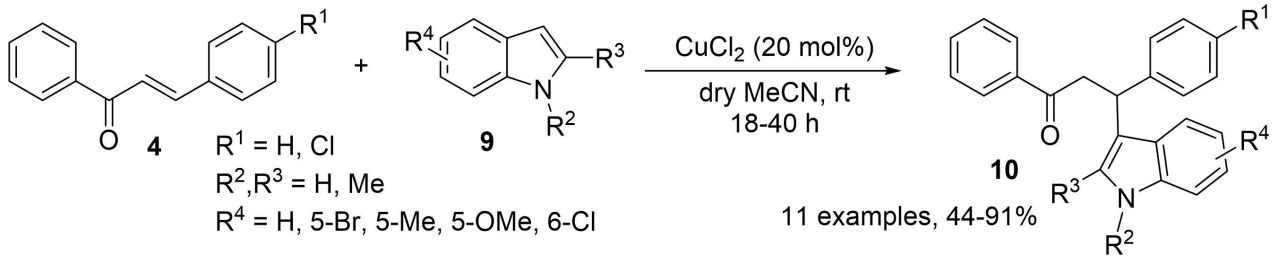
1,4-Conjugate addition of substituted indoles **9** to chalcones **4** using a catalytic amount of copper(II) chloride in dry acetonitrile at room temperature provided a range of 1,3-diaryl-3-(indol-3-yl)propan-1-one derivatives **10** (Scheme 4).[86]



Scheme 2. Chitosan supported copper(II)-catalyzed β-borylation of chalcones **4**, in water.

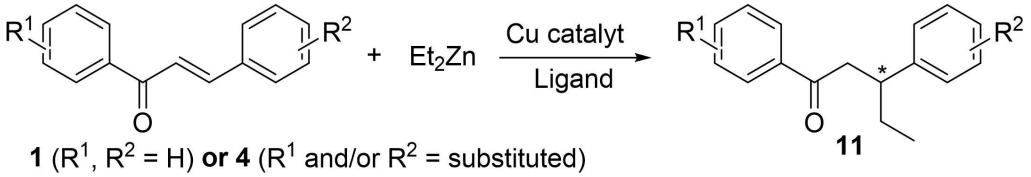


Scheme 3. Copper(II)-catalyzed β-silylation reaction of chalcones **4**, in water.



Scheme 4. Copper(II)-catalyzed 1,4-conjugate addition of indoles **9** to chalcones **4**.

Other carbon–carbon bond formation through 1,4-conjugate addition reactions has been promoted by organocopper reagents. Various chiral external ligands were synthesized and applied in the asymmetric conjugate addition reaction of diethyl zinc to chalcones **4** to produce 1,3-diarylpentan-1-ones **11**, using different copper(I) and copper(II) catalysts (Scheme 5). The most types were phosphorous-based ligands derived from 2,2'-dihydroxy-1,1'-dinaphthyl (BINOL) or modified binaphthols such as phosphonites **12**–**14** (entries 1–3, Table 1),[87] phosphites **15** (entry 4, Table 1),[88] phosphor-



Scheme 5. Enantioselective copper-catalyzed 1,4-conjugate addition of diethylzinc to chalcones **4**.

Table 1. Reaction conditions and yields obtained in the copper-catalyzed 1,4-conjugate addition of diethyl zinc to chalcones **4**, using different external chiral ligands **12**–**87**, according to Scheme 5.

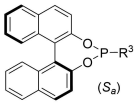
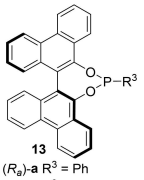
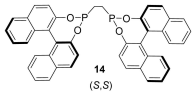
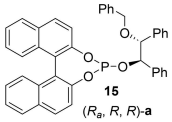
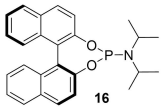
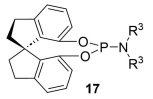
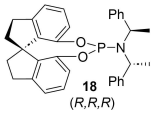
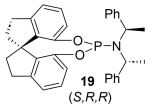
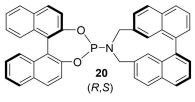
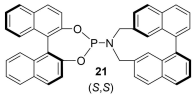
Entry	Chalcone	Catalyst	Ligand (L)	Conditions	Yield of **11**[a]	Ref.
1	**1**	$Cu(OTf)_2$	 **12** S_a = (*S*)-BINOL (S_a)-**a** R^3 = Ph (S_a)-**b** R^3 = Me (S_a)-**c** R^3 = *t*-Bu (S_a)-**d** R^3 = 2-$OMeC_6H_4$ (S_a)-**e** R^3 = cyclohexyl	toluene, −30 °C	**a**, 63 %ee (*R*) **b**, 43 %ee (*R*) **c**, 82 %ee (*R*) **d**, 47 %ee (*R*) **e**, 60 %ee (*R*)	[87]
2	**1**		 **13** (R_a)-**a** R^3 = Ph (S_a)-**b** R^3 = Me (S_a)-**c** R^3 = *t*-Bu (S_a)-**d** R^3 = 2-$OMeC_6H_4$ (S_a)-**e** R^3 = cyclohexyl		**a**, 53 %ee (*S*) **b**, 63 %ee (*R*) **c**, 80 %ee (*R*) **d**, 63 %ee (*R*) **e**, 74 %ee	
3	**1**		 **14** (*S,S*)		43 % ee (*R*)	
4	**1**	$Cu(OTf)_2$	 **15** (R_a, *R*, *R*)-**a** (S_a, *R*, *R*)-**b**	toluene, −40 °C, 90 min	**a** 66 %, 48 % ee (*S*) **b** 61 %, 11 % ee (*R*)	[88]
5	**1** **4**	$Cu(OTf)_2$	 **16**	toluene, −20 °C, 16 h	85 %, 89 % ee 11 examples, 30–94 % 15-89 % ee	[89]
6	**1** **4** (R^1 = H)	$Cu(OTf)_2$	 **17** (*R*)-**a** R^3 = Me (*R*)-**b** R^3 = Et (*R*)-**c** R^3 = *i*-Pr (*R*)-**d** R^3 = cyclohexyl	toluene, −20 °C, 8 h	**a**, 68 %, 37 % ee (*R*) **b**, 87 %, 52 % ee (*R*) **c**, 89 %, 71 % ee (*R*) **d**, 87 %, 64 % ee (*R*) **c**, 2 examples, 80–87 % 44–76 % ee **d**, 2 examples, 74–77 % 40–72 % ee	[90]
7	**1**		 **18** (*R,R,R*)		65 %, 70 % ee (*R*)	
8	**1**		 **19** (*S,R,R*)		70 %, 30 % ee (*S*)	
9	**1** **4** (R^1 = H)	$Cu(OTf)_2$	 **20** (*R,S*)	toluene, −40 °C, 1–4 h	95 %, 72 % ee (*S*) 2 examples, 63–87 %, 40–70 % ee	[91]
10	**1**		 **21** (*S,S*)		97 %, 72 % ee (*R*)	

Table 1. continued

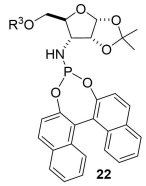
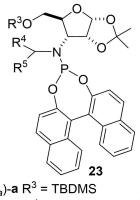
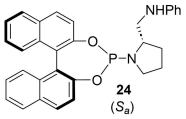
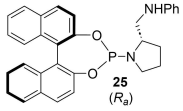
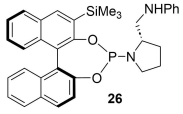
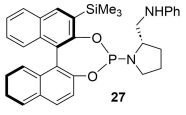
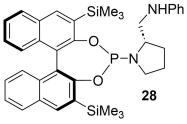
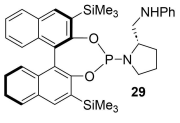
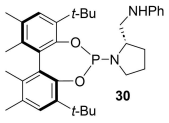
Entry	Chalcone	Catalyst	Ligand (L)	Conditions	Yield of **11**[a]	Ref.
11	**1**	$Cu(OTf)_2$	 **22** (S_a)-**a** R^3 = TBDMS; (R_a)-**b** R^3 = TBDMS; (S_a)-**c** R^3 = TBDPS; (S_a)-**d** R^3 = Tr; (S_a)-**e** R^3 = *n*-Pr; (S_a)-**f** R^3 = Piv	toluene, −20 °C, 4–4.5 h	**a**, 72 %, 59 % ee (*R*) **b**, 48 %, 21 % ee (*S*) **c**, 75 %, 37 % ee (*R*) **d**, 78 %, 4 % ee (*R*) **e**, 74 %, 45 % ee (*R*) **f**, 73 %, 37 % ee (*R*)	[92]
12	**1**	$Cu(OTf)_2$	 **23** (S_a)-**a** R^3 = TBDMS, R^4 = 4-MeOC$_6$H$_4$, R^5 = H; (S_a)-**b** R^3 = TBDMS, R^4 = cyclohexyl, R^5 = H; (S_a)-**c** R^3 = TBDMS, R^4,R^5 = Me; (S_a)-**d** R^3 = TBDMS, R^4 = Ph, R^5 = H; (R_a)-**e** R^3 = TBDMS, R^4 = Ph, R^5 = H; (S_a)-**f** R^3 = *n*-Pr, R^4 = Ph, R^5 = H	toluene, −20 °C, 3–10 h	**a**, 82 %, 75 % ee (*R*) **b**, 79 %, 71 % ee (*R*) **c**, 30 %, 16 % ee (*R*) **d**, 81 %, 77 % ee (*R*) **e**, 85 %, 23 % ee (*S*) **f**, 81 %, 76 % ee (*R*)	[92]
13	**1**	$Cu(OTf)_2$	 **24** (S_a)	toluene, −20 °C, 15 h	**24**/Cu = 1, 93 %, 54 % ee (*S*) **24**/Cu = 2, 85 %, 46 % ee (*S*)	[93]
14	**1**		 **25** (R_a)		**25**/Cu = 1, 55 %, 8 % ee (*R*) **25**/Cu = 2, 47 %, 9 % ee (*R*)	
15	**1**		 **26**		**26**/Cu = 1, 66 %, 28 % ee (*R*) **26**/Cu = 2, 34 %, 23 % ee (*R*)	
16			 **27**		**27**/Cu = 1, 67 %, 37 % ee (*R*) **27**/Cu = 2, 54 %, 36 % ee (*R*)	
17			 **28**		**28**/Cu = 1, 50 %, 30 % ee (*S*) **28**/Cu = 2, 60 %, 26 % ee (*S*)	
18			 **29**		**29**/Cu = 1, 27 %, 16 % ee (*R*) **29**/Cu = 2, 37 %, 20 % ee (*R*)	
19			 **30**		**30**/Cu = 1, 70 %, 62 % ee (*S*) **30**/Cu = 2, 73 %, 45 % ee (*S*)	

Table 1. continued

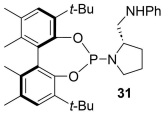
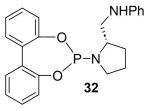
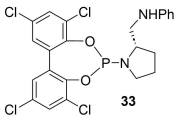
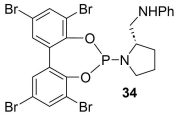
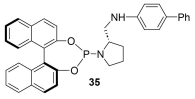
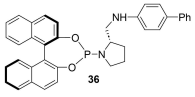
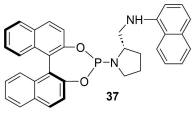
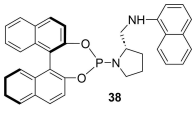
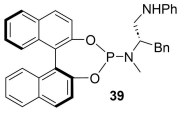
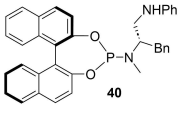
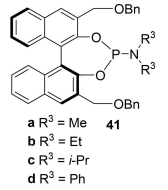
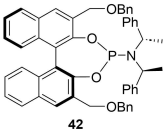
Entry	Chalcone	Catalyst	Ligand (L)	Conditions	Yield of **11**[a]	Ref.
20			 **31**		**31**/Cu = 1, 51 %, 8 % ee (*S*) **31**/Cu = 2, 38 %, 4 % ee (*S*)	
21			 **32**		**32**/Cu = 1, 17 %, 34 % ee (*S*) **32**/Cu = 2, 0 %, -% ee	
22			 **33**		**33**/Cu = 1, 15 %, 4 % ee (*S*) **33**/Cu = 2, 16 %, 12 % ee (*S*)	
23			 **34**		**34**/Cu = 1, 17 %, 7 % ee (*S*) **34**/Cu = 2, 20 %, 8 % ee (*S*)	
24			 **35**		**35**/Cu = 1, 73 %, 54 % ee (*S*) **35**/Cu = 2, 46 %, 55 % ee (*S*)	
25			 **36**		**36**/Cu = 1, 78 %, 18 % ee (*R*) **36**/Cu = 2, 62 %, 20 % ee (*R*)	
26			 **37**		**37**/Cu = 1, 65 %, 36 % ee (*R*) **37**/Cu = 2, 53 %, 25 % ee (*R*)	
27			 **38**		**38**/Cu = 1, 90 %, 60 % ee (*S*) **38**/Cu = 2, 77 %, 72 % ee (*S*)	
28			 **39**		**39**/Cu = 1, 96 %, 56 % ee (*S*) **39**/Cu = 2, 82 %, 26 % ee (*S*)	
29			 **40**		**40**/Cu = 1, 90 %, 43 % ee (*R*) **40**/Cu = 2, 89 %, 46 % ee (*R*)	
30	**1**	$Cu(OTf)_2$	 **41** **a** R^3 = Me **b** R^3 = Et **c** R^3 = *i*-Pr **d** R^3 = Ph	toluene, −40 °C, 48 h	**a**, 74 %, 57 % ee (*R*) **b**, 76 %, 70 % ee (*R*) **c**, 85 %, 87 % ee (*R*) **d**, 80 %, 49 % ee (*R*)	[94]
31			 **42**		65 %, 58 % ee (*R*)	

Table 1. continued

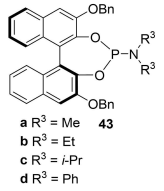
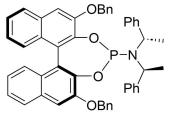
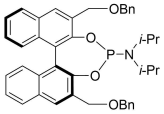
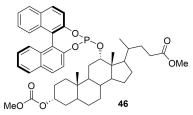
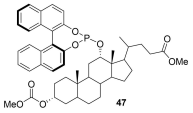
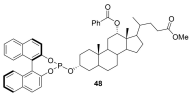
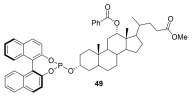
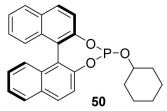
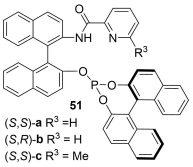
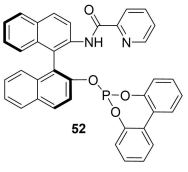
Entry	Chalcone	Catalyst	Ligand (L)	Conditions	Yield of **11**[a]	Ref.
32			 **a** R^3 = Me **43** **b** R^3 = Et **c** R^3 = *i*-Pr **d** R^3 = Ph		**a**, 84 %, 0 % ee (*R*) **b**, 76 %, 5 % ee (*R*) **c**, 72 %, 53 % ee (*R*) **d**, 80 %, 30 % ee (*R*)	
33			 **44**		70 %, 68 % ee (*R*)	
34	**4**	$Cu(OTf)_2$	 **45**	toluene, −40 °C, 48 h	21 examples, 20–83 % 39–93 % ee	[94]
35	**1** **4** (R^1 = Ph)	$Cu(OTf)_2$	 **46**	toluene, −70 °C, 3–20 h	86 %, 76 % ee (*S*) 3 examples, 22–84 % 16–78 % ee	[95]
36	**1**	$Cu(OTf)_2$	 **47**	toluene, −70 °C, 3 h	88 %, 40 % ee (*R*)	[95]
37			 **48**		88 %, 58 % ee (*S*)	
38			 **49**		85 %, 6 % ee (*R*)	
39			 **50**	toluene, −70 °C, 20 h	46 %, 32 % ee (*S*)	
40	**1**	$[Cu(CH_3CN)_4]BF_4$	 **51** (*S*,*S*)-**a** R^3 =H (*S*,*R*)-**b** R^3 = H (*S*,*S*)-**c** R^3 = Me	toluene, −10 °C, 12 h	**a**, 92 %, 91 % ee (*S*) **b**, 15 %, 54 % ee (*S*) **c**, 73 %, 96 % ee (*S*)	[96,97]
41			 **52**		14 %, 34 % ee (*R*)	[96]

Table 1. continued

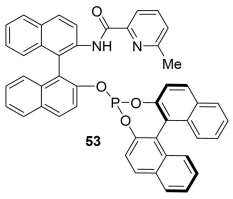
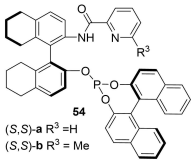
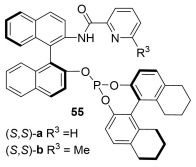
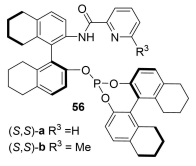
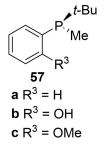
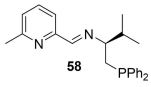
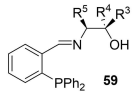
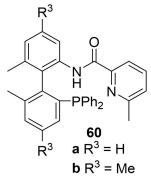
Entry	Chalcone	Catalyst	Ligand (L)	Conditions	Yield of **11**[a]	Ref.
42	**4**	$[Cu(CH_3CN)_4]BF_4$	 **53**	toluene, −10 °C, 12 h	6 examples 31–86 %, 74–97 % ee	[96]
43	**1** **4**	$[Cu(CH_3CN)_4]BF_4$	 **54** (*S*,*S*)-**a** R^3 =H (*S*,*S*)-**b** R^3 = Me	toluene, −20 °C, 12 h	**a**, 91 %, 93 % ee (*S*) **b**, 72 %, 94 % ee (*S*) **a**, 6 examples, 41–92 % 67–97 % ee **b**, 6 examples, 48–93 % 86-97 % ee	[98]
44	**1** **4**	$[Cu(CH_3CN)_4]BF_4$	 **55** (*S*,*S*)-**a** R^3 =H (*S*,*S*)-**b** R^3 = Me	toluene, −20 °C, 12 h	**a**, 54 %, 91 % ee (*S*) **b**, 40 %, 86 % ee (*S*) **a**, 6 examples, 5–71 % 24–95 % ee **b**, 6 examples, 14–57 % 41-83 % ee	[98]
45	**1** **4**	$[Cu(CH_3CN)_4]BF_4$	 **56** (*S*,*S*)-**a** R^3 =H (*S*,*S*)-**b** R^3 = Me	toluene, −20 °C, 12 h	**a**, 37 %, 49 % ee (*S*) **b**, 50 %, 81 % ee (*S*) **a**, 5 examples, 18–37 % 33–50 % ee **b**, 6 examples, 13–50 % 46-85 % ee	[98]
46	**1**	$Cu(OTf)_2$	 **57** **a** R^3 = H **b** R^3 = OH **c** R^3 = OMe	Et_2O, 0 °C, 12–18 min	**a**, 84 %, 26 % ee **b**, 84 %, 77 % ee **c**, 81 %, 61 % ee	[99]
47	**1** **4**	CuOTf	**57 b**	CH_2Cl_2, 0 °C, 0.3–1 h	88 %, 85 % ee (*R*) 7 examples, 84–98 % 61-96 %ee	[99]
48	**1**	$Cu(OTf)_2$	 **58**	CH_2Cl_2, 0 °C, 5 h	90 %, 71 % ee (*R*)	[100]
49	**1**	$Cu(acac)_2$	 **59** **a** R^3,R^4 = H, R^5 = Bn **b** R^3 = Ph, R^4 = H, R^5 = Bn **c** R^3,R^4 = Ph, R^5 = Bn **d** R^3,R^4 = Ph, R^5 = *i*-Pr	toluene, 0 °C, 16 h	**a**, 100 %, 14 % ee (*S*) **b**, 95 %, 21 % ee (*S*) **c**, 100 %, 48 % ee (*S*) **d**, 91 %, 5 % ee (*S*)	[101]
50	**1** **4**	$Cu(acac)_2$	**59 c**	hexane/Et_2O (1 : 1), −40 °C, 16 h	100 %, 83 % ee (*S*) 12 examples, 89–98 % 78–97 % ee	[101]
51	**1** **4**	$[Cu(CH_3CN)_4]BF_4$	 **60** **a** R^3 = H **b** R^3 = Me	toluene, −10 °C, 3 h	**a**, 79 %, 92 % ee (*R*) **b**, 84 %, 91 % ee (*R*) **a**, 6 examples, 38–81 % 90-95 % ee **b**, 6 examples, 47–82 % 87-96 % ee	[102]

Table 1. continued

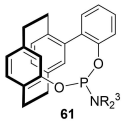
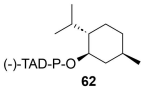
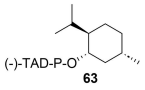
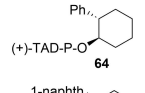
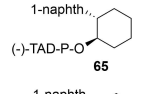
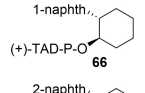
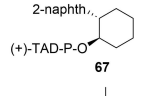
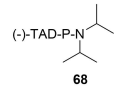
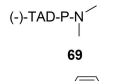
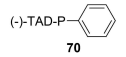
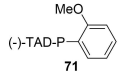
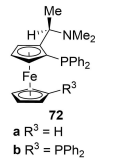
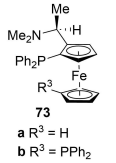
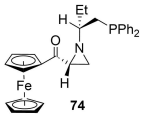
Entry	Chalcone	Catalyst	Ligand (L)	Conditions	Yield of **11**[a]	Ref.
52	**1** **4**	$Cu(OTf)_2$	 **61** (*S*)-**a** R^3 = Me (*S*)-**b** R^3 = Et (*S*)-**c** R^3 = *i*-Pr	hexane/toluene, −20 °C or 0 °C, 2–12 h	**a**, 92 %, 88 % ee (*R*) **b**, 94 %, 95 % ee (*R*) **c**, 89 %, 82 % ee (*R*) **b**, 12 examples, 90–98 %, 55–95 % ee	[103]
53	**1**	$Cu(OTf)_2$	 (-)-TAD-P-O **62**	−20° to −10 °C, 2 h	64 %, 0 % ee	[104]
54			 (-)-TAD-P-O **63**	−20° to 10 °C, 3 h	51 %, 21 % ee (R)	
55			 Ph (+)-TAD-P-O **64**	−20° to −10 °C, 3 h	96 %, 50 % ee (*S*)	
56			 1-naphth (-)-TAD-P-O **65**	−20° to −10 °C, 3 h	90 %, 17 % ee (*R*)	
57			 1-naphth (+)-TAD-P-O **66**	−20° to −10 °C, 3 h	99 %, 30 % ee (*S*)	
58			 2-naphth (+)-TAD-P-O **67**	−20° to −10 °C, 3 h	84 %, 25 % ee (*S*)	
56			 (-)-TAD-P-N **68**	−20° to −10 °C, 6 h	37 %, 13 % ee (*R*)	
60			 (-)-TAD-P-N **69**	−20 °C, 4.5 h	60 %, 3 % ee (*S*)	
61			 (-)-TAD-P **70**	−5 °C to rt, 24 h	55 %, 7 % ee (*R*)	
62			 MeO (-)-TAD-P **71**	−20 °C, 7 h	48 %, 8 % ee (*R*)	
63	**1** **4**	$Cu(OTf)_2$	 Me H NMe_2 PPh_2 Fe R^3 **72** **a** R^3 = H **b** R^3 = PPh_2	toluene, 0 °C, 10 h; then rt, 38 h	**a**, 60 %, 41 % ee (*R*) **b**, 30 %, 15 % ee (*R*) **a**, 12 examples, 40–96 % 10–92 % ee	[105]
64	**1** **4**		 Me Me_2N H Ph_2P Fe R^3 **73** **a** R^3 = H **b** R^3 = PPh_2		**a**, 60 %, 41 % ee (*S*) **b**, 31 %, 15 % ee (*S*) **a**, 6 examples, 80–95 % 81–91 % ee	[105]
65	**1**	$Cu(OTf)_2$	 Et H PPh_2 O N Fe H **74**	toluene, 0 °C, 4 h	66 %, 10 % ee (*S*)	[106]

Table 1. continued

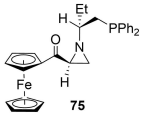
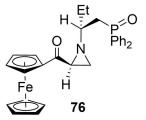
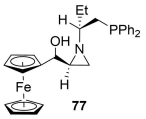
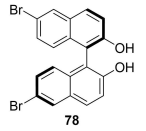
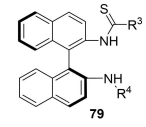
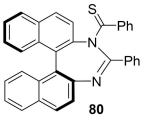
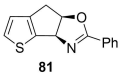
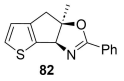
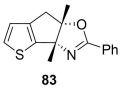
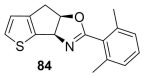
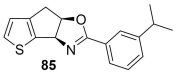
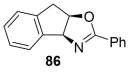
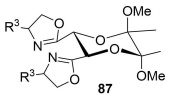
Entry	Chalcone	Catalyst	Ligand (L)	Conditions	Yield of **11**[a]	Ref.
66			 **75**		75%, 50% ee (*R*)	
67			 **76**		51%, 14% ee (*S*)	
68			 **77**		71%, 14% ee (*S*)	
69	**1**	$Cu(OTf)_2$	**75**	1,2-DCE, −20 °C, 4 h	89%, 88% ee 13 examples, 59–96% 70–92% ee	[106]
	4					
70	**1**	CuSPh Cy_2NMe	 **78**	toluene, 0 °C, 5 h	95%, 9% ee (*R*)	[107]
71	**1**	$[Cu(CH_3CN)_4]ClO_4$	 **79** (S_a)-**a** R^3 = Ph, R^4 = Et (S_a)-**b** R^3 = Me, R^4 = Et (S_a)-**c** R^3 = Me, R^4 = Bn (S_a)-**d** R^3 = Ph, R^4 = Bn	toluene, 10 °C, 48 h	**a**, 47%, 51% ee (*R*) **b**, 63%, 8% ee (*R*) **c**, 39%, 7 ee (*R*) **d**, 32%, 52%ee (*R*)	[108]
	4				**a**, 3 examples, 25–36% 51–73% ee	
72	**1**	$[Cu(CH_3CN)_4]ClO_4$	 **80**	toluene, 10 °C, 48 h	21%, 3%ee (*R*)	[108]
73	**1**	$Cu(OTf)_2$	 **81**	solvent, −20 to 0 °C, 6 h	toluene, 61%, 51% ee (*S*) Et_2O, 51%, 53% ee (*S*)	[109]
74			 **82**		toluene, 58%, 70% ee (*R*) Et_2O, 49%, 79% ee(*R*)	
75			 **83**		toluene, 58%, 58% ee (*R*) Et_2O, 40%, 65% ee (*R*)	
76			 **84**	toluene, −20 to 0 °C, 6 h	58%, 47% ee (*S*)	
77			 **85**		55%, 43% ee (*S*)	
78			 **86**	Et_2O, −20 to 0 °C, 6 h	50%, 32% ee (*S*)	

Table 1. continued

Entry	Chalcone	Catalyst	Ligand (L)	Conditions	Yield of **11**[a]	Ref.
79	**1**	$Cu(OTf)_2$	 **87** **a** R^3 = (*S*)-Ph **b** R^3 = (*R*)-Ph **c** R^3 = (*S*)-*i*-Pr **d** R^3 = (*S*)-*t*-Bu	toluene, 0 °C, 17 h	**a**, 46% ee (*S*) **b**, 3% ee (*R*) **c**, 31% ee (*S*) **d**, 31% ee (*S*)	[110]

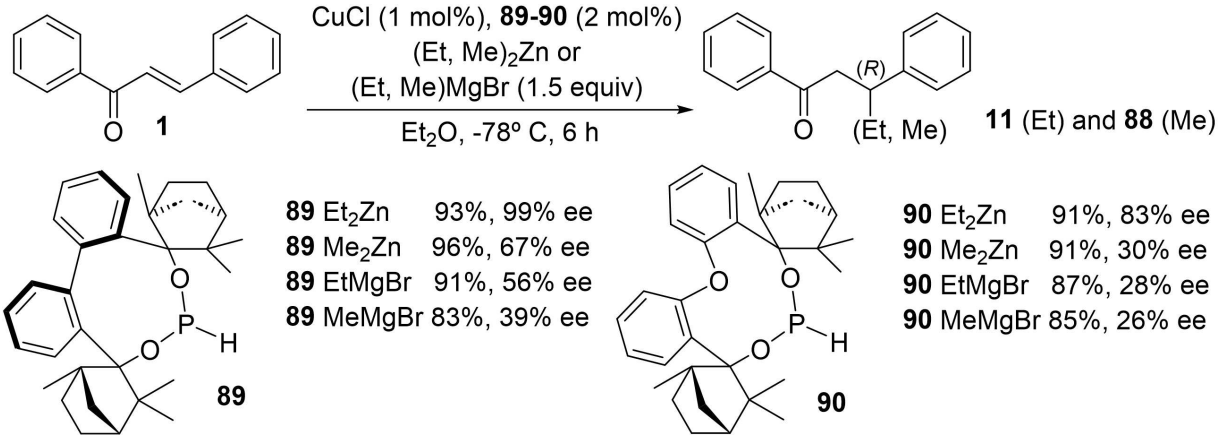
[a] Letters **a–f**, if appear, correspond to the ligand used.

