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Coordination Chemistry Reviews 141 (1995)
153–369

COORDINATION CHEMISTRY REVIEWS

Transition metals in organic synthesis. Annual survey covering the year 1993

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Received 24 September 1994

Contents

SSDI 0010-8545(94)06003-7

Keywords: Transition metals; Organic synthesis

1. General comments

This annual survey covers the literature for 1993 dealing with the use of transition metal intermediates for organic synthetic transformations. It is not a comprehensive review but is limited to reports of discrete systems that lead to at least moderate yields of organic compounds, or that allow unique organic transformations, even if low yields are obtained. Catalytic reactions that lead cleanly to a major product and do not involve extreme conditions are also included. This is not a critical review, but rather a listing of the papers published in the title area.

The papers in this survey are grouped primarily by reaction type rather than by organometallic reagent, since the reader is likely to be more interested in the organic transformation effected than the metal causing it. Oxidation, reduction, and hydroformylation reactions are specifically excluded, and will be covered in a different annual survey. Also excluded are structural and mechanistic studies of organometallic systems unless they present data useful for synthetic application. Finally, reports from the patent literature have not been surveyed since patents are rarely sufficiently detailed to allow reproduction of the reported results.

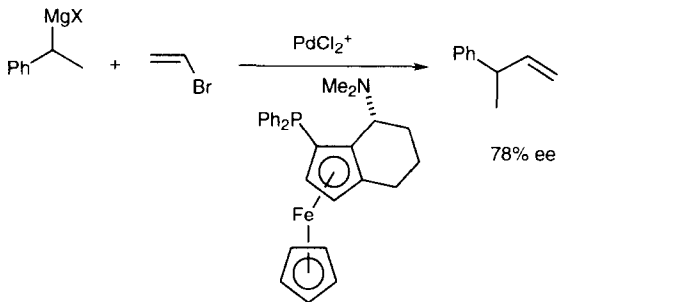
2. Carbon–carbon bond-forming reactions

2.1. Alkylations

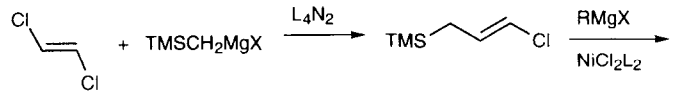
2.1.1. Alkylation of organic halides, tosylates, triflates, acetates, and epoxides

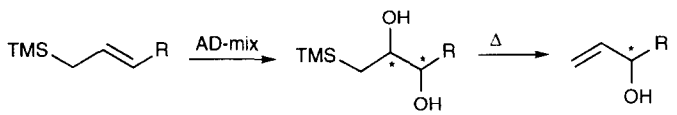
The interest in metal-catalyzed Grignard reactions is waning, and only a single example of asymmetric induction, in poor enantiomeric excess (EE), was reported

(Eq. (1)) [1]. Allyl silanes were prepared by the nickel-catalyzed coupling of trimethylsilylmethyl Grignard reagents with vinyl halides (Eq. (2) [2] and Eq. (3) [3]). Aryl Grignards coupled to neopentyl iodides in the presence of nickel salts (Eq. (4)) [4]. Nickel complexes catalyzed the cyanation of aryl triflates (Eq. (5)) [5]. Vinyl sulfides were alkylated by Grignard reagents in the presence of nickel salts (Eq. (6)) [6].



(1)





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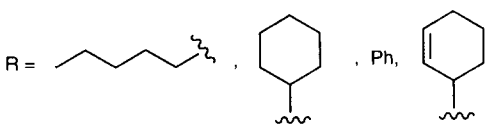

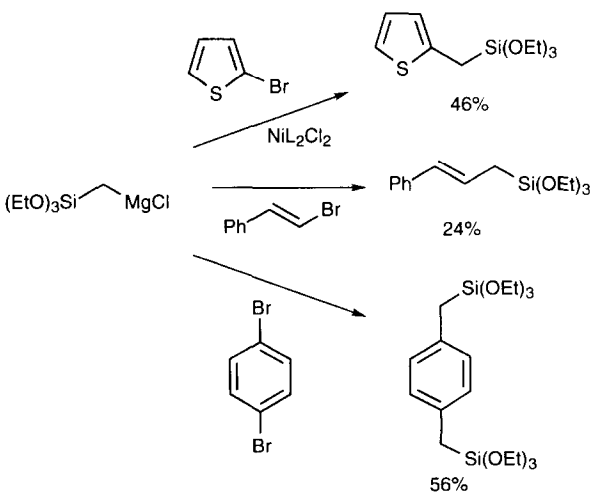

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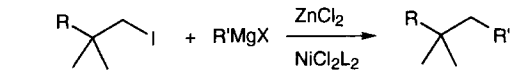
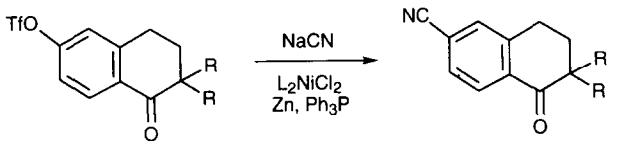
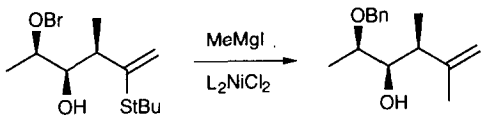


74-88% (4)

Ph = $PhCH_2$, Me R' = Me, Ph, oTol, 1-Naph, pCF_3Ph, $2,4(MeO)_2Ph$



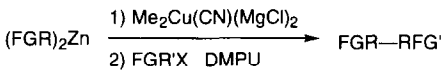
77% (5)



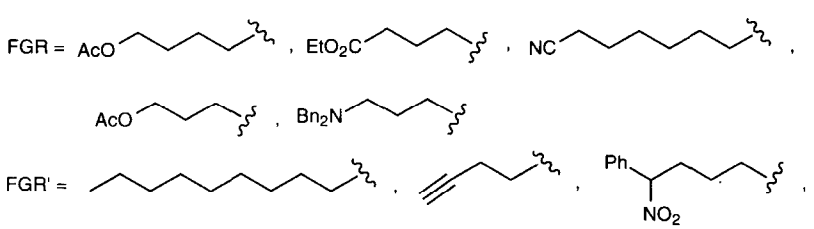
and (6)

54-64%

The reagent produced by the reaction of lithium dialkyl cuprates with trimethylsilyl cyanide was studied by nuclear magnetic resonance [7], as was the solution composition of Gilman's reagents [8]. Preparation and reactions of polyfunctionalized organozinc reagents in organic synthesis was reviewed (217 references) [9]. Functionalized organozinc reagents were coupled via cuprate chemistry (Eq. (7) [10] and Eq. (8) [11]). The full details of the preparation of highly activated copper via reaction of copper iodide–phosphine complexes with sodium naphthalenide has appeared [12]. These are efficient for the preparation of allyl copper species (Eq. (9)) [13,14].

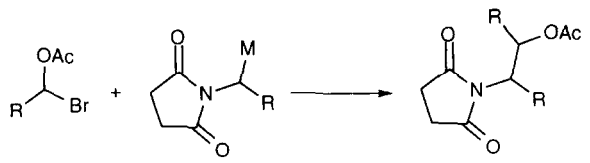


70-90%



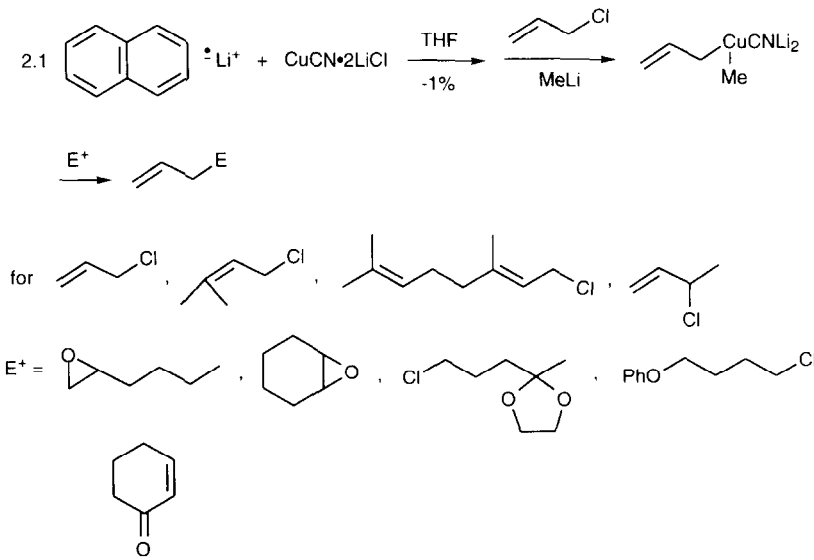
(7)

Bn, pCNPh



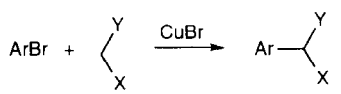
(8)

M = ZnCl, CuCN



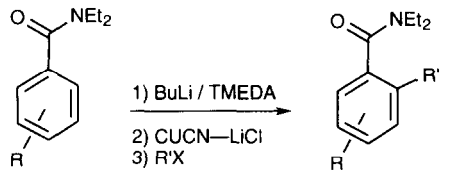
(9)

Aryl halides were alkylated by malonates (Eq. (10)) [15,16]. *Ortho*-lithiated benzamides were alkylated via their cuprates (Eq. (11)) [17], as were dihalobenzenes (Eq. (12)) [18]. Cephalosporin-derived vinyl triflates were alkylated by dialkyl cuprates (Eq. (13)) [19]. Perfluoroalkyl halides coupled to polyfluoroarenes in the presence of copper salts [20]. Vinyl halides were perfluoromethylated by "CF_3Cu" (Eq. (14)) [21]. Mesylated α-alkoxytin reagents were alkylated by cuprates (Eq. (15)) [22]. Vinyl zinc reagents participated in a range of organometallic reactions (Eq. (16)) [23]. Biscuprates spiroannellated β-chloroenones (Eq. (17)) [24]. Copper(I) chloride effected the cyclization of vinyl stannanes with vinyl iodides (Eq. (18)) [25].

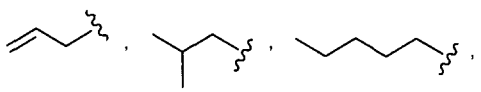


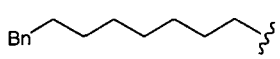
(10)

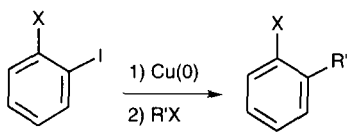
X, Y = CO_2Me, CN Ar = Ph, pMeOPh, oMeOPh, oNO_2Ph, pNO_2Ph, α-Naphth, pClPh



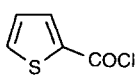
30-90% (11)

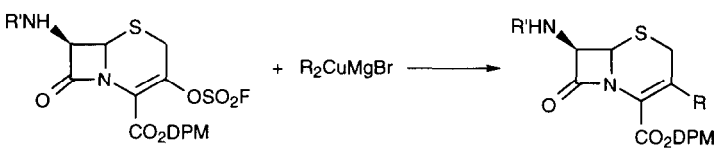
R = H, 3,5(MeO), 2MeO, 2,4(MeO)$_2$ R' = 



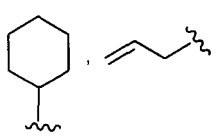


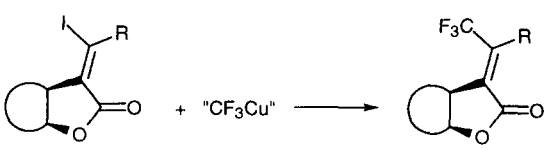
X = Cl, F (12)

R'X = MeI, BnBr, PhCOCl, MeCOCl, 

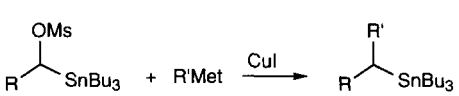


56-90%

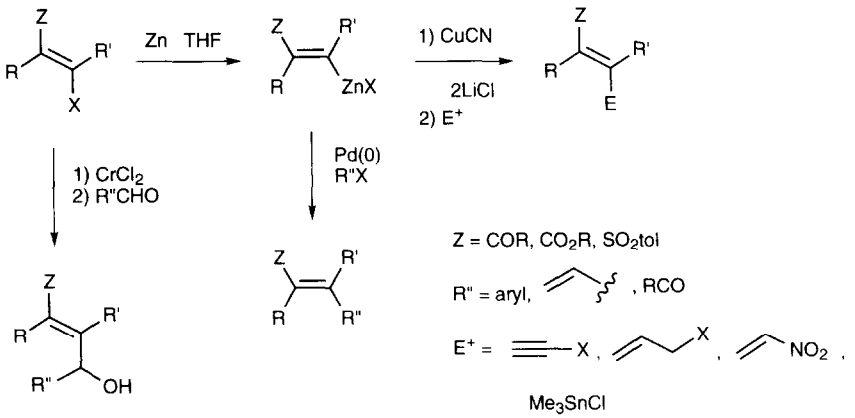
R = Me, Et, Bu, tBu,  (13)



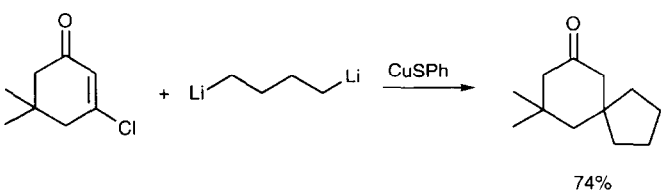
(14)



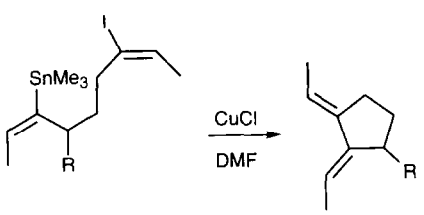
good yields (15)



(16)

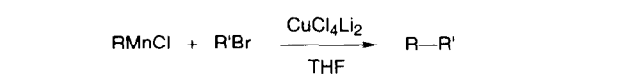


(17)

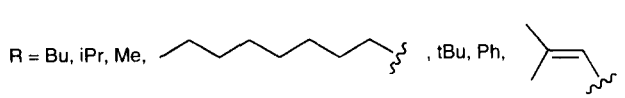


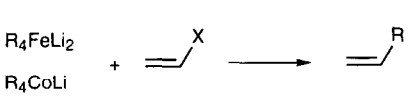
(18)

Organomanganese complexes alkylated aliphatic (Eq. (19)) [26] and alkenyl iodides [27]. Alkyl iron and cobalt reagents alkylated vinyl halides, including fluorides (Eq. (20)) [28]. Vinyl zirconium species from hydrozirconation of alkynes alkylated epoxides (Eq. (21)) [29] and allyl halides (Eq. (22)) [30]. Cationic iron complexes of hexamethyl benzene were peralkylated (Eq. (23)) [31].

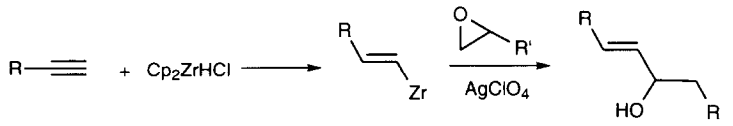


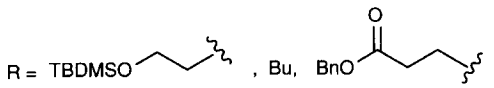
(19)



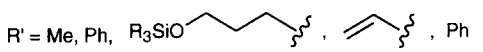


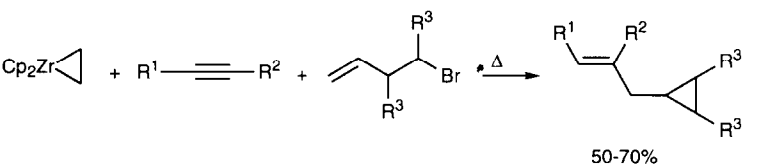
(20)



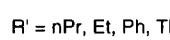


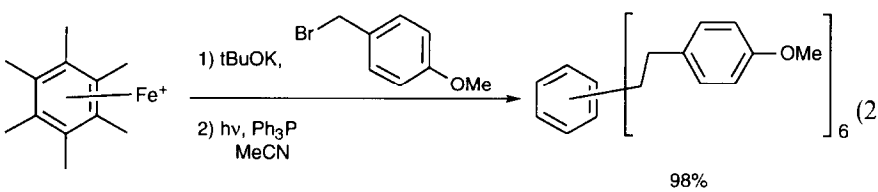
(21)





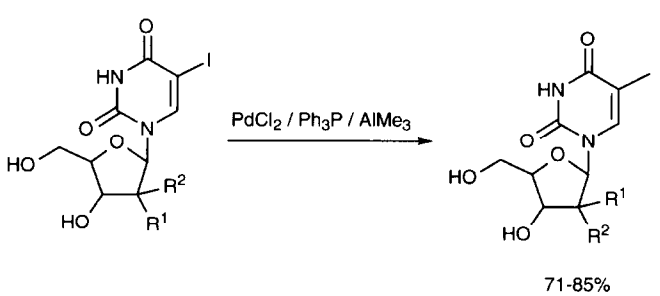
(22)





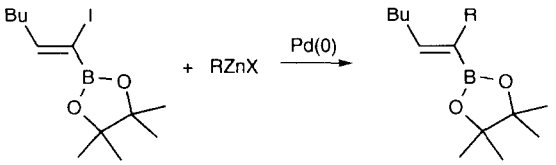
(23)

Treatment of palladium(II) acetate with one equivalent of tributylphosphine in THF led to a very active Pd(0) homogeneous catalyst solution [32]. Dibenzylidene acetone was shown to be a better ligand for L_2Pd than is phosphine, and $Pd(dba)_2$ plus 2L was 5 times slower and $Pd(dba)_2$ plus 4L was 7 times slower in oxidative addition reactions than was L_4Pd [33]. The mechanism of oxidative addition of aryl halides to Pd(0) was studied [34]. Synthetic transformations of vinyl and aryl triflates were reviewed (296 references) [35]. Palladium catalyzed the methylation of iodonucleosides by trimethyl aluminum (Eq. (24)) [36] and the alkylation of aryl halides by α-cyanosulfones [37].



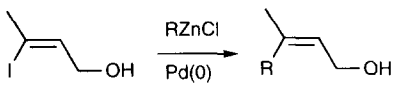
(24)

The coupling of organozinc halides with organic halides catalyzed by palladium was a generally useful reaction (Eq. (25) [38], Eq. (26) [39], Eq. (27) [40], Eq. (28) [41], Eq. (29) [42], Eq. (30) [43], Eq. (31) [44], Eq. (32) [45], Eq. (33) [46,47], and Eq. (34) [48]).

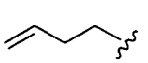
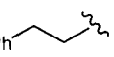
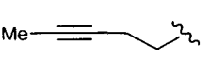
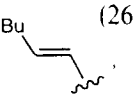


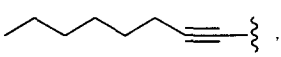
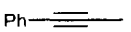
40-87% (25)

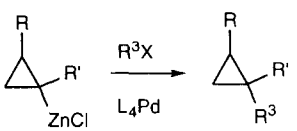
R = Et, Bn, Ph, $TMSCH_2$,  , Bn 



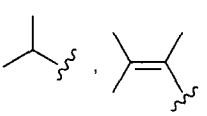
60-90%

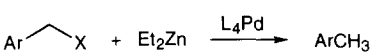
R = Bu, nC_6, iBu, Bn,  , Ph  , Me  , Bu  ,

pMePh, oMeOPh,  , Ph  , pClPh (26)

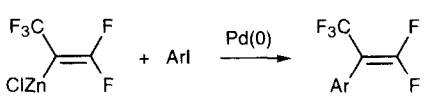


60-70% (27)

R = Ph, $BnOCH_2$, C_7 R^1 = Bn R^3 = Ph, pAcOPh, 

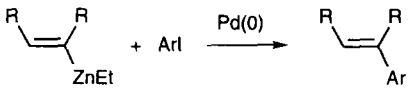


(28)



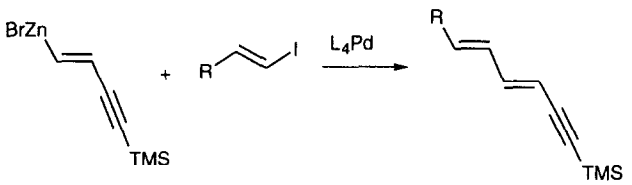
45-75% (29)

Ar = Ph, pNO_2Ph, mNO_2Ph, oNO_2Ph, pMeOPh, pBrPh, $pEtO_2CPh$, oFPh, oClPh, oMePh, $3,5(CF_3)_2Ph$



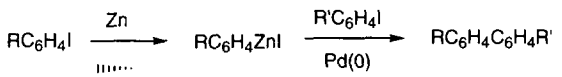
38-74% (30)

R = nPr, Et Ar = Ph, 1-Naph, , pMeOPh, mBrPh, $pMeO_2CPh$



78-91% (31)

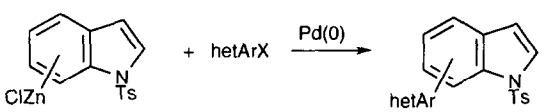
R = , , ,



(32)

R = $oMeO_2C$, oCN, oCl, oCF_3, oBr, oMeCO, $mMeO_2C$, pPr, pOMe, oOMe

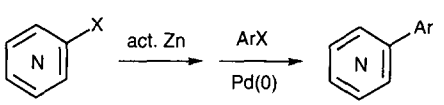
R' = H, pMeCO, pNO_2, pCl, pCO_2Me



40-90% (33)

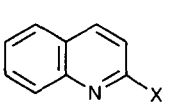
indole = 2, 3, 4, ZnCl

Ar = Ph, , , , , sub

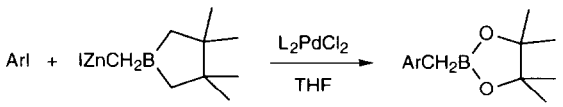


40-90%

for , , , , , , (34)

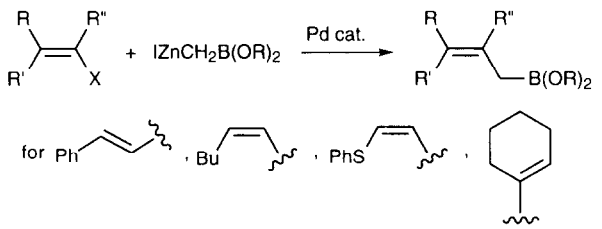


Boronates could be introduced into aryl (Eq. (35)) [49] and vinyl (Eq. (36)) [50] halides via palladium-catalyzed coupling reactions of zinc reagents.



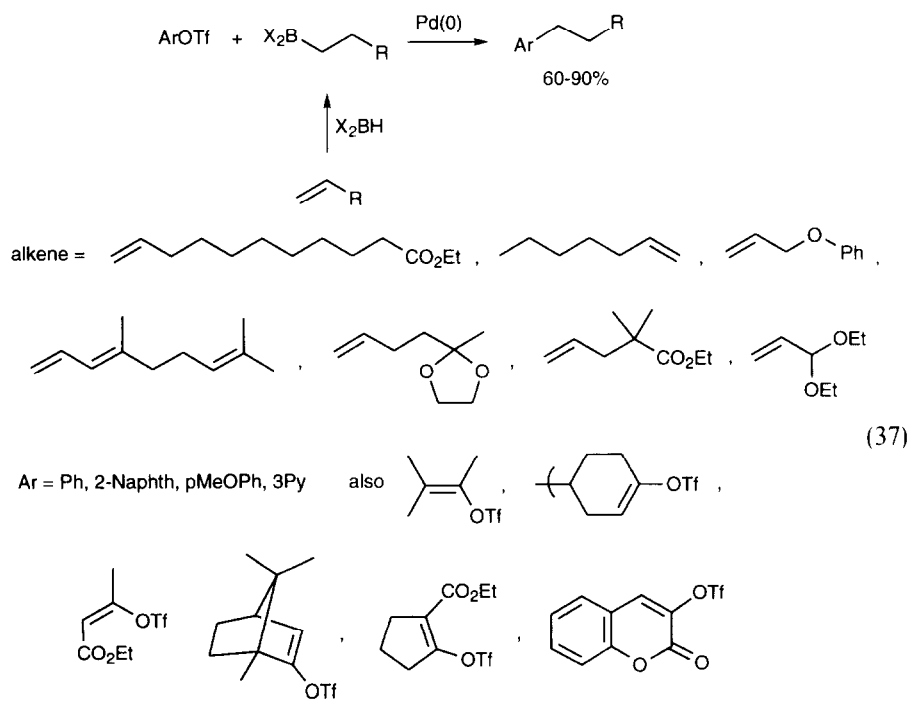
(35)

Ar = Ph, pMeOCH$_2$OPh, pMeO$_2$CPh, oMeO$_2$CPh, oMeSCH$_2$Ph, oNCPh, oBrPh, oHOPh, oMeOPh

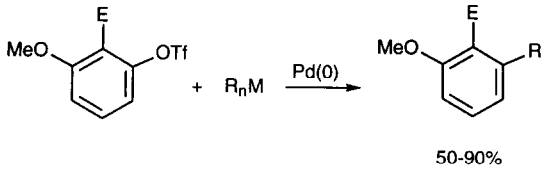


(36)

Palladium-catalyzed cross-coupling reactions of organoboronic acids with organic electrophiles was reviewed (72 references) [51]. This process has proven to be quite useful in organic synthesis with alkyl boronates (Eq. (37) [52], Eq. (38) [53], Eq. (39) [54]), vinyl boronates (Eq. (40) [55], Eq. (41) [56], Eq. (42) [57]), aryl boronates (Eq. (43) [58], Eq. (44) [59], Eq. (45) [60], Eq. (46) [61], Eq. (47) [62], Eq. (48) [63]), and heteroaryl boronates (Eq. (49) [64], Eq. (50) [65], and Eq. (51) [66]).



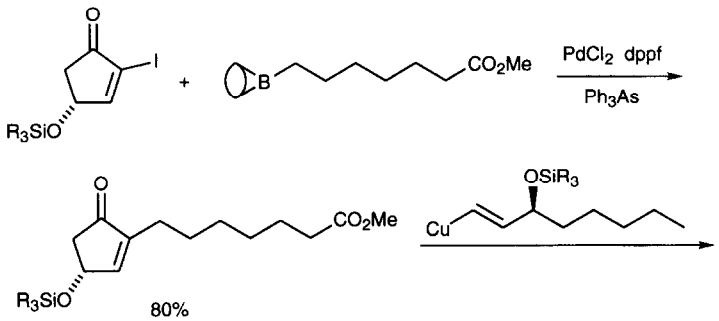
(37)



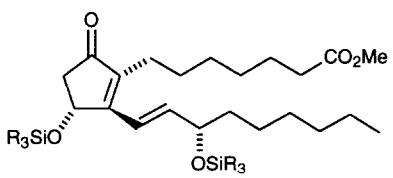
(38)

E = Me, CO_2NEt_2, CO_2Me

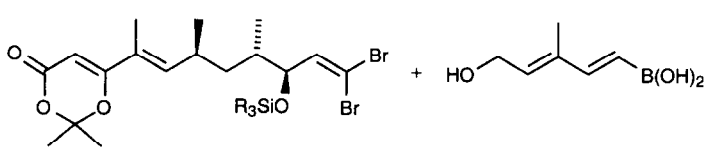
R = Ph, Me, ≡—Ph M = $B(OH)_2$ R_3Sn

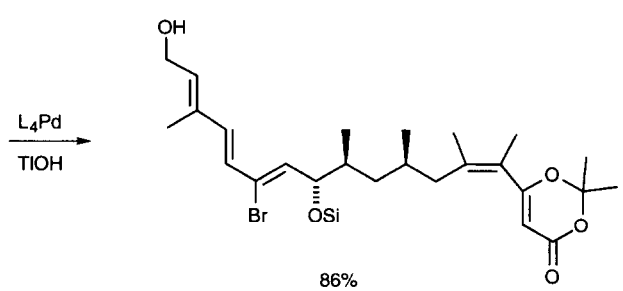


(39)

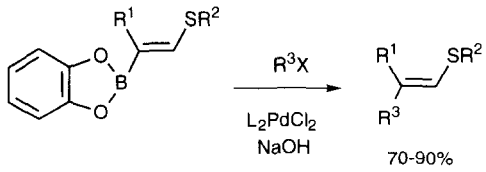


80%

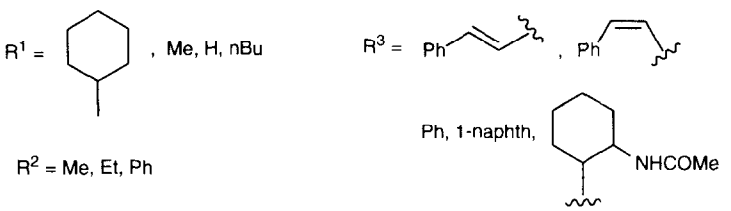


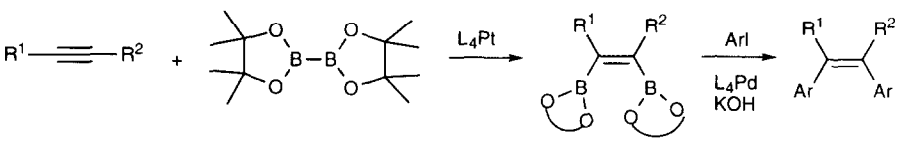


(40)

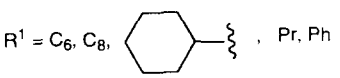


(41)

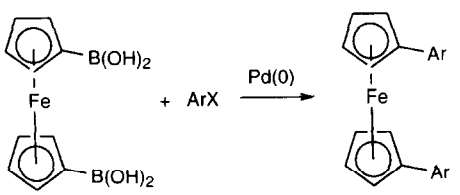




(42)



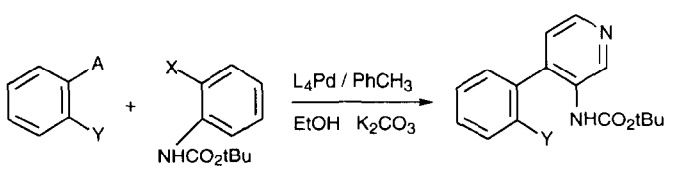
R^2 = H, Pr, Ph



(43)

50-90%

Ar = Ph, oFPh, mFPh, pFPh, oClPh, mClPh, pBrPh

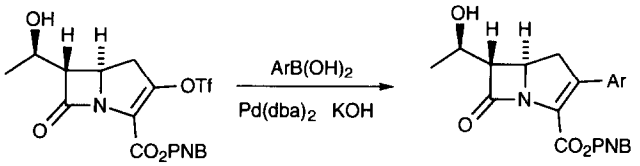


(44)

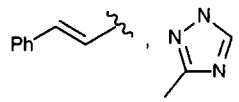
84-99%

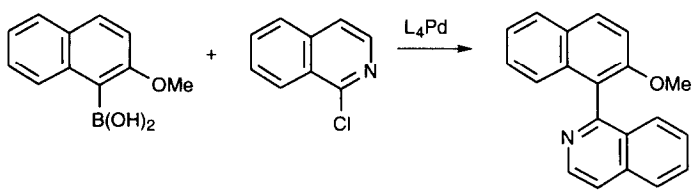
A = $B(OH)_2$

Y = F, OMe, NHCOtBu, NH_2

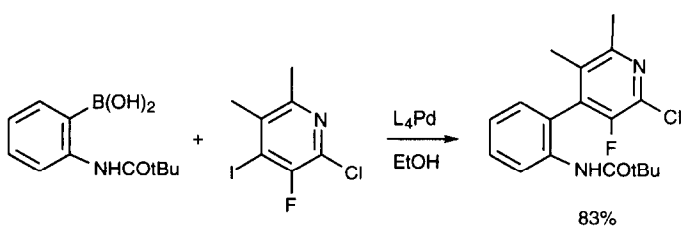


40-80% (45)

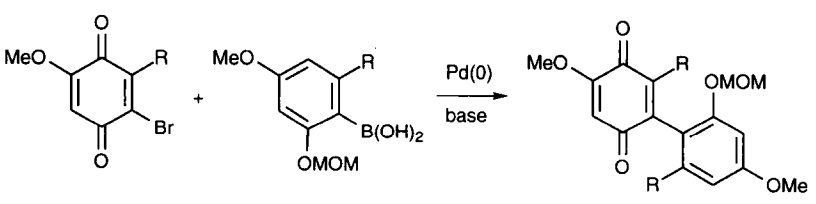
Ar = Ph, 2,4Cl_2Ph, oMePh, pMeOPh, pCF_3Ph, mCNPh, mNO_2Ph, pR_3SiOCH_2Ph, pHOCH_2Ph, 3-furyl, 2-thiophene, 



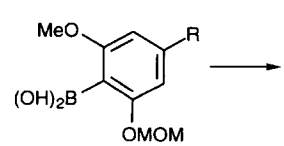
96% (46)



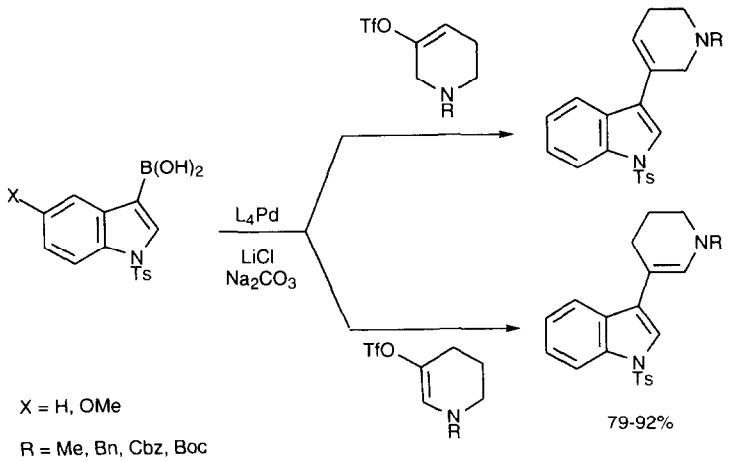
83% (47)



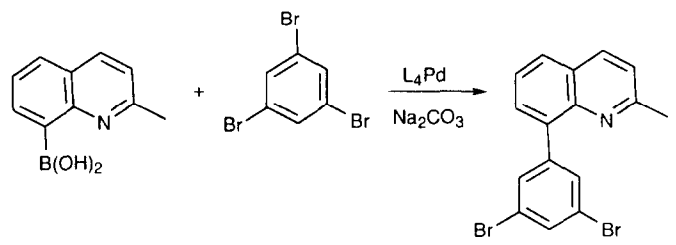
30% (48)

but 

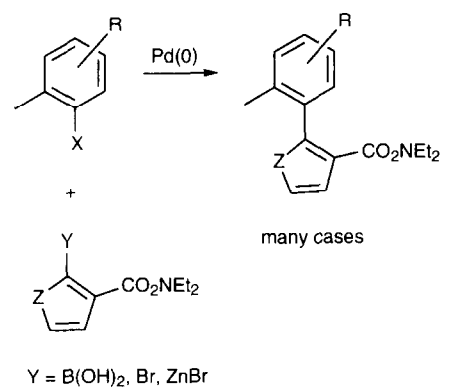
60%



(49)

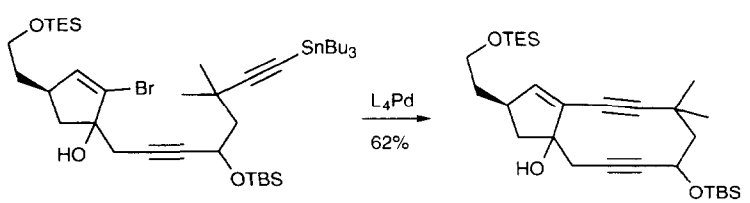


(50)

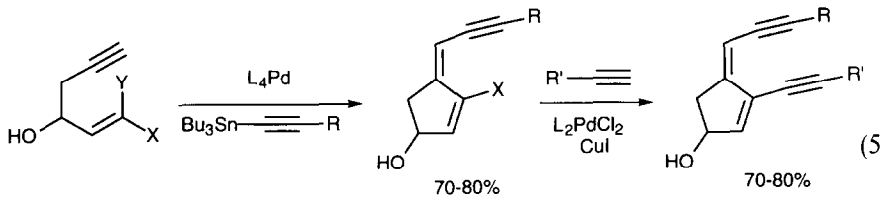


(51)

Oxidative addition–transmetallation from tin has also continued to be extensively utilized in synthesis. Acetylenic tin reagents (Eq. (52) [67], Eq. (53) [68], Eq. (54) [69], and Eq. (55) [70]) were useful for the synthesis of enynes. Vinyl tin reagents



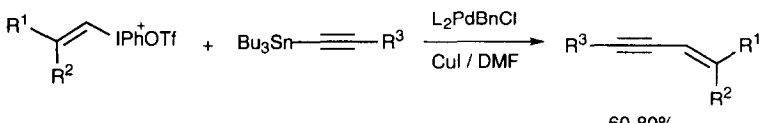
(52)



(53)

R = CH_2OTBS, $CH(OEt)_2$

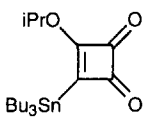
R' = $CH(OEt)_2$ $CH_2OTBDMS$, Ph



R^1 = Me, Bu, Et

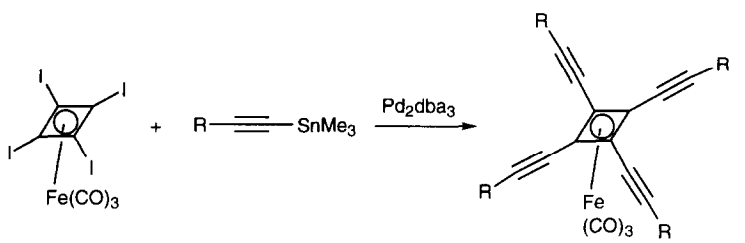
R^2 = Me, Bu, Et

R^3 = Ph, tBuCO



also coupled

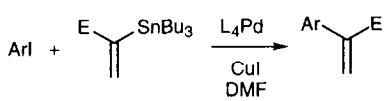
(54)



R = tBu, TMS, , H

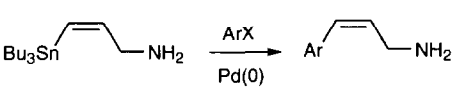
(55)

were extensively used to synthesize multiply unsaturated systems, and coupled efficiently to aryl halides (Eq. (56) [71], Eq. (57) [72], Eq. (58) [73]), aryl triflates (Eq. (59) [74], Eq. (60) [75]), and vinyl triflates (Eq. (61) [76]). Tin coupling to



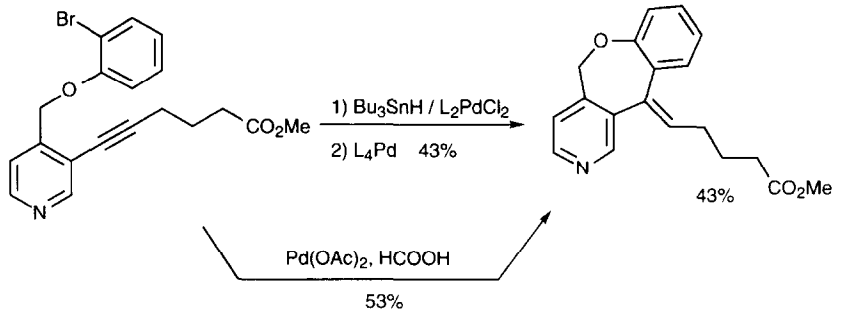
(56)

Ar = Ph, pNO_2Ph, pCF_3Ph, pCH_3COPh, $pMeO_2CPh$, pMePh, pBrPh, pMeOPh, 6-MeO-2-napht.

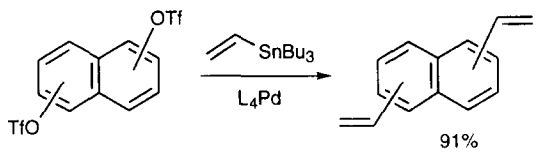


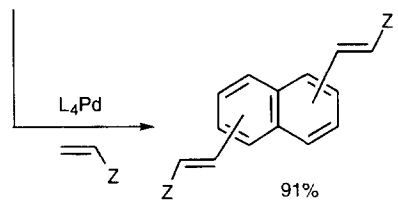
(57)

Ar = Ph, , pCNPh, pMeOPh, oCHOPh, oCO_2Et, Ph, oMeCOPh



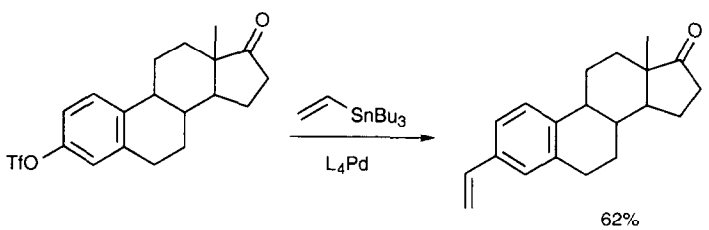
(58)



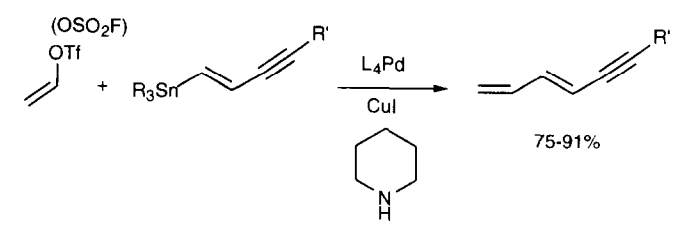


(59)

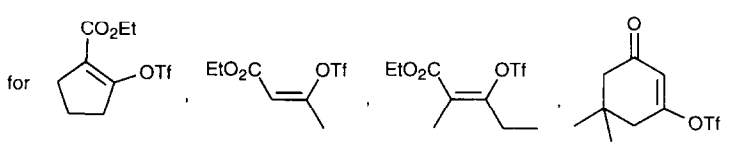
1,2; 1,3; 1,4; 1,5; 1,6; 1,7; 2,3; 2,6; 2,7



(60)

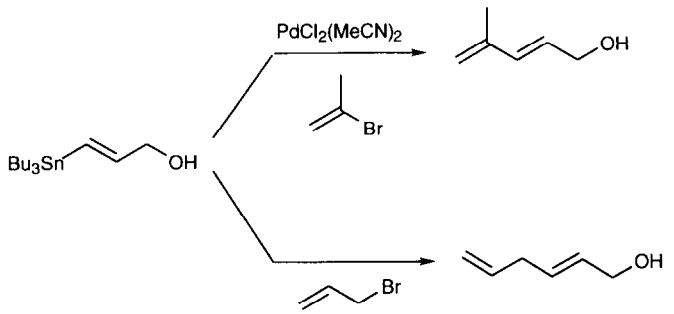


(61)

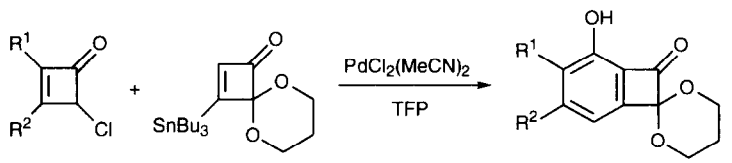


and R' = TMS, H

vinyl halides was also efficient in both simple (Eq. (62) [77], Eq. (63) [78], Eq. (64) [79]), and more complex systems (Eq. (65) [80], Eq. (66) [81], Eq. (67) [82], Eq. (68) [83], Eq. (69) [84], and Eq. (70) [85]).



(62)

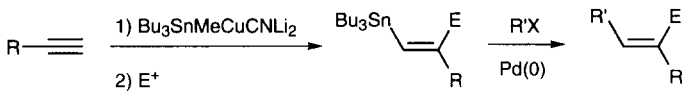


56-99%

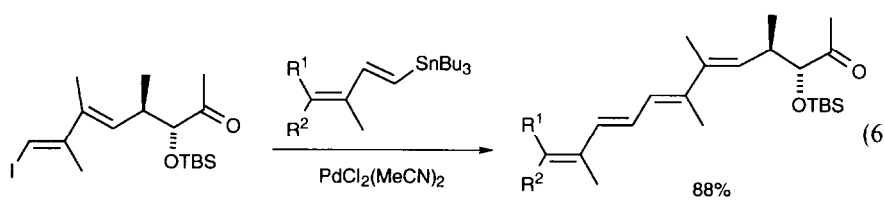
(63)

R^1 = Me, nBu, sBu, tBu, Ph, Et

R^2 = OiPr, Et, Ph, Me



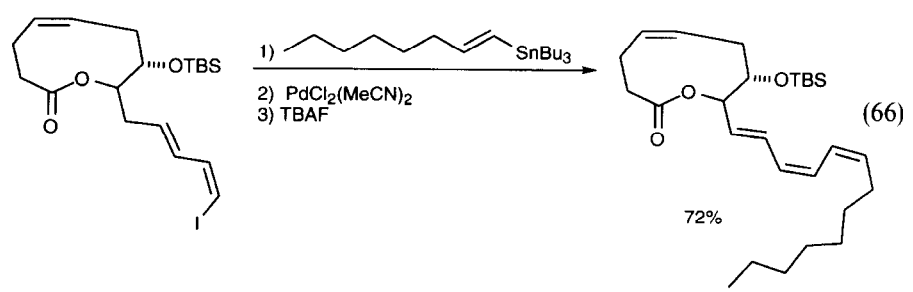
(64)



88%

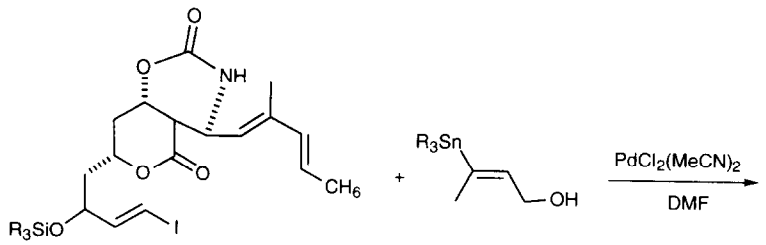
(65)

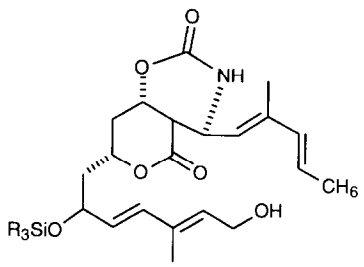
R = H, CN



72%

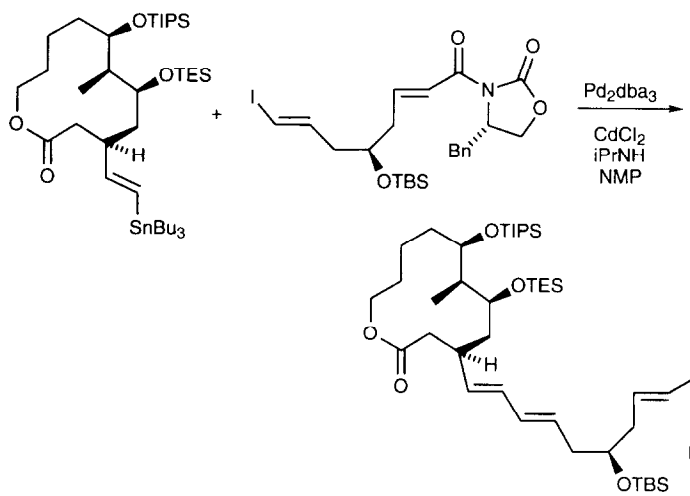
(66)


O
O
NH
O
O
CH6
R3SiO
I
+
R3Sn
OH
PdCl2(MeCN)2
DMF

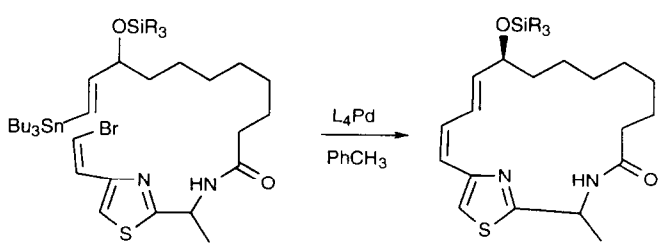

O
O
NH
O
O
CH6
R3SiO
OH

90%

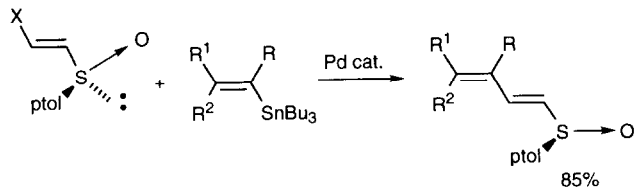
(67)


OTIPS
OTES
O
O
H
SnBu3
+
I
O
O
N
O
Bn
OTBS
Pd2dba3
CdCl2
iPrNH
NMP
OTIPS
OTES
O
O
H
O
N
O
Bn
OTBS

(68)

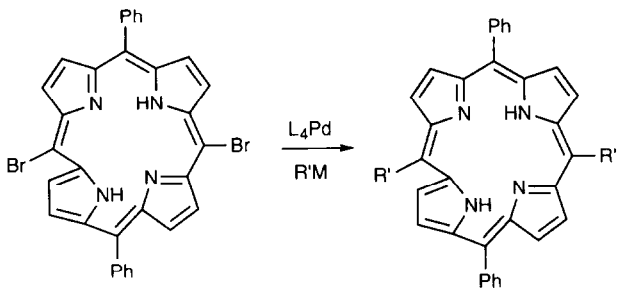

OSiR3
Bu3Sn
Br
N
HN
O
S
L4Pd
PhCH3
OSiR3
N
HN
O
S

(69)

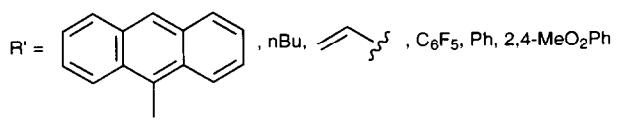


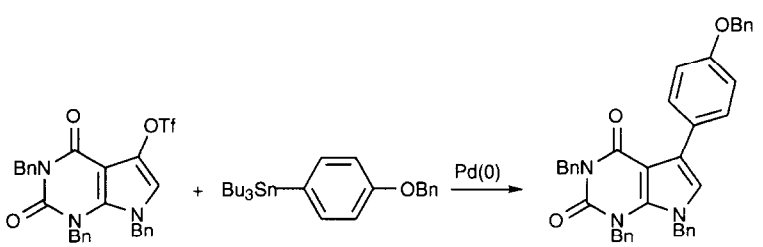
(70)

The full details of palladium-catalyzed coupling of aryl stannanes to vinyl triflates have appeared [86]. Aryl tins couple to porphyrin bromides (Eq. (71)) [87], heteroaromatic triflates (Eq. (72)) [88], aryl triflates (Eq. (73) [89], Eq. (74) [90], Eq. (75) [91]), and α-chlorocyclobutenones (Eq. (76)) [92].

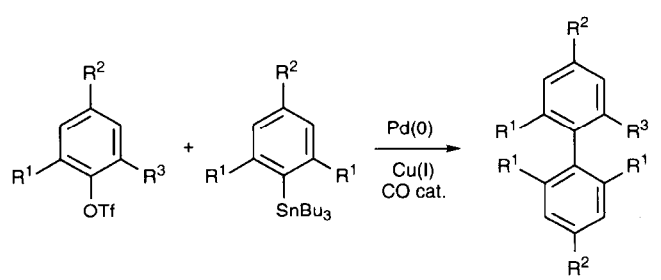


(71)

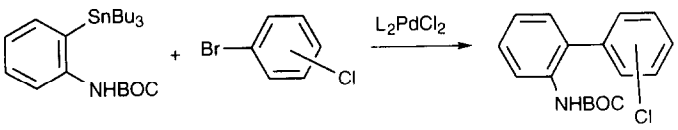




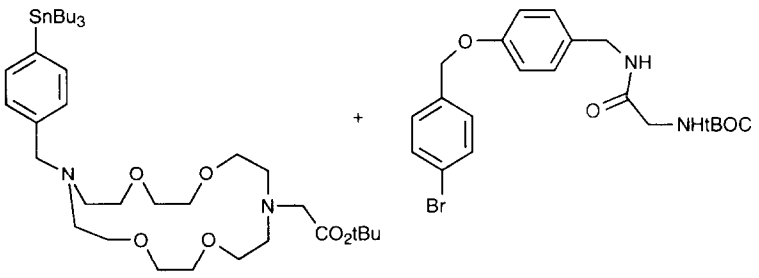
(72)

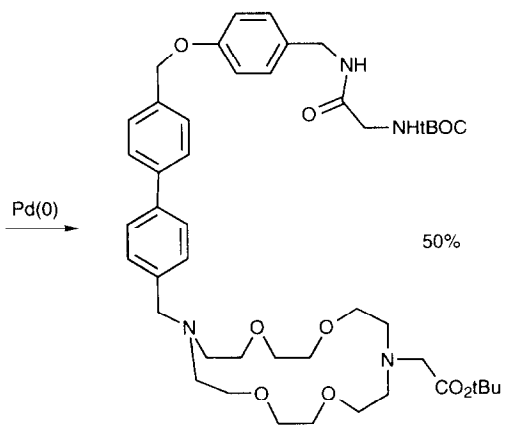


(73)

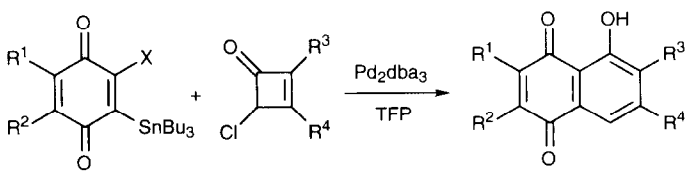


(74)





(75)

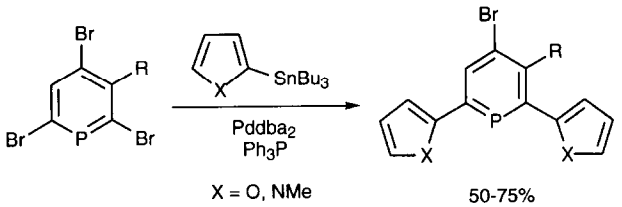


75-95%

(76)

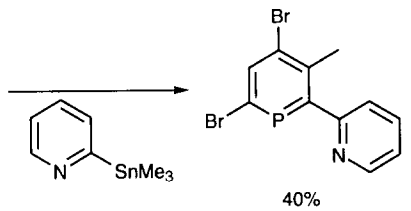
R^1 = Me, iPr
R^2 = Ph
R^3 = Me, tBu, Ph, Et
R^4 = iPrO, Ph, Me, Et

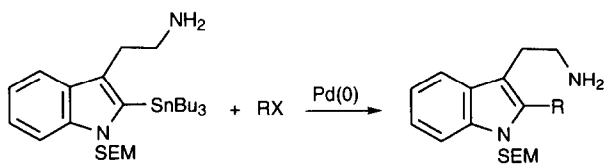
Palladium also catalyzes the coupling of halides with heteroaromatic tin compounds. These include furanyl tins (Eq. (77)) [93], indolyl tins (Eq. (78)) [94], thiophenyl tins (Eq. (79)) [95], pyridyl tin (Eq. (80) [96], Eq. (81) [97], Eq. (82) [98]), and quinolinyl tins (Eq. (83)) [99]. Non-aromatic heterocyclic tin reagents also couple (Eq. (84) [100], Eq. (85) [101], and Eq. (86) [102]).



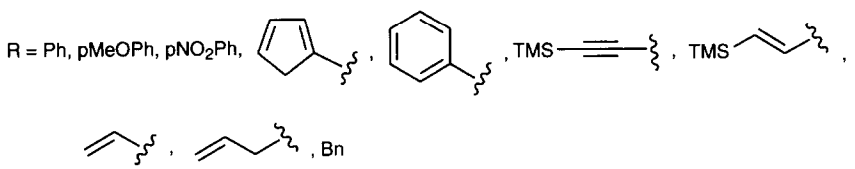
(77)

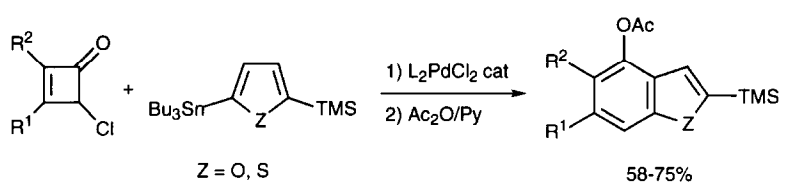
and





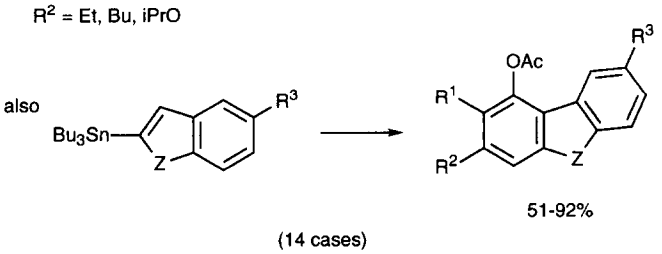
(78)

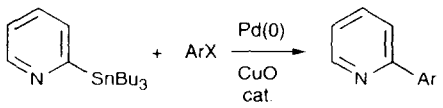




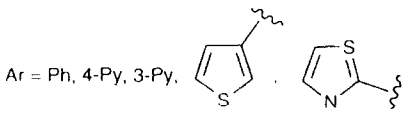
R^1 = Et, Me, nBu
R^2 = Et, Bu, iPrO

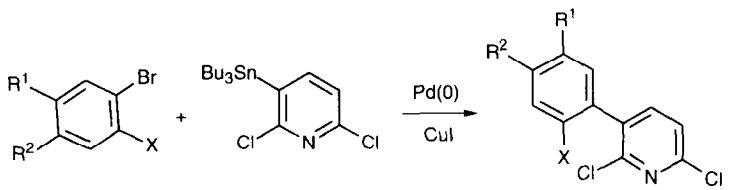
(79)





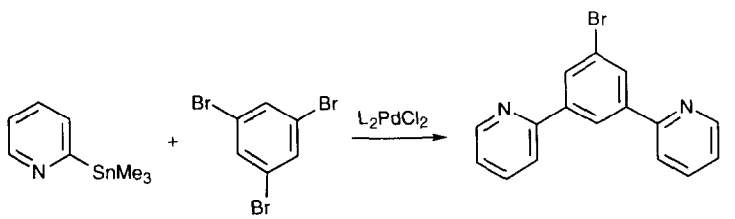
(80)



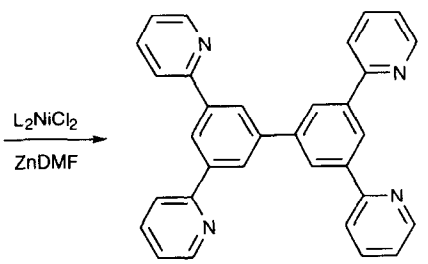


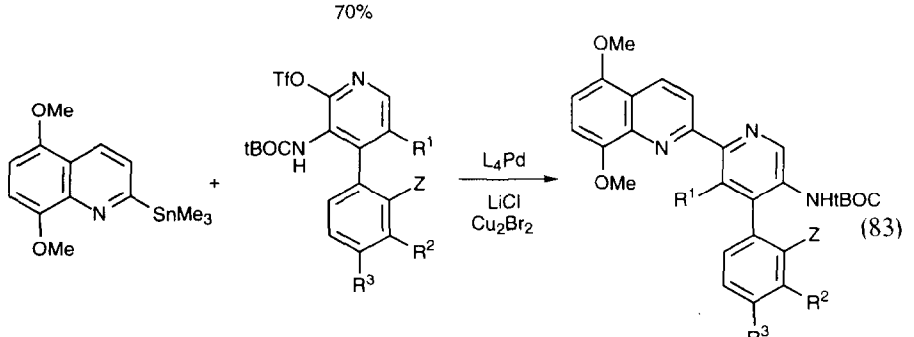
(81)

R^1 = H, F, Me
R^2 = NO_2, H, CF_3, MeO



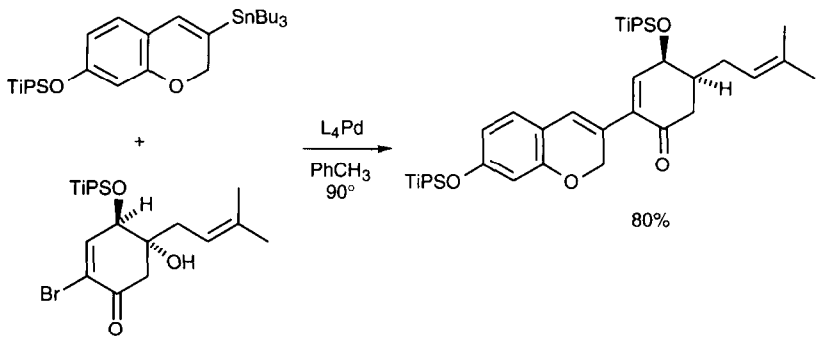
(82)



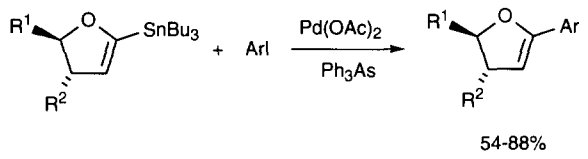


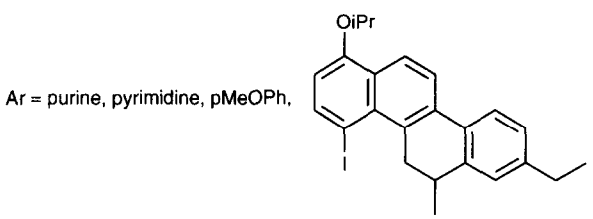
(83)

R's = OMe, H, Me
Z = H, OBn, $OCONEt_2$

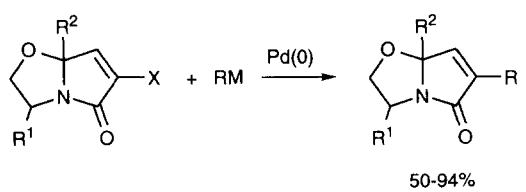


(84)



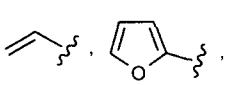


(85)

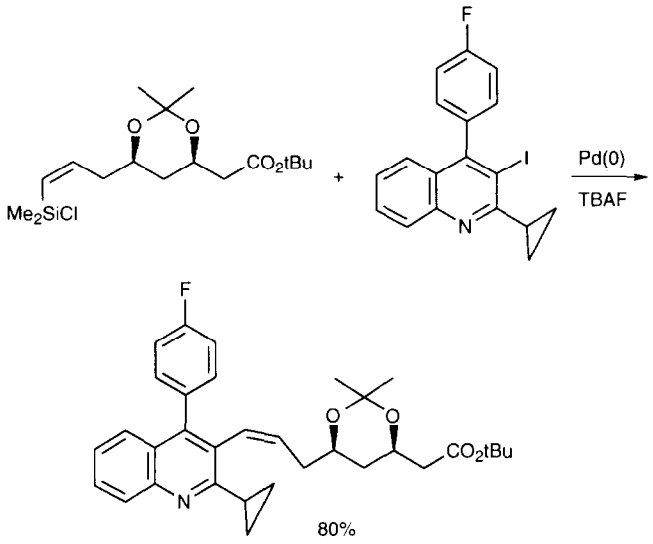


(86)

X = Br, I M = Bu_3Sn, 9BBN, $B(OH)_2$

R = Ph,  , pMeOPh, oMePh

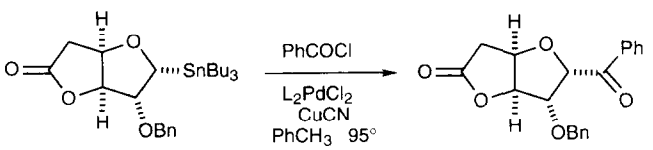
Vinyl silanes (Eq. (87)) [103] and boranes [104] also coupled to halides.



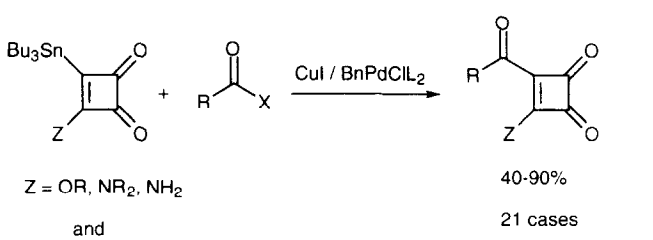
(87)

2.1.2. Alkylation of acid derivatives

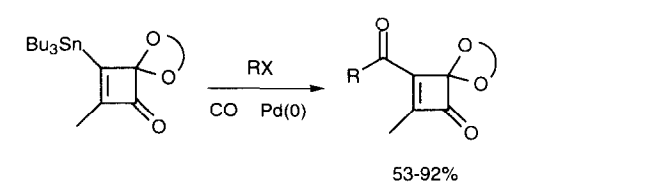
The preparation of allylic ketones via acylation of allylic mercurials was the topic of a dissertation [105]. Acid chlorides alkylated organotin reagents under palladium catalysis (Eq. (88) [106], Eq. (89) [107], Eq. (90) [108], and Eq. (91) [109]). Alkyl iron (Eq. (92)) [110], copper (Eq. (93)) [111], and zinc (Eq. (94) [112], Eq. (95) [113]) alkylated acid halides.

