CHAPTER 6.4

Six-Membered Ring Systems: With O and/or S Atoms

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6.4.1 INTRODUCTION

The large number of publications in 2013 dedicated to *O*- and *S*-six-membered ring systems highlights the importance of these heterocycles.

The chemistry and biological activity of the family of plants *Hyacinthaceae*, and of their homoisoflavanone main constituents (13NPR1165) and of the fungal polyketide metabolites azaphilones (13CR4755) and various aspects on the isolation, synthesis, and biological activity of angular tricyclic benzofurans and related natural products of fungal origin (13NPR941) and marine polyketide psymberin (13AGE10960) have been surveyed. A review on the history of natural product synthesis covers the early phase of this subject, where it was the method of choice to confirm the proposed structure of a natural product, to the challenges of the twenty-first century (13AGE123).

Recent studies on the identification, biological applications, and biosynthesis of mainly *C*-prenyl flavonoids and xanthones along with other small *C*-prenylated phenolics (13COR1067), and on the structure of different phenolic compounds (e.g., flavonoids, coumarins, xanthones, chalcones, lignins, and lignans) and their metabolic pathways, together with the most important results in the treatment and prevention of cancer (13ACMC1236), have appeared. Patent information on therapeutic and cosmetic applications of mangiferin, a natural *C*-glucoside xanthone (13EOTP1561), and of natural and synthetic xanthones possessing antioxidant activity (13CME4481) has been surveyed.

An overview on the structure and pharmacological properties of catechin prodrugs and analogs includes a discussion on the bioavailability and toxicity of tea catechins (13NPR1438). Recent developments on the synthesis of proanthocyanidins (13H2225), on the structure, synthesis, and

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chemical reactivity of naturally occurring pterocarpans (13CR1614) and on the structure, synthesis, and biological activity of polycyclic xanthone natural products (13NPR382) have also been reviewed.

Enzymatic methods for the synthesis of 5-hydroxy-2-(hydroxymethyl)-4*H*-pyran-4-one (kojic acid) esters are reviewed. This naturally occurring organic acid is a fungal secondary metabolite having several biological applications, but its prominent applications are in the cosmetic and skin health industries (13CPA573).

Reports on efficient and enantioselective total synthesis of natural products highlights (+)-coriandrone A and B (13OBC6686), diospongins A and B (13T7706), englerin A and B, orientalol E and F, and oxyphyllol (13CEJ2539). The synthesis of natural tetrahydroxanthones leptosphaerin G, penexanthone B, and blennolide B involving an intramolecular radical protocol to diastereoselectively introduce a variety of substituents at carbon C-4a was accomplished (13CEJ10836).

Discussions of specific reagents include the use of chiral hypervalent iodine(III/V) compounds in the diastereoselective synthesis of isocoumarins (13CEJ17244), the synthesis and reactivity of enaminonitriles of pyrano[2,3-*c*]pyrazole and related compounds (13SC2685) and the transformation of *cis*-1-tosyl-2-tosyloxymethyl-3-(trifluoromethyl)aziridine into the corresponding 1,4-benzodithiin, 1,4-benzoxathiin, and 1,4-benzodioxin derivatives (13CEJ5966). Further examples include 4-hydroxycoumarin in multicomponent reactions (13H1415) and the application of allenamides (13CR4862), arylglyoxals (13CR2958), benzynes (13OBC191), and propargyl vinyl ethers (13CC2272) as versatile building blocks in the synthesis of several families of six-membered oxygen heterocycles. A microreview focused on the role of coinage metal catalysts in the 1,2-addition of O–H to three types of C═C bonds, unactivated alkenes, conjugated alkenes and allenes, which can be used in the stereoselective synthesis of pyran-type compounds. The importance of Brønsted acid catalysis in these reactions is also highlighted (13EJO1027).

Synthetic fragrance chemistry, namely of pyran and chroman-type compounds, describes the catalytic activation of olefins by metal triflates and triflimides (13CEJ3270). Interest continues in the synthesis of long-wavelength fluorescein analogues and their application as fluorescent probes (13CEJ6538) and in the synthesis and physical properties of fluorinated tetrahydropyran-based liquid crystals to be used as displays in electronic devices (13AGE8880).

A great number of surveys covering synthetic and reactivity aspects on oxygen and sulfur six-membered heterocyclic compounds have been given:

(1) synthetic strategies leading to several types of pyrans and of their derivatives utilizing benzoylacetonitriles as starting precursor since 1985 (13JICS1085); (2) the synthesis of polyfunctionalized pyrans, thiopyrans, and their condensed benzo- and naphtho derivatives, focusing on developments of greener synthetic approaches as multicomponent and solventless reactions and ecofriendly heterogeneous catalysis (13AHC241); (3) the general synthesis, biological activities, and structure–activity relationships of different classes of chromenes (13FMC1647), the synthetic routes and reactivity of 3-nitro-2*H*-chromenes (13RCR1081) and of 2-chromanols (13ARK101); (4) the synthesis and reactions of sulfur analogues of partially fluorinated pyrones, chromones, coumarins, and isocoumarins (13JSC432); and (5) the structure, chemistry, and pharmacology of naphthoflavones, and related benzothioflavones, benzoflavanones, benzoflavans and benzochalcones (13MRMC1357).

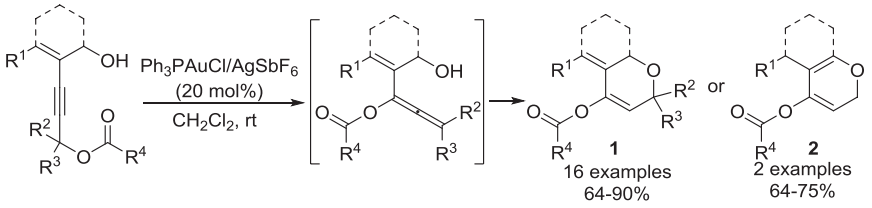
Discussions on specific reactions dedicated to the synthesis of natural products bearing six-membered oxygen heterocycles covers Mukaiyama aldol reaction in total synthesis (13AGE9097), Prins-type cyclizations (13EJO1193) and the Suzuki–Miyaura reaction in the synthesis of several classes of flavonoids (13MOL4739). Other relevant reactions include those on catalytic asymmetric inverse-electron-demand Diels–Alder reactions (13CR5515), the Staunton–Weinreb annulation reaction ([13T3747]), and palladium-catalyzed carbonylative synthesis of heterocycles (13CR1). A review covers a domino Knoevenagel-hetero-Diels–Alder (hDA) reaction for the synthesis of aminochromene annulated heterocycles (13SC1577).