amidites **16–45** (entries 5–34, Table 1),[89–94] deoxycholic acid-phosphites **46–50** (entries 35–39, Table 1)[95] and phosphite-pyridines **51–56** (entries 40–45, Table 1).[96–98] Other ligands bearing phosphorous atoms include *o*-phosphino phenol derivatives **57** (entries 46–47, Table 1),[99] phosphine-pyridines **58–60** (entries 48–51, Table 1),[100–102] [2.2]paracyclo phane-derived phosphoramidites **61** (entry 52, Table 1),[103] cyclic phosphites derived from 2,3-*O*-isopropylidene-1,1,4,4-tetra-phenylthreitol (TADDOL) **62–71** (entries 53–62, Table 1)[104] and ferrocenyl-phosphines ligands **72–77** (entries 63–69, Table 1).[105,106]

Some BINOL- **78** (entry 70, Table 1)[107] and 2,2'-diamine-1,1'-dinaphthyl (BINAM)-based **79–80**[108] ligands without phosphorous atom (entries 71–72, Table 1), and oxazoline-type derivatives **81–87** (entries 73–79, Table 1)[109,110] have also been successfully used in the enantioselective catalytic conjugate addition of diethyl zinc to chalcones (Scheme 5 and Table 1). A comprehensive overview on the enantioselective copper-catalyzed 1,4-conjugate addition of organometallic reagents to α,β-unsaturated compounds, in which chalcones are included, was published by Jerphagnon *et al.* in 2009.[111]

Brüllingen *et al.* studied the influence of biphenyl-bisfenchol-based ligands **89–90** in the enantioselective Cu(I)-catalyzed 1,4-conjugate addition of organozinc [$(Et, Me)_2Zn$] and organomagnesium [(Et, Me)MgBr] reagents to parent chalcone **1**, using diethyl ether as solvent at −78 °C for 6 h. Cu/**89** catalytic system induced the higher enantioselectivity for all the alkylation agents, being higher for the organozinc reagents than that of Grignard reagents. Thus, Et_2Zn as alkylating reagent yields (*R*)-1,3-diphenylpentan-1-one **11** with 99% ee; using Me_2Zn, (*R*)-1,3-diphenylbutan-1-one **88** is obtained with 67% ee; using EtMgBr as alkylating reagent led to the formation of (*R*)-product **11** with 56% ee and with MeMgBr, (*R*)-product **88** is produced with 39% ee (Scheme 6). In the absence of ligands, racemic 1,4-conjugate addition products are obtained.[112]

Chemoselective 1,4-conjugate addition of alkyl- and aryl magnesium halides (I, Br) to chalcones mediated by copper(II) on a 4 Å molecular sieves support in refluxing diethyl ether for 6 h furnished 1,4-conjugate addition products 3-(alkyl/aryl)-1,3-diarylpropan-1-ones, in moderate to good yields.[113,114]



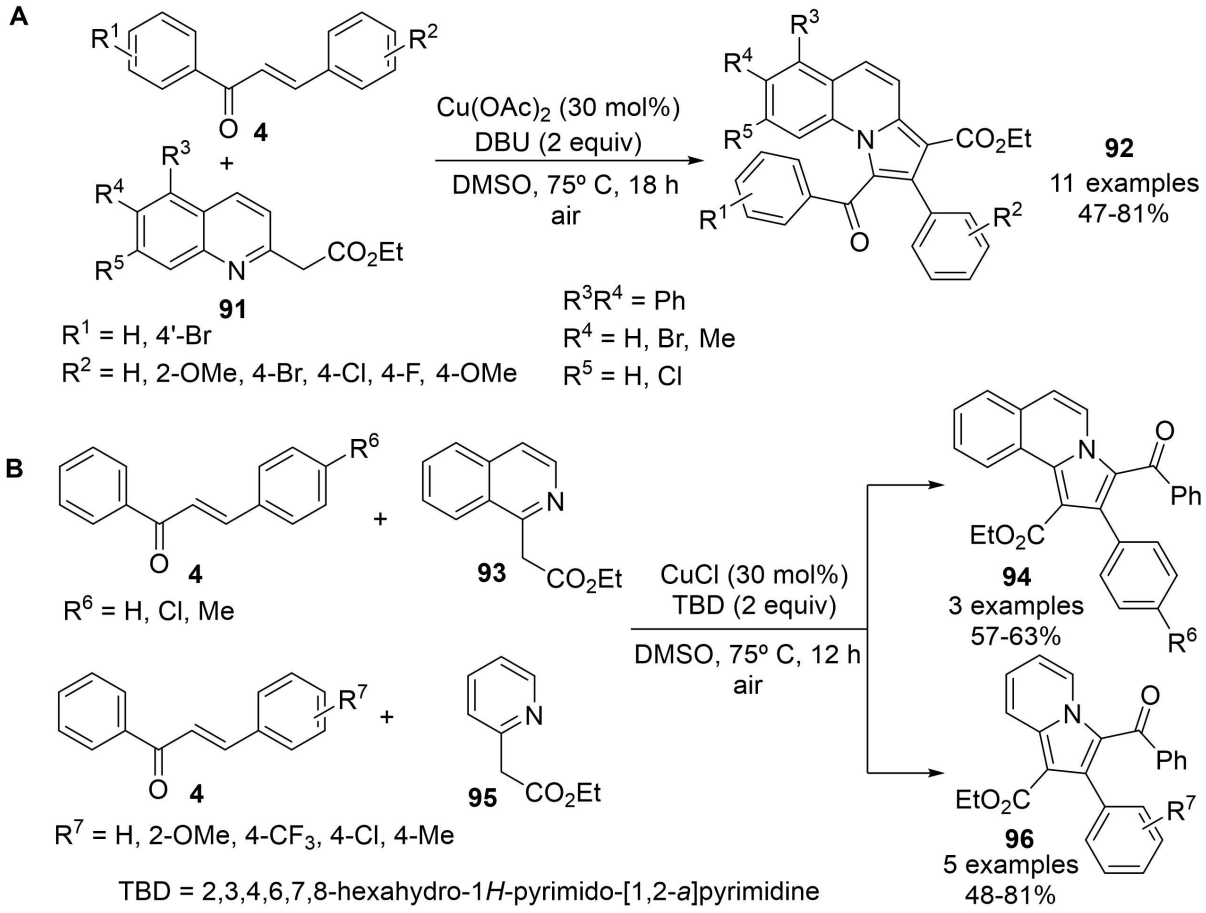
Scheme 6. Enantioselective copper(I)-catalyzed 1,4-conjugate addition of organozinc and Grignard reagents to chalcone **1**.

2.2. Cycloaddition Reactions

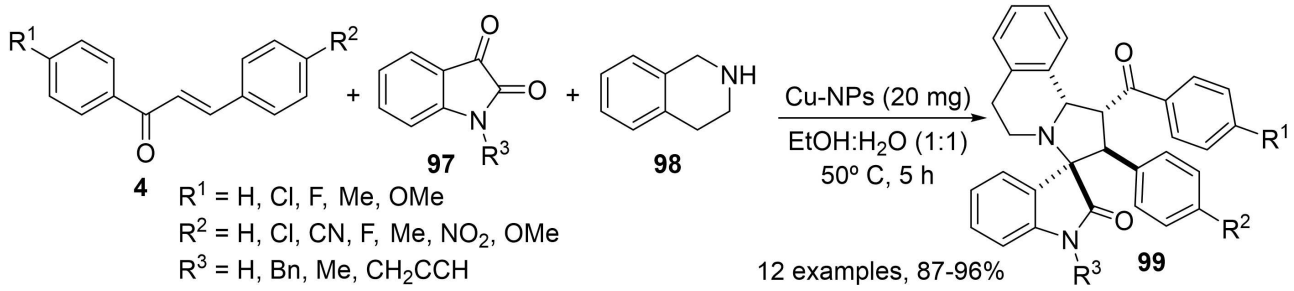
Diversely substituted *NH*-pyrrole-2-carboxylate/2,5-dicarboxylates are readily achieved through copper(II) acetate-promoted oxidation/[3+2] cycloaddition/aromatization cascade reaction of ethyl 2-(benzylamino)acetate/iminodiacetates to chalcones, respectively, in the presence of triethylamine in DMF at 100 °C for 8 h, under an atmosphere of air.[115]

One-pot two-steps synthesis of *NH*-pyrrole-2-carboxylates results from cyclocondensation reaction of chalcones with glycine esters in the presence of acetic acid and pyridine at reflux followed by oxidation promoted by DDQ, 1.2 or 2 equiv. of copper(II) acetate or by copper(I) chloride under air atmosphere. Both cyclization and oxidation reactions were performed under microwave irradiation. The reaction was extended to the microwave-assisted synthesis of *NH*-pyrrole-2-carboxamides starting from chalcones and glycine amides in refluxing pyridine followed by oxidation promoted by 1.2 or 2 equiv. of copper(II) acetate.[116] Copper(II) acetate also mediated aerobic oxidative [3+2] cycloaddition reaction of chalcones **4** with ethyl (quinolin-2-yl)acetates **91** in the presence of DBU in DMSO at 75 °C to deliver pyrrolo[1,2-*a*]quinolines **92**, using air as terminal oxidant (Scheme 7, route A). Moreover, some pyrrolo[2,1-*a*]isoquinolines **94** and indolizines **96** were obtained through copper(I)-catalyzed reaction of chalcones **4** with, respectively, ethyl (isoquinolin-1-yl)acetates and **93** ethyl (pyridin-2-yl)acetates **95**, employing 2,3,4,6,7,8-hexahydro-1*H*-pyrimido-[1,2-*a*]pyrimidine (TBD) as base in DMSO at 75 °C under air atmosphere (Scheme 7, route B).[117] A series of spiroxindolinone polycyclic compounds **99** were synthesized through 1,3-dipolar cycloaddition reaction of chalcones with azomethine ylides, generated *in situ* from isatins **97** and 1,2,3,4-tetrahydroisoquinoline **98**, induced by copper(II) oxide nanoparticles immobilized on microcrystalline cellulose in a 1 : 1 mixture of ethanol:water at 50 °C for 5 h (Scheme 8).[118]

A wide range of 2,5-diaryloxazoles can be prepared via oxidative cyclization reaction of benzylic amines with chal-



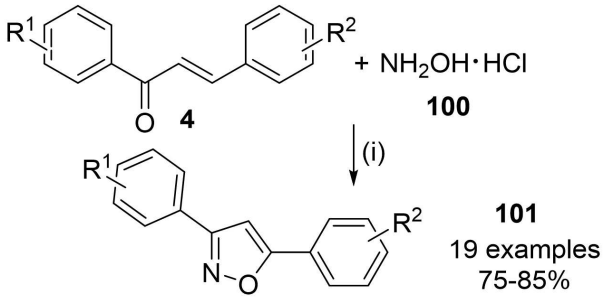
Scheme 7. Copper-catalyzed aerobic oxidative [3+2] cycloaddition reaction of chalcones **4** with ethyl (quinolin-2-yl)acetates **91** (route A), ethyl (isoquinolin-1-yl)acetates **93** and ethyl (pyridin-2-yl)acetates **95** (route B).



Scheme 8. Copper oxide nanoparticles-catalyzed 1,3-dipolar cycloaddition reaction of chalcones **4** with isatins **97** and 1,2,3,4-tetrahydroisoquinoline **98**.

cones mediated by copper(II) bromide, pyridine, potassium carbonate and lithium bromide in refluxing dry toluene for 11 h, using oxygen as clean oxidant.[119] The same copper catalyst promotes oxidative cyclization reaction of hydroxylamine hydrochloride **100** with chalcones **4** carried out in the presence of oxone in ethanol at 80 °C to give 3,5-diarylisoxazoles **101**, in high yields (Scheme 9).[120]

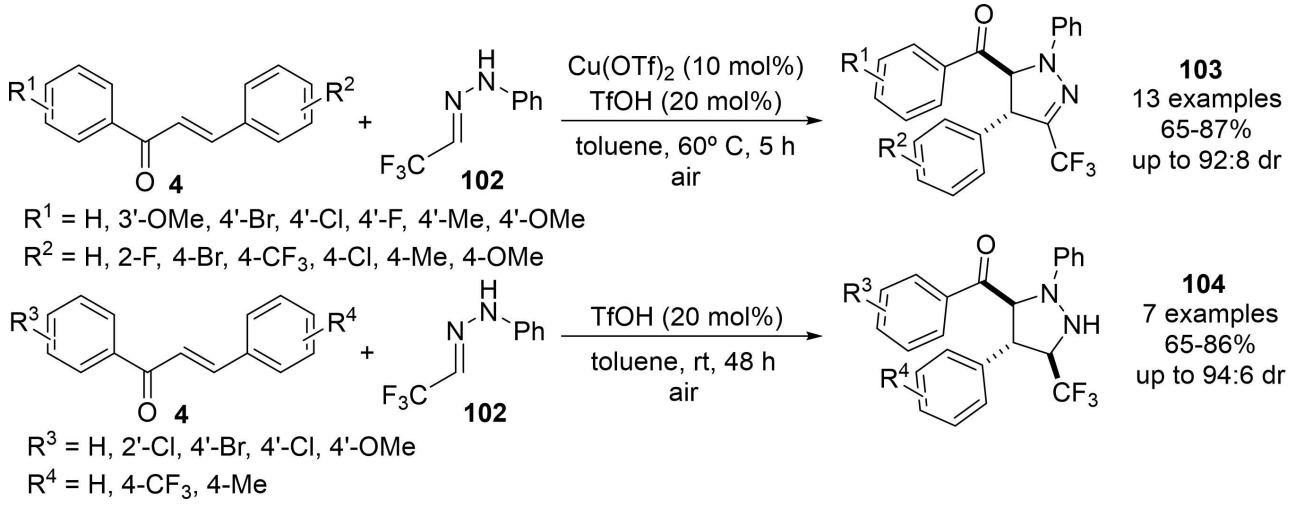
One-pot 1,2-addition–cyclocondensation reaction of chalcones with arylhydrazines mediated by copper(II) triflate in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) ionic liquid and subsequent oxidative aromatization is time-controlled: for 20–30 min of reaction, 1,3,5-triarylpyrazolines are obtained as major products (60–84 %); if the reaction is extended for 1–3 h, oxidation takes place to obtain 1,3,5-triarylpyrazoles in 71–84 % yield.[121] Under dual catalysis of copper(II) triflate and triflic acid, diastereoselective 1,3-dipolar cycloaddition reaction of chalcones **4** with trifluoroacetaldehyde phenylhydrazone **102** in toluene at 60 °C afforded 4-aryl-5-aryloxy-1-phenyl-3-trifluoromethyl pyrazolines **103**. Moreover, if the reaction is promoted solely by triflic acid in toluene at room temperature, a series of 4-aryl-5-aryloxy-1-phenyl-3-trifluoromethylpyrazolidines **104** was obtained (Scheme 10).[122]



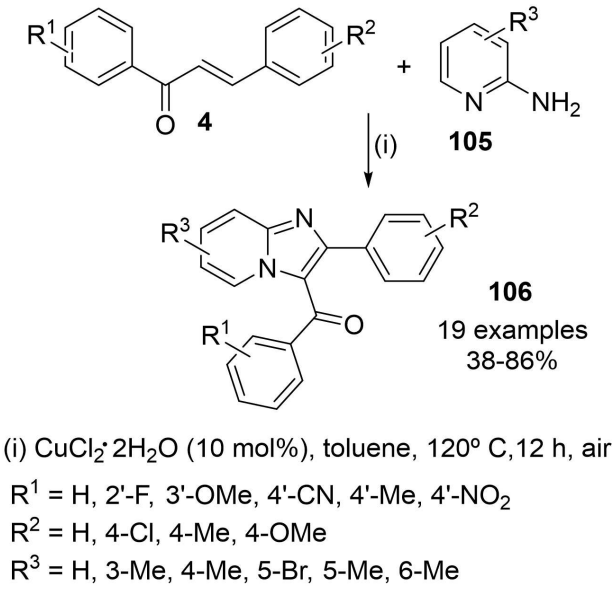
Scheme 9. Copper(II) bromide-catalyzed oxidative cyclization reaction of chalcones **4** with hydroxylamine hydrochloride **100**.

A wide range of 3-aroylimidazo[1,2-*a*]pyridines **106** arose from tandem reaction of chalcones **4** with 2-aminopyridines **105** mediated by copper(II) chloride dihydrate in toluene at 120 °C for 12 h under air atmosphere (Scheme 11),[123] copper(II) acetate hydrate and 1,10-phenanthroline in 1,2-dichlorobenzene at 120 °C for 12 h under molecular oxygen atmosphere[124] and promoted by $CuFe_2O_4$ superparamagnetic nanoparticle catalyst in the presence of molecular iodine in 1,4-dioxane for 7 h and using oxygen as oxidant.[125] In the former case, the proposal mechanism involves: i) copper-catalyzed 1,4-conjugate addition of 2-aminopyridine to chalcone to give the Michael adduct, 1,3-diphenyl-3-(pyridin-2-ylamino)propan-1-one; ii) tautomerization; iii) pyridinium nitrogen binding to copper catalyst and simultaneously reaction with the enol to form a cyclic Cu(II) intermediate; iv) oxidation followed by reductive elimination; v) oxidative aromatization under aerobic conditions. The catalytic cycle is completed by conversion of Cu(I) into Cu(II) species under aerobic conditions. In the latest protocol involving the use of iodine, the authors speculated that the reaction may proceed through the formation of α-iodochalcone followed by nucleophilic substitution with 2-aminopyridine to β-position. The final oxidation of the α,β C–C single bond is facilitated by the copper species in the presence of oxygen as oxidant.

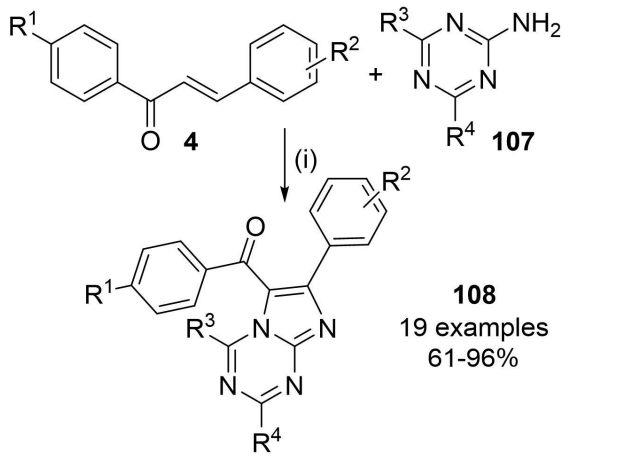
Li *et al.* reported a regioselective copper(II)-catalyzed oxidative cyclization reaction of chalcones **4** with 2-amino-1,3,5-triazines **107** in the presence of iodine in refluxing chlorobenzene under oxygen atmosphere to afford aroylimidazo[1,2-*a*][1,3,5]triazines **108** in good to excellent yields (Scheme 12).[126] The proposed mechanism includes Michael addition of 2-amino-1,3,5-triazines to chalcones and subsequent reaction with iodine to form intermediate **B**; binding of triazine nitrogen and enolic carbon simultaneously



Scheme 10. Diastereoselective 1,3-dipolar cycloaddition reaction of chalcones **4** with trifluoroacetaldehyde phenylhydrazone **102**, with and without copper(II) catalysis.



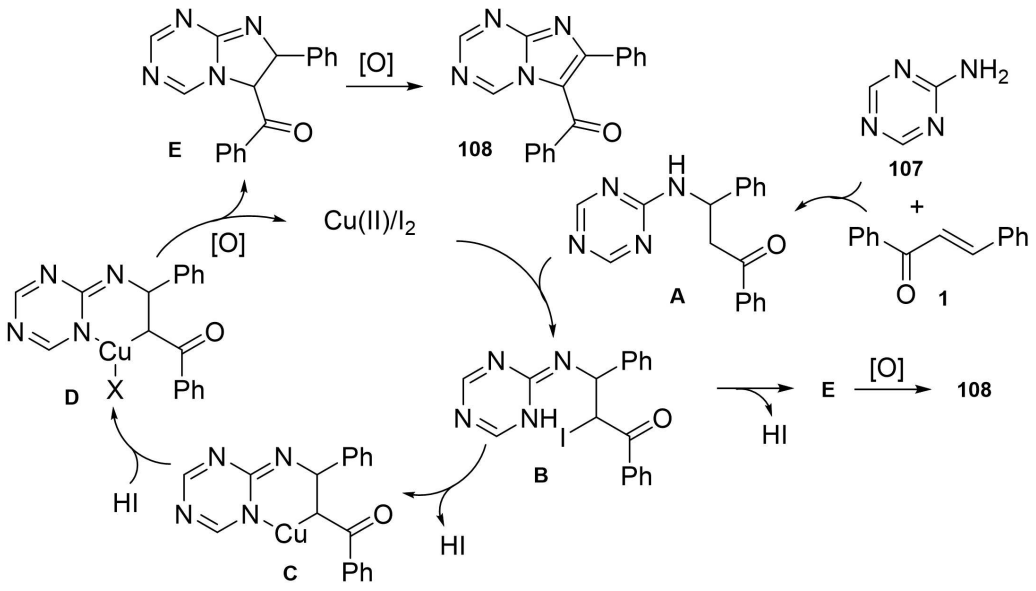
Scheme 11. Copper(II)-catalyzed tandem reaction of chalcones **4** with 2-aminopyridines **105**.



Scheme 12. Copper(II)-catalyzed oxidative cyclization reaction of chalcones **4** with 2-amino-1,3,5-triazines **107**.

to form the organocopper intermediate **C**; oxidation by oxygen to afford cyclic copper intermediate **D**; metal reductive elimination to give intermediate **E**. On the other hand, intermediate **B** also could directly undergo the intramolecular nucleophilic displacement to form the cyclic product **E**. Finally, dehydrogenative aromatization of **E** forms to desired product **108**. Copper(I) species is converted into the copper(II) system in the presence of oxygen and iodine to take part in the next catalytic cycle (Scheme 13).

A series of chalcones underwent oxidative cycloaddition reaction with sodium azide promoted by a catalytic amount of copper(I) iodide in DMF at 110 °C for 6 h to afford 4,5-disubstituted 2*H*-[1,2,3]-triazoles, in high yields.[127] The synthesis of *N*-2-aryl substituted [1,2,3]-triazoles occurred via oxidative cycloaddition reaction of chalcones with sodium azide and post-triazole arylation using aryl halides, promoted

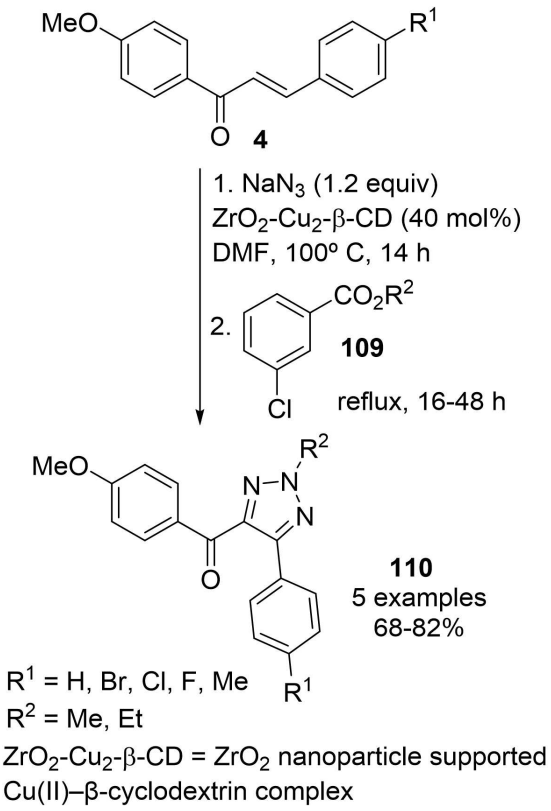


Scheme 13. Proposed mechanism for the synthesis of aroylimidazo[1,2-*a*][1,3,5]triazine **108** ($R^1 = R^2 = R^3 = H$).

by: (i) a catalytic amount of a binuclear copper(I) complex containing *N*′,*N*′-bis{(1*H*-indol-3-yl)methylene}oxalohydrazide ligand, in DMF at 50–100 °C for 22 h;[128] (ii) copper(II) oxide in DMF at 80 °C for 24 h[129] or at 100 °C for 20 h[130] and (iii) magnetic $CuFe_2O_4$ nanoparticles.[131] It is important to highlight that the methodology using copper(II) salts requires the use of stoichiometric amounts of the catalysts. More *N*-2-aryl substituted [1,2,3]-triazoles were prepared in excellent yields through multicomponent reaction of chalcones with sodium azide and aryl fluorides, in equimolar amounts, promoted by chitosan copper(II) oxide nanocomposite in refluxing DMF for 4 h.[132]

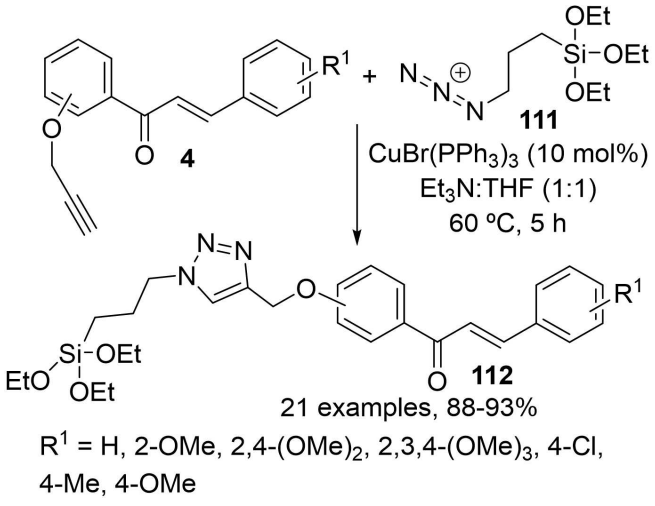
One-pot synthesis of 2-alkyl-5-aryl-4-aroyl[1,2,3]-triazoles **110** was accomplished through 1,3-dipolar cycloaddition reaction of chalcones **4** with sodium azide in DMF mediated by ZrO_2 nanoparticle supported Cu(II)-β-cyclodextrin complex followed by alkylation reaction using alkyl 3-chlorobenzoates **109** as alkylating agents (Scheme 14). The prepared nanocatalyst is easily regenerated and reused over four times with only a slight loss of the catalytic activity.[133]

1,3-Dipolar cycloaddition reaction of organic azides with alkynes, via Huisgen method, has been applied in the functionalization of a series of chalcones bearing azide or alkyne units linked to A- or B-ring, leading to the synthesis of [1,2,3]-triazole-chalcone hybrids with promising biological properties. Thus, 2'-propargyloxy chalcones underwent cycloaddition reaction with benzyl azide promoted by copper(I) iodide in DMF under microwave irradiation[134,135] and by copper(II) sulfate in the presence of sodium ascorbate in a 1 : 1 mixture of *t*-butanol:water at room temperature[136] to give

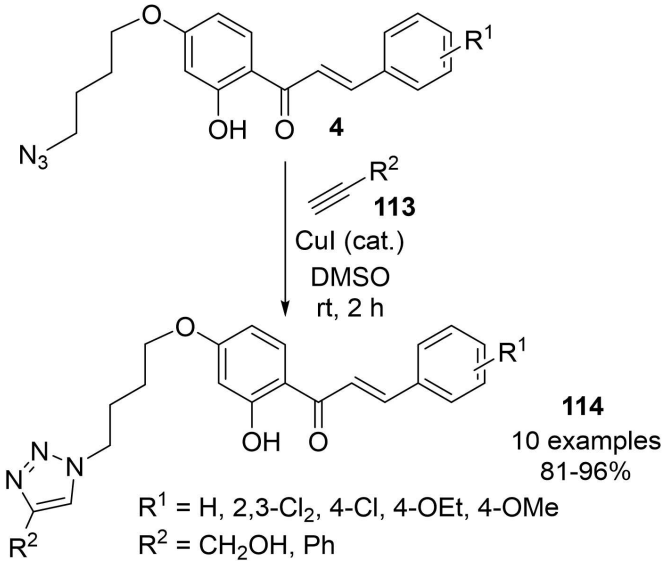


Scheme 14. 1,3-Dipolar cycloaddition reaction of chalcones **4** with sodium azide, mediated by ZrO_2 nanoparticle supported Cu(II)–β-cyclodextrin complex, followed by alkylation.

diversely substituted 1-benzyl-1*H*-[1,2,3]-triazole-chalcone conjugates. Copper(II) sulfate/sodium ascorbate (or ascorbic acid) catalytic system was also applied in the reaction of *O*-propargylated chalcone derivatives with aromatic azides in a mixture of DMF/water at room temperature[137,138] or under microwave irradiation[139] to furnish 1-aryl-1*H*-[1,2,3]-triazole-chalcone conjugates. Singh *et al.* used a different copper catalyst, bromotris(triphenylphosphine)copper(I), in the presence of triethylamine/THF solvent system for the functionalization of *O*-propargylated chalcones **4** with 3-azidopropyltriethoxysilane **111** giving access to 1*H*-[1,2,3]-triazole-tethered triethoxysilane-chalcone derivatives **112** (Scheme 15).[140]



Scheme 15. Synthesis of 1*H*-[1,2,3]-triazole-tethered triethoxysilane-chalcone hybrids **112** via copper(I)-catalyzed 1,3-dipolar cycloaddition reaction *O*-propargylated chalcones **4** with 3-azidopropyltriethoxysilane **111**.