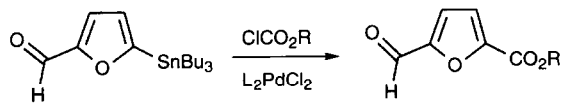


(88)

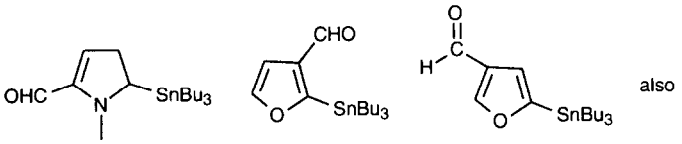


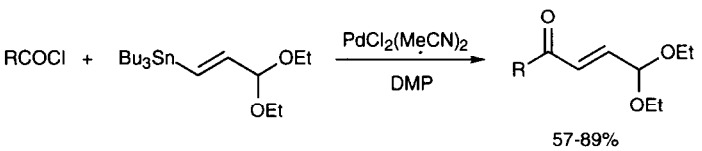
(89)



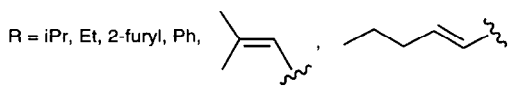


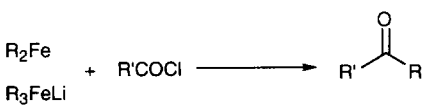
(90)



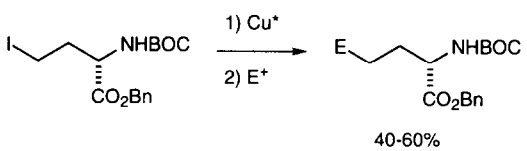


(91)

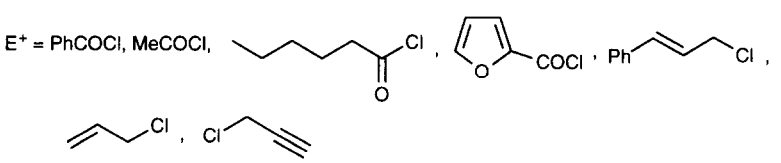


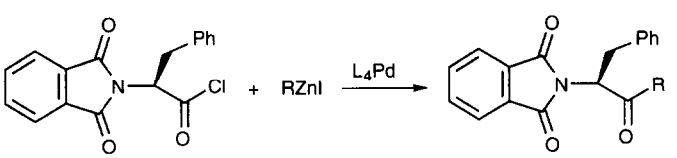


(92)

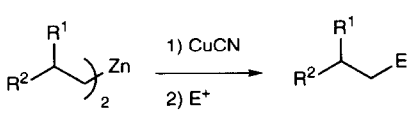


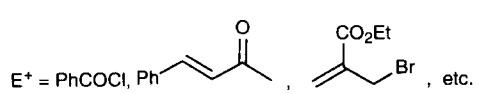
(93)





(94)



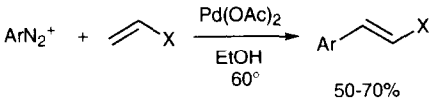


(95)

2.1.3. *Alkylation of olefins*

The Heck reaction (palladium-catalyzed oxidative addition–olefin insertion) continues to be developed and exploited for organic synthesis. 4-bromoanisole was used to arylate a variety of acrylic and cinnamic acid derivatives [114]. The use of substituted phenanthrolines as ligands for the Heck reaction resulted in mild conditions [115]. By changing the length of the tether in chelating bis-diisopropylphosphines the stereochemistry of the Heck arylation of styrene could be changed from cis to trans [116].

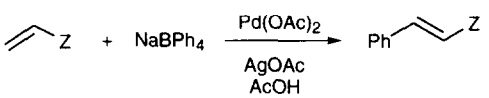
Aryl diazonium salts (Eq. (96)) [117] and tetraphenylborate (Eq. (97)) [118] arylated alkenes. Aryl bromides (Eq. (98)) [119], bromopyrazines (Eq. (99)) [120] and bromoindoles (Eq. (100)) [121] all arylated alkenes under Heck conditions.



(96)

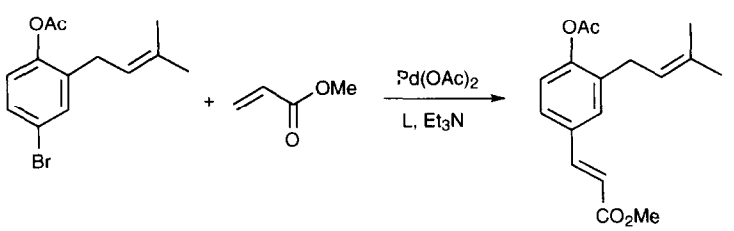
X = CO_2Me, CN

Ar = pMeOPh, oMeOPh, pClPh, $oMeO_2CPh$, mClPh, pBrPh



(97)

Z = CO_2Et, CN, Ph, CH_3

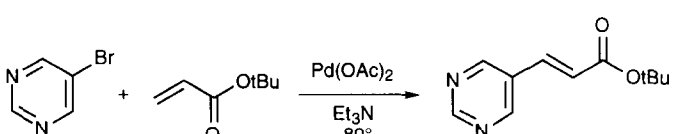


(98)

33%

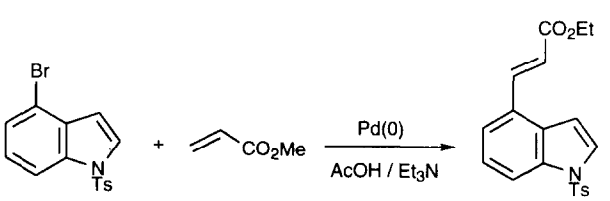
(I)

96%



(99)

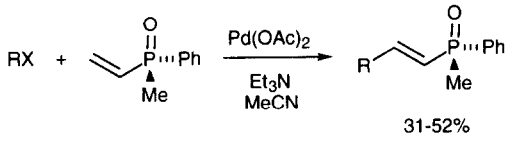
67%



(100)

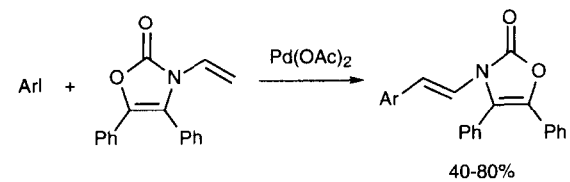
82%

Vinyl phosphonates (Eq. (101)) [122], carbamates (Eq. (102)) [123], and ethers (Eq. (103)) [124] underwent Heck arylation, as did bridged bicyclic alkenes (Eq. (104)) [125]. Palladium(0) catalyzed the addition of α-iodoperfluoroketenes to alkenes (Eq. (105)) [126].



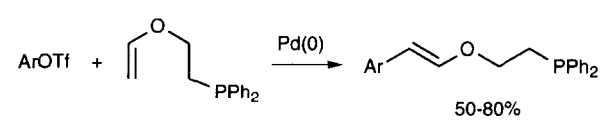
(101)

R = Ph, 3 BrPh, 2 CHOPh, 2HOCH2Ph, 3-Py, Ph , TMS



(102)

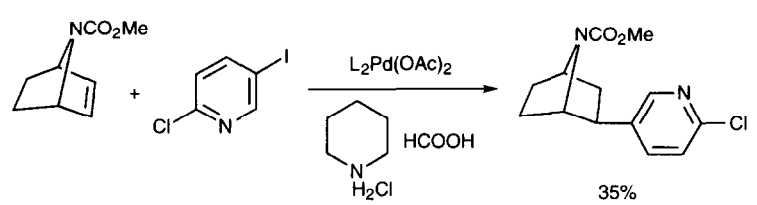
Ar = Ph, oFPh, mFPh, pClPh, pMePh, oMeOPh, pMeOPh, pHOPh, 3-Py, 5- indolyl



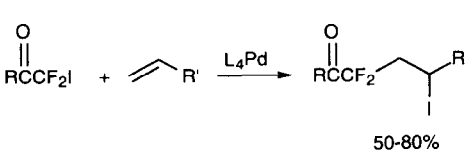
(103)

Ar = 1-Nap, 8-quin, pMeCOPh, pNO2Ph, mCNPh, pNHAcPh, oMeO2CPh, oMeCOPh

PPh2 directs terminal attack.



(104)

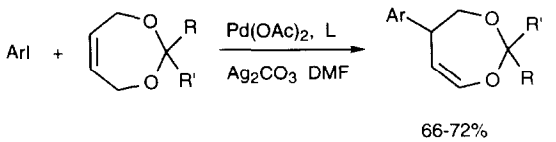


10 cases

(105)

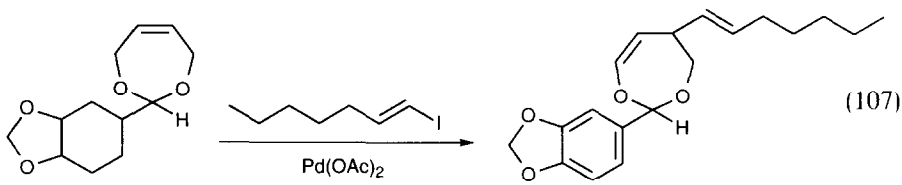
Acetals of 2-butene-1,4-diol underwent Heck arylation (Eq. (106)) [127,128] and vinylation (Eq. (107)) [129]. 2,3-dihydrofuran was asymmetrically arylated under Heck conditions [130], (Eq. (108)) [131,132]. Under high pressure (10 kbar) the

EE increased [133]. Water promoted the Heck arylation of dihydrofuran by iodopurine and pyrimidine bases (Eq. (109)) [134].

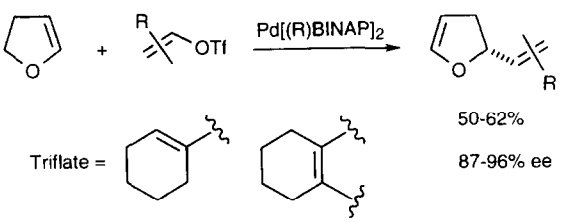


(106)

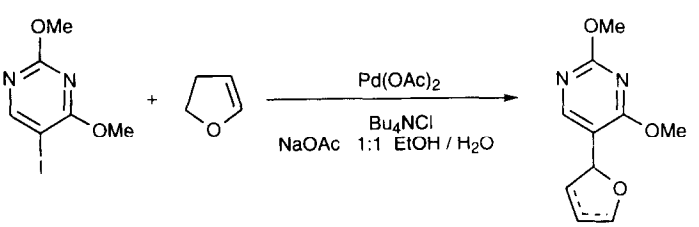
Ar = Ph, pMePh, pMeOPh, pEtO2CPh



(107)

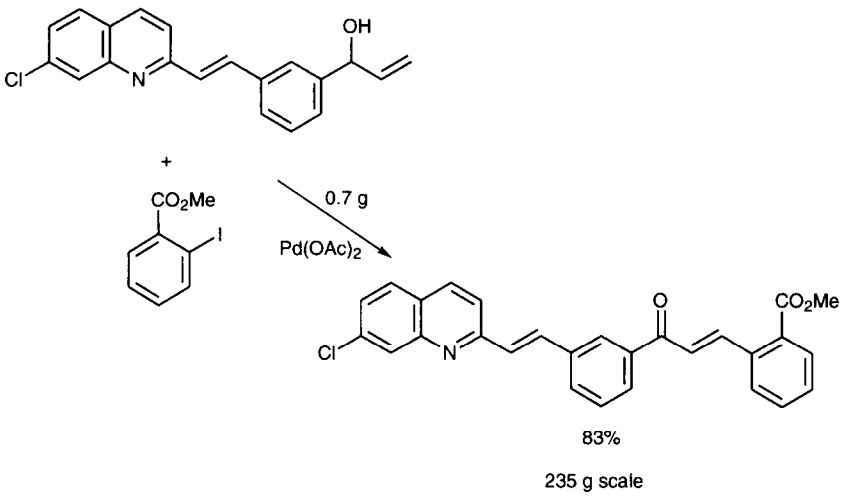


(108)

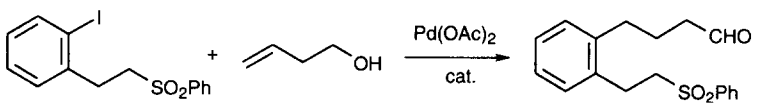


(109)

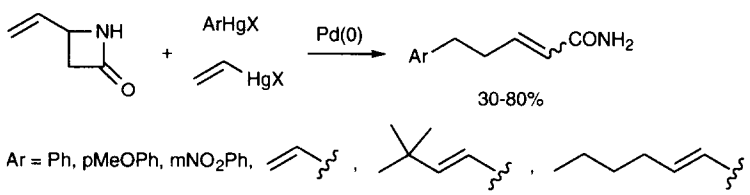
Heck arylation of allylic alcohols (Eq. (110)) [135] and more distantly unsaturated alcohols produced carbonyl compounds (Eq. (111)) [136]. Vinyl β-lactams underwent ring opening when arylated (Eq. (112)) [137], as did bridged bicyclic systems (Eq. (113)) [138]. In contrast, allyl amines were arylated without rearrangement (Eq. (114)) [139]. The course of arylation of vinyl boranes depended on reaction conditions (Eq. (115)) [140].



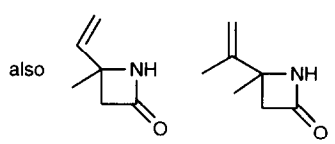
(110)

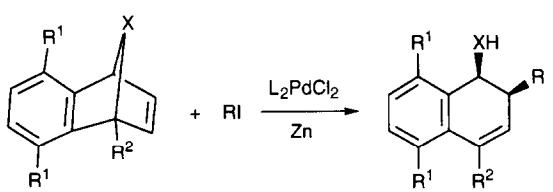


(111)

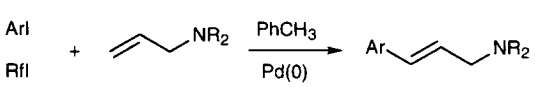


(112)

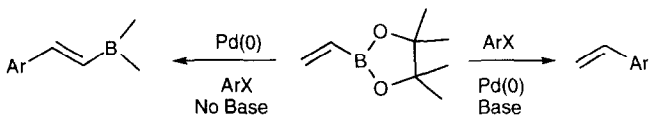




(113)

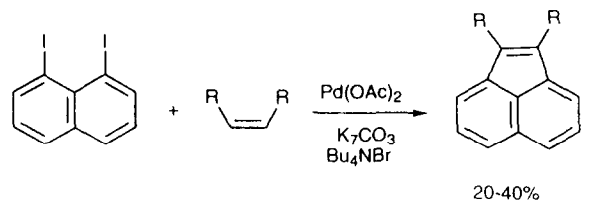


(114)

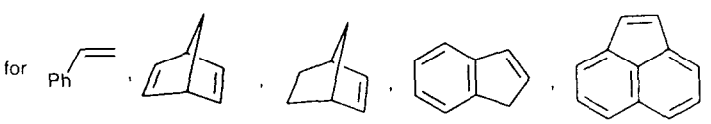


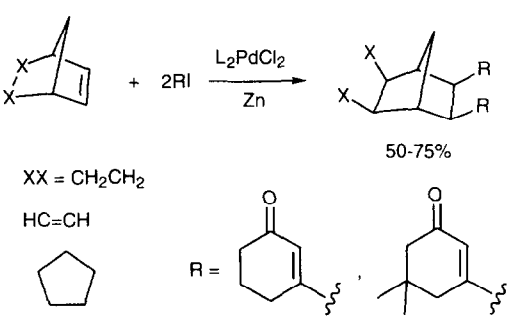
(115)

Alkenes could be dialkylated under palladium catalysis (Eq. (116) [141] and Eq. (117) [142]).



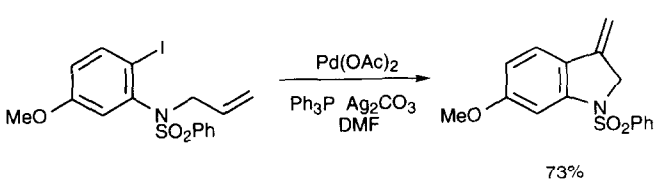
(116)



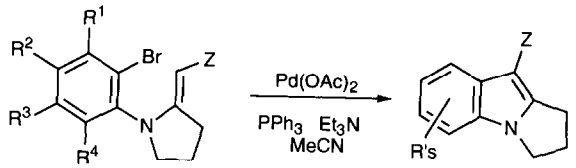


(117)

Intramolecular Heck reactions have become very important for forming rings. Indoles (Eq. (118) [143], Eq. (119) [144], Eq. (120) [145]), oxindoles (Eq. (121)) [146], and benzothiophenes (Eq. (122)) [147] have all been synthesized by this chemistry.



(118)

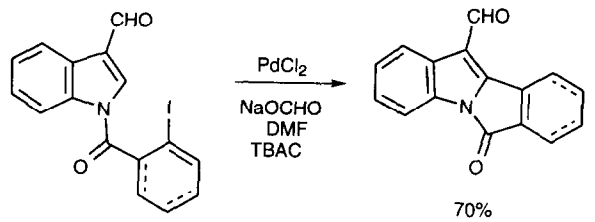


60-80%

(119)

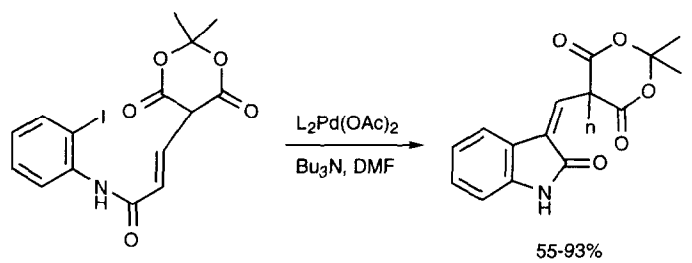
R^1 = H, Me, OMe

Z = CO_2Et, CN, COPh, COMe



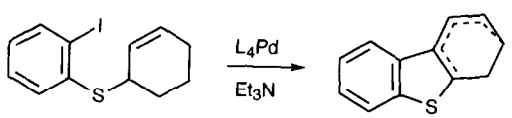
70%

(120)



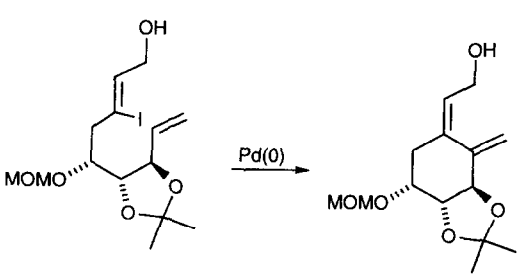
55-93%

(121)



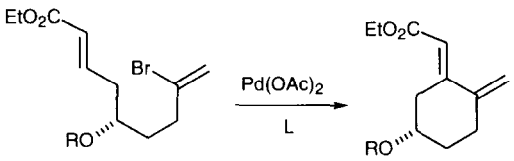
(122)

Carbocycles were also readily formed by intramolecular Heck arylation of olefins (Eq. (123) [148], Eq. (124) [149], Eq. (125) [150], Eq. (126) [151]) as were cyclic ethers (Eq. (127) [152] and Eq. (128) [153]).



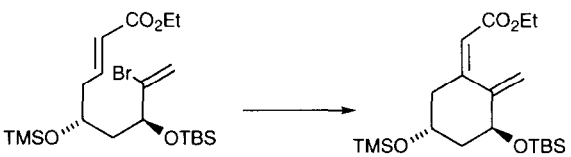
58%

(123)



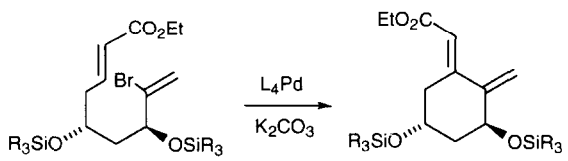
72%

and



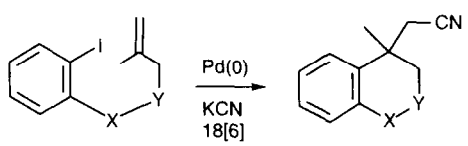
(124)

86%

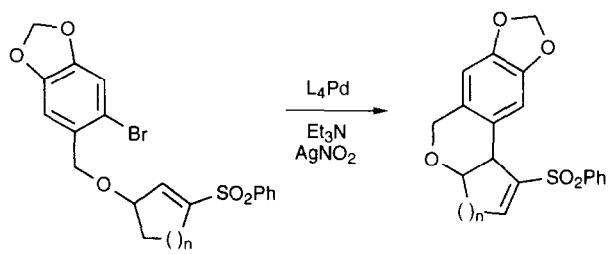


(125)

92%

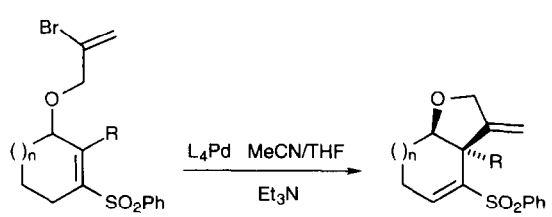


(126)



(127)

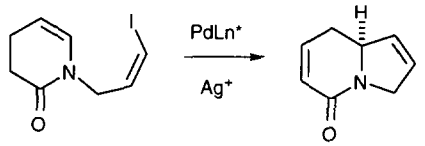
n = 1 97%
n = 2 57%



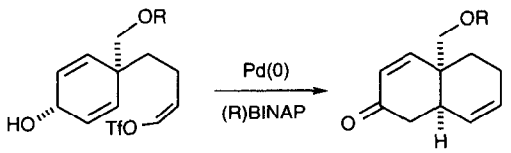
(128)

n = 1 73%
n = 2 58%

By using chiral ligands, asymmetric Heck reactions were achieved (Eq. (129) [154] and Eq. (130) [155,156]).

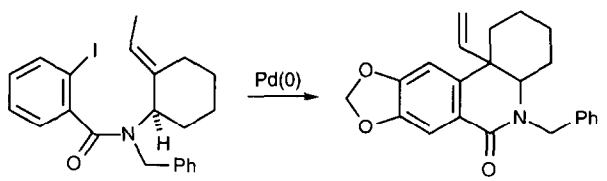


(129)

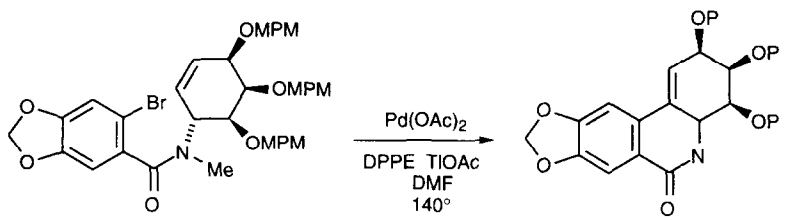


(130)

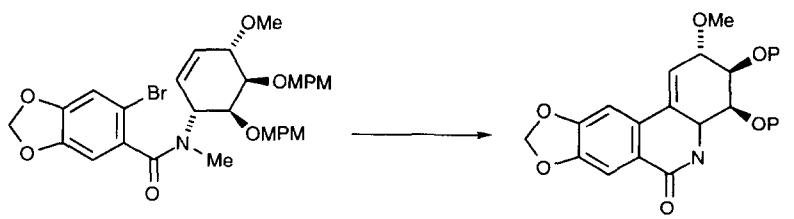
Palladium-catalyzed polyene cyclizations have been reviewed (23 references) [157]. Intramolecular Heck reactions are particularly effective with highly functionalized systems (Eq. (131) [158], Eq. (132) [159], Eq. (133) [160], Eq. (134) [161], Eq. (135) [162], Eq. (136) [163]) and quaternary centers (Eq. (137) [164], Eq. (138) [165], Eq. (139) [166], and Eq. (140) [167]).



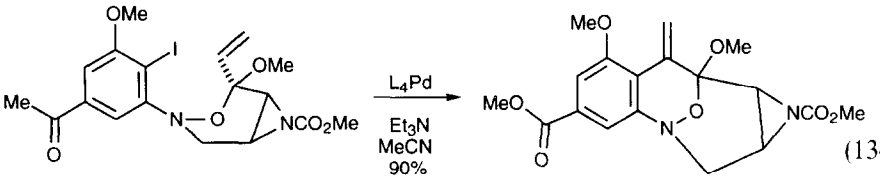
(131)



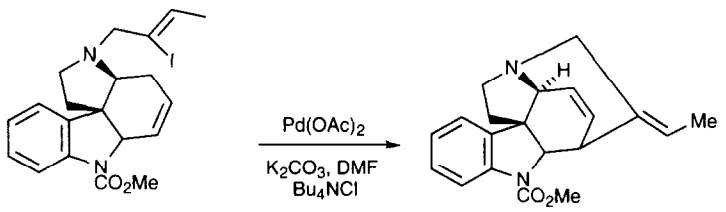
(132)



(133)



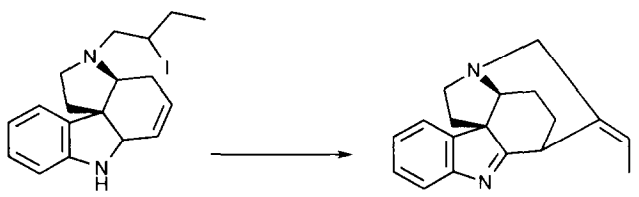
(134)



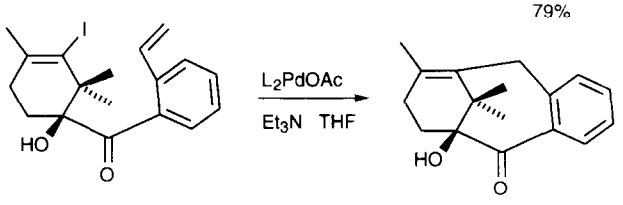
84%

and

(135)



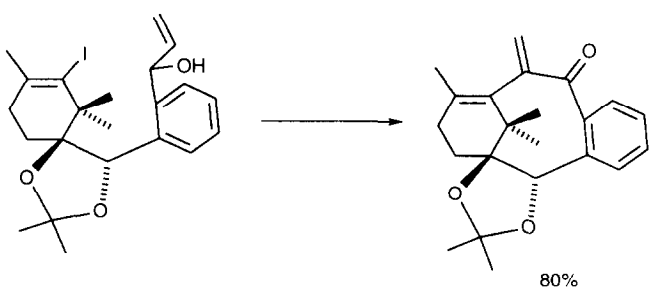
79%



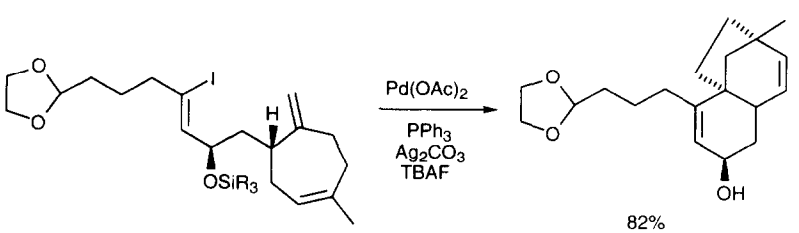
52%

and

(136)

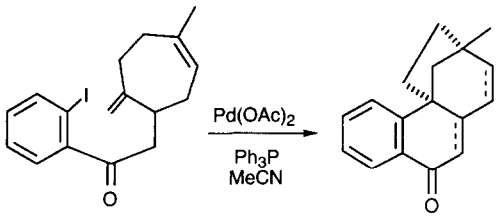


80%

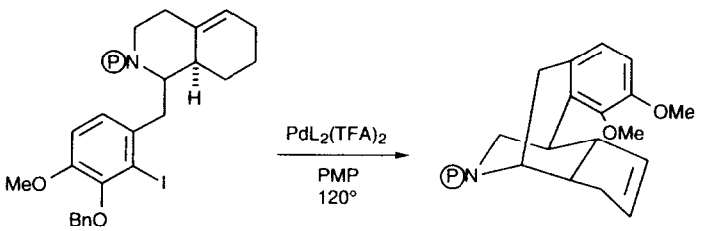


(137)

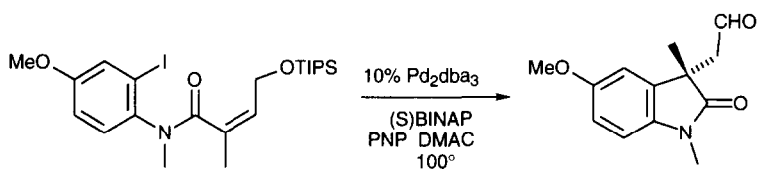
82%



85% (14 g scale) (138)

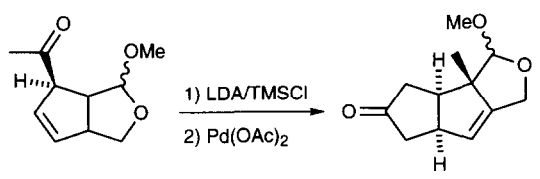


60% (139)

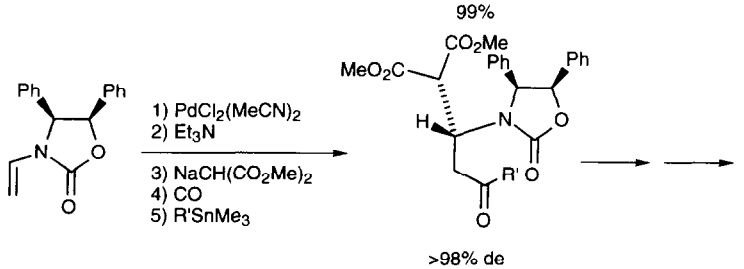


84% 95% ee (140)

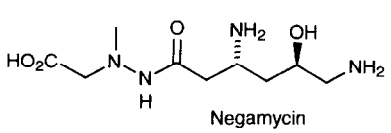
Palladium(II) catalyzed the alkylation of olefins by silylenol ethers (Eq. (141)) [168,169] and stabilized carbanion (Eq. (142)) [170].



99% (141)



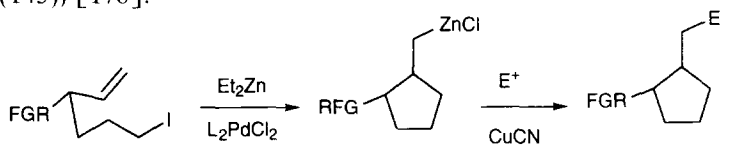
>98% de (142)



Negamycin

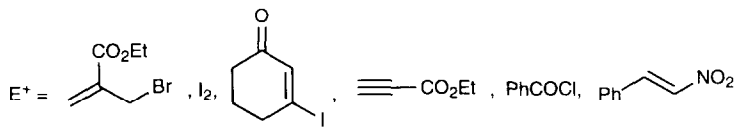
Palladium catalyzed the cyclization of iodohexenes to give cyclic organozinc reagents which could be further functionalized (Eq. (143)) [171–173]. Chiral rhodium complex catalyzed asymmetric cyclization of enols was reviewed (40 references) [174] and was used to make chiral cyclic compounds (Eq. (144) [175] and Eq. (144a) [176]).

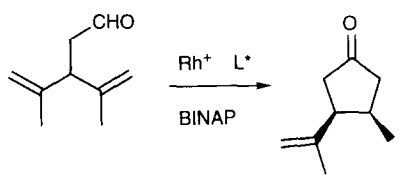
Copper salts catalyzed the addition of CF_3CCl_3 to alkenes to introduce the CF_3CCl_2CCCl subgroup [177]. Vinyl triflates were alkylated by stannanes in the presence of palladium catalysts. The group transferred depended on the solvent (Eq. (145)) [178].



(143)

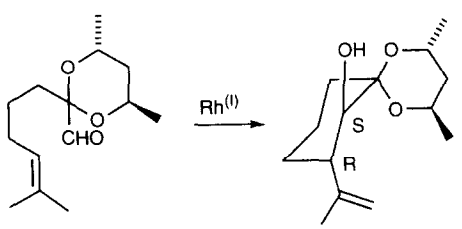
RFG = H, Ph, pNCPh, pPirOPh





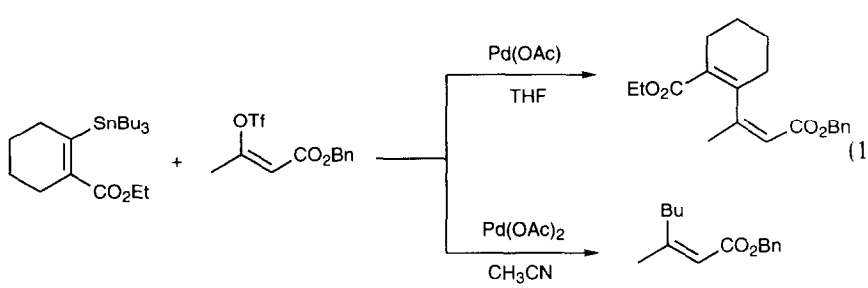
(144)

84% >99% ee



(144a)

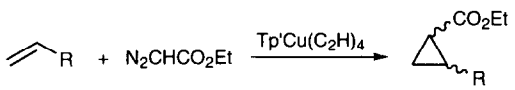
53% 71% de



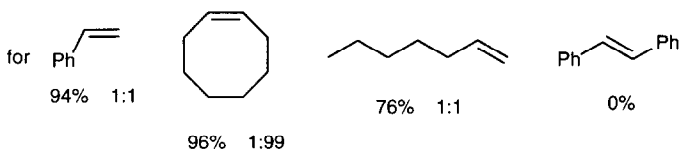
(145)

2.1.4. Decomposition of diazoalkanes and other cyclopropanations

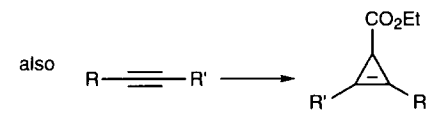
Carbene reactions of diazoesters with σ bonds as an effective method for alkoxycarbonylmethylenation of organic compounds were the subject of a review [179]. Copper (Eq. (146)) [180], iron (Eq. (147)) [181], ruthenium (Eq. (148)) [182], osmium (Eq. (149)) [183], and rhodium (Eq. (150) [184], and Eq. (151) [185]) complexes all catalyzed the cyclopropanation of alkenes by diazo compounds.

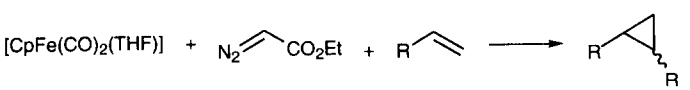


Tp' = hydrotris(3,5-dimethyl-1-pyrazolyl)borate

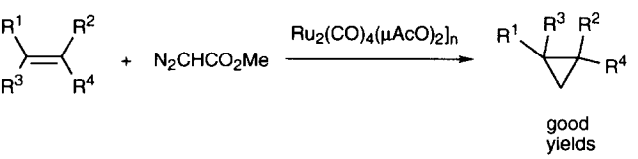


(146)

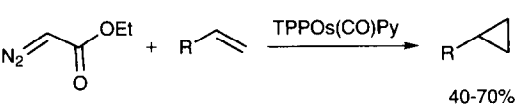




(147)

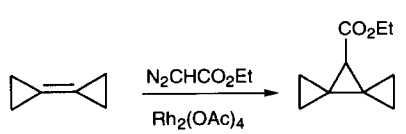


(148)

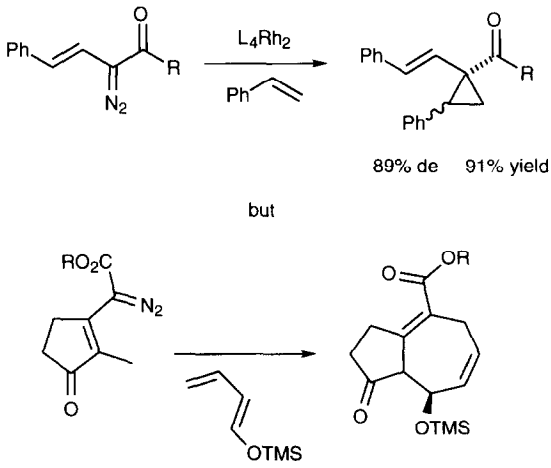


(149)

TPP = tetraphenylporphyrin

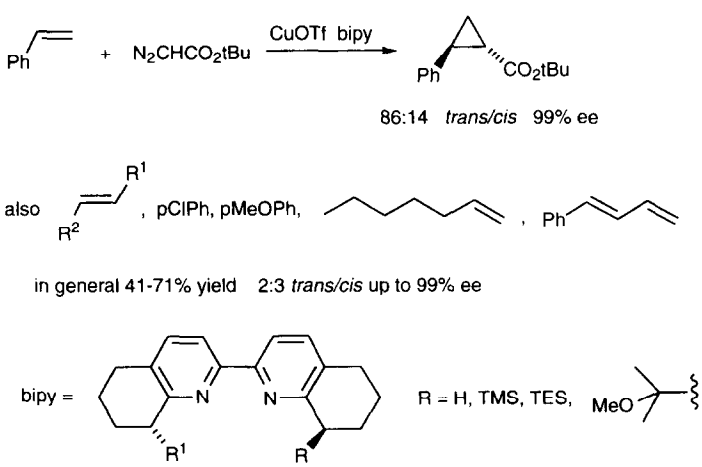


(150)

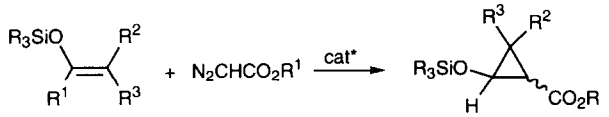


(151)

The use of chiral ternary copper(II) complexes in asymmetric synthesis of chrysanthemic acids has been developed [186,187]. The use of chiral rhodium(II) carboxamides for catalysts for enantioselective metal carbene transformations has been reviewed (63 references) [188]. These same complexes have been studied to provide comparisons for catalysis of cyclopropanation, cyclopropenations and CH insertion reaction of diazoalkanes [189]. The MEPy (pyroglutamic ester) ligand was most effective. The catalyst $Rh_2[(4S)$-4-phenyl-oxazolidine-2-one$]_4$ showed lower enantioselectivity but favored cyclopropanation [190]. Asymmetric cyclopropanation was catalyzed by chiral bipyridyl copper complexes (Eq. (152) [191,192], Eq. (153) [193]), and chiral rhodium(II) complexes (Eq. (154)) [194]. Copper also catalyzed intramolecular cyclopropanations (Eq. (155)) [195]. Modest asymmetric induction was observed with chiral diazoesters (Eq. (156)) [196].

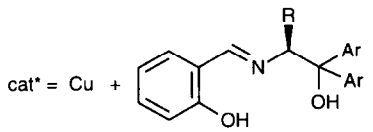


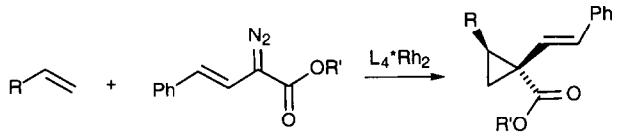
(152)



modest yields
wide range of ee's

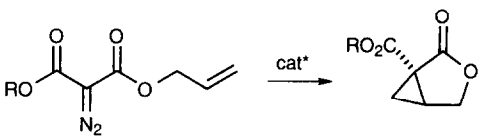
(153)





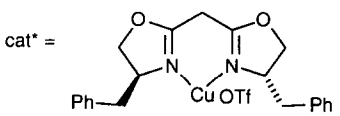
(154)

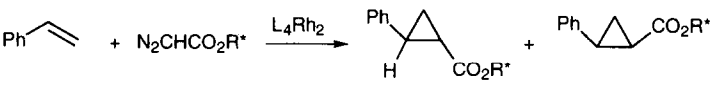
R = Ph, pClPh, AcO, EtO, nBu, Et, iPr



32% ee 70% yield

(155)

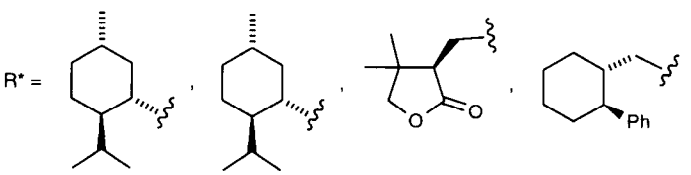




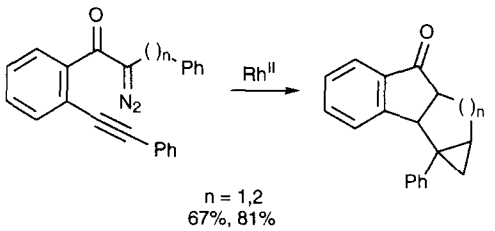
de 5-70% de 13-88%

21-82% yield

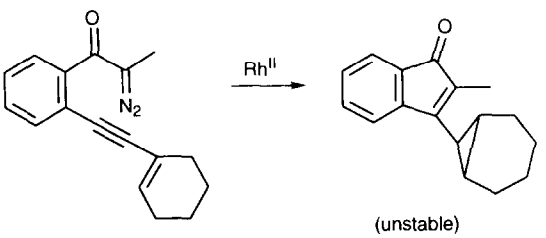
(156)



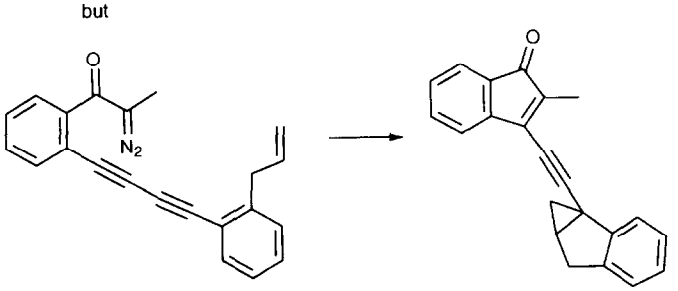
Metal-catalyzed intramolecular cyclization reactions of alkynyl α-diazoketones were the topic of a thesis [197]. This type of process was used to synthesize a variety of ring systems (Eq. (157) [198], Eq. (158) [199], Eq. (159) [200], and Eq. (160) [201]).



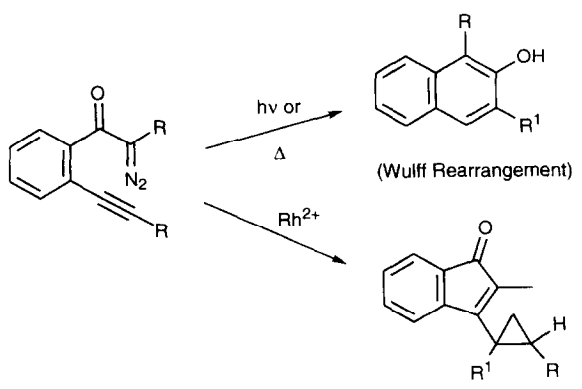
(157)



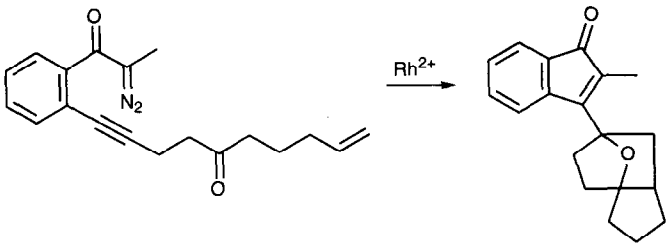
but



(158)



(159)



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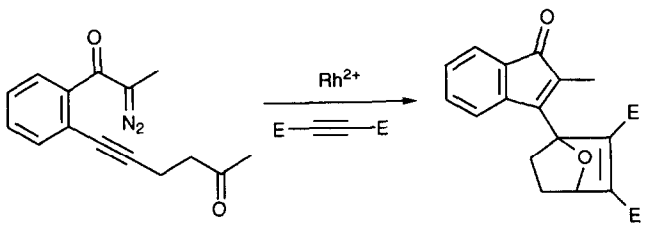
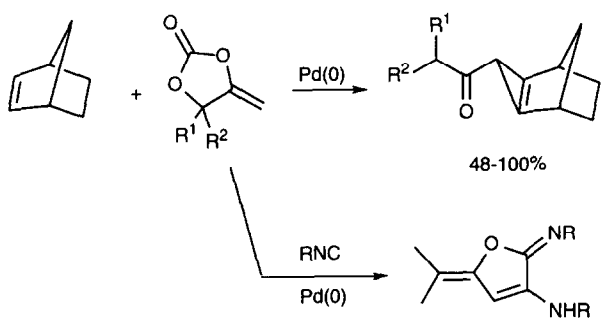


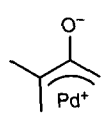
(160)

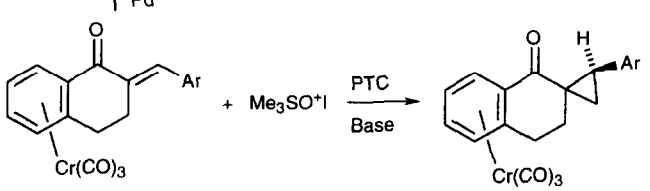
An *Organic Synthesis* procedure for the synthesis of 1,1-diphenyl cyclopropane via iron methylene transfer reagents was published [202]. Palladium(0) catalyzed the unusual cyclopropanation of norbornene in Eq. (161) [203]. Complexation to chromium resulted in exclusive endo cyclopropanation of unsaturated tetralones (Eq. (162)) [204].



(161)

via

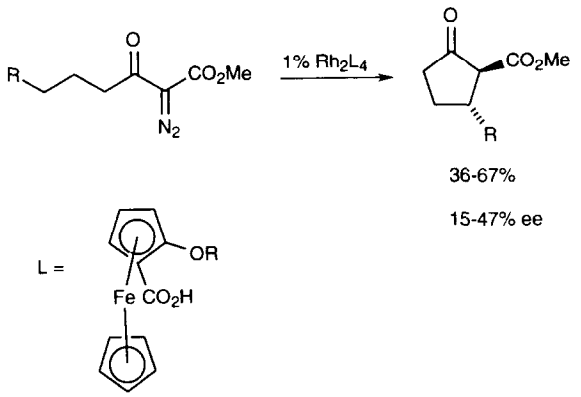




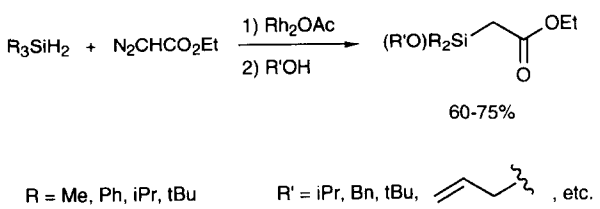
(162)

Ar = Ph, pMePh, pMeOPh

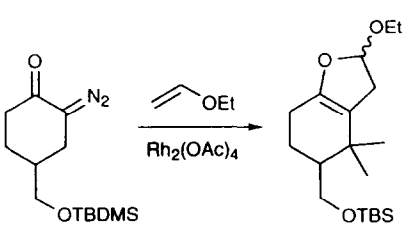
Ligand effects on the partitioning of rhodium(II) catalyzed diazo decomposition reactions between cyclopropanation, CH insertion, and aromatic substitution have been studied in detail [205,206]. The rhodium-catalyzed diazo–CH insertion process was used to make cyclopentanones (Eq. (163)) [207]. Other miscellaneous diazo decomposition reactions are seen in Eq. (164) [208, Eq. (165) [209], and Eq. (166) [210].



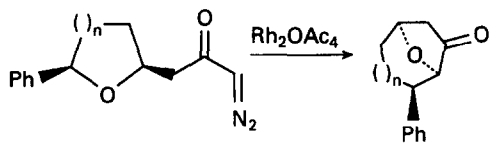
(163)



(164)



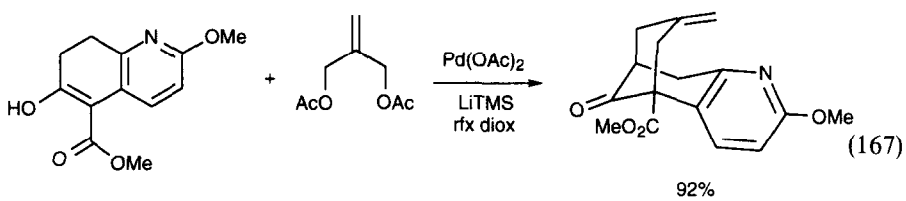
(165)



(166)

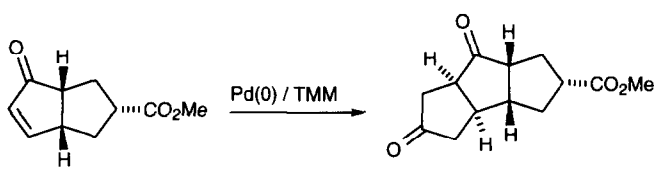
2.1.5. Cycloadditions

Palladium(0) complexes catalyzed a number of cycloadditions involving trimethylenemethane complex intermediates (Eq. (167) [211,212], Eq. (168) [213], Eq. (169) [214], and Eq. (170) [215]).



92%

(167)



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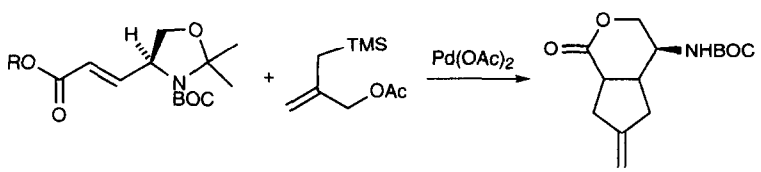
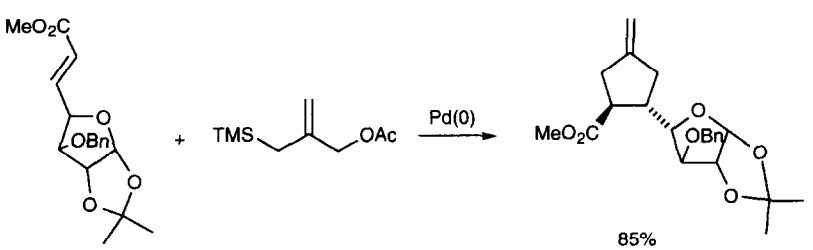
(168)



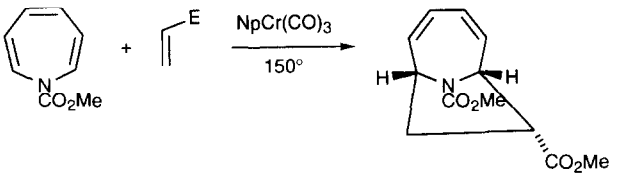
(169)



85%

(170)

Chromium tricarbonyl fragments catalyzed the photochemical and thermal cycloaddition reactions of cycloheptatrienes (Eq. (171) [216] and Eq. (172) [217]).



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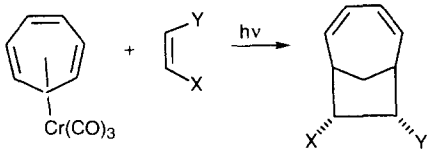
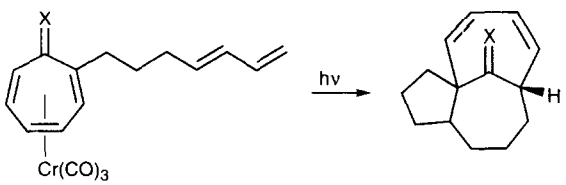
77%

(171)



40-90%



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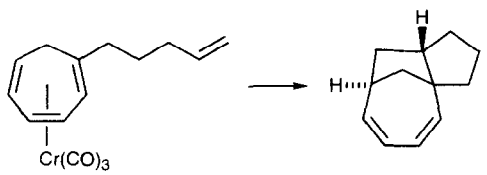
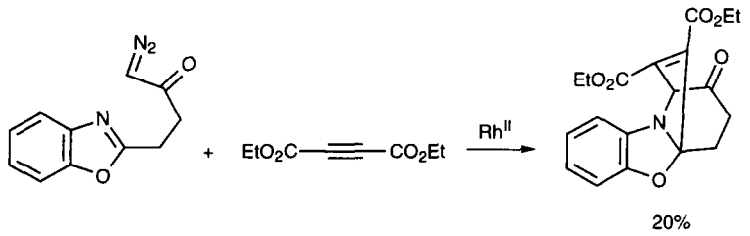
(172)



65%

Synthetic applications of carbonyl ylides generated via tandem cyclization cycloaddition reactions of rhodium carbenoids have been reviewed [218]. Ylide formation–cycloaddition reactions of rhodium-catalyzed diazodecompositions have been studied for steric and electronic effects in the partitioning between ylide formation and insertion [219]. This class of reaction has been used to make a variety of heterocycles (Eq. (173) [220], Eq. (174) [221], and Eq. (175) [222]).



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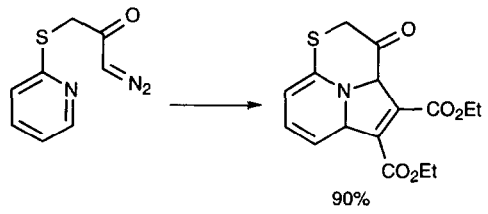
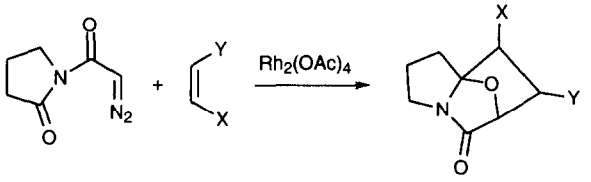
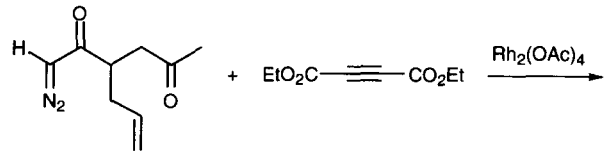
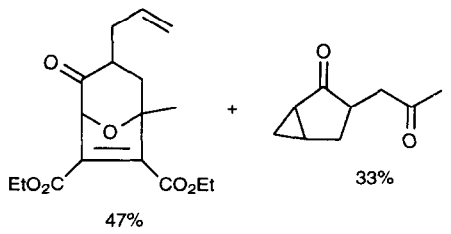


(173)



(174)

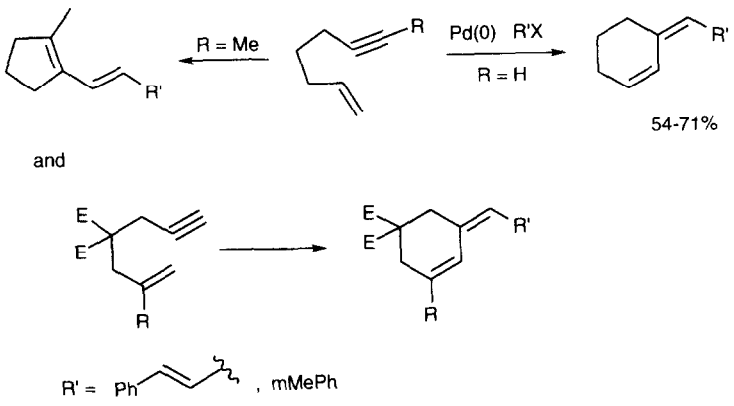




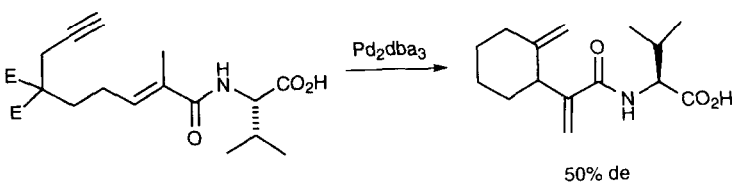
(175)

The regioselectivity of palladium-catalyzed enyne cyclization could be changed by the substitution pattern on the substrate (Eq. (176)) [223]. The presence of a carboxylic acid in the substrate facilitated the cyclization (Eq. (177)) [224]. The product depended very much on the nature of the catalyst (Eq. (178)) [225]. Multiple

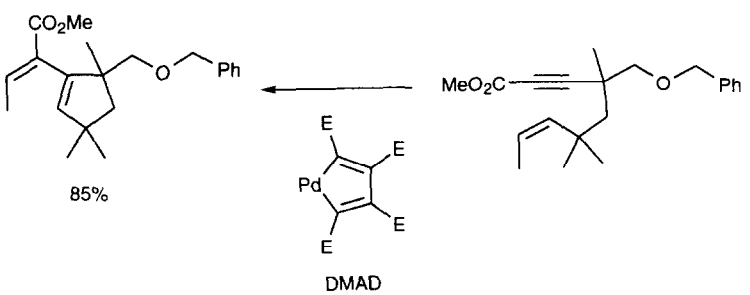
cyclizations could be achieved (Eq. (179) [226], Eq. (180) [227], and Eq. (181) [228]), culminating in the formation of seven rings (Eq. (182)) [229]. Other uses are seen in Eq. (183) [230] and Eq. (184) [231].



(176)



(177)



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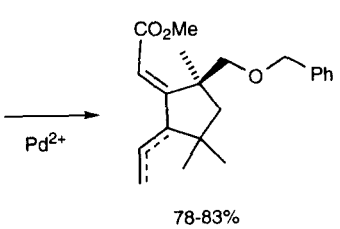

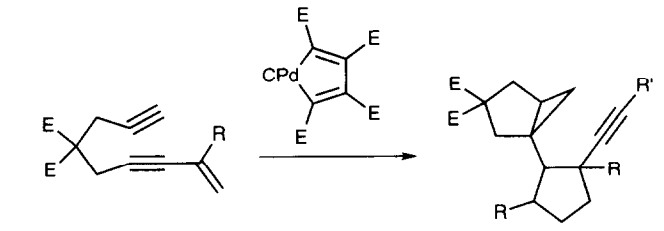
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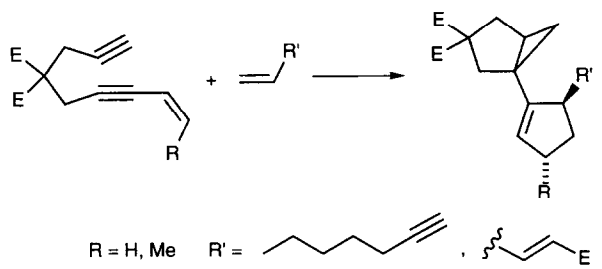
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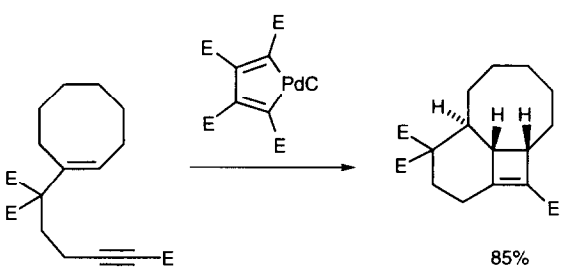
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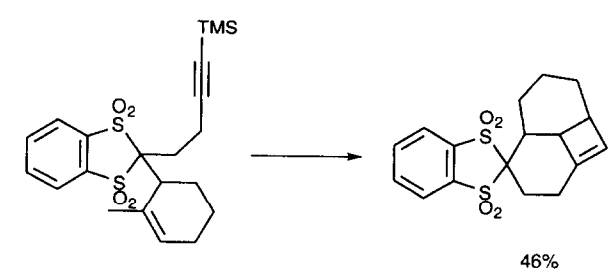
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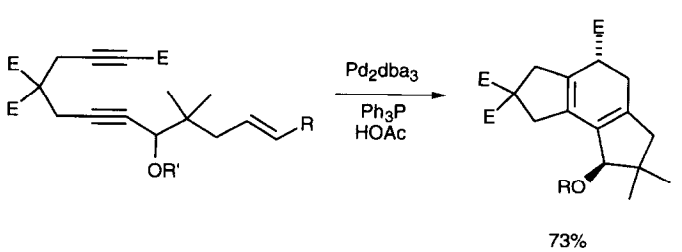
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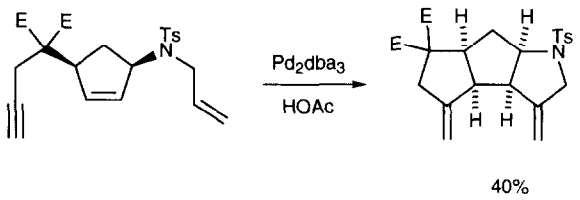

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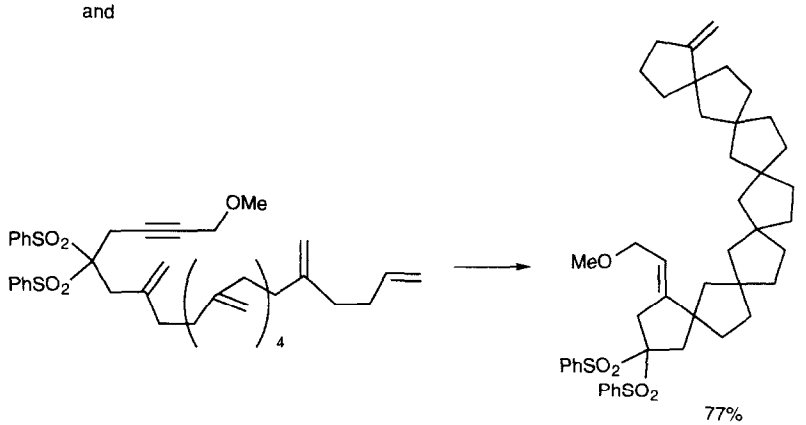
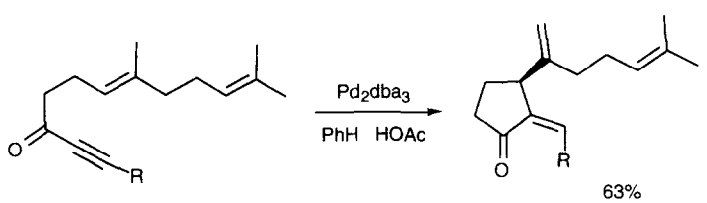


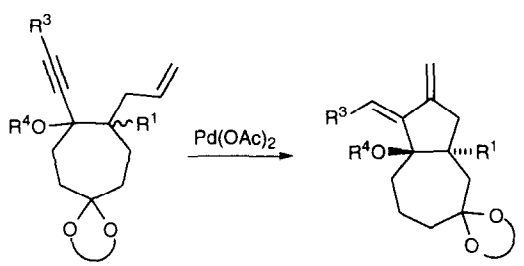
77%

(182)



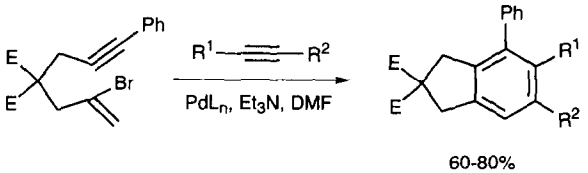
63%

(183)

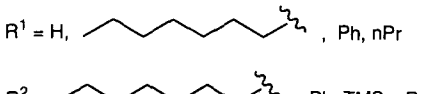


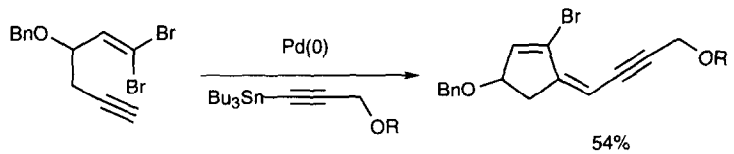
(184)

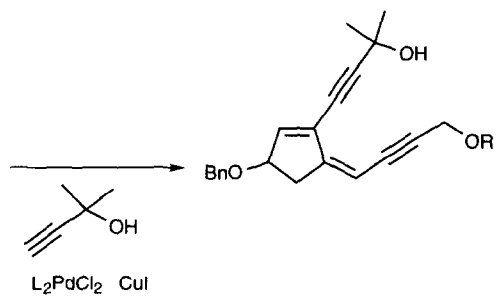
Enyne cyclization was also achieved by oxidative addition–insertion processes (Eq. (185)) [232] and oxidative addition–insertion–transmetallation (Eq. (186) [233] and Eq. (187) [234]).



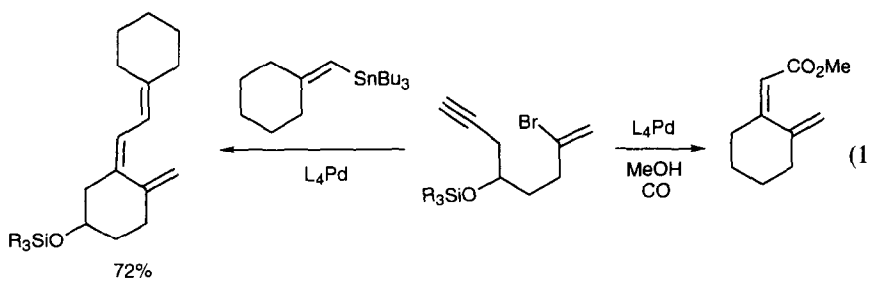
(185)





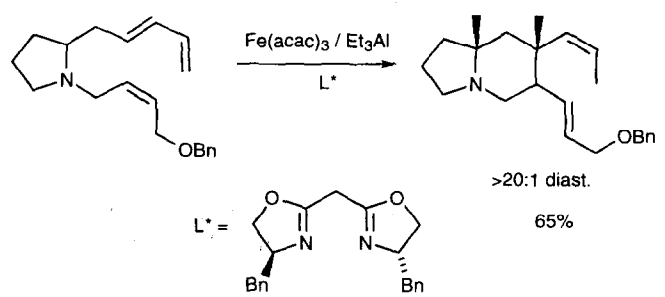


(186)

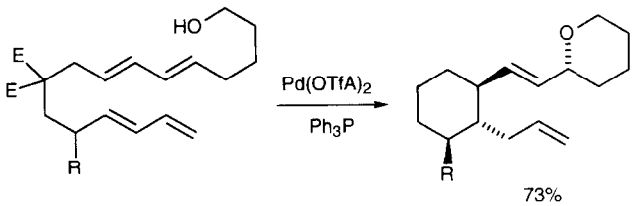


(187)

Polyenes were cyclized by iron- (Eq. (188)) [235] and palladium- (Eq. (189)) [236] assisted telomerization reactions.

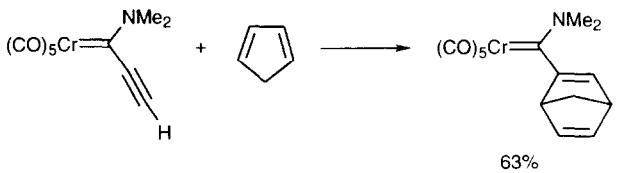


(188)

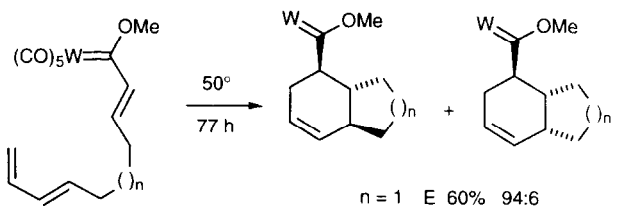


(189)

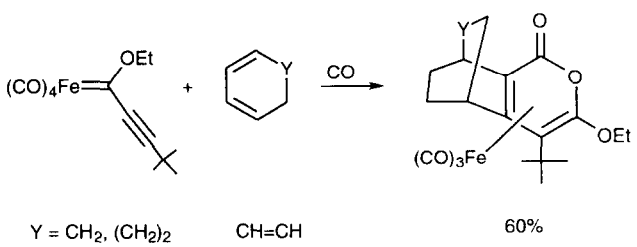
Unsaturated chromium carbene complexes (Eq. (190)) [237], tungsten carbene complexes (Eq. (191)) [238], and iron carbene complexes (Eq. (192)) [239] underwent efficient Diels–Alder cycloadditions with dienes. Chromium-complexed chiral acrylate esters controlled the stereochemistry of Diels–Alder cycloaddition (Eq. (193)) [240]. Chromium-complexed benzocyclobutanones underwent Diels–Alder cycloadditions (Eq. (194)) [241].