Mechanistic studies are an important tool to understand how the biosynthesis of natural products occurs in nature and how to mimic their synthesis in the laboratory. Progress in this field includes the biomimetric synthesis of flavonolignan diastereomers in milk thistle (13JOC7594) and the chemoenzymatic synthesis of tetrahydropyran-containing polyketides (13AGE13215). In the synthetic domain, DFT calculations and experimental assays have been carried out to explain the multiple mechanisms involved in the palladium(II)-catalyzed S_N2' reactions of allylic alcohols to prepare chiral tetrahydropyran derivatives (13JOC7664).

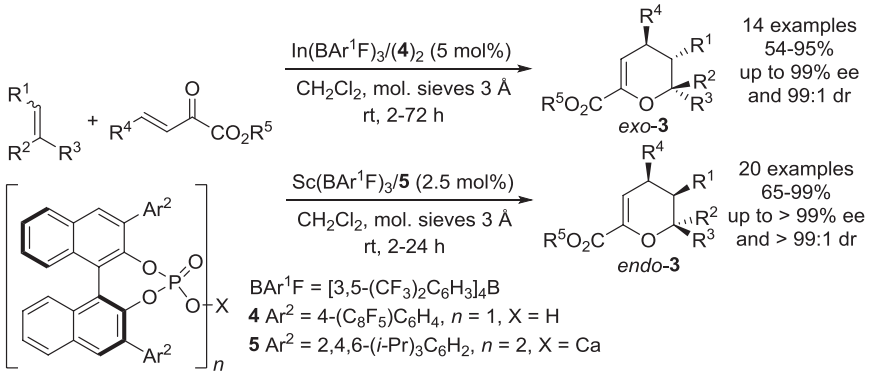
6.4.2 HETEROCYCLES CONTAINING ONE OXYGEN ATOM

6.4.2.1 Pyrans

Allenes are proposed as intermediates in the gold(I)-catalyzed cycloisomerization of β-hydroxy propargylic esters to afford dihydro-2*H*-pyrans **1**/2*H*-pyrans **2** (Scheme 1) (13T8002).



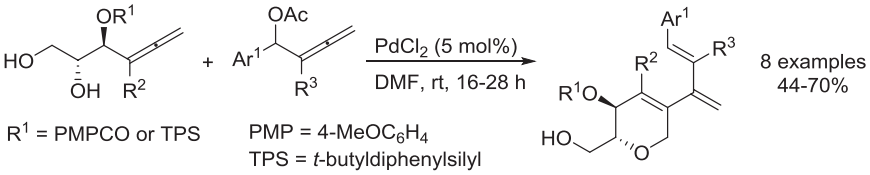
Scheme 1



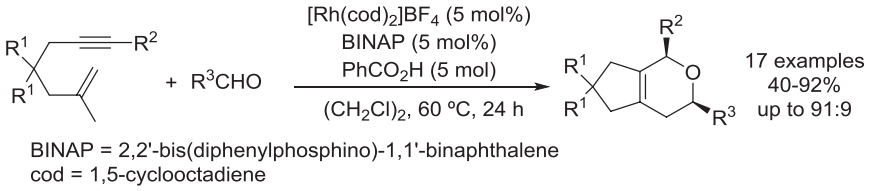
Scheme 2

Under solvent free-conditions, ethylenediammonium diacetate mediates the Knoevenagel-type condensation of cyclic 1,3-dicarbonyl compounds and α,β-unsaturated aldehydes to prepare 2*H*-pyran derivatives (13SC208).

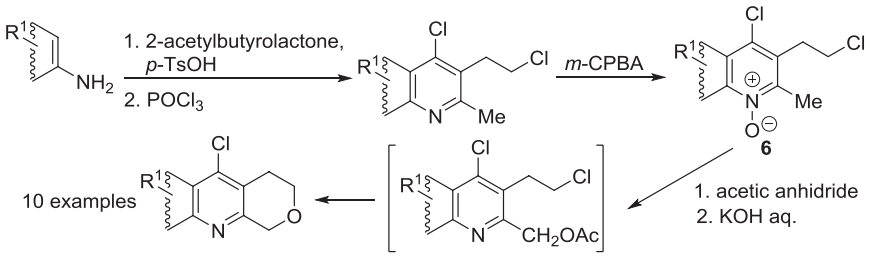
3,4-Dihydro-2*H*-pyrans can be enantio- and diastereoselectively prepared from [4 + 2] cycloaddition reactions of nitroalkenes with oxadienes catalyzed by an *N*-heterocyclic carbene (NHC) (13CEJ4441) and from simple olefins with β,γ-unsaturated α-ketoesters catalyzed by a chiral binary acid synergistically combining a chiral phosphoric acid with a metal salt. A simple exchange of transition metal ion from In(III) to Sc(III) changes the stereochemistry of the formed adducts from *exo*-**3** to *endo*-**3** (Scheme 2) (13AGE9786). Other chiral derivatives are achieved via organocatalytic hydration–aldol–inverse-electron-demand oxa-Diels–Alder domino reaction of alkyl aldehydes and alkynyl aldehydes (13OL204) and inverse-electron-demand Diels–Alder reaction of alkyl aldehydes with α,β-unsaturated ketoesters mediated by modularly designed organocatalysts (13CEJ6976), with high diastereo- and enantioselectivities. 4-Fluoroalkylated 3,4-dihydro-2*H*-pyrans are selectively prepared by one-pot annulation reaction of



Scheme 3



Scheme 4

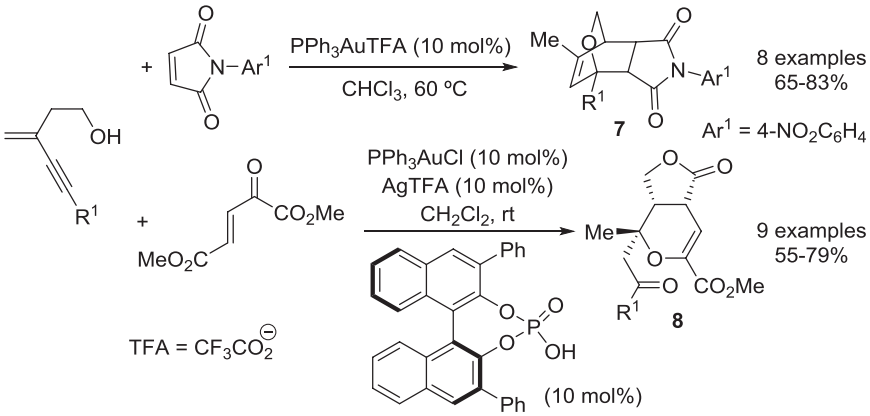


Scheme 5

β-fluoroalkylated α,β-unsaturated ketones with various enamines (13T1521).