Scheme 16. Synthesis of [1,2,3]-triazole-chalcone conjugates **114** via copper(I)-catalyzed cycloaddition reaction of azidochalcones **4** with terminal alkynes **113**.

On the other hand, Yadav *et al.* proposed a greener protocol for the synthesis of 1-(aryl or benzyl)-1*H*-[1,2,3]-triazole-chalcone conjugates by reacting propargyloxychalcones with aromatic azides or with sodium azide and various benzyl bromides, respectively, in presence of cellulose supported copper nanoparticles, in water at 70 °C.[141,142]

A variety of [1,2,3]-triazole-chalcone conjugates **114** was also achieved in a very efficient manner through cycloaddition reaction of azidochalcones **4** with terminal alkynes **113** catalyzed by copper(I) iodide in DMSO at room temperature (Scheme 16)[143] or employing copper(II) sulfate, in the presence of sodium ascorbate[144,145] or generated from ascorbic acid and sodium hydroxide,[146] in a 1 : 1 mixture of *n*-butanol: water at room temperature.

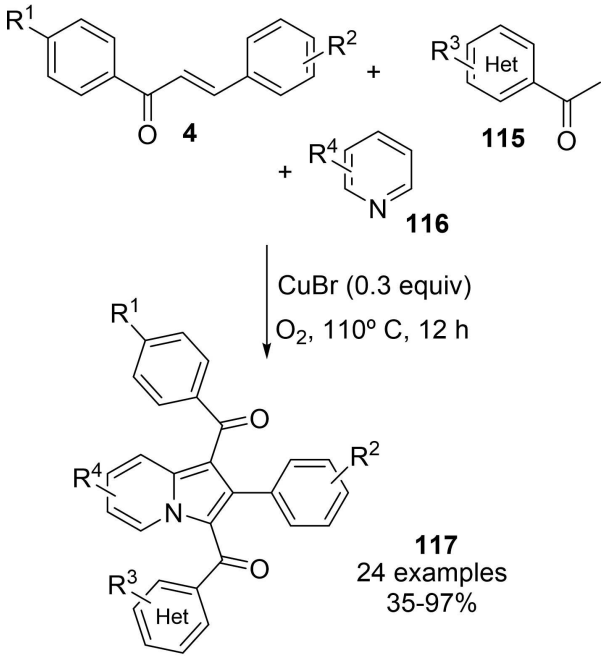
2.3. Multicomponent Reactions

The synthesis of 1,3,5-triaryl-4-(organylselanyl)pyrazoles was accomplished via multicomponent reaction of chalcones with arylhydrazines and diorganoyl diselenides under dual catalysis of copper(I) bromide and 2,2′-bipyridine, in refluxing acetic acid for 48 h.[147] The same copper catalyst is applied in multicomponent reaction of chalcones **4** with acetophenones **115** and pyridines **116**, using oxygen as oxidant, under solvent-free conditions at 110 °C for 12 h to afford polyfunctionalized indolizines **117** (Scheme 17).[148] Further derivatives can be obtained from one-pot reaction of chalcones with benzyl bromides and pyridines mediated by copper(II) acetate and potassium carbonate in DMF at 120 °C for 8 h, under oxygen atmosphere.[149]

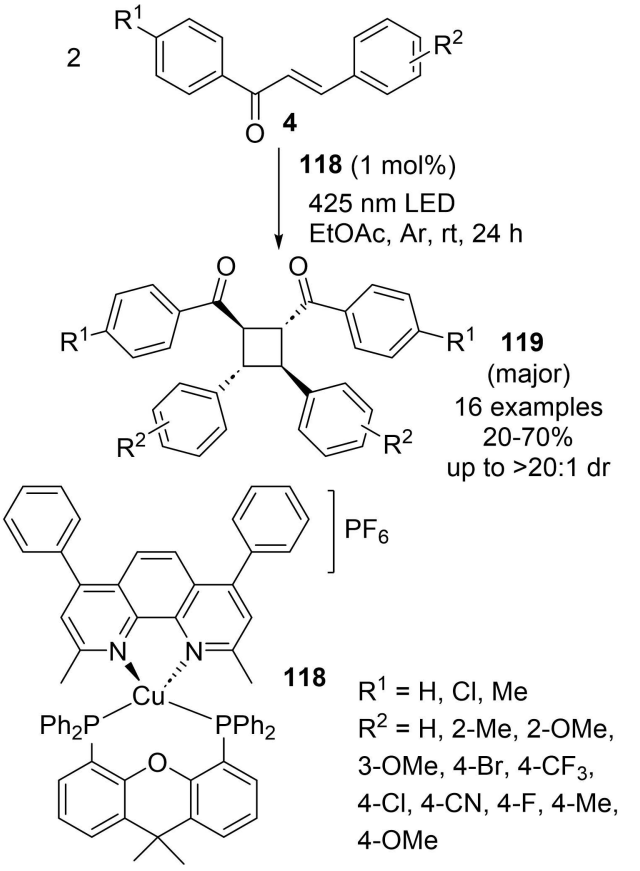
Three-component reaction of chalcones with propanone and thiocarbohydrazide in dry ethanol at room temperature for 2 h followed by addition of copper(0) nanoparticles delivered 5-[(3,5-diaryl)-4,5-dihydro-1*H*-pyrazol-1-yl]-2,2-diphenyl-2,3-dihydro-1,3,4-thiadiazoles, in 66–91 % yield.[150]

2.4. Other Reactions

A mixture of copper(II) chloride dihydrate, an excess of lithium sand and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl in THF at room temperature promoted the complete reduction of chalcone to the respective 1,3-diphenylpropan-1-ol in 63 % yield.[151] Meanwhile, reduction of the C=C double bond of chalcones into 1,3-diarylpropan-1-ones was accompanied using copper(I) iodide as catalyst, in the presence of bis(pinacolato)diboron, cesium carbonate and methanol in anhydrous THF at room temperature for 30 min.[76]



Scheme 17. Synthesis of indolizines **117** via copper(I)-catalyzed multicomponent reaction of chalcones **4** with acetophenones **115** and pyridines **116**.



Scheme 18. Photodimerization reaction of chalcones **4** promoted by copper(I) complex **118**.

Visible-light-promoted photocatalytic reactions have emerged as powerful tools in organic synthesis and Wu *et al.* developed a protocol for the [2+2] photodimerization of chalcones **4** catalyzed by heteroleptic copper(I) complex **118** in ethyl acetate at room temperature, under argon atmosphere. The 1,2-diaroyl-3,4-diarylcyclobutane products **119** were obtained in moderate to good yields and with high diastereoselectivity (Scheme 18).[152]

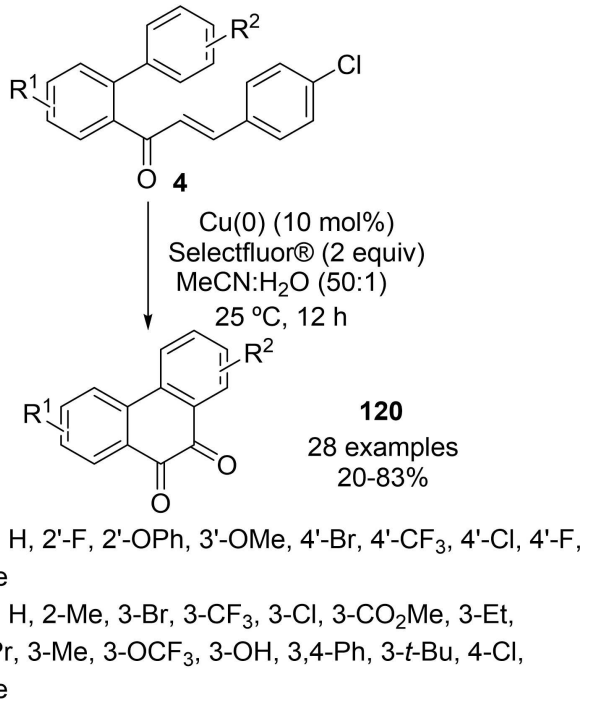
A mixture of (*E*,*Z*)-stereoisomers of α-aryl- and α-aroylchalcones underwent Nazarov cyclization reaction promoted by copper(II) triflate in dry dichloromethane at room temperature to afford *trans*-indanones as major products, after purification in silica gel flash chromatography.[153] Under dual catalysis of copper(0) and Selectfluor®, diversely substituted 2'-arylchalcones suffered oxidative C–C bond cleavage/annulation reactions in a 50:1 mixture of acetonitrile:water at 25 °C to give a variety of substituted 9,10-phenanthraquinones in 20–83% yield (Scheme 19).[154] The same catalytic system is used for the epoxidation of chalcones in a 400:1 mixture of acetonitrile:water at room temperature affording the corresponding 1,3-diaryl-2,3-epoxypropan-1-ones, in good to excellent yields.[155]

Copper(I)-catalyzed tandem *N*-arylation and 1,4-conjugate addition of 2-bromochalcones **4** with cyclic enaminones **121** in the presence of 1,10-phenanthroline and potassium carbonate in DMSO at 130 °C furnished a variety of 9-(2-aryl-2-oxoethan-1-yl)-1,2,3,4-tetrahydroacridin-1-ones **122** (Scheme 20).[156]

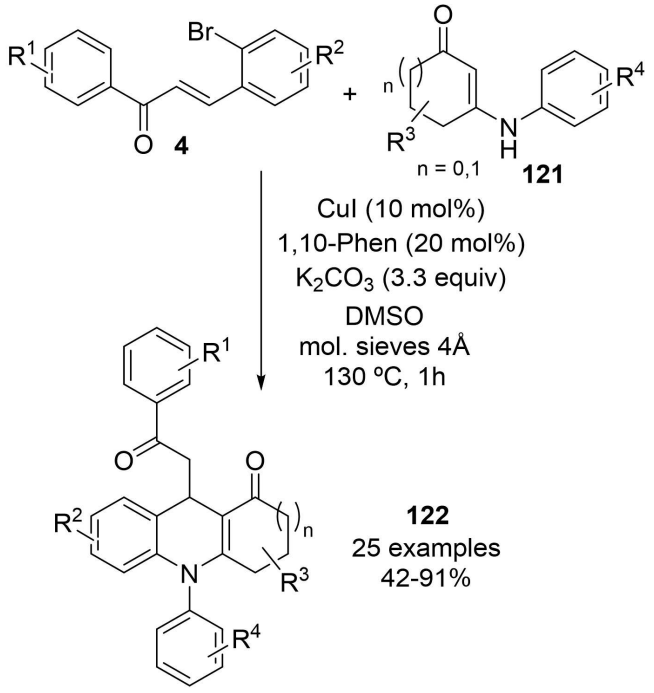
3. Palladium-Catalyzed Reactions

3.1. Hydrogenation

Several methods have been established for the selective reduction of chalcones C=C double bond or accompanied by additional carbonyl reduction, mediated by palladium catalysts. In the former case, although the risk associated with the manipulation of hydrogen is very high, this gas has been widely applied in the catalytic hydrogenation of the chalcones C=C double bond to afford 1,3-diarylpropan-1-ones pro-



Scheme 19. Cu(0)/Selectfluor® system-promoted oxidative annulation reaction of 2'-arylchalcones **4**.



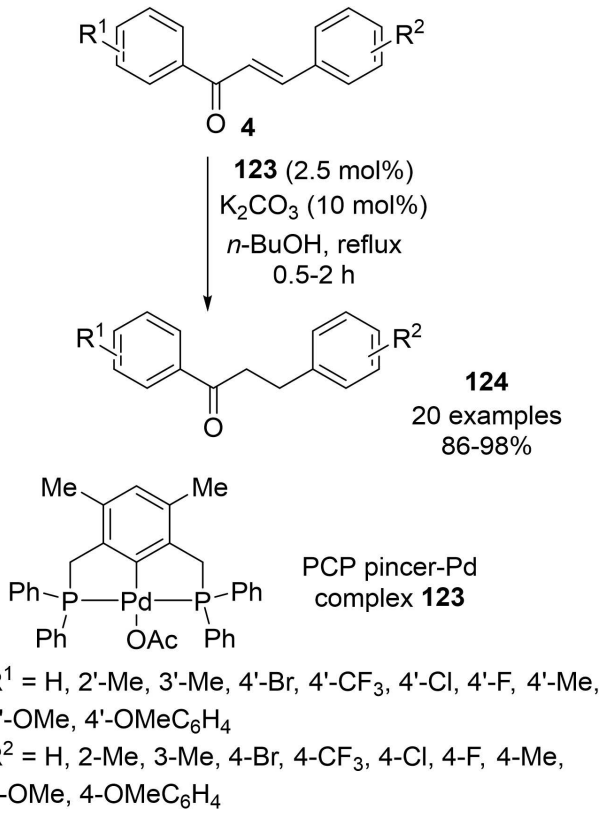
Scheme 20. Copper(I)-catalyzed tandem *N*-arylation and 1,4-conjugate addition reaction of 2-bromochalcones **4** with cyclic enaminones **121**.

moted by palladium(0) on carbon in ethyl acetate,[157] palladium(0) on carbon in in the presence of diphenylsulfide in methanol,[158] palladium(II) acetate in the presence of triphenylphosphine in toluene,[159] palladium(II) acetate supported on silk-fibroin in methanol,[160] palladium(II) salts supported on porous glass in ethyl acetate,[161] palladium(II) chloride supported on celite-polyaniline in methanol,[162] palladium nanoparticles supported on phosphorus-doped porous organic polymer in ethanol,[163] layered double hydroxides supported nano palladium catalyst in ethanol,[164] palladium nanoparticles on 3-(aminopropyl) triethoxysilane (APTES) modified SBA-15 in water,[165] palladium nanoparticles immobilized on lipoic acid functionalized SBA-15 in acetonitrile,[166] palladium-supported graphene oxide in an 1 : 1 mixture of ethanol:water,[167] palladium nanoparticles supported on *N*-doped hierarchically porous carbon in ethanol[168] and thermoregulated phase-transfer palladium nanocatalyst using $Ph_2P(CH_2CH_2O)_{22}CH_3$ as ligand in an 1 : 1 mixture of pentan-1-ol:water.[169]

Alternatively, formic acid can be used a versatile, inexpensive and nontoxic hydrogen donor in the catalytic transfer hydrogenation of chalcones promoted by palladium(II) acetate,[170] polypyrrole stabilized palladium nanoparticles,[171] recyclable heterogeneous palladium nanoparticles on *N*,*O*-dual doped hierarchical porous biomass-derived carbon[172] or used in combination in an 1 : 1 mixture with ammonium formate mediated by C_3N_4 nanosheets/reduced graphene oxide supported palladium nanocatalyst[173] and nitrogen-enriched porous carbon supported palladium nanoparticles.[174]

Easily accessible and inexpensive butan-1-ol was also used simultaneously as hydrogen donor and solvent in the chemoselective hydrogenation of chalcones **4** catalyzed by PCP pincer-palladium complex **123** (cyclic palladium complex incorporating carbon/two phosphorous atoms–palladium bonds) in the presence of potassium carbonate at reflux (Scheme 21).[175]

The reduction of the chalcones C=C double bond can also proceed by addition of ammonium formate to palladium immobilized ionic liquid catalyst[176] and palladium nanoparticles in aqueous medium,[177] and by addition of ammonium formate[178] or triethylsilane[179] to palladium(0) on charcoal catalyst to generate *in situ* molecular hydrogen and afford the corresponding 1,3-diarylpropan-1-ones. Alternatives were to apply resin-supported formate as hydrogen donor and palladium acetate as catalyst in DMF at 70 °C[180] and silica-supported palladium chloride as catalyst and a combination of



Scheme 21. Palladium-catalyzed hydrogenation of chalcones **4** to give 1,3-diarylpropan-1-ones **124**.

methanol:formic acid/water (1 : 2 : 3) as hydrogen source and irradiate in a domestic microwave oven within 50–52 minutes.[181]

In the case of carbonyl reduction, Andrade and Silva reported a catalytic transfer hydrogenation of chalcones promoted by palladium(0) on carbon and using ammonium formate as hydrogen donor, in methanol at room temperature, to furnish the corresponding saturated alcohols, 1,3-diarylpropan-1-ols, in 83–100 % yield.[182] Complete reduction of parent chalcone was also accomplished via heterogenous palladium on carbon-ethylenediamine complex catalysis, using methanol as solvent at room temperature for 24 h to give 1,3-diphenylpropan-1-ol in 99 % yield.[183] Palladium-catalyzed conjugate reduction of chalcones to afford 1,2-diaryl-2,3-dideuteropropan-1-ones can be readily achieved by combination of hexamethyldisilane as reductant and deuterium oxide as deuterium source in DMAc at 60 °C for 24 h.[184]

3.2. 1,4-Conjugate Additions

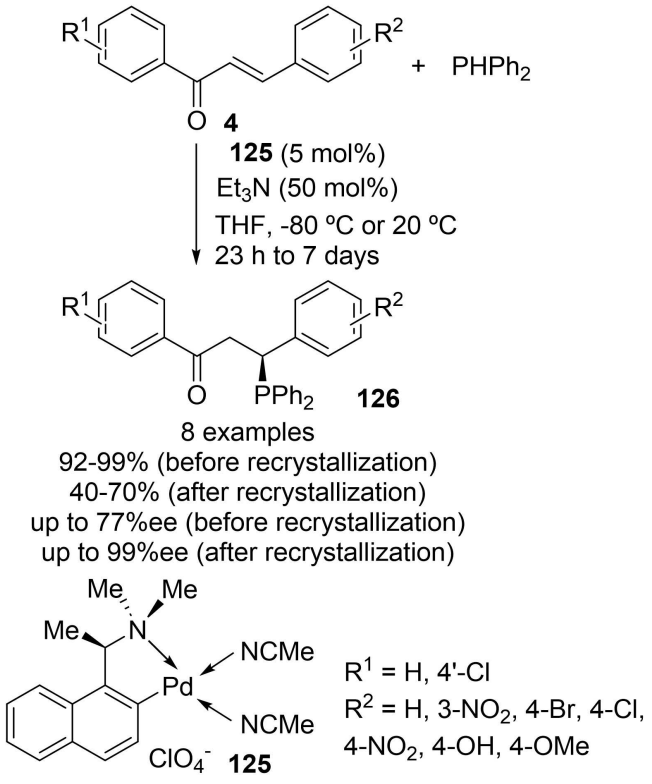
Few (1,3-diarylpropyl-3-oxo)carbamic esters were produced in 41–68 % yield via palladium(II)-mediated aza-Michael reaction of ethyl or benzyl carbamate to various chalcones in the presence of trimethylsilyl chloride in dichloromethane at room temperature for 24 h.[185]

The palladium(II)-catalyzed non-asymmetric addition of silylphosphine reagents introduced by Trepohl *et al.* was highly selective for chalcones. Thus, conjugate phosphination of (*Z*)- and (*E*)-chalcone with *t*-BuMe$_2$Si-PPh$_2$ and Me$_2$PhSi-PCy$_2$ in a 10 : 1 mixture of 1,4-dioxane:water at 60 °C for 16 h gave the corresponding diphenyl- and dialkylphosphinyl adducts which suffer subsequent oxidation with hydrogen peroxide at room temperature for 2 h to produce phosphine-oxide adducts. Moreover, it is known that the synthesis of phosphine-oxides is usually preferred instead of tertiary phosphines since these phosphines are quite air sensitive and difficult to handle and to obtain. From the results we can infer that higher yields were obtained for (*Z*)-adducts (91 and 80 %, respectively) than for (*E*)-adducts (78 and 74 %, respectively).[186]

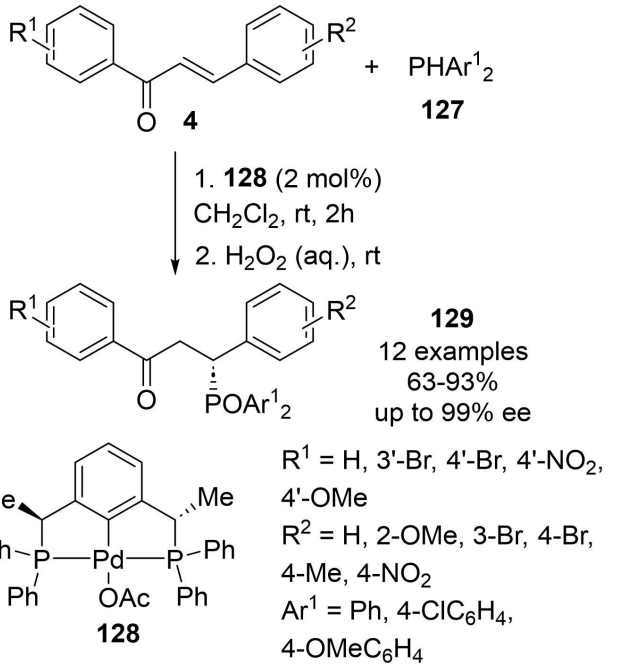
The use of chiral phosphines is a practical and efficient strategy to convert achiral compounds into enantioenriched products, incorporating several functionalities in the phosphine unit.[187,188] Thus, Huang *et al.* prepared the chiral azapalladacycle complex **125** (cyclic palladium complex incorporating one nitrogen–palladium bond) to be applied in the asymmetric hydrophosphination of chalcones **4** with diphenylphosphine, carried out in the presence of triethylamine in THF to afford 3-(diphenylphosphanyl)-1,3-diphenylpropan-1-ones **126**. In some cases, good enantioselectivities were achieved after simple recrystallization (Scheme 22).[189]

Shortly after, the same research group synthesized a new chiral phosphapalladacycle and screened its effectiveness in the same hydrophosphination reaction. It was found that phosphorous-containing complex was better catalyst than the amino analogue, considering the reduced reaction time, improved yields and enantioselectivity achieved.[190] In a similar protocol, four chiral phosphapalladacycle complexes functionalized with a malonate moiety were prepared to induce asymmetric hydrophosphination of chalcone with diphenylphosphine to obtain the corresponding chiral tertiary phosphine, in quantitative yields.[191] Employing *rac*-methylphenylphosphine as phosphinating agent, asymmetric hydrophosphination of chalcones mediated by the previously mentioned phosphapalladacycle complex, using triethylamine as base and THF as solvent at −80 °C, furnished the corresponding chiral methylphenylphosphine chalcone adducts in excellent yields and with good diastereo- and enantioselectivities.[190]

Several cyclic palladium complexes incorporating carbon/two heteroatoms–palladium bonds known as pincer-palladium complexes, can also be applied in the hydrophosphination reaction of chalcones. The studies reported by Li *et al.* on the palladium-catalyzed asymmetric 1,4-conjugate addition of alkylphenylphosphines to chalcones involved two different



Scheme 22. Asymmetric hydrophosphination of chalcones **4** with diphenylphosphine promoted by chiral azapalladacycle complex **126**.



Scheme 23. Asymmetric hydrophosphination of chalcones **4** with diarylphosphines **127** promoted by chiral PCP pincer-palladium complex **128** and subsequent oxidation.

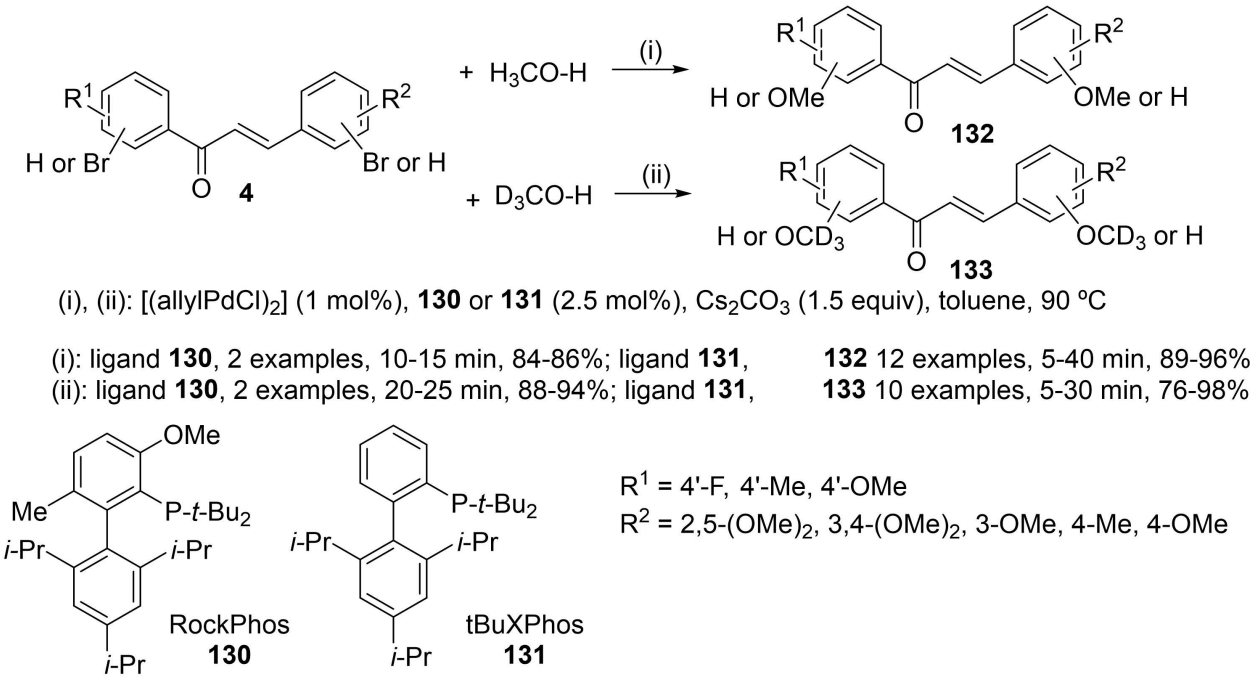
pincer-palladium complexes. The addition of methylphenylphosphine occurred under the catalysis of a bisimidazoline (NCN) pincer-palladium complex in the presence of potassium acetate in toluene at −5 °C for 24 h followed by the addition of borane dimethylsulfide to give a mixture of diastereomers of the phosphine adduct bearing methyl, phenyl and hydroborane substituents. A similar protocol was used for the addition of isopropylphenylphosphine to chalcones, however, a bisphosphine (PCP) pincer-palladium complex was applied to achieve better diastero- and enantioselectivity in the adducts obtained.[192]

In 2010, Feng *et al.* screened a couple of chiral PCP pincer-palladium catalysts to promote asymmetric addition of diphenylphosphine to parent chalcone followed by oxidation with hydrogen peroxide to afford diphenylphosphine-oxide chalcone adduct in good to excellent yields and enantioselectivity. Additionally, the optimal conditions were tested in the asymmetric addition of several diarylphosphines **127** to various chalcones **4** to provide the corresponding chiral phosphine-oxide derivatives **129** (Scheme 23).[193] Other pincer-palladium complexes were synthesized for the catalytic asymmetric hydrophosphination of chalcones with diphenylphosphine[194,195] or diarylphosphines[196,197] and subsequent oxidation to produce the respective chiral phosphine-oxides.

3.3. Substitution Reactions

Palladium-catalyzed C–O cross-coupling reactions have appeared as an important alternative for the traditional alkoxylation of phenols which requires strong basic medium, harsh reaction conditions and high temperatures.