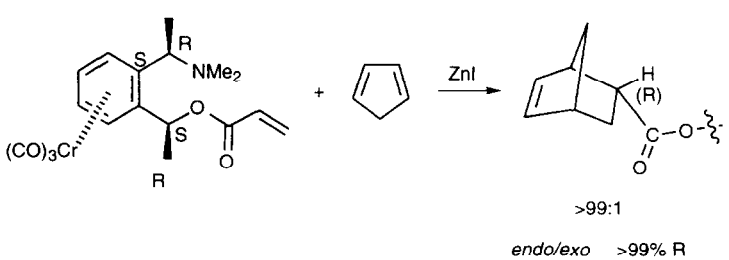
(190)



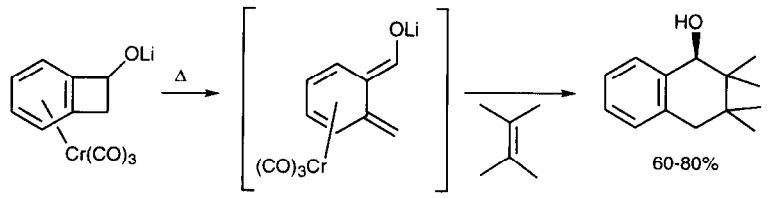
(191)



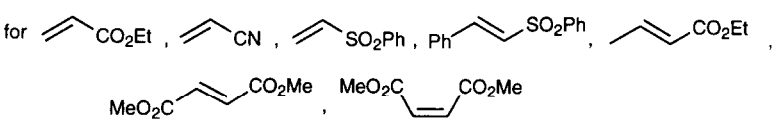
(192)



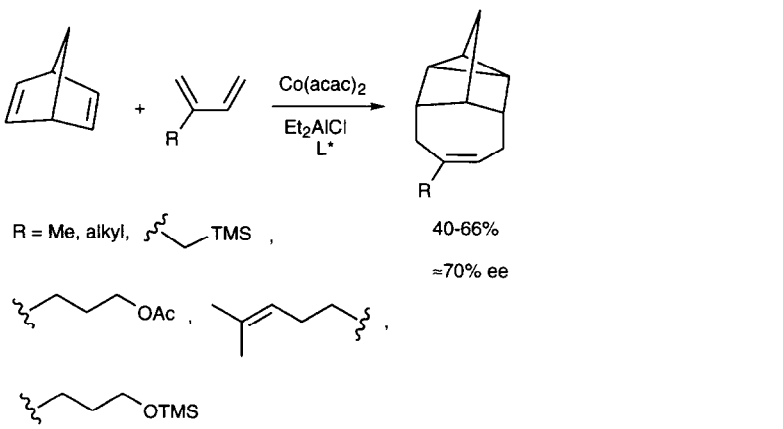
(193)



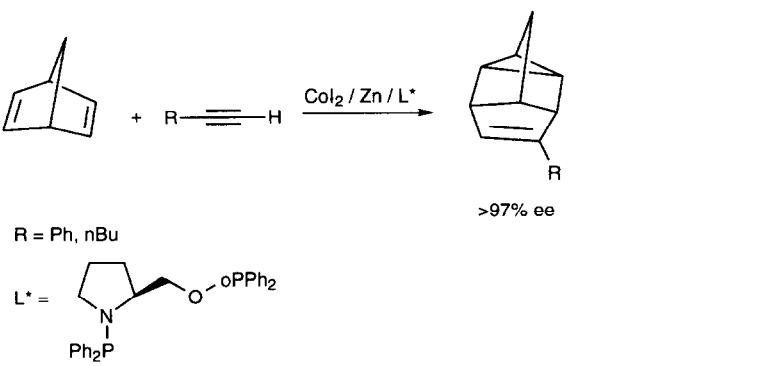
(194)



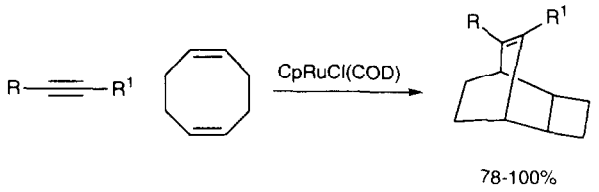
Reduced cobalt complexes catalyzed 4+4 and 4+2 cycloaddition of norbornadiene (Eq. (195) [242] and Eq. (196) [243]). Ruthenium (Eq. (197)) [244] and rhodium (Eq. (198)) [245] catalyzed alkyne cycloadditions to polyenes. Metalated dienes (Eq. (199)) [246], enones (Eq. (200)) [247], and cyclopentadienes (Eq. (201)) [248] all underwent cycloaddition reactions. Palladium and platinum catalyzed the selective cycloadditions of dipropargyl acetylenedicarboxylate (Eq. (202)) [249].



(195)



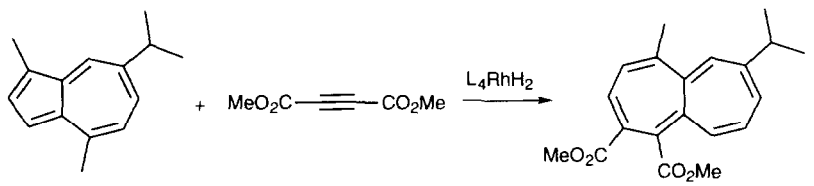
(196)



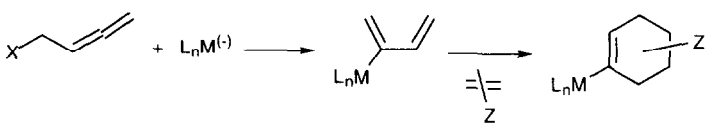
78-100% (197)

R = Me, Et, R_3SiOCH_2H

R^1 = CH_2OH, CH_3OSiR_3, CO_2Me, MeO_2C



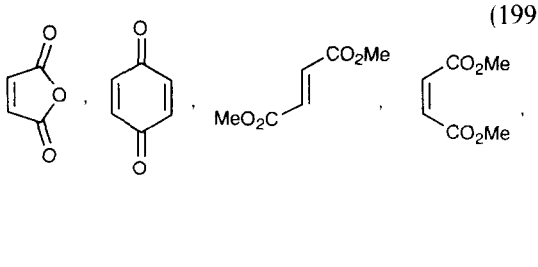
80% (198)

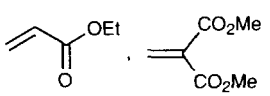


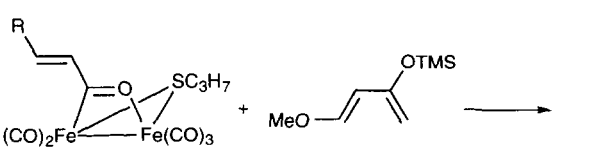
(199)

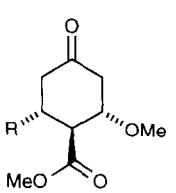
L_nM = $L(DMG)_2Co$

alkenes MeO_2C—≡—CO_2Me ,



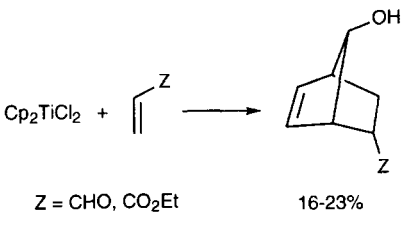






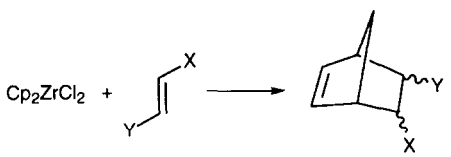
exo selective

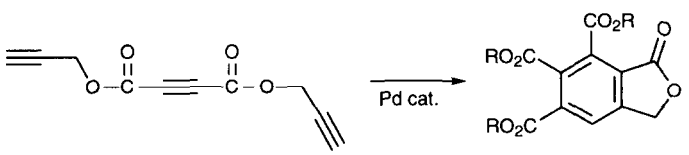
60% (200)



(201)

and

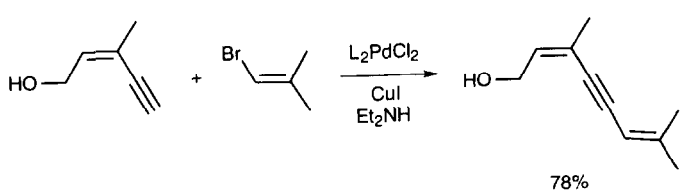




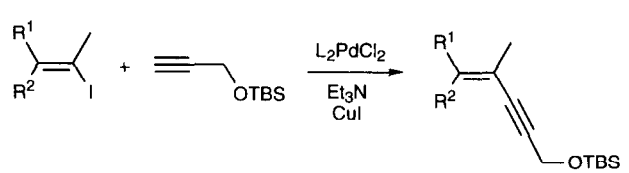
(202)

2.1.6. *Alkylation of alkynes*

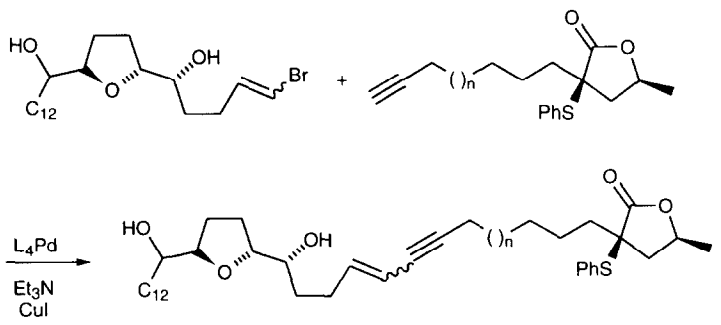
Palladium-catalyzed reactions of alkynes with vinyl bromides and aryl halides were the topic of a dissertation [250]. This was a widely used procedure to form enynes (Eq. (203) [251], Eq. (204) [252], Eq. (205) [253], Eq. (206) [254], Eq. (207) [255], Eq. (208) [256]). The full range of coupling substrates has been studied (Eq. (209)) [257].



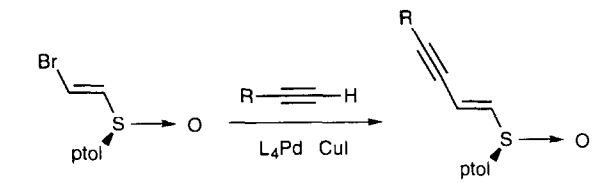
(203)



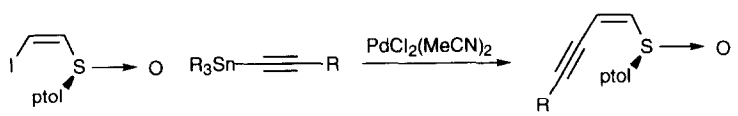
(204)



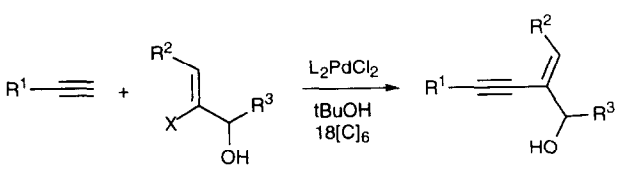
(205)



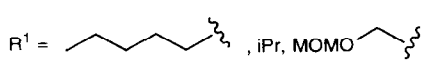
and



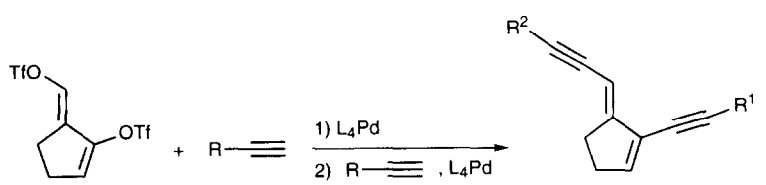
(206)



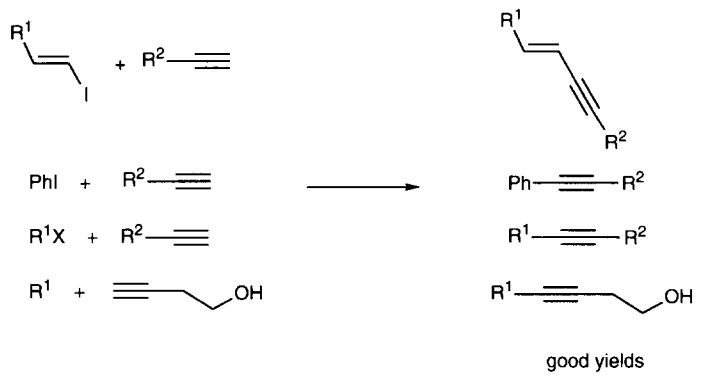
(207)



R^2 = H, Bu R^3 = H, Et, Me

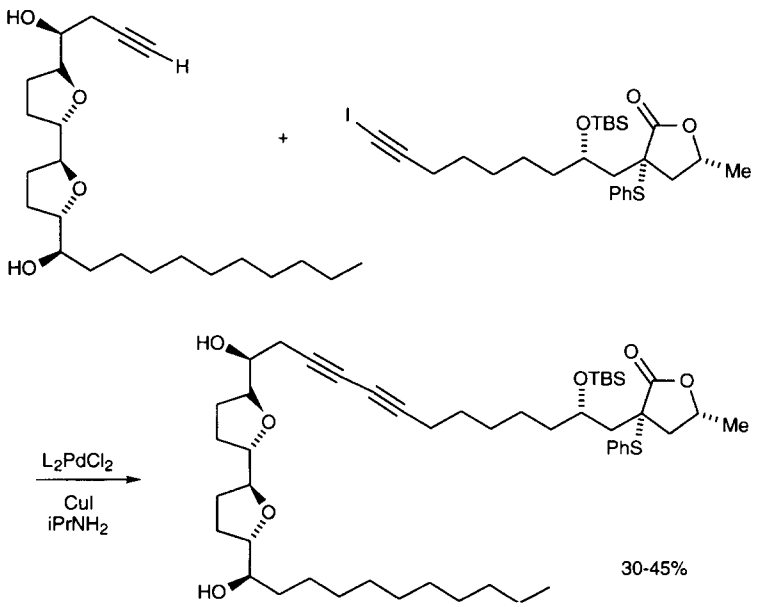


(208)

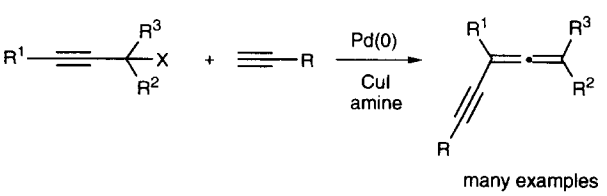


(209)

Alkynyl halides (Eq. (210)) [258] and propargyl halides (Eq. (211)) [259] also coupled to alkynes under these conditions.

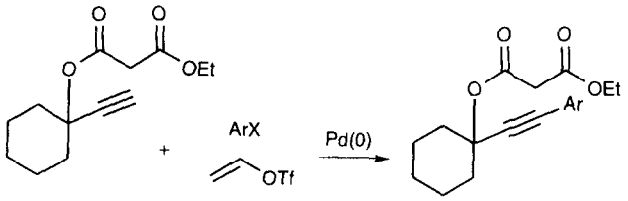


(210)

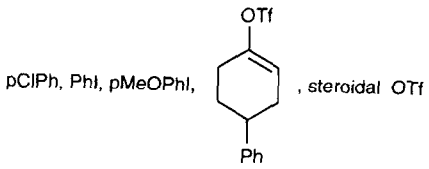


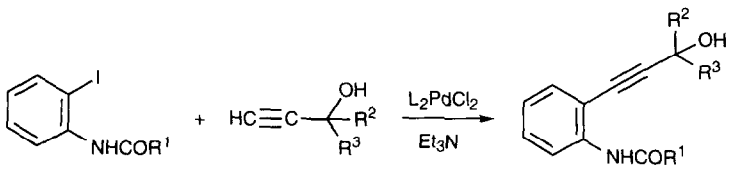
(211)

The palladium-catalyzed coupling of alkynes to aryl halides or triflates was also a popular pursuit (Eq. (212) [260], Eq. (213) [261], Eq. (214) [262], Eq. (215) [263], Eq. (216) [264], Eq. (217) [265], Eq. (218) [266], and Eq. (219) [267]).



(212)

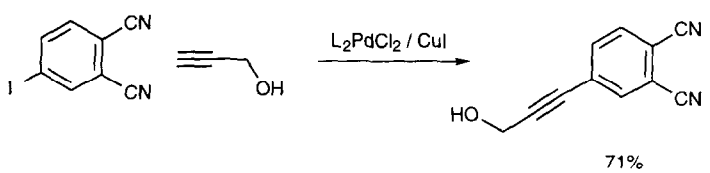




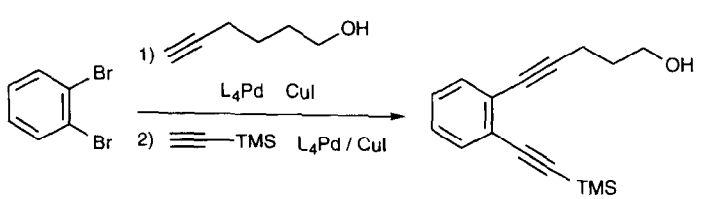
(213)

R^1 = Me, CF_3 R^2 = H, Me, Ph, pMePh, oMePh, pMeOPh, oMeOPh

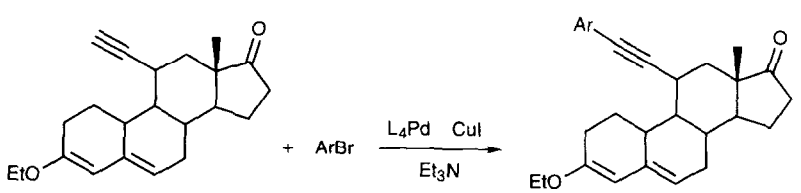
R^3 = H, Me



(214)



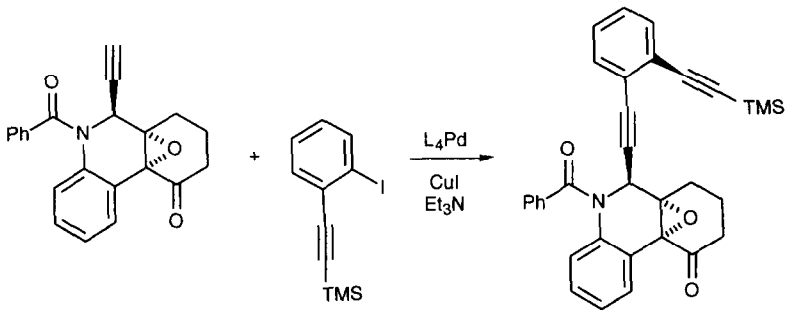
(215)



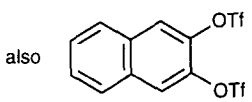
36-83%

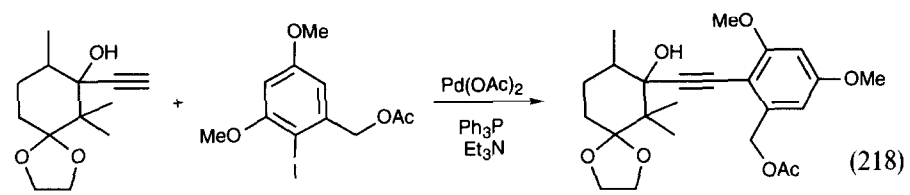
(216)

Ar = pMe_2NPh, mNO_2Ph, 3Py

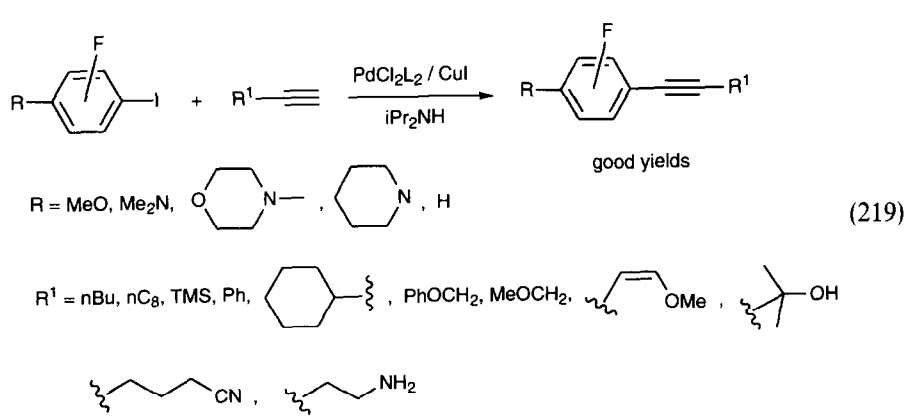


(217)



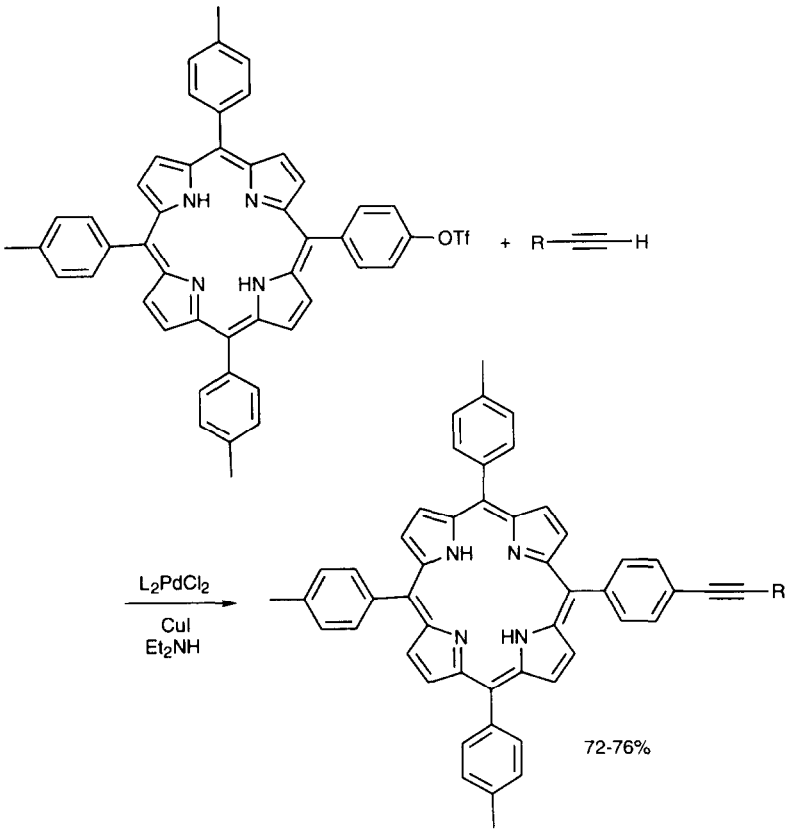


(218)

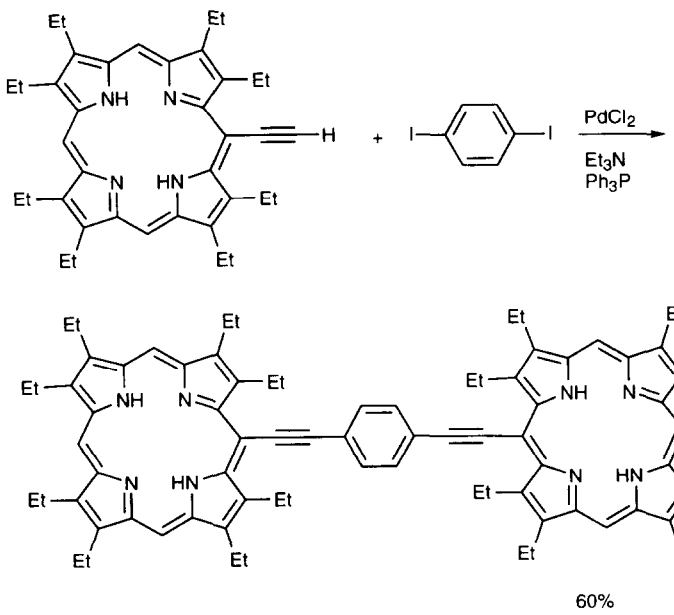


(219)

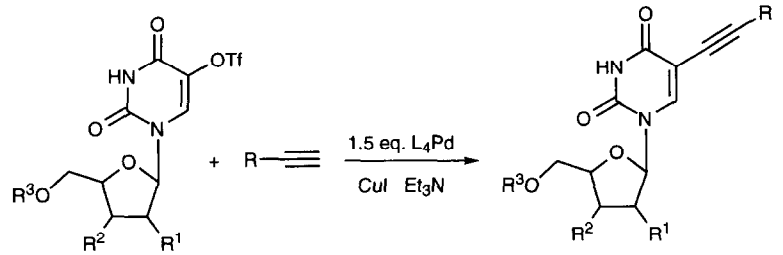
Heteroaromatic halides including porphyrins (Eq. (220) [268], Eq. (221) [269]), nucleosides (Eq. (222) [270], Eq. (223) [271]), imidazoles (Eq. (224)) [272], and indoles (Eq. (225)) [273] all coupled cleanly to alkynes.


NH
N
N
HN
OTf
+ R—≡—H
L2PdCl2
CuI
Et2NH
R
72-76%

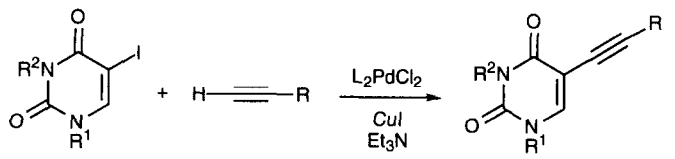
(220)


Et
NH
N
N
HN
H
+
I
I
PdCl2
Et3N
Ph3P
60%

(221)

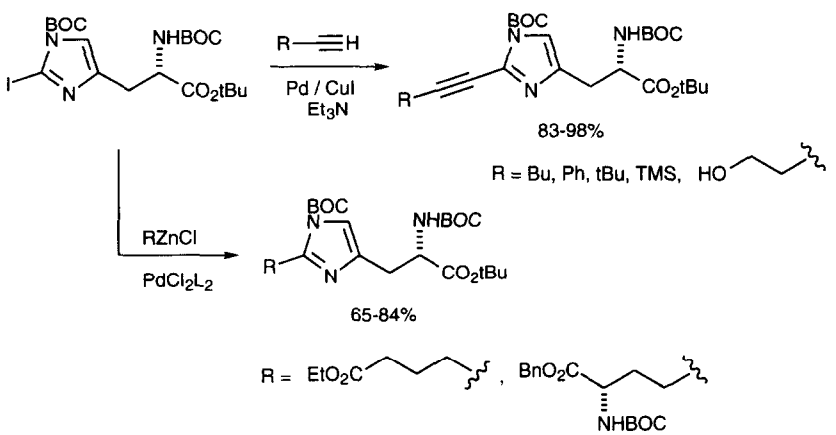


(222)

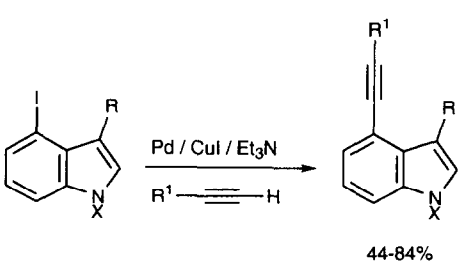


(223)

R = PhCO, pMeOPhCO, PhCHOH, CH_2OH, pMePh, oMePh

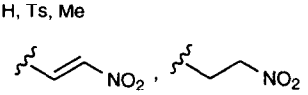


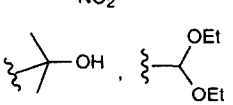
(224)



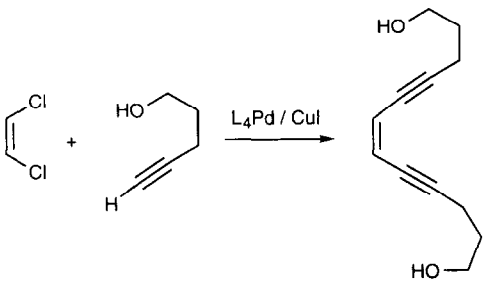
(225)

X = H, Ts, Me

R = 

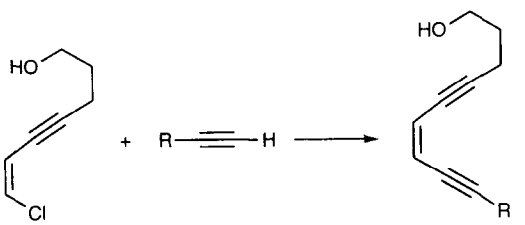
R^1 = TMS, nBu, CHOH, 

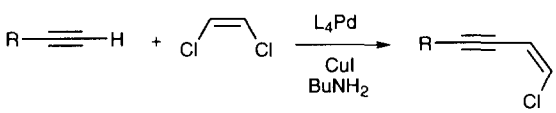
This palladium-catalyzed alkylation of alkynes has been extensively used in the synthesis of ene–diyne antitumor antibiotics, a topic which has been reviewed (38 references) [274]. Examples are seen in Eqs. (226)–(232) (from Refs. [275–281] respectively).

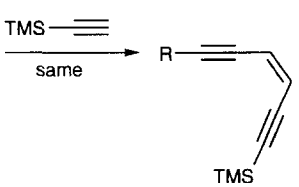


and

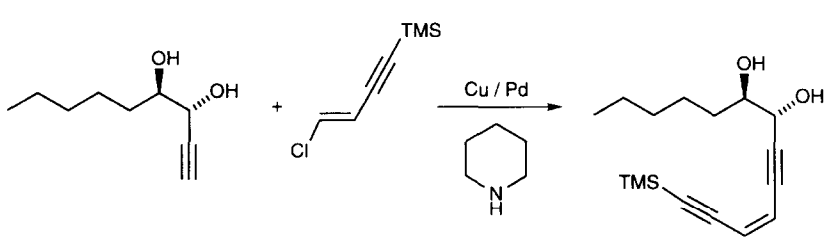
87% (226)



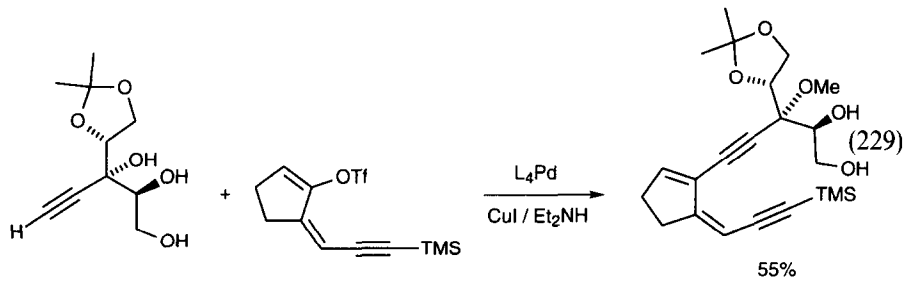




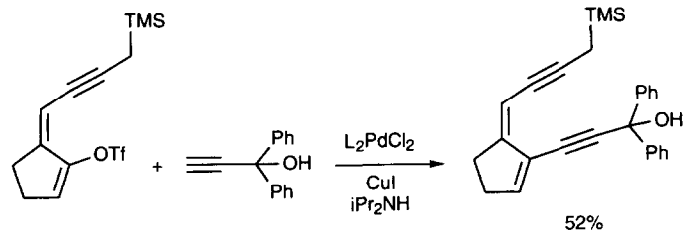
$R = R_3Si$ (227)



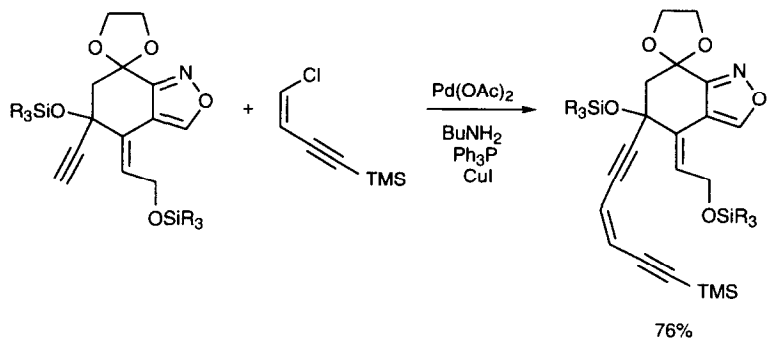
75% (228)



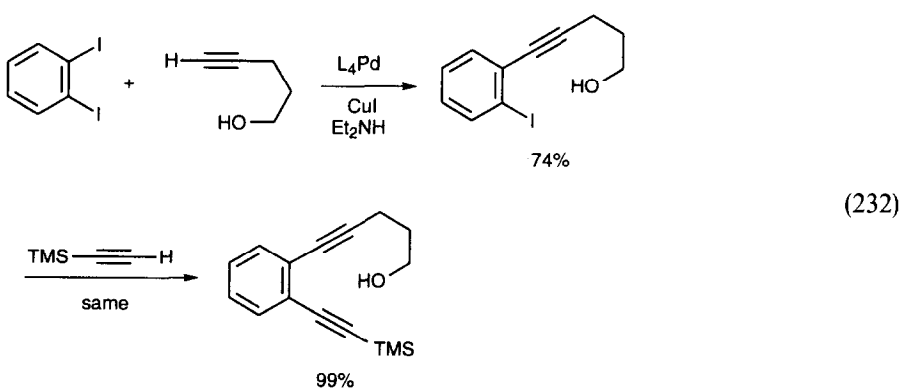
(229)



(230)

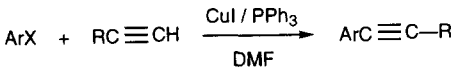


(231)



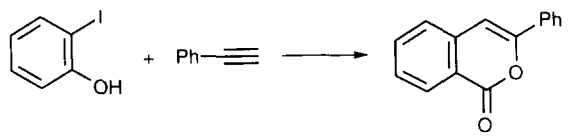
(232)

Copper salts directly coupled alkynes to aryl halides (Eq. (233)) [282], to nitrones (Eq. (234)) [283], and to acetylenic halides (Eq. (235)) [284]. Cuprates added to alkynes to generate allenes (Eq. (236)) [285] or vinyl cuprates (Eq. (237)) [286].



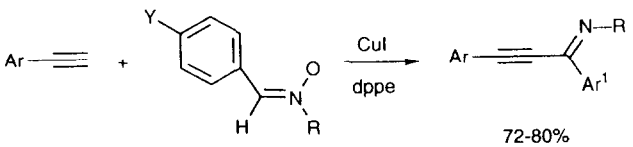
13 cases

and



19%

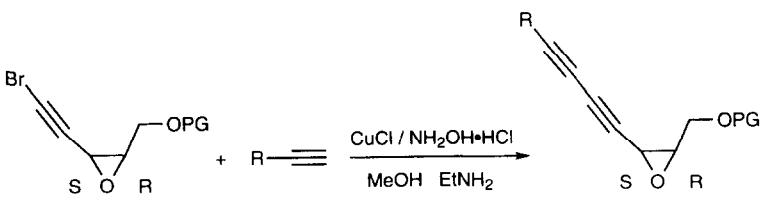
(233)



72-80%

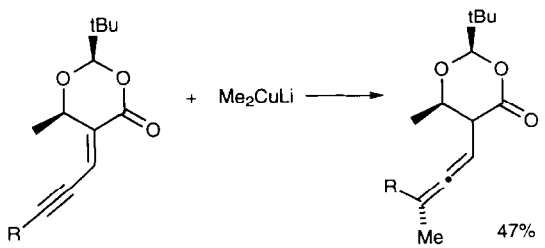
(234)

Ar = Ph, pMeOPh, pMePh Y = H, Me, Cl R = Ph, Me



50-90%

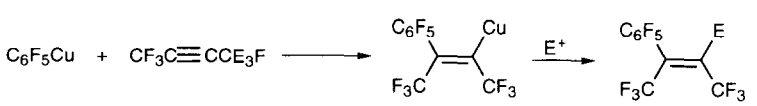
(235)

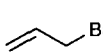
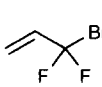


47%

94% this enantiomer

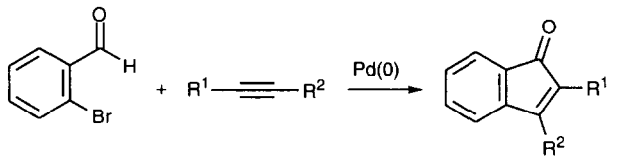
(236)



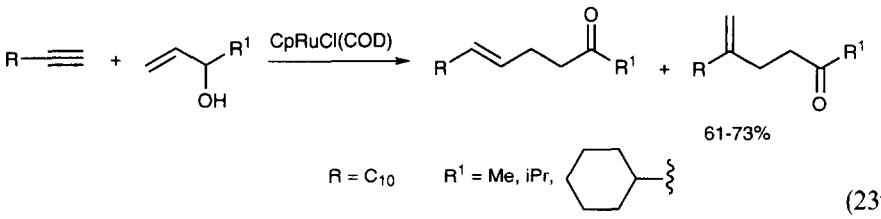
E = C_6F_5I, PhI, MeI,  ,  , CF_3CF_3COCl

(237)

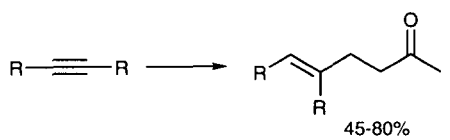
Palladium(0) catalyzed the reaction of alkynes with *o*-bromobenzaldehyde to produce indenones (Eq. (238)) [287]. Ruthenium complexes catalyzed the reaction between alkynes and allylic alcohols to produce enones (Eq. (239)) [288]. Alkynes inserted into nickelocyclopentanes (Eq. (240)) [289]. Palladium(II) catalyzed the addition of allylic halides to alkynes (Eq. (241)) [290]. Zirconocycles also underwent reaction with alkynes (Eq. (242) [291] and Eq. (243)) [292]).

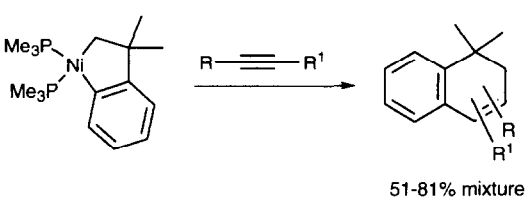


(238)

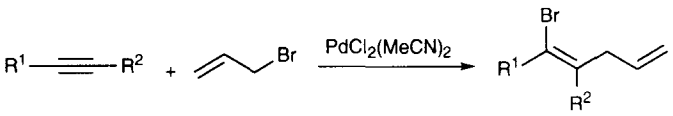


(239)





(240)

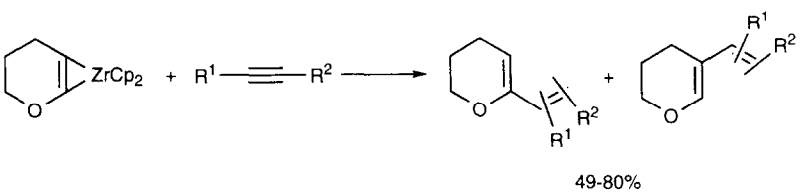


(241)

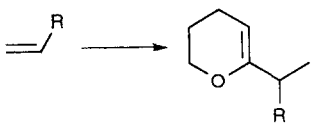
R^1 = Bu, TMS, Ph, H, $EtCH_2$

R^2 = H, COMe

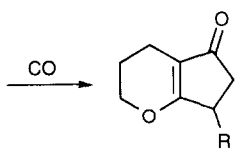
49-72%



49-80%

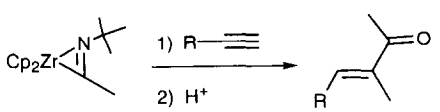


(242)



R^1 = Pr, TMS, nBu

R^2 = Pr, Me, H



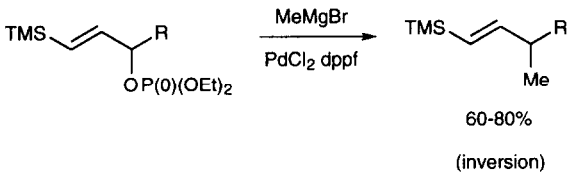
(243)

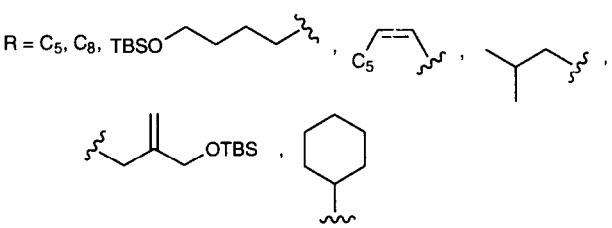
R = H, TMS, Ph

2.1.7. Alkylation of allyl, propargyl, and allenyl systems

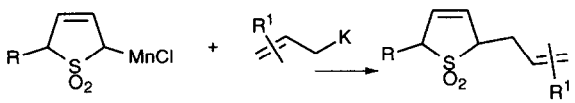
Silica-supported palladium complexes catalyzed the regioselective allylation of Grignard reagents [293]. The stereochemistry of the cross-coupling of crotyl alcohol derivatives with aryl magnesium bromide in the presence of chiral ligands was studied [294]. Palladium catalyzed the alkylation of allyl phosphonates by methyl Grignard reagents (Eq. (244)) [295]. Organomanganese derivatives of 3-sulfolenes cross-coupled with allyl and propargyl bromides (Eq. (245)) [296].

In the palladium-catalyzed alkylation of allylic acetates by stabilized carbanions, the reaction is reversible, and the kinetic product can rearrange to the more stable product [297]. The regioselectivity of alkylation of dienyl acetates was dependent on counterion (Eq. (246)) [298]. The stereoselectivity was related to the stereochemistry of the acetate (Eq. (247)) [299]. Enzyme oxidation of dienes was combined with palladium-catalyzed allylic reactions to give chiral products (Eq. (248)) [300].

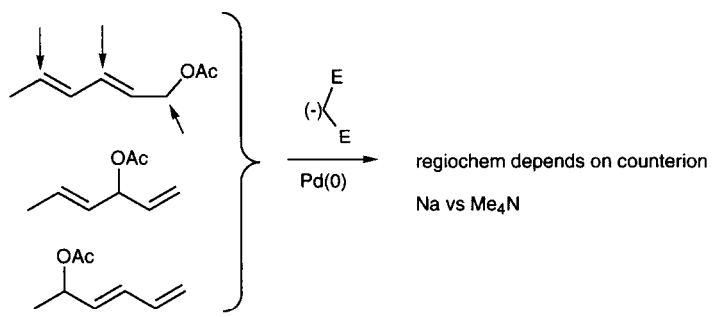




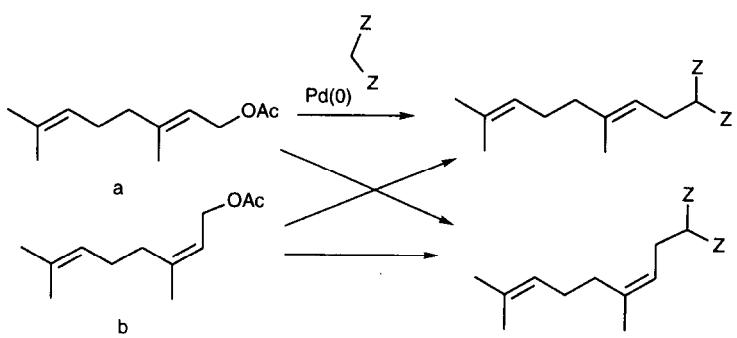
(244)



(245)

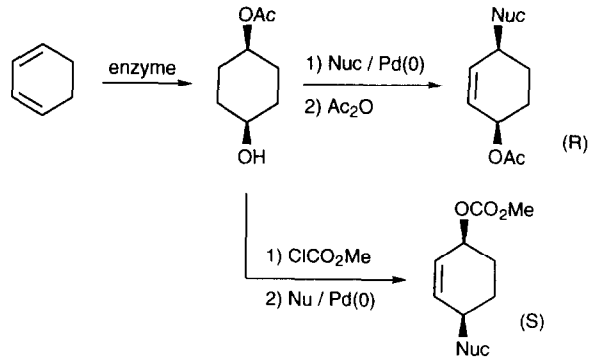


(246)



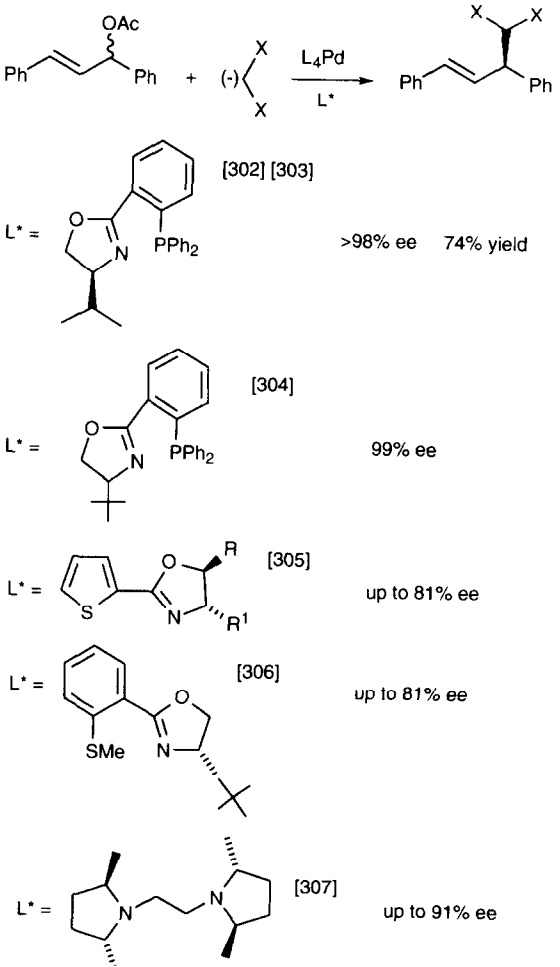
a	88:12	71%
b	36:66	43%

(247)



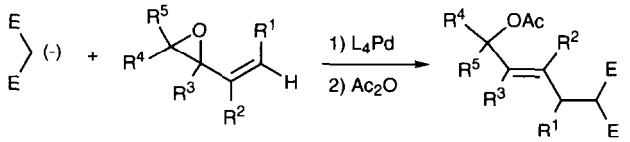
(248)

Palladium-catalyzed asymmetric allylic alkylation of racemic allyl acetates was reviewed (19 references) [301]. Everybody seems to have discovered that chiral oxazoline ligands were effective for this process (Eq. (249)) [302–306]. Chiral diamines also worked [307].

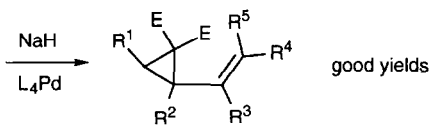


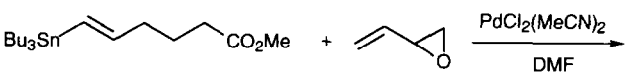
(249)

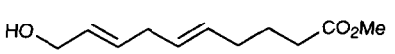
Palladium catalyzed the allylic alkylation of vinyl epoxides by stabilized carbanions (Eq. (250)) [308], by vinyl stannanes (Eq. (251)) [309] and by aryl and vinyl halides (Eq. (252)) [310]. Vinyl oxetanes (Eq. (253)) [311] and vinyl β-lactams (Eq. (254)) [312] were also alkylated under palladium catalysis. Rhodium catalyzed the alkylation of allyl alcohols by alkynes (Eq. (255)) [313].



(250)

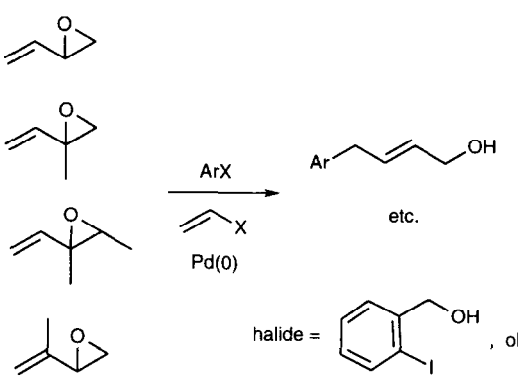




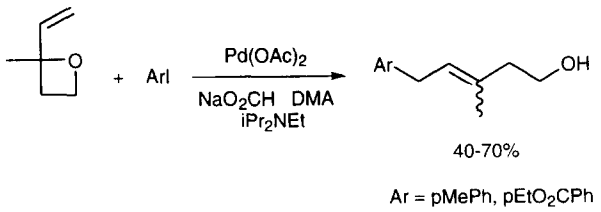


93%

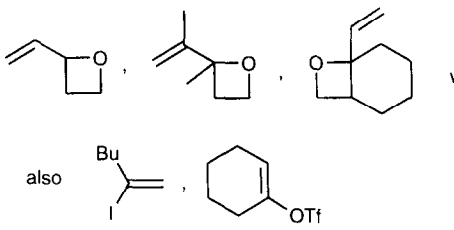
(251)

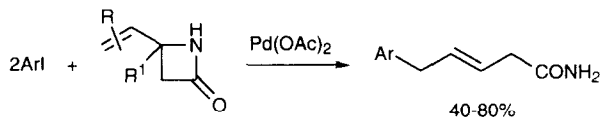


(252)

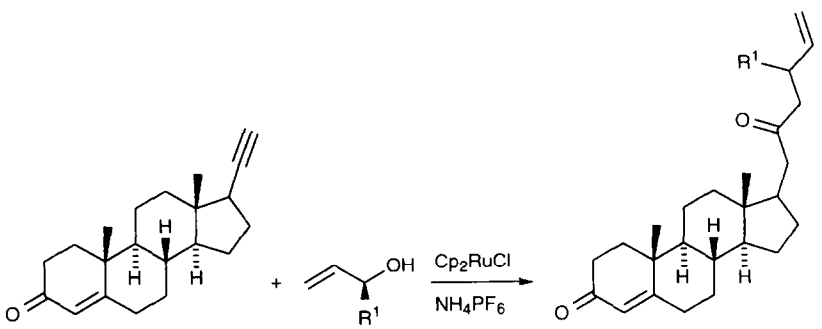


(253)



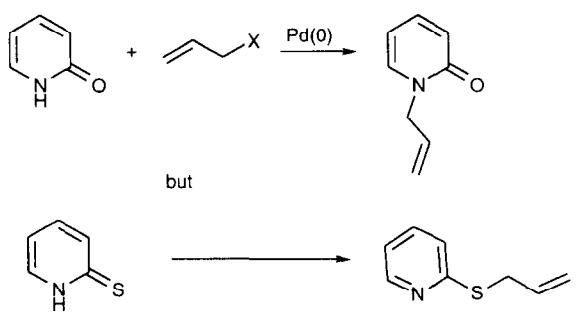


(254)



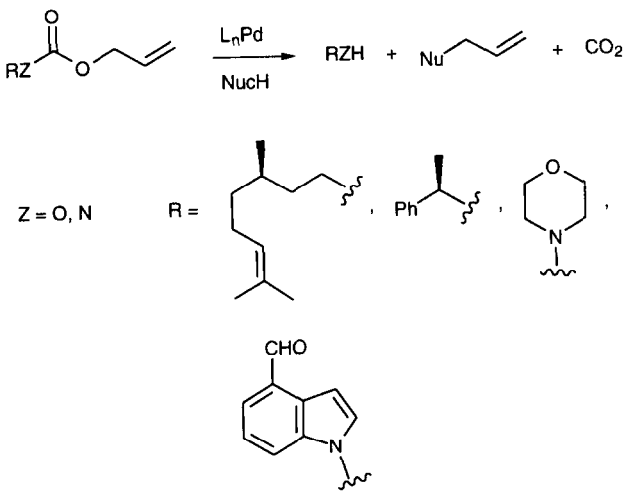
(255)

Palladium(0) catalyzed the alkylation of uracils at nitrogen, but thiouracils at sulfur (Eq. (256)) [314]. It also catalyzed the S-alkylation of five-membered ambident

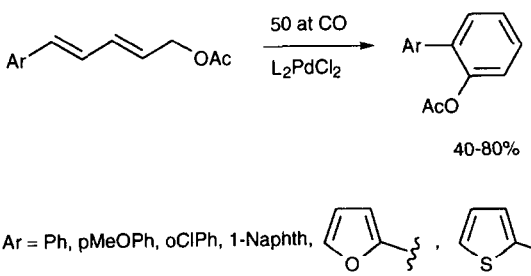


(256)

sulfur nucleophiles [315]. Palladium(0) effectively catalyzed the removal of allyl ester protecting groups (Eq. (257)) [316]. It also catalyzed a strange cycloaromatization of aryl dienylacetates (Eq. (258)) [317].

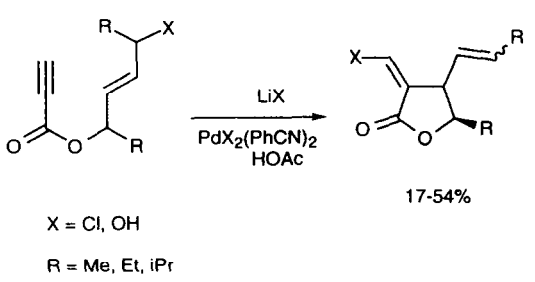


(257)

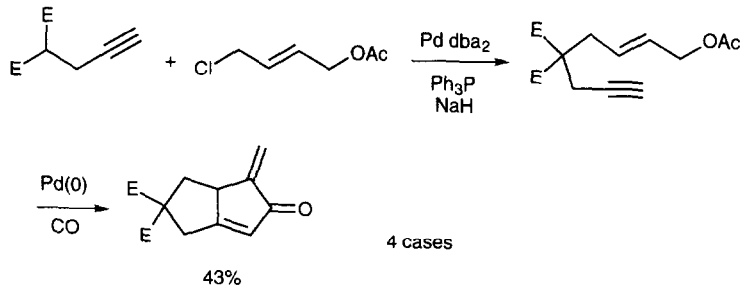


(258)

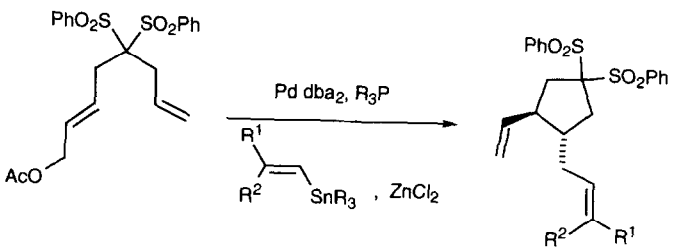
Palladium catalyzed the cyclocoupling of alkynes (Eq. (259) [318,319], Eq. (260) [320]) and alkenes (Eq. (261)) [321] into allylic systems. Rhodium catalyzed a similar process (Eq. (262)) [322]. Other allyl alkylations are seen in Eq. (263) [323] and Eq. (264) [324].



(259)



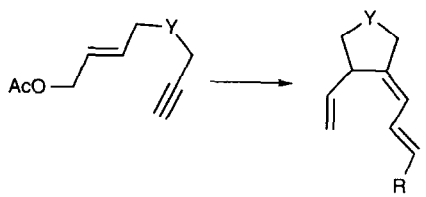
(260)

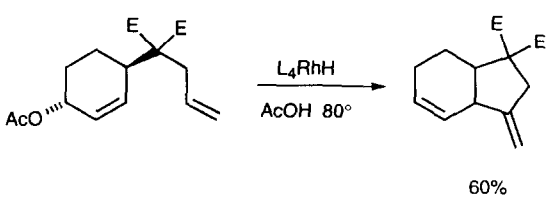


R^1 = H, TMS, CH_2OTHP, CH_2NFMOC 65-85%

R^2 = H, CO_2Et_2 (261)

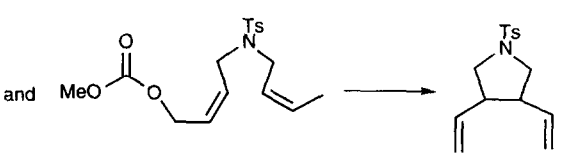
and

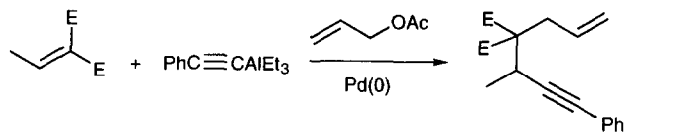


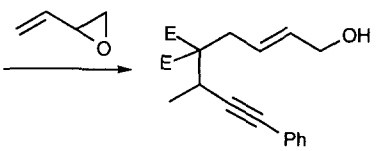


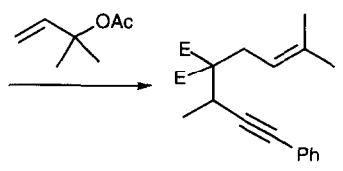
(262)

and

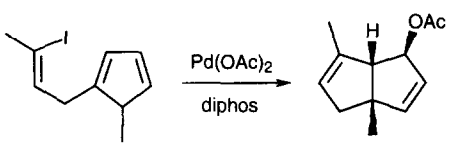






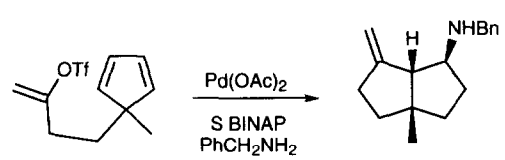


(263)



52%

and

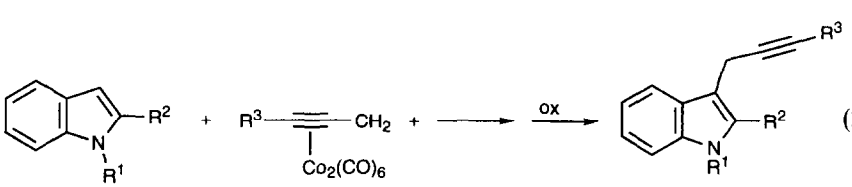


76%

(264)

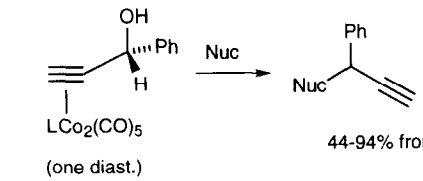
Cobalt-stabilized propargyl cations were alkylated by indoles (Eq. (265)) [325], trimethylcylsilylenol ethers (Eq. (266)) [326] and oxazolidinone enolates (Eq. (267)) [327]. This last process was used in the synthesis of thienamycin [328].

Iron carbonyl catalyzed allylic alkylations (Eq. (268) [329] and Eq. (269) [330]). Ruthenium catalyzed the alkylation of allyl carbonates (Eq. (270)) [331].

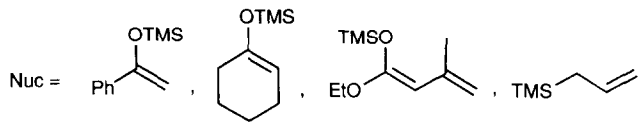


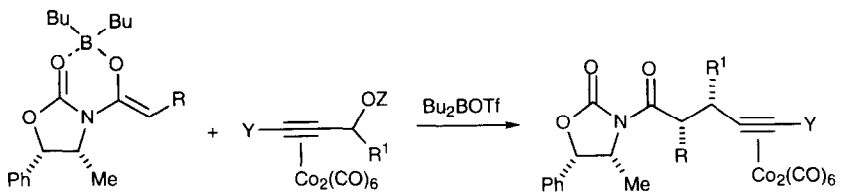
50%

(265)



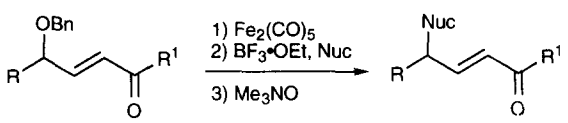
(266)





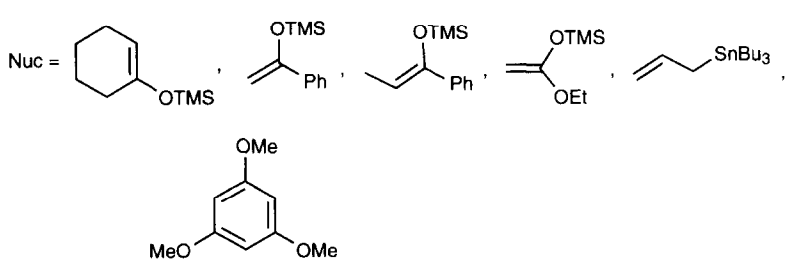
(267)

highly diastereoselective

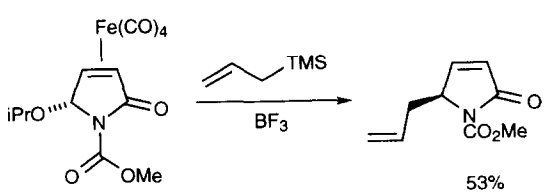


50-80%

R^1 = Me, iPr, Ph R = Me, H, Et

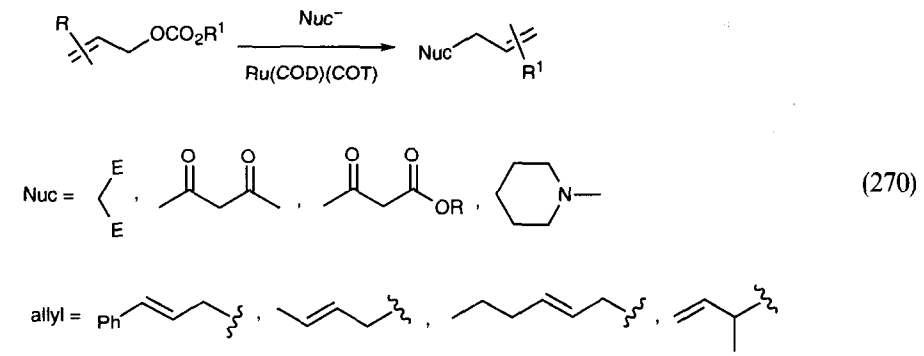


(268)



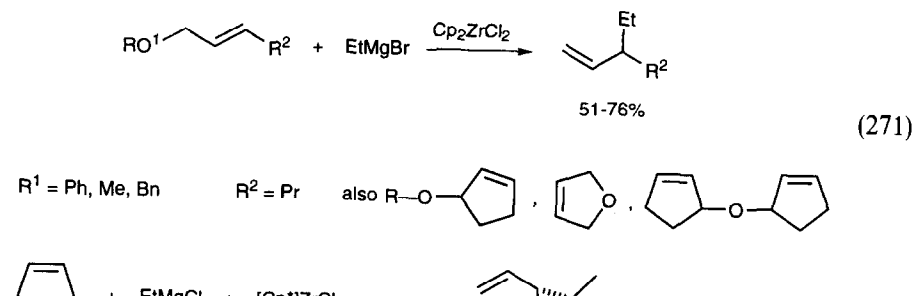
(269)

53%
55% ee

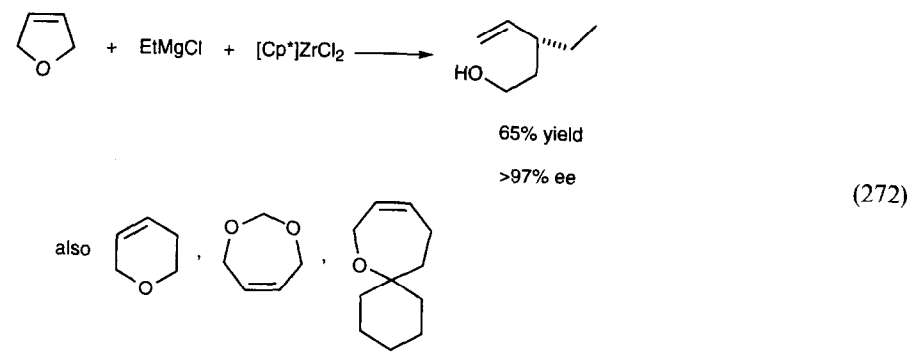


(270)

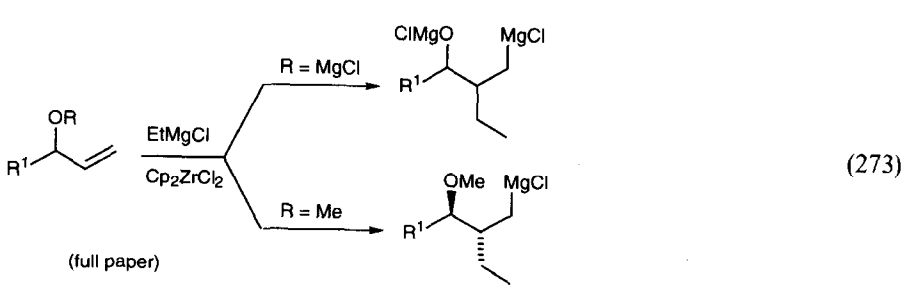
Zirconocene dichloride catalyzed the alkylation of allyl ethers by Grignard reagents (Eq. (271) [332] and Eq. (272) [333]). The zirconium-catalyzed addition of Grignards to allylic alcohols was the subject of a full paper (Eq. (273) [334] and Eq. (274) [335]). Dibutylcuprate effected a bridgehead allylic alkylation (Eq. (275)) [336].