A reductive homocondensation of (*E*)-benzylidenepyruvate esters promoted by $P(NMe_2)_3$ affords polyfunctionalized 3,4-dihydro-2*H*-pyrans (13OL1926). Enantiopure 5,6-dihydro-2*H*-pyrans are accessible from a chemo- and regio-controlled palladium(II)-catalyzed domino reaction of β,γ-allenediols with α-allenic acetates (Scheme 3) (13CEJ14233).

$PtCl_2$ catalyzes the enantiospecific cycloisomerization of 1,6-enynes to afford cyclopropane-fused 3,4-dihydro-2*H*-pyrans in good yields and high stereospecificity (13OL1772). A one-pot cycloisomerization–hDA reaction of 1,6-enynes with unactivated aldehydes is catalyzed by a rhodium complex and a Brønsted acid to produce a wide range of cyclopentane-fused 5,6-dihydro-2*H*-pyrans (Scheme 4) (13OL2120). Other heterocyclic-fused 5,6-dihydro-2*H*-pyrans arise from a multistep sequence involving a rearrangement of pyridine *N*-oxides **6** with acetic anhydride followed by one-pot hydrolysis and intramolecular Williamson ether formation (Scheme 5) (13SC1092).

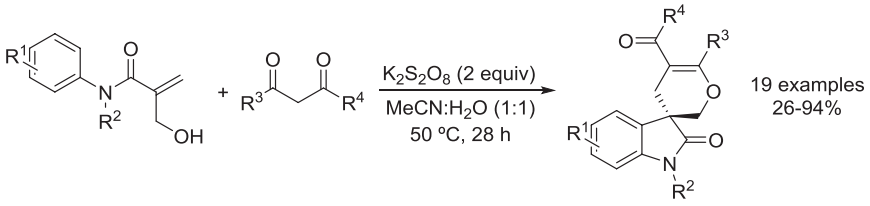


Scheme 6

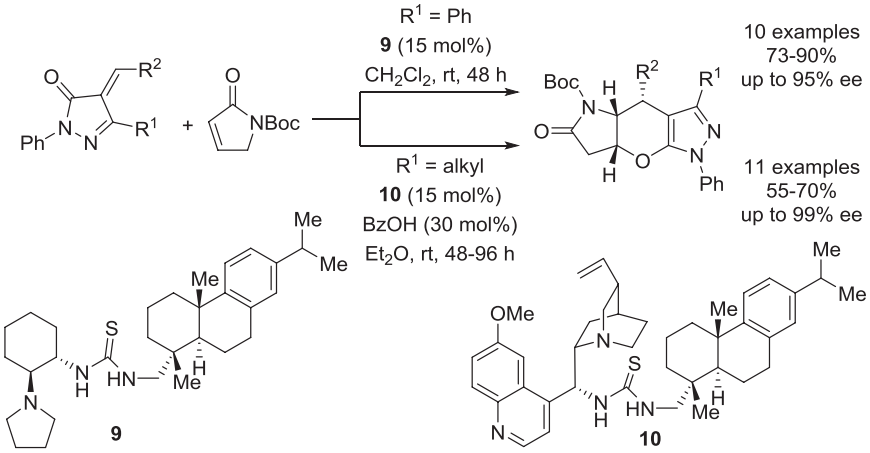
Under gold catalysis, 2*H*-pyrans formed from enyne alcohols can participate as 1,3-dienes in Diels–Alder reactions with *N*-(4-nitrophenyl) maleimide to afford tricyclic products **7** or as dienophiles in inverse-electron-demand hDA reactions with (*E*)-dimethyl 4-oxopent-2-enedioate to provide 3,4-dihydro-2*H*-pyrans **8** (Scheme 6). The stereoselectivity in this last reaction is obtained using a combination of the gold complex and a chiral copper Lewis acid formed in situ from $Cu(OTf)_2$ and a bisoxazoline derivative (13OBC6707). Another asymmetric inverse-electron-demand hDA reaction using 3-formylchromone as heterodiene and 3-vinylindoles as dienophiles promoted by a chiral bifunctional tertiary amine thiourea catalyst provided a series of chromanone-fused 3,4-dihydro-2*H*-pyrans (13JOC10233). A similar reaction between 2-oxoindolin-3-ylidenes and vinyl ethers catalyzed by a chiral calcium phosphate led to indole-fused 3,4-dihydro-2*H*-pyrans (13CEJ9754).

A metal-free oxidative spirocyclization of hydroxymethylacrylamide with 1,3-dicarbonyl compounds provides a range of spirooxindole 3,4-dihydro-2*H*-pyrans, in moderate to good yields. This strategy involves the formation of two C–C bonds and one C–O bond in one step (Scheme 7) (13OL5254).

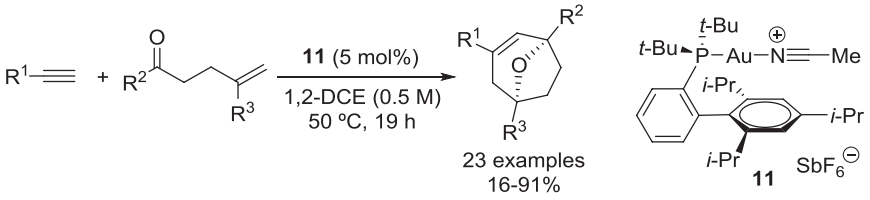
An efficient and diastereoselective synthesis of 5,6-dihydro-2*H*-pyran-2-acetates involves a Prins cyclization of acrylyl enol ethers mediated by TMSOTf. This strategy was used in the total synthesis of the natural compound (+)-civet (13JOC12182). Highly functionalized tricyclic dihydropyranopyrrolidin-2-ones are formed by a catalytic β,γ-selective Diels–Alder [4 + 2] annulation of α,β-unsaturated γ-butyrolactams, in good yields and enantioselectivities (Scheme 8) (13AGE11329).