Rangarajan *et al.* have developed a protocol that involves palladium(II)-catalyzed C–O cross-coupling reaction of activated chalcone bromides with methanol and methanol-d_4 using BrettPhos as ligand, cesium carbonate as base and toluene as solvent, at 85 °C under argon atmosphere, to provide the corresponding methoxy and methoxy-d_3 chalcones.[198] One year later, the same group applied another palladium catalytic system for the methoxylation and deuteromethoxylation of 3/3'- and 4/4'-bromochalcones **4**. Using *t*BuXPhos **131** as ligand provided a higher number of alkoxylated derivatives, and with shorter reaction time than using RockPhos ligand **130**, to obtain similar yields of the obtained products (Scheme 24). Moreover, the efficiency of the *t*BuXPhos catalyst system towards the rapid coupling of 4-bromochalcones with alkyl alcohols (ethanol, propan-1-ol and butan-1-ol) pointed out that the increase of the alkyl chain led to an



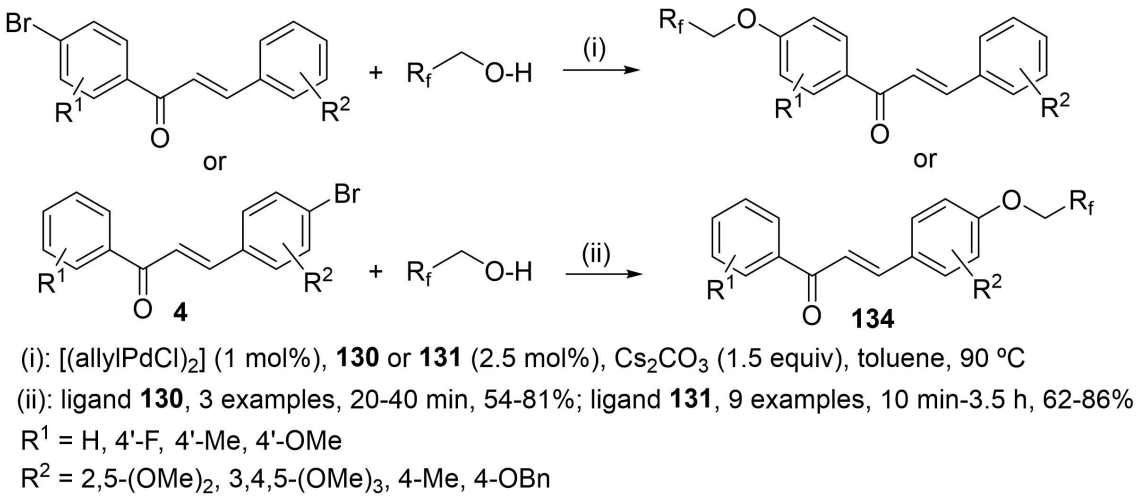
Scheme 24. Palladium(II)-catalyzed methoxylation and deuteromethoxylation of 3/3'- and 4/4'-bromochalcones **4**.

increase in the reaction time and a decrease in the yields of the corresponding alkoxylated chalcones.[199]

Palladium-catalyzed 2,2,2-trifluoroethoxylation of various 4'- and 4-bromochalcones was also studied by Rangarajan *et al.*, using $Pd_2(dba)_3$ as catalyst in the presence of cesium carbonate in toluene, at 90 °C under argon atmosphere. Both ligands, *t*BuXPhos and JohnPhos, were effective towards the coupling reaction to produce 4'- or 4-(2,2,2-triflluoroethoxy)chalcones. No coupling product of 3'-bromo-4-methylchalcone with 2,2,2-trifluoroethanol was obtained.[200] In a continuous work, they also tested palladium(II)-catalyzed 2-fluoroethoxylation of several substituted bromochalcones, being both ligands *t*BuXPhos and RockPhos efficient in the 2-fluoroethoxylation of 4'- and 4-bromochalcones in short reaction time (5–100 min). The protocol was extended to the coupling reaction of 3'- and 3-bromochalcones with 2-fluoroethanol and longer reaction time was required to obtain the corresponding products, compared with the 4'- and 4-bromo analogues. Only one successful example of 2-fluoroethoxylation of 2-bromochalcone was recorded and the product (*E*)-2-fluoroethoxy-4'-methoxychalcone was isolated in 48% yield with the Pd/RockPhos catalyst system. Palladium(II)-mediated 1*H*,1*H*-perfluoroalkoxylation reaction of 4'- and 4-bromo chalcones with higher perfluoro-alcohols was also accomplished in moderate to good yields (Scheme 25).[201] Damas *et al.* described a single example of microwave-assisted aminocarbonylation reaction of 4-iodochalcone with allylamine mediated by palladium(II) acetate, using molybdenum hexacarbonyl as alternative CO source and DBU as base in 1,4-dioxane at 125 °C for 5 min to deliver (*E*)-*N*-allyl-4-(3-oxo-3-phenylprop-1-en-1-yl)benzamide in 25%, after silica gel column chromatography purification.[202]

3.4. Cross-Coupling Reactions

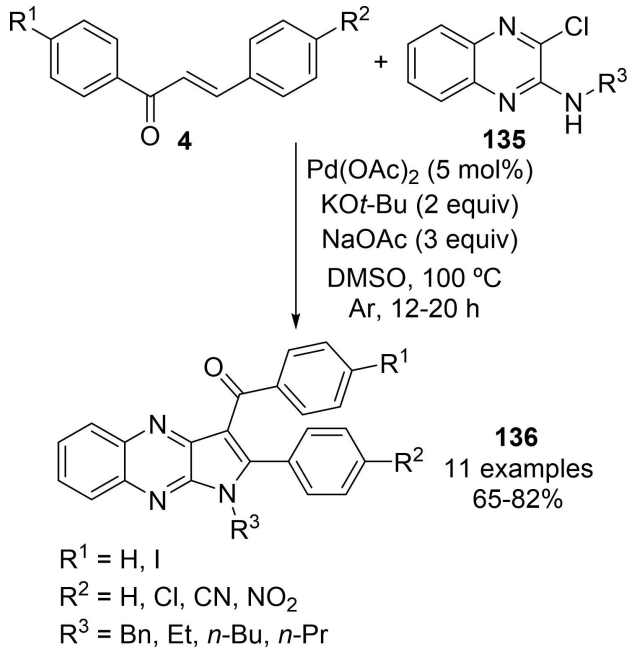
Palladium-mediated cross-coupling reactions are a powerful strategy for the construction of C–C and C-heteroatom bonds. Da Costa *et al.* reported a protocol on the Heck reaction of chalcones with aryl iodides to provide β-arylchalcones. It involved the use of palladium(II) acetate, tri(*o*-tolyl)phosphine, potassium carbonate in DMF at 120 °C for 8 h and the products (*E*)-β-arylchalcones ($E:Z > 96:4$) were obtained in moderate to excellent yields, after precipitation. The authors also synthesized α,β-diarylchalcones via a sequential α-bromination of β-arylchalcones with bromine in refluxing chloroform followed by Suzuki cross-coupling reaction with arylboronic acids using a simple catalytic system based on palladium(II) acetate, triphenylphosphine and potassium carbonate in an 1:1 mixture of toluene:ethanol at 75 °C for 2 h, in 60–99% yield over two steps.[203] Regioselective synthesis of 3-acyl-1-alkyl-2-arylpyrrolo[2,3-*b*]quinoxalines **136** was accomplished via palladium(II) acetate-catalyzed Heck coupling/heteroannulation reactions of chalcones **4** with *N*-(alkyl/benzyl)-3-chloroquinoxaline-2-amines **135** in the



Scheme 25. Palladium(II)-catalyzed 1*H*,1*H*-perfluoroalkoxylation of 4'- and 4-bromochalcones **4**.

presence of potassium *t*-butoxide and sodium acetate in DMSO at 100 °C (Scheme 26).[204]

Vieira *et al.* described a green approach for the Suzuki coupling reaction of various chalcones bearing halogen atoms in A- and B-ring with different arylboronic acids mediated by palladium(II) acetate and potassium fluoride, using PEG-400 as solvent at 110 °C under microwave irradiation, to give the respective arylated chalcones in A- and B-rings.[205]



Scheme 26. Palladium(II)-catalyzed Heck coupling/heteroannulation reactions of chalcones **4** with *N*-(alkyl/benzyl)-3-chloroquinoxaline-2-amines **135**.

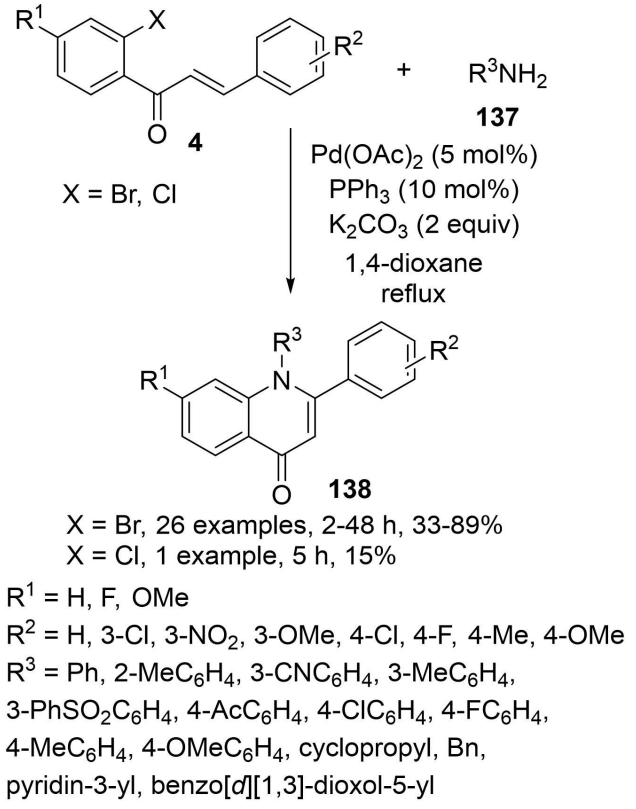
Buchwald–Hartwig coupling/Michael addition reactions of 2'-halo chalcones **4** with primary aliphatic and aromatic amines **137** mediated by palladium(II) acetate, triphenylphosphine and potassium carbonate in refluxing 1,4-dioxane led to the synthesis of 1-(alkyl/aryl)-2-aryl-4*H*-quinolin-4-ones **138** (Scheme 27). Palladium catalyst plays a dual role in Buchwald–Hartwig coupling reaction and in catalytic dehydrogenation.[206]

Various 4-bromo- and 4'-bromochalcones underwent palladium(II)-catalyzed C–O cross-coupling reaction with ethyl acetohydroxamate using two supporting ligands, namely *t*BuXPhos and cataCXium®PIntB, in the presence of cesium carbonate in toluene at 60 °C, under argon atmosphere, to produce the corresponding chalcone 4- and 4'-ethanimidates.[207]

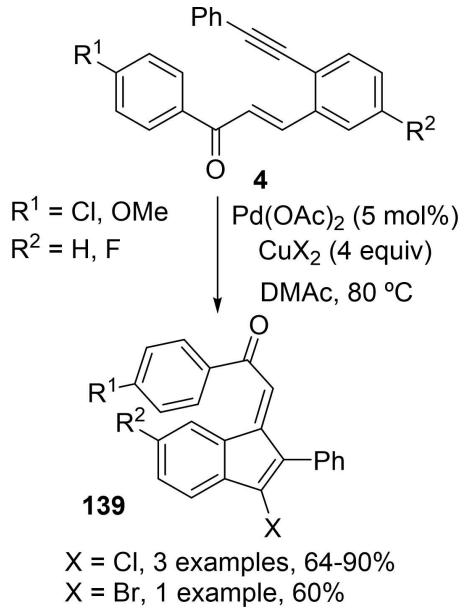
3.5. Intramolecular Reactions

Few 3-chloro-2-phenyl-1-methylideneindenes **139** were obtained via tandem reaction of 2-(phenylethynyl)chalcones **4** mediated by palladium(II) acetate in the presence of copper(II) chloride in DMAc at 80 °C. The reaction with copper(II) bromide leds to the formation of the 3-bromoindene analogue (Scheme 28).[208]

The synthesis of 3-acetoxy-(2-methoxymethyl)-1-(2-phenyl-2-oxoethyl)indene was achieved via palladium(II) acetate-catalyzed reaction of 2-(methoxyethynyl)chalcone in the presence of 1,10-phenanthroline monohydrate in an 1 : 1 mixture of acetic acid:1,4-dioxane at 90 °C for 12 h, under nitrogen atmosphere, in 91% yield. Treating the same chalcone with palladium(II) acetate and lithium bromide in acetic acid at 50 °C for 23 h yielded the respective 3-bromoindene derivative in 86%.[209]



Scheme 27. Palladium(II)-catalyzed Buchwald–Hartwig coupling/Michael addition reactions of 2'-halochalcones **4** with primary aliphatic and aromatic amines **137**.



Scheme 28. Synthesis of 3-halo-1-methylidene-2-phenylindenes **139** via tandem reaction of 2-(phenylethynyl)chalcones **4**, promoted by palladium(II) acetate in the presence of copper(II) halides.

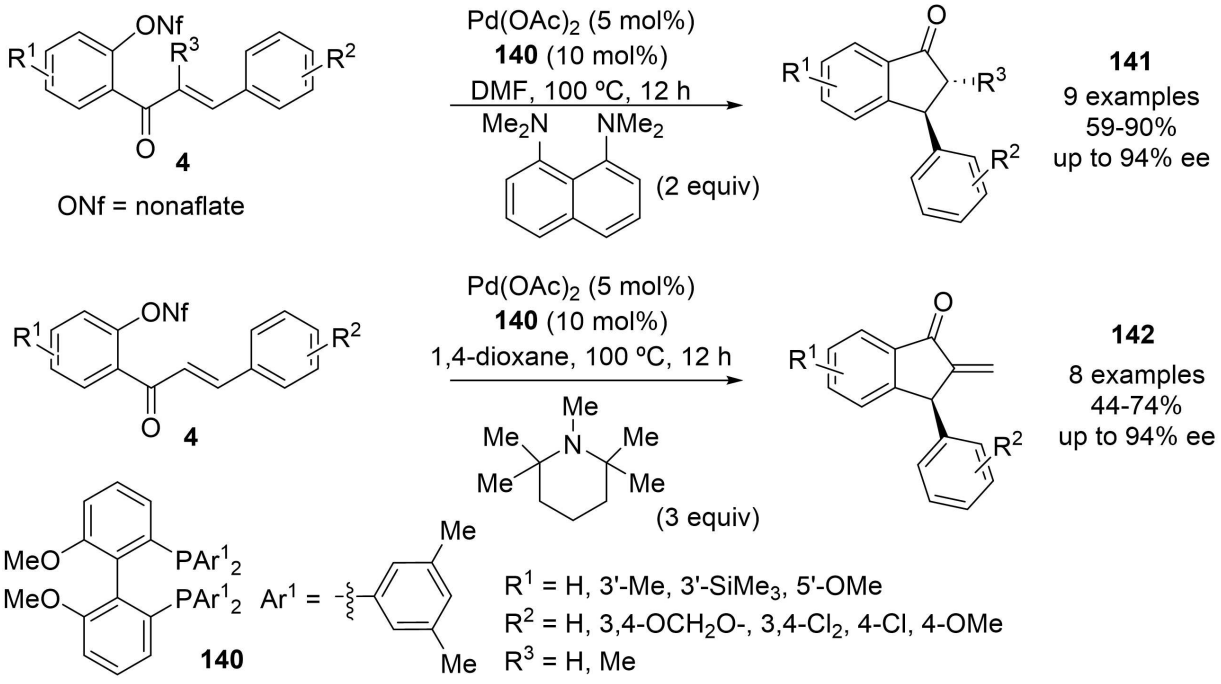
Mphahlele and Maluleka reported a palladium(II) chloride-promoted heteroannulation reaction of (*E*)-2'-amino-3'-(arylethynyl)-5-bromochalcones in acetonitrile at 90 °C for 3 h to give (*E*)-3-aryl-1-(2-aryl-5-bromo-1*H*-indol-7-yl)prop-2-en-1-ones in 53–75 % yield.[210]

Intramolecular reductive cyclization of 2'-substituted chalcones in the presence of palladium complexes was dependent on the chiral bisphosphine ligands used and the leaving groups on chalcone core. For 2'-bromo derivative, 3-phenylindan-1-one was obtained as main product along with the reductive cyclization product, 2-methyl-3-phenyl-1*H*-inden-1-one. Cyclization of 2'-triflate derivative produced 3-phenylindan-1-one as main product and smaller amounts of 2-phenyl-4*H*-chroman-1-one. Cyclization of 2'-mesyloxy- and methoxycarbonyloxy-substituted chalcones under similar conditions gave solely 2-phenyl-4*H*-chroman-4-one.[211] An enantioselective version of the reductive-Heck reaction of 2'-nonaflate chalcones **4** mediated by palladium(II) acetate is base-controlled: using proton sponge [1,8-bis(dimethylamino)naphthalene] in DMF delivered a series of chiral 3-arylindan-1-ones **141** while the use of 1,2,2,6,6-pentamethylpiperidine as base in 1,4-dioxane furnished 3-aryl-2-methyleneindan-1-ones **142** (Scheme 29).[212] Further 3-arylindan-1-ones were synthesized through palladium(II)-catalyzed intramolecular reductive cyclization of 2'-bromochalcones carried out in the presence of *N*,*N*-diisopropylethylamine and benzoic acid in ethylene glycol at 90–100 °C[213] and in the presence of *N*,*N*-dimethylcyclohexyl amine in DMF, under conventional heating conditions (155 °C, 1–2 h) and microwave irradiation (160 °C, 15 min). Although it was not observed major differences in the yields obtained by the two methods, an higher number of derivatives was isolated in the microwave-assisted protocol.[214]

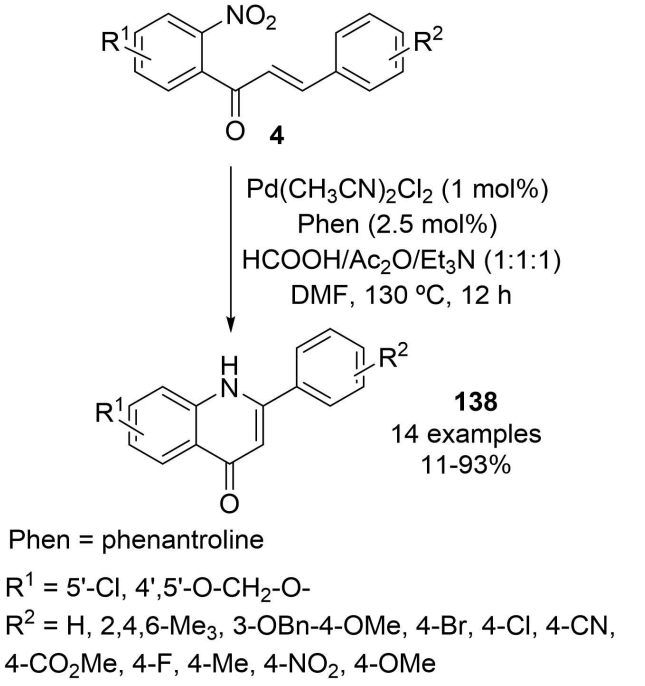
Microwave-assisted intramolecular Mizoroki-Heck coupling reaction of 2'-bromochalcones promoted by palladium(II) chloride in the presence of an aurone-based α,β-unsaturated carbonyl-amino bidentate ligand and potassium carbonate in propan-2-ol at 70 °C for 13–15 min produced a couple of 3-aryl-1*H*-inden-1-ones.[215] In turn, 2'-nitrochalcones **4** underwent palladium(II)-catalyzed reductive cyclization reaction in the presence of phenanthroline, acetic anhydride, triethylamine and formic acid as CO surrogate in DMF to produce a wide variety of 2-aryl-4*H*-quinolin-4-ones **138** (Scheme 30).[216] Replacing formic acid by phenyl formate and DMF for acetonitrile at 140 °C for 3 h, cyclization of 2'-nitrochalcone led to (1*H*-indol-2-yl)(phenyl) methanone.[217,218]

3.6. Other Reactions

Palladium(0)-catalyzed asymmetric inverse-electron-demand oxa-Diels–Alder (IED-hDA) reaction of α-cyanochalcones



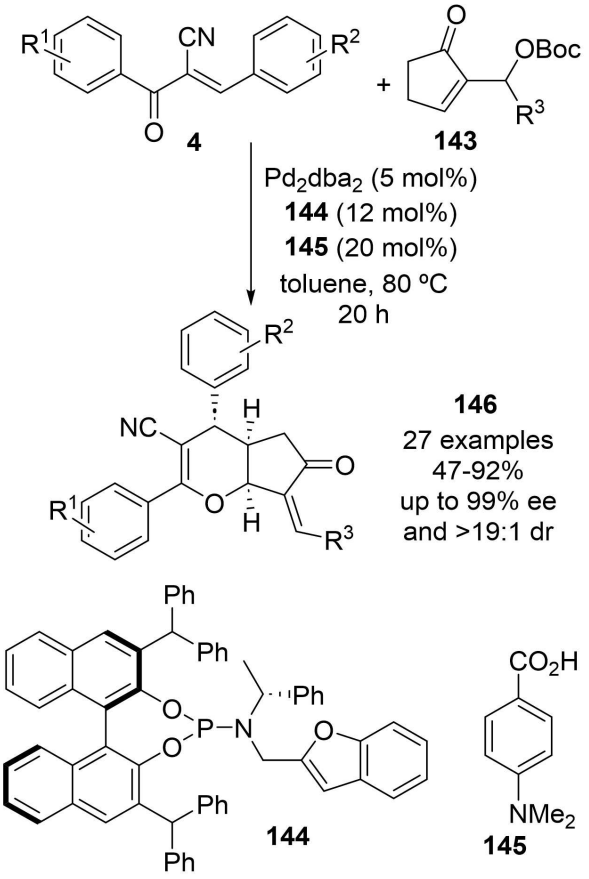
Scheme 29. Palladium(II)-catalyzed enantioselective reductive-Heck reaction of 2'-nonaflate chalcones **4**, in the presence of two different bases.



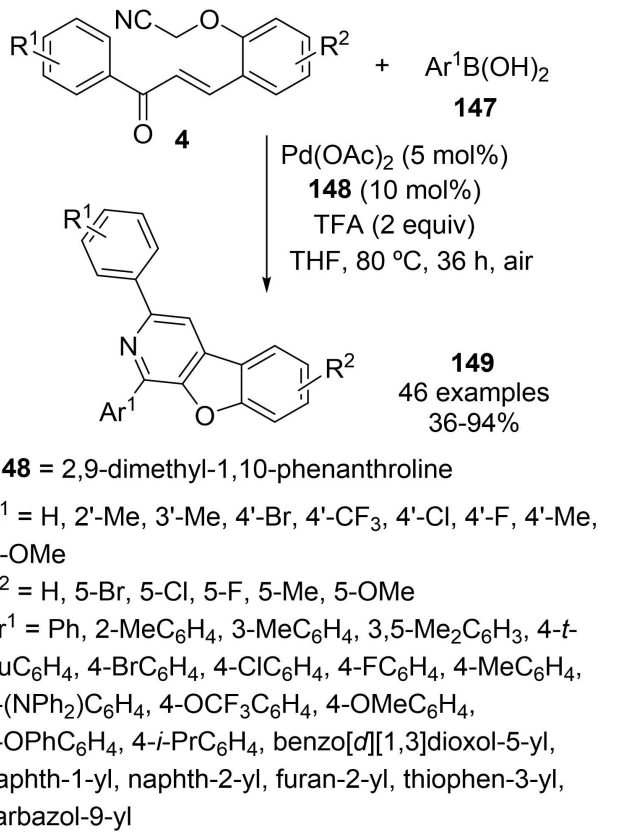
Scheme 30. Synthesis of 2-aryl-4*H*-quinolin-4-ones **138**, via palladium(II)-catalyzed reductive cyclization reaction of 2'-nitrochalcones **4**.

with carbonates of 4-hydroxycyclopent-2-en-1-ones was ligand controlled: employing a bifunctional monophosphine ligand from a chiral aminoalcohol in dichloromethane at room temperature afforded *exo*-cycloadducts 2,4-diaryl-5-oxo-tetrahydrocyclopenta [*b*]pyran-3-carbonitriles and using a proline-derived bisphosphine ligand in an 1 : 1 mixture of chloroform : toluene at room temperature provided the respective *endo*-cycloadducts.[219] More α-cyanochalcones **4** underwent palladium(0)-catalyzed asymmetric IED-hDA reaction with Morita–Baylis–Hillman carbonates **143**, derived from cyclopent-2-en-1-one and various aldehydes, using a BINOL-derived ligand **144** and 4-(dimethylamino)benzoic acid **145** in toluene to produce polysubstituted 2,4-diaryl-7-[(*E*)-benzylidene]-6-oxo-4,4a,5,6,7,7a-hexahydrocyclopenta[*b*]pyran-3-carbonitriles **146**, with excellent diastereo- and enantioselectivities (Scheme 31).[220]

Xiong *et al.* published a new strategy for the rapid synthesis of 1,3-diarylbenzofuro[2,3-*c*]pyridines involving a palladium(II)-catalyzed cascade reaction of 2-(cyanomethoxy)chalcones with arylboronic acids employing 2,9-dimethyl-1,10-phenanthroline and trifluoroacetic acid in THF at 80 °C for 36 h, under air atmosphere. The procedure was extended to reaction with thiophen-3-ylboronic acid giving access to various 3-aryl-1-(thiophen-3-yl)benzofuro[2,3-*c*]pyridines (Scheme 32). These transformations involve the formation of C–C/C–C/C–N bonds through nitrile carbopalladation, intramolecular Michael addition, cyclization and aromatization reactions.[221] The same group prepared other 3-arylbenzofuro[2,3-*c*]pyridines bearing thienyl, furanyl, pyrrol-



Scheme 31. Palladium(0)-catalyzed asymmetric IED-hDA reaction of α-cyanochalcones **4** with Morita–Baylis–Hillman carbonates **143**.



Scheme 32. Synthesis of 1,3-diarylbenzofuro[2,3-c]pyridines **149**, via palladium(II)-catalyzed cascade reaction of 2-(cyanomethoxy)chalcones **4** with arylboronic acids **147**.

yl, and indolyl groups at C-1 involving a palladium(II)-catalyzed cascade reaction of 2-(cyanomethoxy) chalcones with thiophenes, furans, pyrroles and indoles, respectively. The conditions used were palladium(II) acetate as catalyst, 2,2'-bipyridine and acetic acid as additives, silver trifluoroacetate as oxidant and *N*-methylacetamide as solvent, at 80–120 °C for 48 h, under nitrogen atmosphere.[222]

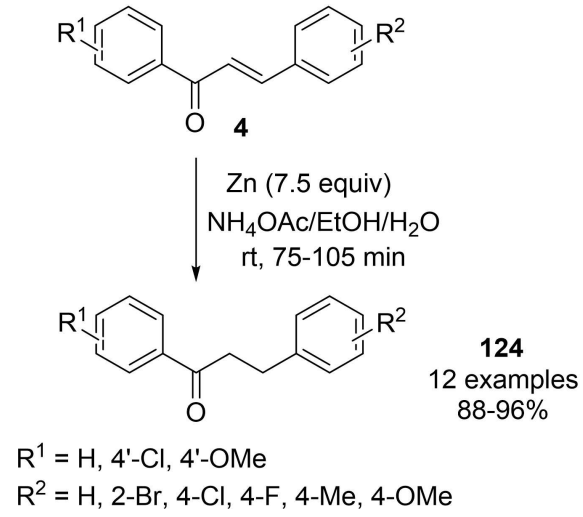
4. Zinc-Catalyzed Reactions

4.1. Hydrogenation

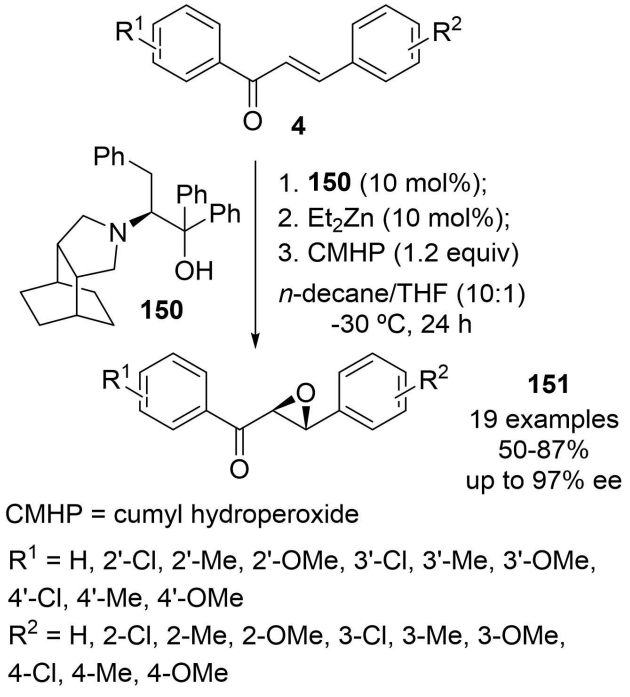
Selective reduction of C=C double of substituted chalcones **4** was accomplished by mixing vigorously with zinc powder and ammonium acetate in the presence of 95% ethanol and water, at room temperature. The corresponding 1,3-diarylpropan-1-ones **124** were obtained in excellent yields, after recrystallization in ethanol (Scheme 33).[223] Replacing ammonium acetate by ammonium chloride and using the same reaction conditions, selective 1,4-reduction of other chalcones was also performed with high yields and selectivity.[224]

4.2. Epoxidation

Various zinc alkylperoxides were prepared and applied in the epoxidation of Cα=Cβ double of parent chalcone, using unsaturated *N,N*-bidentate ligands and *t*-butylhydroperoxide as oxidant, in toluene at 0 °C.[225] Other epoxy ketones resulted from the asymmetric epoxidation of chalcones **4** in the presence of cumyl hydroperoxide (CMHP), diethylzinc and chiral pyrrolidinyl alcohol ligand **150** as cocatalyst in a 10:1 mixture of decane:THF. The products **151** were obtained in moderate to good yields and enantioselectivity up to 97% (Scheme 34).[226]



Scheme 33. Synthesis of 1,3-diarylpropan-1-ones **124**, via selective hydrogenation of chalcones **4** promoted by zinc powder.