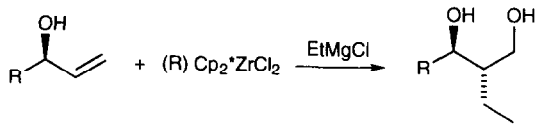
(271)



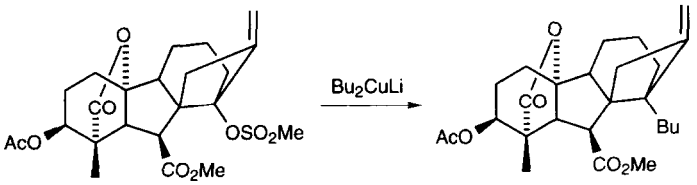
(272)



(273)



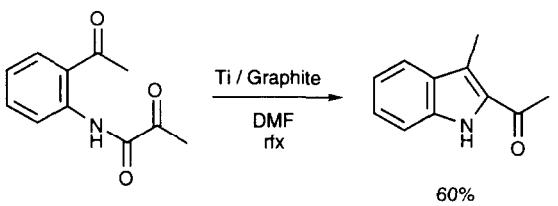
(274)



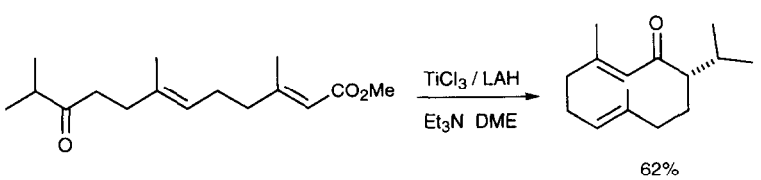
(275)

2.1.8. Coupling reactions

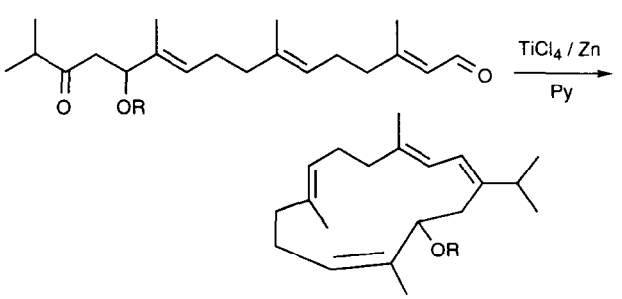
The stereochemistry of titanium(0)-induced pinacol coupling was the subject of a theoretical study [337]. This process (McMurray coupling) was useful for forming small (Eq. (276)) [338], medium (Eq. (277) and (278) [339–340]), and large (Eq. (279)) [341] rings. Cross-coupling of ketones with acid chlorides and esters was also achieved (Eq. (280)) [342].



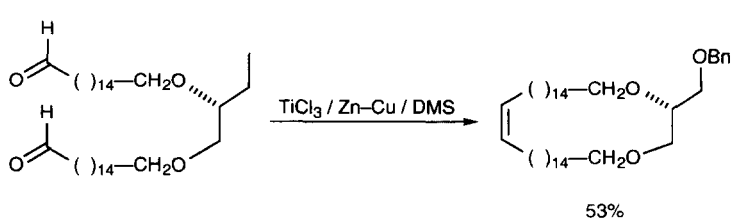
(276)



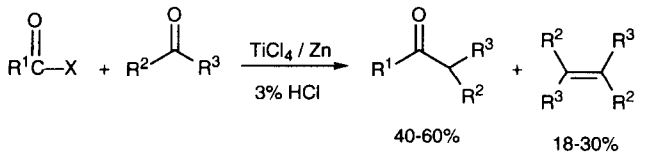
(277)



(278)

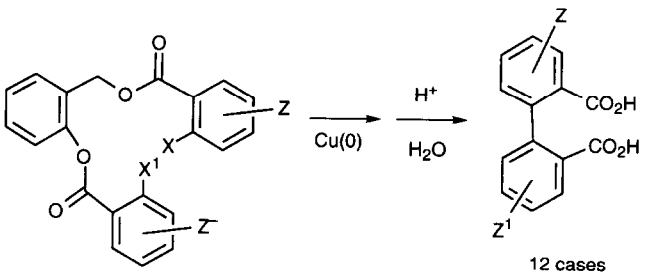


(279)

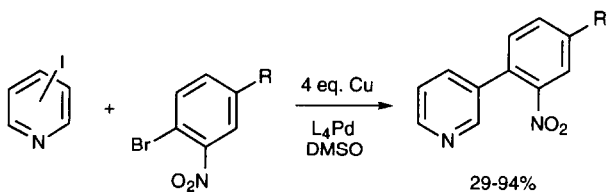


(280)

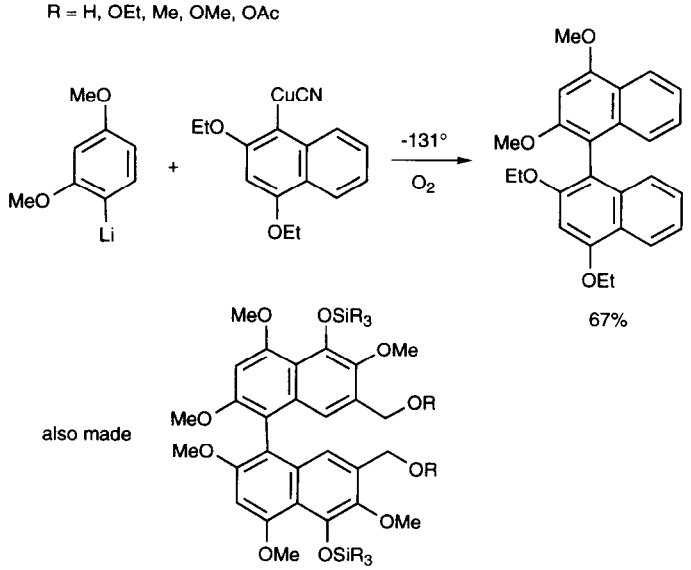
Unsymmetrical biaryls were made by linked Ulmann coupling (Eq. (281)) [343], by Pd–Cu-catalyzed cross-coupling (Eq. (282)) [344] and by very low temperature cuprate coupling (Eq. (283) [345] and Eq. (284) [346]). Cationic rhodium complexes coupled cresols (Eq. (285)) [347]. Gem divinyl halides were coupled to cumulenes by lithiation–copper coupling (Eq. (286)) [348].



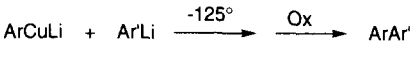
(281)



(282)



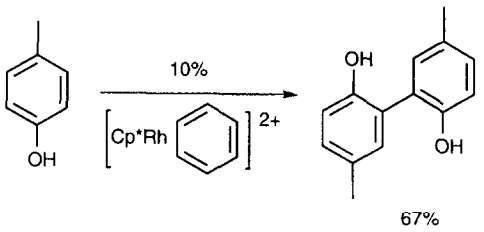
(283)



Ar = oMeOPh, Ph, oMePh, 2Cl,4CF$_3$Ph

Ar' = 3F,4MePh, 2Cl,4CF$_3$Ph, 3MeOPh, 4MeOPh

(284)

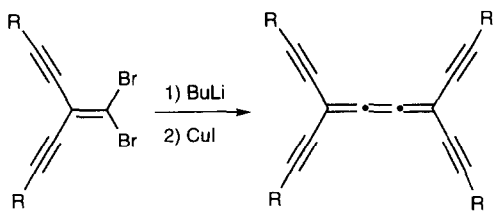


67%

always ortho coupling

10 cases

(285)



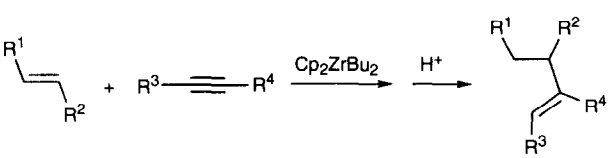
42-55%

R = TMS, TIPS

(286)

Zirconocene coupled alkynes to alkenes (Eq. (287) [349], Eq. (288) [350]) and alkynes to alkynes (Eq. (289)) [351]. Zirconacyclopentenes incorporated a variety of unsaturated substrates (Eq. (290)) [352].

Palladium or nickel catalyzed the dimerization of aryl triflates (Eq. (291)) [353], vinyl stannanes (Eq. (292)) [354], chloropyridines (Eq. (293)) [355], and aryl halides (Eq. (294)) [356] in the presence of reducing agents. Palladium catalyzed the coupling of vinyl or aryl halides to distannylalkanes (Eq. (295) [357,358], Eq. (296) [359], and Eq. (297) [360]).



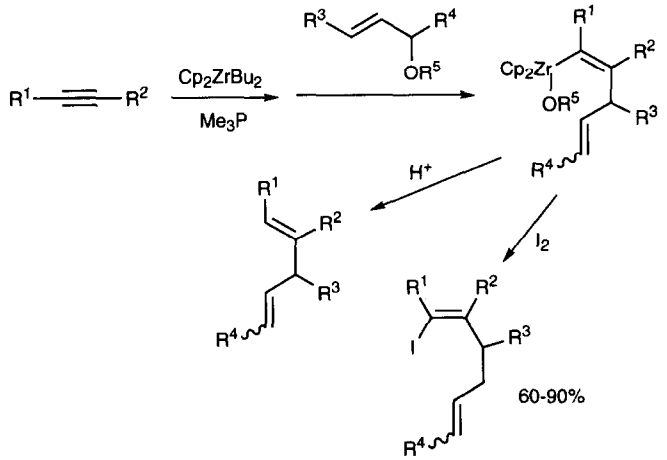
20 cases good yields

(287)

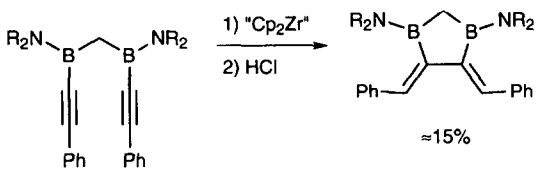
R^1 = H, nC_6, Ph, TMS, Bu_3Sn

R^2 = H

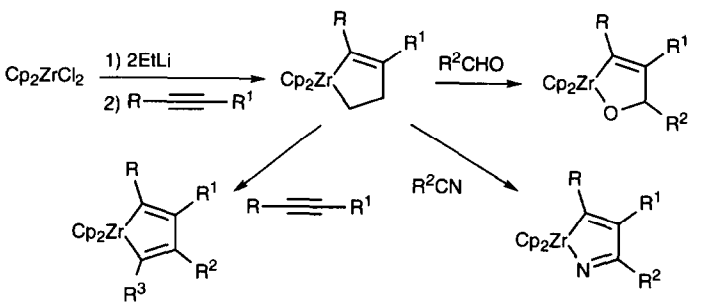
R^4,R^3 = Et, Bu, TMS, Ph



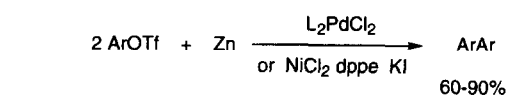
(288)



(289)

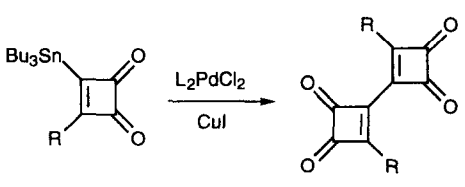


(290)

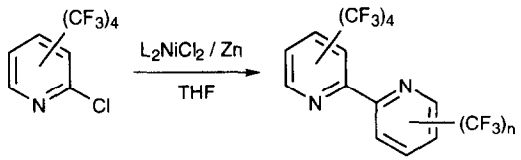


(291)

Ar = 1-Napht, pNCPh, pCF3Ph, pEtO2CPh, pClPh, Ph, oMePh, pMeOPh



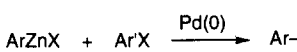
(292)



20-35%

(293)

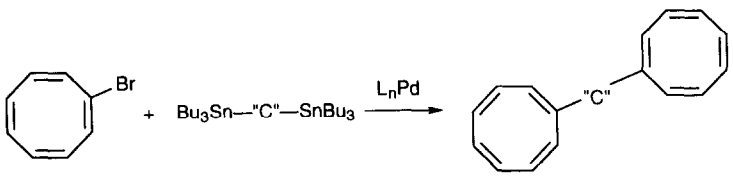
3-CF_3, 4-CF_3, 5-CF_3, 6-CF_3, 3,5$(CF_3)_2$



49-90%

≈20 cases

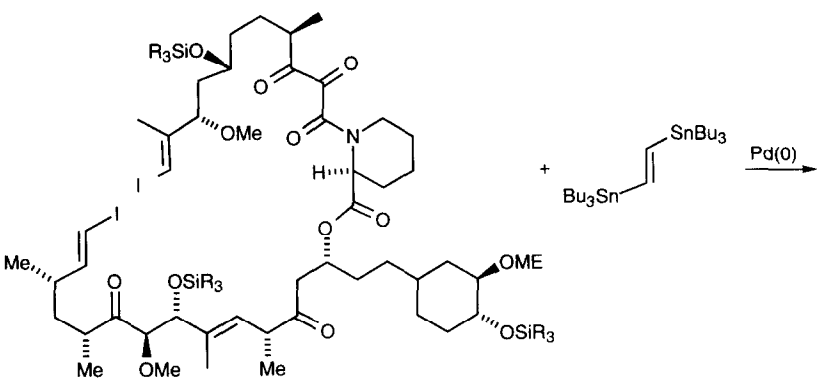
(294)



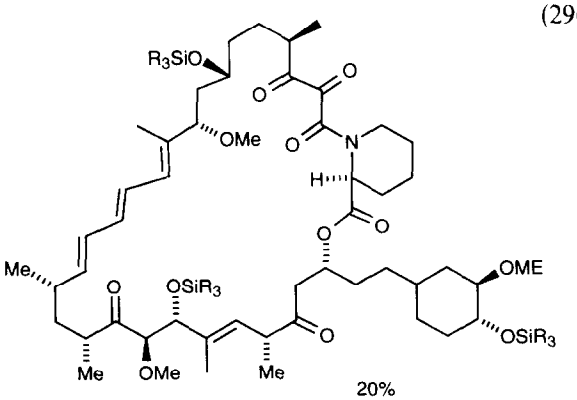
30-60%

(295)

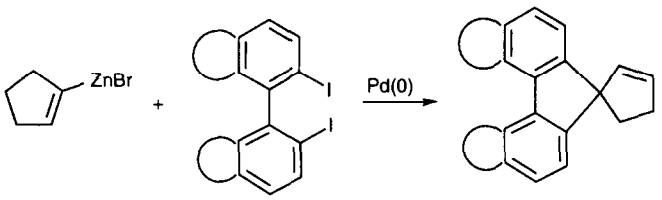
"C" = —C≡C— , , ,



(296)

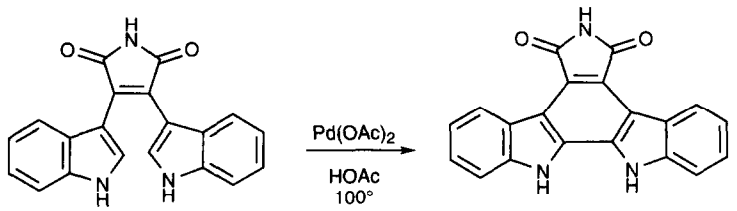


20%

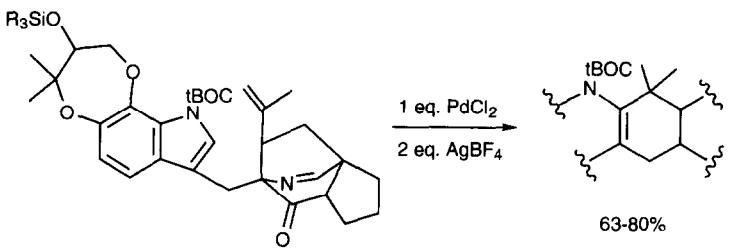


85% (297)

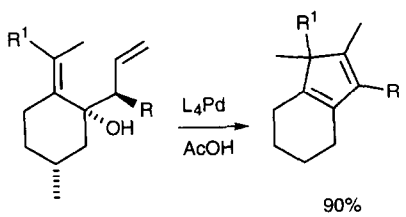
Palladium catalyzed the coupling of two indoles (Eq. (298)) [361], an alkene with an indole (Eq. (299)) [362] and two alkenes (Eq. (300)) [363]. σ alkyliron complexes coupled on decomposition (Eq. (301) [364], Eq. (302) [365], and Eq. (303) [366]).



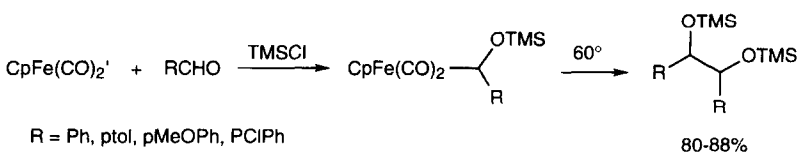
75% (298)



63-80% (299)

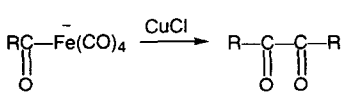


90% (300)

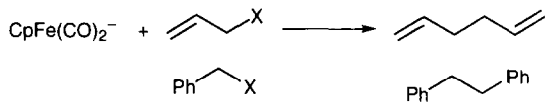


R = Ph, ptol, pMeOPh, PClPh

80-88% (301)

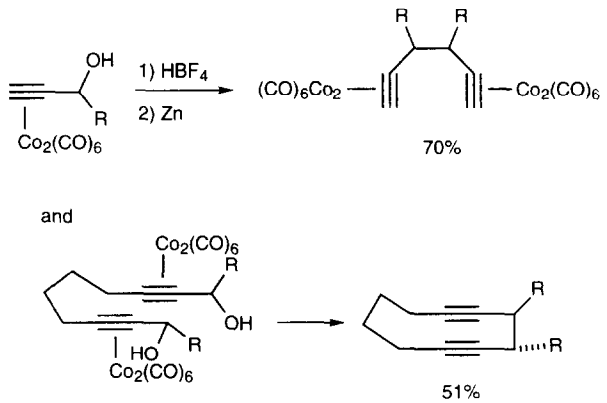


(302)

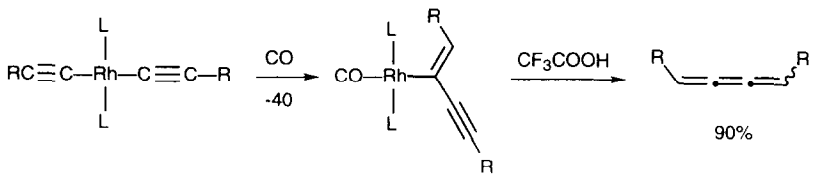


(303)

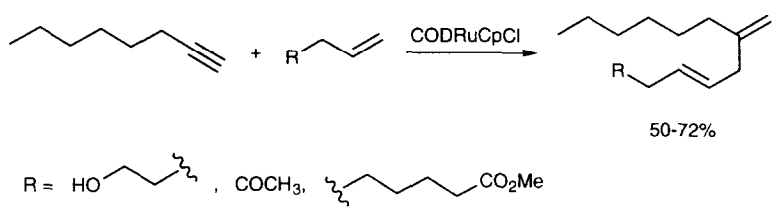
Ruthenium porphyrin complexes catalyzed the dimerization of ethyl diazoacetates at a rate of one turnover per second [367]. Cobalt-complexed propargyl cations underwent radical dimerization (Eq. (304)) [368]. Alkynes were coupled by rhodium complexes (Eq. (305)) [369]. Ruthenium complexes also catalyzed the coupling of alkynes to alkenes (Eq. (306)) [370].



(304)



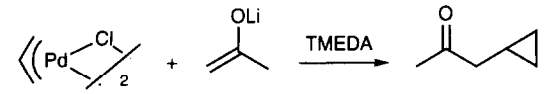
(305)

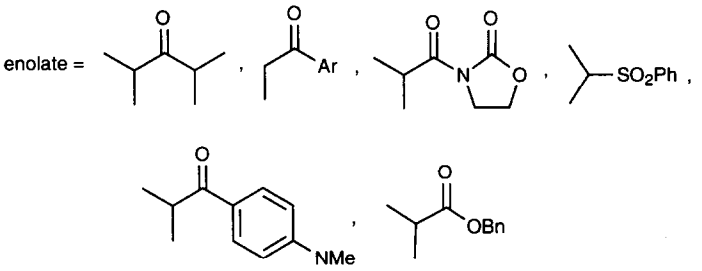


(306)

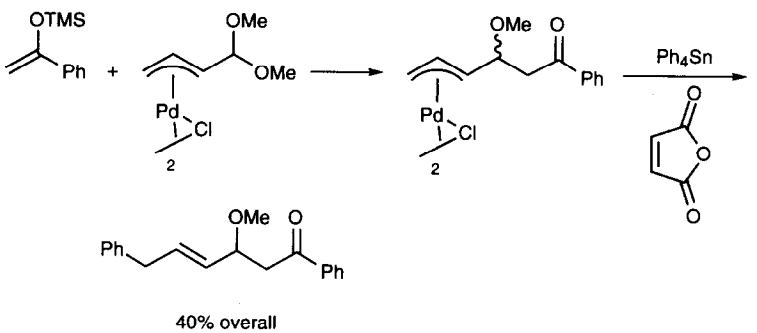
2.1.9. *Alkylation of π allyl complexes*

π allylpalladium complexes underwent alkylation at the central carbon with enolates as nucleophiles, in the presence of TMEDA (Eq. (307)) [371]. They also activated α-positions to nucleophilic attack (Eq. (308)) [372]. Functionalized organocuprates attacked π allyliron complexes at the less substituted terminus [373]. π allylnickel halides alkylated iodoimidazoles (Eq. (309)) [374]. Aldehydes were alkylated by π allylmolybdenum complexes (Eq. (310)) [375].

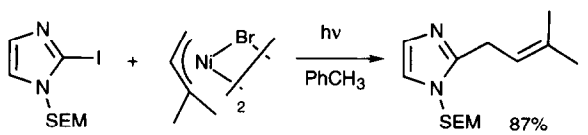




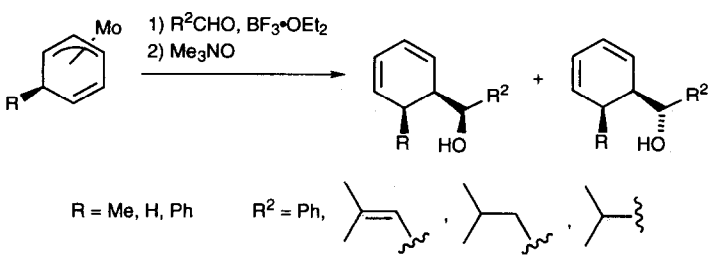
(307)



(308)



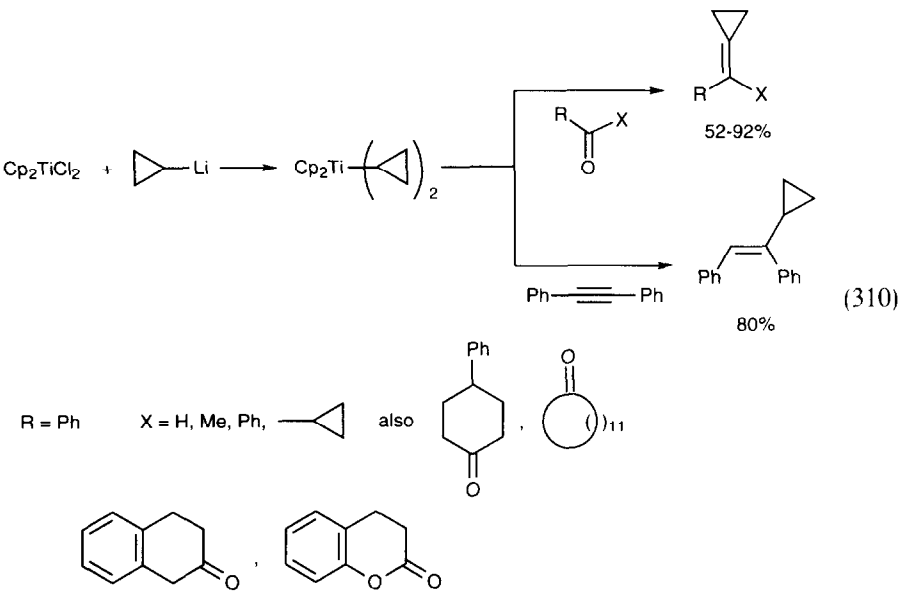
(309)



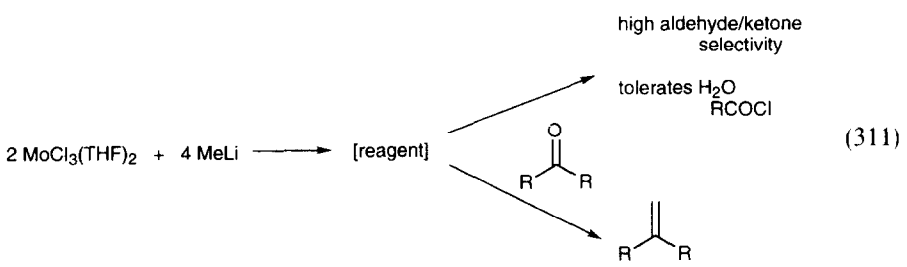
(309a)

2.1.10. Alkylation of carbonyl compounds

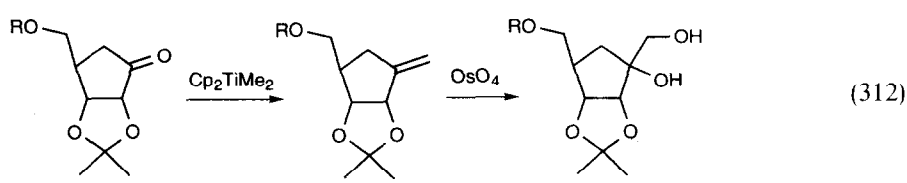
Carbonyl methylenation and alkylidenation using titanium-based reagents has been reviewed [376]. New reagents for cyclopropanylidation (Eq. (310)) [377] and selective methylenation (Eq. (311)) [378–380] have been developed. The Petasis reagent (Eq. (312)) [381] and Tebbe's reagent (Eq. (313)) [382] methylenated complex systems. A titanium reagent to produce allenes from aldehydes has been developed (Eq. (314)) [383]. Allenylstannanes converted aldehydes to 1,3-dienes in the presence of Cp_2ZrHCl (Eq. (315)) [384]. Alkynes methylenated aldehydes in the presence of reduced tantalum species (Eq. (316)) [385].



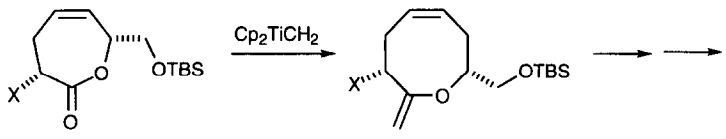
(310)

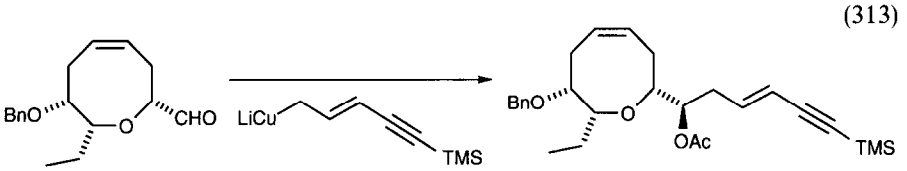


(311)

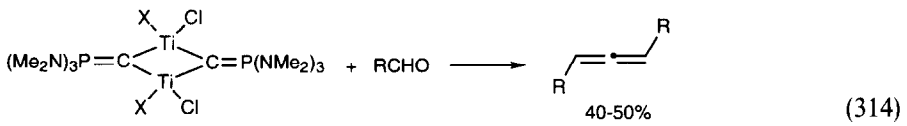


(312)

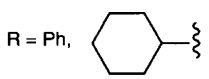


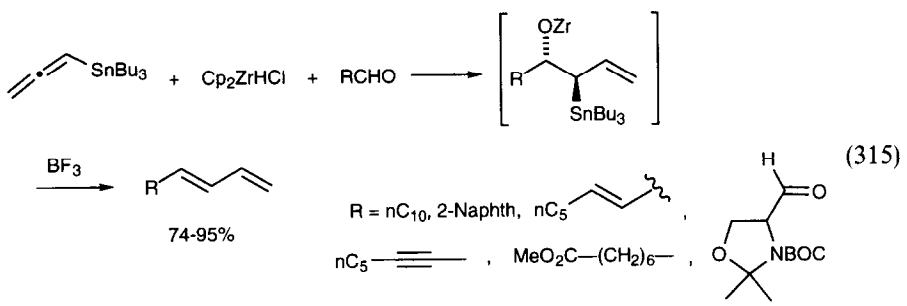


(313)

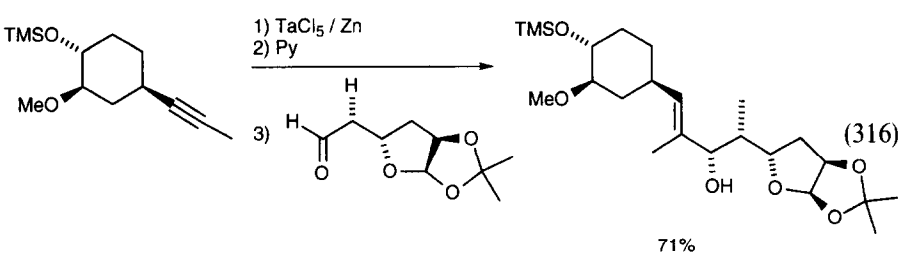


(314)





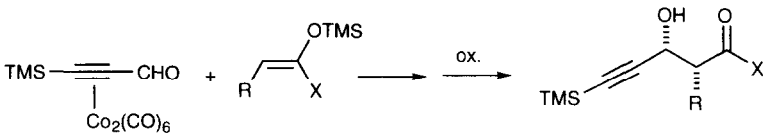
(315)



71%

(316)

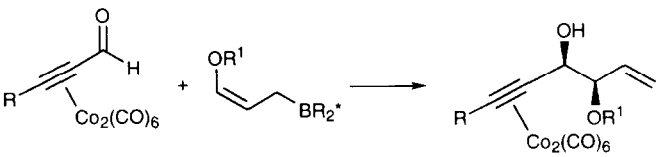
Cobalt-complexed propargaldehydes underwent aldol reactions with high *syn* selectivity (Eq. (317) and (318) [386–388]). Iron-complexed dienals were cleanly alkylated (Eq. (319) [389] and Eq. (320) [390]). Chromium complexation was used to control stereochemistry in the alkylation of aldehydes (Eq. (321) [391] and Eq. (322) [392]), and to control the reactivity of benzocyclobutane dione (Eq. (323) [393]).



84=90% >98% *syn*

R = Me, Et, iPr
R^1 = X = SR, OMe

(317)

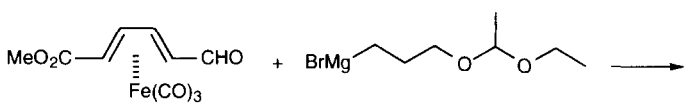


60-76% yield
>96% ee

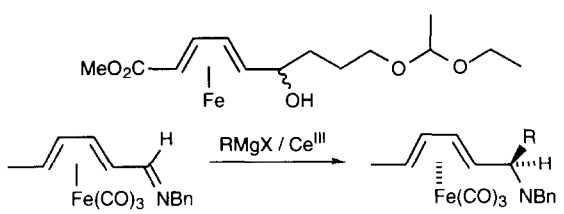
R = Ph, Me, H R^1 = Me, $MeOCH_3$

R* = isocampheyl

(318)

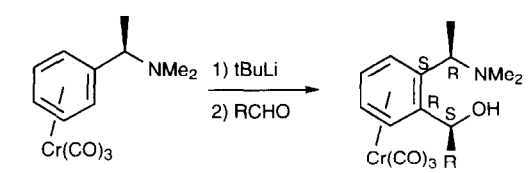


(319)



95% ≈100% de

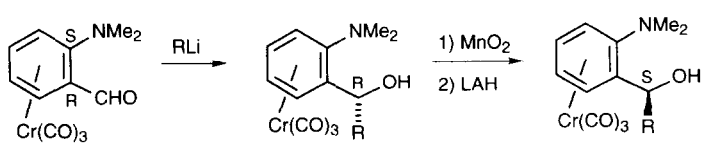
(320)



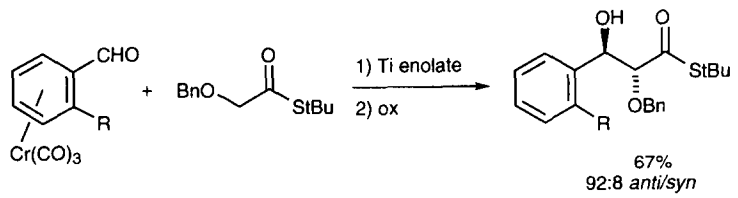
84-94%

and

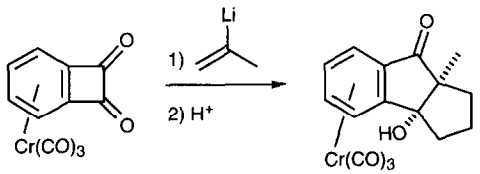
(321)

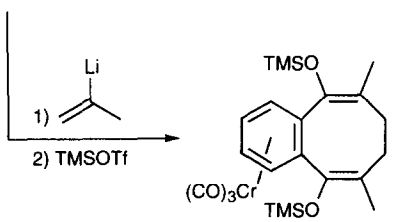


R = Me 92:8
Ph 73:27
H 1:99



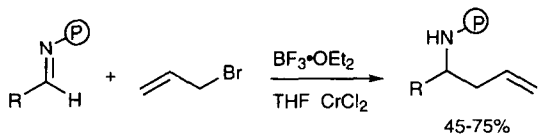
(322)



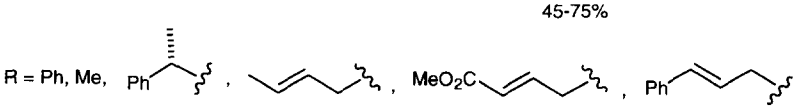


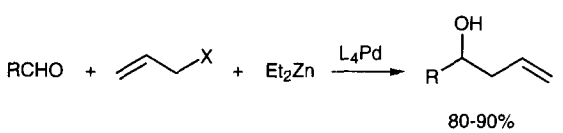
(323)

Imines were alkylated by allyl bromides in the presence of chromium(II) (Eq. (324)) [394]. Palladium catalyzed the allylation of aldehydes by allyl phenyl ethers in the presence of diethyl zinc (Eq. (325)) [395]. Cationic rhodium or iridium(I) complexes catalyzed the allylation of aldehydes by allyl stannanes (Eq. (326)) [396].

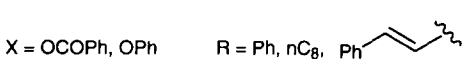


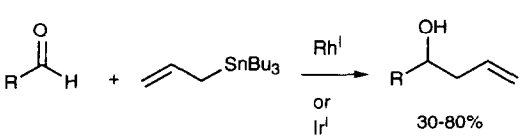
(324)





(325)

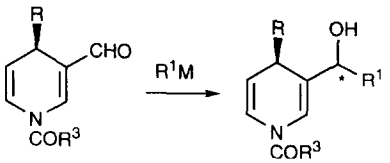




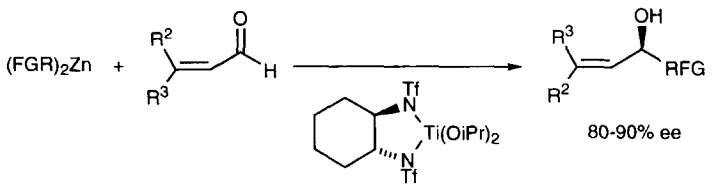
(326)

R = Ph, pMeOPh, 3,4,5-$(MeO)_3$Ph

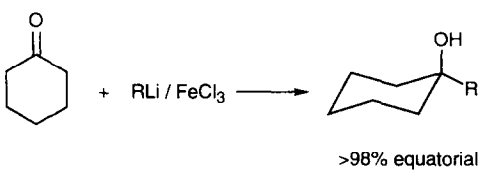
Miscellaneous alkylations of carbonyl compounds are shown in Eq. (327) [397], Eq. (328) [398] and Eq. (329) [399].



(327)

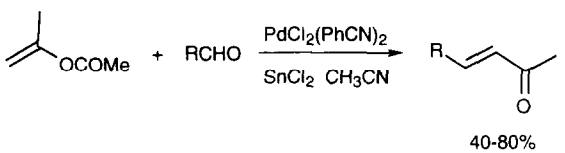


(328)



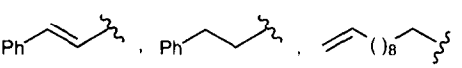
(329)

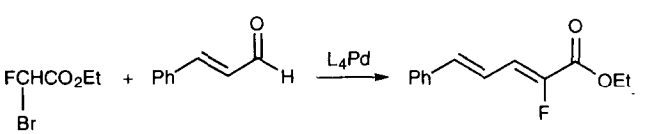
Palladium(II) complexes catalyzed the alkylation of aldehydes by enol ethers to give enones (Eq. (330)) [400] and by fluorinated bromo esters (Eq. (331)) [401]. An ester was alkylated by an aryl halide using palladium(0) catalysts (Eq. (332)) [402]. Zirconium diene complexes coupled to ketones and metal carbonyls (Eq. (333)) [403].



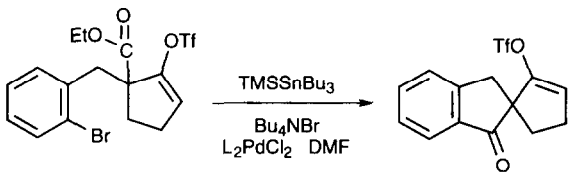
(330)

R = Ph, pMeO$_2$Ph, pMeOPh, mMeOPh, pMeOPh,

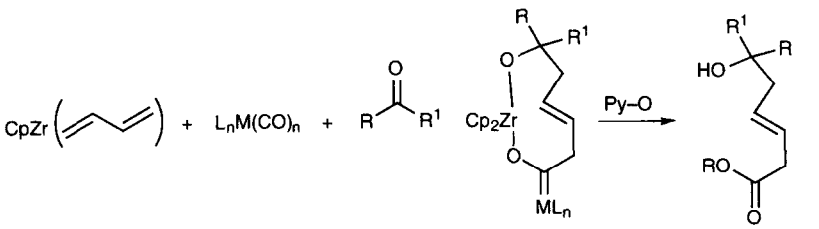
oNO$_2$Ph, pNO$_2$Ph, pCNPh, pClPh, 



(331)



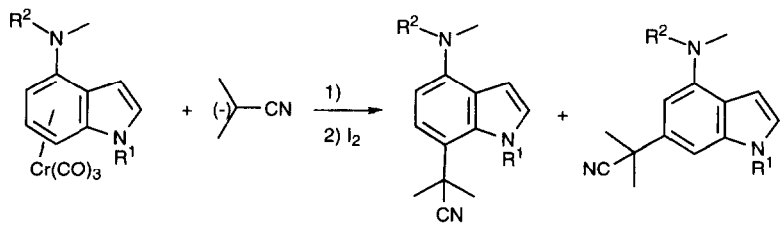
31% (332)



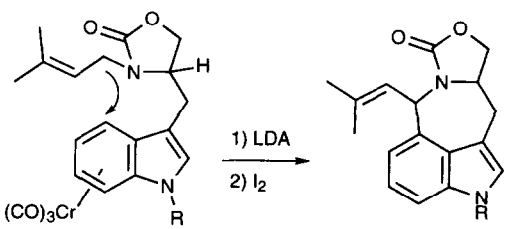
good yields (333)

2.1.11. Alkylation of aromatic carbonyls

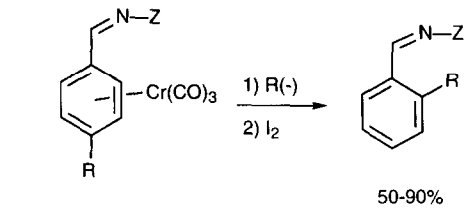
Reviews entitled "(η^6-Arene)chromium complexes in organic synthesis" (34 references) [404] and "Arenechromium tricarbonyl catalyzed reactions in organic synthesis" (72 references) [405] have appeared. The regioselectivity of alkylation of indoles complexed to chromium was a function of the substituent on the indole (Eq. (334)) [406]. Ergot alkaloids were prepared by related chemistry (Eq. (335)) [407]. Chromium-complexed benzaldehyde imines underwent efficient orthoalkylation (Eq. (336)) [408]. Chromium-complexed C-2 symmetric benzaldehyde acetals underwent diastereoselective *o*-lithiation–alkylation (Eq. (337)) [409].



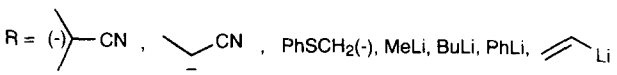
from 0:100 for R^1 = Ts, R^2 = Me
to 100:0 for R^1 = Me, R^2 = Ts or TBDMS (334)



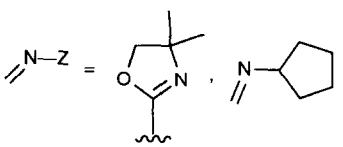
77% (335)

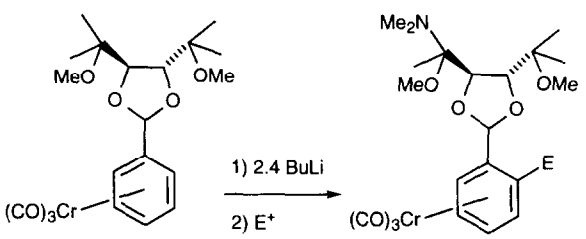


50-90%



(336)

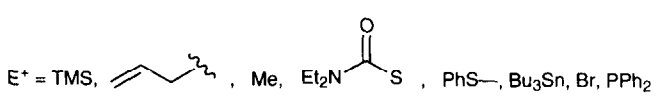




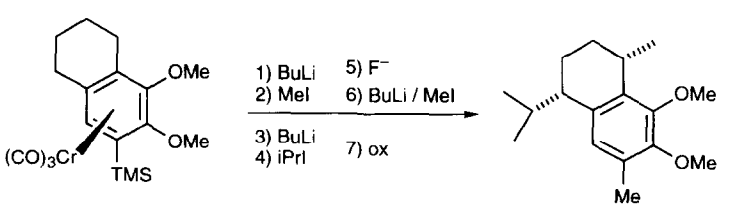
(337)

62-84%

86-95% de

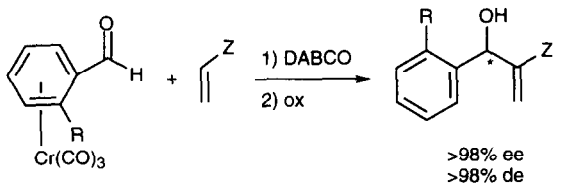


Arene chromium tricarbonyl stabilized benzylic carbocations were the topic of a review (39 references) [410]. Multiple applications of this process to an optically active chromium arene complex resulted in alkylation with high enantioselectivity (Eq. (338)) [411]. Chromium arene complexes were resolved by lipase [412]. Optically active chromium benzaldehyde complexes were alkylated with high stereoselectivity (Eq. (339) [413] and Eq. (340) [414]).

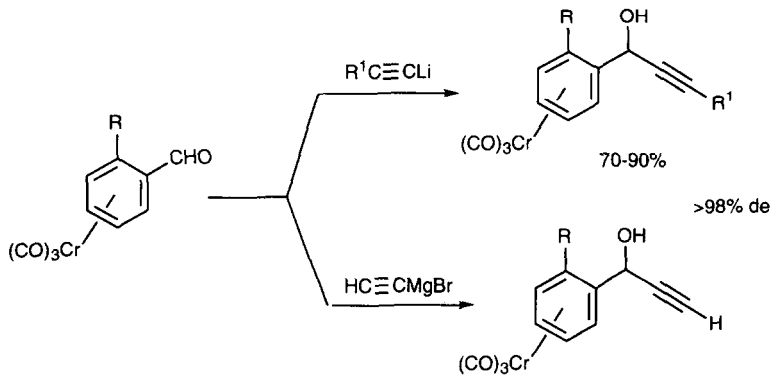


(338)

>95% ee

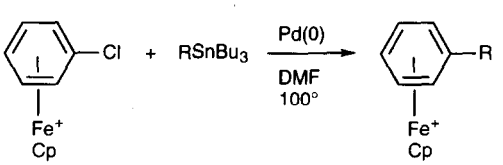


(339)



(340)

Cationic iron chlorobenzene complexes were readily alkylated (Eq. (341) [415] and Eq. (342) [416]). Cationic manganese arene complexes were diastereoselectively alkylated by chiral enolates (Eq. (343)) [417]. Cationic rhenium isoquinoline complexes were alkylated by carbanions stereoselectively (Eq. (344)) [418].



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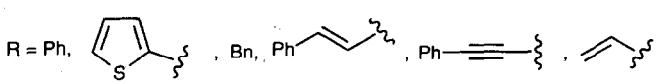

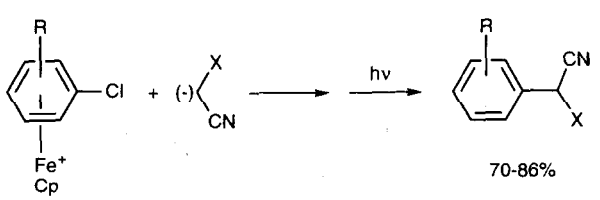

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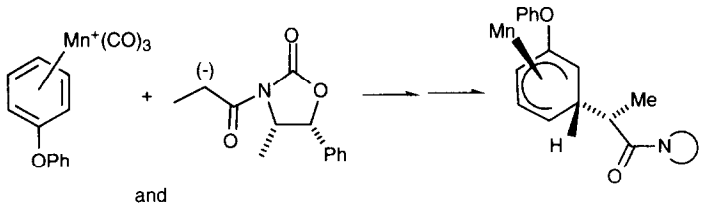

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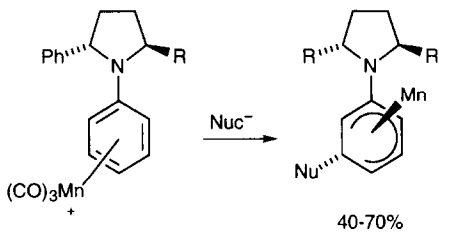
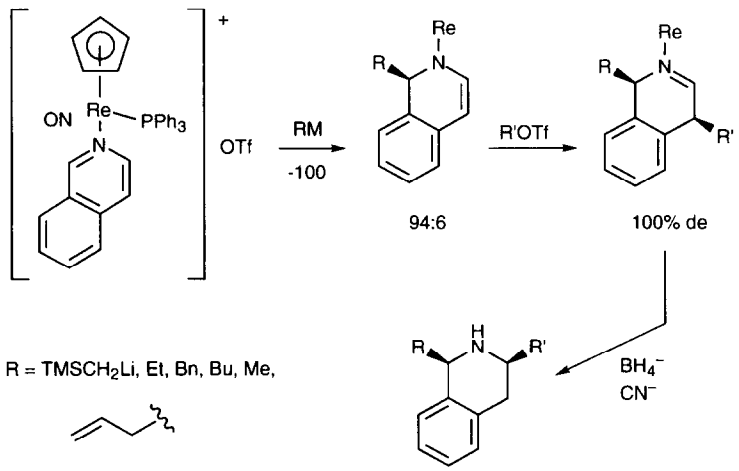


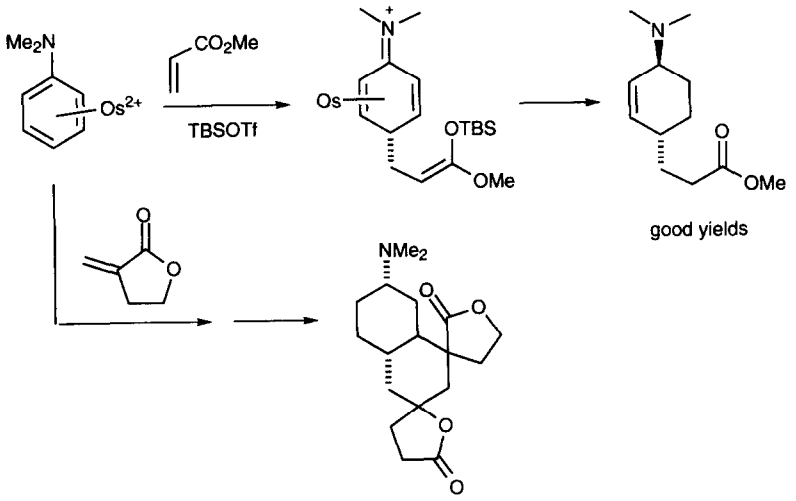


(344)

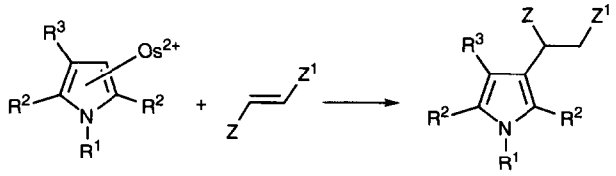
Osmium(II) complexes of dimethylaniline (Eq. (345)) [419] and pyrroles (Eq. (346)) [420] were subject to nucleophilic attack. Palladium catalyzed the alkylation of arenes by alkenes (Eq. (347)) [421] and by aryl triflates (Eq. (348)) [422]. Rhodium-catalyzed carbenoid insertions were used to alkylate arenes (Eq. (349)) [423].

2.1.12. *Alkylation of dienyl and diene complexes*

η^4-diene metal carbonyl complexes and their applications in organic synthesis were the topic of a review (23 references) [424]. Iron diene complexes were resolved by lipase (Eq. (350)) [425] or via their diastereomeric amide complexes (Eq. (351)) [426]. The amide group in tricarbonyl iron complexes of cyclohexadiene carboxamides interacted with the metal and altered the reactivity [427]. Cycloheptadienone complexes were cleanly α-alkylated (Eq. (352)) [428]. A total synthesis of the DIHETEs which heavily utilized iron diene complexes has appeared [429].

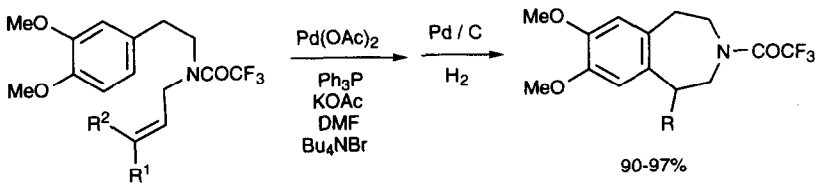


(345)



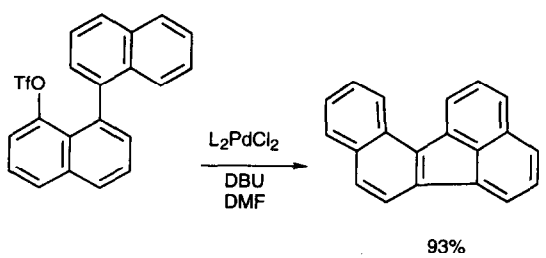
(346)

R's = H, Me, CO_2Me, 3Py Z = CO_2Me, CN



(347)

R^2, R^1 = H, Me



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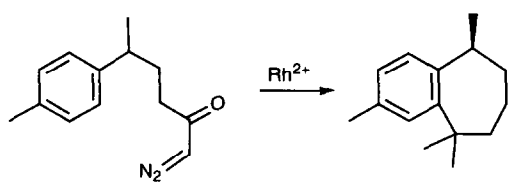
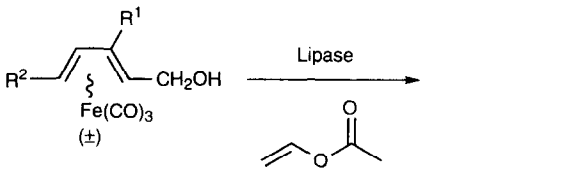
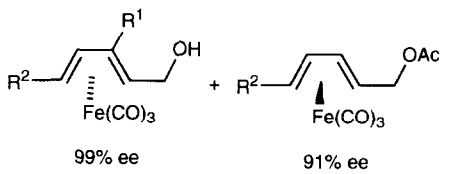
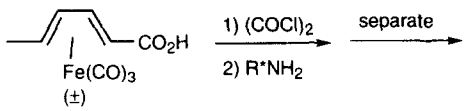


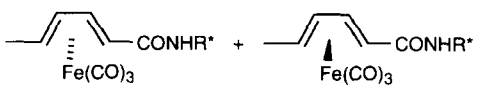
(349)



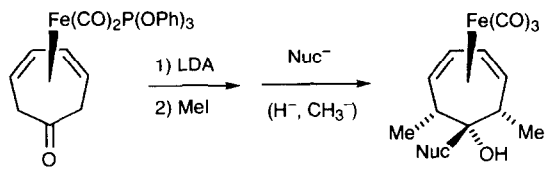
(350)





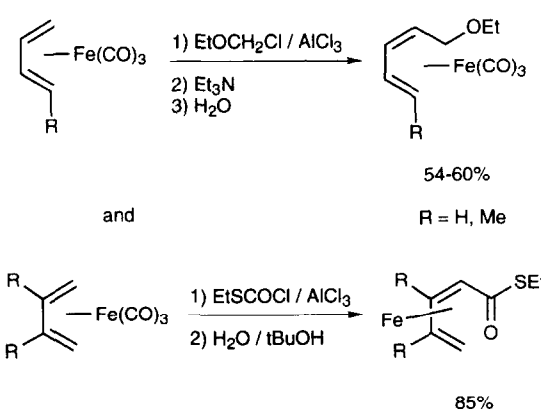


(351)

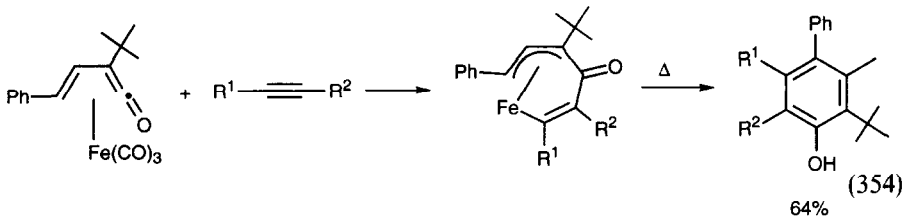


(352)

Iron diene complexes underwent electrophilic alkylation and acylation (Eq. (353)) [430]. Iron vinyl ketene complexes inserted alkynes and oxidatively closed (Eq. (354)) [431].

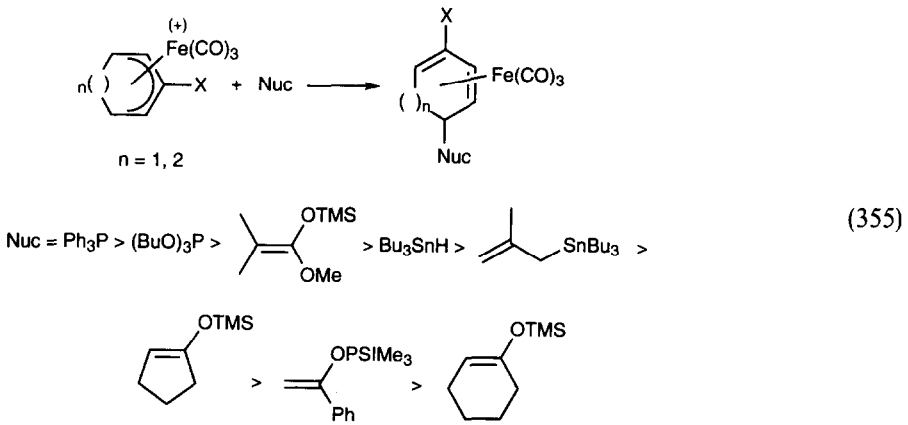


(353)

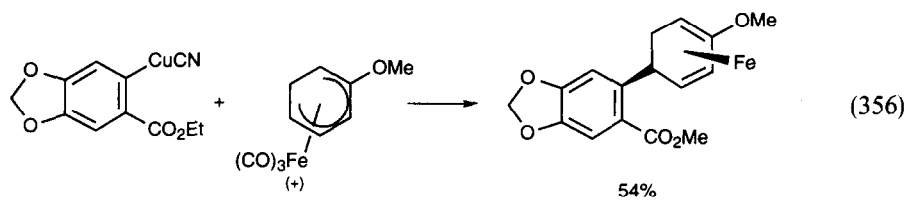


(354)

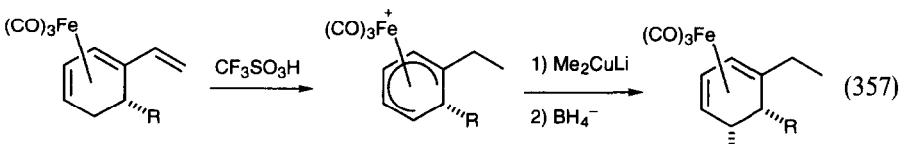
Regioselective nucleophilic additions to (η^4-diene) cobalt complexes was the topic of a dissertation [432]. Cationic dienyliron complexes underwent attack by a wide range of nucleophiles (Eq. (355) [433], Eq. (356) [434], Eq. (357) [435], Eq. (358) [436], and Eq. (359) [437]). This chemistry was used in the synthesis of a variety of alkaloids (Eq. (360) [438], Eq. (361) [439], Eq. (362) [440], and Eq. (363) [441]). Iron cyclooctadienyl complexes were also subject to nucleophilic attack (Eq. (364)) [442].



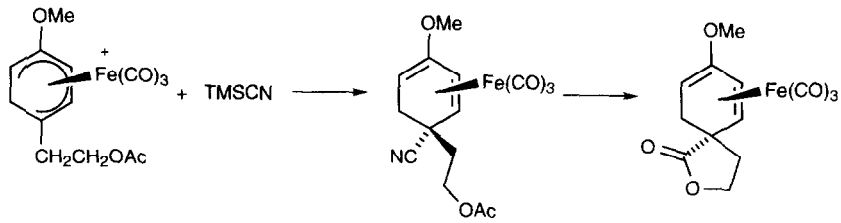
(355)



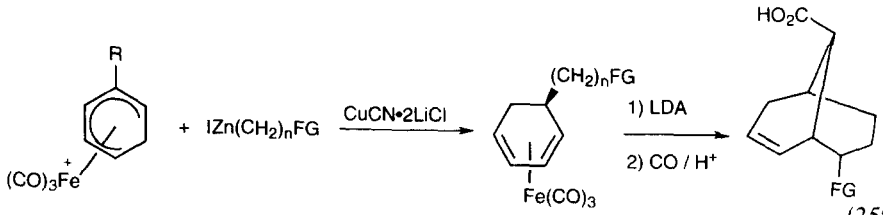
(356)



(357)

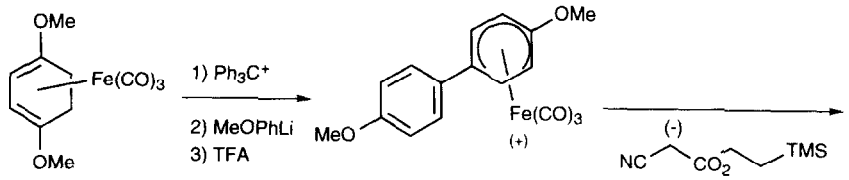


(358)

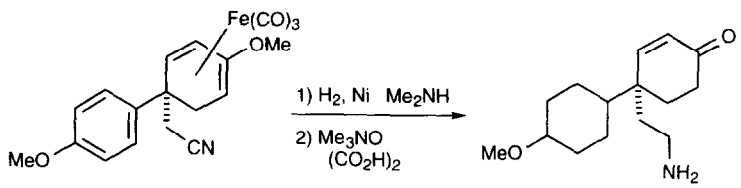


40-70%

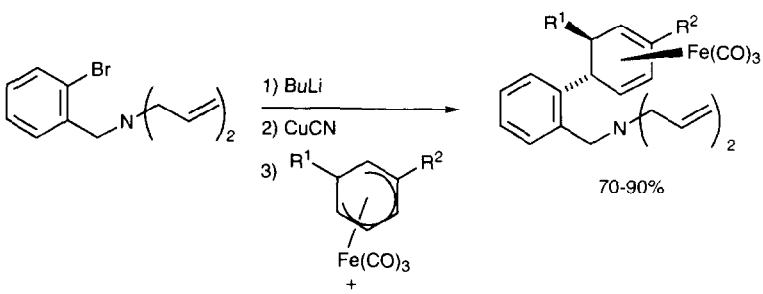
(359)



(360)

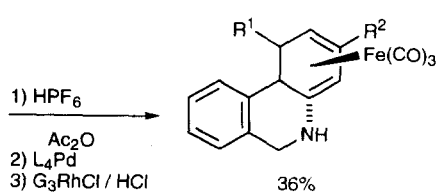


40% overall
(±) Me Joubertiamine



70-90%

(361)



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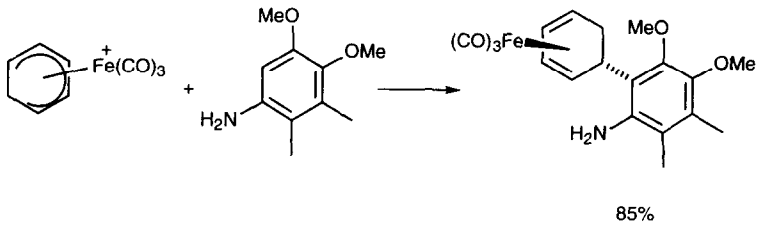
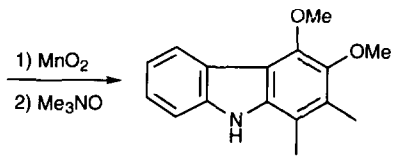
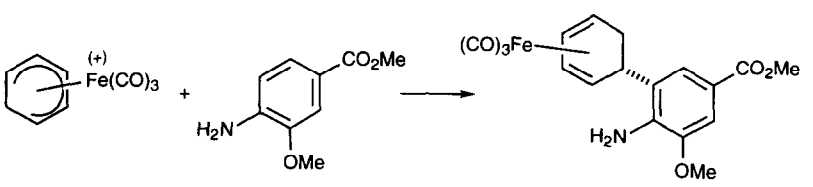


85%

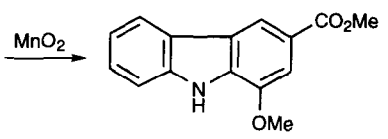
(362)



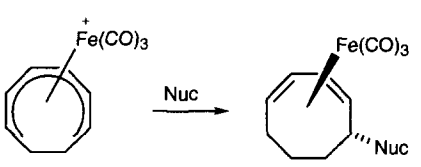
42%



(363)



54%

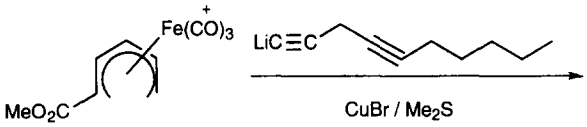


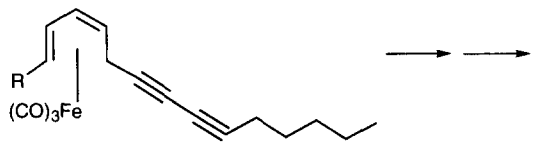
60-80%

(364)

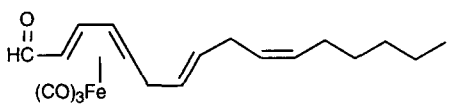
Nuc =  , PhSH, Me_2CuLi

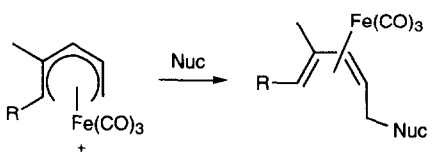
Acyclic dienyliron complexes were also readily alkylated (Eq. (365) [443] and Eq. (366) [444]). Cationic manganese (Eq. (367)) [445] and molybdenum (Eq. (368)) [446] diene complexes were also alkylated.





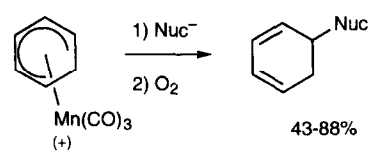
70% (365)



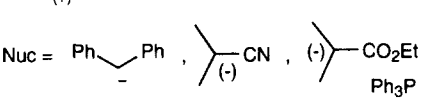


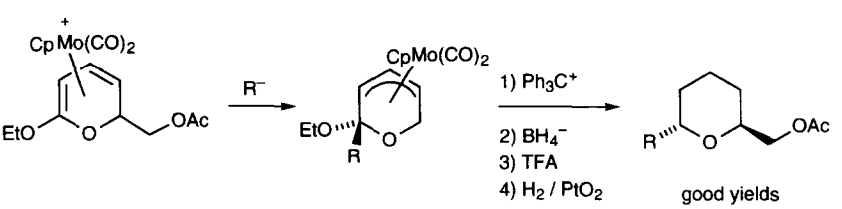
(366)

Nuc = MeLi / CuBr or 

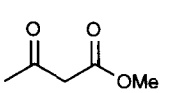


43-88% (367)

Nuc = 

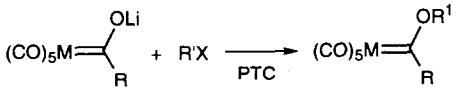


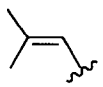
(368)

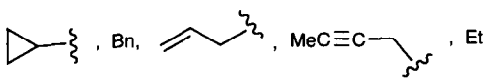
R⁻ = H⁻, Me⁻, Et, ptolyl,  , BuC≡C—  , MeO_2CH_2—  , 

2.1.13. Metal carbene reactions [447]

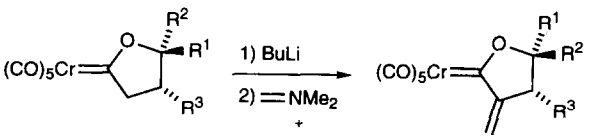
Organic synthesis with metal carbene complexes has been reviewed [447]. Fisher carbene complexes: preparation from alkyl iodides was the topic of a dissertation [448] and the subject of a paper (Eq. (369)) [449]. Cyclic alkoxycarbene complexes were α-vinylated (Eq. (370)) [450].



R = Me, nBu, Ph, 

R^1 = Me, nPr, nBu, iPr, secBu, tBu, 5-hexenyl,  , Bn, , MeC≡C, Et

(369)



17-74%

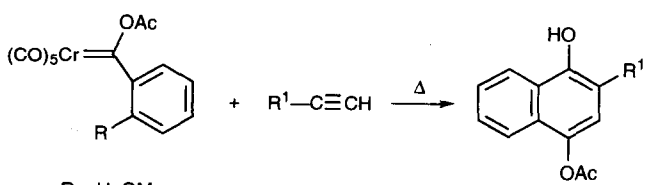
R^1 = Me, CH_2Cl, CH_2Br, H

R^2 = H, Me

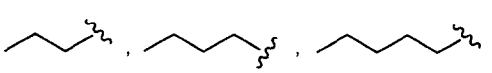
R^3 = H, Me $(CH_2)_4$ $(CH_2)_5$

(370)

The Dötz benzannellation reaction of chromium carbene complexes with alkynes was improved by sonocation or adsorption on silica [451,452]. Acetoxycarbene complexes underwent the Dötz reaction efficiently (Eq. (371)) [453]. Cyclic carbenes, directly available from propargyl ethers also formed hydroquinones efficiently (Eq. (372)) [454]. Phosphaalkynes formed phosphabenzenes (Eq. (373)) [455], and quinones could be homologated onto porphyrins (Eq. (374)) [456]. Combined Diels–Alder reaction–benzannelation was efficient (Eq. (375)) [457], combined Michael addition–benzannelation less so (Eq. 376)) [458]. Molybdenum carbene complexes reacted with alkynes to give quinones, indanones, and furans, depending on the substrate [459]. The mechanism of the process was studied (Eq. (377)) [460].