Scheme 7



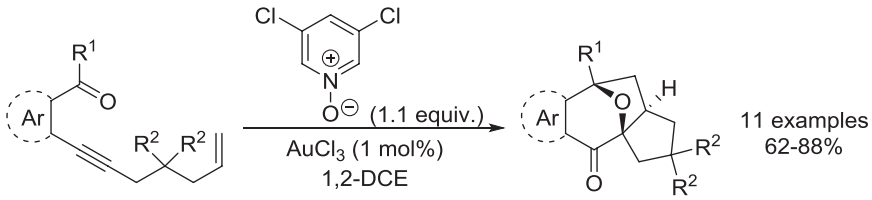
Scheme 8



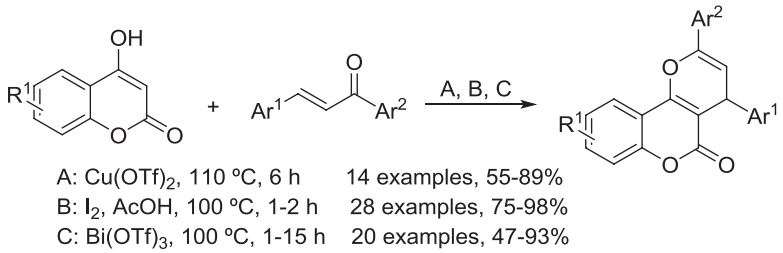
Scheme 9

8-Oxabicyclo[3.2.1]oct-3-ene derivatives can be prepared by a gold(I)-catalyzed cycloaddition reaction of alkynes with oxoalkenes (Scheme 9) (13CEJ3547). In a similar procedure, a gold(III) catalyst mediates an efficient oxidative domino cyclization–cycloaddition reaction of enyne aldehydes and ketones to give polyfunctionalized tetracyclic ketoethers (Scheme 10) (13CEJ14787).

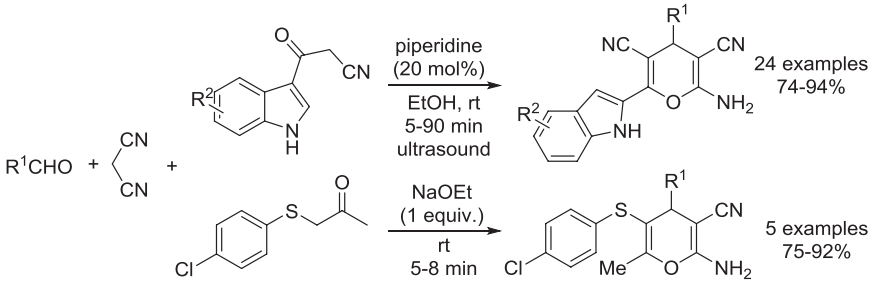
Coumarin-fused 4*H*-pyrans can be achieved through the tandem reaction of 4-hydroxycoumarins with chalcones mediated by iodine/acetic acid



Scheme 10



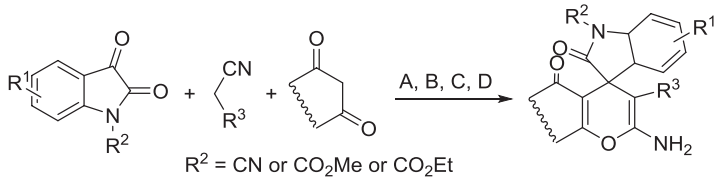
Scheme 11



Scheme 12

(13SC3044) and by copper(II) triflate (13TL3892) or $Bi(OTf)_3$ under solvent-free conditions (Scheme 11) (13TL3773).

2-Amino-3-carbonitrile-4*H*-pyrans are obtained in moderate to good yields by grinding ethyl acetoacetate, [(2-aryl)methylene]malononitriles and ammonium acetate at room temperature (13SC465). Further examples are accomplished by the one-pot three-component reactions of aldehydes and malononitrile with 3-cyanoacetyl indoles under ultrasound irradiation (13JHC244) or with 1-[(4-chlorophenyl)sulfanyl]acetone in sodium ethoxide at room temperature (Scheme 12) (13SC2763). Benzylidenecycloalkane-fused 2-amino-3-carbonitrile-4*H*-pyrans result from the reaction of α,α′-bis(substituted-benzylidene)cycloalkanones with malononitrile using a catalytic amount of piperidine in refluxing ethanol (13JHC625), while



A: carbon-SO_3H, EtOH, reflux, 3-6 h 16 examples, 78-94%
B: HMT, H_2O, 60 °C, 20-150 min 35 examples, 60-95%
C: DBU, H_2O, reflux, 5-55 min 28 examples, 75-90%
D: H_2O, 80 °C, μW, 8-12 min 12 examples, 87-95%

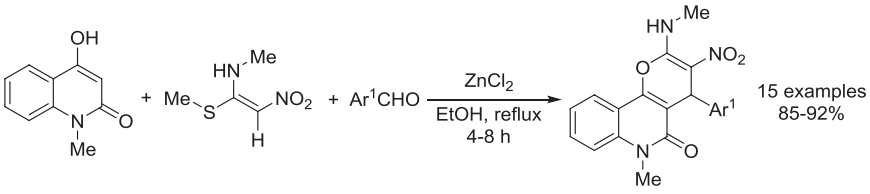
Scheme 13

heterocyclic-fused 2-amino-3-carbonitrile-4*H*-pyrans arise from the multicomponent reaction of heterocyclic 1,3-diones, aldehydes, and malononitrile in the presence of stabilized nickel nanoparticles in ethylene glycol (13SC2294) or in catalyst-free conditions (13SC2073).

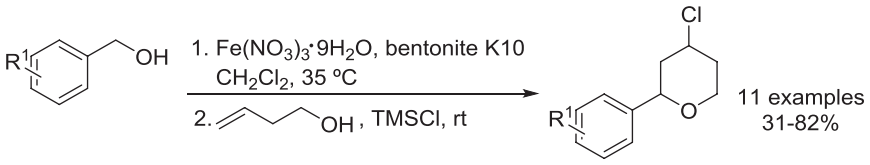
A wide range of spirooxindole 2-amino-4*H*-pyrans are readily available in good yields from the one-pot three-component reaction of isatins, malononitrile/cyanoacetic esters, and cyclic and acyclic 1,3-dicarbonyl compounds catalyzed by a bioglycerol-derived carbon sulfonic acid (13TL2466), hexamethylenetetramine (HMT) (13JHC61), or 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (13SC3239) in water and also in aqueous media without catalyst under microwave irradiation (Scheme 13) (13JHC599). Other spiro derivatives were synthesized from the four-component reaction of isatins/ninhydrin, malononitrile/cyanoacetic ester, diamines and cyclic 1,3-dicarbonyl compounds (13JHC608, 13TL3487), or dialkyl acetylenedicarboxylates (13TL5434). Yet more examples arise from the reaction of isatins, 2-cyanoacetamide, cyclic 1,3-dicarbonyl compounds, and aliphatic alcohols (13JHC272).

One-pot four-component reactions of carbonyl compounds, hydrazines, malononitrile, and β-ketoesters mediated by meglumine (13T9931), cetyltrimethylammonium chloride in aqueous medium (13SC1721), or in the absence of catalyst under ultrasound irradiation in water (13JHC1174) are versatile routes for the synthesis of pyrazole-fused 2-amino-3-carbonitrile-4*H*-pyrans. Quinolinone-fused 3-nitro-4*H*-pyrans result from the $ZnCl_2$-catalyzed three-component reaction of 4-hydroxy-1-methylquinolin-2(1*H*)-one, nitroketene *N*,*S*-dimethyl acetal, and various aromatic aldehydes, in excellent yields (Scheme 14) (13TL3248).