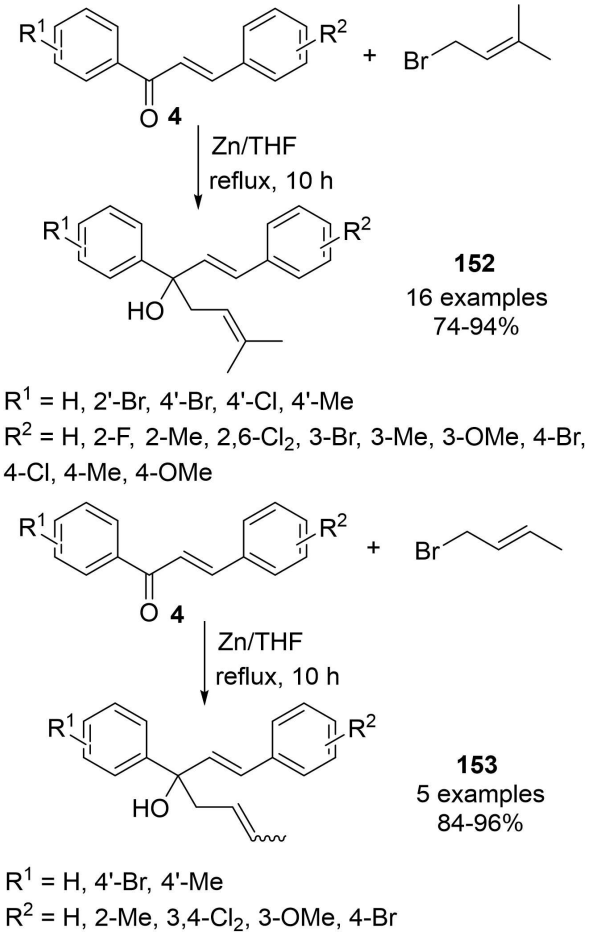


Scheme 34. Asymmetric epoxidation of chalcones **4**, promoted by diethylzinc and cumyl hydroperoxide.

4.3. Addition Reactions

α-Regioselective 1,2-addition reaction of prenylzinc, generated *in situ* from zinc and prenyl bromide, to a series of chalcones in refluxing THF led to the synthesis of 1,3-diaryl-6-methylhepta-1,5-diene-3-ols **152**, in high yields. Using crotylzinc, various 1,3-diarylhepta-1,5-dien-3-ols **153** were efficiently obtained (Scheme 35).[227] On the other hand, regioselective 1,4-conjugate addition of prenylzinc to a series of chalcones was accomplished in the presence of the Lewis acid tin(IV) chloride in refluxing THF for 16 h to provide the respective 1,3-diarylhept-5-en-1-ones. The strategy was extended to geranylzinc to give the corresponding 1,4-α-adducts.[228] A couple of 3-(indol-3-yl)-1,3-diphenylpropan-1-ones were obtained through 1,4-conjugate addition of chalcone with indoles promoted by zinc bromide supported on hydroxyapatite in refluxing acetonitrile.[229]

Three Reformatsky reagents, prepared from the reaction of methyl 1-bromocycloalkanecarboxylates (cyclobutane, cyclopentane and cyclohexane) with zinc, underwent both 1,2- and 1,4-addition reaction with chalcones, in the presence of a catalytic amount of mercuric chloride and hexamethylphosphoramide in anhydrous ethyl acetate. The 1,4-adducts suffer subsequent cyclization reaction to produce the corresponding spiro-3,4-dihydropyran-2-one derivatives: 7,9-diaryl-



Scheme 35. Regioselective 1,2-addition reaction of prenylzinc and crotylzinc to chalcones **4**.

6-oxaspiro[3.5]non-7-en-5-ones, 8,10-diaryl-7-oxaspiro[4.5]dec-8-en-6-ones and 3,5-diaryl-2-oxaspiro[5.5]undec-3-en-1-ones, respectively.[230,231]

Enantioselective conjugate addition of zinc homoenolates, generated *in situ* via ring opening of various 1-substituted cyclopropanols **154** promoted by a zinc aminoalkoxide catalyst, to various chalcones **4** in the presence of 4 Å molecular sieves and *N*,*N*'-dimethylpropylene urea as solvent afforded 1,6-diketone intermediates, which undergo, upon heating, intramolecular aldol condensation to produce a wide variety of 1-acyl-2,4-diarylcyclopentenes **156** (Scheme 36).[232]

4.4. Other Reactions

Catalytic asymmetric Friedel–Crafts alkylation reaction of pyrrole with chalcones catalyzed by dinuclear zinc catalysts in THF at room temperature for 24 h delivered a wide variety of (*S*)-1,3-diaryl-3-(1*H*-pyrrol-2-yl)propan-1-ones, in high yields and with excellent enantioselectivity. The reaction doesn't occur with *N*-protected pyrroles.[233,234]

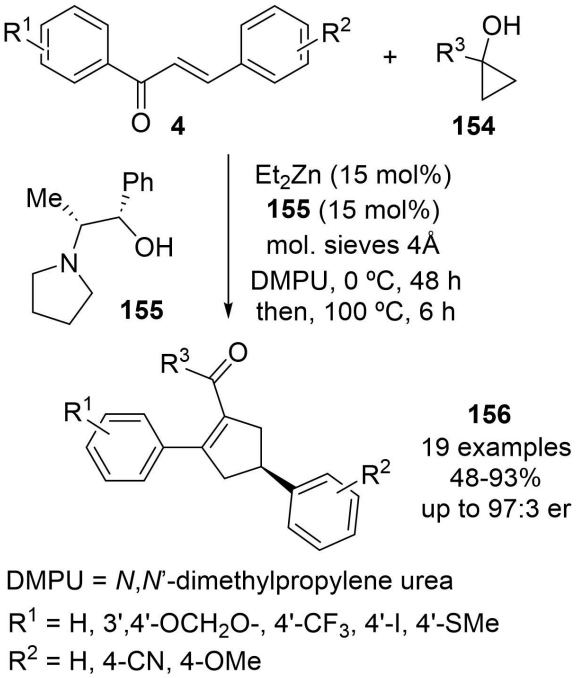
Liang *et al.* developed a facile one-pot synthesis of 3,5-diaryl-3,4-dihydro-2*H*-pyrroles involving Michael addition of chalcones with nitroalkanes conducted by aqueous sodium hydroxide in DMF at room temperature, *in situ* reduction of the adducts formed, promoted by zinc/aqueous hydrochloric acid system, and finally intramolecular cyclization reaction.[235] Diversely substituted pyrimidines **158** were synthesized in good to excellent yields through multicomponent reaction of chalcones **4** with 2-(1*H*-benzimidazol-2-yl)guanidine (**157**, X = N), 2-(1,3-benzothiazol-2-yl)guanidine (**157**, X = S) or 2-(1,3-benzoxazol-2-yl)guanidine (**157**, X = O), promoted by a $Zn(L\text{-proline})_2$ catalyst in a 2 : 3 mixture of water:ethanol at reflux (Scheme 37).[236]

Zinc triflate mediated one-pot [3 + 3] cascade annulation reaction of chalcone with 2-amino-4*H*-chromen-4-ones in DMF at room temperature for 1–3 h and subsequent addition of DDQ in 1,2-DCE at room temperature for 2 h and the 2,4-diphenyl-5*H*-chromeno[2,3-*b*]pyridine-5-ones were isolated in good yields.[237] Enantioselective Michael/transesterification tandem reaction of *o*-ester chalcones **4** with α-hydroxy indanones **159** using a dinuclear zinc catalyst in THF, delivered an array of spiro[indanone-2,3'-isochroman-1-one] derivatives **161**, in good yields and with excellent diastereo- and enantioselectivity (Scheme 38).[238]

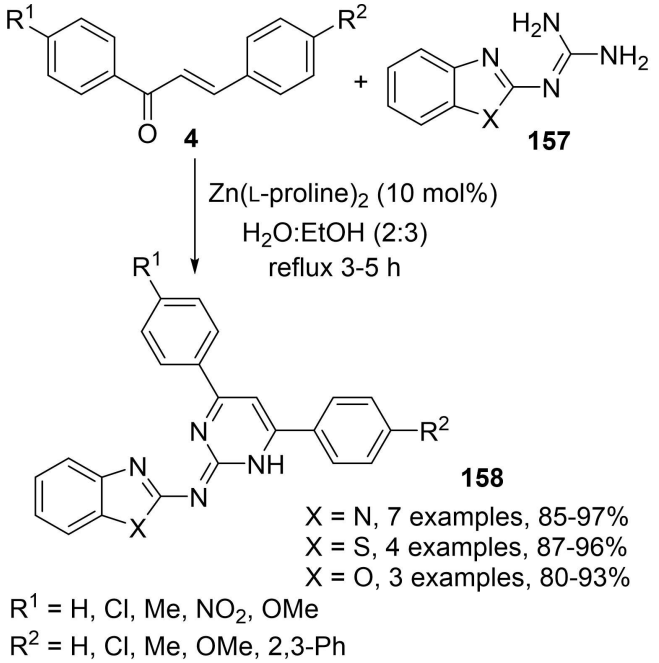
5. Iron-Catalyzed Reactions

5.1. Addition Reactions

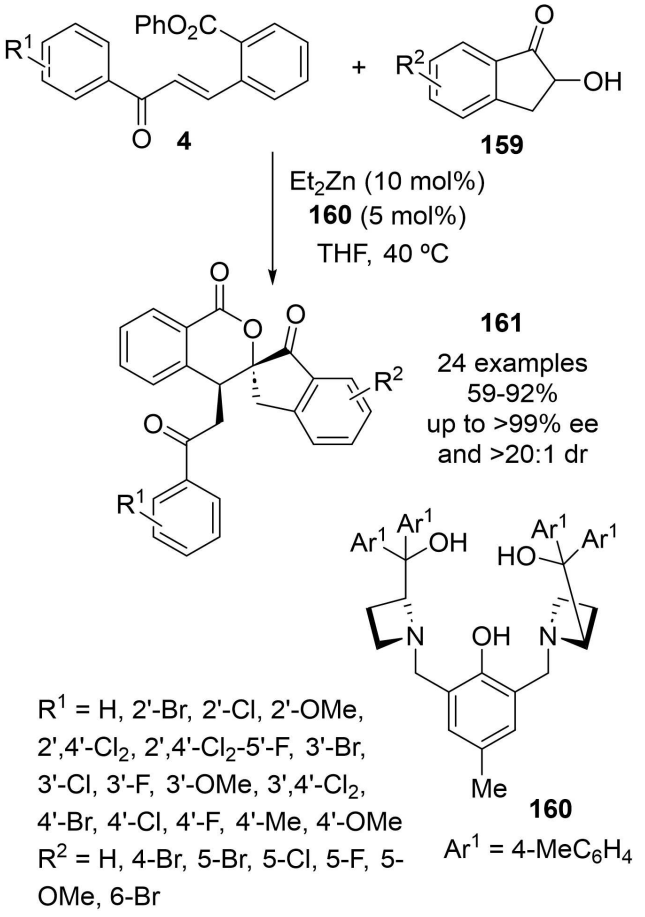
Iron is one of the most abundant metals in the earth's crust, approx. 4.7 wt% and many of their salts are cheap, easily available, non-toxic and environmentally benign. Iron(III) chloride mediated Michael addition of chalcones with acyclic



Scheme 36. Enantioselective conjugate addition of zinc homoenolates to chalcones **4**, followed by intramolecular aldol condensation reaction.



Scheme 37. Multicomponent reaction of chalcones **4** with 2-(1*H*-benzimidazol-2-yl)guanidine (**157**, X = N), 2-(1,3-benzothiazol-2-yl)guanidine (**157**, X = S) or 2-(1,3-benzoxazol-2-yl)guanidine (**157**, X = O), promoted by a $Zn(L\text{-proline})_2$.



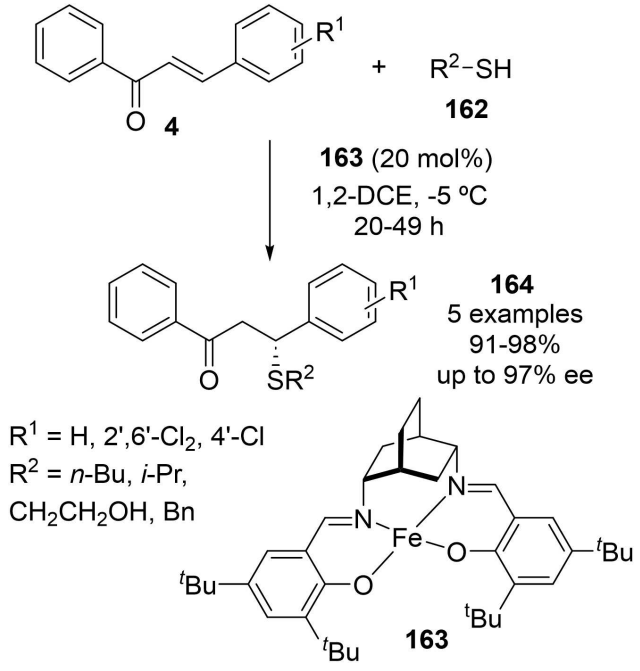
Scheme 38. Tandem reaction of *o*-ester chalcones **4** with α-hydroxy indanones **159**, promoted by a dinuclear zinc catalyst.

1,3-dicarbonyl compounds in toluene at room temperature for 12 h to give the respective 3-substituted 1,3-diarylpropan-1-ones.[239] Under dual catalysis of iron(III) chloride and trimethylsilyl chloride, Sakurai–Michael addition of chalcones with allyltrimethylsilane in dichloromethane at room temperature for 3 h furnished a series of 3-allyl-1,3-diarylpropan-1-ones.[240] In turn, an iron(II) catalyst induced Sakurai–Michael-type addition of chalcones with allylbenzenes and inactivated alkenes using 2,4,6-collidine as base and a combination of triisopropylsilyl triflate and lithium bis(trifluoromethanesulfonyl)imide as Lewis acids in toluene at 80 °C for 16 h and acidic workup in 1,4-dioxane at room temperature for 30 min to give 3-(allyl-substituted)-1,3-diarylpropan-1-ones.[241]

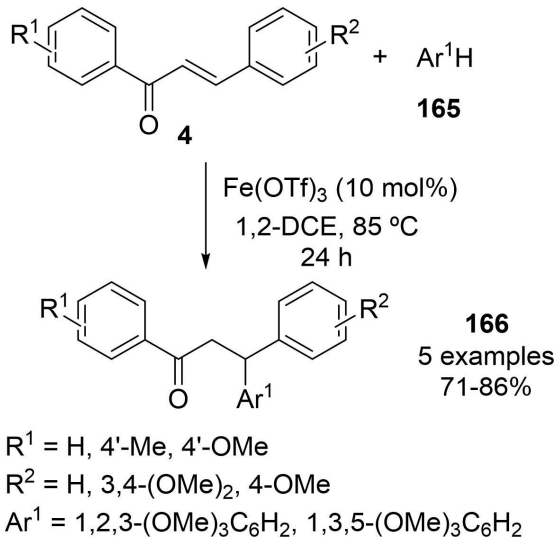
Aza-Michael addition of parent chalcone with a couple of carbamates, using iron(III) chloride hexahydrate/trimethylsilyl chloride catalyst system, in dichloromethane at room temperature yielded the 3-aminated 1,3-diphenylpropan-1-ones in 50–52 % yield.[242] Iron(III)-salen complex based on a chiral *cis*-2,5-diaminobicyclo[2.2.2]octane scaffold **163** mediated asymmetric sulfa-Michael addition of aliphatic thiols **162** to chalcones **4** in 1,2-DCE to form 3-(alkylthio)-1,3-diarylpropan-1-ones **164**, in excellent yields and enantioselectivity (Scheme 39).[243]

Iron(III) salts as Lewis acids can also be used in Friedel–Crafts-type alkylation reactions. Thus, iron(III) chloride in the presence of acetylacetone catalyzed Friedel-Crafts alkylation reaction of indoles with various chalcones, using methanol as solvent at room temperature for 12 h, to give 1,3-diaryl-3-(indol-3-yl)propan-1-ones.[244] Further derivatives arose from the reaction of indoles with chalcones promoted by iron(III) triflate in 1,2-DCE at 80 °C for 12 h. The authors used the same Lewis acid to promote hydroarylation reaction of chalcones **4** with arenes **165** in 1,2-DCE to provide 1,3,3-triarylpropan-1-ones **166**, in good yields (Scheme 40).[245]

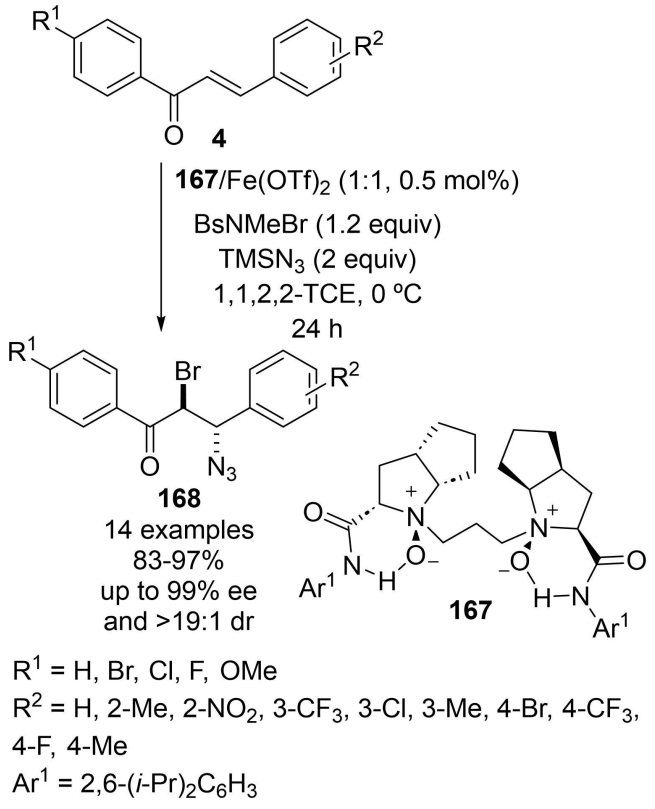
Under low loading of a chiral *N*,*N*′-dioxide **167**/iron(II) triflate complex, bromoazidation of chalcones **4** occurred in the presence of *N*,4-dibromo-*N*-methylbenzenesulfonamide (BsNMeBr) as electrophilic bromine reagent, trimethylsilyl azide ($TMSN_3$) as nucleophilic azide and 1,1,2,2-tetrachloroethane as solvent to produce 1,3-diaryl-3-azido-2-bromopropan-1-ones **168**, in high yields and with excellent diastereo- and enantioselectivities (Scheme 41). This protocol was also extended to chloro- and iodoazidation of parent chalcone.[246]



Scheme 39. Iron(III)-mediated asymmetric sulfa-Michael addition of aliphatic thiols **162** to chalcones **4**.



Scheme 40. Iron(III) triflate-mediated hydroarylation reaction of chalcones **4** with arenes **165**.



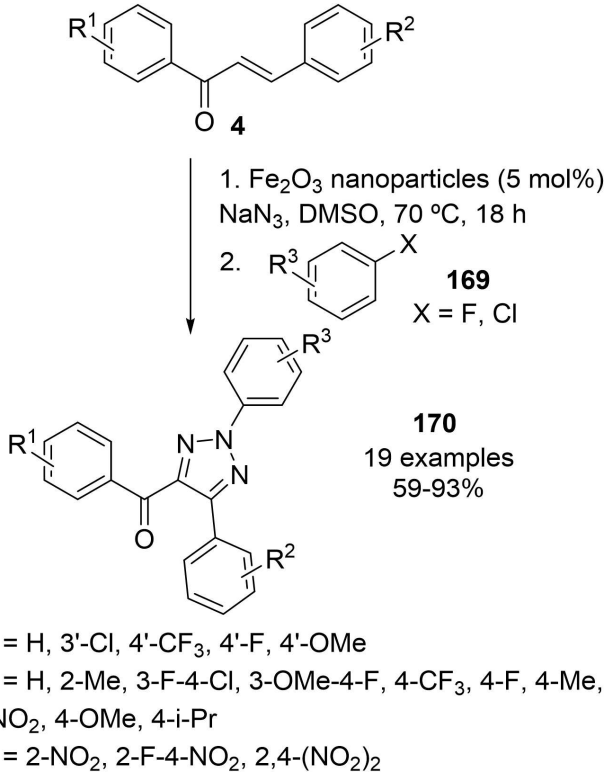
Scheme 41. Bromoazidation of chalcones **4**, promoted by a chiral *N,N'*-dioxide **167**/iron(II) triflate complex.

5.2. Other Reactions

Iron tricarbonyl complex bearing an electron-rich cyclopentadienone ligand promoted chemoselective reductive hydrogenation of chalcones in the presence of cesium carbonate in propan-2-ol at 70 °C for 16 h to afford 1,3-diarylpropan-1-ones.[247]

The synthesis of various 1-(2-aryl-2-oxoethyl)-3-haloindenes was accomplished via iron(III) halides-promoted intramolecular nucleophilic addition and cyclization reactions of *o*-alkynylarene chalcones in refluxing 1,2-DCE for 2 h.[248] Substituted 2'-nitrochalcones underwent tandem reduction of the nitro group and Michael addition using iron powder in concentrated hydrochloric acid at 100 °C to produce (±)-2-aryl-2,3-dihydro-4*H*-quinolin-4-ones, in good yields.[249]

High yields of 1-(3,5-diaryl-4,5-dihydro-1*H*-pyrazol-1-yl)-3-(4-chlorophenyl)isoquinolines resulted from the condensation reaction of chalcones with 3-(4-chlorophenyl)-1-hydrazino isoquinoline, followed by dehydration and cyclization reactions, mediated by iron oxide nanoparticles in refluxing ethanol for 30 min.[250] Iron oxide nanoparticles also promoted the tandem three-component reaction of chalcones **4** with sodium azide in DMSO under air atmosphere followed by the addition of aryl halides **169** and the reaction continued for 4 h to yield 2,5-diaryl-4-aroyl-2*H*-[1,2,3]-triazoles **170** (Scheme 42). This strategy involves oxidative 1,3-dipolar



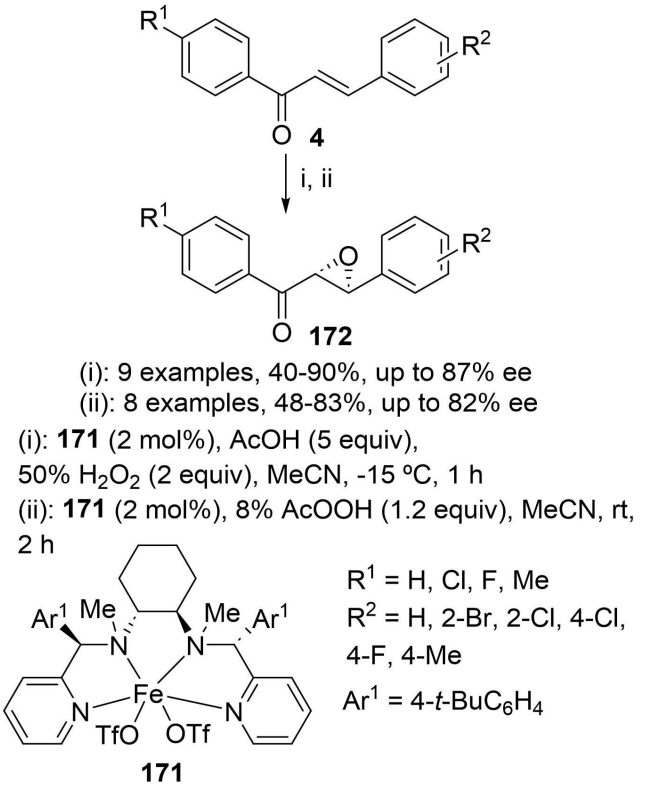
Scheme 42. Three-component reaction of chalcones **4** with sodium azide and aryl halides **169**, promoted by iron oxide nanoparticles.

cycloaddition reaction and regioselective *N*-2-arylation sequence.[251]

Kannan *et al.* synthesized a chiral iron(III)-dendrimer to mediate domino Michael and aldol reactions of chalcones with 1,4-dithiane-2,5-diol in a 2 : 1 mixture of toluene:1,2-DCE at 0 °C for 60 h to deliver a series of 5-aryl-4-aroyltetrahydrothiophen-3-ols, up to 85 : 15 er.[252]

A chiral iron(II) complex bearing a tetradentate ligand based on a ethylenediamine backbone **171** was synthesized to conduct the asymmetric epoxidation of chalcones **4** using hydrogen peroxide as oxidant in the presence of acetic acid in acetonitrile at −15 °C or using peracetic acid as oxidant in acetonitrile at room temperature, to give the corresponding epoxychalcones **172** with similar efficiency (Scheme 43).[253] Using a chiral iron(II) complex bearing a dipyrrolidine backbone, asymmetric epoxidation reaction of few chalcones with hydrogen peroxide in the presence of 2-ethylhexanoic acid in acetonitrile at −30 °C for 30 min gave the respective epoxychalcones in 56–84 % yield and 94–97 % ee.[254]

Lyakin *et al.* reported the use of iron and manganese complexes with chiral bipyrrolidine-derived aminopyridine ligands for the asymmetric epoxidation of chalcone with hydrogen peroxide in acetonitrile and applying various carboxylic acids as additives namely, methanoic, ethanoic, butanoic, isobutanoic, pentanoic, hexanoic, 2-ethylhexanoic and pivalic acids.[255] Years later, this research group studied the asymmetric epoxidation of chalcone employing the same iron complexes in the presence of various oxidants (hydrogen peroxide, *t*-butyl hydroperoxide, cumene hydroperoxide, peracetic acid and *m*-chloroperbenzoic acid) in acetonitrile at 0 °C and provided some insights about the epoxidation mechanisms.[256]

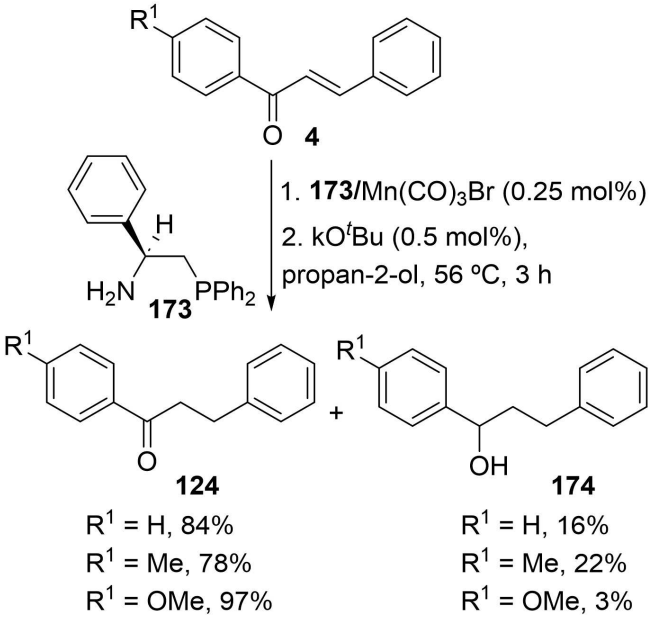


Scheme 43. Asymmetric epoxidation of chalcones **4**, promoted by chiral iron(II) complex **171**.

6. Manganese-Catalyzed Reactions

6.1. Hydrogenation

A manganese(I) complex bearing a β-amino phosphine ligand derived from phenylglycine **173** was an efficient catalyst to promote 1,4-transfer hydrogenation of chalcones **4** in propan-2-ol followed by addition of potassium *t*-butoxide to give 1-aryl-3-phenylpropan-1-ones **124** as main products along with small amounts of the respective 1-aryl-3-phenylpropan-1-ols **174** (Scheme 44).[257] Parent chalcone can also be reduced to 1,3-diphenylpropan-1-one by using 1 molar equiv. of manganese(I) complex containing a triazine backbone and linked to phosphines bearing phenyl groups as catalyst, 2 equiv. of potassium *t*-butoxide in THF at room temperature for 5 min, in quantitative yield. To promote the additional reduction of the carbonyl group, the reaction had to occur in the presence of 2 equiv. of catalyst and 4 equiv. of base in



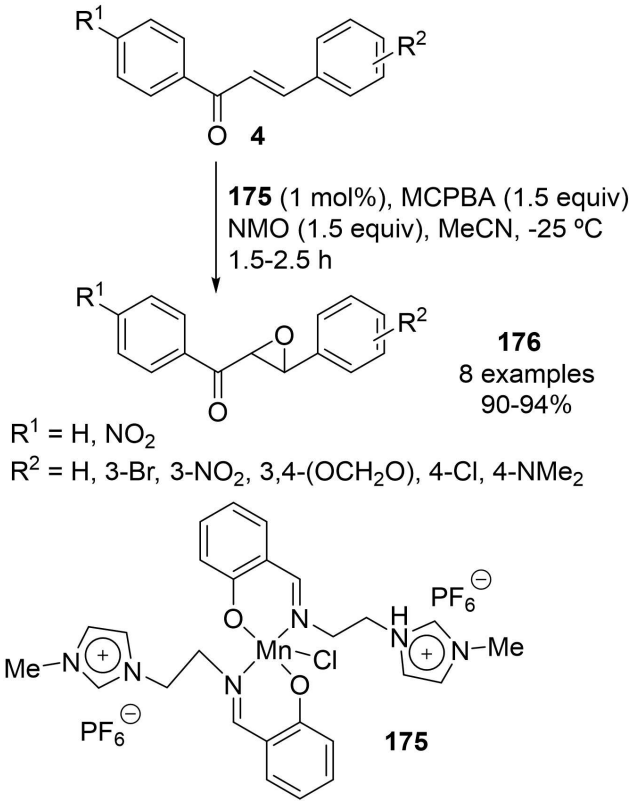
Scheme 44. Hydrogenation of chalcones **4**, promoted by a manganese(I) complex, followed by addition of potassium *t*-butoxide.