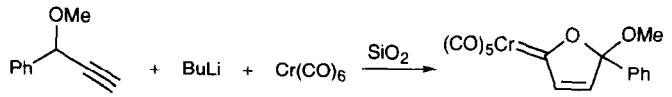


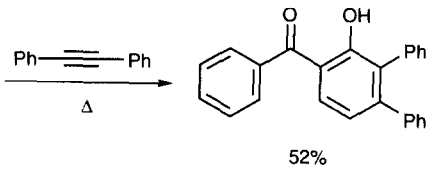
R = H, OMe

R^1 = 

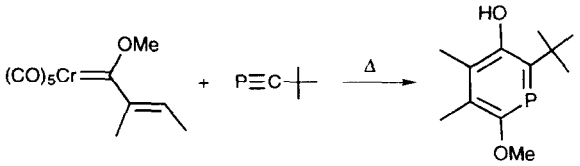
47-71%

(371)

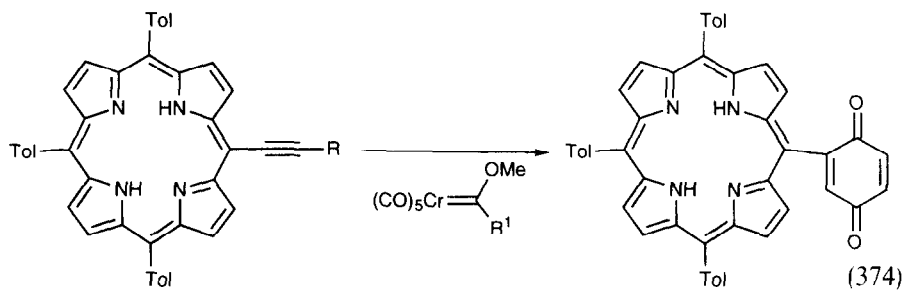




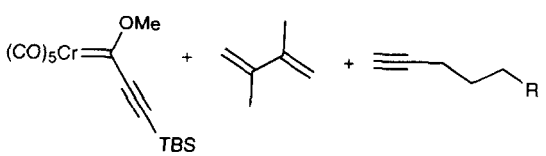
(372)

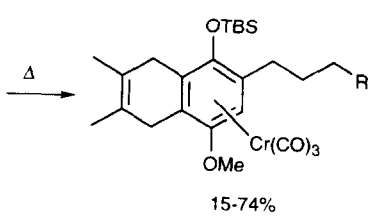


(373)

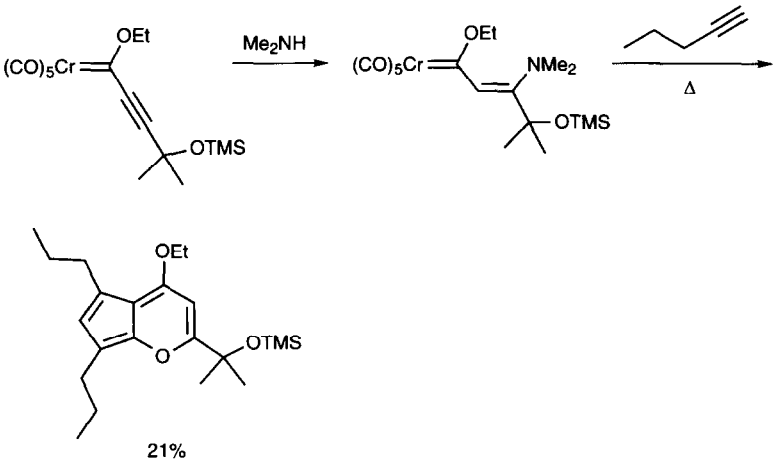


(374)

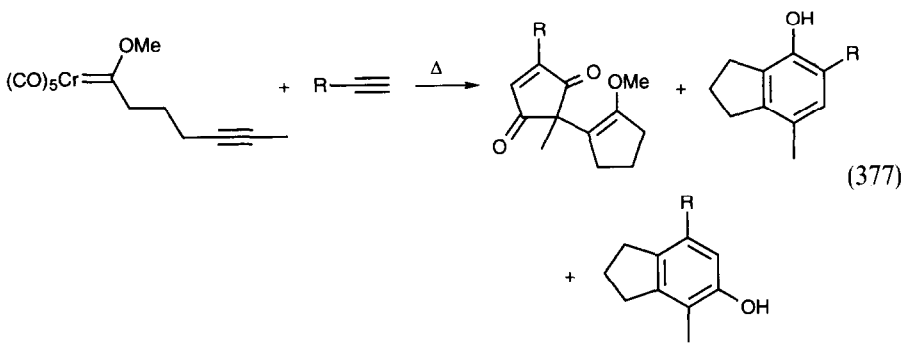




(375)

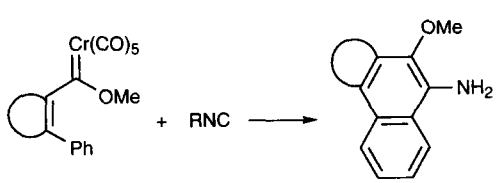


(376)

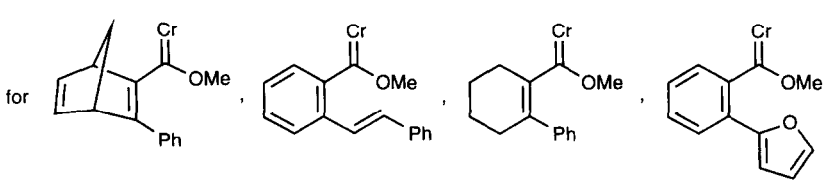


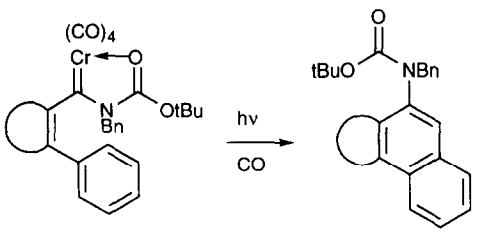
(377)

Dienyl carbene complexes underwent isonitrile insertions to give aminoarenes (Eq. (378)) [461] and underwent photochemical benzannelation (Eq. (379)) [462]. The regioselectivity of this process was examined (Eq. (380)) [463].

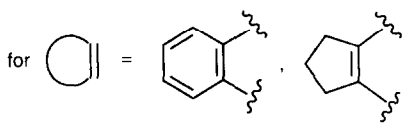


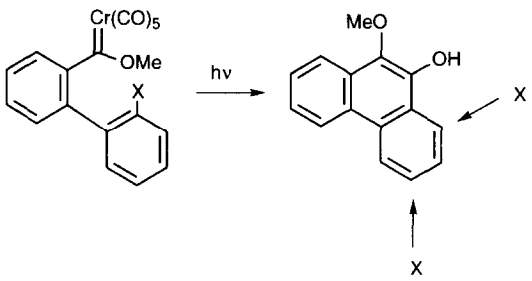
(378)





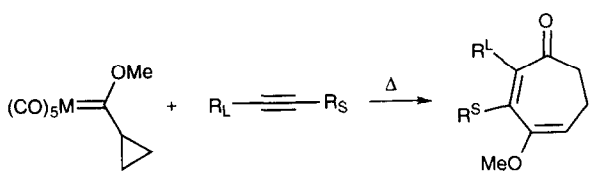
(379)



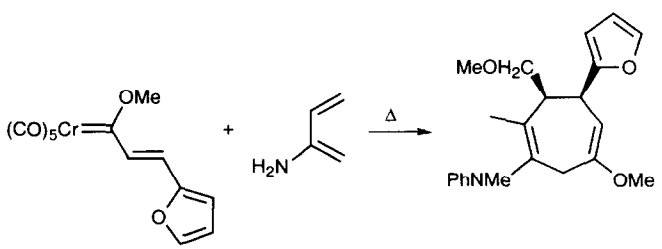


(380)

Cyclopropyl carbenes reacted with alkynes to give cyclooctadienones (Eq. (381)) [464,465]. Seven-membered carbacycles were produced from vinyl carbene complexes and aminodienes (Eq. (382)) [466].

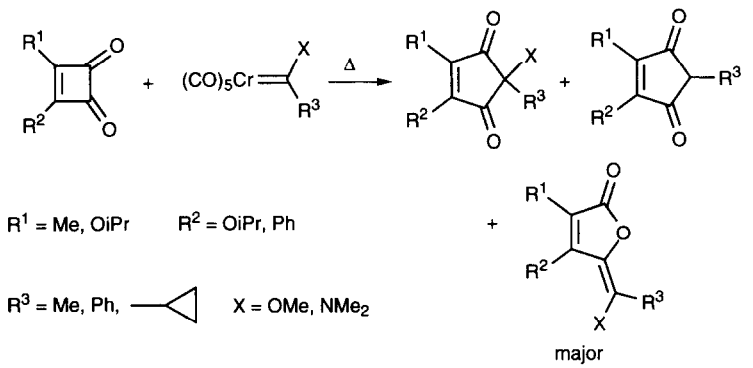


(381)

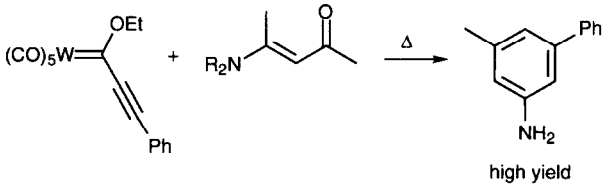


(382)

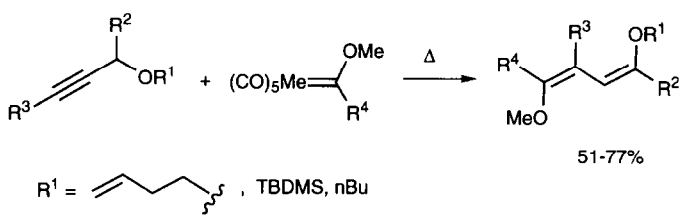
Carbene complexes also underwent a number of unusual reactions of limited scope (Eq. (383) [467], Eq. (384) [468], Eq. (385) [469], Eq. (386) [470], and Eq. (387) [471]). Photolysis of carbyne complexes produced cyclopentenones (Eq. (388)) [472].



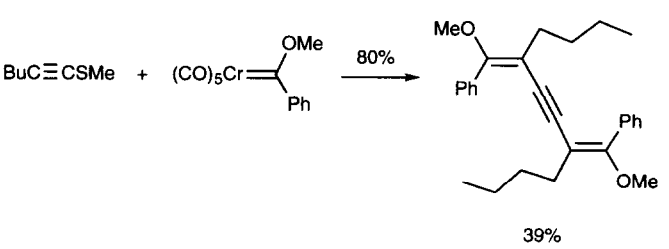
(383)



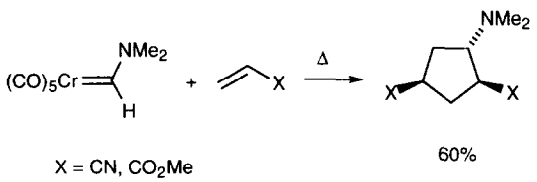
(384)



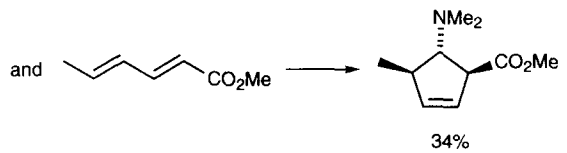
(385)

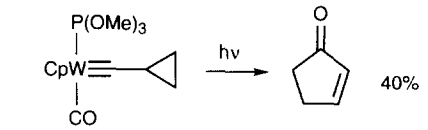


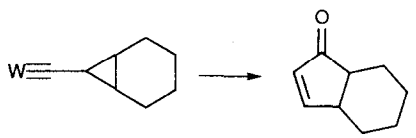
(386)



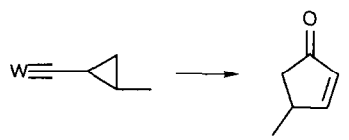
(387)





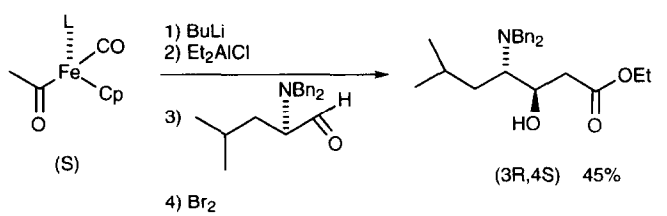


(388)

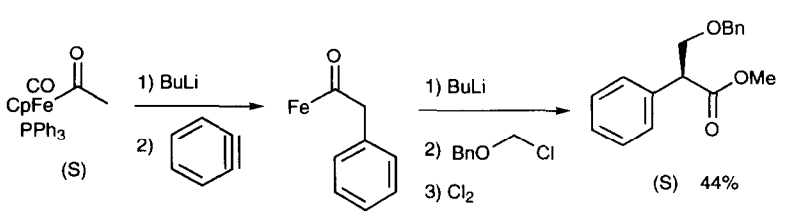


2.1.14. Alkylation of metal acyl enolates

Racemic iron acetyl complexes were resolved by classical methods [473]. Statin was synthesized using optically active iron acyl enolate chemistry (Eq. (389)) [474] as were optically active α-esters (Eq. (390)) [475].



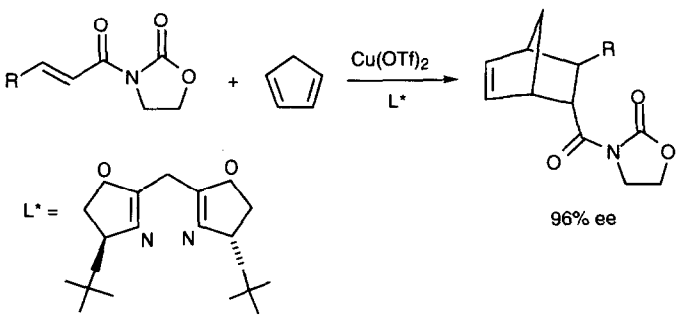
(389)



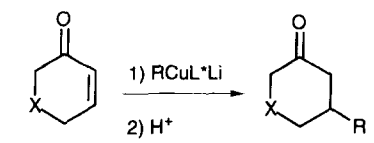
(390)

2.2. Conjugate addition

Asymmetric induction via organocopper conjugate addition reactions was the topic of a dissertation [476]. This could be achieved by using chiral ligands (Eq. (391) [477], Eq. (392) [478], and Eq. (393) [479]) or chiral enones (Eq. (394) [480], Eq. (395) [481], Eq. (396) [482], Eq. (397) [483], and Eq. (398) [484]).

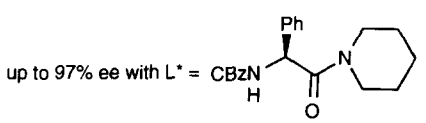


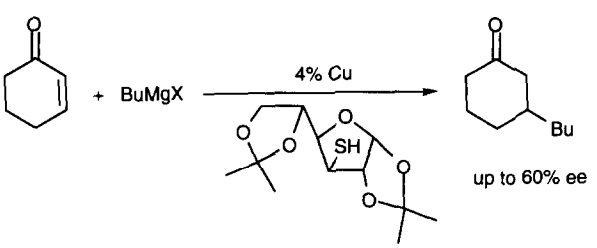
(391)



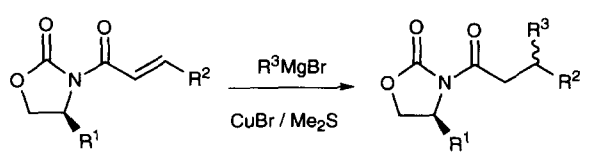
X = $(CH_2)_n$ n = 0-3 R = Me, Bu, Ph

(392)





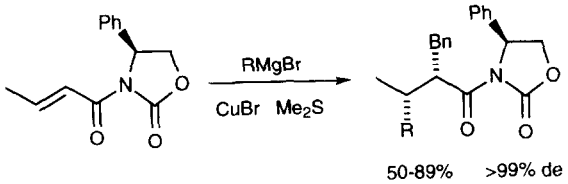
(393)



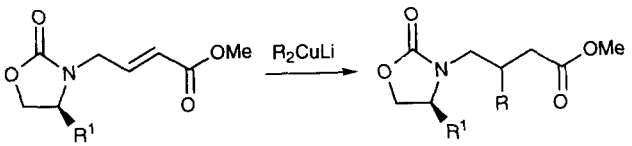
(394)

R^1 = Bn, Ph R^2 = Me, Ph

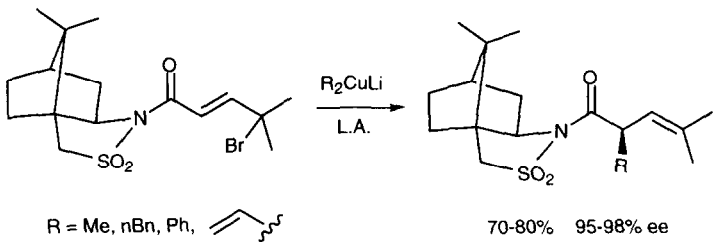
R^3 = Ph, Me, pMeOPh, 2,4$(MeO)_2$Ph



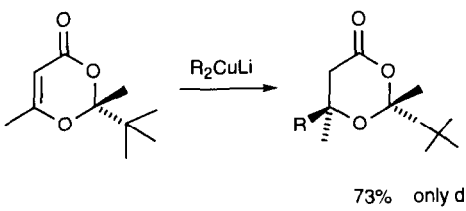
(395)



(396)

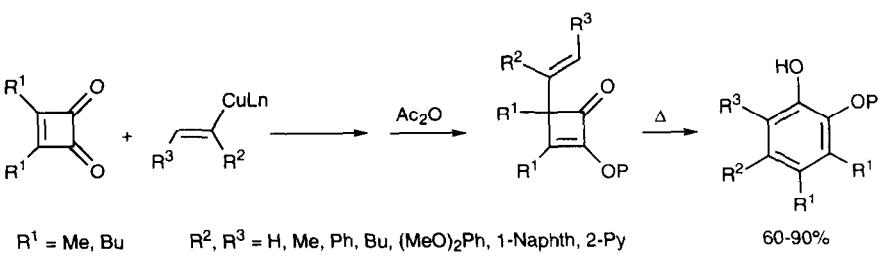


(397)

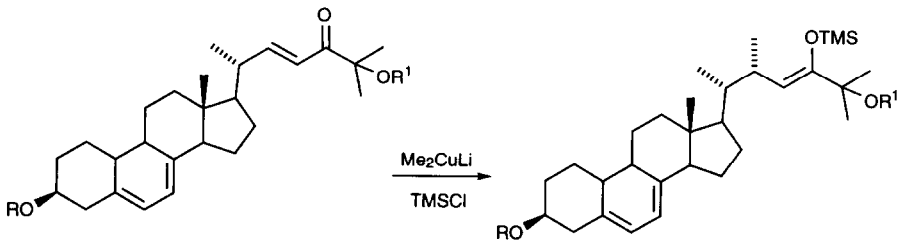


(398)

Cyclobutene diones were converted to phenols via conjugate addition of vinyl cuprates, followed by thermolysis (Eq. (399)) [485]. Trimethylsilyl chloride promoted the conjugate addition of cuprates to enones to give trimethylsilylenol ethers (Eq. (400) [486], Eq. (401) [487], and Eq. (402) [488]).

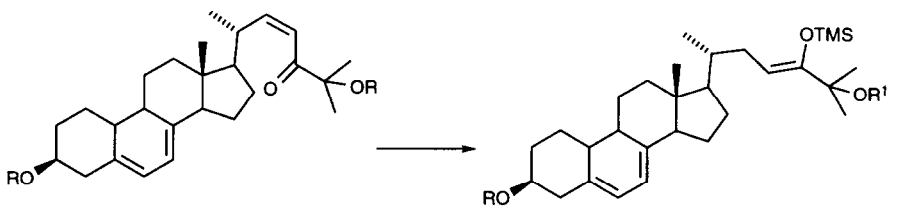


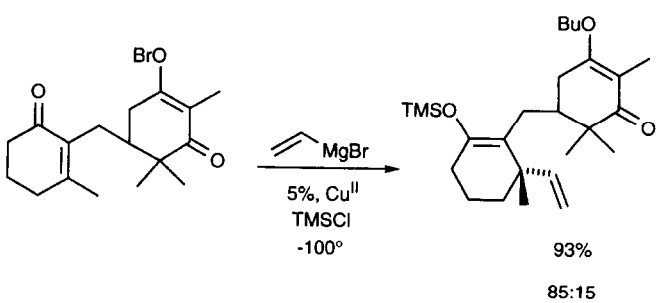
(399)



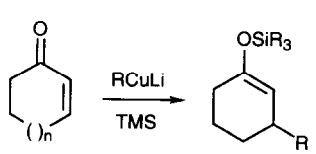
(400)

and

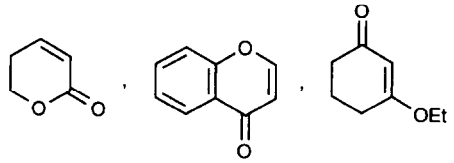




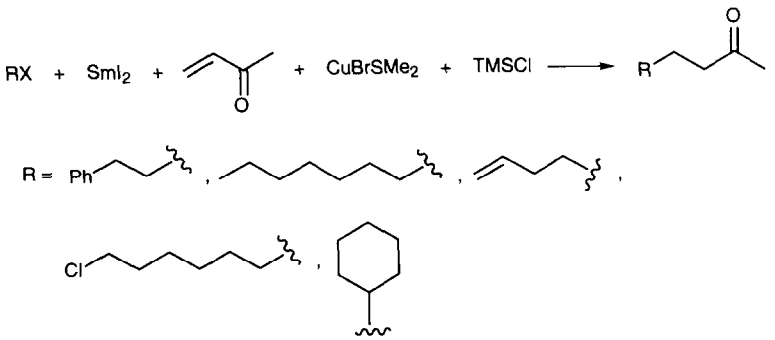
(401)



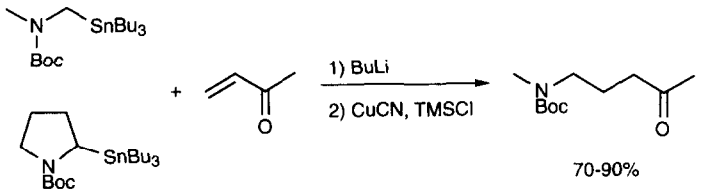
(402)

n = 1, 2 R = Me, Bu, tBu also 

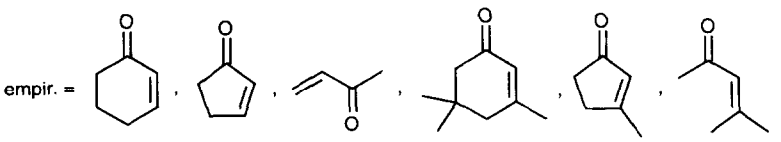
Copper catalyzed conjugate additions of other organometallics, including samarium (Eq. (403)) [489], tin (Eq. (404)) [490], aluminum (Eq. (405)) [491], and zirconium (Eq. (406)) [492].

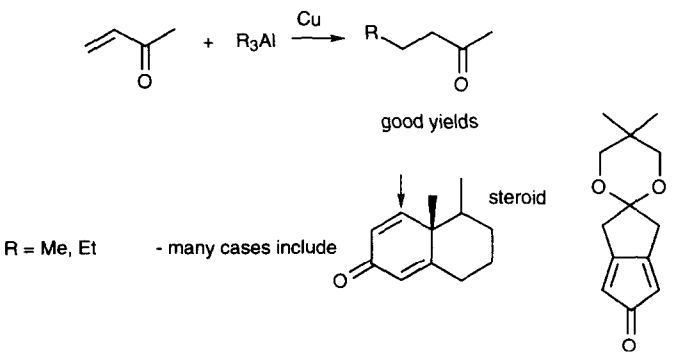


(403)

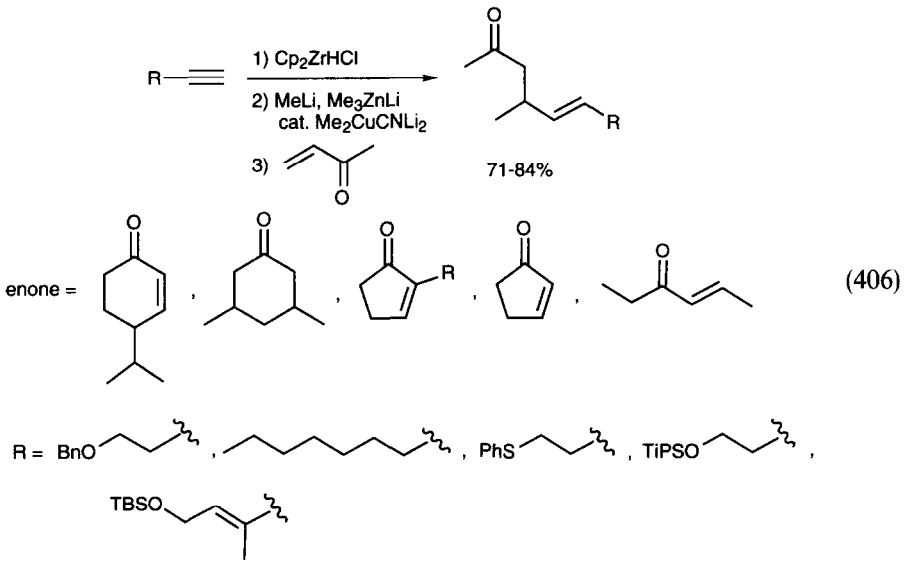


(404)





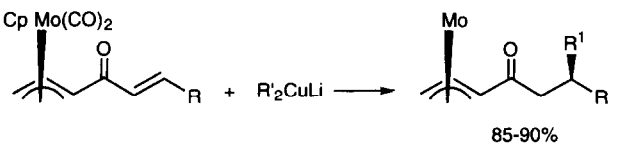
(405)



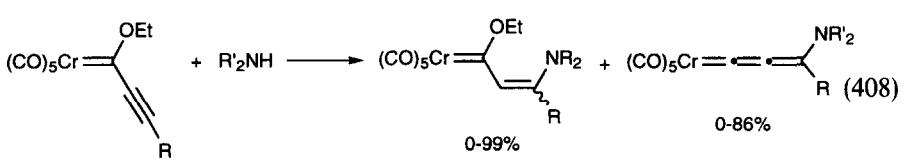
(406)

Cuprates added 1,4 to enones having π allyl molybdenum groups present (Eq. (407)) [493]. Unsaturated chromium carbene complexes underwent a variety of conjugate addition reactions (Eq. (408) [494], Eq. (409) [495], Eq. (410) [496], and Eq. (411) [497]). Chromium carbene anions Michael added to enones (Eq. (412)) [498].

The chromium tricarbonyl complex of benzyl copper added 1,4 to methyl vinyl ketone [499]. Nickel and palladium complexes catalyzed the conjugate alkylation of enones by organozinc reagents (Eq. (413)) [500]. Conjugated iron acyl enolates were 1,4 alkylated by stabilized carbanions (Eq. (414)) [501]. Osmium(II) complexes of steroidal phenols Michael added to enones (Eq. (415)) [502]. Iron carbonyl anions promoted the alkylation of enones by ketones (Eq. (416)) [503].

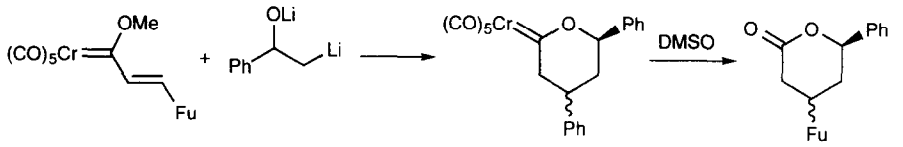


(407)



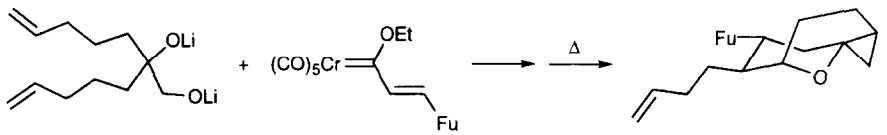
(408)

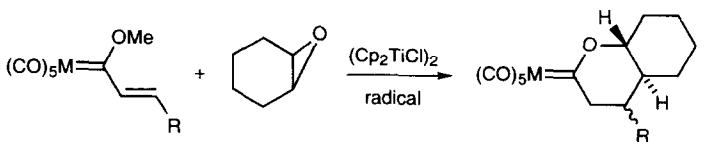
depends on amine



(409)

and ≈50%

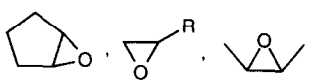


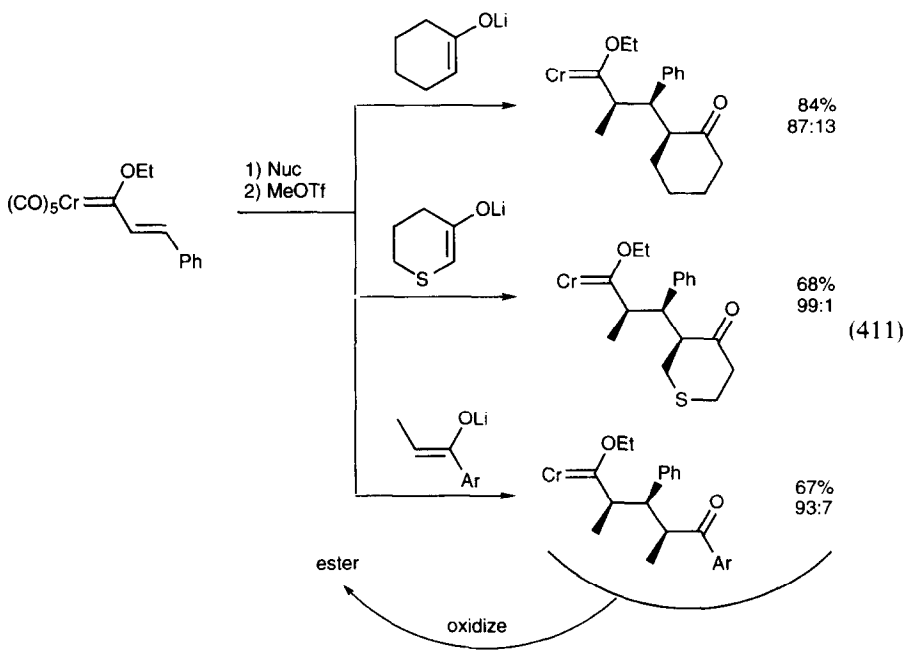


40-60%

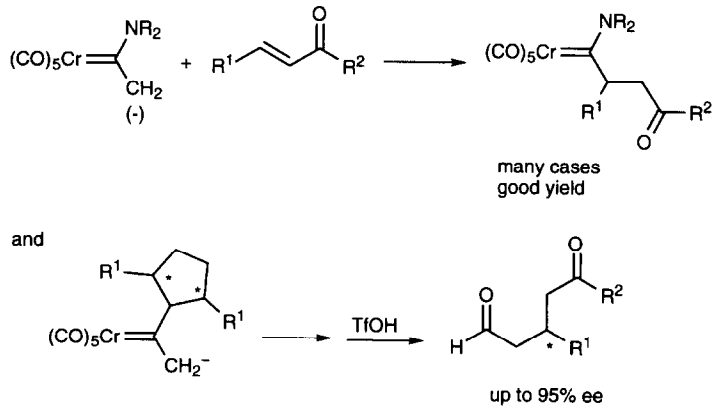
(410)

R = Me, Ph, iPr also

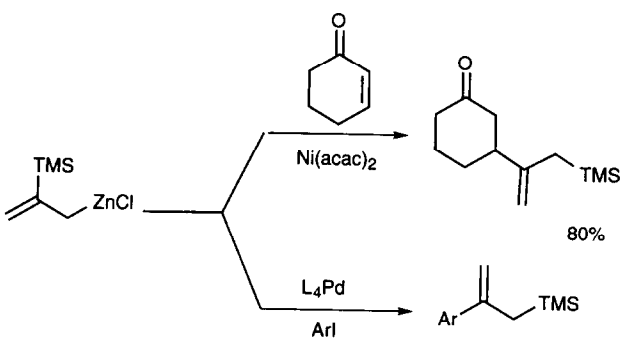




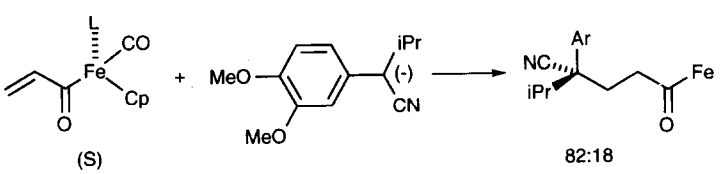
(411)


(CO)5Cr
NR2
CH2
(-)
R1
R2
O
many cases
good yield
and
TfOH
CH2−
up to 95% ee

(412)


TMS
ZnCl
Ni(acac)2
80%
L4Pd
ArI
Ar
TMS

(413)


L
CO
Fe
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(S)
MeO
MeO
iPr
(-)
CN
NC
Ar
iPr
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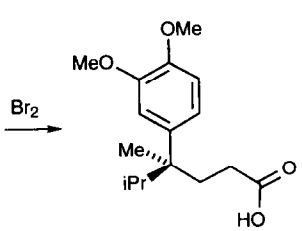
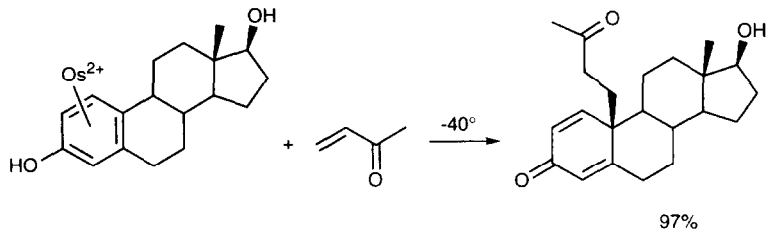
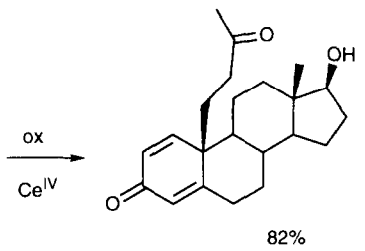
82:18

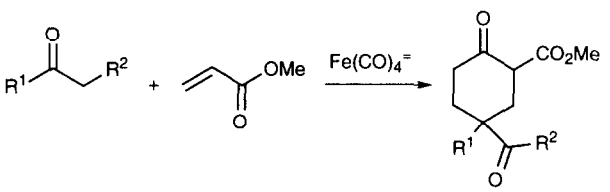
(414)

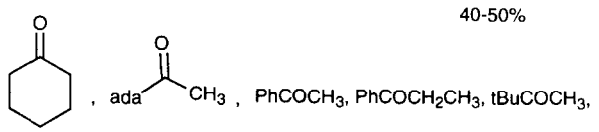

Br2
OMe
MeO
Me
iPr
O
HO



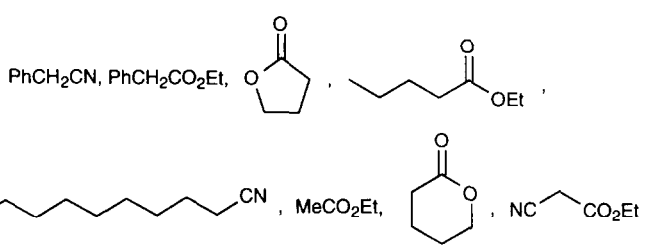
(415)







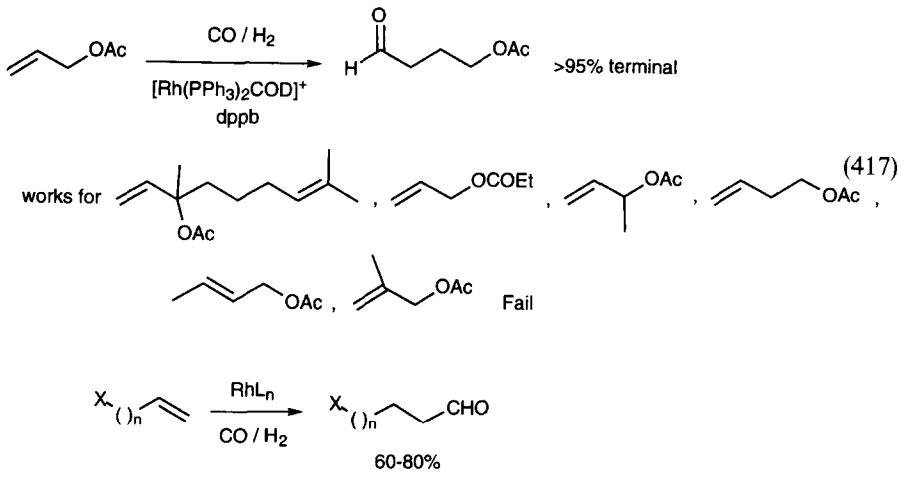
(416)



2.3. *Acylation reactions (excluding hydroformylation)*

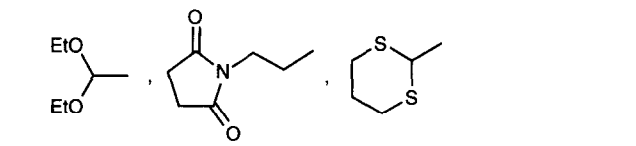
2.3.1. *Carbonylation of alkenes and arenes*

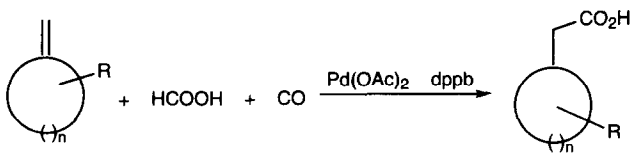
Hydroformylation, oxidation and reduction have been reviewed for 1991 (879 references) [504]. A variety of functionalized olefins undergo hydroformylation (Eq. (417) [505] and Eq. (418) [506]). Palladium catalyzed the hydrocarboxylation of alkenes (Eq. (419)) [507–509].



(417)

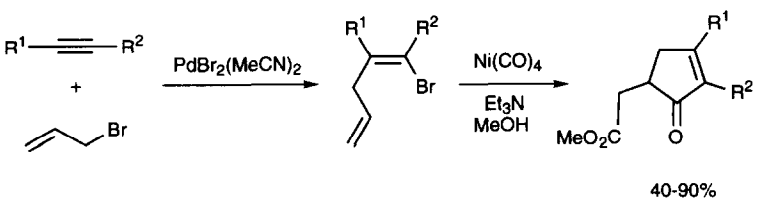
(418)



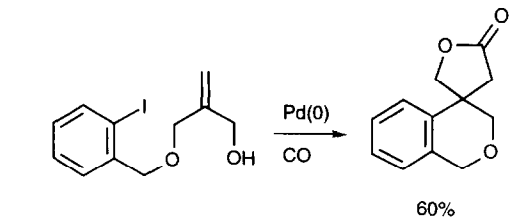


(419)

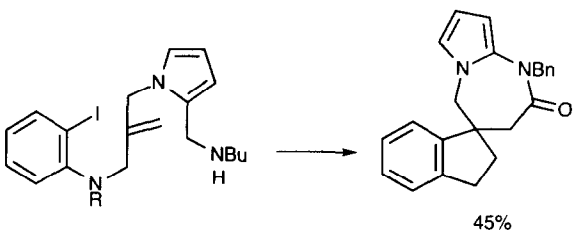
Palladium catalyzed a number of cyclocarbonylation reactions (Eq. (420) [510], Eq. (421) [511], Eq. (422) [512], Eq. (423) [513], and Eq. (424) [514]). Carbonylative cyclization of unsaturated carboxylic acids was studied extensively [515,516].

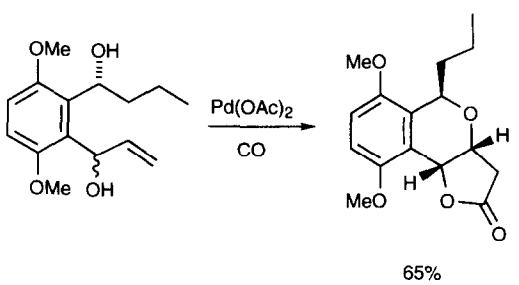


(420)

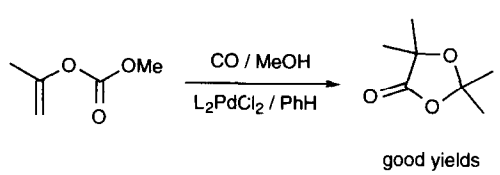


(421)

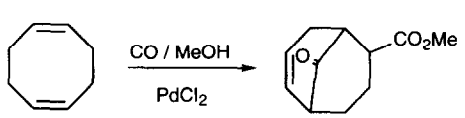




(422)

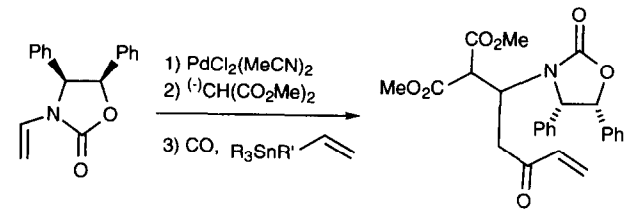


(423)



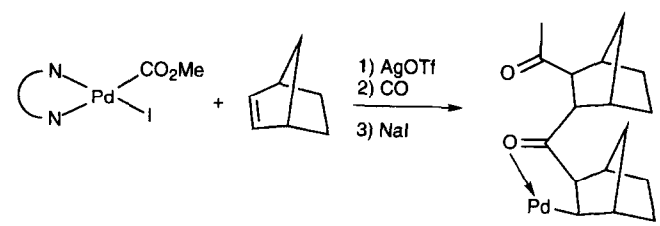
(424)

Palladium also promoted a number of less conventional carbonylation reactions (Eq. (425) [517], Eq. (426) [518], and Eq. (427) [519]). Iron allyl complexes were used in a two-step cyclocarbonylation (Eq. (428)) [520]. Manganese cyclocarbonylated ω-olefinic malonates (Eq. (429)) [521]. Rhodium catalyzed the conversion of homoallylic amines to lactams (Eq. (430)) [522]. Zirconium complexes promoted a cyclocarbonylation used in the synthesis of dendrobine (Eq. (431)) [523].

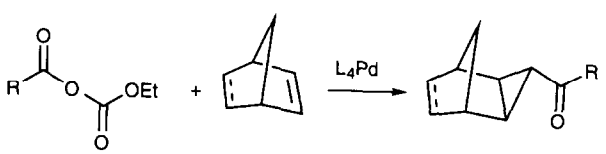


good yields
high ee

(425)



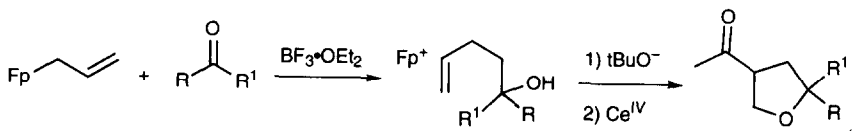
(426)



50-99%

R = Me, Ph

(427)

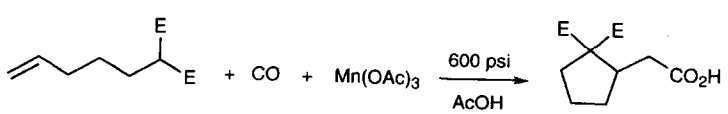


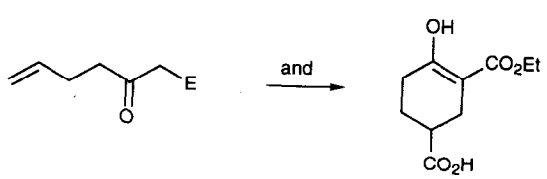
20-40%

(428)

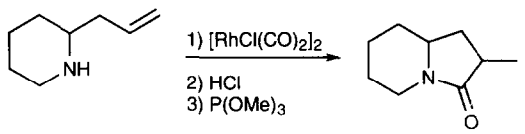
R = Ph, pNO2Ph, mMeOPh

R1 = H, CH3 (CH2)6

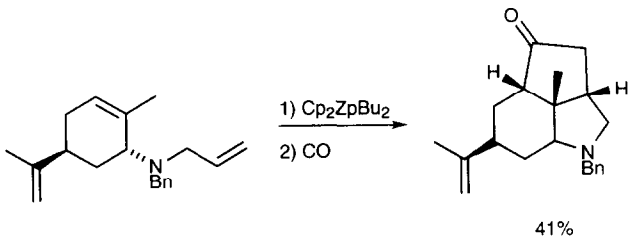




(429)



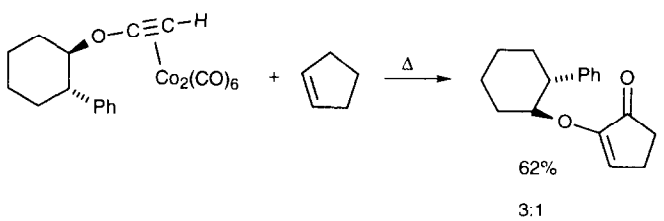
(430)



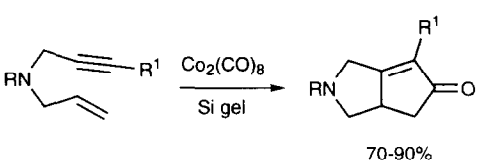
(431)

2.3.2. Carbonylation of alkynes (including the Pauson–Khand reaction)

Enantioselective Pauson–Khand reactions were the subject of a review (6 references) [524]. Only low stereoselectivity was achieved using chiral alkoxyacetylenes as the alkyne component (Eq. (432)) [525]. Both amine oxides and dimethylsulfoxide promoted the Pauson–Khand reaction [526]. This process was used to synthesize nitrogen heterocycles (Eq. (433) [527], Eq. (434) [528], Eq. (435) [529]), oxygen heterocycles (Eq. (436)) [530], and carbocycles (Eq. (437) [531], Eq. (438) [532]). Ligands attached to the alkyne member accelerated the reaction (Eq. (439)) [533]. Cyclopropanes participated in Pauson–Khand reactions (Eq. (440)) [534].



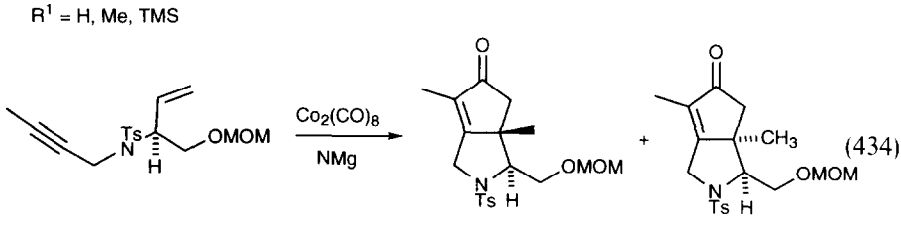
(432)



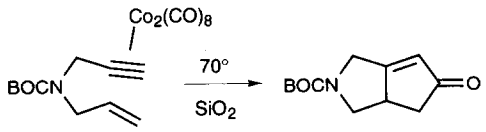
(433)

R = Ac, BOC, CBz, Tos, PhCO

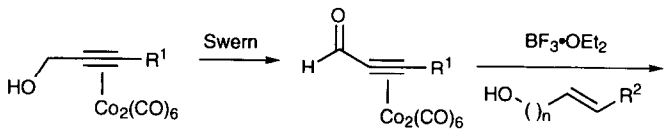
R^1 = H, Me, TMS

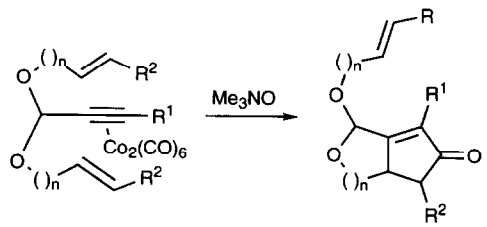


(434)

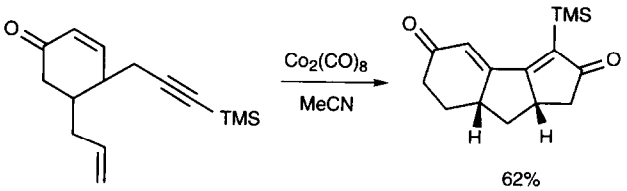


85% (435)

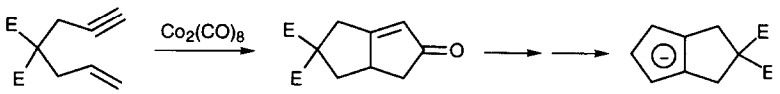




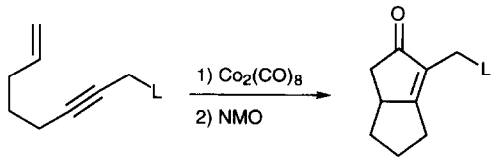
40-90% (436)



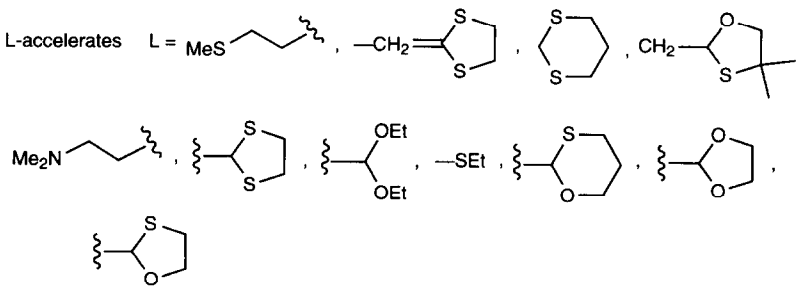
62% (437)

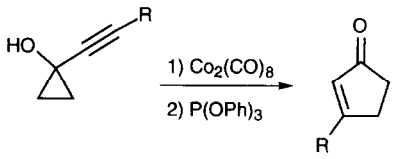


(438)



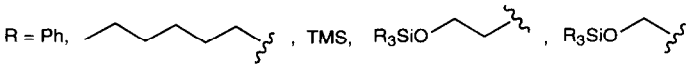
40-90%

L-accelerates L =  (439)

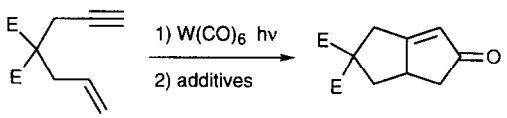


61-92%

(440)



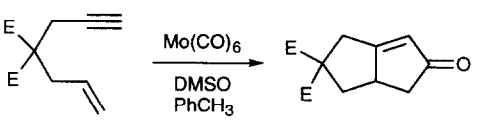
Pauson–Khand-type cyclizations were also catalyzed by tungsten hexacarbonyl (Eq. (441)) [535], molybdenum hexacarbonyl (Eq. (442)) [536], and chromium carbonyl fluorides (Eq. (443)) [537]. Chromium carbene complexes also promoted cyclocarbonylation of enynes (Eq. (444)) [538], while iron carbonyl cyclocarbonylated diynes (Eq. (445)) [539]. Palladium(0) catalyzed the cyclocarbonylation of enyne carbonates (Eq. (446)) [540].



60%

10 cases

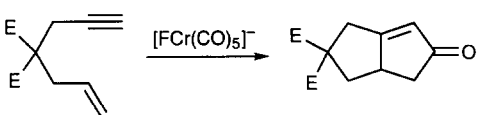
(441)



60-80%

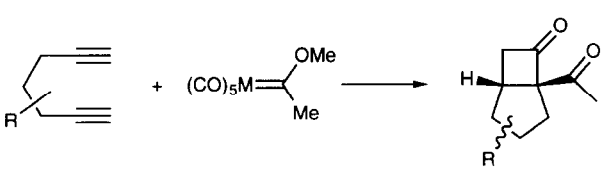
9 cases

(442)



59%

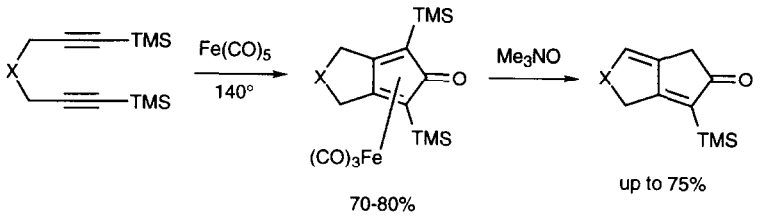
(443)



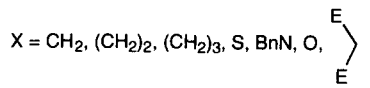
30-60%

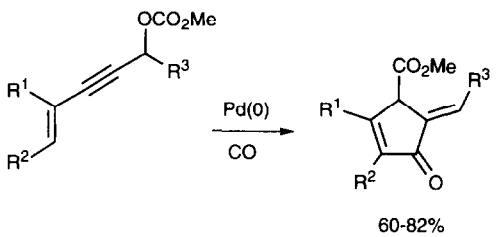
high diastereoselectivity

(444)



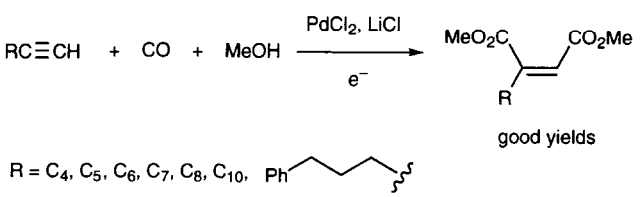
(445)



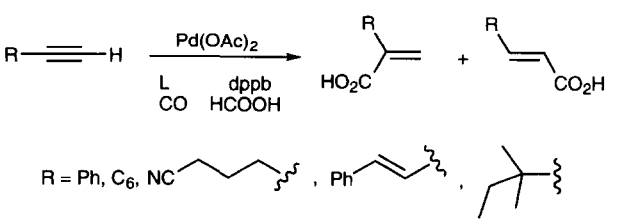


(446)

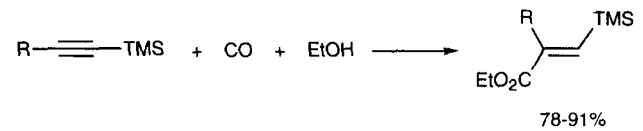
Palladium-catalyzed carbonylation of 2-alkynyl carbonates and 2,3-alkadiene carbonates was reviewed (37 references) [541]. Palladium catalyzed the dicarboxylation of alkynes (Eq. (447)) [542] and the hydrocarboxylation of alkynes (Eq. (448) [543], Eq. (449) [544], and Eq. (450) [545]). Diynes were cyclocarbonylated (Eq. (451)) [546].



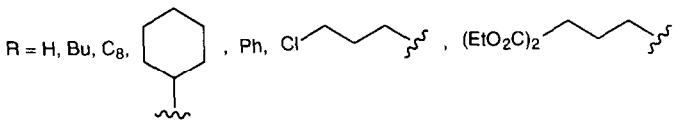
(447)

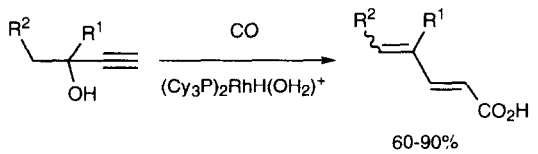


(448)

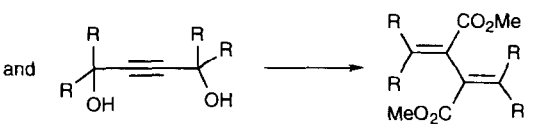


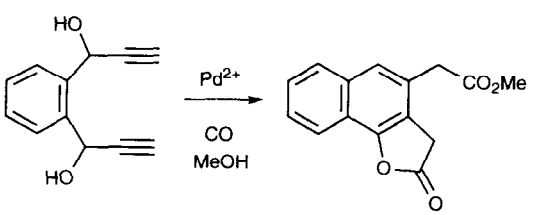
(449)





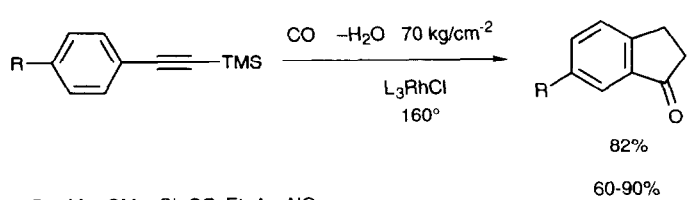
(450)



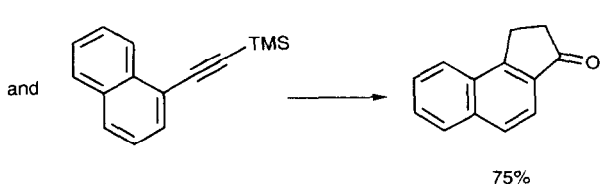


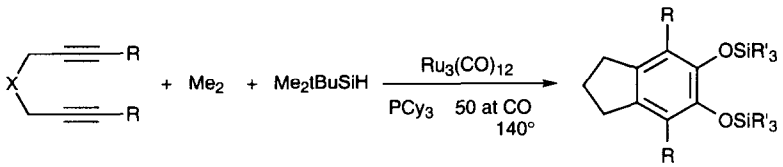
(451)

Rhodium(I) complexes catalyzed the cyclocarbonylation of trimethylsilyl alkynes (Eq. (452)) [547]. Ruthenium (Eq. (453)) [548] and rhodium (Eq. (454) [549], Eq. (455) [550], and Eq. (456) [551]) catalyze silylformylation of alkynes.



(452)





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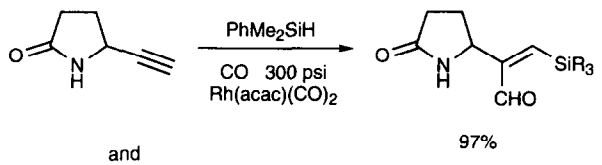

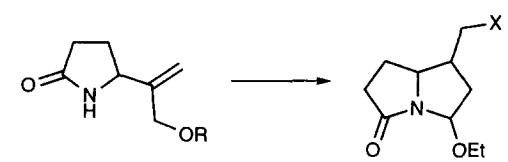

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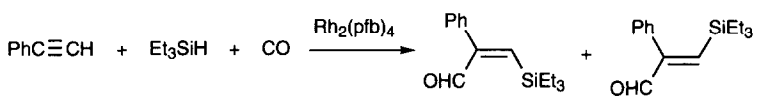
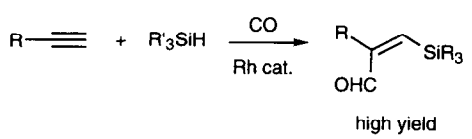
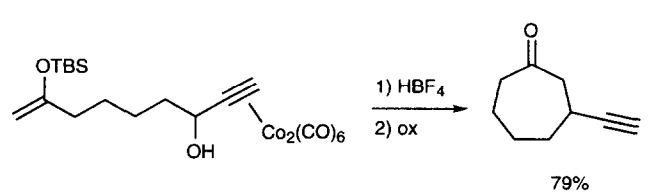


(455)



(456)

The nickel carbonyl promoted carbonylative cycloaddition of alkynes and allyl halides for the synthesis of 2-cyclopentenone derivatives was the topic of a review (21 references) [552]. Cobalt propargyl alcohols cyclized to cycloheptanones (Eq. (457)) [553]. Alkynes were carbonylated by very unusual zirconium chemistry (Eq. (458)) [554]. Allenes were cyclocarbonylated by palladium (Eq. (459)) [555] and iron carbonyl (Eq. (460)) [556].



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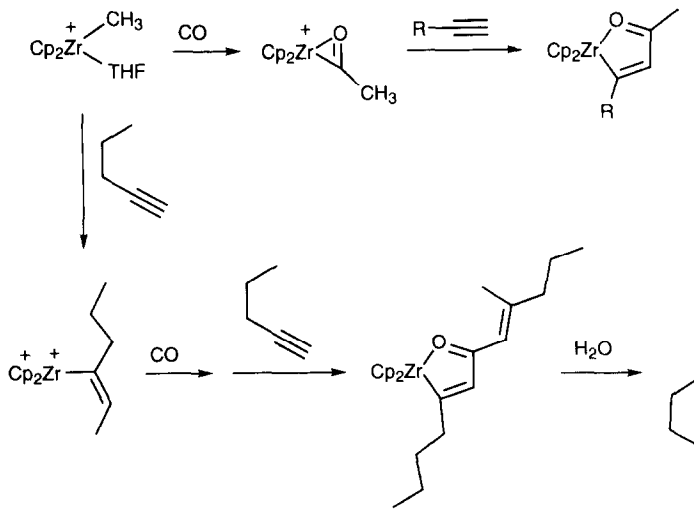
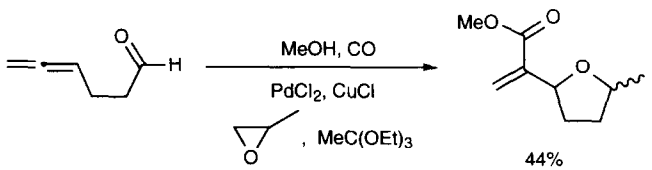
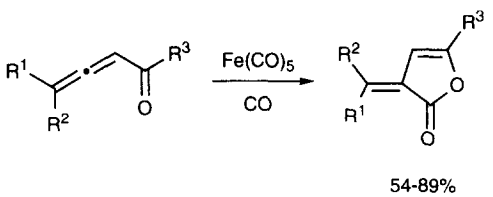


(458)



(459)



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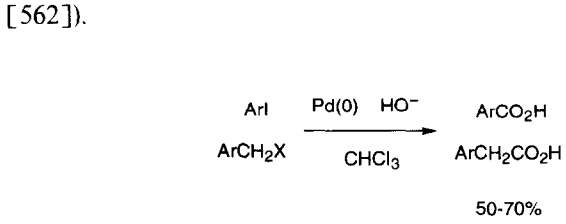
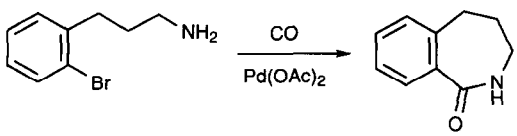


(461)

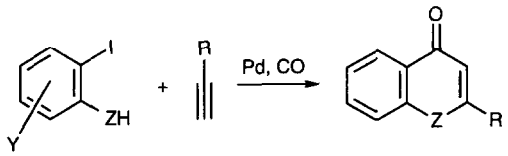
Ar = Ph, pMePh, mMePh, oMePh, pMeOPh, mMeOPh, pClPh, mClPh, 1-naphth

2.3.3. Carbonylation of halides and triflates

Palladium(0) complexes catalyzed the carboxylation of aryl and benzyl halides (Eq. (461) [557] and Eq. (462) [558]). Alkynes could be incorporated to give pyrones (Eq. (463)) [559]. Palladium also catalyzed the carbonylation of arylboronic acids (Eq. (464)) [560] and unsaturated stannanes (Eq. (465) [561] and Eq. (466) [562]).

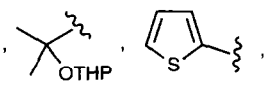


low yield (462)

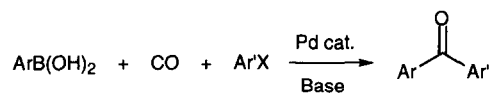


40-60%

Z = O, NH (463)

R = Ph, pMeOPh, C_5, C_6, $THPOCH_2$, AcO 

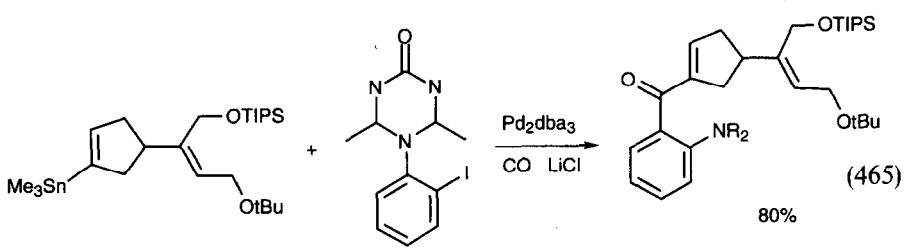
1-Naphth, pMePh



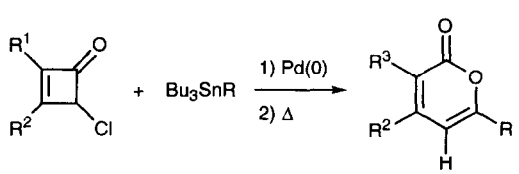
60-89% (464)

Ar = Ph, pFPh, pBrPh, 1-Naphth, pMeOPh, 1,3,5-Me_3Ph

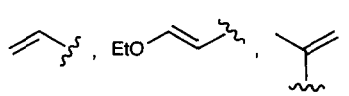
Ar' = pNO_2Ph, pMeO_2CPh, Ph, pMe_2NPh, oPy, oMePh, PFPh



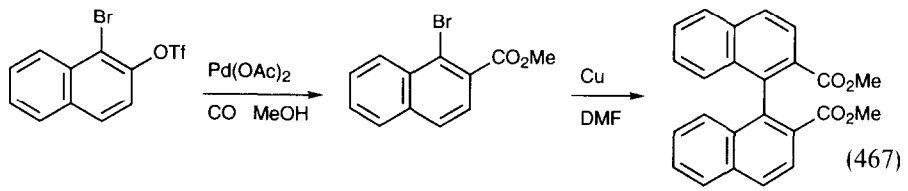
80% (465)



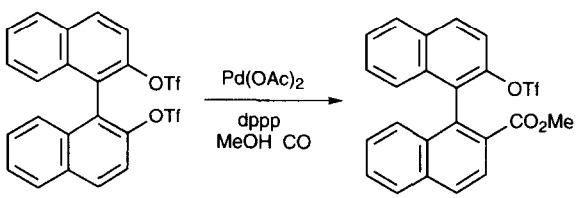
60-90% (466)

R = Ph, pClPh, pMeOPh, 2-furyl, 3-furyl, 2-thienyl, 

Palladium(0) complexes catalyzed the carbonylation of aryl triflates (Eq. (467) [563], Eq. (468) [564], Eq. (469) [565], Eq. (470) [566]) and aryliodonum species (Eq. (471)) [567].