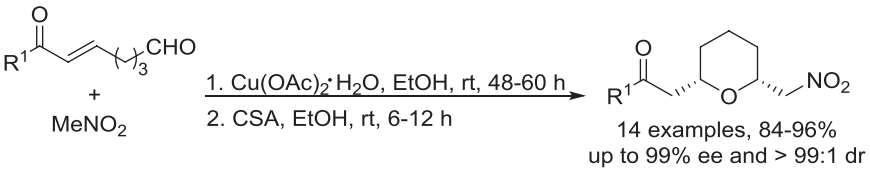
Several studies were dedicated to the construction of the tetrahydropyran scaffold in the total synthesis of natural products, namely (−)-brevisamide (13OBC6751), (−)-blepharocalyxin D (13OL2046), bryostatins



Scheme 14



Scheme 15

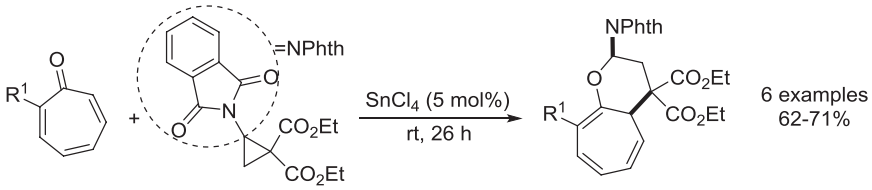


Scheme 16

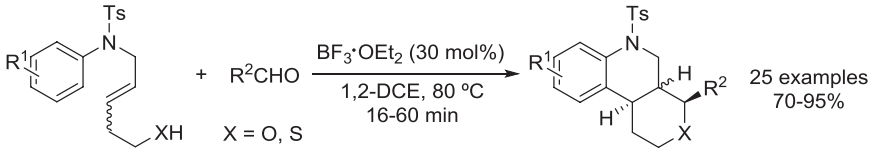
(13CC10211, 13S1815), (+)-centrolobine (13TA196), 5-*epi*-diospongin A (13TA196), tubulexins (13AGE410), pectenotoxin-4 (13AGE2491) and in the synthesis of unnatural enantiomers of polyol, polyene macrolides (13EJO6584). L-Glutamic acid was used as starting material in a kilogram-scale synthesis of (*S*)-3-aminotetrahydropyran, a synthetic intermediate in the preparation of Janus kinase 1 inhibitors (13SL987).

Iron nitrate supported on bentonite induces the sequential oxidation of benzyl alcohols, and Prins cyclization of the aldehydes formed, with homoallylic alcohols and trimethylsilyl chloride to provide 2-aryl-4-chlorotetrahydro-2*H*-pyrans (Scheme 15) (13SL1781).

TMSOTf promotes the diastereoselective synthesis of 2,6-disubstituted tetrahydropyrans through Prins–pinacol reaction of 2-methylene-1,4-diols with acetals (13SL2292) and multicomponent Prins cyclization of allylsilyl alcohols with aliphatic and aromatic aldehydes (13JOC104, 13OL5234). Highly stereoselective 2,6-*cis*-disubstituted tetrahydropyrans are readily available through the copper(II)-mediated Henry reaction of nitromethane with 7-oxo-hept-5-enals followed by intramolecular oxa-Michael addition using a catalytic amount of camphorsulfonic acid (CSA) (Scheme 16) (13OL2922).



Scheme 17



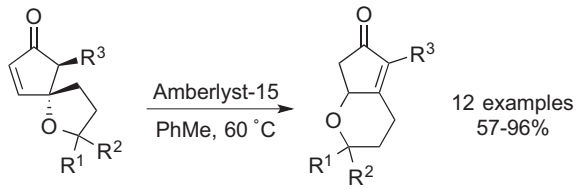
Scheme 18

Highly substituted tetrahydropyrans are diastereo- and enantioselectively prepared from the reaction between carbamates, boron esters, and two different aldehydes via one-pot lithiation–borylation, allylation, and Prins cyclization process (13TL49). Regio- and diastereoselective $SnCl_4$-catalyzed [8 + 3] cycloaddition reactions of tropone derivatives and donor-acceptor aminocyclopropanes lead to tetrahydrocyclohepta[*b*]pyrans, in good yields (Scheme 17) (13OL4928). A similar procedure uses $Ni(ClO_4)_2{\cdot}6H_2O$ as catalyst (13CC10406).

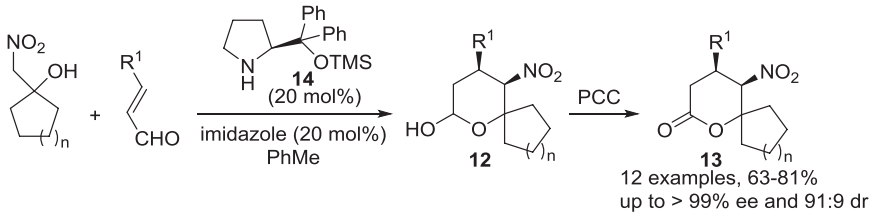
Tandem Prins biscyclization of sugar-derived homoallylic alcohols with aldehydes in the presence of $In(OTf)_3$ and *p*-toluenesulfonic acid (*p*-TsOH) affords sugar-annulated furotetrahydropyrans (13SL1263). A series of quinoline-fused tetrahydro-2*H*-(thio)pyrans can also be synthesized through a Prins cascade cyclization of homoallylic alcohols (mercaptans) with aldehydes. The stereoselectivity of the reaction is controlled by the geometry of the olefin: (*Z*)-olefins afford *cis*-fused products, whereas (*E*)-olefins give *trans*-fused products (Scheme 18) (13JOC8161).

6,8-Dioxa[3.2.1]bicycles, prepared from a metal-free 1,3-stereoselective conjugate addition of alkenylboronic acids or potassium alkenyltrifluoroborates to δ-oxygen-substituted α,β-unsaturated carbonyl compounds, are intermediates in the stereodivergent synthesis of 4-alkenyl-2,6-disubstituted tetrahydro-2*H*-pyrans (13JOC12825). Molecular rearrangement of spirocyclic ethers promoted by Amberlyst-15 gives access to a range of cyclopentenone-fused tetrahydro-2*H*-pyrans (Scheme 19) (13EJO6237).