THF at 120 °C for 4 h to produce the 1,3-diphenylpropan-1-ol in 88 % yield.[258]

6.2. Epoxidation

Farooq and Ngaini in their review on the one-pot and two-pot strategies for the synthesis of epoxychalcones systematize the catalysts described in the literature to achieve this goal, including the metal-based ones.[259] The synthesis of epoxychalcone has been accomplished via enantioselective epoxidation of chalcone employing manganese transition metals such as aminopyridine based Mn complexes [$LMn^{II}(OTf)_2$] in the presence of hydrogen peroxide as oxidant, acetic acid[260,261] or 2-ethylhexanoic acid[262] as additive, in acetonitrile; in the presence of peracetic acid as oxidant in acetonitrile at 0 °C;[263] in the presence of peracetic acid as oxidant or using hydrogen peroxide in acetic acid in acetonitrile at 0 °C;[264] using various terminal oxidants (hydrogen peroxide, alkyl hydroperoxides, peroxyacids, and iodosylarenes) in a mixture of acetonitrile: dichloromethane at 0 °C[265] and mediated by $Mn(acac)_3$, using nanosheets of layered double hydroxides of amino acid Schiff bases as chiral ligands in dichloromethane at 20 °C for 3 h followed by the addition of iodosylbenzene for 24 h.[266]

Other chalcones underwent enantioselective epoxidation reactions using hydrogen peroxide as oxidant, catalyzed by manganese(II) complexes with tetradentate nitrogen ligands, derived from diamines in the presence of acetic acid in acetonitrile at room temperature[267] or at −20 °C,[268] derived from aminopyridines and graphene oxide in acetonitrile at −20 °C[269] and derived from rigid chiral diamines in a 3 : 6 : 1 mixture of acetic acid:acetonitrile:dichloromethane at −40 °C.[270] A non-asymmetric version for the epoxidation of chalcones **4** involves the use of manganese(III)–Schiff base complex with covalently attached imidazolium tags **175** as catalyst, *m*-chloroperoxybenzoic acid (MCPBA) as oxygen source, *N*-methylmorpholine *N*-oxide (NMO) as co-oxidant in acetonitrile to produce epoxychalcones **176** in excellent yields (Scheme 45). The catalyst was reused five times without loss of activity.[271]



Scheme 45. Non-asymmetric epoxidation of chalcones **4**, promoted by manganese(III)–Schiff base complex **175**.

6.3. Other Reactions

Diastereoselective synthesis of 2,3-disubstituted *cis*-5-aryl-4-benzoyl-4,5-dihydrofurans was prompted via [3 + 2] oxidative addition reaction of acyclic 1,3-dicarbonyl compounds with chalcones mediated by manganese(III) acetate in the presence of sodium acetate in acetic acid at 80 °C for 5–23 h, under argon atmosphere.[272] The same catalyst promoted oxidative cyclization reaction of chalcones with dimedone in glacial acetic acid at 80 °C under nitrogen atmosphere to give 3-aryl-2-benzoyl-6,6-dimethyl-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-ones. This protocol can also be applied using an equimolar mixture of manganese(III) acetate and copper(II) acetate as catalytic system, although with lower yields.[273]

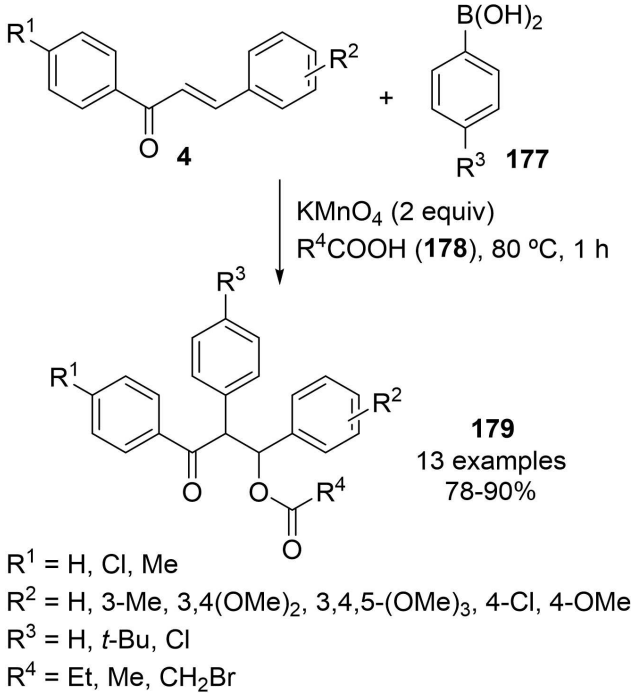
Regio- and diastereoselective β-acyloxy-α-arylation of chalcones **4** occurred using arylboronic acids **177** as aryl source, aliphatic carboxylic acids **178** as acyloxyl source and potassium permanganate as oxidant to afford the corresponding 3-acyloxy-1,2,3-triarylpropan-1-ones **179**, in high yields (Scheme 46). Potassium permanganate/carboxylic acid system generates *in situ* the Mn(III) species for the activation of the reaction.[274]

7. Nickel-Catalyzed Reactions

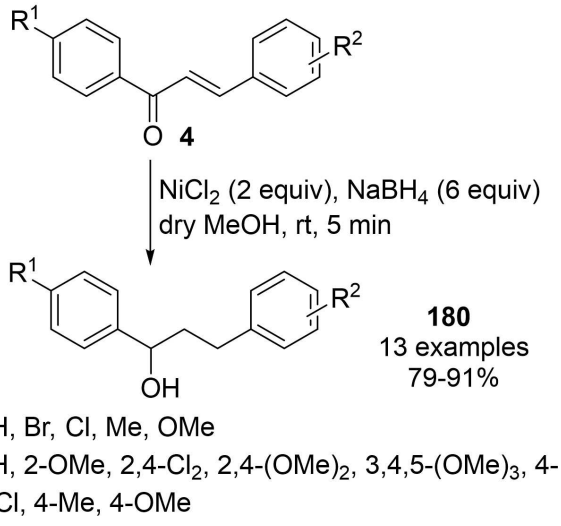
7.1. Hydrogenation

Nickel is an abundant base metal, often used a base coat prior to plating to provide increased protection to corrosion, with balanced global distribution and low toxicity that it is much cheaper than noble metals such as palladium and rhodium.[275]

Alonso *et al.* synthesized nickel(0) nanoparticles from nickel(II) chloride, lithium metal and a catalytic polymer-supported arene, for the chemoselective hydrogenation of the parent chalcone C=C bond using ethanol as hydrogen source



Scheme 46. Regio- and diastereoselective β-acyloxy-α-arylation of chalcones **4** with arylboronic acids **177** and aliphatic carboxylic acids **178**, promoted by potassium permanganate.



Scheme 47. Full reduction of chalcones **4**, promoted by nickel boride.

in THF at 0 °C.[276] Years later, Zaramello *et al.* prepared other nickel(0) nanoparticles for the same propose and the reaction occurred under mild reaction conditions, i. e., low hydrogen pressure, temperature and catalyst loading. The best catalyst, Ni-octanoic acid@SiO_2 system, could be reused up to 10 times without significant loss of activity.[277] Nickel boride, generated *in situ* from anhydrous nickel(II) chloride and sodium borohydride, promoted a rapid, efficient and full reduction of chalcones **4** to the corresponding 1,3-diarylpropan-1-ols **180**, in dry methanol at ambient temperature for 5 min (Scheme 47).[278]

7.2. Addition Reactions

Similarly, to the enantioselective copper(II)-catalyzed 1,4-conjugate addition of diethylzinc to chalcones, various organonickel catalysts has been prepared to this propose. Thus, asymmetric conjugate addition of diethylzinc to chalcone promoted by $Ni(acac)_2$ and using bipyridine-derived amino alcohols as ligands, in acetonitrile at −35 °C for 16 h, produced 1,3-diphenylpentan-1-one in high yields. The reaction also occurred using 2,2'-bipyridyl as co-ligand at the same time.[279]

Other chiral ligands were synthesized to mediate enantioselective nickel-catalyzed conjugate additions of diethylzinc to chalcones and include β-amino alcohols such as (*S*)-valine-derived amino alcohol possessing a piperidine ring and two flexible phenethyl groups,[280] five pyrrolidinylmethanols derived from L-proline,[281] six norephedrine-based chiral ligands,[282] a 2-(aminoalkyl)phenol and four 1-(aminoalkyl)naphth-2-ols;[283] α-amino amides derived from natural amino acids (alanine, valine, phenylalanine, isoleucine, and phenylglycine);[284] five derivatives of (1*R*,2*S*,3*R*)-3-mercaptocamphan-2-ol[285] and a couple of bipyridines combined with monoterpenoid fragments.[286] To note that similar results has been reached in this type of reactions using nickel(II) and copper(II) salts, being $Ni(acac)_2$ a cheaper and more accessible reagent than copper(II) triflate, commonly used in these cases.

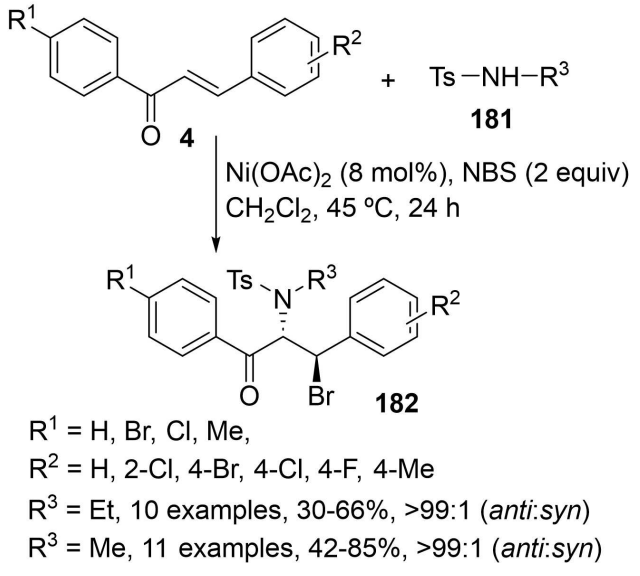
The divinylalane reagent, $[(CH_2{=}CH)_2Al(\mu\text{-}OCH_2CH_2NMe_2)]_2$, was applied in the 1,4-conjugate addition to chalcone, promoted by $Ni(acac)_2$ in toluene at 20 °C for 12 h, to produce 1,3-diphenyl-3-vinylpropan-1-one in 50% yield.[287] Microwave-assisted ligand-free 1,4-conjugate addition of arylboronic acids to chalcones mediated by nickel(II) nitrate hexahydrate in the presence of potassium hydroxide in 1,4-dioxane at 110 °C for 10–30 min under nitrogen atmosphere prompted the corresponding 1,3,3-triarylpropan-1-ones, in good to excellent yields.[288] The β-boration of chalcones with bis(pinacolato)diboron occurred under the same conditions, but replacing potassium hydroxide to cesium carbonate, and the respective 1,3-diaryl-3-borylated propan-1-ones were obtained also in good to excellent yields.[289] The synthesis of 1,3-diaryl-2-[*N*-(ethyl/methyl)-*N*-*p*-toluenesulfonyl]-3-bromopropan-1-ones **182** was accomplished via aminobromination of chalcones **4** mediated by nickel(II) acetate and combinations of *N*-ethyl-*p*-toluenesulfonamide **181** (R^3 = Et)/NBS and *N*-methyl-*p*-toluenesulfonamide **181** (R^3 = Me)/

NBS, respectively, in dichloromethane at 45 °C (Scheme 48).[290]

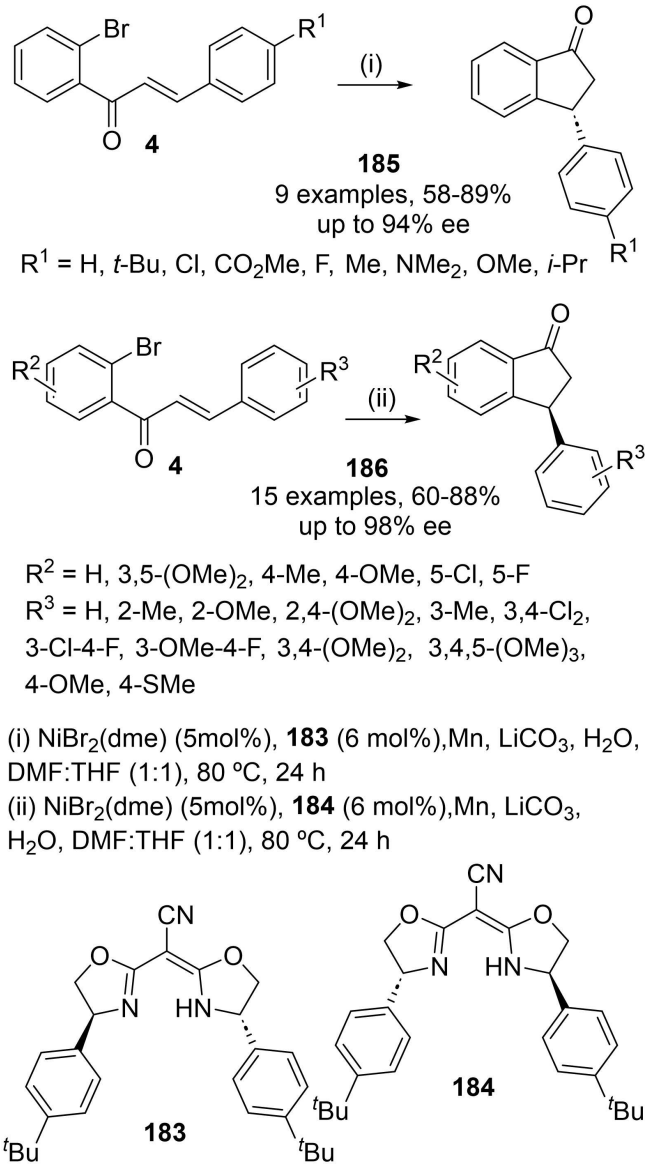
7.3. Other Reactions

Nickel(II)-catalyzed reductive cyclization reaction of 2'-bromo chalcones **4** employing semicorrins ligands (**183** and **184**), manganese powder, lithium carbonate and water in an 1 : 1 mixture of DMF : THF at 80 °C furnished the 5-*endo-trig* products, 3-arylindan-1-ones **185** and **186**, in high yields. Chalcones bearing *p*-substituted in A ring afforded the corresponding products in higher enantioselectivity with catalyst **183** while chalcones bearing *ortho* or *meta*-substituents on aryl rings provided the respective products in higher enantioselectivity with catalyst **184** (Scheme 49).[291]

Tabatabaeian *et al.* prepared a nickel(II)-pyridylimine complex anchored into a metal-organic-framework (MOF) cavity to catalyze the epoxidation of chalcones and bischalcones using hydrogen peroxide or bleach in methanol at room temperature. This heterogeneous catalysis took place under ultrasound irradiation (12–38 min) and without irradiation (50–200 min), with similar good yields, but with a reduced reaction time, in the former case.[292]



Scheme 48. Aminobromination of chalcones **4** with *N*-ethyl-*p*-toluene sulfonamide (**181**, R^3 = Et)/NBS and *N*-methyl-*p*-toluenesulfonamide (**181**, R^3 = Me)/NBS, mediated by nickel(II) acetate.



Scheme 49. Nickel(II)-catalyzed reductive cyclization reaction of 2'-bromochalcones **4**.

8. Ruthenium-Catalyzed Reactions

8.1. Hydrogenation

Carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) was applied as catalyst in the chemoselective transfer hydrogenation of chalcone in the presence of benzene in propan-2-ol to produce 1,3-diphenylpropan-1-one in 81 % yield.[293] Other example of transfer hydrogenation of chalcone was performed employing formic acid, sodium formate or sodium carbonate/propan-2-ol as the hydrogen source, using half-sandwich ruthenium(II) complexes in aqueous media. All the complexes

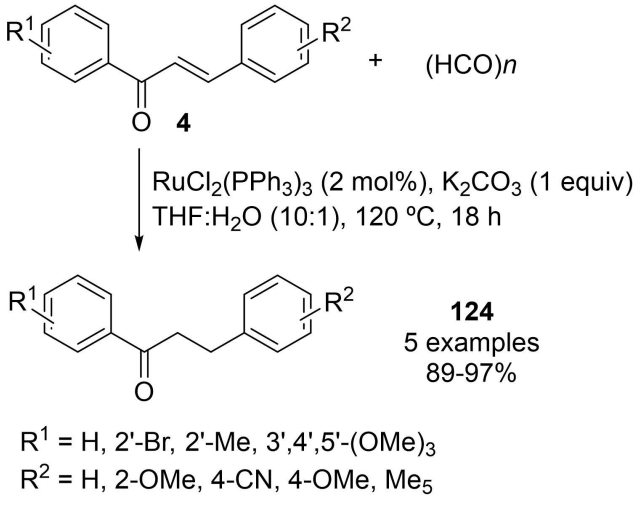
selectively hydrogenate the C=C bond, being the total conversion and selectivity highest in acidic solution, to afford 1,3-diphenylpropan-1-one as main reduction product.[294]

Selective hydrogenation of chalcone to 1,3-diphenylpropan-1-one was also accomplished under atmospheric hydrogen pressure and using a thermoregulated phase-transfer ruthenium nanocatalyst in an 1:1 mixture of water:pentan-1-ol.[295] A ruthenium(II) *N,N,N*-pincer-type bipyridylidine amide complex was applied in the catalytic transfer hydrogenation of chalcone in the presence of potassium hydroxide in refluxing propan-2-ol to provide 1,3-diphenylpropan-1-one in 33% yield, along with acetophenone, benzaldehyde, and their hydrogenated products.[296] Various 1,3-diarylpropan-1-ones were synthesized via ruthenium(II)-mediated selective hydrogenation of chalcones using paraformaldehyde in water as hydrogen generator and potassium carbonate as base, in THF (Scheme 50).[297]

Patil and Pratihar developed a solvent (methanol *vs* ethanol)- and base (potassium *vs* lithium carbonate)-assisted switchable selectivity for the ruthenium(II)-catalyzed tandem hydrogenation of chalcones in the presence: (i) of potassium carbonate in ethanol formed saturated ketones 1,3-diarylpropan-1-ones, exclusively; (ii) of potassium carbonate in methanol α-methylation occurred and produced saturated ketones 1,3-diaryl-2-methylpropan-1-ones as main products along with small amounts of the corresponding saturated ketones, in some cases; (iii) of lithium carbonate in methanol, solely hydrogenation took place to form saturated ketones, although with lower conversion rates than those obtained with potassium carbonate.[298]

A single example of reduction of chalcone followed by α-methylation induced by a ruthenium(II)-catalyst, using lithium *t*-butoxide as base and methanol as methylation agent furnished 2-methyl-1,3-diphenylpropan-1-one in 74% yield.[299]

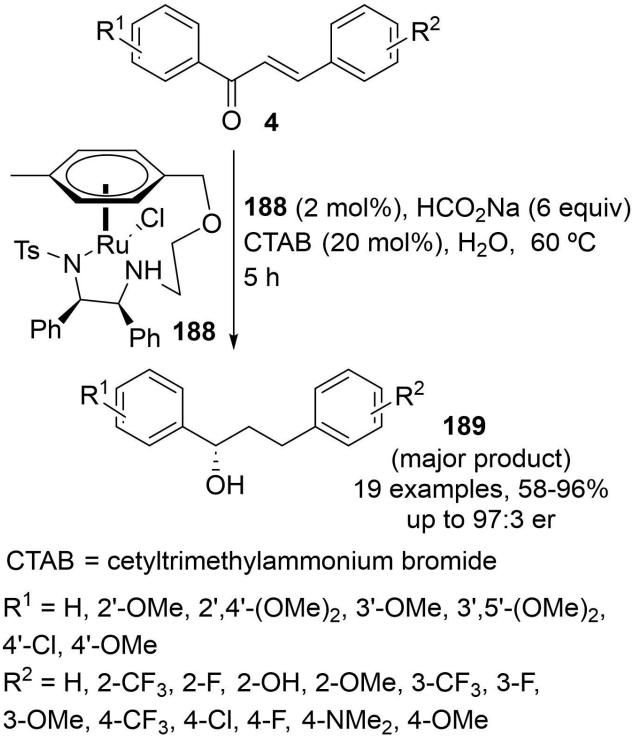
Yadav and Gupta synthesized a ruthenium(II) hydride complex supported with a coumarin-amide-base ligand to promote transfer hydrogenation of chalcone, using propan-2-ol as solvent and hydrogen source, giving access to 1,3-diphenylpropan-1-ol in quantitative yield.[300] Other 1,3-diarylpropan-1-ols were obtained as major products from ruthenium(II)-catalyzed asymmetric transfer hydrogenation of chalcones using sodium formate as hydrogen source in presence of cetyltrimethylammonium bromide in water (Scheme 51). Smaller amounts of 1,3-diarylpropan-1-ones and 1,3-diarylprop-2-en-1-ols were also isolated, in some cases.[301]



Scheme 50. Ruthenium(II)-mediated selective hydrogenation of chalcones **4**.

8.2. Addition Reactions

Li *et al.* reported the asymmetric Michael addition of malononitrile to chalcones catalyzed by $RuCl_2[(R,R)\text{-DPEN}](PPh_3)_2$ in the presence of cesium acetate and cesium hydroxide in toluene at −10 °C for 24–70 h to afford 1,3-diaryl-4,4-dicyanobutan-1-ones in 18–99% yield and up to 82% ee. In addition, the reaction of diethyl malonate to chalcone occurred smoothly at room temperature and furnished the adduct with 77% yield and 33% ee, after 40 h of reaction.[302] The Michael-type addition of substituted



Scheme 51. Ruthenium(II)-mediated asymmetric transfer hydrogenation of chalcones **4**.

benzaldehyde derived hydrazones to chalcones under the catalysis of $[Ru(p\text{-cymene})Cl_2]_2$, using triphenylphosphine as ligand and potassium phosphate as base in refluxing water for 6 h under argon atmosphere prompted the alkylated products 1,3,4-triarylbutan-1-ones, in moderate to good yields.[303]

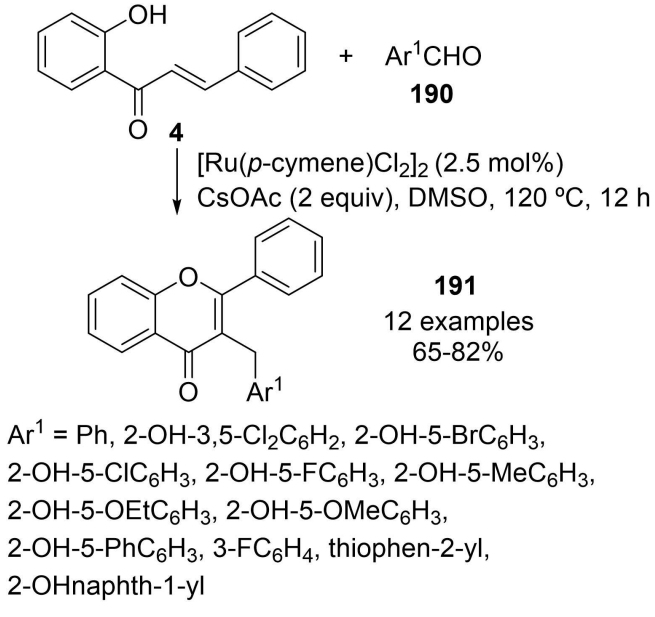
Three $Cp^*Ru(PPh_3)(PR_3)Cl$ complexes were applied in the atom transfer radical addition of CCl_4 to chalcone in the presence of 2,2′-azobis(2-methylpropionitrile) (AIBN) in toluene-d_8. The yields of 3-chloro-1,3-diphenyl-2-(trichloromethyl)propan-1-one, predominantly in a *trans*-configuration, were determined by ^1H NMR spectroscopy and varied from 41 to 58%.[304] A single example of 3-(indol-3-yl)-1,3-diphenylpropan-1-one was synthesized in 80% yield via 1,4-conjugate addition of indole to chalcone mediated by ruthenium(III) chloride in refluxing methanol for 3 h.[305]

A broad range of 2'-acrylate chalcones were synthesized via regioselective *ortho*-C–H activation of chalcones with acrylates in presence of $[Ru(p\text{-cymene})Cl_2]_2$ as catalyst, copper(II) acetate hydrate as oxidant and silver hexafluoroantimonate as additive in refluxing 1,2-DCE for 24 h.[306] The same catalyst promoted C–H activation of 2'-hydroxychalcone **4** with aromatic aldehydes/salicylaldehydes **190**, carried out in the presence of cesium acetate in DMSO at 120 °C to deliver highly substituted 3-benzyl-2-phenyl-4*H*-chromen-4-ones **191** (Scheme 52).[307]

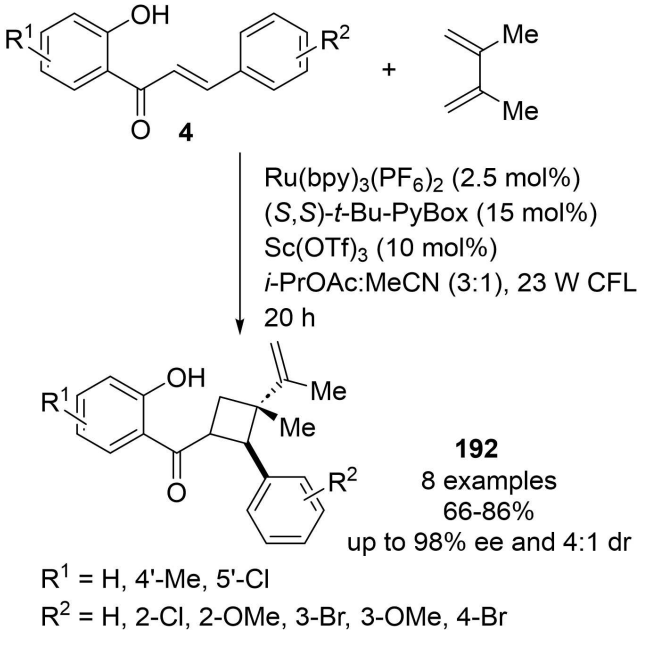
8.3. Cycloaddition Reactions

Jernei *et al.*, along with copper(I)-catalyzed alkyne-azide cycloaddition reaction, also studied ruthenium(II)-promoted cycloaddition reaction of azido chalcones with readily available diastereomeric cinchona-derived 9,10-didehydroquinine or 9,10-didehyroquinidine alkynes, carried out in the presence of ascorbic acid and sodium hydroxide in an 1:1 mixture of butan-1-ol:water at room temperature to give the related cinchona-chalcone hybrids with a 1,2,3-triazole linker, in low yields (31–60%).[146] Asymmetric [2+2] photocycloaddition reaction of 2′-hydroxychalcones **4** with 2,3-dimethylbuta-1,3-diene using the Lewis acid tris(bipyridyl)ruthenium(II) hexafluorophosphate as catalyst in the presence of (*S*,*S*)-*t*-Bu-PyBox, scandium(III) triflate in a 3:1 mixture of isopropyl acetate:acetonitrile at room temperature provided the corresponding 2-aryl-3-(2-hydroxyaroyl)-1-methyl-1(prop-1-en-2-yl)cyclobutanes **192** (Scheme 53). The protocol was applied to other substituted and unsubstituted dienes[308] as well as for styrene olefins to form 1,2-diaryl-3-(2-hydroxybenzoyl)cyclobutanes.[309]

Various 1,2-diaryl-3,4-dibenzoylcyclobutanes were obtained from light-induced homocoupling [2+2] cycloaddition reaction of chalcones promoted by a ruthenium-based supramolecular cage catalyst at room temperature under nitrogen atmosphere. All substrates generated *syn*-HH diastereomers as the major photoproducts.[310]



Scheme 52. Ruthenium(II)-catalyzed C–H activation of 2'-hydroxychalcone **4** with aromatic aldehydes/salicylaldehydes **190**.



Scheme 53. Ruthenium(II)-catalyzed asymmetric [2+2] photocycloaddition reaction of 2′-hydroxychalcones **4** with 2,3-dimethylbuta-1,3-diene.