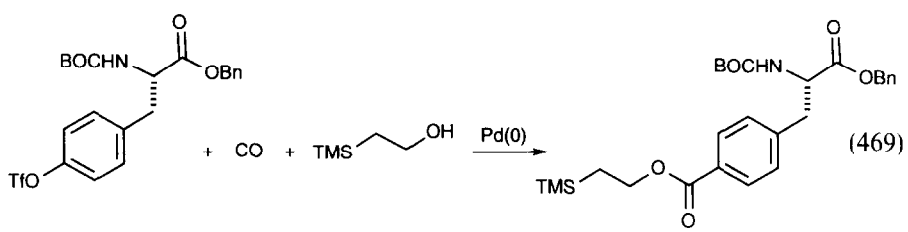


(467)



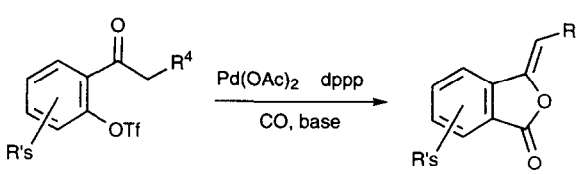
(468)

83%



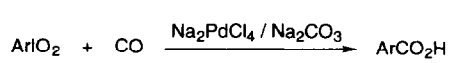
(469)

87%



(470)

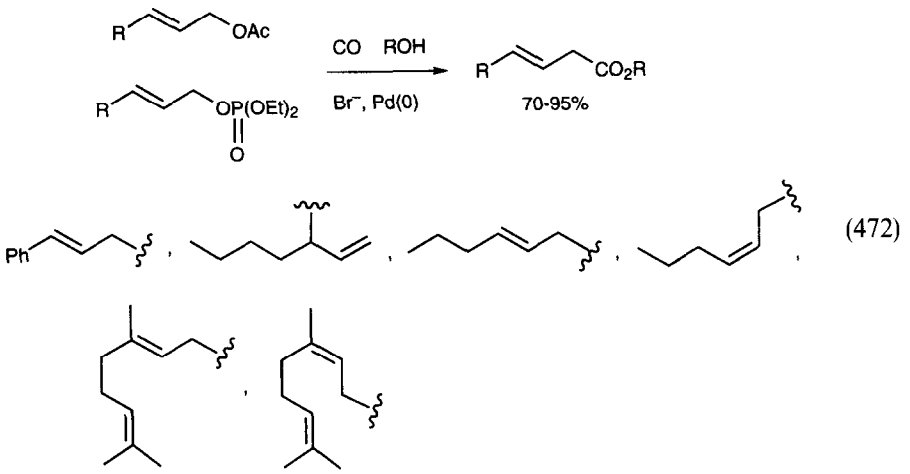
74-94%



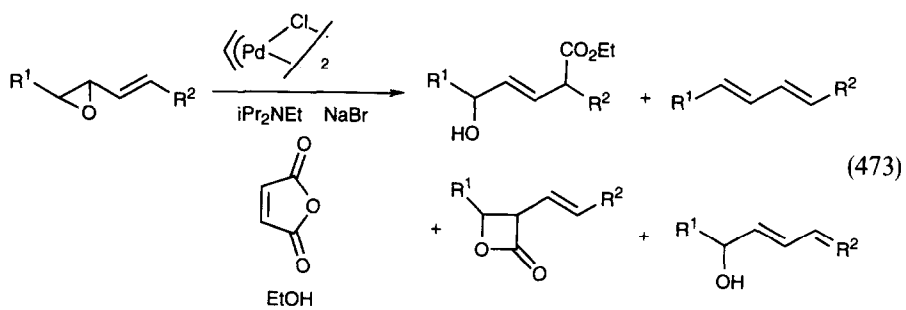
(471)

Ar = Ph, pMePh, oMePh, mMePh, mClPh, pClPh, mBrPh, pBrPh, pNO_2Ph, pMeOPh

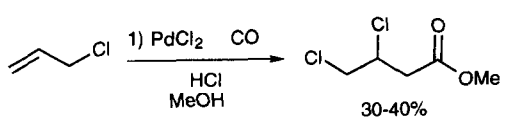
Allyl acetates and phosphonates were carbonylated by palladium(0) catalysts in the presence of bromide (Eq. (472)) [568]. 1,4-diacetoxy-2-butenes were decarbonylated [569]. The palladium-catalyzed carbonylation of vinyl epoxides resulted in complex mixtures (Eq. (473)) [570]. Palladium also catalyzed the strange carbonylation of allylic chlorides in Eq. (474) [571].



(472)

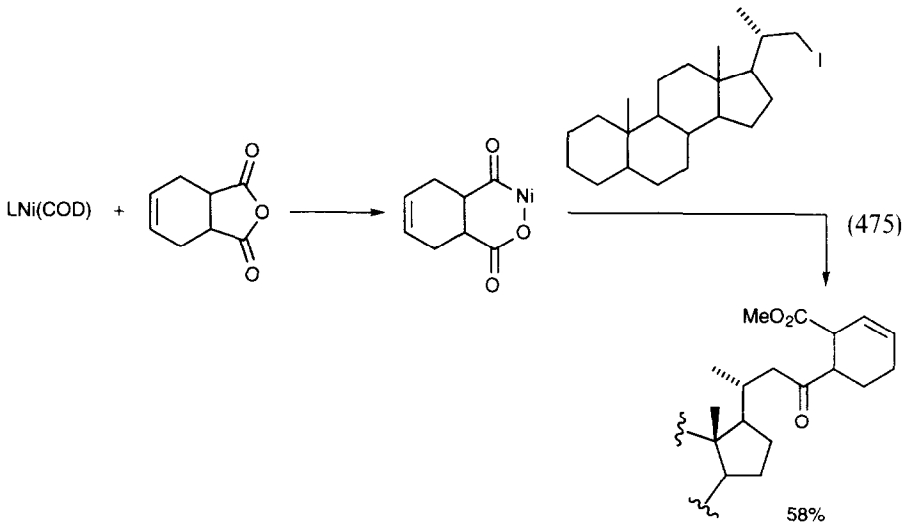


(473)

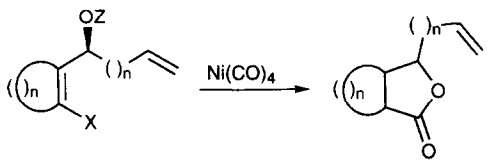


(474)

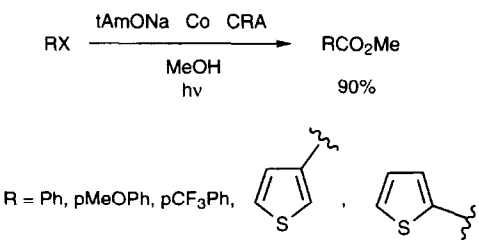
Cyclic nickel acyl complexes acylated steroidal iodides (Eq. (475)) [572]. Nickel carbonyl cyclocarbonylated olefinic halides (Eq. (476)) [573]. Aryl halides were carbonylated by cobalt CRAs (Eq. (477)) [574].



(475)



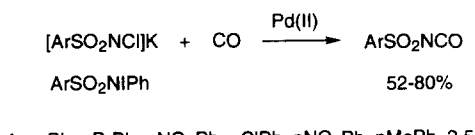
(476)



(477)

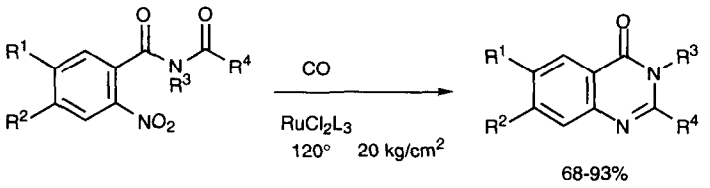
2.3.4. *Carbonylation of nitrogen compounds*

Palladium catalyzed the production of aryl sulfonylisocyanates (Eq. (478)) [575]. Ruthenium catalyzed the reductive cyclization of nitro imides (Eq. (479)) [576].



(478)

Ar = Ph, oBrPh, oNO2Ph, pClPh, pNO2Ph, pMePh, 3,5-Cl2Ph



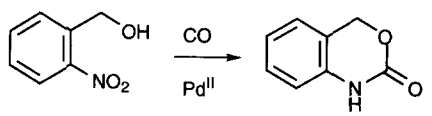
(479)

R^1 = H, Me $R^3 = R^4$ = Me, $(CH_2)_3$, $(CH_2)_5$, $(CH_2)_6$

R^2 = H, Cl R^4 = Bn

2.3.5. *Carbonylation of oxygen compounds*

o-nitrobenzyl alcohol was cyclocarbonylated by palladium catalysts (Eq. (480)) [577].



(480)

good yields

2.3.6. *Miscellaneous carbonylations*

There were none.

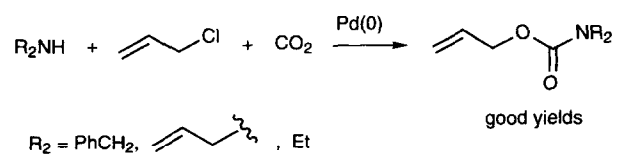
2.3.7. *Decarbonylations*

There were none.

2.3.8. *Reactions of carbon dioxide*

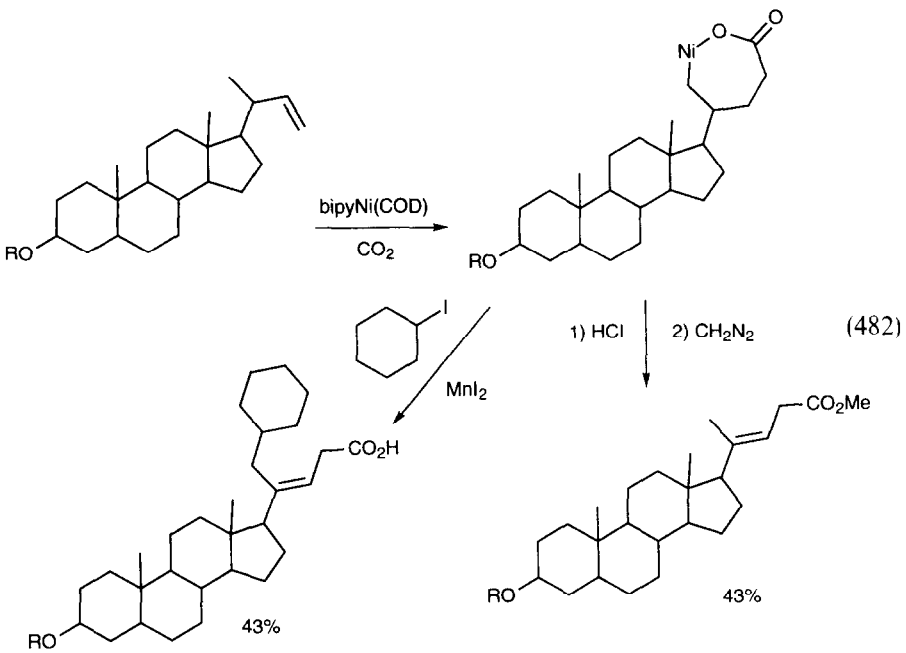
The chemistry of carbon dioxide at metal centers was the subject of a review (189 references) [578]. Palladium catalyzed the carboxylation of allyl chlorides (Eq. (481)) [579]. Nickel(0) complexes catalyzed the carboxylation of dienes (Eq. (482)) [580]. Titanium-catalyzed Grignard reactions were used to produce butenolides (Eq. (483)) [581].

Palladium(0) catalyzed the dicarboxylation of propargyl carbonates (Eq. (484)) [582,583] and allyl carbamates (Eq. (485)) [584].

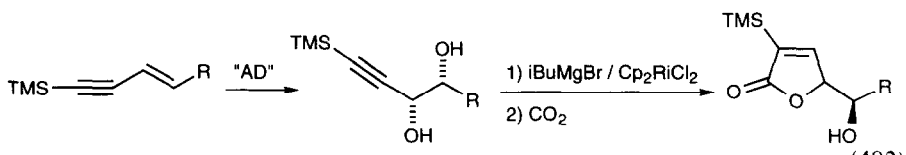


(481)

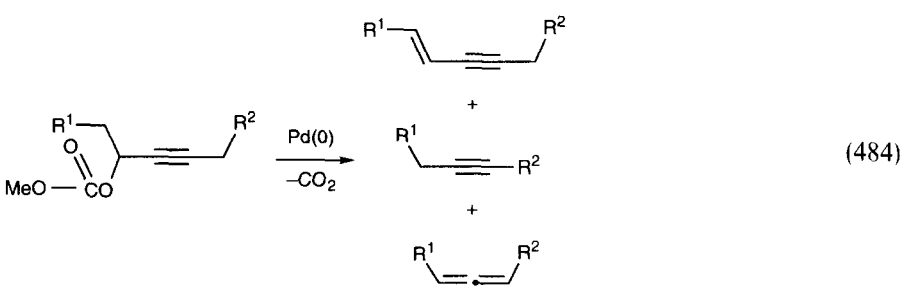
good yields



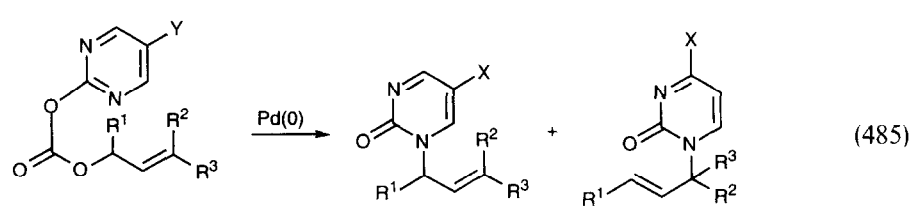
(482)



(483)



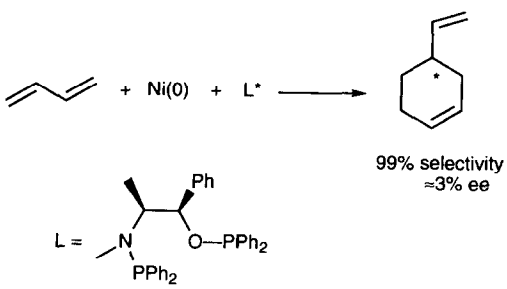
(484)



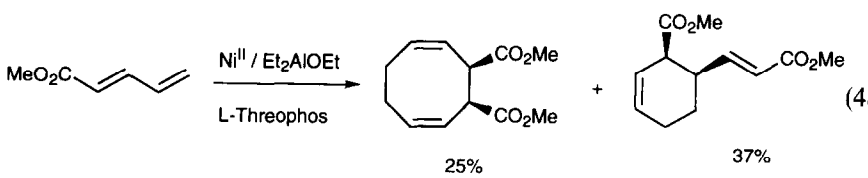
(485)

2.4. Oligomerization (including cyclotrimerization of alkynes and metathesis polymerization)

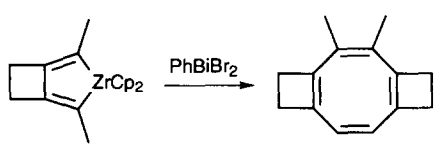
Nickel atoms in ethanol catalyzed the linear and cyclodimerization of 1,3-dienes [585]. Nickel(0) complexes catalyzed the cyclodimerization of butadiene to vinyl cyclohexene with high selectivity but virtually no EE (Eq. (486)) [586]. Dienic esters cyclodimerized to cyclooctadienes (Eq. (487)) [587]. Octaethylporphyrin nickel complexes were dimerized by a free radical process [588]. A bismuth complex dimerized a zirconacyclobutene (Eq. (488)) [589].



(486)

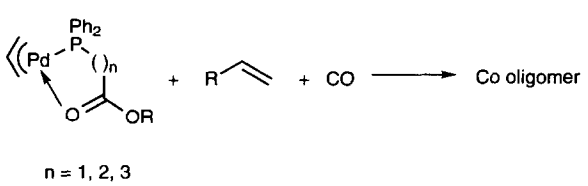


(487)

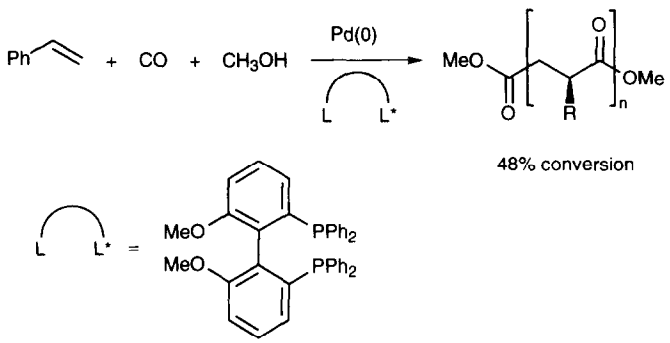


(488)

Palladium(0) catalyzed the co-oligomerization of alkenes and carbon monoxide (Eq. (489) [590] and Eq. (490) [591]).

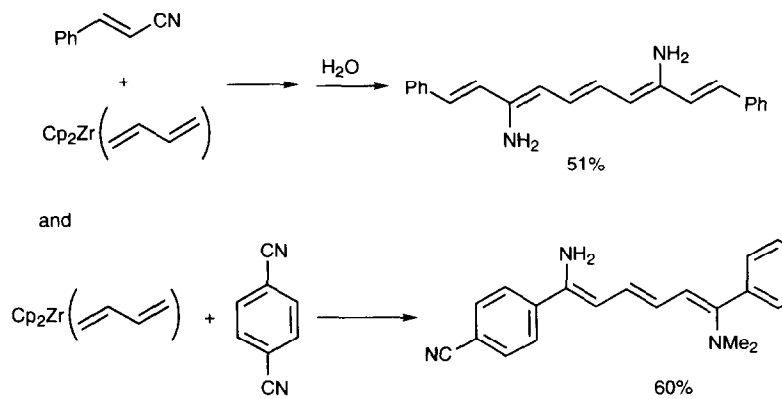


(489)



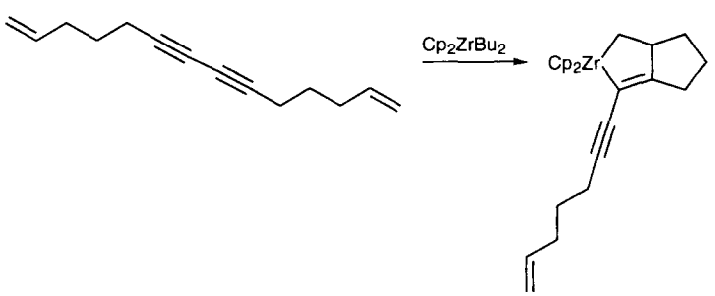
(490)

Palladium catalysts promoted the telomerization of isoprene with secondary amines [592] with aniline [593] and the telomerization of butadiene with methanol [594]. Acrylonitrile condensed with zirconium butadiene complexes (Eq. (491)) [595].

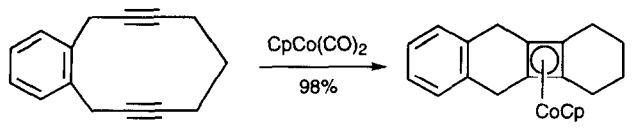


(491)

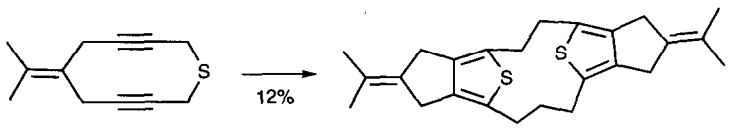
"Zirconocene" cocyclodimerized enynes (Eq. (492)) [596]. A review dealing with production of phenylenes from cobalt-catalyzed cyclotrimerization of alkynes (22 references) [597] has appeared. This same cyclotrimerization was effective for the synthesis of a range of alkyne cyclodimers and trimers (Eq. (493) [598], Eq. (494) [599], Eq. (495) [600], and Eq. (496) [601]). These same catalysts cocyclotrimerized alkynes and nitriles to produce nitrogen heterocycles [602,603].

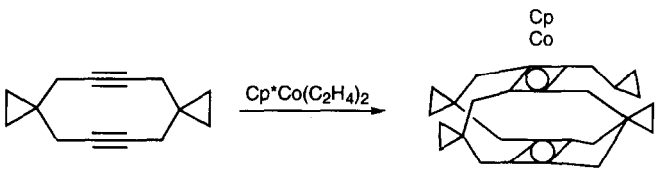


(492)

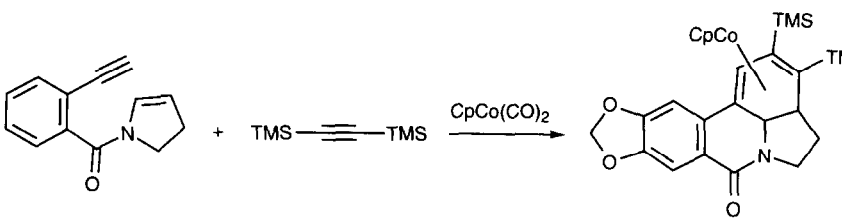


and (493)

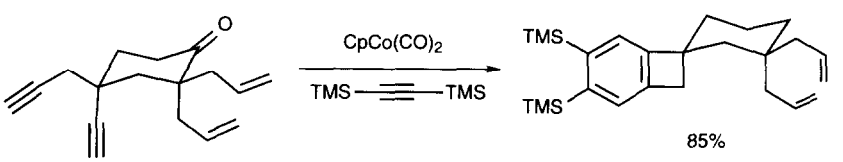


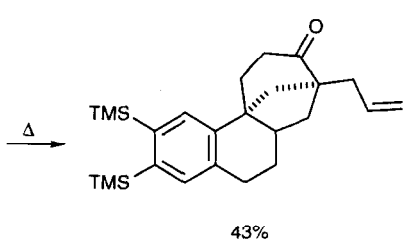


(494)



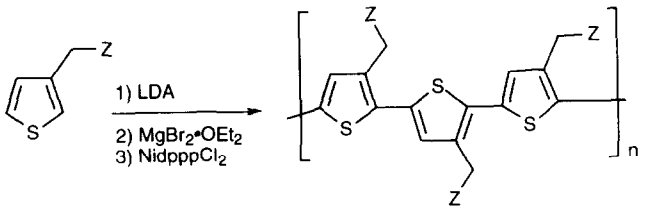
(495)





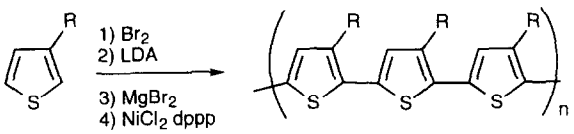
(496)

Polythiophenes were synthesized by nickel-catalyzed Grignard coupling of bromothiophenes (Eq. (497) [604], Eq. (498) [605], and Eq. (499) [606]) and by palladium-catalyzed coupling of bisthiophenebisstannanes with bisbromobisthiophene (Eq. (500)) [607]. Polyphenyls were made by similar chemistry (Eq. (501) [608] and Eq. (502) [609]).



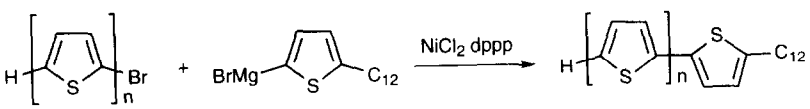
≈65% MW = 71,000 (497)

Z = MeS, MeO, MeO–(CH2CH2O)–, MeO–(CH2CH2O)2–



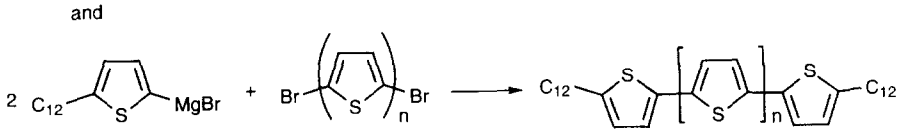
33-65% (498)

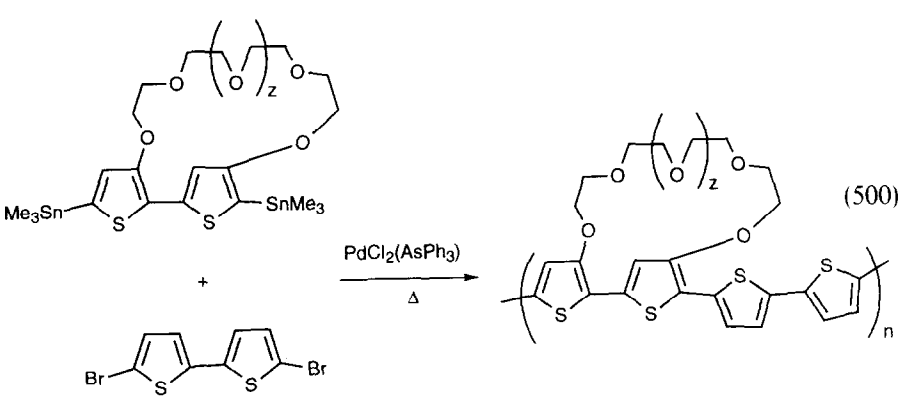
R = nBu, nC6, nC8, nC12



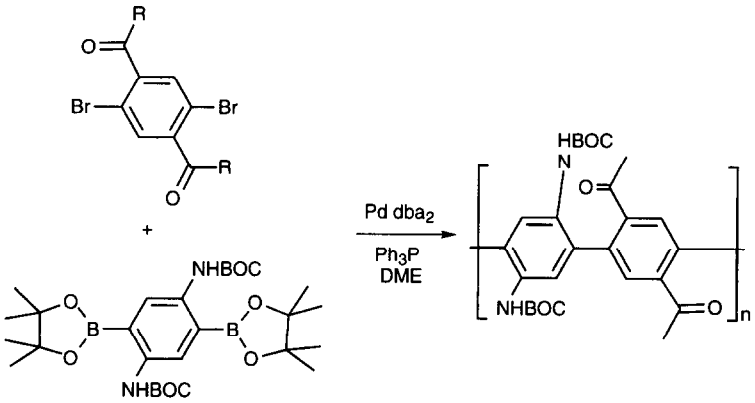
n = 1, 2, 3 59-61% (499)

and

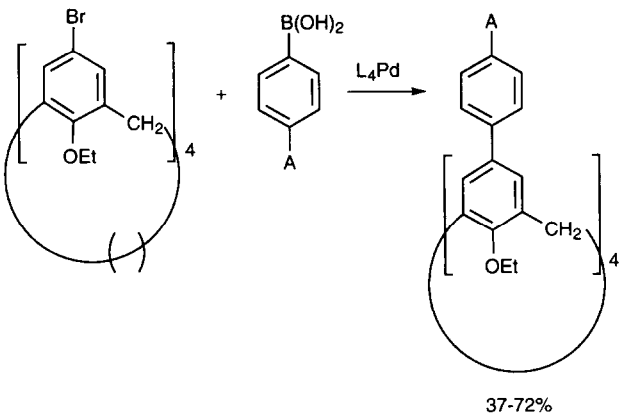




(500)



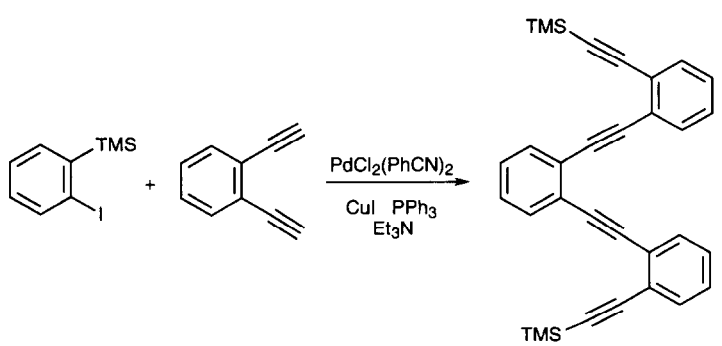
(501)



37-72%

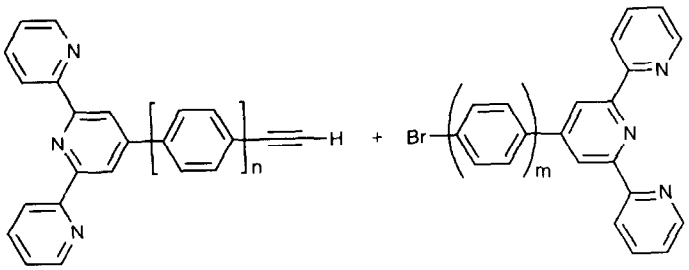
(502)

Aryl acetylene oligomers were synthesized using palladium–copper coupling (Eq. (503) [610], Eq. (504) [611], and Eq. (505) [612]). Dendrimers were synthesized this way (Eq. (506) [613] and Eq. (507) [614]).

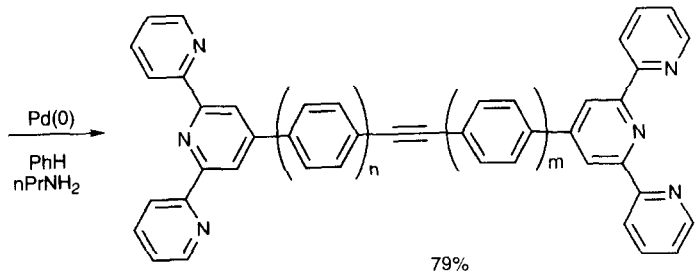


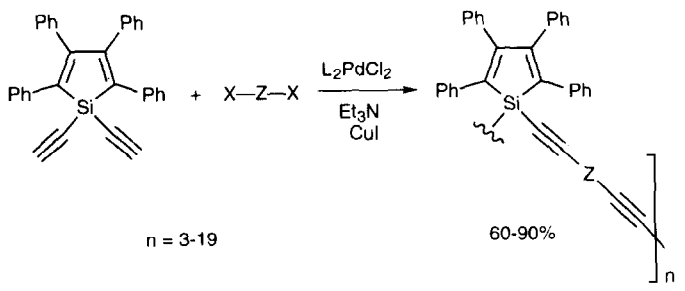
(503)

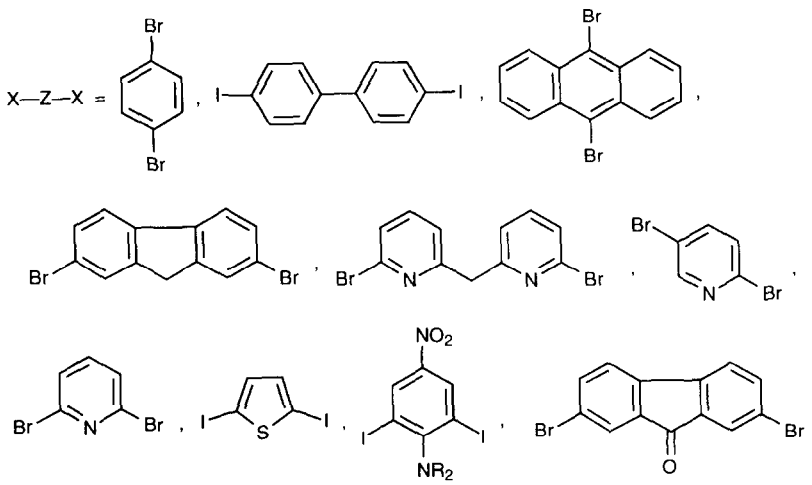
etc.



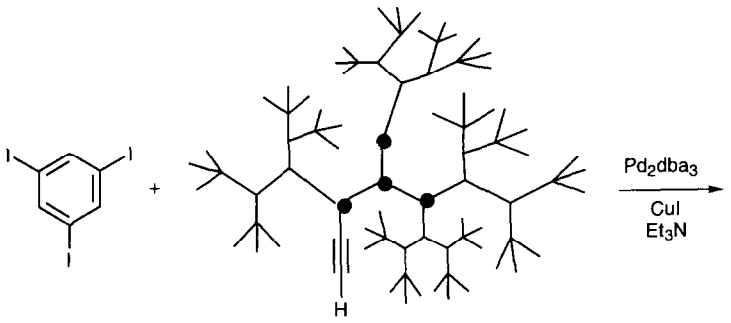
(504)



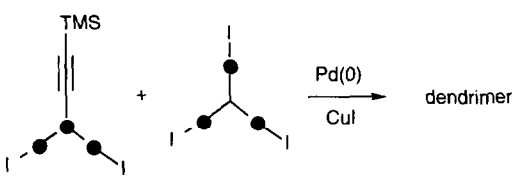




(505)

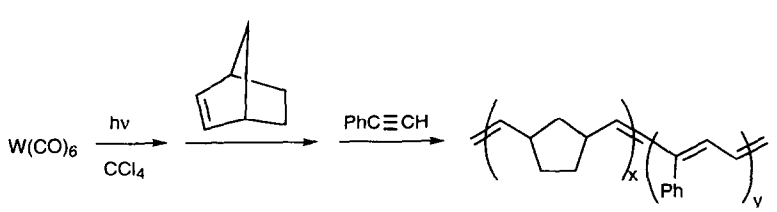


(506)

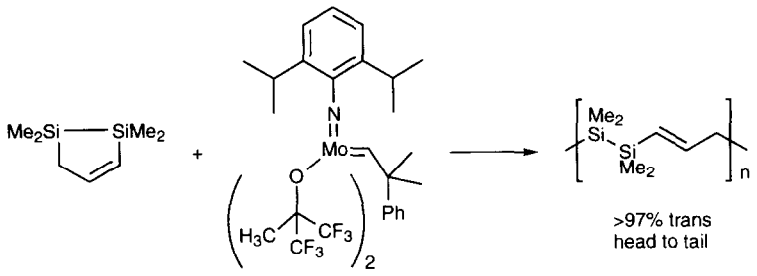


(507)

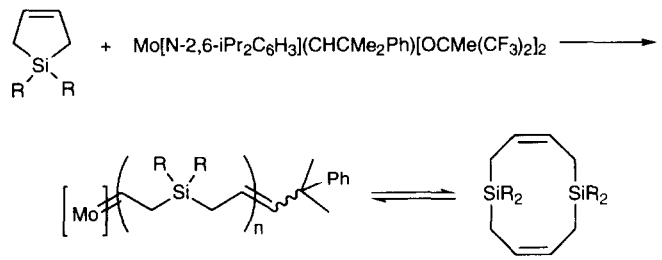
Ring opening metathesis of norbornene was catalyzed by Cp_2TiR_2 complexes [615]. Chiral molybdenum complexes catalyzed ROMP of substituted norbornadienes to give all cis highly tactic polymer [616]. Photolysis of molybdenum hexacarbonyl in carbon tetrachloride and norbornene led to living polymers which incorporated alkynes (Eq. (508)) [617]. Cyclic and vinyl and allyl silanes underwent ROMP (Eq. (509) [618] and Eq. (510) [619]).



(508)



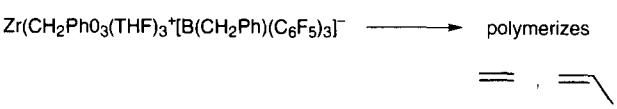
(509)



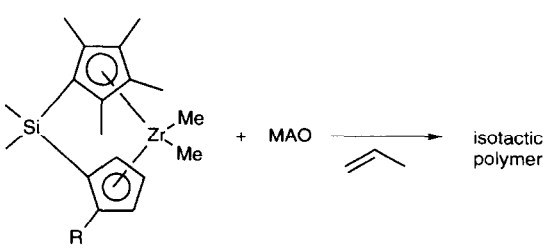
(510)

Base-free cations for zirconium-catalyzed Ziegler–Natta polymerization of alkenes were developed (Eq. (511) [620] and Eq. (512) [621]). Non C-2 symmetric Ziegler–Natta catalysts were developed (Eq. (513) [622] and Eq. (514) [623]). Titanium complexes catalyzed syndiotactic polymerization of styrene (Eq. (515)) [624]. Methylene cyclobutenes (Eq. (516)) [625] and 1,5-hexadiene (Eq. (517)) [626] were Ziegler–Natta polymerized. Vinylzirconium complexes reacted with aldehydes in an unusual way (Eq. (518)) [627].

(511)

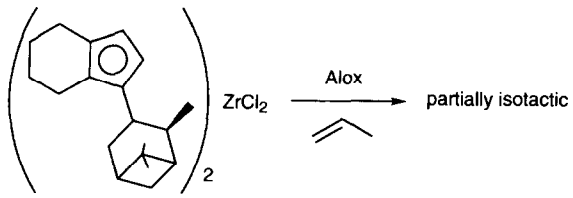


(512)

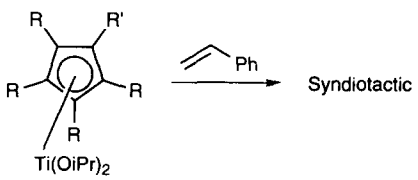


(513)

R = menthyl, neomenthyl



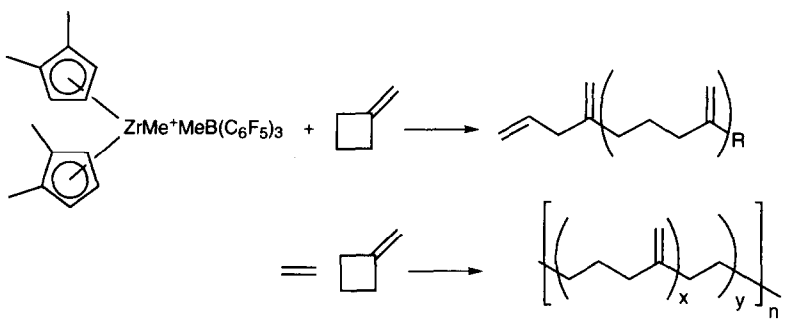
(514)



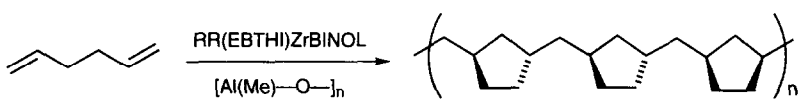
(515)

R' = H, PPh_2, $SiMe_3$

R = H, Me, Ph

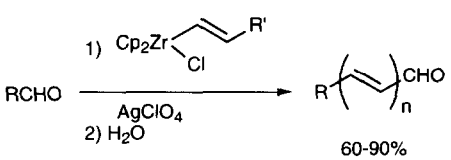


(516)



(517)

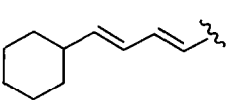
80% trans



60-90%

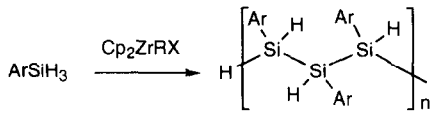
n = 1, R' = OEt n = 2, R' = Z, CH=CHOMe

R = Cp, , Ph, , $MeO_2C—(CH_2)_8$,



(518)

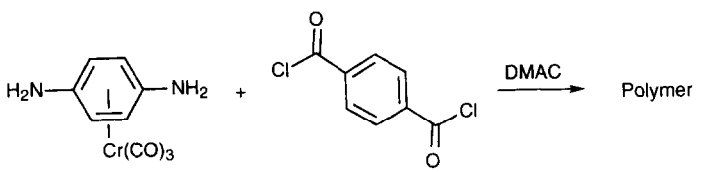
Zirconium complexes oligomerized arylsilanes (Eq. (519)) [628]. Chromium complexes of paraphenylenediamine were copolymerized with paraphthalic acid (Eq. (520)) [629].



40-90%

Ar = Ph, mMePh, mCF3Ph, pCF3Ph

(519)

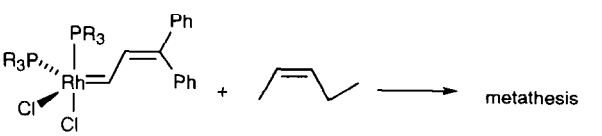


(520)

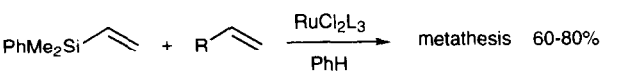
2.5. Rearrangements

2.5.1. Metathesis

"Olefin metathesis: a new tool in the synthesis of organic sulfur compounds" was the title of a review (4 references) [630], as was "Catalytic metathesis of olefins" (137 references) [631]. The WCl_5–1,1,3,3-tetramethyl-1,3-disilacyclobutane system catalyzed metathesis of functionalized alkenes [632]. Rhenium–tin systems catalyzed metathesis of silicon-containing olefins [633]. Other useful metathesis systems are seen in Eq. (521) [634], Eq. (522) [635], Eq. (523) [636], Eq. (524) [637] and Eq. (525) [638].

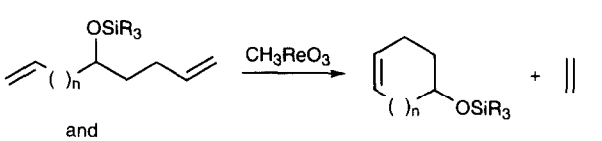


(521)

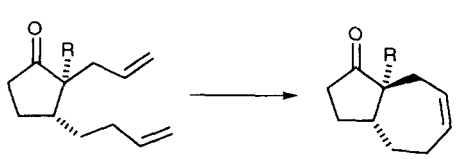


R = C5, C7, C8, C11, C16, Ph

(522)

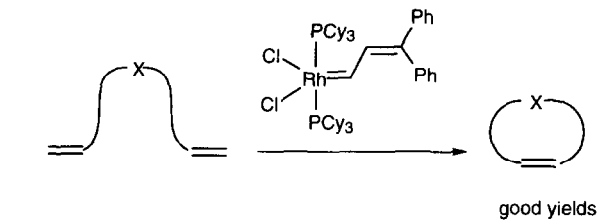


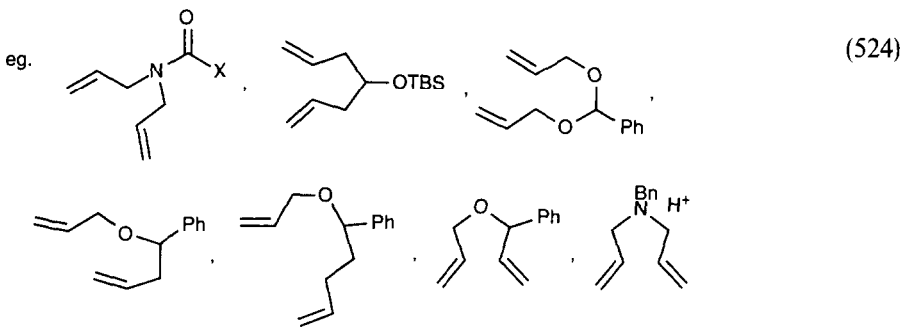
and



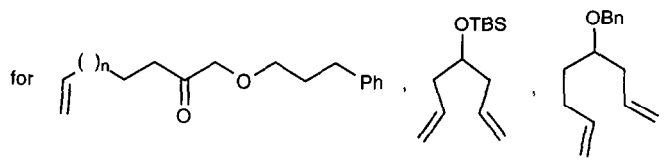
40-80%

(523)





(524)



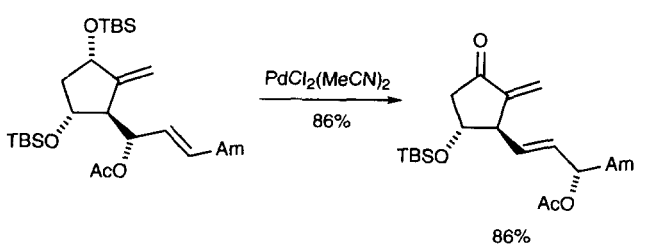
(525)

2.5.2. Olefin isomerization

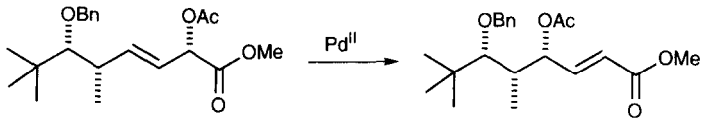
Titanocene dichloride catalyzed alkenes and cycloalkenes [639].

2.5.3. Rearrangement of allylic and propargylic compounds

A dissertation entitled "Palladium II catalysis: kinetics on a [3,3]-allylic ester rearrangement" has appeared [640]. Palladium(II) catalyzed the rearrangements of allylic acetates with a high degree of stereoselectivity (Eq. (526) [641], Eq. (527) [642], and Eq. (528) [643]). Trichloroimidates also rearranged (Eq. (529)) [644]. Nickel(0) catalyzed the rearrangement of cyclopropyl dienes (Eq. (530)) [645].

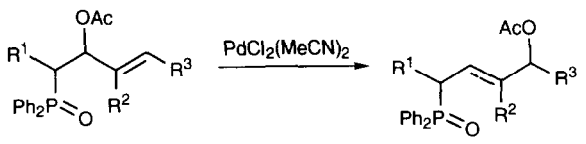


(526)



and

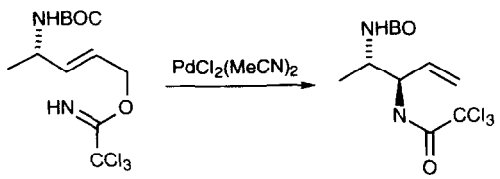
(527)



(528)

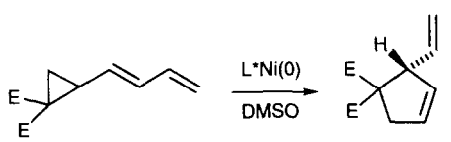
Regiospecific away from P

Stereoselective (E) suprafacial



(529)

48%



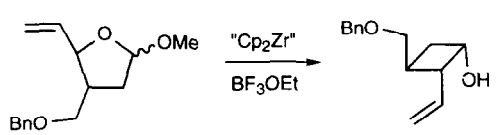
(530)

90% ee

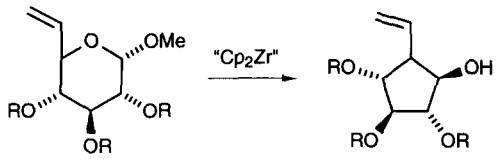
L* = [MOD-DIOP] 77% yield

2.5.4. *Skeletal rearrangements*

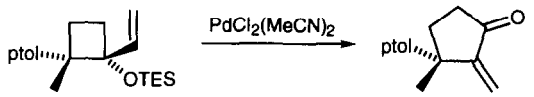
Zirconocene isomerized allyl acetals (Eq. (531) [646] and Eq. (532) [647]). Palladium isomerized vinylcyclopropanes to cyclopentanones (Eq. (533)) [648]. Rhodium catalyzed the rearrangements of cyclopropyl cyclobutenones to cycloheptadienones (Eq. (534)) [649].



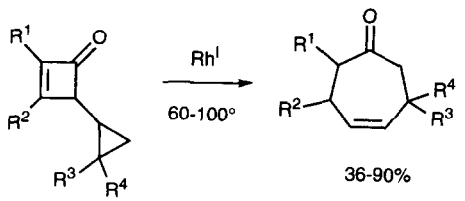
(531)



40-70% (532)



86% (533)

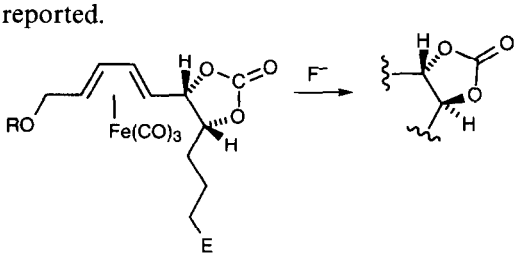


36-90% (534)

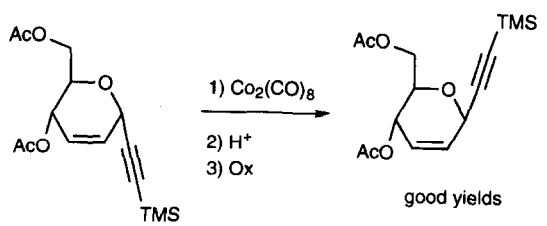
R^1 = H, nBu, Me, Et R^3 = H, Me, Ph
R^2 = Ph, nBu, iPrO, Et R^4 = H, Me

2.5.5. *Miscellaneous rearrangements*

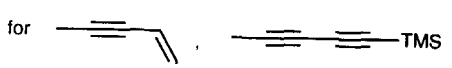
A review entitled "Tandem cyclopropanation/Cope rearrangement: a general method for the construction of seven membered rings" has appeared (42 references) [650]. Two epimerizations (Eq. (535) [651] and Eq. (536) [652]), a series of Wulff rearrangements (Eq. (537)) [653] and an olefin isomerization (Eq. (538)) [654] were also reported.

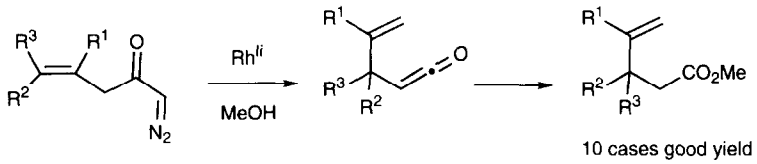


(535)

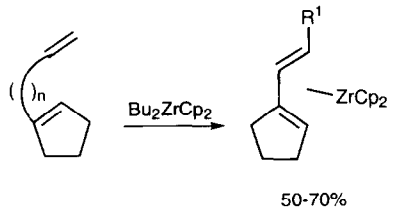


(536)





(537)

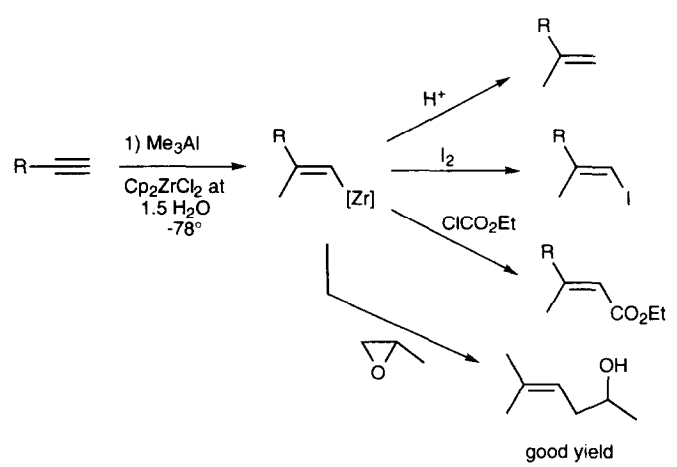


(538)

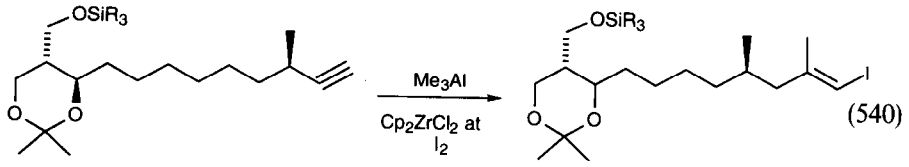
3. Functional group preparation

3.1. Halides

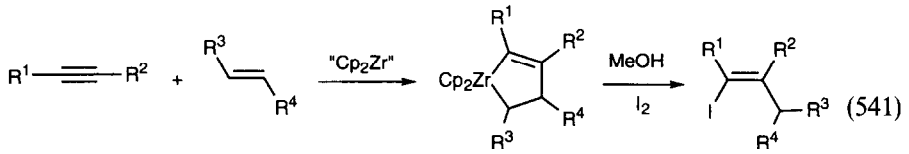
A small amount of water dramatically accelerated the zirconium-catalyzed carbalumination of alkynes, for the production of a range of functional groups (Eq. (539)) [655]. Vinyl iodides were prepared in this way (Eq. (540) [656] and Eq. (541) [657]). Titanium effected similar chemistry (Eq. (542)) [658]. Palladium catalyzed the conversion of alkenes to chlorohydrins (Eq. (543)) [659] and the iodoperfluoroalkylation of alkenes (Eq. (544)) [660]. Platinum(II) ring opened a cyclopropane to give chlorination (Eq. (545)) [661].



(539)

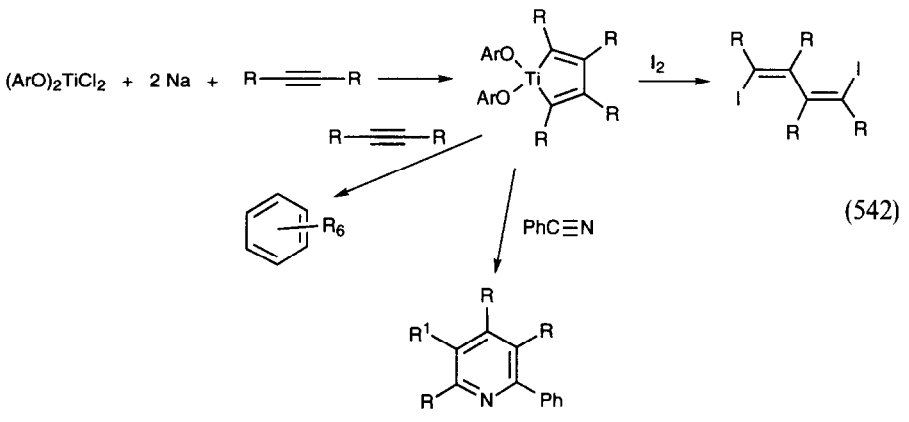


(540)

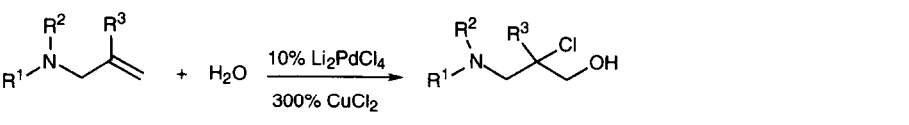


(541)

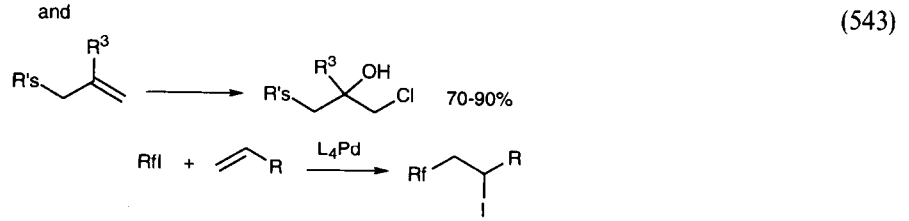
$R^2 = R^1$ = nPr, Ph, Et R^3 = H, TMS R^4 = H



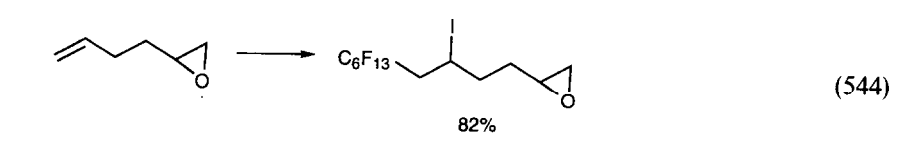
(542)



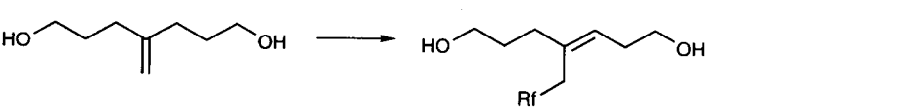
and

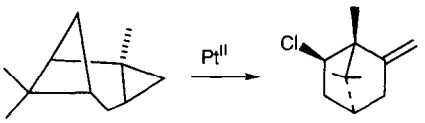


(543)



(544)

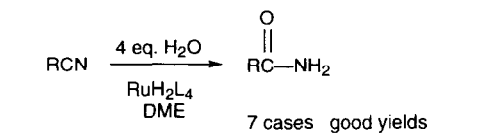




95% (545)

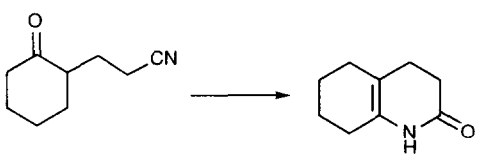
3.2. Amides, nitriles

Rhodium hydrides catalyzed the hydrolysis of nitriles (Eq. (546)) [662]. Palladium–ruthenium complexes catalyzed the reductive carbonylation of nitroaromatics to carbamates (Eq. (547)) [663]. Rhodium carbonyl clusters catalyzed the conversion of allyl phosphonates to amides (Eq. (548)) [664]. Nickel(0) catalyzed the opening of anhydrides to amides (Eq. (549)) [665].

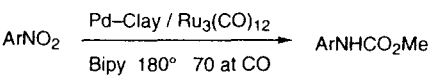


7 cases good yields

and



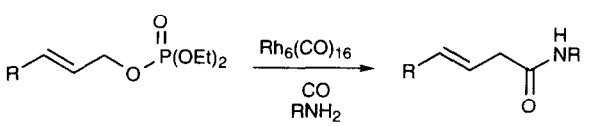
40-80% 11 cases (546)



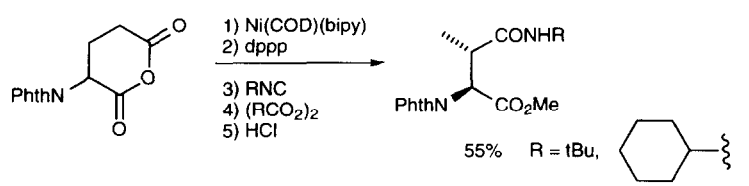
60-90% (547)

Ar = pMePh, oMePh, 2-Naph, 1-Naph

and $Ar(NO_2)_2 \longrightarrow Ar(NHCO_2Me)_2$

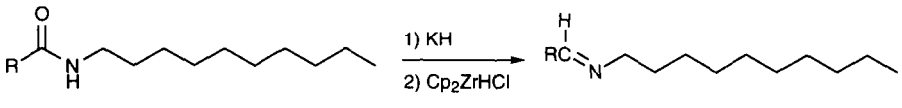


70-85% (548)

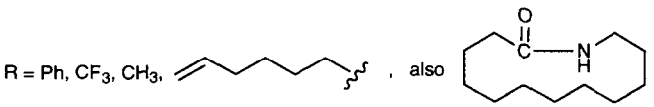


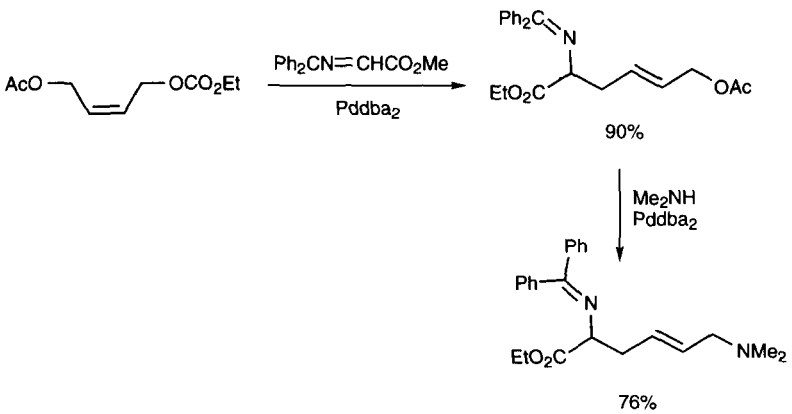
55% R = tBu, (549)

Imines (Eq. (550) [666] and Eq. (551) [667]), imidates (Eq. (552)) [668], amidines (Eq. (553) [669] and Eq. (554) [670]) and azo compounds (Eq. (555)) [671] were prepared by organometallic methods.

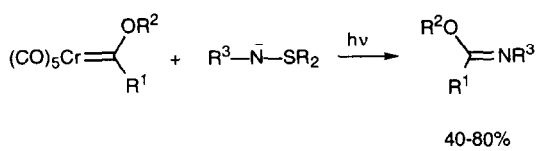


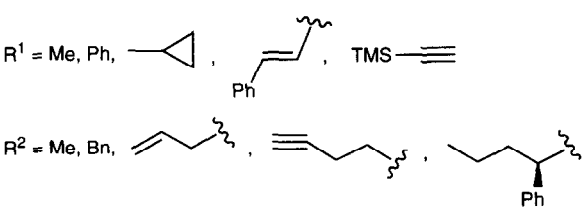
(550)



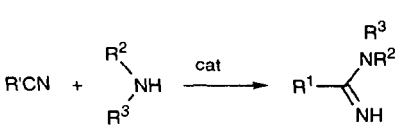


(551)

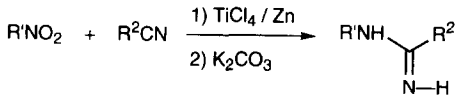




(552)



(553)

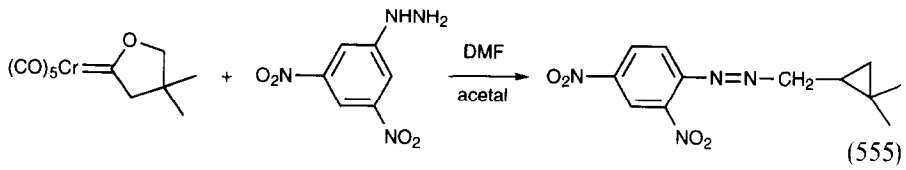


43-79%

(554)

R^1 = pClPh, mClPh, Ph

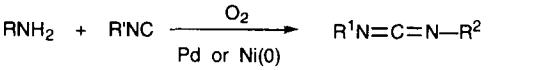
R^2 = pClBn, Bn, Ph



6%

(555)

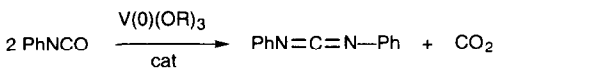
Carbodimides were made by palladium-catalyzed reaction of amines with isonitriles (Eq. (556)) [672] and from dicarboxylations of isocyanates (Eq. (557)) [673]. Allyl acetates were converted to nitriles by palladium-catalyzed reaction with trimethylsilyl cyanide (Eq. (558)) [674]. Palladium catalyzed the conversion of vinyl triflate to acrylonitriles (Eq. (559)) [675].



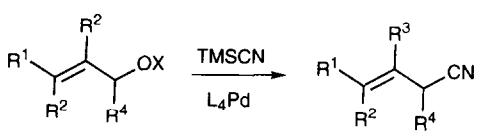
40-80%

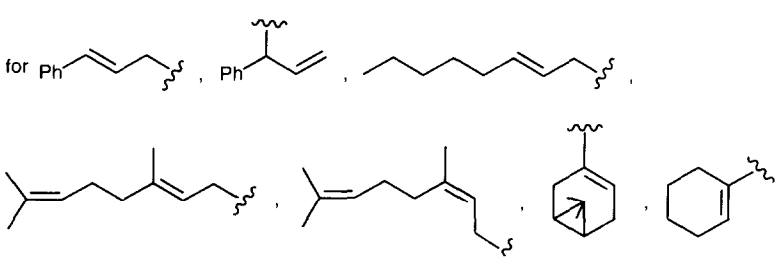
(556)

R = pMePh, pMeOPh, 3,5-Cl_2Ph R^1 = tBu,

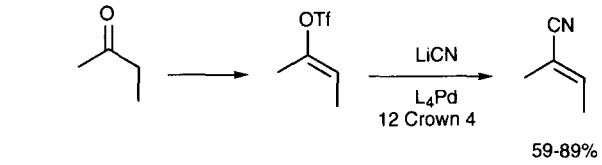


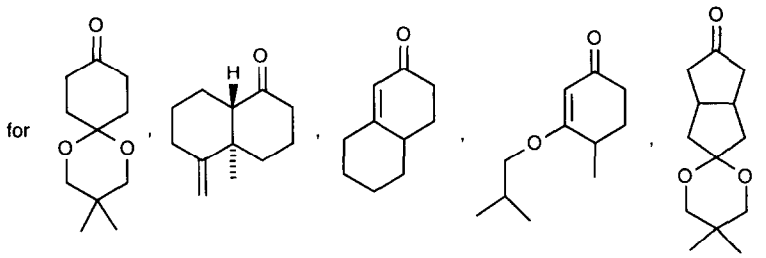
(557)





(558)

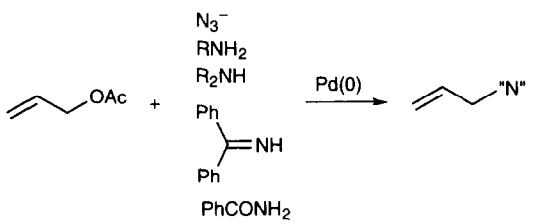




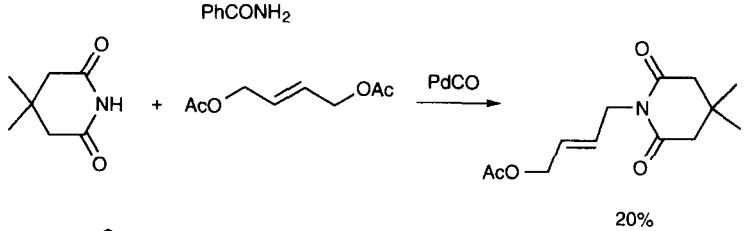
(559)

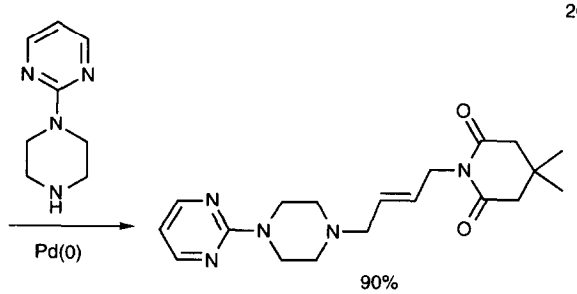
3.3. Amines, alcohols

Palladium(0) catalyzed the allylic amination of allyl acetates (Eq. (560) [676], Eq. (561) [677], Eq. (562) [678], and Eq. (563) [679]), and the deallylation of allyl amines (Eq. (564)) [680]. γ-alkoxy acids were aminated via their η^3-allyliron complex (Eq. (565)) [681]. Cobalt propargyl cations were aminated (Eq. (566)) [682]. Cupration of ynamines led to a vinyl copper which could be transferred (Eq. (567)) [683]. Methylated aryl amines were dealkylated via their arenechromium tricarbonyl adduct (Eq. (568)) [684].