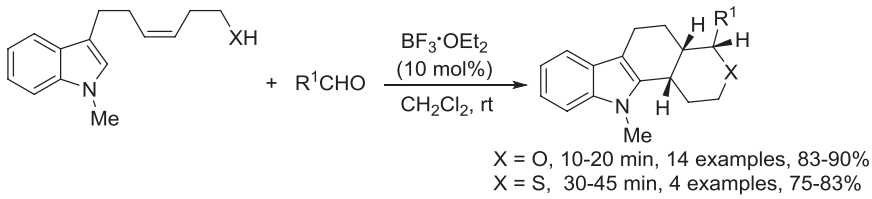
Spiro 2-hydroxytetrahydro-2*H*-pyrans **12** result from the asymmetric organocatalytic Michael–hemiacetalization reaction of



Scheme 19



Scheme 20



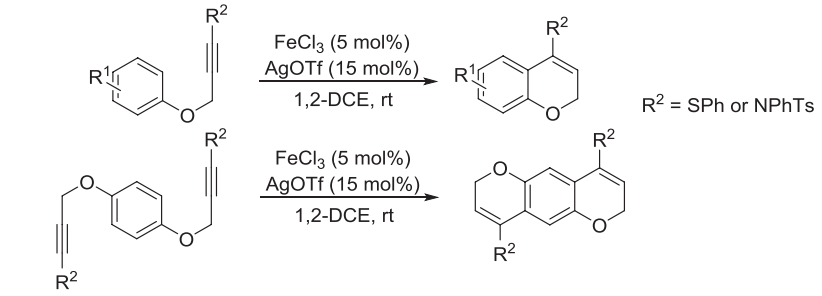
Scheme 21

1-nitromethylcycloalkanols with α,β-unsaturated aldehydes and subsequent in situ oxidation with pyridinium chlorochromate (PCC) to provide spiro tetrahydro-2*H*-pyran-2-ones **13** (Scheme 20) (13TL2546).

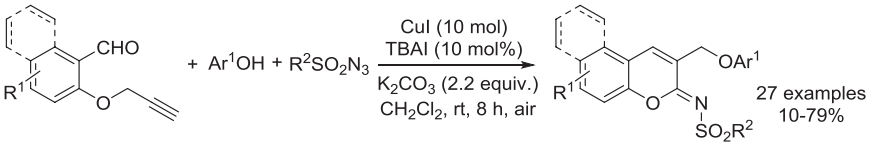
Tetracyclic-fused tetrahydropyrans arise from intramolecular 1,3-dipolar cycloaddition of 7-formyl-8-allyloxyquinoline with secondary amino acids or alkyl hydroxylamines in the presence of the ionic liquid [Bmim][PF_6] (13TL4339) and Prins–Friedel–Crafts cyclization of 6-heterocyclic-hex-3-en-1-ol with various aldehydes using a catalytic amount of $BF_3{\cdot}OEt_2$ (13TL1392). This last strategy was also applied for the synthesis of tetrahydro-2*H*-thiopyrans starting from the corresponding thiol (Scheme 21) (13TL1392).

6.4.2.2 [1]Benzopyrans and Dihydro[1]benzopyrans (Chromenes and Chromans)

The enantioselective synthesis of cedrelin A and methylated paralycolin B utilizes a palladium(II)-catalyzed asymmetric intramolecular Friedel–Crafts



Scheme 22

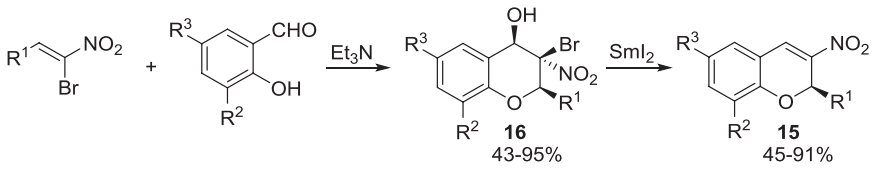


Scheme 23

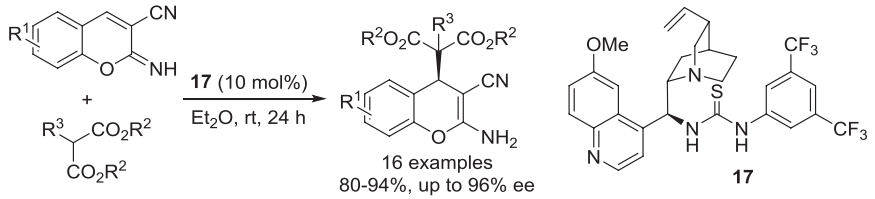
allylic alkylation of phenols as a key step for the chromene ring formation (13T5913). The total synthesis of other biologically active natural compounds with a chromene scaffold, such as eryvarin H and 13 derivatives (13OBC5782) and hirtellanine A (13EJO1356), results from Friedel–Crafts acylation-type reactions.

A few examples of 2*H*-chromenes result from the intramolecular hydroarylation of oxygen-tethered arylalkynyl phenyl sulfides and sulfonamides, catalyzed by $FeCl_3$ and AgOTf. A twofold intramolecular selective 6-*endo* hydroarylation protocol led to bicyclic products (Scheme 22) (13EJO533). Under mild conditions, the electrophilic intramolecular twofold iodoarylation of diynyl diethers with iodine monochloride affords high yields of 4,4′-bis(2*H*-chromenes) (13JOC11382).

Salicylaldehydes afford 2,2-difluoro-2*H*-chromenes through a tandem reaction with ethyl 3-bromo-3,3-difluoropropionate mediated by 1,4-diazabicyclo[2.2.2]octane (DABCO) (13T10820). Functionalized 2*H*-chromene-2-thiones arise from the $AlCl_3$-promoted Pechmann condensation of phenols with β-oxodithioesters, under solvent-free conditions (13TL183). CuI catalyzes the three-component cascade reactions of salicylaldehydes, terminal akynes, and 2-azidoacetonitrile (13OL2986) and of ynals, phenols, and sulfonyl azides (Scheme 23) (13OL3828) to give a wide range of 2-imino-2*H*-chromenes.