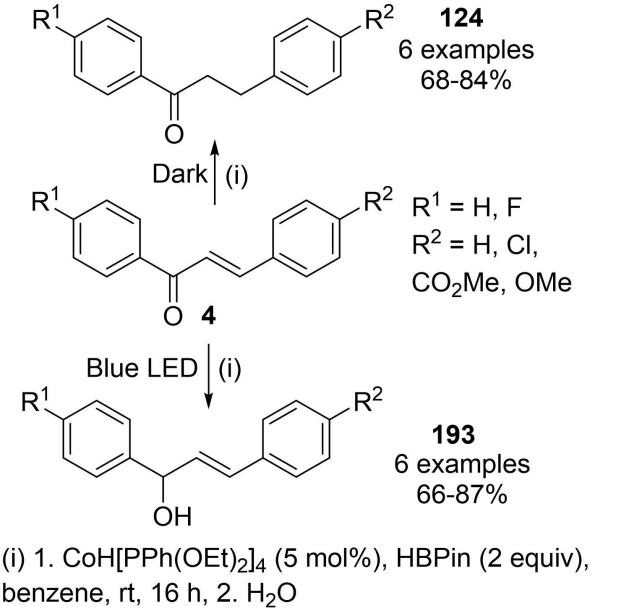
9. Cobalt-Catalyzed Reactions

Aramini *et al.* studied the selective reduction of parent chalcone using the dual catalytic system of sodium borohydride:cobalt(II) chloride to afford quantitatively the 1,4-reduced product (1,3-diphenylpropan-1-one) as well as the totally reduced compound (1,3-diphenylpropan-1-ol) by simple changes in the experimental conditions: the former was obtained as main product using a 1 : 2.5 : 2 ratio of substrate: $NaBH_4$:$CoCl_2$ in methanol and the last was obtained in 98 % yield using a 1 : 8.1 : 3 ratio of substrate:$NaBH_4$:$CoCl_2$ in aqueous micellar solution of cetyltrimethylammonium bromide.[311] On the other hand, Yadav *et al.* proposed a selective reduction of C=O of chalcone promoted by a cobalt(II) catalyst in the presence of potassium hydroxide as base and propan-2-ol as both hydrogen source and solvent, at 80 °C for 7 h to achieve 1,3-diphenylprop-3-en-1-ol in 78 % yield,[312] while Jiang *et al.* reported C=C double bond reduction of several chalcones mediated by a cobalt(II) catalyst in the presence of indium power and propan-2-ol in toluene at 80 °C for 24 h to provide 1,3-diarylpropan-1-ones.[313]

Other 1,3-diarylpropan-1-ones were prompted through hydrogenation of chalcones mediated by cobalt nanoparticles supported on the biomass-derived carbon from bamboo shoots in the presence of tetrabutylammonium iodide in water.[314] Interestingly, Beltran *et al.* published a regioselective reduction of chalcones **4** depending on the presence or absence of light, mediated by a cobalt hydride catalyst and pinacolborane in benzene at room temperature followed by aqueous workup: (i) in dark light conditions, 1,4-reduction takes place to afford 1,3-diarylpropan-1-ones **124**; (ii) in blue LED irradiation conditions, 1,2-addition occurs and the corresponding 1,3-diarylprop-2-en-1-ols **193** were formed (Scheme 54).[315]

Under phase transfer conditions, chiral cobalt(III) complexes catalyzed the asymmetric epoxidation reaction of chalcones with aqueous hydrogen peroxide, in the presence of potassium *t*-butoxide in methyl *t*-butyl ether (MTBE) at room temperature, under argon atmosphere, to give the respective epoxychalcones with a high conversion rate and enantiomeric purity up to 58 %.[316–318]

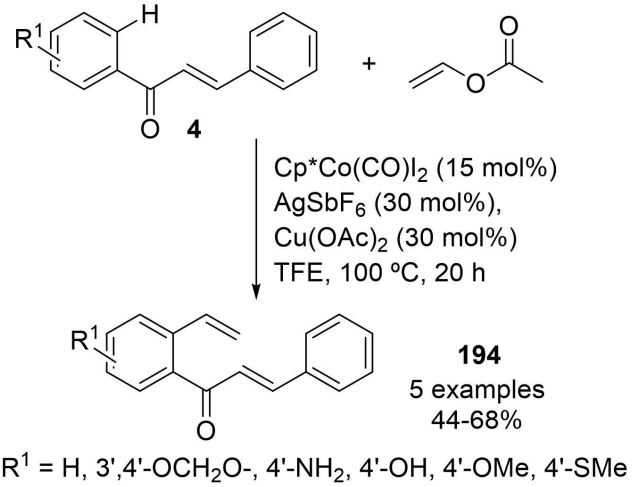
Chen *at al.* prepared a cobalt complex, prepared *in situ* from cobalt(II) acetate and a C_2-symmetric chiral nitrogen-containing ligand bearing a spirobisindane backbone, for the asymmetric Michael addition of malonates to chalcones, using diethyl zinc as base and ethanol as solvent, at room temperature for 60 h to produce 2-(1,3-diaryl-3-oxopropyl)malonates in 70–78 % yield and with modest enantioselectivity.[319] The synthesis of 1,3,3-triarylpropan-1-ones can be efficiently achieved through C–H bond addition of 2-arylpyridines to chalcones in THF at 100 °C for 24 h.[320] Cobalt(III)-catalyzed *ortho*-C–H vinylation reaction of chalcones **4** with vinyl acetate in the presence of silver hexafluoroantimonate and copper(II) acetate in TFE prompted few 2'-vinylchalcone derivatives **194** (Scheme 55).[321]



Scheme 54. Cobalt(II)-mediated regioselective reduction of chalcones **4**, in the absence and in presence of light.

10. Rhodium-Catalyzed Reactions

Various 1,3-diarylpropan-1-ones could be synthesized via selective hydrogenation of chalcones C=C double bond induced by a rhodium(I) catalyst in dichloromethane,[322] by a cationic rhodium(I) complex in the presence of triphenylphos-



Scheme 55. Cobalt(III)-mediated *ortho*-C–H vinylation reaction of chalcones **4** with vinyl acetate.

phine as ligand and using γ-valerolactone as green solvent,[323] by a rhodium(I)-modified nanodiamonds using a surface-immobilized catechol phosphane ligand in methanol,[324] and using a rhodium(III) hydride complex in methanol.[325] High conversion rates were observed in the chemoselective rhodium(I)-catalyzed transfer hydrogenation reaction of chalcones in the presence of ammonium formate as hydrogen donor in the ionic liquid [bmim][$BuSO_4$] at 90 °C for 15 min to give 1,3-diarylpropan-1-ones.[326] Methanol was also applied as an effective hydrogen source for the highly chemoselective transfer hydrogenation reaction of a wide variety of chalcones mediated by a rhodacycle in the presence of potassium carbonate at reflux for 1 h, providing the corresponding 1,3-diarylpropan-1-ones in good to excellent yields.[327]

Enantioselective synthesis of chiral 3-arylindan-1-ones was prompted via asymmetric intramolecular 1,4-addition of 2'-pinacolborane chalcones mediated by a rhodium(I) dimer and using simple mono-Phos as chiral ligand in the presence of potassium phosphate in toluene at 80 °C.[328] Various 3-aroyl-3-arylindan-1-ones were obtained from rhodium(III)-catalyzed [4 + 1] oxidative cyclization of chalcones with internal alkynes in the presence of silver hexafluoroantimonate and copper(II) acetate hydrate in DME at 130 °C for 13 h. From this reaction was also possible to isolate the aromatic aldehydes resulting from the cleavage of the C=C double bond of chalcones.[329] Under the same reaction conditions at 100 °C, 2′-hydroxychalcones **4** reacted with diphenyl acetylene, via C–C bond cleavage and C–H bond functionalization, to deliver a series of *cis*-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-1-ones **195**. In addition, when chalcone is substituted in A-ring or different symmetric diphenyl or diaryl acetylenes **198** were used, products appear as a mixture of two regioisomers, **196:197** and **199:200**, respectively. Moreover, using alkyl phenyl acetylenes **201**, only products **202** were isolated (Scheme 56).[330]

Yu *et al.* applied a rhodium(III) catalyst for the selective hydroarylation reaction of maleimides to chalcones, via *ortho*-C–H bond activation, conducted in the presence of silver hexafluoroantimonate and sodium acetate in 1,2-DCE at 100 °C for 6 h, under nitrogen atmosphere, to produce 2'-(2,5-dioxopyrrolidin-3-yl)chalcones.[331] The same rhodium(III) catalyst in the presence of silver hexafluoroantimonate promoted conjugate 1,4-conjugate addition of aryl C–H bonds to chalcones in acetic acid at 60 °C for 24 h to form 1,3,3-triarylpropan-1-ones.[332] Parent chalcone underwent vinylic C–H activation with *N*,*N*-di(but-2-yn-1-yl)-4-methylbenzenesulfonamide preceded by aromatic C–H activation reaction using [Rh(cod)(biphep)]BF_4 [biphep: 2,2'-bis-(diphenylphosphino)-1,1'-biphenyl] as catalyst, in dichloromethane at room temperature for 1 h to give (2*E*,4*Z*)-4-[(*Z*)-4-ethylidene-1-tosylpyrrolidin-3-ylidene]-1,3-diphenylpent-2-en-1-one in 97 % yield.[333] A huge variety of aryl(3'-aryl-2',3'-dihydro-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,1'-inden]-2′-yl) methanones can be prepared through rhodium(III)-catalyzed [3 + 2]-spiroannulation reaction of chalcones with 3-aryl-2*H*-benzo[*b*][1,4]-oxazines as cyclic ketimines using sodium acetate in TFE at 100 °C, in good to excellent yields and with high diastereoselectivity (Scheme 57).[334]

11. Iridium-Catalyzed Reactions

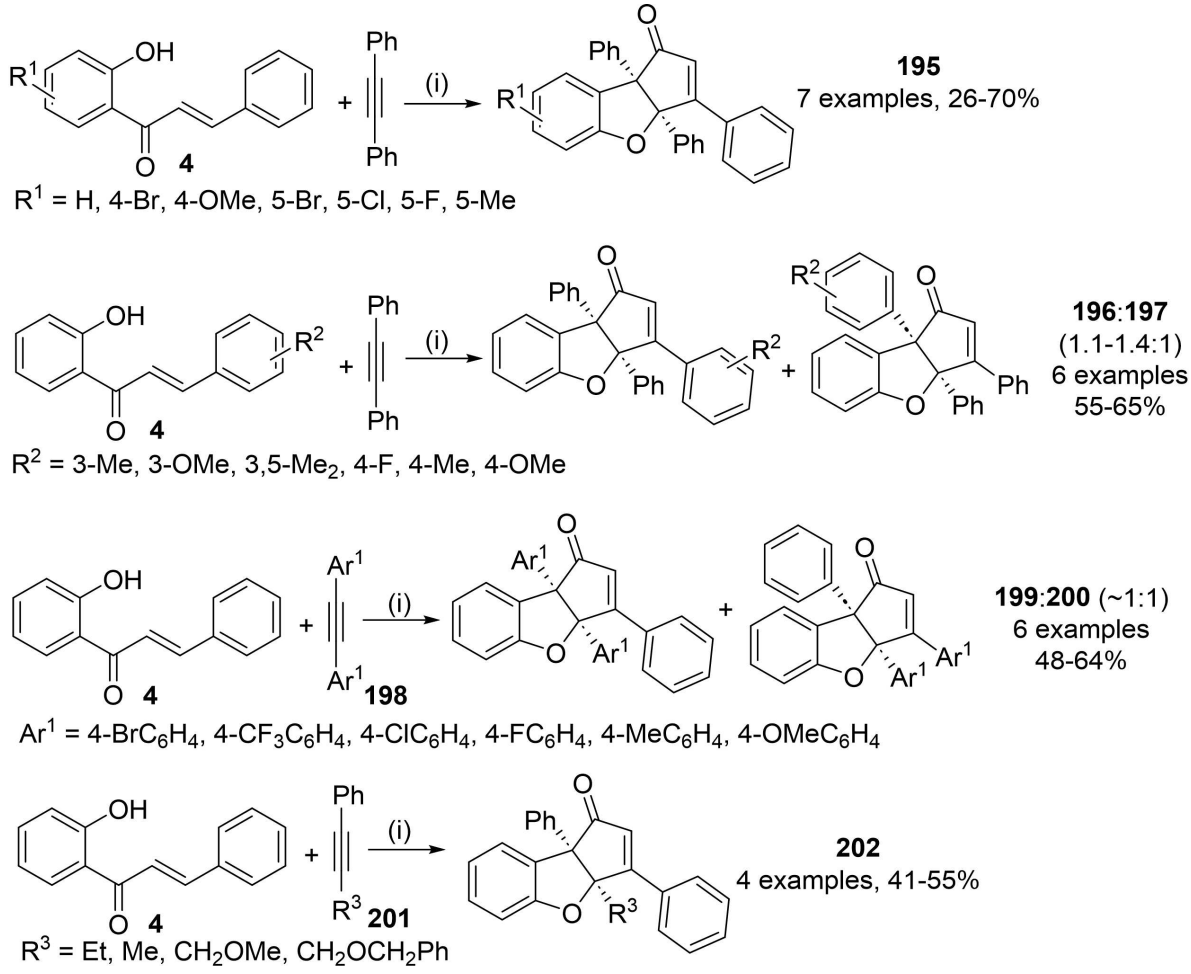
The methodology developed by Császár *et al.* for the asymmetric hydrogenation of chalcones promoted by an iridium(P,N,N) complex is controlled by the size of the ligand: a five-membered P,N chelate induced higher C=C hydrogenation to form 1,3-diarylpropan-1-ones while six-membered P,N chelate switched chemoselectivity for C=O hydrogenation to produce 1,3-diarylprop-2-en-1-ols.[335] Chemoselective transfer hydrogenation of chalcones catalyzed by dichloro(pentamethylcyclopentadienyl) iridium(III) dimer in propan-2-ol (as hydrogen source and solvent) at 85 °C for 5 h was base-controlled: using potassium carbonate formed 1,3-diarylpropan-1-ones while switching to potassium hydroxide 1,3-diarylpropan-1-ols were obtained.[336] One year later, a bis(protic *N*-heterocyclic carbene)iridium(III) complex was applied in the transfer hydrogenation of chalcone in the presence of potassium hydroxide in propan-2-ol at 95 °C for 30 min and 1,3-diphenylpropan-1-one was obtained in 97 % yield.[337]

A wide range of 1,3-diaryl-2-methylpropan-1-ones was prepared via iridium(III)-induced tandem reductive methylation of chalcones conducted in the presence of cesium hydroxide hydrate in methanol at 120 °C for 24 h (Scheme 58).[338]

Regio- and diastereoselective intermolecular [2 + 2] photodimerization reaction of chalcones **4** promoted by an iridium(III) catalyst in 1,4-dioxane at room temperature under an argon atmosphere provided a mixture of isomers of 1,2-diaroyl-3,4-diarylcyclobutanes **207**, in an *anti*-head-to-head configuration, in 38–86 % yields. Under similar conditions, the cross [2 + 2] photodimerization of chalcones **4** with 1,1-diphenyl ethylene in 1,2-DCE afforded 2-aryl-3-benzoyl-1,1-diphenyl cyclobutanes **208**, in a *trans*-configuration (Scheme 59).[339] Another iridium(III) catalyst promoted [2 + 2] photocycloaddition reaction of chalcones in anhydrous DMF at room temperature to form a couple of 1,2-diaryl-3,4-dibenzoylcyclobutanes.[340]

12. Silver-Catalyzed Reactions

Nájera *et al.* reported the 1,3-dipolar cycloaddition reaction of chalcone with azomethine ylides (glycine aldimino esters) using a chiral phosphoramiditesilver(I) perchlorate complex as catalyst, triethylamine as base, in toluene at −20 °C to form

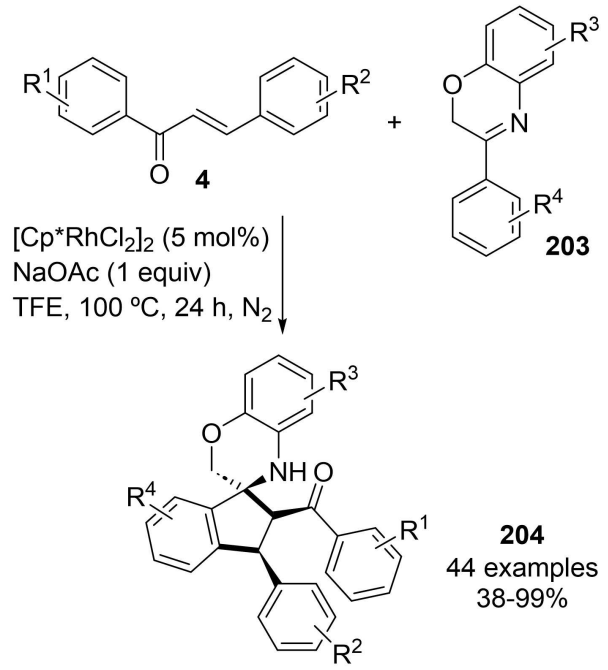


Scheme 56. Rhodium(III)-catalyzed C–C bond cleavage and C–H bond functionalization for the synthesis of 3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-1-ones from the reaction of chalcones **4** with diphenyl acetylene or aryl acetylenes **198** and **201**.

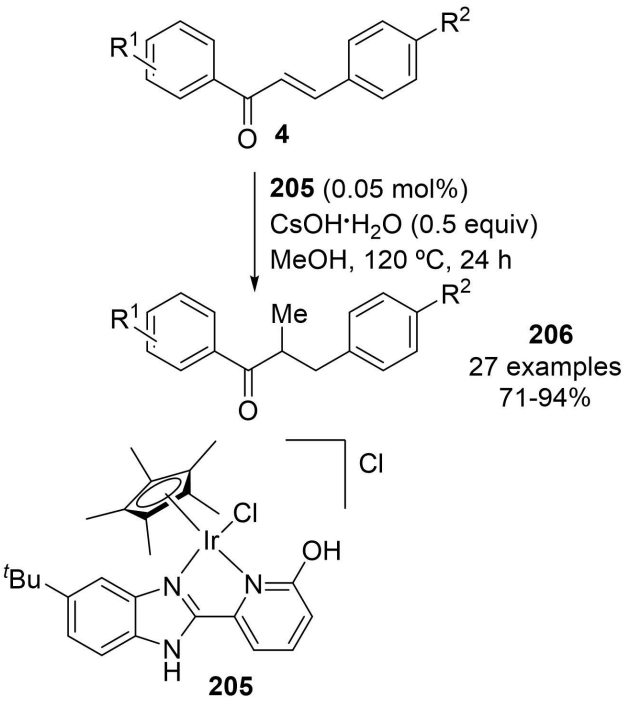
the *endo*-products, methyl (2*S*,3*R*,4*S*,5*R*)-3,5-diaryl-4-benzoyl-pyrrolidine-2-carboxylates in 70–81% yields and excellent enantioselectivity.[341] Later, the same research group made a comparison study of the 1,3-dipolar cycloaddition reaction of chalcone **1** with similar ylides **209** catalyzed by binap-gold(I) [Binap: 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl)] and binap-silver trifluoroacetate complexes in the presence of triethylamine in toluene at room temperature for 24 h. Gold catalyst furnished higher yields and enantiomeric excess values than the silver complex, for the synthesis of the *endo*-products **210** (Scheme 60).[342]

On the other hand, Li *et al.* reported an enantiodivergent synthesis of *endo*-pyrrolidine-2-carboxylates from 1,3-dipolar cycloaddition reaction of various chalcones with similar ylides using brucine diol as ligand: (i) using silver fluoride as catalyst in the presence of *t*-butanol in THF at −15 °C for 48–72 h provided (2*R*,3*S*,4*R*,5*S*)-products; (ii) using copper(I) triflate as catalyst in the presence of DBU and phenol in TCE (1,1,2-trichloroethane) at −15 °C for 48–72 h afforded (2*S*,3*R*,4*S*,5*R*)-products.[343] Highly substituted (2*R*,3*R*,4*S*,5*S*)-3,5-diaryl-4-benzoylpyrrolidine-2-carboxylates were obtained as *exo*-products of [3 + 2] cycloaddition reaction of chalcones with glycine aldimino esters promoted by silver(I) fluoride and Xing-Phos ligand in an 1 : 1 mixture of THF:ethanol at −20 °C for 12–24 h.[344]

Asymmetric Michael addition initiated cyclization reaction for the [3 + 2] cycloaddition of chalcones **4** with aldimino ester **209** promoted by silver acetate/Xing-Phos system in the presence of *N*,*N*-dimethylaminocyclohexane in methanol at −20 °C followed by acidic workup (HCl) prompted *cis*-Δ(1)-3,4-diaryldihydropyrroline-2-carboxylates **211**. Furthermore, replacing HCl for triflic acid (TfOH) and subsequent basic



Scheme 57. Rhodium(III)-catalyzed [3 + 2]-spiroannulation reaction of chalcones **4** with 3-aryl-2*H*-benzo[*b*][1,4]-oxazines **203**.



Scheme 58. Iridium(III)-mediated tandem reductive methylation of chalcones **4**.

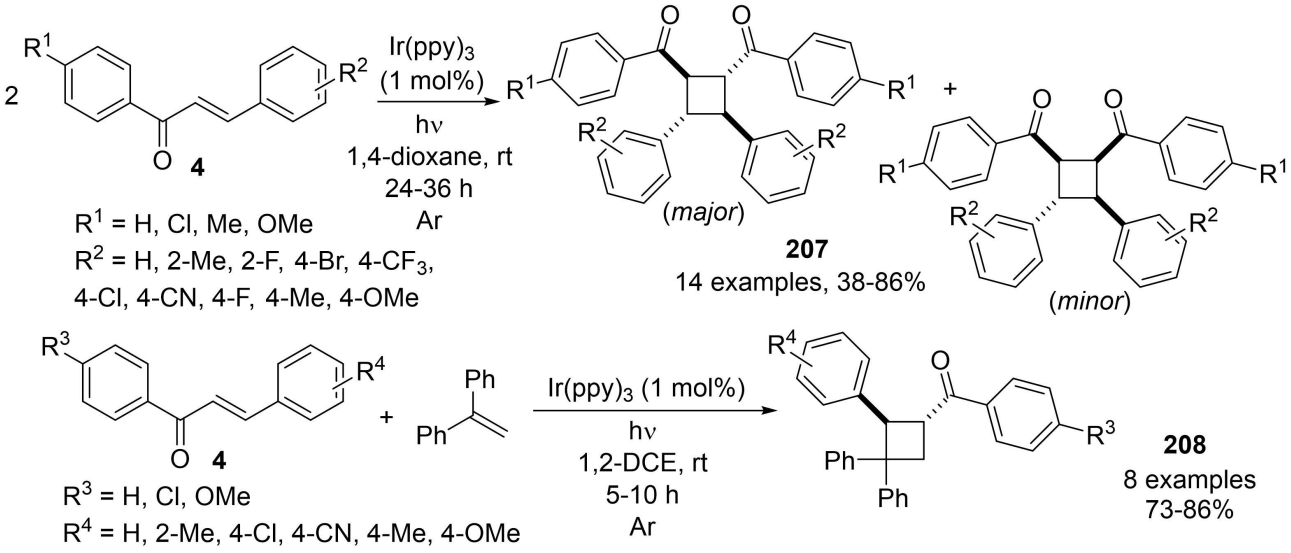
(DBU) workup, led to the stereodivergent synthesis of the *trans*-configured products **212** (Scheme 61).[345]

13. Other Transition Metal-Catalyzed Reactions

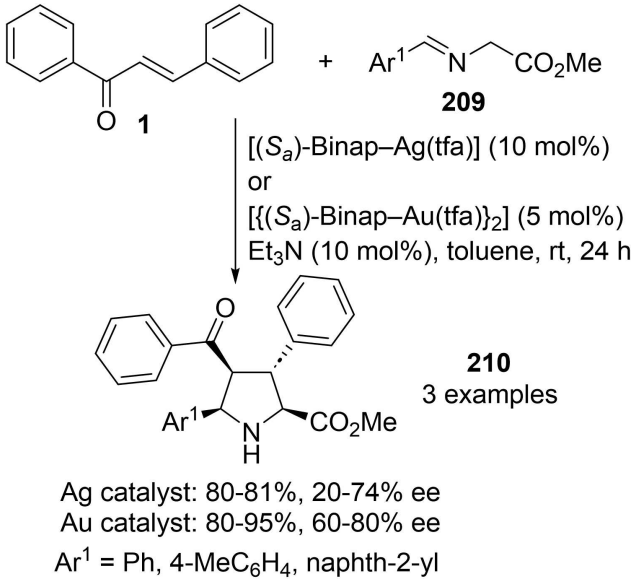
Indium metal was not a successful reducing agent for selective reduction of C=C double bond of chalcone. Using acetic acid in refluxing THF provided the reduced 1,3-diphenylpropan-1-one in only 23% yield and the cyclo-dimerized 2-benzoyl-1,3,4-triphenylcyclopentanol as major product (59%).[346] Applying ammonium chloride in an 1:1 mixture of ethanol: water at reflux, the ketone product was obtained in 30% yield.[347] However, indium hydride, generated *in situ* from a catalytic amount of indium(III) chloride and sodium borohydride in acetonitrile, reduced selectively the chalcones C=C double bond: quenching the reaction mixture with water provided the corresponding 1,3-diphenylpropan-1-ones,[348] while quenching with methanol 1,3-diarylpropan-1-ols were obtained as major products,[349] in excellent yields.

Indium(III) bromide mediated 1,4-conjugate addition reaction of indoles to chalcone in dichloromethane at room temperature afford 3-(indol-3-yl)-1,3-diphenylpropan-1-ones and with thiols give 3-(arylthio)-1,3-diphenylpropan-1-ones. Moreover, using a catalytic amount of the same catalyst, 1,4-conjugate addition 2-methylindole to chalcone in dichloromethane and subsequent 1,2-addition of trimethylsilyl cyanide produced 1-cyano-1-trimethylsilyloxy-3-(2-methylindol-3-yl)propane in 52% yield.[350] More examples of 3-(alkyl/arylthio)-1,3-diarylpropan-1-ones **213** can be achieved from 1,4-conjugate addition of aliphatic and aromatic thiols **162** to chalcones **4** mediated by indium(III) chloride in dry methanol at room temperature (Scheme 62).[351]

In situ generation of hydrogen peroxide, using ethanol as solvent and (polyvinylpyrrolidone)-stabilized nanogold catalytic system, was applied in the aerobic epoxidation of chalcone in the presence of a stoichiometric amount of potassium hydroxide at 27 °C for 15 h. The corresponding epoxide



Scheme 59. Iridium(III)-mediated intermolecular [2 + 2] photodimerization reaction of chalcones **4** and cross [2 + 2] photodimerization of chalcones **4** with 1,1-diphenylethylene.