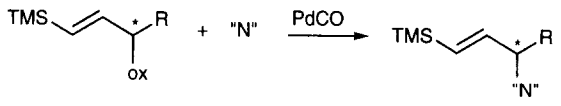


(560)





(561)

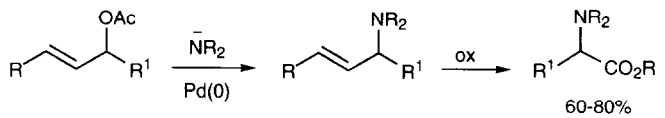


>98% ee 40-90% yield

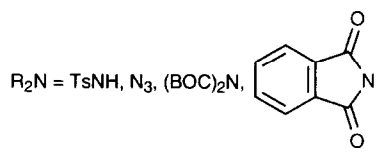
"N" = $BuNH_2$, $TsNH_2$, N_3

R = C_5, iBu, , Ph

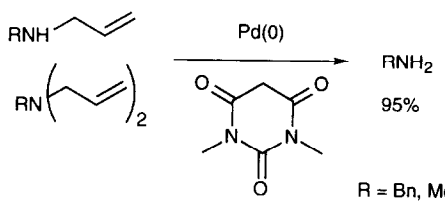
(562)



60-80%

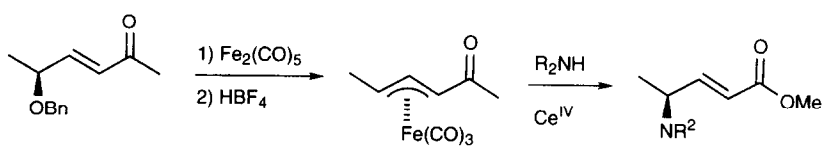


(563)



R = Bn, $MeOCCH_2$, tBu

(564)

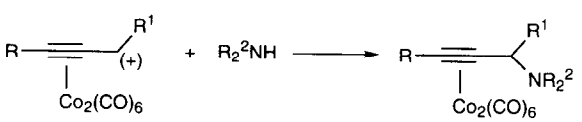


83% >95% ee

51-91%

>95% ee

(565)



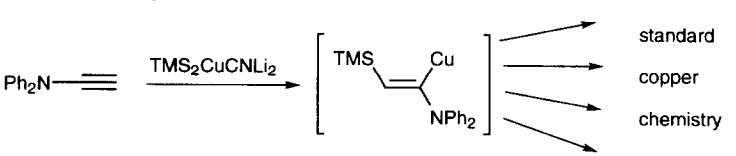
60-70%

(566)

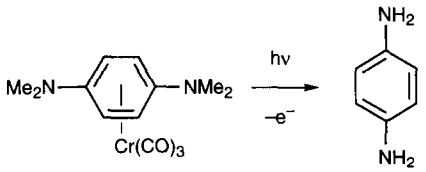
R = H, Me, TMS

R^1 = H, Me

R^2 = wide range of amines

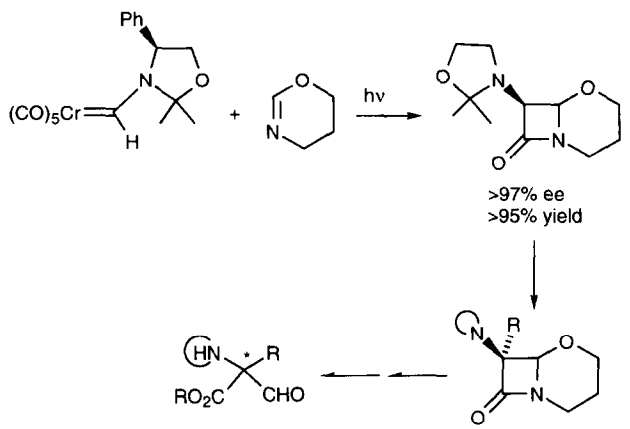


(567)

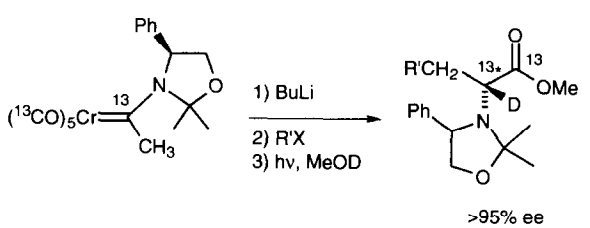


(568)

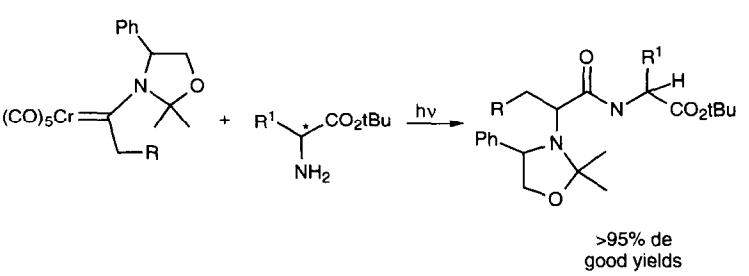
Asymmetric synthesis of amino acids via transition metal complexes was the subject of a symposium report [685]. Chromium carbene complexes were used in the synthesis of α-alkyl amino acids (Eq. (569)) [686], isotopically labelled amino acids (Eq. 570)) [687] and to incorporate amino acids into peptides (Eq. (571)) [688]. Amino acids containing iron dienyl fragments were prepared to label peptides (Eq. (572)) [689].



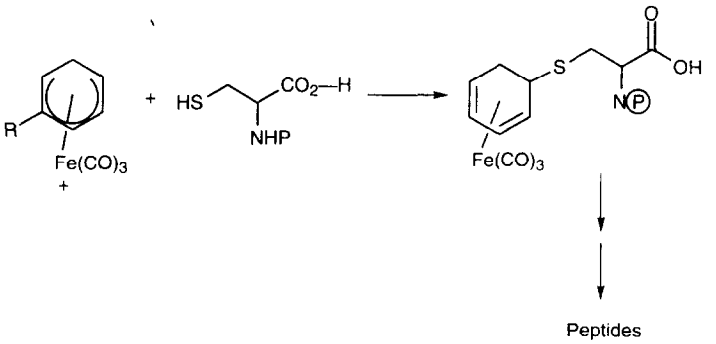
(569)



(570)

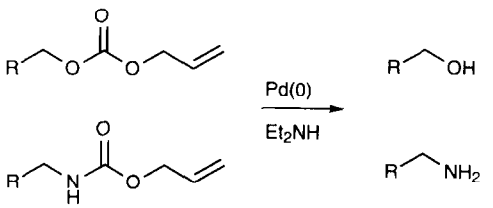


(571)



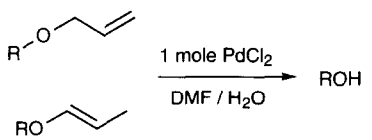
(572)

Palladium(0) (Eq. (573) [690] and Eq. (574) [691]) and zirconocene (Eq. (575)) [692] deallylated allyl ethers. Palladium(0) catalyzed the reduction of epoxides (Eq. (576) [693], Eq. (577) [694], and Eq. (578) [695]). Copper amide complexes opened epoxides to amino alcohols (Eq. (579)) [696].



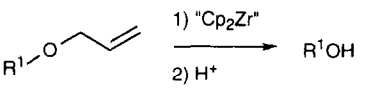
(many classes, β-lactams, sugars, amino acids etc.)

(573)

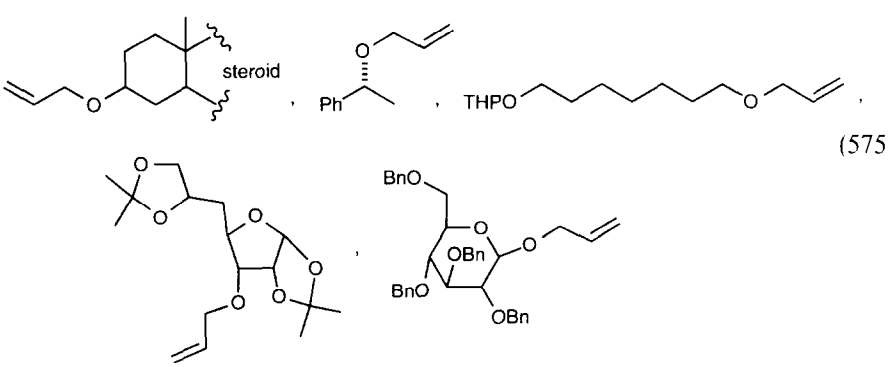


R = sugars, at anomeric carbon

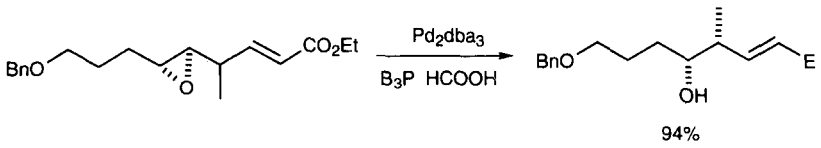
(574)



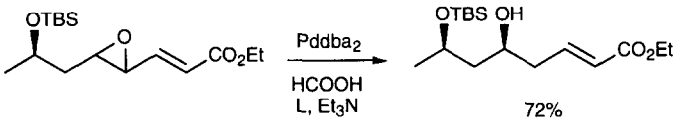
50-97%



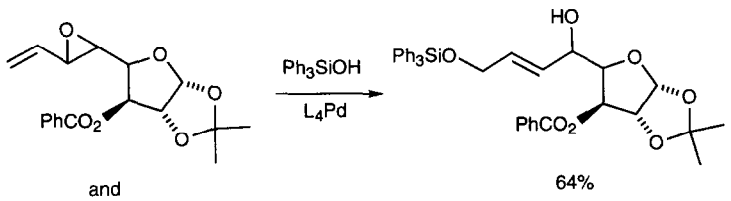
(575)



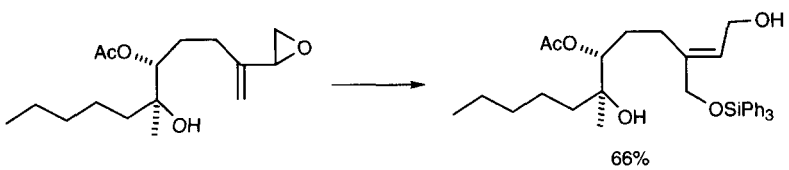
(576)

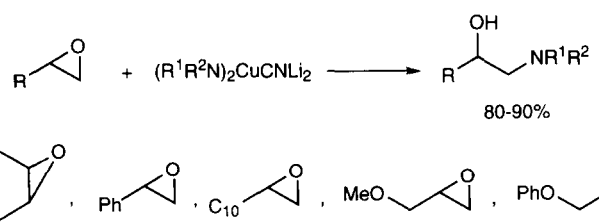


(577)



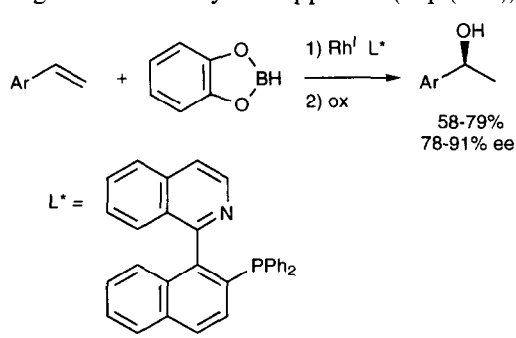
(578)



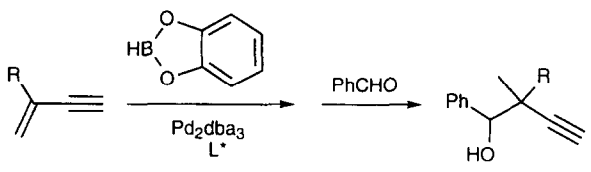


(579)

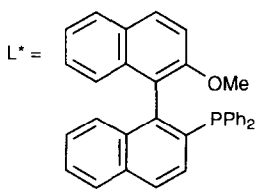
Chiral rhodium complexes catalyzed the asymmetric hydroboration of styrenes (Eq. (580)) [697]. Palladium catalyzed the coupling of boranes to aldehydes (Eq. (581)) [698]. Chromium complexes of chiral aryl aminoalcohols catalyzed the asymmetric addition of diethyl zinc to aldehydes (Eq. (582)) [699]. Zirconium aldehyde complexes alkylated ketones (Eq. (583)) [700]. The full paper on Cu homologation chemistry has appeared (Eq. (584)) [701].

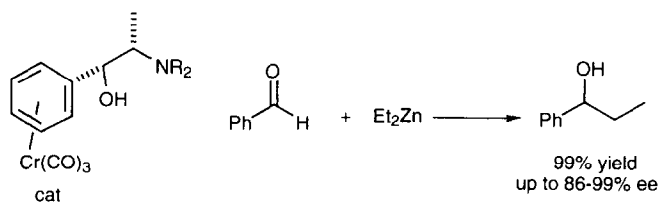


(580)

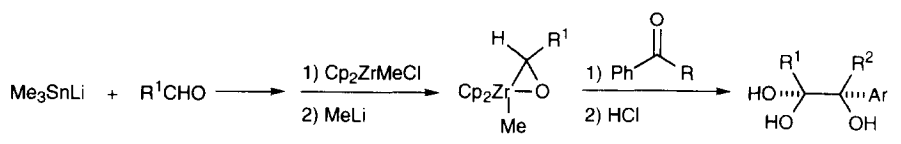


up to 61% ee (581)



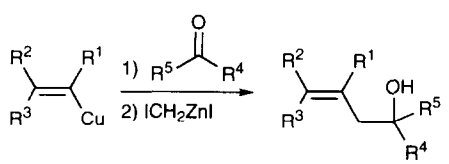


99% yield
up to 86-99% ee (582)

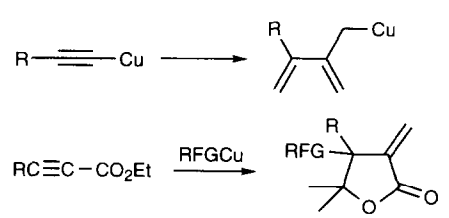


57-78%

R^1 = pMePh, Ph, iBu, Et Ar = ptolyl, Ph R^2 = H, Ph, Me (583)



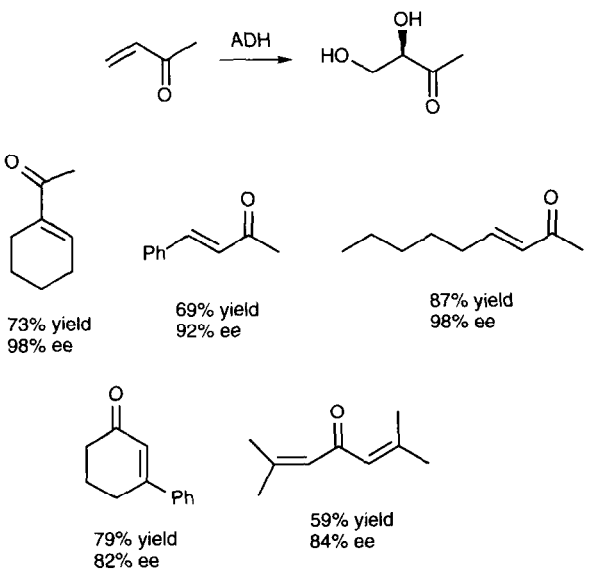
and



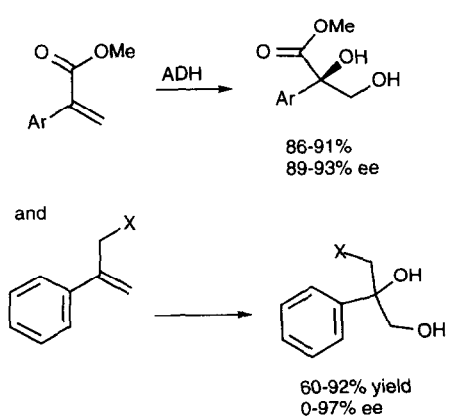
(584)

Asymmetric dihydroxylation of olefins catalyzed by osmium tetroxides was the subject of a review (22 references) [702]. A review dealing with asymmetric oxidation reactions involving Mn(III) salen complex has also appeared (10 references) [703].

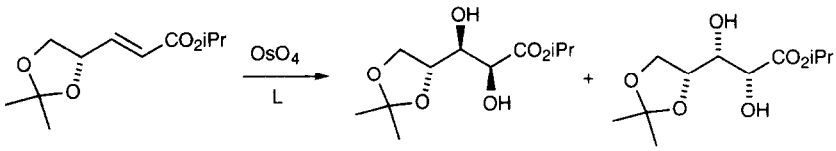
A full paper detailing the synthesis and crystal structure of cinchona alkaloids for use in the catalytic cis hydroxylation of alkenes has appeared [704]. Bis cinchona alkaloid substituted pyrimidines gave high EEs in the cis hydroxylation of terminal alkenes [705]. The effect of ligands on the selectivity for cis hydroxylation of various alkene types has been probed [706,707]. Functionalized alkanes were asymmetrically dihydroxylated (Eq. (585) [708], Eq. (586) [709], Eq. (587) [710], Eq. (588) [711], Eq. (589) [712], Eq. (590) [713], Eq. (591) [714], and Eq. (592) [715]). Olefins could be resolved using the ADH reaction (Eq. (593)) [716]. A C-2 symmetric diamine was an efficient ADH ligand (Eq. (594)) [717].



(585)

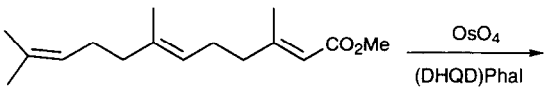


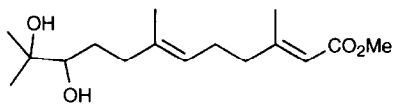
(586)



(587)

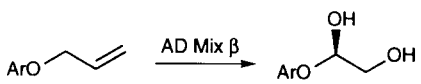
from 39:1 to 1:7 depending on L





(588)

R(+) 98% ee S(-) 92% ee

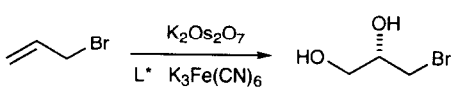


85-95% yield

(589)

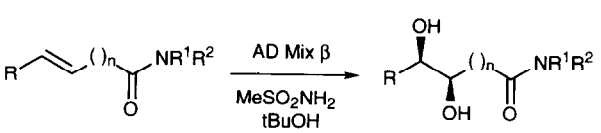
Ar = pMeOPh, pMeOPh, pClPh, Ph >90% ee

Ar = oMeOPh, oMePh, oClPh, oNCPh 20-60% ee



61-74%
72% ee

(590)

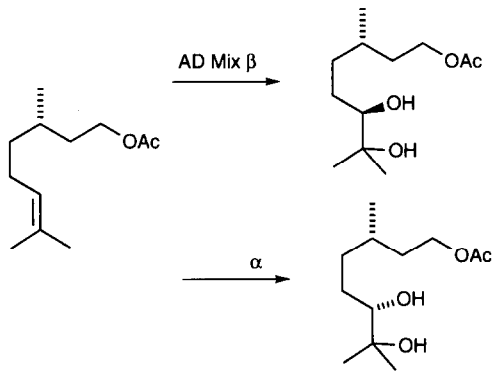


(591)

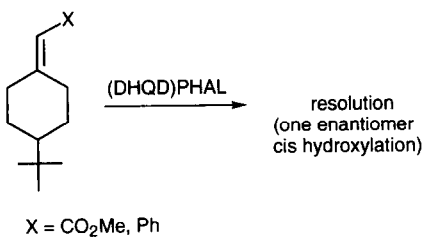
n = 0, 1

R = Ph, Bu, Cs

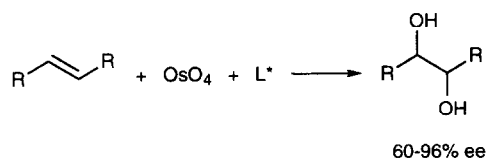
80-97% 93-98% ee

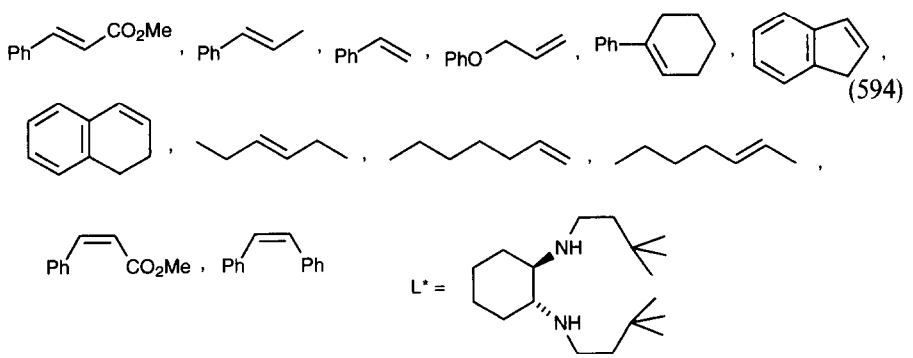


(592)



(593)

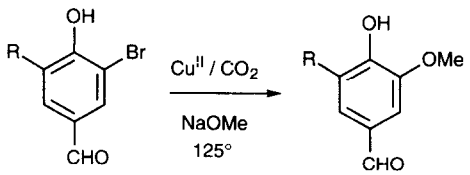




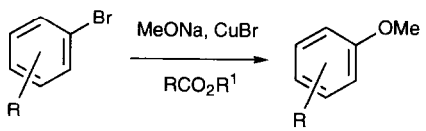
(594)

3.4. Ethers, esters, acids

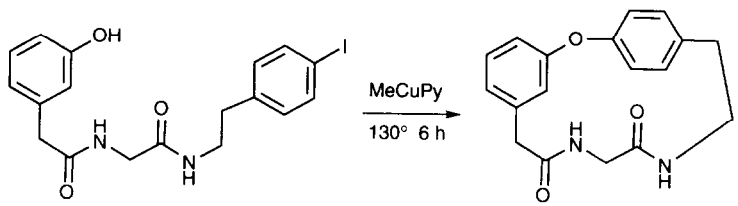
Copper salts promoted the alkoxylation of aryl halides (Eq. (595) [718], Eq. (596) [719], and Eq. (597) [720]). Palladium cleaved propargyl enol ethers (Eq. (598)) [721]. Ketal formation was catalyzed by a number of metals (Eq. (599) [722], Eq. (600) [723] and Eq. (601) [724]).



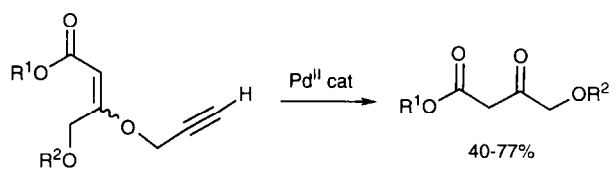
99% (595)



(596)



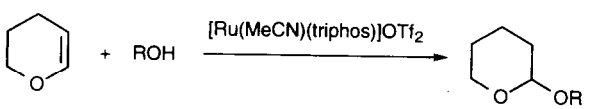
40% (597)



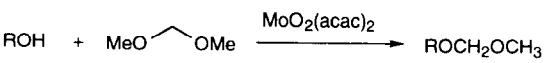
40-77% (598)

R^1 = Me, Et, nBu, Bn

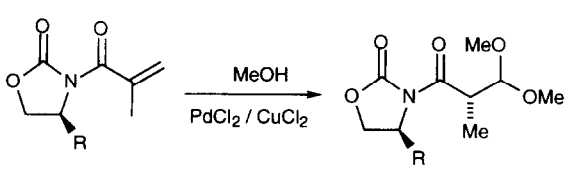
R^2 = THP, DEE



(599)



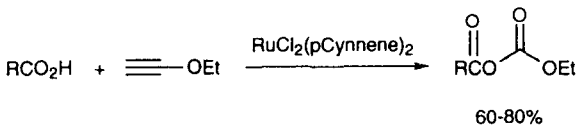
63-90%
12 cases (600)



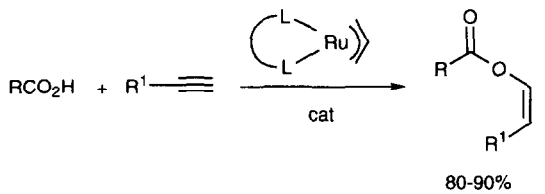
60-80%

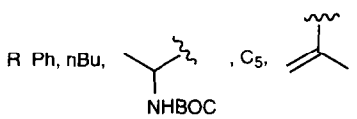
23-95% ee (601)

Ruthenium complexes catalyzed the reaction of acids with alkynes to give enol ethers (Eq. (602) [725], Eq. (603) [726], and Eq. (604) [727]). Synthesis of dicarboxylic acids by transition metal catalyzed oxidative cleavage of fatty acids was reviewed (57 references) [728]. Palladium(II) catalyzed the bis acetoxylation of dienes (Eq. (605) [729] and Eq. (606) [730,731]) and the allylic acetoxylation of cyclohexene (Eq. (607)) [732].

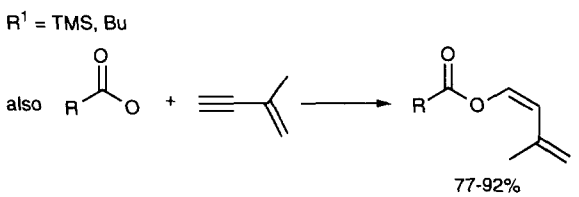


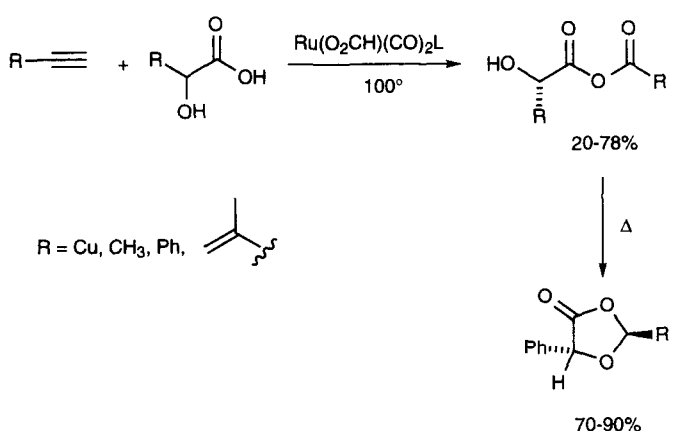
(602)



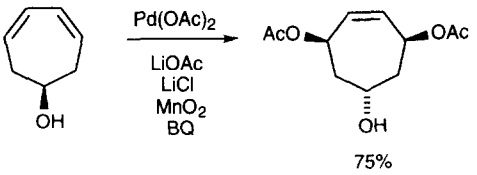


(603)

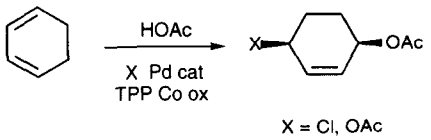




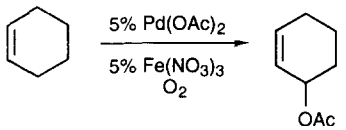
(604)



(605)

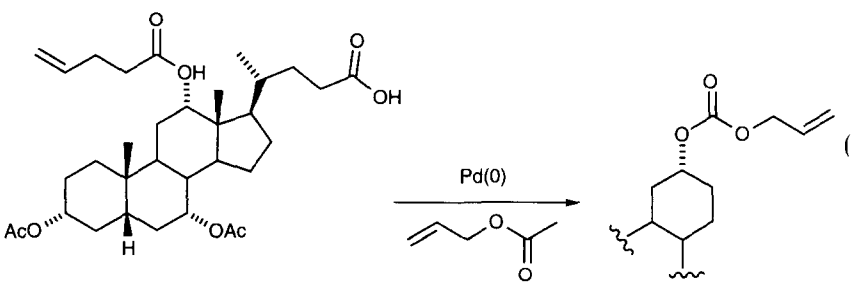


(606)

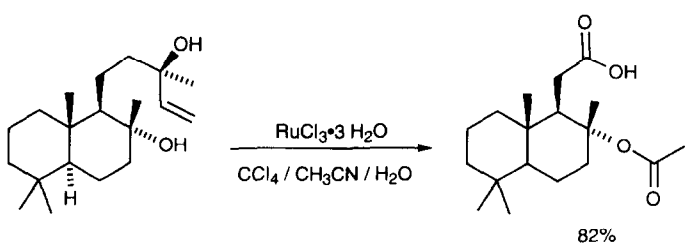


(607)

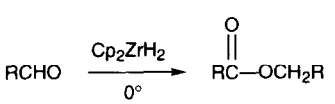
Palladium(0) catalyzed the allylcarboxylation of a steroidal alcohol (Eq. (608)) [733]. Two other ester forming reactions are shown in Eq. (609) [734] and Eq. (610) [735].

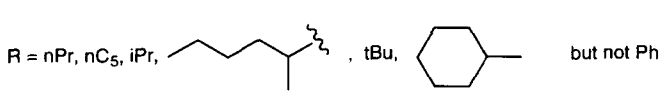


(608)



(609)

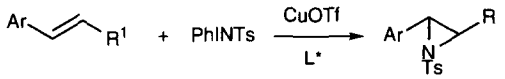


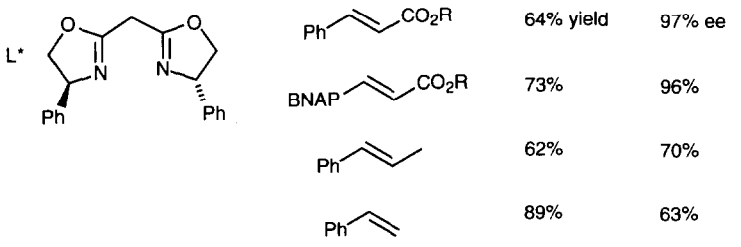


(610)

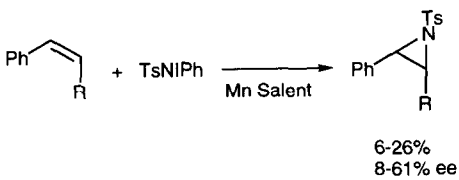
3.5. Heterocycles

Olefins were converted to N-tosyl aziridines using copper–bis oxazole catalysts (Eq. (611)) [736], manganese salen complexes (Eq. (612)) [737] and copper salen complexes (Eq. (613)) [738].

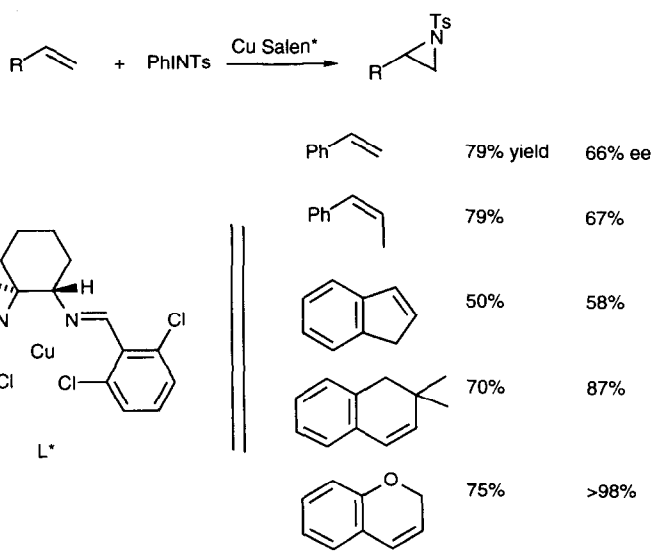




(611)



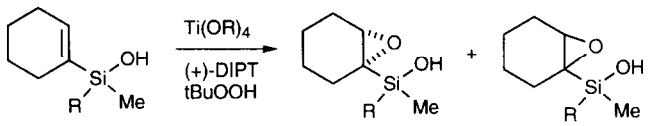
(612)



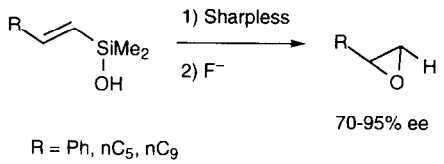
(613)

Dissertations entitled "Asymmetric catalytic epoxidations of simple olefins" [739] and "Asymmetric epoxidation and cyclopropanation of alkenes catalyzed by 'chiral wall' metalloporphyrins" [740] have appeared. Asymmetric epoxidation using chiral

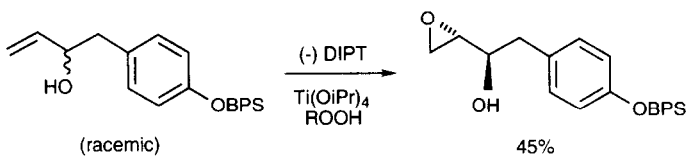
salen complexes has been reviewed [741]. Alkenyl silanols underwent efficient Sharpless epoxidation (Eq. (614) [742] and Eq. (615) [743]). Racemic allylic alcohols were resolved by Sharpless epoxidation (Eq. (616)) [744].



(614)

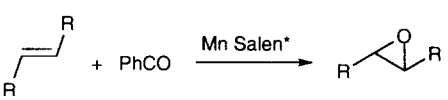


(615)

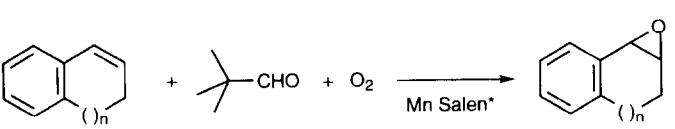


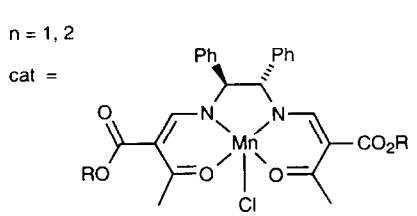
(616)

Optically active manganese salen complexes catalyzed the epoxidation of alkenes (Eq. (617) [745], Eq. (618) [746] and Eq. (619) [747]). Epoxidation and hydroxylation were reviewed (382 references) [748]. Alkenes were epoxidized by periodate in the presence of manganese porphyrin complexes [749] and by sodium bromite in the presence of copper ions [750]. Shape-selective olefin epoxidation catalyzed by metallo picnic basket porphyrins was reported [751]. The properties of MCPBA, singlet oxygen, and $VO(acac)_2$–*t*BuOOH for the epoxidation of allylic alcohols were compared [752].

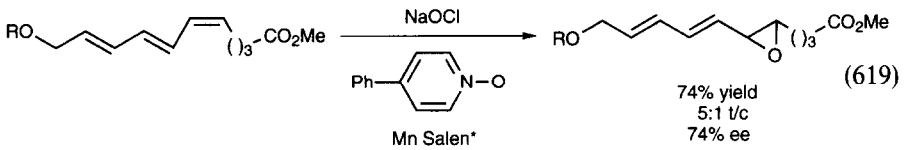


(617)



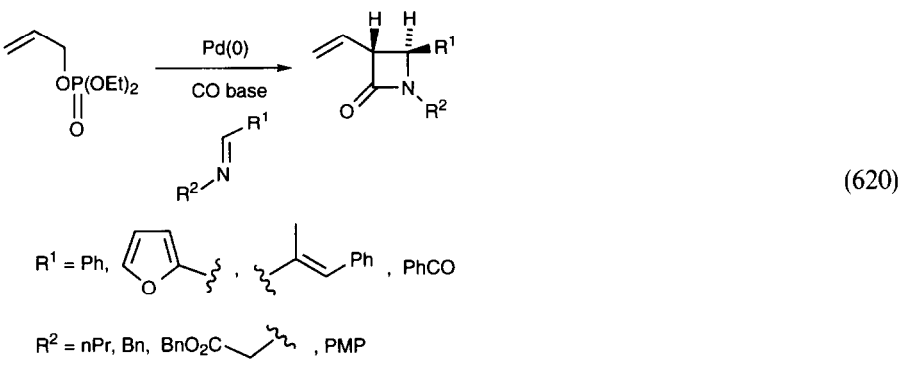


(618)

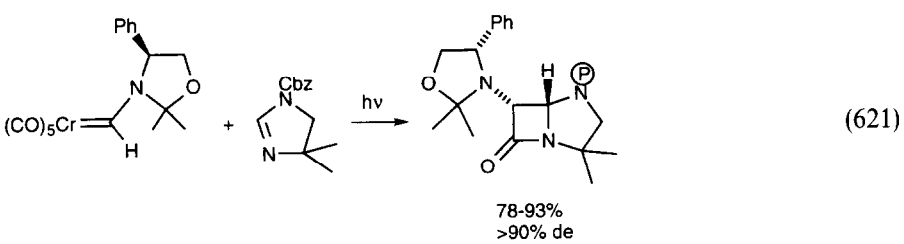


(619)

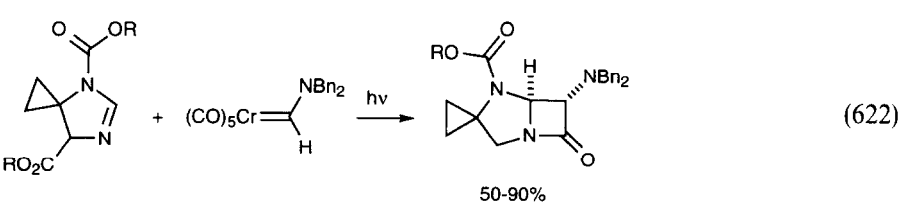
β-lactams were synthesized by palladium-catalyzed cyclocarbonylation of imines with allyl phosphonates (Eq. (620)) [753], by chromium carbene complex photochemistry (Eq. (621) [754] and Eq. (622) [755]) and by rhodium(II)-catalyzed NH insertion (Eq. (623)) [756]. β-azetidinones were synthesized by copper-catalyzed NH insertion (Eq. (624)) [757]. β-lactam antibiotics containing ferrocene were made [758].



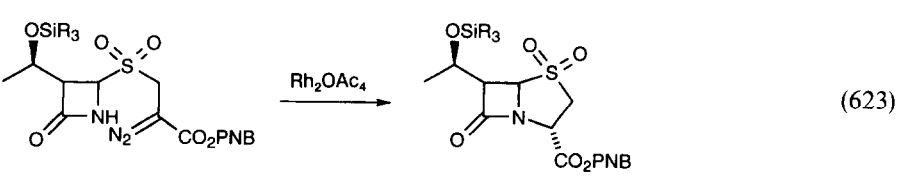
(620)



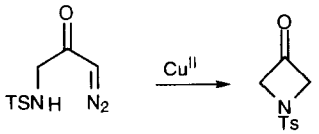
(621)



(622)

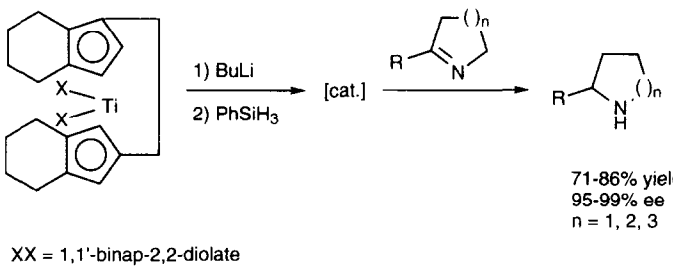


(623)

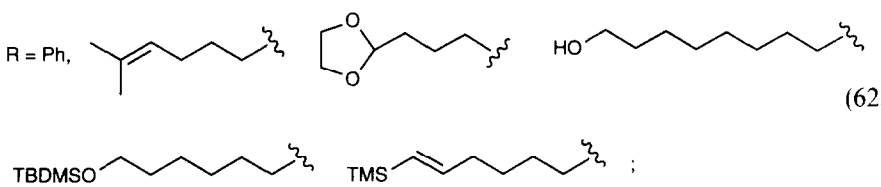


(624)

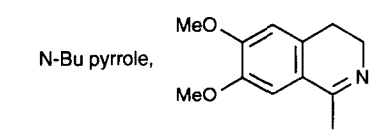
Cyclic imines were reduced to saturated nitrogen heterocycles using titanocene-based catalysts (Eq. (625)) [759]. Palladium(0) cyclized amino allyl ethers (Eq. (626)) [780], amino allenes (Eq. (627)) [761] and amino vinyl halides (Eq. (628)) [762]. Amino alkynes were cyclized by titanium complexes (Eq. (629)) [763].

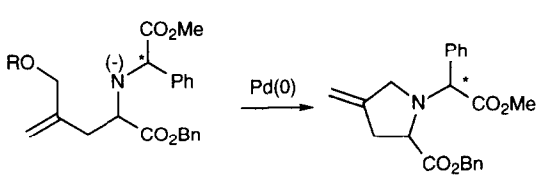


XX = 1,1'-binap-2,2-diolate



(625)

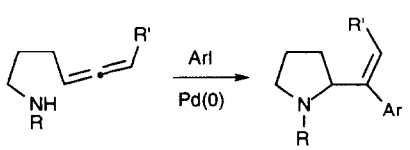




(626)

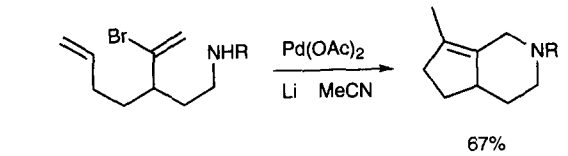
70-90% de

50-65% yield



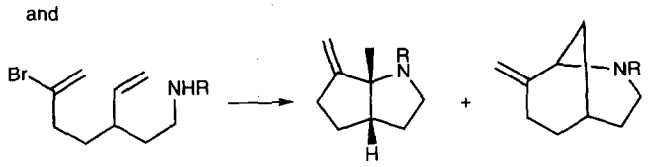
(627)

67-80%



67%

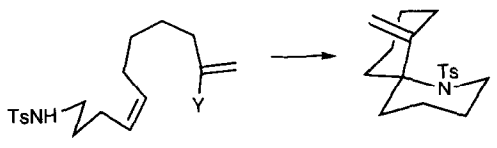
and



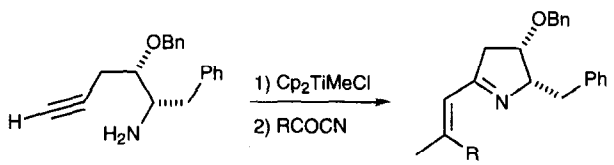
78%

(628)

and



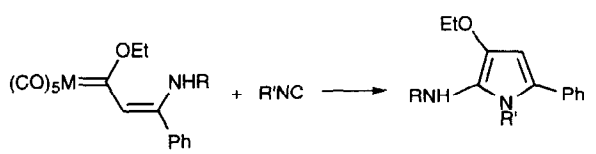
67%



80%

(629)

Pyrroles were synthesized from carbene complexes and isonitriles (Eq. (630)) [764] and from propargyl amines (Eq. (631)) [765]. Pyrrolidinones were made by ruthenium-catalyzed atom transfer cyclization (Eq. (632) [766] and Eq. (633) [767]), by palladium trimethylenemethane chemistry (Eq. (634)) [768] and [6+2] cycloaddition to chromium cycloheptatriene complexes (Eq. (635)) [769].

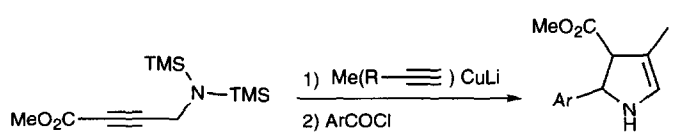


>90%

(630)

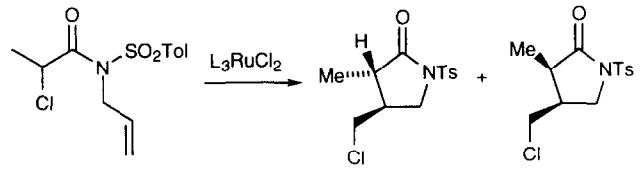
R = Ph, iPr, Bn

R' = Cy, tBu

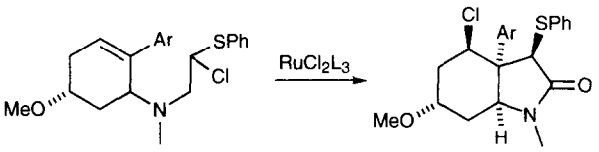


30-60%

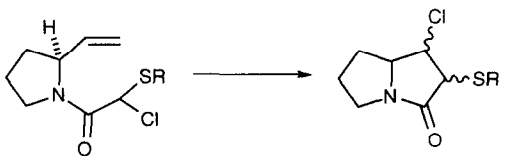
(631)



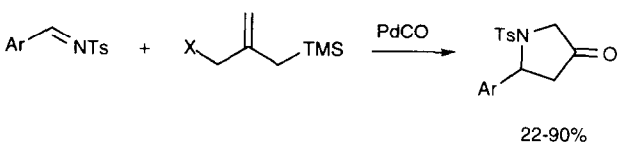
(632)



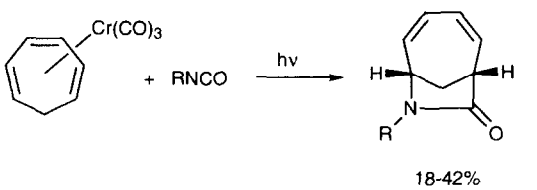
and



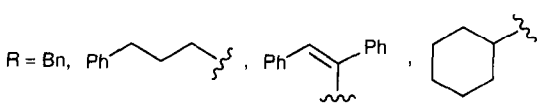
(633)



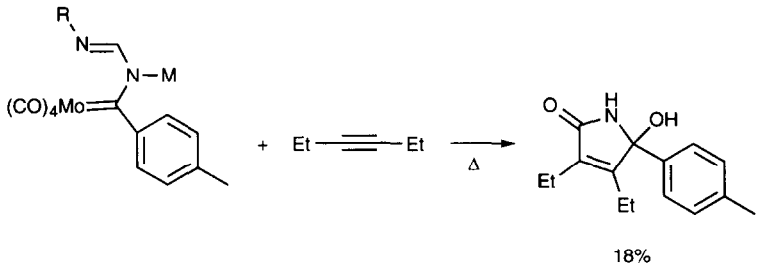
(634)



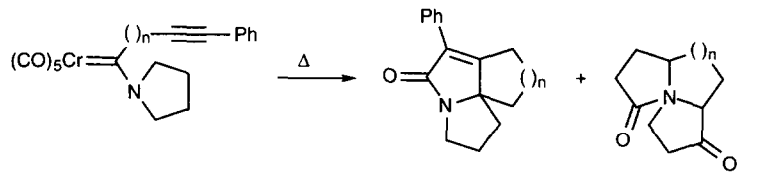
(635)



Group 6 carbene complexes were used to synthesize pyrrolidinones (Eq. (636) [770] and Eq. (637) [771]).

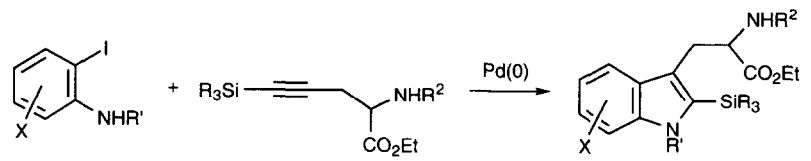


(636)

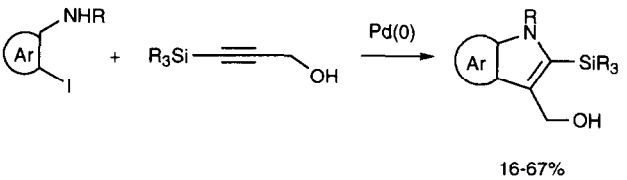


(637)

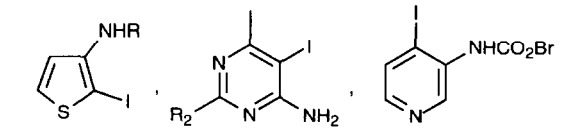
Palladium catalyzed the conversion of *o*-iodoanilines to indoles (Eq. (638) [772] and Eq. (639) [773]), as well as the cyclization of N-attached aryl halides into the indole nucleus (Eq. (640)) [774] and the cyclization of *o*-nitrostyrenes to indoles (Eq. (641)) [775]. Indoles were also synthesized from chromium carbene complexes (Eq. (642)) [776] and iron diene complexes (Eq. (643)) [777].

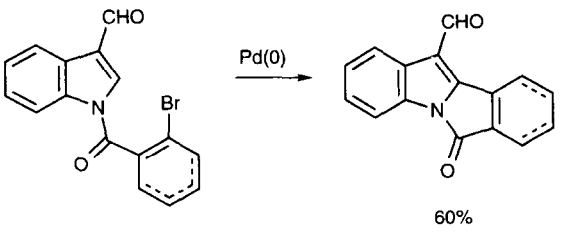


(638)

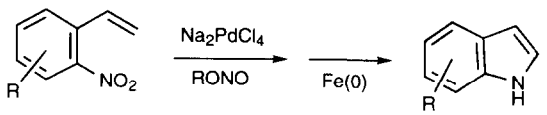


(639)

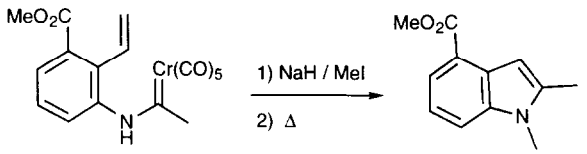




(640)

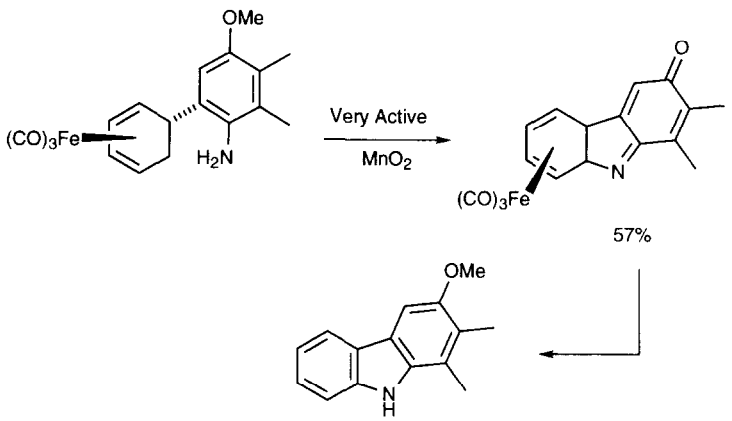


(641)



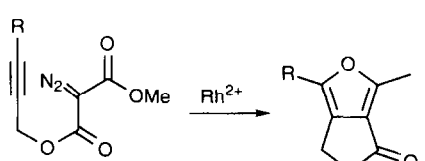
11%

(642)



(643)

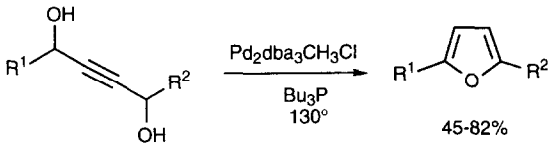
The synthesis of furans via rhodium(II)-catalyzed reactions of acetylenes with α-diazocarbonyls was developed into an *Organic Synthesis* preparation [778] (Eq. (644) [779]). Palladium catalyzed the production of furans from propargyl alcohols (Eq. (645)) [780], acetylenic ketones (Eq. (646)) [781] and vinyl halide plus *o*-iodoanisole (Eq. (647)) [782]. Cobalt complexed vinyl ketenes formed furans (Eq. (648)) [783].



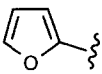
70%

R = H, Me, Ph, TMS, nC_5

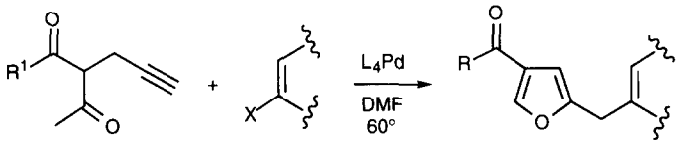
(644)



(645)

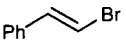
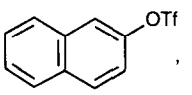
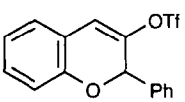
R^1 = Me, Et, nBu, iPr,  , nC_{16}, nC_7

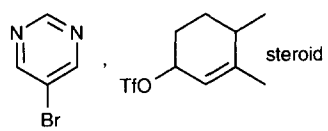
R^2 = Me, Et, H, iPr

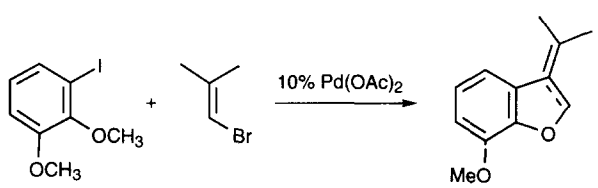


R = Me, OEt X = Br, OTf, I

(646)

alkene =  , PhI, pClPhI, pMeO2CPhI,  , 

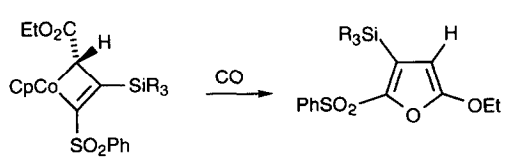




(647)

82%

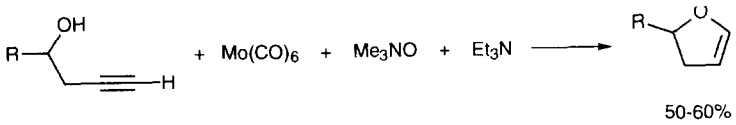
"C–H of OCH_3 activated!"



(648)

Molybdenum carbonyl (Eq. (649)) [784] and palladium(II) in the presence of indium(III) (Eq. (650)) [785] produced dihydrofurans. Tetrahydrofurans were produced by palladium-catalyzed cyclization of allenic alcohols (Eq. (651)) [786],

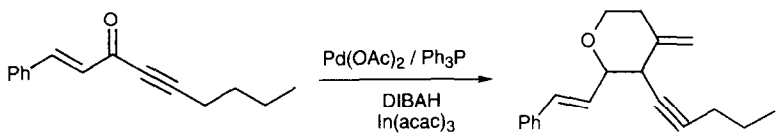
rhodium(I)–tin(II)-catalyzed cyclization of olefinic ketones (Eq. (652)) [786], zirconium-assisted reactions of epoxides (Eq. (653)) [788], and the oxidation of hydroxy η^3-allylmolybdenum complexes (Eq. (654)) [789].



50-60%

(649)

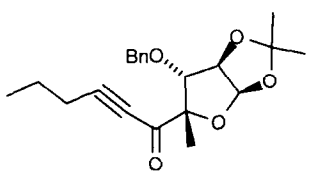
R = Ph, CH_2OH, $PivOCH_2$, $TBSOCH_2$

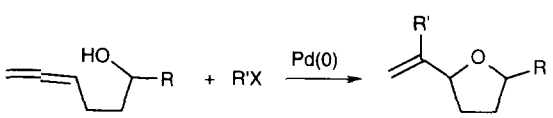


78%

(650)

also

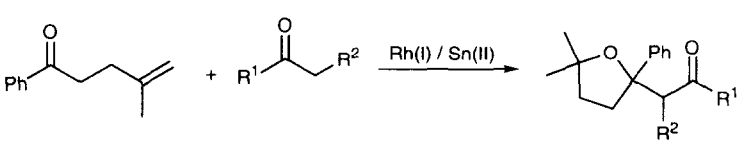




40-60%

30 cases

(651)

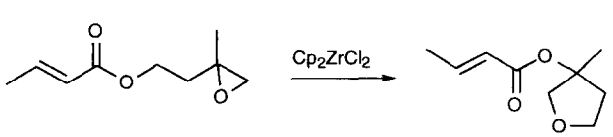


R^1 = Me, Ph,  , Et

R^2 = H, Me, $(CH_2)_3$

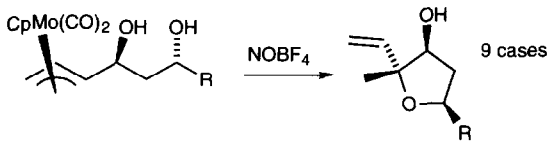
60-80% conversion
25-50% yield

(652)



78%

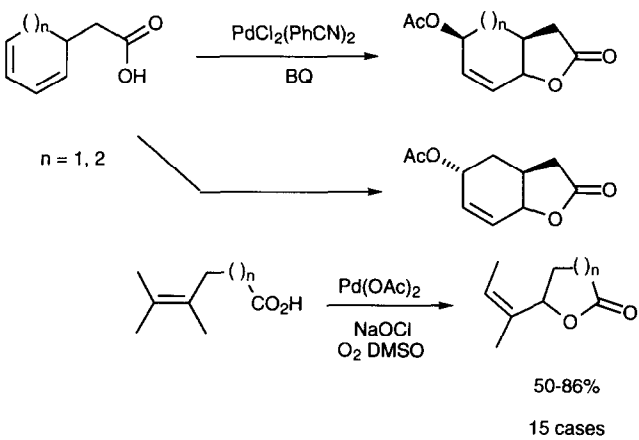
(653)



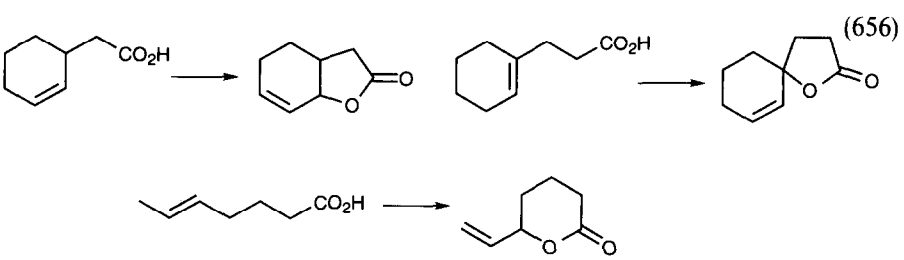
(654)

44-50% R = Ph, pMeOPh

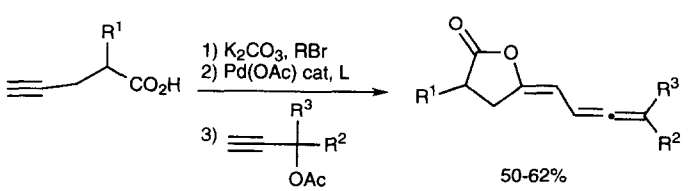
Butyrolactones were made by palladium-catalyzed attack of carboxylic acids on dienes (Eq. (655)) [790], alkenes (Eq. (656)) [791], and alkynes (Eq. (657)) [792]. Oxidation of δ-olefinic esters led to butyrolactones (Eq. (658)) [793]. Cuprates added to δ-ketoesters to give butyrolactones (Eq. (659)) [794]. Alkynes combined with *o*-iodobenzoic acid to produce lactones (Eq. (660)) [795].



(655)

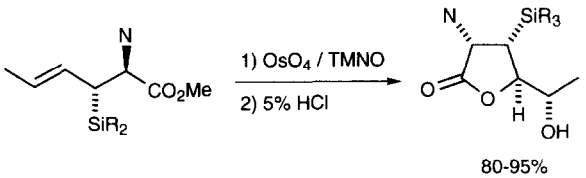


(656)

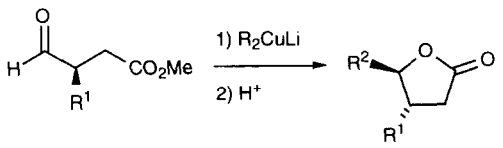


(657)

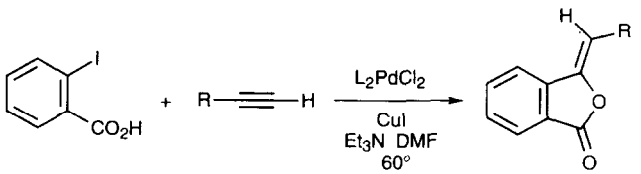
R^1 = H, Me R^2 = H, Me, Ph R^3 = Me, Ph $(CH_2)_5$



80-95% (658)

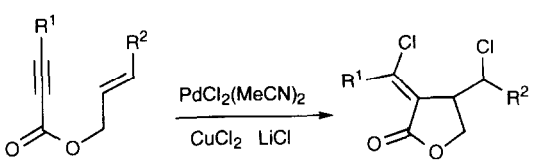


95:5 *trans/cis* (659)



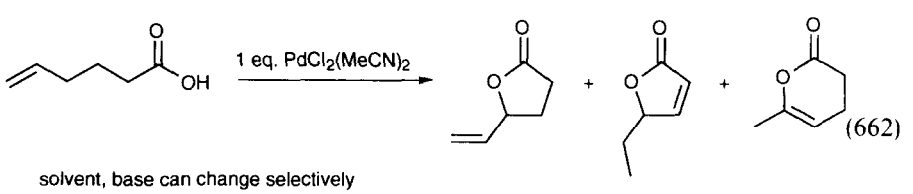
(660)

Palladium cyclized unsaturated esters (Eq. (661)) [796,797] and acids (Eq. (662)) [798] to α-methylene lactones. Butenolides were prepared by the palladium-catalyzed reaction of β-bromoacrylic acid with alkynes (Eq. (663)) [799] and from chromium carbene photochemistry (Eq. (664)) [800]. Tetrahydrothiophene was made by titanium coupling (Eq. (665)) [801].



50-94% (661)

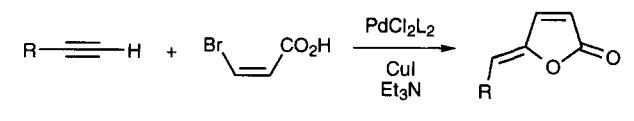
R^1 = H, Me R^2 = Ph, H



(662)

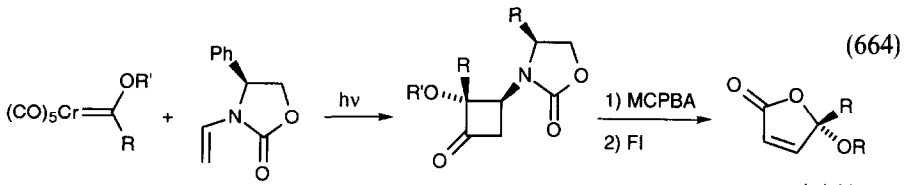
solvent, base can change selectively

good yields

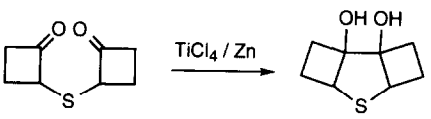


(663)

R = Ph, C_5, C_7, CH_2OH, PhCH(OH), $THPOCH_2$, Me_2C(OH), $MeOCH_2$

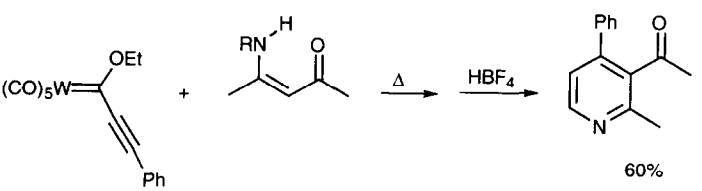


(664)

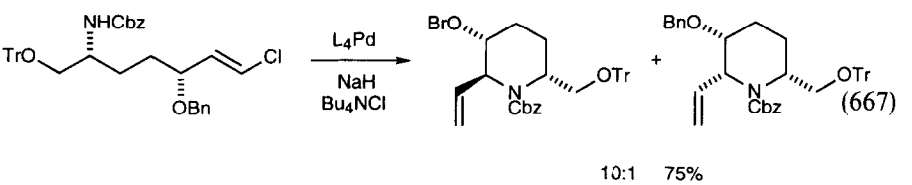


(665)

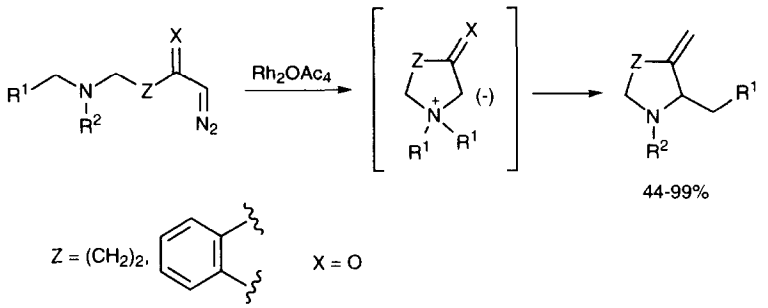
Alkynyl carbene complexes reacted with vinylogous amides to produce pyridines (Eq. (666)) [802]. Piperidines were produced by palladium-catalyzed allyl amination (Eq. (667)) [803]. Six-membered nitrogen heterocycles were prepared by metal-catalyzed decomposition of diazo compounds (Eq. (668) [804], Eq. (669) [805], and Eq. (670) [806]). Triols and amines reacted to form perhydroazepines under ruthenium catalysis (Eq. (671)) [807].



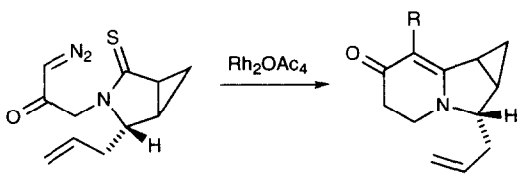
(666)



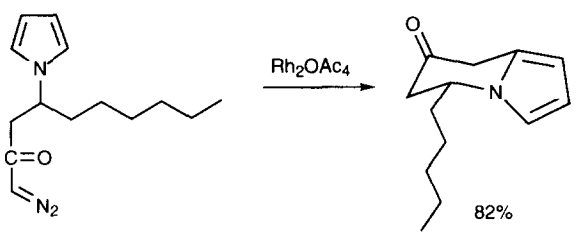
(667)



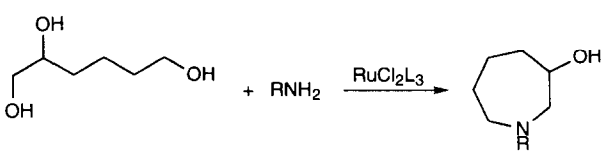
(668)



(669)

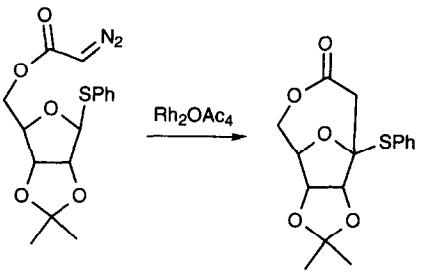


(670)

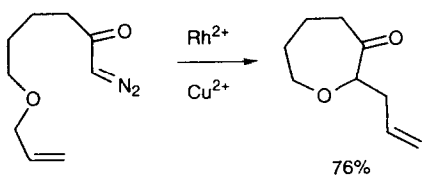


(671)

Oxygen heterocycles were also produced by rhodium-catalyzed CH insertion processes (Eq. (672) [808] and Eq. (673) [809]) and by palladium-catalyzed processes (Eq. (674) [810] and Eq. (675) [811]) including palladium-catalyzed telomerization (Eq. (676)) [812]. Asymmetric dihydroxylation (Eq. (677)) [813] and copper-catalyzed atom transfer chemistry (Eq. (678)) [814] also produced oxygen heterocycles.