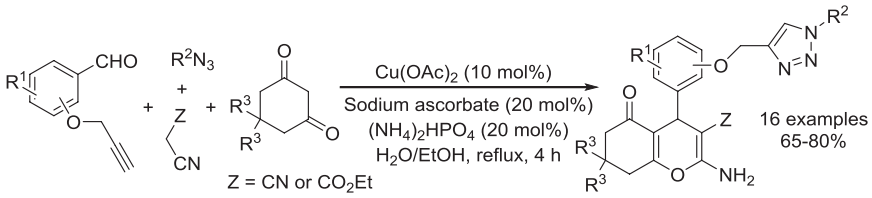
Scheme 24



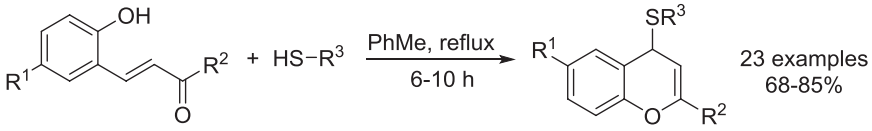
Scheme 25

3-Substituted 2*H*-chromenes result from the reaction of *O*-propargyl salicylaldehydes with active methylene compounds mediated by CuI/$(NH_4)_2HPO_4$ (13T82). A range of chiral 3-nitro-2*H*-chromenes were prepared from an organocatalyzed (*trans*-4-hydroxyprolinamide as catalyst and 4-nitrophenol as cocatalyst) domino oxa-Michael–Henry reaction of salicylaldehydes and *trans*-β-nitroolefins (13EJO5431), while 2-*C*-glycosyl-3-nitro-2*H*-chromenes **15** are available through a triethylamine-promoted tandem Michael–Henry reaction of sugar-derived *gem*-bromonitroalkenes with salicylaldehydes followed by a SmI_2-mediated β-elimination of the resulting 3-bromo-4-hydroxy-2*H*-chromans **16** (Scheme 24) (13JOC12831).

Under catalyst-free conditions, the reaction of 2-hydroxychalcone derivatives with electron-withdrawing substituted acetonitriles affords cyano-functionalized 2-aryl-4*H*-chromenes. The reaction with malononitrile in the presence of sodium bicarbonate provides 2-amino-3-carbonitrile-4*H*-chromenes in excellent yields at room temperature (13S334). Further 2-amino-3-carbonitrile-4*H*-chromenes were attained through a domino Rauhut–Currier-type reaction–cyclization–isomerization process involving cyclohexen-2-one and alkylidenemalononitriles under metal-free conditions and using a Lewis basic tertiary amine as catalyst (13OL5534). High yields and enantioselectivity of 2-amino-3-carbonitrile-4*H*-chromenes result from the conjugate addition of malonates to 2-imino-3-nitrochromenes promoted by a quinine-thiourea catalyst **17** (Scheme 25) (13OBC400) and from the tandem Michael addition–cyclization reaction of functionalized *o*-2-nitrovinylphenols with malononitrile catalyzed by a chiral bifunctional squaramide (13TA953).



Scheme 26

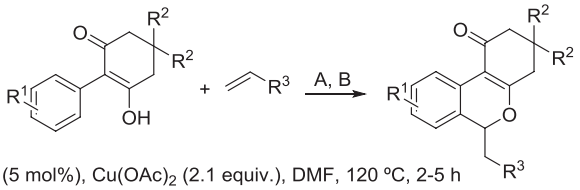


Scheme 27

Similar derivatives are also obtained from the three-component reactions of salicylaldehydes, malononitrile, and dialkyl/diphenylphosphites catalyzed by 1,1,3,3-tetramethylguanidine under neat conditions (13T10544), substituted resorcinols, isatins, and malononitrile mediated by $Ca(OH)_2$ (13T9682), different enols, aromatic aldehydes, and active methylene nitriles in the presence of a low loading of the organocatalyst potassium phthalimide-*N*-oxyl in water (13T1074), dimedone, benzaldehydes, and malononitrile using water dispersed magnetic nanoparticles of γ-Fe_2O_3 (13TL3344), dimedone or 1-naphthol, aldehydes, and malononitrile in the presence of amino-functionalized MCM-41 catalyst in water (13SC1499) and dimedones, methyl 2-perfluoroalkynoate and active methylene nitriles in methylamine (13T6121). The one-pot four-component reaction of aryloxy propargylated aldehydes, various azides, active methylene compounds, and dimedones gives 2-amino-4*H*-chromene derivatives in high yields (Scheme 26) (13SC486).

A wide range of 4-thio-substituted 2-aryl-4*H*-chromenes is formed when 2-hydroxychalcone derivatives react with various thiols (Scheme 27). Two new C–S and C–O bonds are formed in this catalyst-free domino reaction (13T2430). Chiral phosphoric acids catalyze the photocyclization reduction of 2-hydroxychalcones (13CEJ13658) and the 1,4-reduction of racemic 2,4-diaryl-2*H*-chromen-2-ols (13CEJ9775), both in the presence of the Hantzsch ester, to provide 2,4-diaryl-4*H*-chromenes in good yields and with excellent enantioselectivity.

2′-Bromobiaryl-2-carbaldehydes undergo a tandem reduction followed by palladium(0)-catalyzed and *t*-BuOK-mediated C_{aryl}–$O_{alcoholic}$ coupling to produce benzo[*c*]chromenes, in good yields (13TL1673). Further



A: $Pd(OAc)_2$ (5 mol%), $Cu(OAc)_2$ (2.1 equiv.), DMF, 120 °C, 2-5 h
6 examples, 50-73%
B: $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%), $Cu(OAc)_2$ (2.1 equiv.), K_2CO_3 (2 equiv.), *t*-AmOH, 90 °C, 3-24 h
6 examples, 45-74%

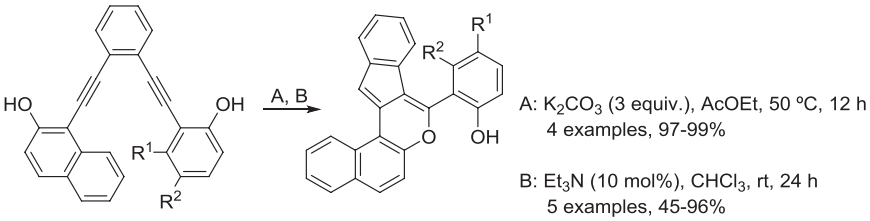
Scheme 28

derivatives are obtained from the treatment of 2-hydroxyphenylboronic acid with β-(2-bromoaryl)-α,β-unsaturated carbonyl compounds mediated by in situ-generated palladium(II) nanoparticles in water (13TL665). 2-Aryl-3-hydroxycyclohexen-2-ones afford tetrahydrobenzo[*c*]chromenes through a palladium(II)- or ruthenium(II)-catalyzed C–H alkenylation reaction with terminal alkenes (Scheme 28) (13OL570).

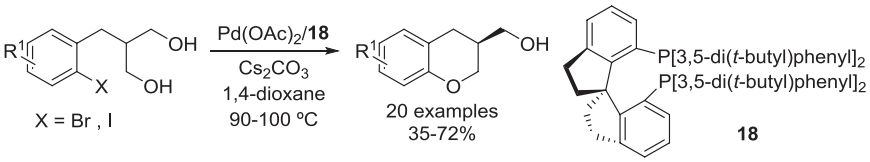
A few examples of naphtho[*c*]chromenes arise from the intramolecular cascade hydroarylation–cycloisomerization reaction of 1-(3-phenoxy-1-propynyl)-2-(1-propynyl)benzene derivatives, catalyzed by a $PtCl_2/PtCl_4$ system (13EJO260). 3-Trifluoromethylated benzo[*f*]chromenes are readily accessible through the one-pot reaction of α,β-unsaturated trifluoromethyl ketones with 2-naphthols carried out in the presence of DBU and concentrated sulfuric acid (13SC2883).