Scheme 60. [(S)-Binap–Ag(tfa)] versus [{(S)-Binap–Au(tfa)}$_2$]-catalyzed 1,3-dipolar cycloaddition of chalcone **1** with iminoesters **209**.

product was obtained in 51% yield.[352] A series of 1,3-diaryl-3-(indolyl-3-yl)propan-1-ones were synthesized in excellent yields from gold-catalyzed Michael-type Friedel-Crafts reaction of indole with chalcones in acetonitrile at room temperature for 3–7 h.[353]

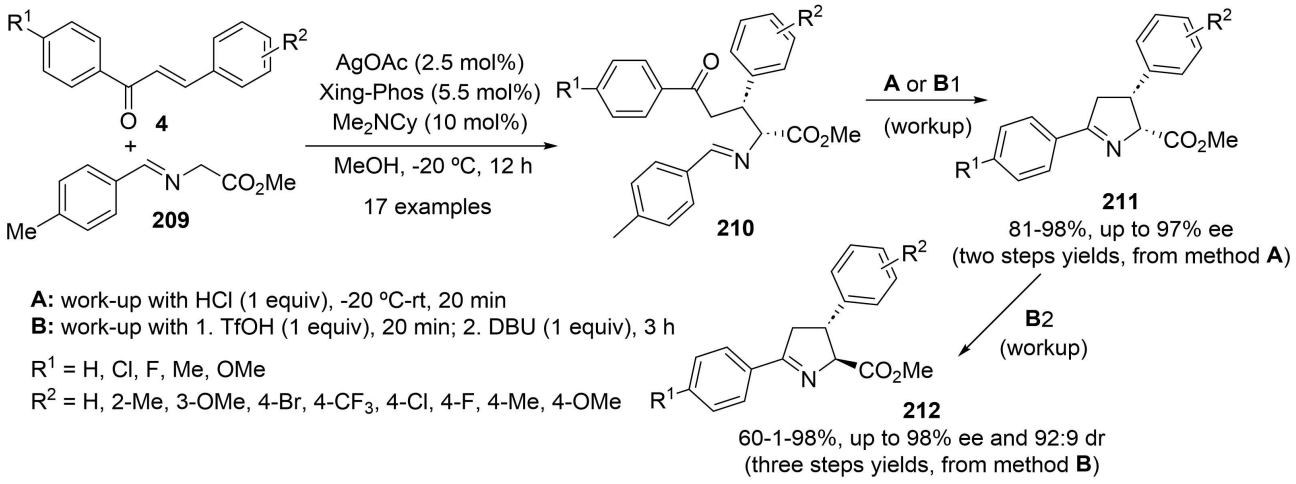
An organosilicon/graphene-supported platinum(II) catalyst was prepared to promote the 1,4-hydrosilylation of chalcones with various hydrosilanes in THF at 60 °C for 3 h and the respective (*Z*)-(1,3-diarylprop-1-enyloxy)silane derivatives were obtained in good to excellent yields.[354]

Zeng *et al.* published a substituent-controlled divergent cascade cycloaddition reaction of chalcones **4** with (2-ethynylaryl)methanols **214** mediated by platinum(II) iodide in toluene at 60 °C: (i) using α-cyanochalcones as starting materials, cascade [2 + 4] cycloaddition reaction takes place to give spirobenzofuran 4,6-diaryl-3,4-dihydro-2*H*-pyran-5-carbonitriles **215**; (ii) using 2'-hydroxychalcones, cascade [4 + 2] cycloaddition reaction occurs to produce oxa-bridged fused heterocycles **216** and **217** (Scheme 63).[355]

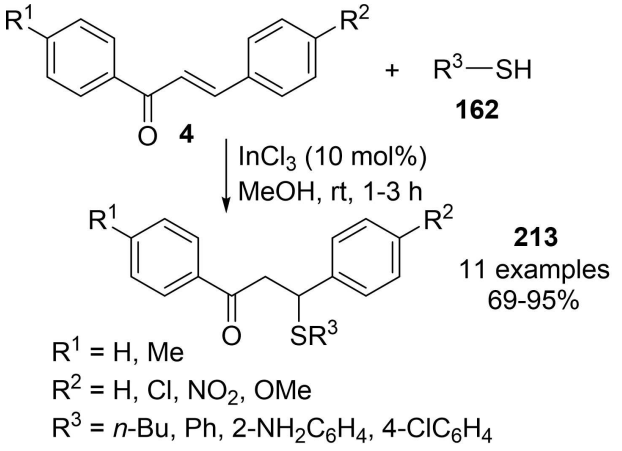
Stereocontrolled cyclodimerization reaction of chalcones mediated by samarium(II) iodide in THF at room temperature furnished 1,2-*cis*-2,3-*trans*-3,4-*trans*-2-benzoyl-1,3,4-triaryl cyclopentanols, in good yields.[356] Various 5-aroyl-2,2,3-triaryl-2,3-dihydrofurans **219** were synthesized through intermolecular reductive cyclization reaction of chalcones **4** with aromatic ketones **218** using SmI_2/Sm catalytic system in THF at room temperature for 20 min (Scheme 64).[357]

1,4-Conjugate addition of ethyl acetoacetate to chalcones promoted by cerium(III) chloride heptahydrate in the presence sodium iodide at room temperature, under solvent-free conditions, afforded ethyl 3,5-diaryl-2,5-dioxopentanoates in 51–93% yields.[358] Three-component reaction of chalcones **4** with primary amines **137** and β-ketoesters mediated by cerium(IV) ammonium nitrate[359] or cerium(IV) oxide nanoparticles (Scheme 65)[360] in ethanol prompted a series of 2-amino-4,6-diaryl-4-hydroxycyclohex-1-ene-1-carboxylic esters **220**.

A titanium complex formed from chiral ligand derived from (*S*)-BINOL and L-prolineamide **221** was prepared to



Scheme 61. Silver(I)-catalyzed Michael addition and subsequent cyclocondensation reaction of chalcones **4** with aldimino ester **209**, with the aid of an acidic workup (Method A) or with the aid of an acidic and subsequent basic workup (Method B).



Scheme 62. 1,4-Conjugate addition reaction of chalcones **4** with aliphatic and aromatic thiols **162**, mediated by indium(III) chloride.

catalyze domino reaction of 2'-hydroxychalcones **4** with *o*-phenylenediamine in THF at −20 °C and the corresponding 2-aryl-4-(2'-hydroxyaryl)-2,3-dihydro-1*H*-1,5-benzodiazepines **222** were formed in high yields and with good enantioselectivity (Scheme 66).[361]

Friedel–Crafts alkylation reaction of chalcones with indoles or pyrroles catalyzed by a chiral *N,N'*-dioxide–scandium triflate complex in dichloromethane at 35 °C under argon atmosphere provided, respectively, 1,3-diaryl-3-(indol-3-yl)propan-1-ones or 1,3-diaryl-3-(pyrrol-2-yl)propan-1-ones.[362]

Asymmetric Diels–Alder reaction of chalcones **4** with 1,3-cyclohexadiene promoted by aluminium chloride bearing an oxazoline containing β-diketiminate-type ligand **223** in deuterated chloroform at room temperature afforded a series of aryl(3-phenylbicyclo[2.2.2]oct-5-en-2-yl)methanones **224**, in high yields and good enantioselectivity (Scheme 67).[363]

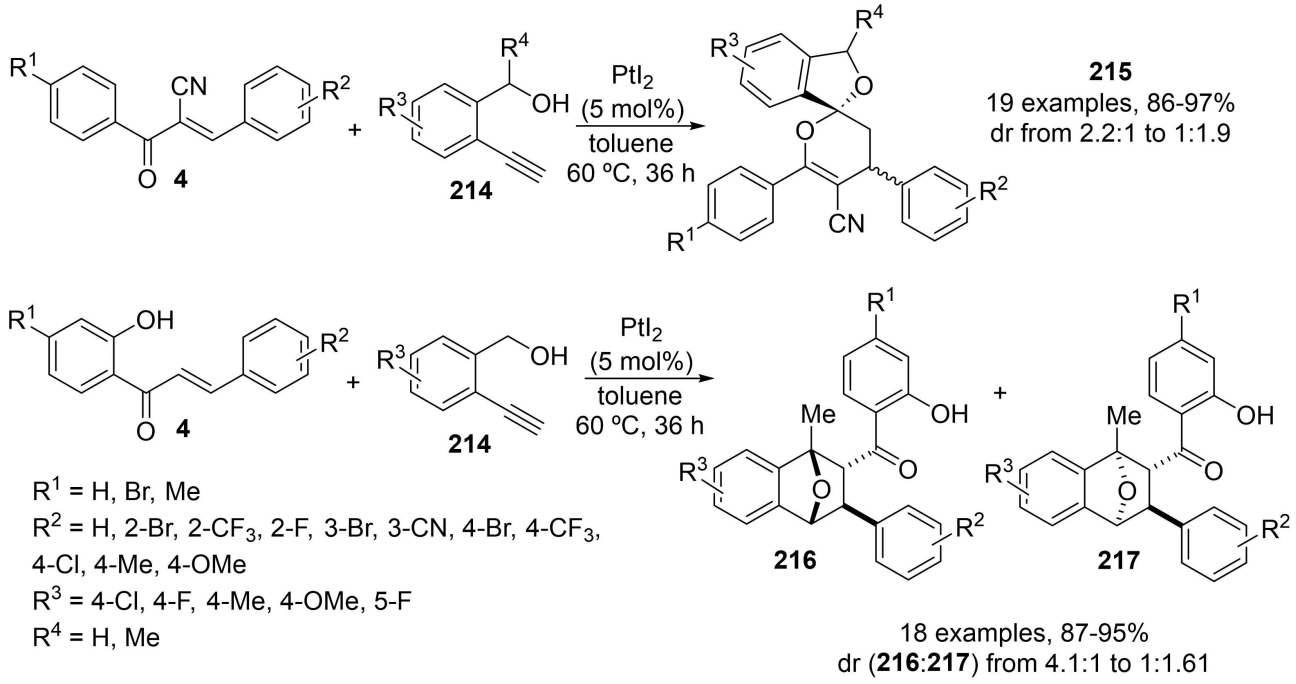
14. Bimetallic-Catalyzed Reactions

Selective transfer hydrogenation reaction of chalcones mediated by copper-palladium alloy nanoparticles decorated on mesoporous graphitic carbon nitride catalyst and ammonia borane in a 3:7 mixture of water:methanol at room temperature,[364] by cobalt-nickel bimetallic nanocatalyst supported on g-C_3N_4 in toluene at 100 °C,[365] by a high-density monolayer of rhodium–diisocyanide on gold surface in ethanol at 25 °C,[366] and by palladium/magnesium-lanthanum mixed oxide catalyst in ethanol at room temperature[367] prompted 1,3-diarylpropan-1-ones, in good to excellent yields.

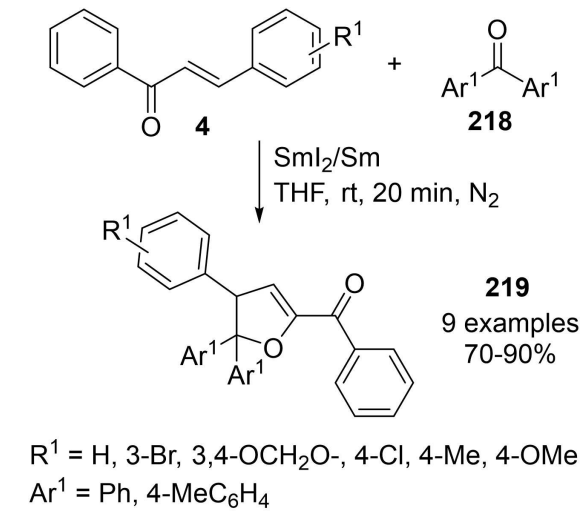
A series of epoxychalcones can be synthesized from enantioselective epoxidation of chalcones using gold nanoparticles supported on titanium(IV) oxide as catalyst in the presence of sodium carbonate and hydrogen peroxide in ethanol at 80 °C.[368]

Bimetallic catalysts, namely iron-palladium catalyst in the presence of acetylacetone[369] and iron-magnesium catalyst in the presence of hexamethylphosphoramide,[370] were involved in the Michael-type Friedel–Crafts reaction of indoles with chalcones in methanol at room temperature to form a variety of 1,3-diaryl-3-(indol-3-yl)propan-1-ones.

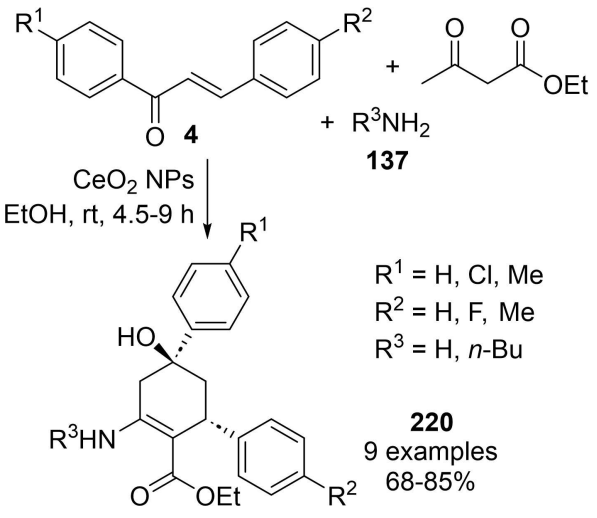
Intramolecular cyclization reaction of 2'-hydroxychalcones **4** into (*Z*)-selective 2-(arylmethylidene)aurones (*Z*)-**226** was accomplished via palladium on gold bimetallic nanoparticle catalyst supported on cerium(IV) oxide **225** in butyl acetate at 100 °C for 24 h under an open air atmosphere (Scheme 68).[371]



Scheme 63. Substituent-controlled divergent cascade cycloaddition reactions of chalcones **4** with (2-ethynylaryl)methanols **214**.

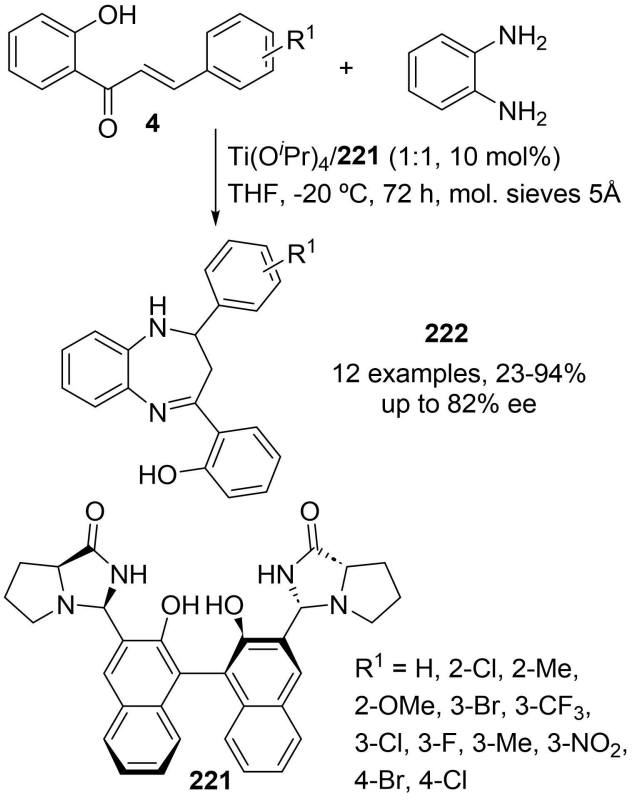


Scheme 64. Reductive cyclization reaction of chalcones **4** with aromatic ketones **218** promoted by SmI_2/Sm catalytic system.

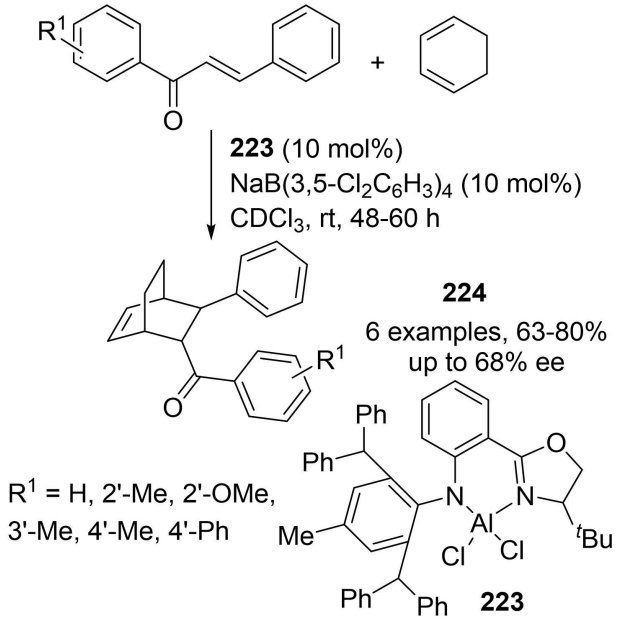


Scheme 65. Three-component reaction of chalcones **4** with primary amines **137** and ethyl acetoacetate, mediated by cerium(IV) oxide nanoparticles.

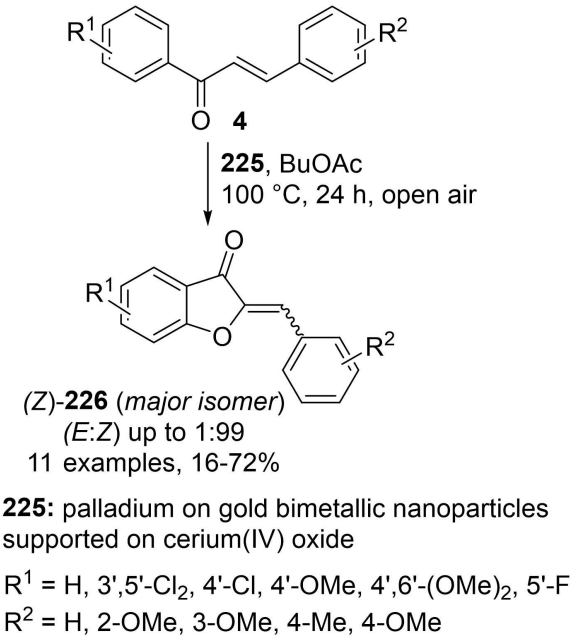
Cyclodimerization reaction of chalcones induced by titanium(IV) chloride-samarium(II) catalytic system in THF at room temperature formed 2-benzoyl-1,3,4-triarylcyclopentanols, in good yields.[372] A dimerization-heteroannulation reaction of a series of chalcones **4** with urea (Scheme 69) and derivatives (system possessing NH_2–C=X functionality) using a heterocatalyst made of bismuth(III) nitrate and zinc(II) chloride immobilized on neutral alumina, under solventless conditions, proceeded in conventional thermal conditions and using a microwave-assisted procedure. 2,4,6-Triaryl-3-benzylpyridines **227** were obtained as major products along with 2,4,6-triarylpyridines **228** in smaller amounts, in both cases. The yields obtained for both compounds were independent of the method used, although shorter reaction times were



Scheme 66. Domino reaction of 2'-hydroxychalcones **4** with *o*-phenylene diamine, mediated by a titanium complex.



Scheme 67. Asymmetric DA reaction of chalcones **4** with 1,3-cyclohexadiene, mediated by aluminium complex **223**.



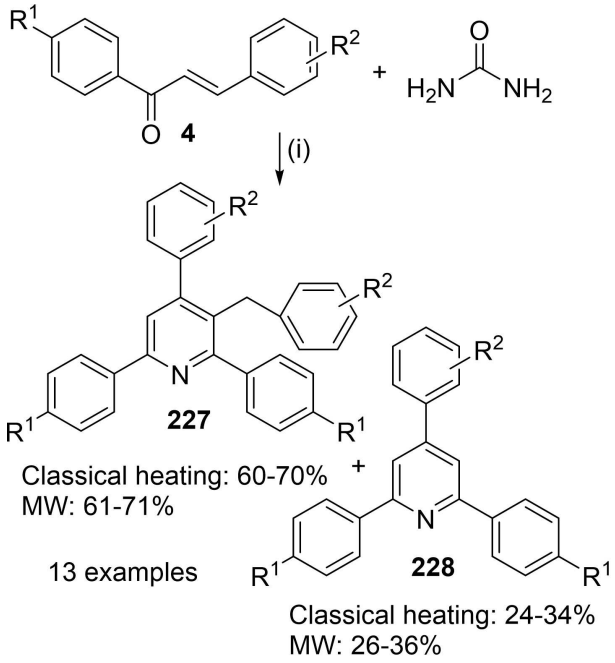
Scheme 68. Intramolecular cyclization reaction of 2'-hydroxychalcones **4**, mediated by palladium on gold bimetallic nanoparticle catalyst supported on cerium(IV) oxide **225**.

required in the microwave-assisted protocol (3.0–3.5 h vs 18–25 min).[373]

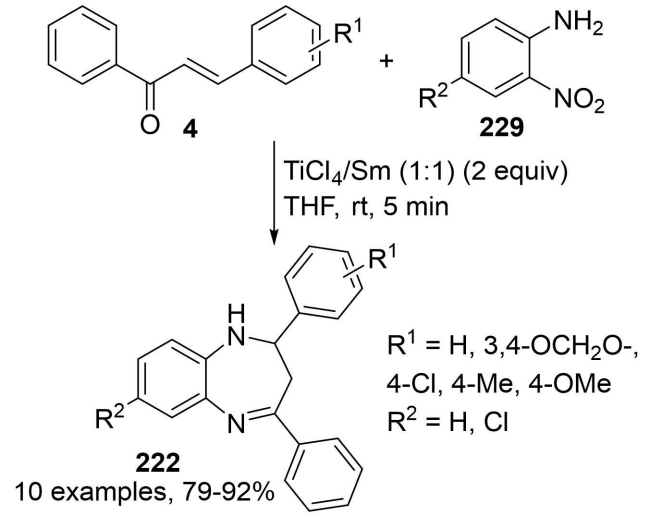
A series of 2,4-diaryl-2,3-dihydro-1*H*-1,5-benzodiazepines **222** was also synthesized via cross-coupling reaction of chalcones **4** with 2-nitroanilines **229** mediated by titanium(IV) chloride-samarium powder catalytic system in THF at room temperature for 5 min (Scheme 70).[374]

Condensation reaction of chalcones with phenylhydrazine in presence of magnetically separable cobalt ferrite nanoparticles in an 1 : 1 mixture of water:ethanol at room temperature delivered 3,5-diaryl-1-phenyl-4,5-dihydro-1*H*-pyrazoles.[375] Copper ferrite superparamagnetic nanoparticle catalyst was applied in the coupling reaction of chalcones **4** with 2-aminopyridines **230** (X = C) or 2-aminopyrimidines **230** (X = N) in the presence of 2 molar equiv. of iodine in 1,4-dioxane at 140 °C to provide aroylimidazo[1,2-*a*]pyridines **231** (X = C) and aroylimidazo[1,2-*a*]pyrimidines **231** (X = N), respectively (Scheme 71).[376] To note that magnetic nanocatalysts are attracting reagents due to their insoluble and paramagnetic nature that make them easily recovered from the reaction medium by using an external magnet, without filtration, centrifugation, or other demanding workup steps.

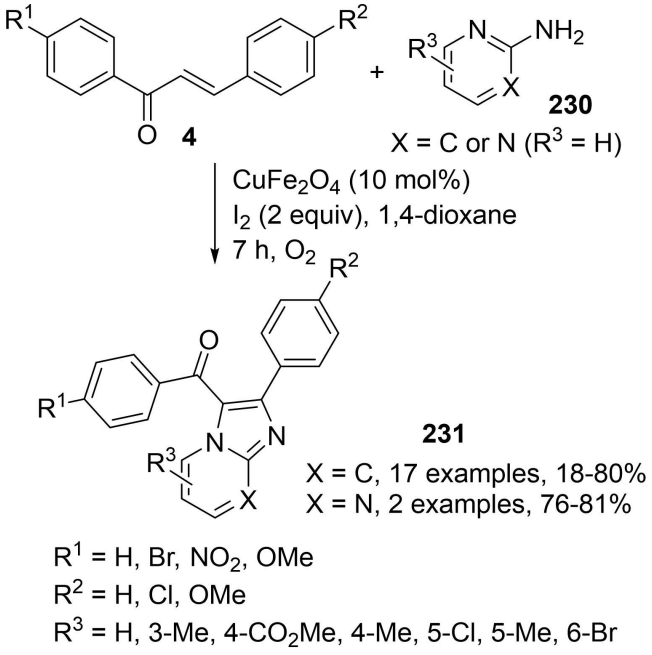
Copper ferrite nanoparticles was also applied in the DA reaction of chalcones with cyclopentadiene in ethanol at 70 °C to give mainly *endo*-adducts, aryl(3-arylbicyclo[2.2.1]hept-5-en-2-yl)methanone, in high yields and good diastereoselectivity. Under the same conditions, a couple of 4'-halochalcones



Scheme 69. Dimerization-heteroannulation reaction of chalcones **4** with urea, promoted by bismuth(III) nitrate and zinc(II) chloride immobilized on neutral alumina, under classical heating conditions and microwave irradiation.



Scheme 70. Cross-coupling reaction of chalcones **4** with 2-nitroanilines **229**, mediated by titanium(IV) chloride-samarium powder catalytic system.



Scheme 71. Coupling reaction of chalcones **4** with 2-aminopyridines **230** (X=C) or 2-aminopyrimidines **230** (X=N), promoted by copper ferrite superparamagnetic nanoparticles.

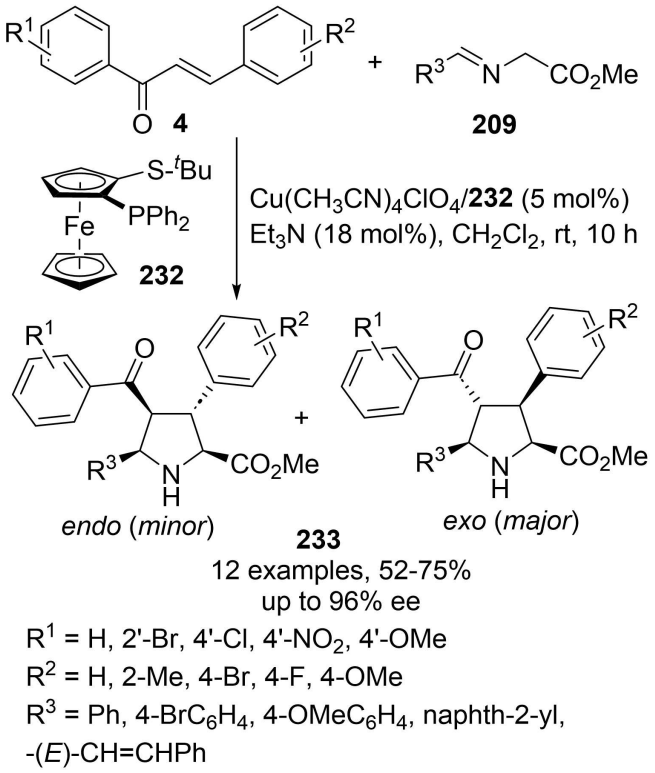
reacted with isoprene to form the corresponding regioisomers, 4-haloaryl(5-methyl-1,2,3,6-tetrahydro-[1,1′-biphenyl]-2-yl)methanones.[377]

Catalytic asymmetric 1,3-dipolar cycloaddition reaction of chalcones with azomethine ylides induced by a copper(I)-ferrocenyl complex[378] or by a silver(I)-ferrophos complex[379] in the presence of triethylamine in dichloromethane afforded *endo*-3,5-diaryl-4-benzoylpyrrolidine-2-carboxylates as major products and with high enantioselectivity. An opposite *exo*-selectivity for the pyrrolidine adducts was accomplished using copper(I)-ironsulphos complexes as catalysts (Scheme 72).[380]

Three porphyrin-based PCP pincer palladium complexes were applied in the 1,4-reduction of chalcone in the presence of potassium carbonate in refluxing butan-1-ol. The catalytic activity was dependent on the inner metal, being the zinc-catalyst the most active among the three complexes tested. To note that the reduction did not occur when either $[PdCl_2(PPh_3)_2]$, $[Pd_2(dba)_3]$, or $Pd(OAc)_2$ were used instead of pincer complexes.[381]

15. Conclusion

A wide variety of chalcones have been applied as starting materials in several metal-catalyzed transformations. The studies included in this review revealed that not only chalcone moiety, involving the carbonyl group and also α,β-unsaturated system, but also the substituents linked to the main core, can



Scheme 72. Asymmetric 1,3-dipolar cycloaddition reaction of chalcones **4** with azomethine ylides **209**, promoted by a copper(I)-ironsulphos **232** complex.

play an important role in the synthesis of diverse heterocyclic compounds.

Undoubtedly, copper was the most used metal for screening the reactivity of chalcones. The transformations involved mainly 1,4-conjugate additions, where several copper(I) and copper(II) complexes were used as efficient catalysts. In addition, a great contribution was given in the beginning of 21st century to the development of novel ligands to the asymmetric copper-mediated addition of diethyl zinc to chalcones. Cycloaddition reactions, multicomponent, intramolecular and other type of reactions were also performed.

The second place was attained for palladium. The prevalent transformations were hydrogenation, 1,4-conjugate additions, substitution, cross-coupling and intramolecular reactions. Then, we can highlight the application of zinc, iron, manganese, nickel and ruthenium catalysts to promote mainly hydrogenation, epoxidation and addition reactions. A smaller contribution for the metal-catalyzed transformation of chalcones was given by cobalt, rhodium, iridium, and silver salts.

Metals such as indium, gold, platinum, titanium, scandium, aluminum, samarium, cerium, and some bimetallic systems were also included in this review.

Most of the protocols were applied to a wide variety of derivatives with a great atom economy, mild reaction conditions, small amounts and quite cheap catalyst systems. These methodologies may involve the use of green energy sources such as LED light and microwave irradiation, the use of green solvents or in solvent-free conditions, and with simple workup processes, some of them with recovery and reuse of the catalyst.

To sum up, the large number of publications concerning the transformation of chalcones under the catalysis of transition metals emphasize the importance and timeliness of this topic and provides insights into the design of novel chalcone-derived compounds, in an efficient and sustainable perspective.

16. List of Abbreviations

Ac	acetyl
acac	acetylacetonate
AcOH	acetic acid
Bmin	1-butyl-3-methylimidazolium acetate
BINAM	2,2'-diamine-1,1'-dinaphthyl
BINOL	2,2'-dihydroxy-1,1'-dinaphthyl
Bn	benzyl
BOX	bis(oxazoline)
Bu	butyl
Cat	catalytic
DA	Diels–Alder
DABCO	1,4-diazabicyclo[2.2.2]octane
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo(5.4.0)undec-7-ene
DCE	dichloroethane
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DMAc	*N*,*N*-dimethylacetamide
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
Et	ethyl
EtOH	ethanol
IED	inverse-electron-demand
LED	light emitting diode
LiHMDS	lithium bis(trimethylsilyl)amide
MCPBA	*m*-chloroperbenzoic acid
Me	methyl
MW	microwave
NBS	*N*-bromosuccinimide
NMO	*N*-methylmorpholine *N*-oxide
NPs	nanoparticles
OTf	triflate
PEG	polyethylene glycol
Phen	phenantroline
Piv	pivaloyl

Ph	phenyl
Pr	propyl
TAD	α,α,α,α-tetraaryl-1,3-dioxolane
TADDOL	α,α,α,α-tetraaryl-1,3-dioxolane-4,5-dimethanol
TBDMS	*t*-butyldimethylsilyl
TBDPS	*t*-butyldiphenylsilyl
TFA	trifluoroacetic acid
TFE	2,2,2-trifluoroethanol
TfOH	triflic acid
THF	tetrahydrofuran
TMS	trimethylsilyl
Tr	trityl
Ts	tosyl

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Conflict of Interest

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

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