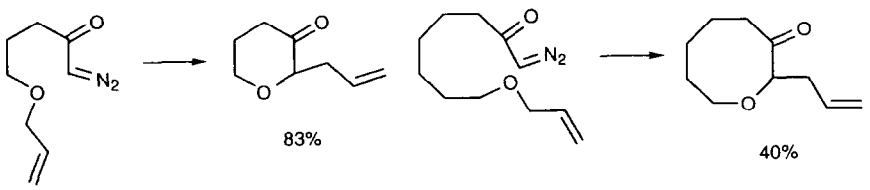


48% (672)

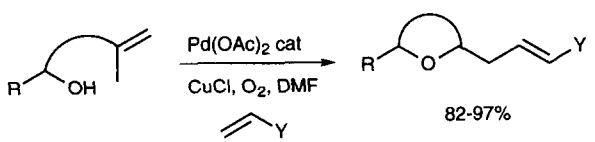


76% (673)

also

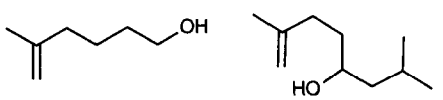


83% 40%

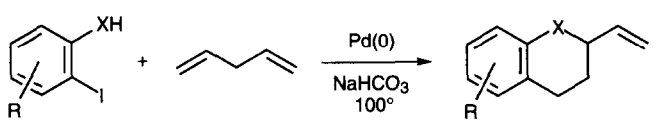


82-97% (674)

also



Y = COMe, CO_2Me, Ph

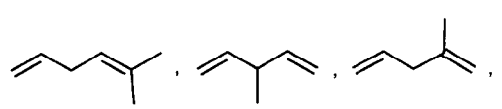


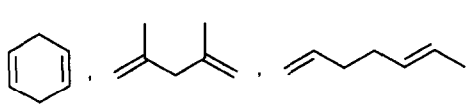
52-88%

X = O, NH

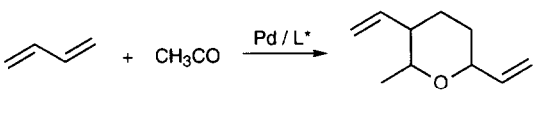
R = H, pMeOH

also





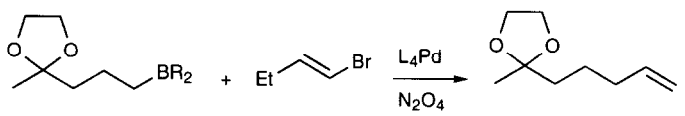
(675)



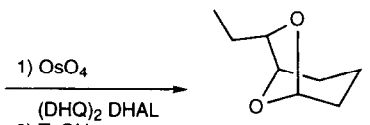
50-70%

20-60% ee

(676)

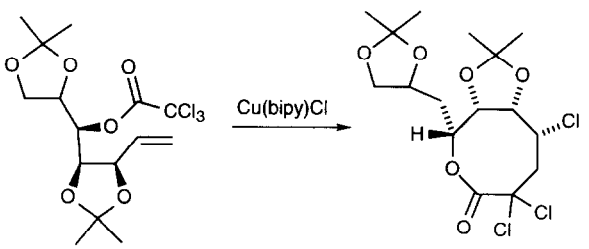


85%



90% 95% ee

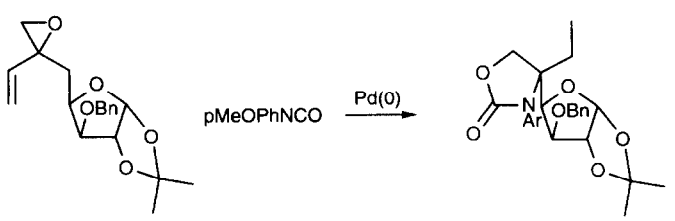
(677)



74%

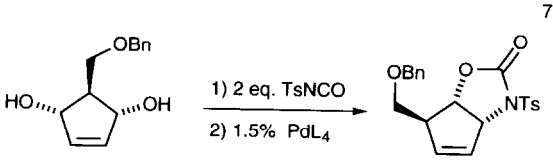
(678)

Five-membered cyclic carbamates were prepared by palladium-catalyzed reaction of vinyl epoxides with isocyanates (Eq. (679)) [815], allylic alcohols with isocyanates (Eq. (680) [816] and Eq. (681) [817]), palladium(II)-catalyzed amination of olefins (Eq. (682)) [818], asymmetric cis hydroxylation of alkenes (Eq. (683)) [819] and unusual titanocene chemistry (Eq. (684)) [820].



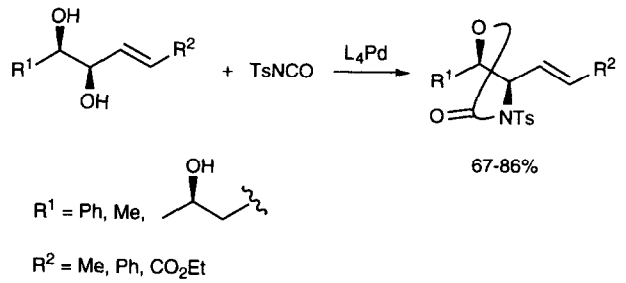
76%

(679)

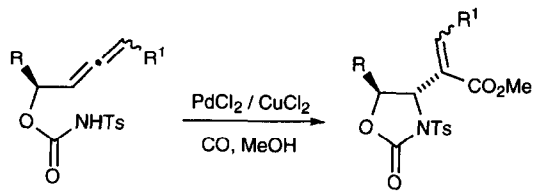


96%

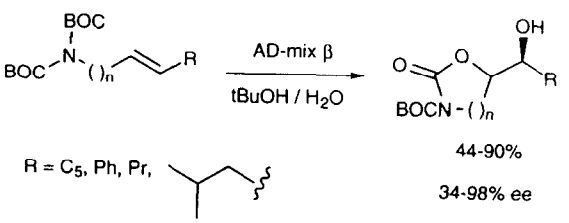
(680)



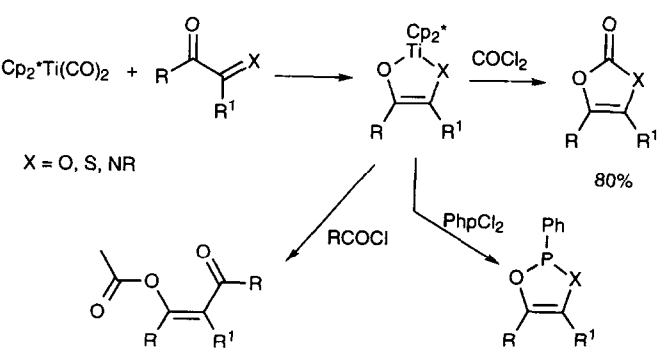
(681)



(682)

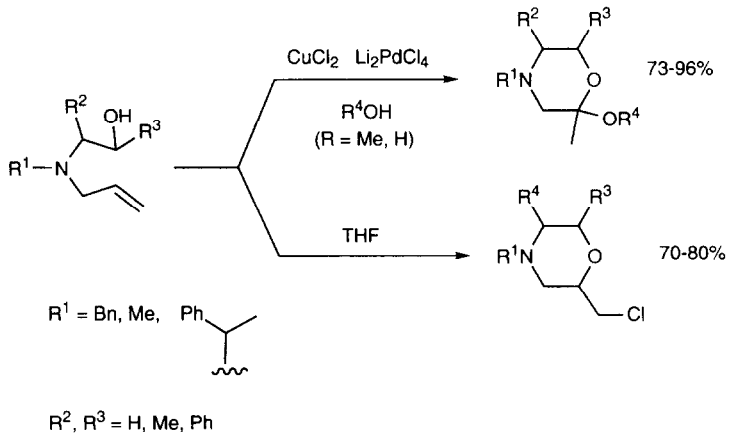


(683)

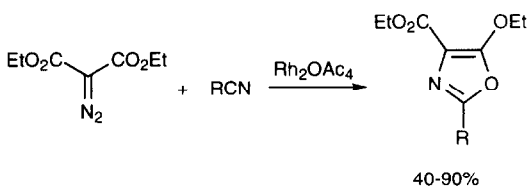


(684)

Morpholines were prepared by palladium-catalyzed alkoxylation of alkenes (Eq. (685)) [821]. Rhodium-catalyzed decomposition of diazo compound with nitriles (Eq. (686)) [822], cycloaddition to arene chromium complexes (Eq. (687) [823] and Eq. (688) [824]), palladium-catalyzed arylation (Eq. (689)) [825] and ruthenium-catalyzed diol oxidation (Eq. (690)) [826] all produced nitrogen heterocycles.

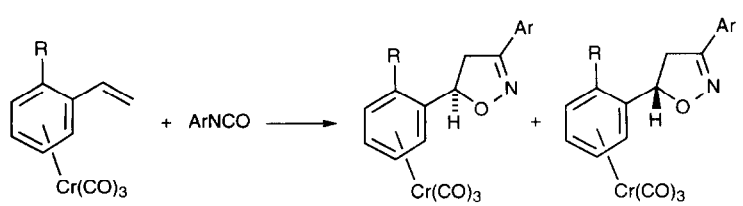


(685)

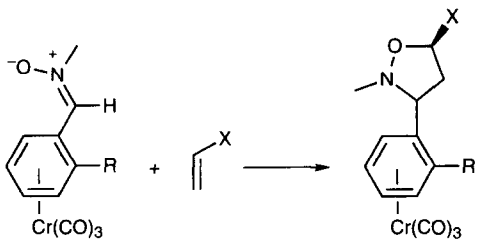


(686)

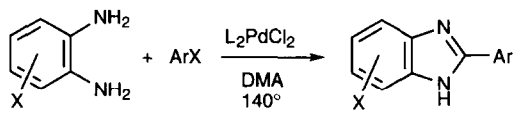
R = Ph, Ph, Me, nC9, Me, NnPr, iPr, tBu, Bn, pClPh, pMePh, pMeOPh, mClPh,



(687)



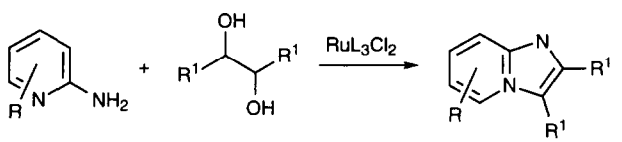
(688)



(689)

Ar = Ph, pMePh, pClPh, pCNPh, pPhPh, $pMeO_2CPh$, 2-Thiophene

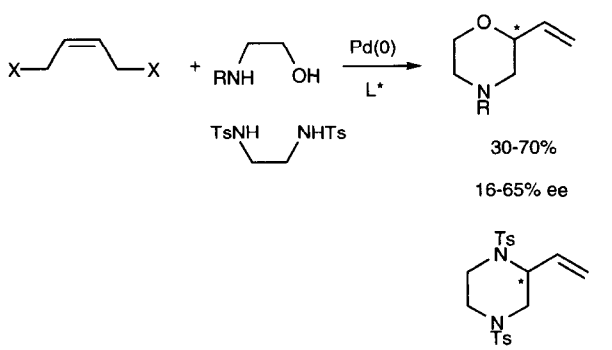
X = oMe, mMe, mMeO, mCl, mCF_3, pPhCO, 2-Naphth



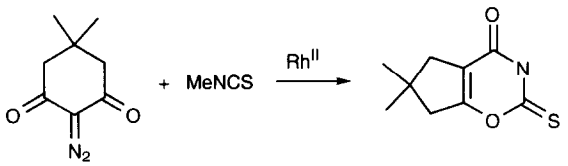
(690)

R = H, 5Me, 5Cl R^1 = Me, $(CH_2)_4$

Morpholines were made by the bisamination of 1,4-diacetoxybutene with palladium catalysis (Eq. (691)) [827]. More complex heterocycles were made by metal-catalyzed diazo decomposition (Eq. (692)) [828]. Transition metal complex catalyzed reductive N-heterocyclization of nitroarenes was the subject of a review (12 references) [829].

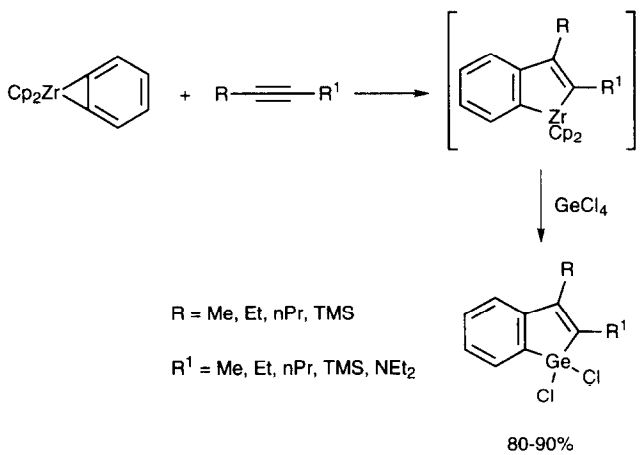


(691)

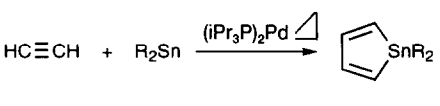


(692)

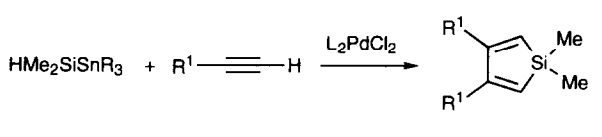
Heterocycles containing germanium (Eq. (693)) [830], tin (Eq. (694)) [831] and silicon (Eq. (695)) [832] were prepared. Heterocycles were prepared by cycloaddition to ylides produced by rhodium(II)-catalyzed decomposition of azo compounds (Eq. (696) [833] and Eq. (697) [834]). Cyclic thioureas were prepared from iron enone chemistry (Eq. (698)) [835]. Other miscellaneous reactions of heterocycles are shown in Eq. (699) [836], Eq. (700) [837], and Eq. (701) [838].



(693)

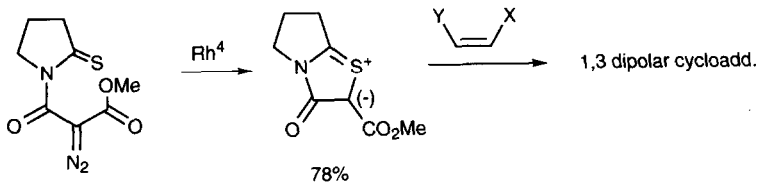


(694)

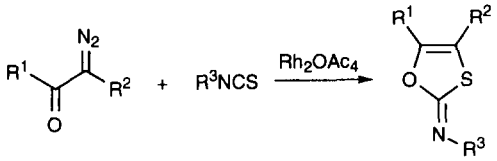


(695)

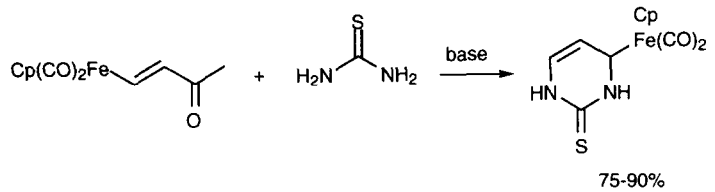
R^1 = Ph, pBrPh, C_8, 1-Naphth, THPO, pMePh, pClPh, 2,4,6-Me_3Ph, Me, BnO



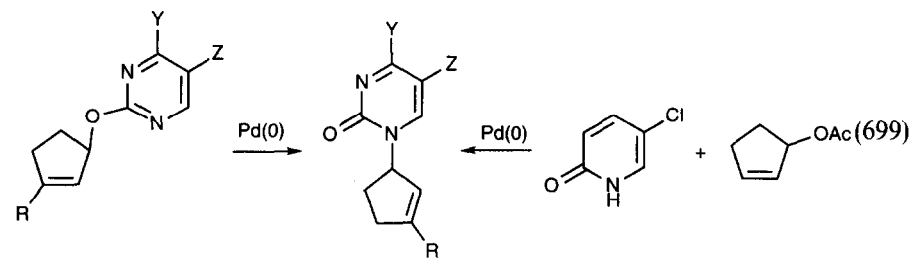
(696)



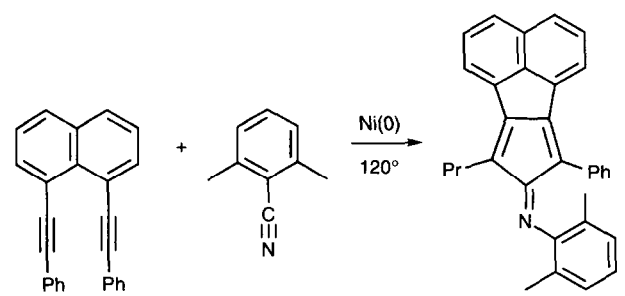
(697)



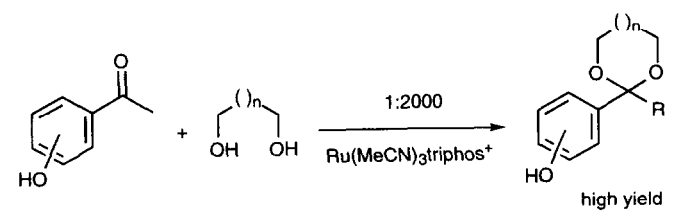
(698)



(699)



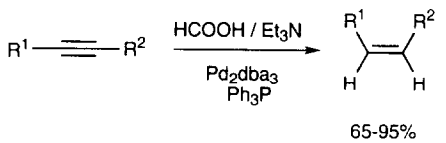
(700)



(701)

3.6. Alkenes, alkanes

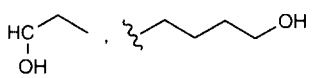
Palladium catalyzed the reduction of alkynes to cis alkenes by formic acid (Eq. (702)) [839] and catalyzed the thioboronation of alkynes (Eq. (703)) [840]. Palladium also catalyzed the production of alkenes by elimination (Eq. (704) [841] and Eq. (705) [842]). Propargyl alcohols were converted to enynes by cobalt complexation (Eq. (706)) [843] and by palladium(II)–stannous chloride (Eq. (707)) [844]. Propargyl acetates were converted to allenes by cuprates (Eq. (708) [845] and Eq. (709) [846]).

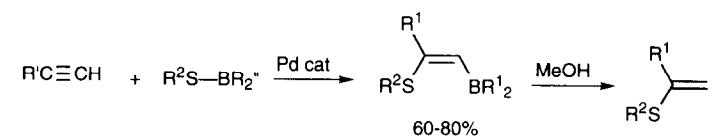


(702)

R^1 = C_8, C_5, Ph, Et

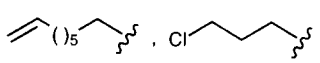
R^2 = H, Me, CO_2Me, CH_2OH, CH_2OTHP, CH_2OTIPS,



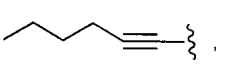


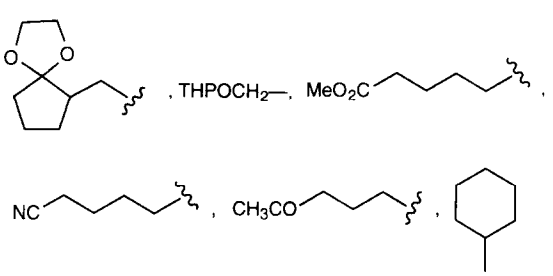
(703)

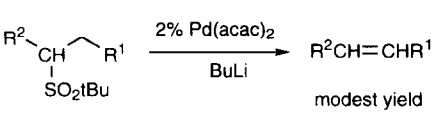
R^1 = C_8,



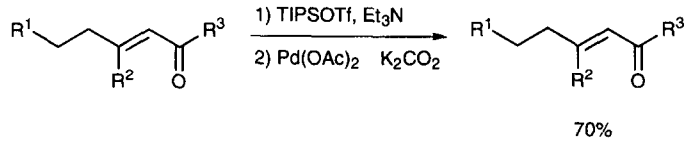
R^3 = Ph,



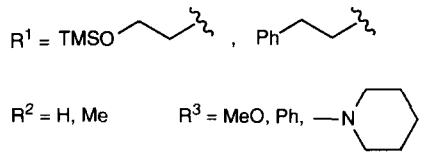




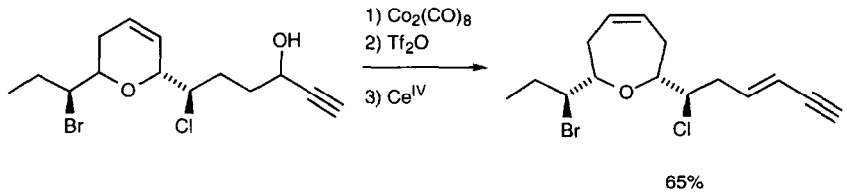
(704)

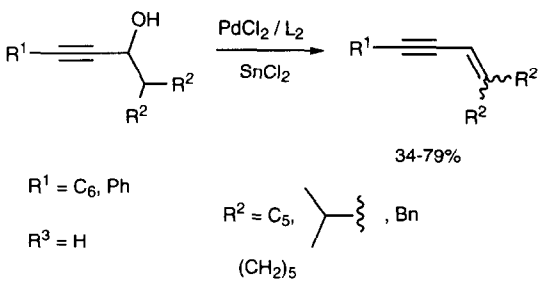


(705)

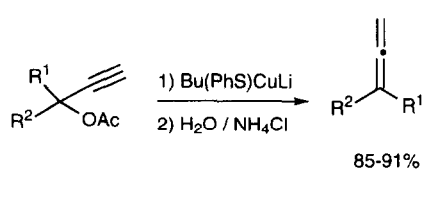


(706)

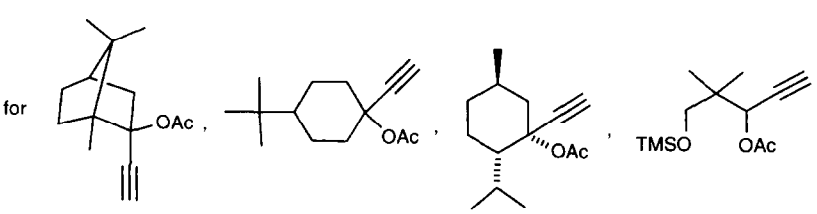


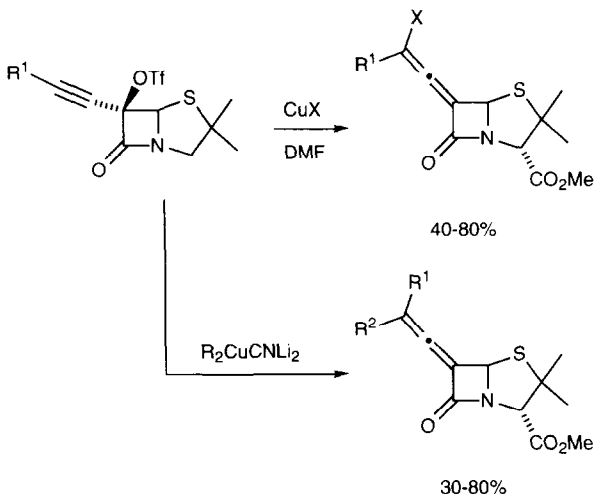


(707)



(708)



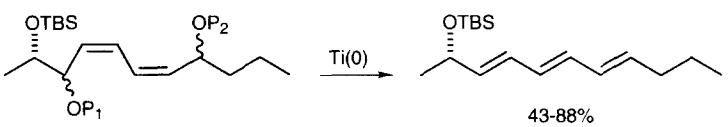


(709)

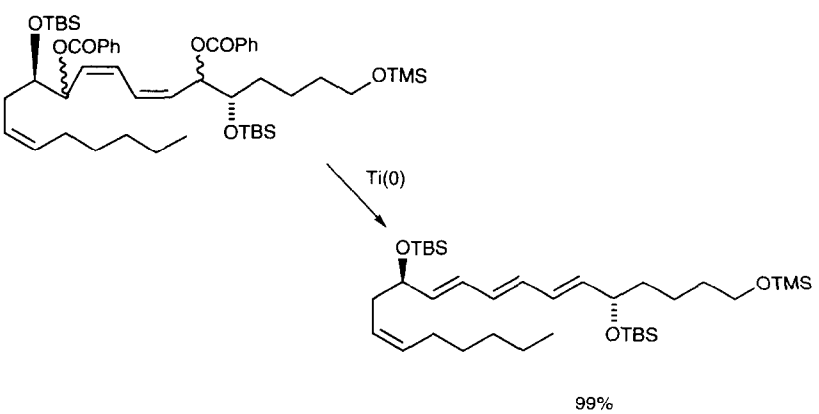
R^1 = H, Me, $TBSOCH_2$, $(EtO)_2CH$, CO_2Et

R^2 = tBu, Me, Ph, oMePh

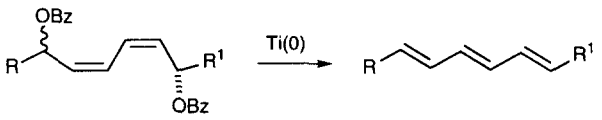
Titanium(0) complexes eliminated allylic esters to give polyenes (Eq. (710) [847], Eq. (711) [848], Eq. (712) [849]) and coupled ketones with nitriles to give alkenes (Eq. (713)) [850]. Ruthenium eliminates HCl from α-chloroketones (Eq. (714)) [851].



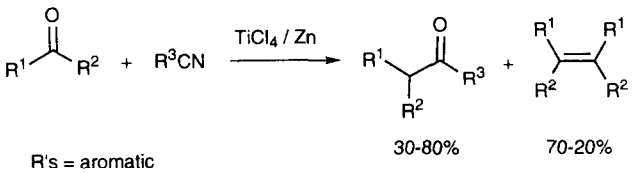
(710)



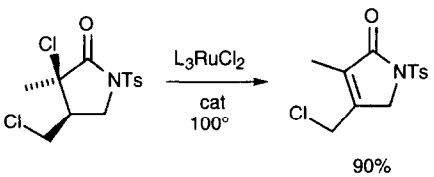
(711)



(712)

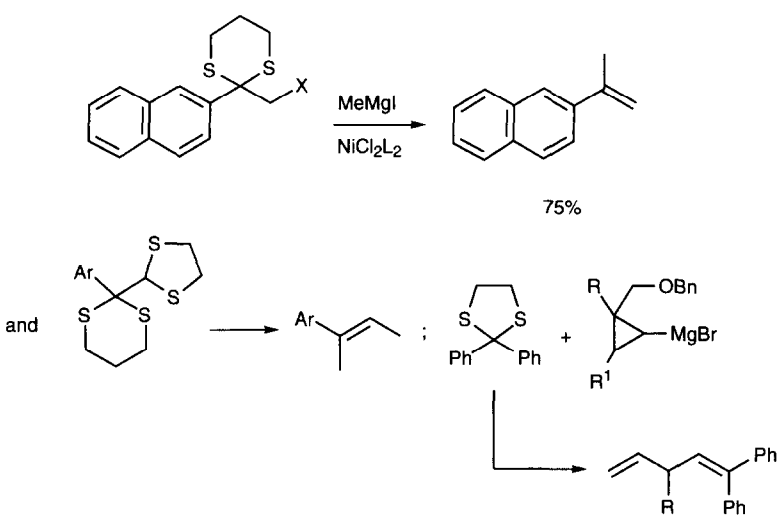


(713)

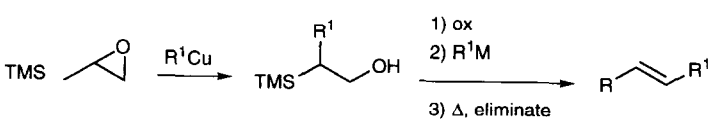


(714)

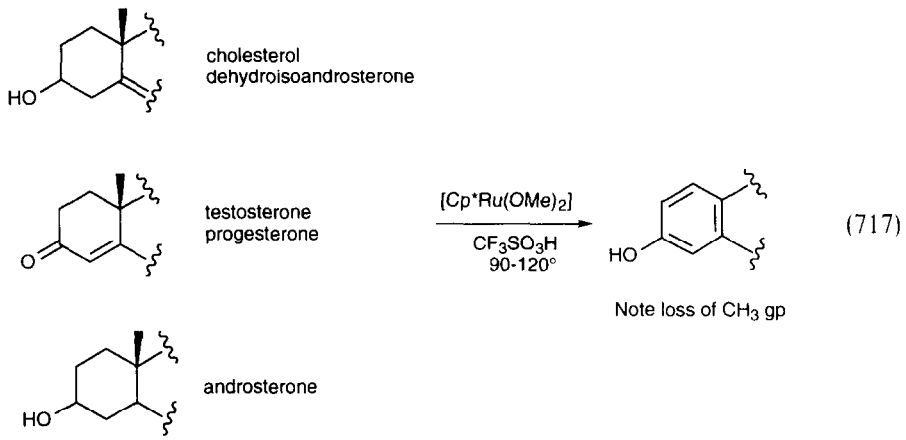
Nickel(II) salts catalyzed the conversion of thioketals to alkenes (Eq. (715)) [852]. α-trimethylsilyl alcohols were converted to alkenes (Eq. (716)) [853]. Ruthenium complexes catalyzed the aromatization of steroidal alcohols (Eq. (717)) [854].



(715)

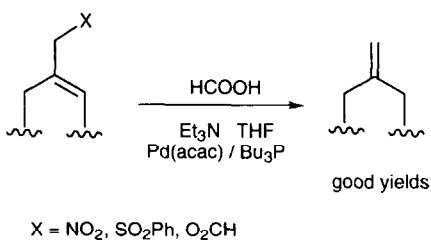


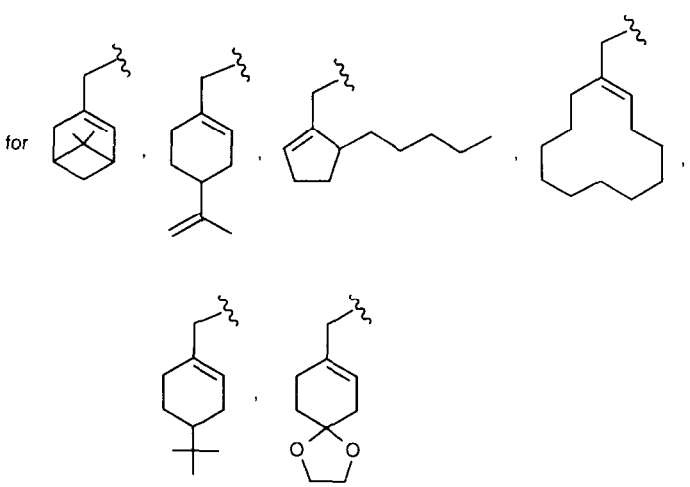
(716)



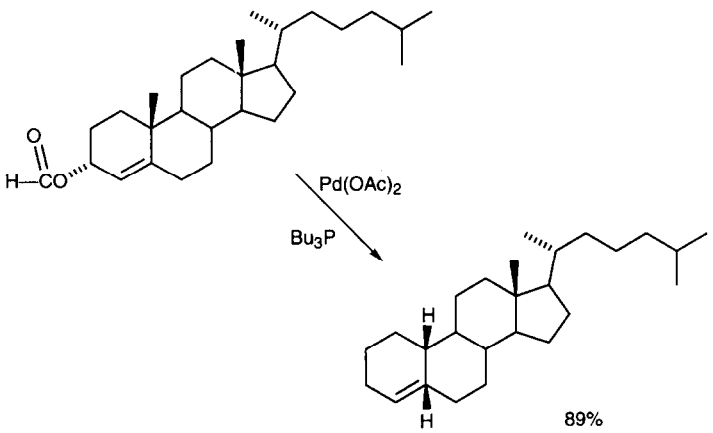
(717)

Group 6 hydride anions reduced α-haloketones to ketones [855]. Palladium(II) catalyzed the reduction of allyl acetates by formic acid (Eq. (718) [856] and Eq. (719) [857]). Chiral titanocenes catalyzed the asymmetric reduction of trisubstituted alkenes (Eq. (720)) [858]. Zirconocene reduced one olefin of dienes (Eq. (721)) [859].

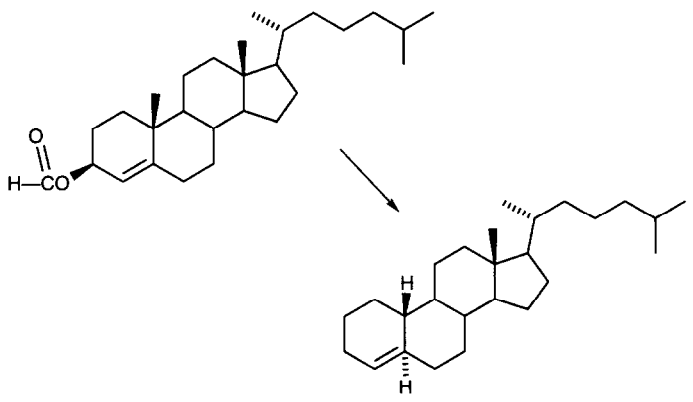


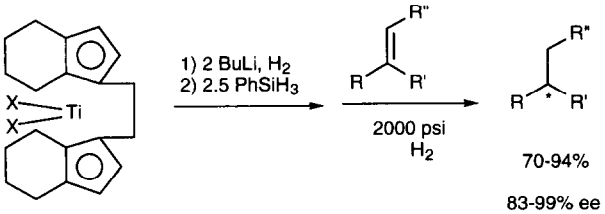


(718)



(719)



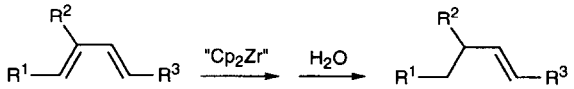


(720)

XX = 1,1-binap-2,2-diolate

R = Ph, pMeOPh

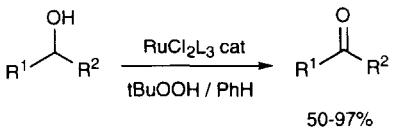
R' = Me R" = Ph, Me, CH_2NBn_2, CH_2OMe

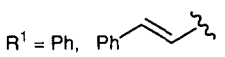


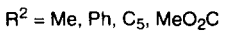
(721)

3.7. Ketones, aldehydes

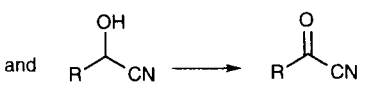
Ruthenium complexes catalyzed the oxidation of alcohols to ketones by *t*-butylhydroperoxides [860], (Eq. (722)) [861], and by air and aldehydes (Eq. (723)) [862]. Alkenes were oxidized to α-hydroxyketones by ruthenium(III) chloride–peracetic acid (Eq. (724)) [863].

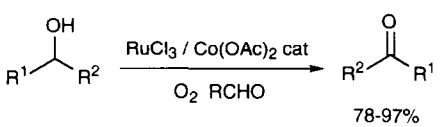


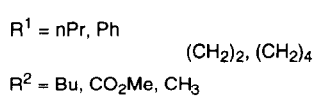




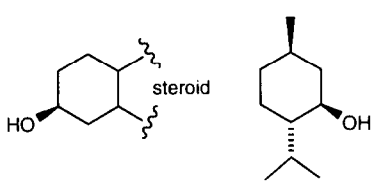
(722)

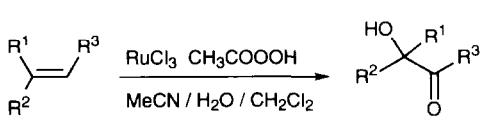




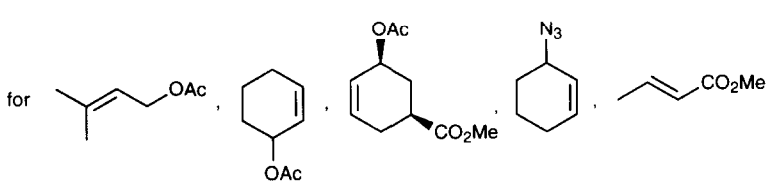


(723)

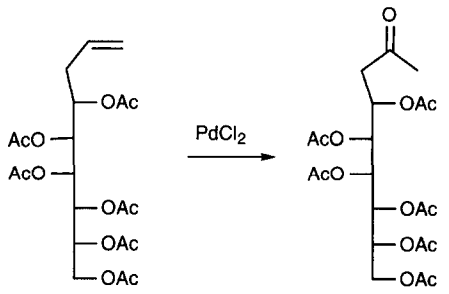




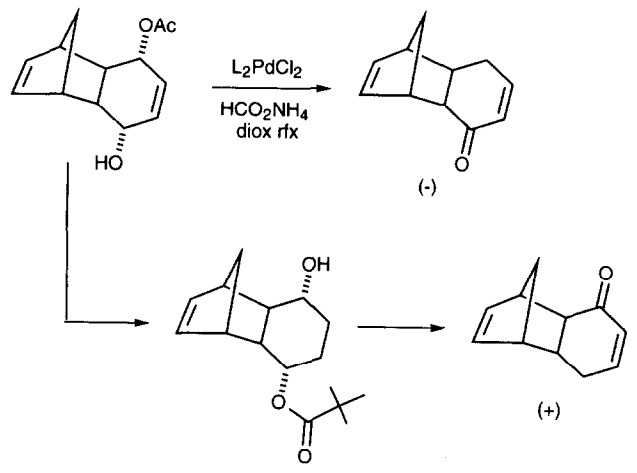
(724)



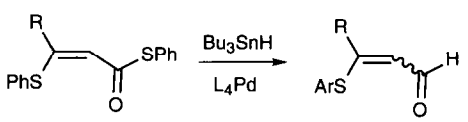
Palladium(II) catalyzed the oxidation of alkenes to methyl ketones (Eq. (725)) [864] and allyl alcohols to ketones (Eq. (726)) [865,866]. Palladium(0) catalyzed the reduction of thioesters to aldehydes (Eq. (727)) [867]. Rhodium catalyzed the silylformylation of epoxides (Eq. (728)) [868].



(725)

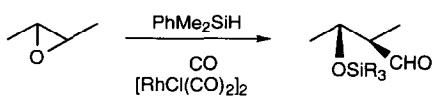


(726)



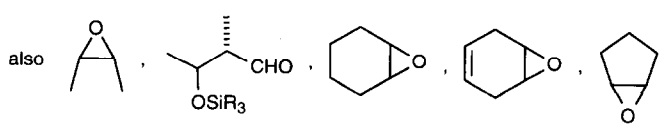
86-98%

(727)

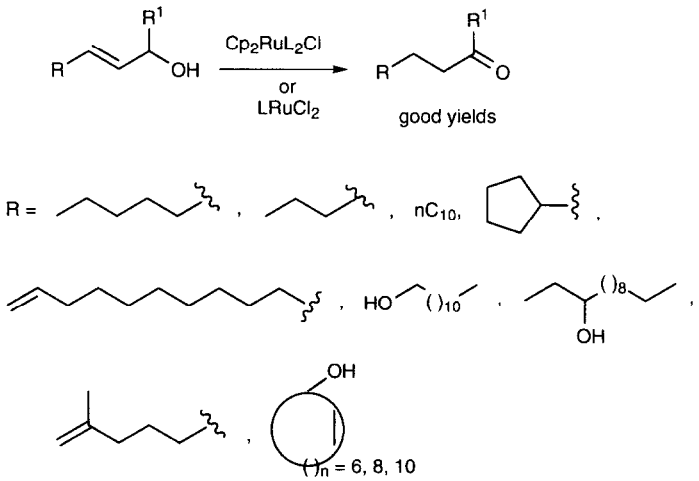


70%

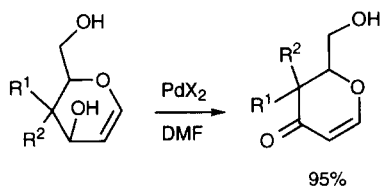
(728)



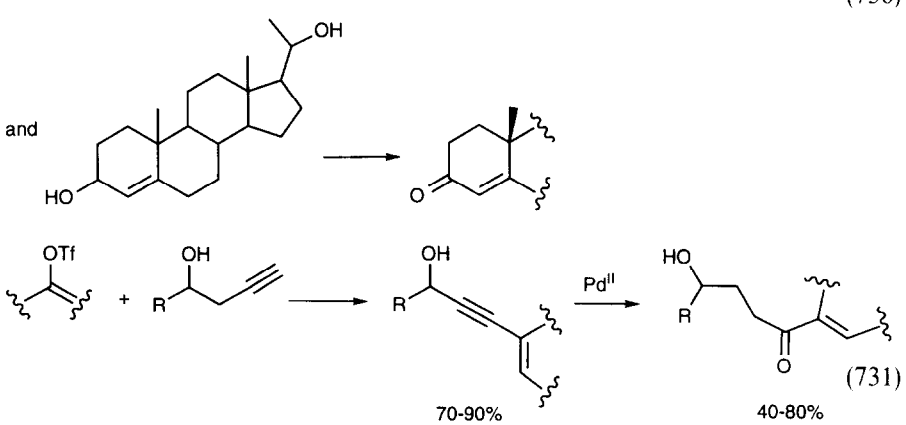
Ruthenium(II) complexes catalyzed the rearrangement of allylic alcohols to aldehydes (Eq. (729)) [869,870] as did palladium(II) (Eq. (730)) [871]. Palladium also catalyzed an unusual rearrangement of acetylenic alcohols (Eq. (731)) [872].



(729)

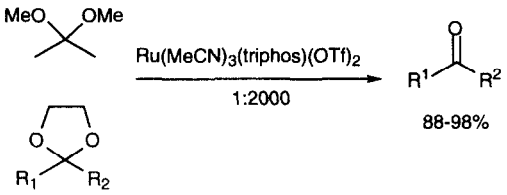


(730)

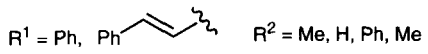


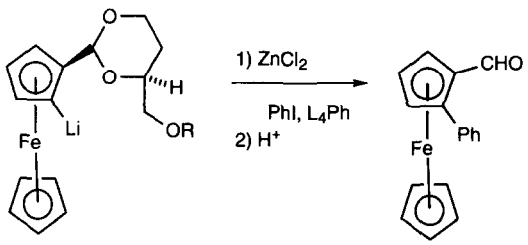
(731)

Ketals were hydrolyzed to ketones by ruthenium(II) cationic compounds (Eq. (732)) [873] and palladium(0) compounds (Eq. (733)) [874]. Chromium carbene complexes were used to make cyclic diketones (Eq. (734)) [875]. Palladium catalyzed the coupling of acid chlorides with aryl zinc reagents to produce ketones (Eq. (735)) [876].

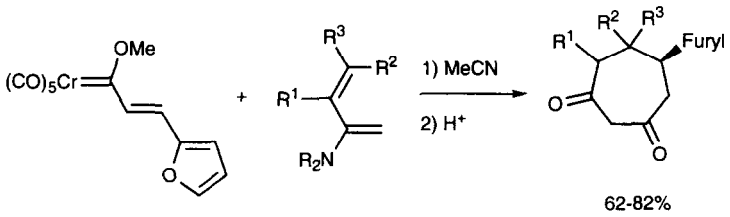


(732)

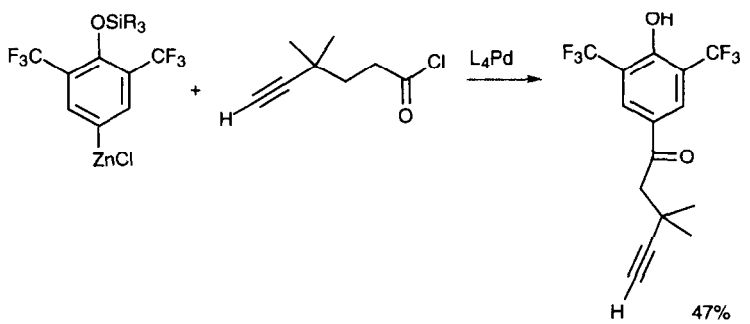




(733)



(734)

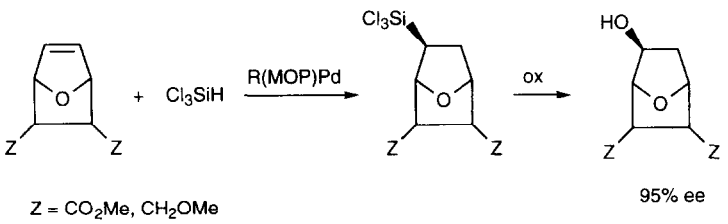


(735)

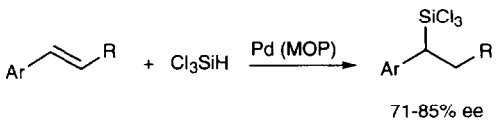
3.8. Organosilicon compounds

Catalytic asymmetric synthesis of optically active alcohols via hydrosilylation of olefins with chiral monophosphine palladium catalysts was reviewed [877] (Eq. (736) [878] and Eq. (737) [879]). Palladium catalyzed the 1,4-hydrosilylation of dienes (Eq. (738)) [880] and conjugated enones (Eq. (739)) [881]. Iridium(I) catalyzed the

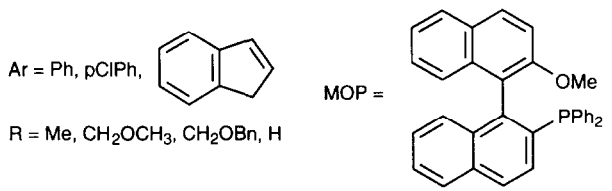
trans hydrosilylation of alkynes (Eq. (740)) [882]. Both rhodium (Eq. (741)) [883] and iron carbonyl (Eq. (742)) [884] catalyzed the dehydrogenerative silylation of olefins.

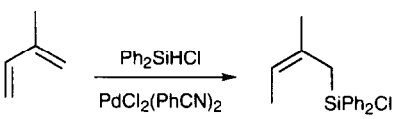


(736)

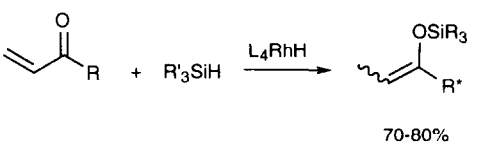


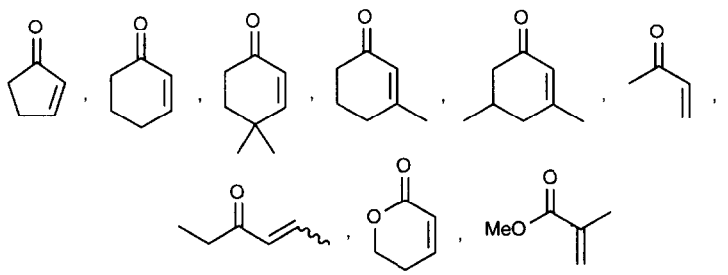
(737)



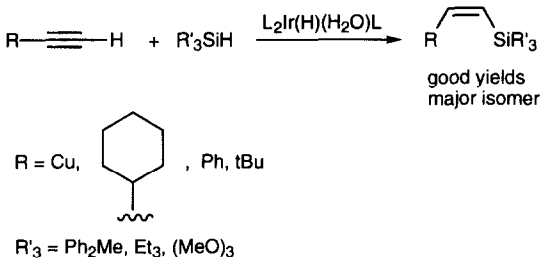


(738)

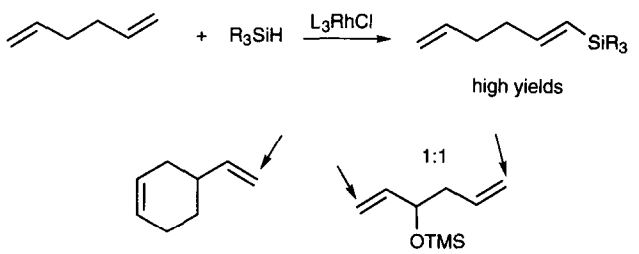




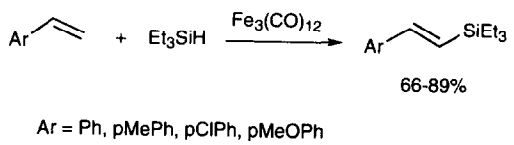
(739)



(740)



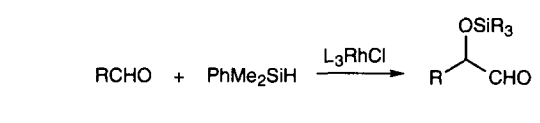
(741)



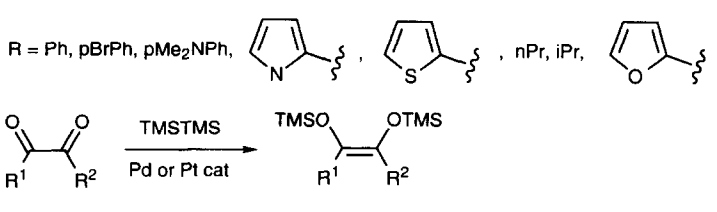
(742)

Ar = Ph, pMePh, pClPh, pMeOPh

Aldehydes were silylformylated using rhodium(I) catalysts (Eq. (743)) [885]. α-diketones were converted to vic-silyl ethers by palladium or platinum catalysts (Eq. (744)) [886]. Rhodium(I) catalyzed the conversion of ketones to silylenol ethers (Eq. (745)) [887]. Silanes cleaved chromium carbene complexes (Eq. (746)) [888]. Palladium(0) complexes catalyzed the strange reaction in Eq. (747)) [889].



(743)



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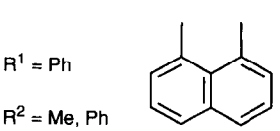
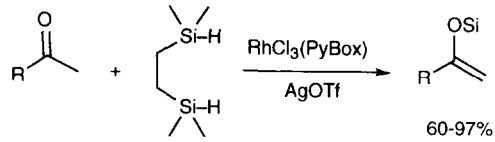
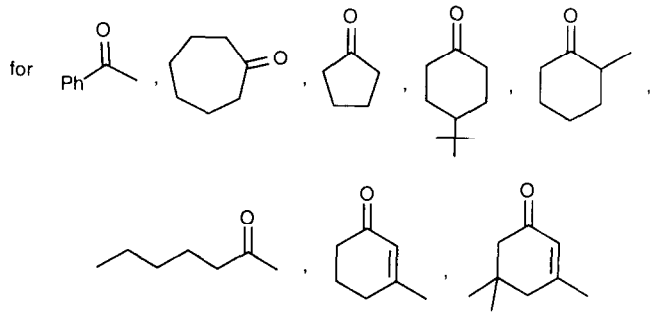
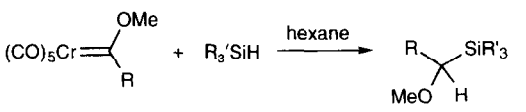
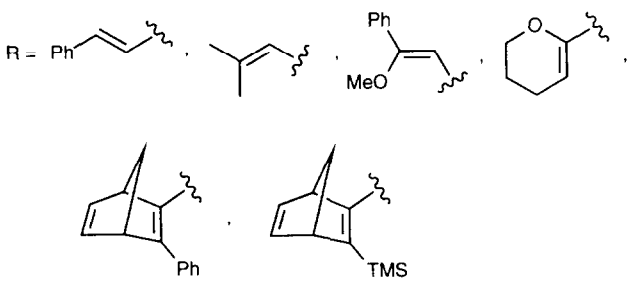



RhCl3(PyBox)
AgOTf
60-97%

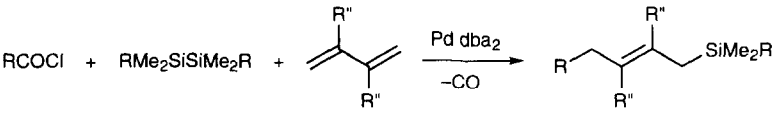

for

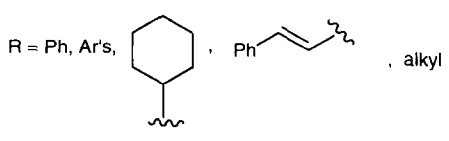
(745)


hexane
40-87%


R =
Ph
MeO
Ph
TMS
R' = Et, Ph

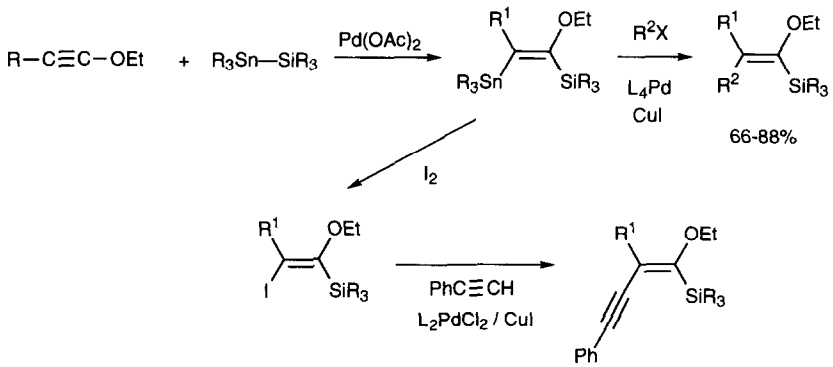
(746)


RCOCl
RMe2SiSiMe2R
Pd dba2
-CO
70-80%

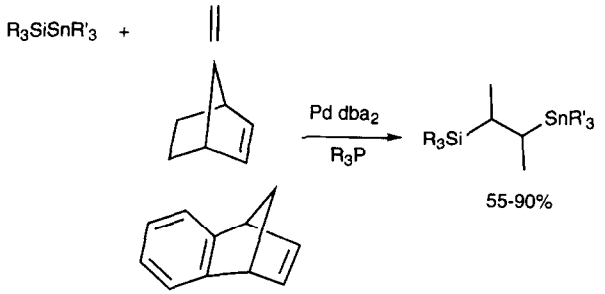

R = Ph, Ar's,
Ph
alkyl
R' = Me, pFPh, Cl
R" = H, Me

(747)

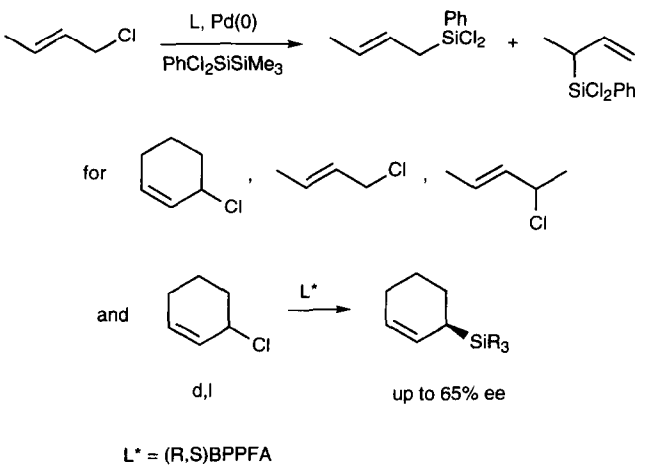
Catalytic reactions involving silylmetallation as the key step have been reviewed (91 references) [890]. Alkynes (Eq. (748)) [891] and alkenes (Eq. (749)) [892] were silylstannylated using palladium catalysts, which also catalyzed the silylation of allyl chlorides (Eq. (750)) [893] and allyl acetates (Eq. (751)) [894].



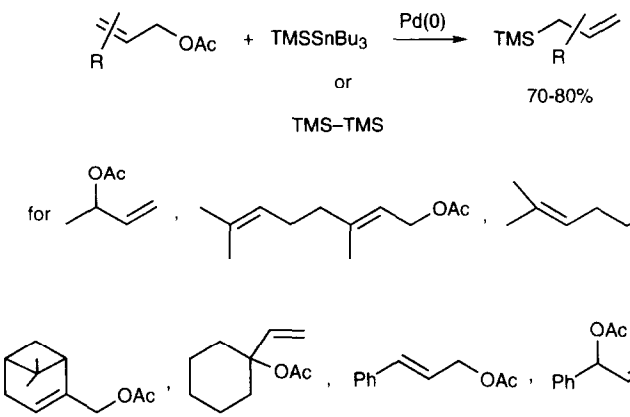
(748)



(749)

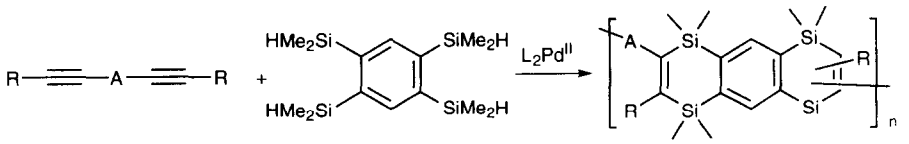


(750)



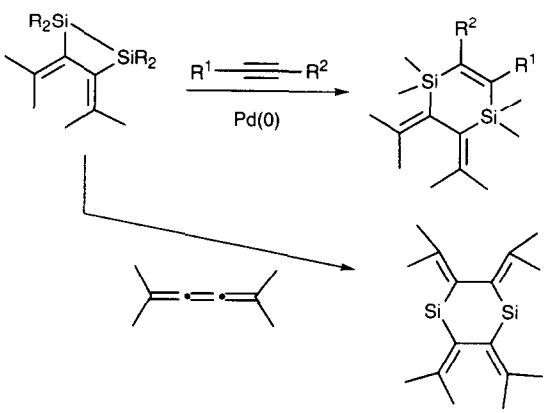
(751)

Platinum ethylene complexes catalyzed the oligomerization of diynes with tetrasilylarenes (Eq. (752)) [895]. Palladium catalyzed the reactions of disilanes with alkynes and dienes (Eq. (753)) [896] and the intramolecular silylation of olefins (Eq. (754)) [897].

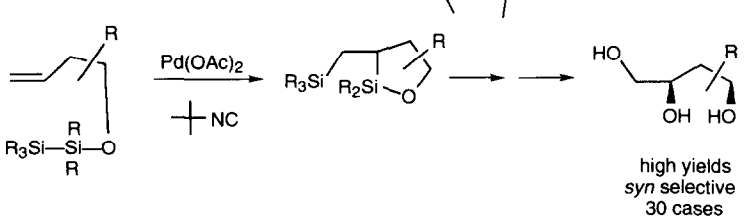


MW 1.2×10^4 (752)

70-90%



(753)

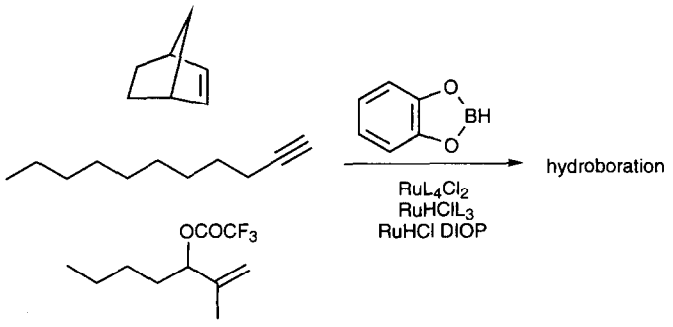


(754)

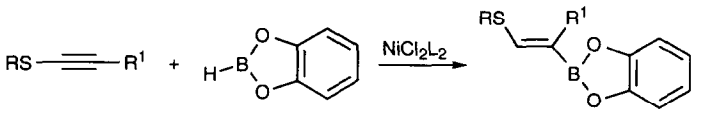
high yields
syn selective
30 cases

3.9. Miscellaneous

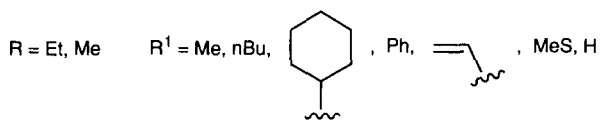
Reactions that are not easily classified are shown in Eqs. (755)–(763), from Refs. [898–906] respectively.

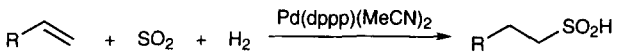


(755)



(756)





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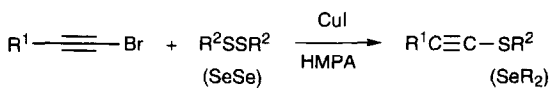
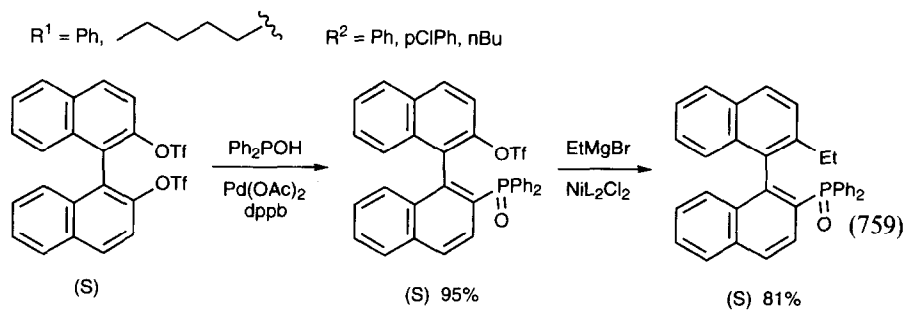
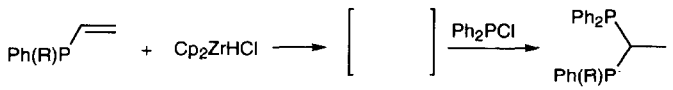


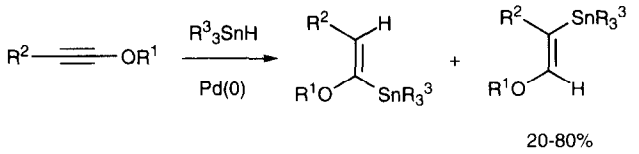
(758)



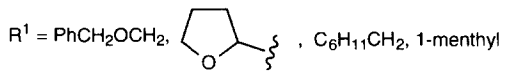
(759)

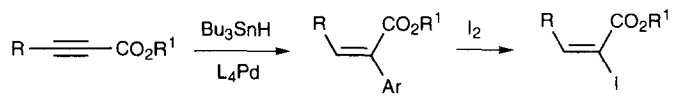


(760)

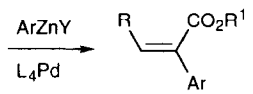


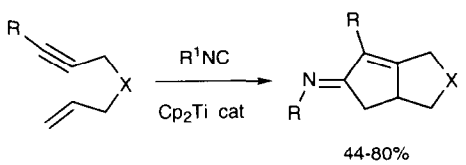
(761)





(762)





(763)

R = Ph, Me

X = O, NPh, E, E

4. Reviews

The following reviews have appeared.

- Transition metals in organic synthesis. Annual survey covering the year 1991 (more than 1069 references) [907]
- Organometallic chemistry. Part 1. The transition elements (more than 301 references) [908]
- New synthetic methodologies using transition metals. Applications to synthesis of biologically active compounds (25 references) [909]
- Homogeneous catalysis of optically active transition-metal complexes and its application to synthesis of bioactive molecules (353 references) [910]
- Homogeneous catalysis by optically active transition-metal complexes and its use in the synthesis of bioactive molecules. II. Carbon–carbon bond formation (299 references) [911]
- Catalytic asymmetric synthesis (17 references) [912]
- Catalytic asymmetric synthesis (21 references) [913]

- Asymmetric catalysis (18 references) [914]
- Application of palladium catalysts to organic synthesis (more than 20 references) [915]
- Selectivity and mechanism in catalytic asymmetric synthesis (34 references) [916]
- Practical ruthenium catalysts for asymmetric syntheses (7 references) [917]
- Stereocontrolled synthesis via chiral aziridines (24 references) [918]
- The +IV oxidation state in organopalladium chemistry. Recent advances and potential intermediates in organic synthesis and catalysis (more than 18 references) [919]
- Approaches to asymmetric synthesis using chiral (propargyl alcohol) pentacarbonyl triphenylphosphine dicobalt(0) and (proparygylium) pentacarbonyl triphenylphosphine dicobalt(0) tetrafluoroborate complexes [920]
- Organometallic compounds in the chemistry of morphine alkaloids (24 references) [921]
- Selectivity control elements for transition metal catalyzed cycloaddition reactions [922]
- Chiral complexes of nickel(II), copper(II) and copper(I) as reagents, catalysts and receptors for asymmetric synthesis and chiral recognition of amino acids (13 references) [923]
- Organometallic chemistry in water (34 references) [924]
- Asymmetric synthesis of α-amino acids (49 references) [925]
- New progress of organometallic compounds in stereoselective synthesis (18 references) [926]
- Silyl-substituted conjugated dienes: Versatile building blocks in organic synthesis (174 references) [927]
- Stereoselective transformations mediated by chiral monocyclopentadienyl titanium, zirconium, and hafnium complexes (49 references) [928]
- Zirconium-promoted carbon–carbon and carbon–heteroatom bond-forming and -cleaving reactions [929]
- Zirconacyclopropanes and zirconacyclopropenes: their formation and reactivity [930]
- Organic synthesis using zirconium compounds (45 references) [931]
- Syntheses of some natural products using zirconium promoted cyclization (12 references) [932]
- Early transition metals in organic synthesis (67 references) [933]
- Hydroalumination of alkynes with aluminum lithium hydride–methanol catalyzed by Cp_2TiCl_2 [934]
- Towards transition metal-catalyzed hydration of olefins; aquo ions, and pyridylphosphine–platinum and palladium complexes [935]
- Transition-metal-catalyzed oxidation. The role of peroxometal complexes (149 references) [936]
- Homogeneous and heterogeneous catalytic oxidations with peroxide reagents (43 references) [937]

● Catalytic oxidations with hydrogen peroxide as oxidant. Peroxometal complexes derived from hydrogen peroxide. Some applications in organic synthesis (70 references) [938]

● Catalytic oxidations with hydrogen peroxide as oxidant. The use of polyoxometalates in reactions with hydrogen peroxide (59 references) [939]

● Ring-reconstruction addition reaction catalyzed with ruthenium (6 references) [940]

● Metal-catalyzed carbon–carbon bond formation in the reaction of β-dicarbonyls with nitriles (45 references) [941]

● Palladium-catalyzed selective hydrogenolysis of alkenyloxiranes with formic acid and its application to organic syntheses (66 references) [942]

● The use of organopalladium chemistry in isotopic carbon incorporation [943]

● Transmetallation reactions in organocopper chemistry (161 references) [944]

● Metal complexes in the synthesis of organic sulfur compounds (106 references) [945]

● Mechanism of formation and cleavage of carbon–carbon bonds in the presence of supported metal catalysts (14 references) [946]

● Chemistry of and with highly active metals (152 references) [947]

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