The application of Vilsmeier–Haack formylation to 4,6-diacetylresorcinol, its Schiff bases and hydrazones leads to a range of polyfunctionalized pyrano-fused 4*H*-chromenes (13SC3329). The three-component reaction of aldehydes, cyclic and acyclic 1,3-dicarbonyl compounds, and 4-hydroxycoumarin mediated by an efficient Lewis acid-surfactant-combined catalyst $Fe(DS)_3$ (DS = dodecyl sulfate) in aqueous media affords coumarin-fused tetrahydrochromenes (13TL3105). A series of indole-fused chromenes arise from the reaction of oxindoles with 2′-hydroxyacetophenones or 2′-hydroxypropiophenones or salicylaldehyde (13H2053), whereas indeno-fused chromenes are available through a base-catalyzed Schmittel cycloisomerization of *o*-phenylenediyne-linked bis(arenol)s (Scheme 29) (13TL7107).

The total synthesis of cannabicyclol, clusiacyclol A and B, iso-eriobrucinol A and B and eriobrucinol involves an oxa-[3 + 3] annulation for the construction of the chroman nucleus and a stepwise cationic [2 + 2] cycloaddition for the cyclobutane formation (13OL3130). The synthesis of



Scheme 29



Scheme 30

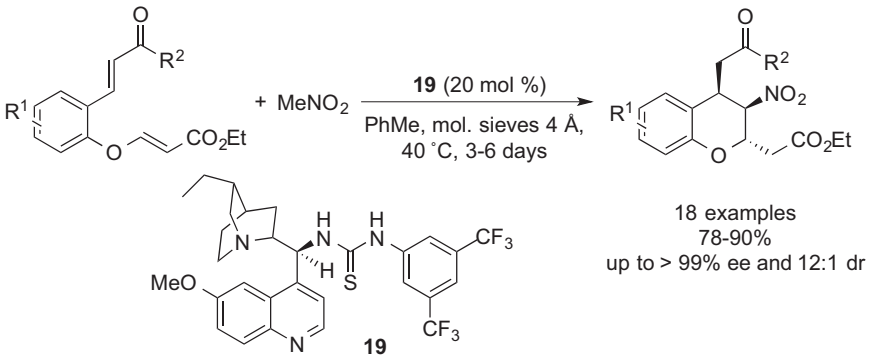
the chroman core of (±)-trichodermatides B and C involves also an oxa-[3 + 3] annulation of α,β-unsaturated aldehydes and 1,3-cyclohexanedione (13TL5567).

A wide range of chromans result from the phosphine-promoted intramolecular conjugation of alkyl halides with electron-deficient olefins (13CC4570) and palladium(II)-catalyzed intramolecular asymmetric *O*-arylation of 2-(2-haloaryl)propane-1,3-diols (Scheme 30) (13OL6022).

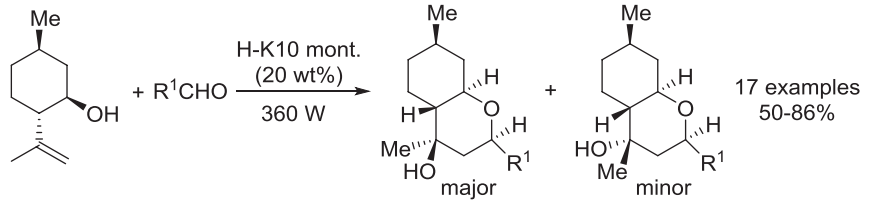
High enantioselectivity is achieved in the asymmetric hydrogenation of 4*H*-chromene-2-carboxylic acids promoted by a chiral spirophosphine oxazoline iridium complex to afford chroman-2-carboxylic acids (13AGE6072).

2-Polysubstituted 3,4-dihydro-3-nitro-2*H*-chromans are obtained from the enantioselective Michael–Michael cascade reaction of chalcone enolates and nitromethane catalyzed by bifunctional thiourea **19** (Scheme 31) (13JOC6488) and tandem Friedel–Crafts alkylation–Michael addition reaction of nitroolefin enoates and 1-methylindole promoted by $Zn(OTf)_2$ (13S601). A squaramide-tertiary amine catalyst promotes the asymmetric sulfa-Michael–Michael cascade reaction of thiosalicylates with nitroalkene enoates which leads to polysubstituted chromans in high yields with excellent stereoselectivities (13OL1190).

Formal inverse-demand [4 + 2] cycloaddition reaction of the *in situ*-generated cationic aryl 2-oxadiene oxocarbenium ions with electron-rich alkenes provides polysubstituted chromans in high yields. The diastereoselectivity is dependent on the substitution pattern of the alkene: generally

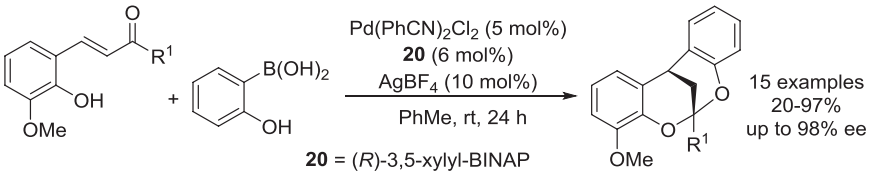


Scheme 31



H-K10 mont. = acid-treated montmorillonite K10

Scheme 32

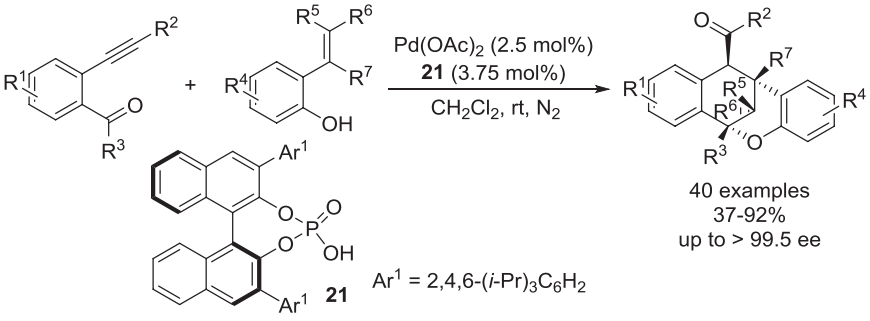


20 = (*R*)-3,5-xylyl-BINAP

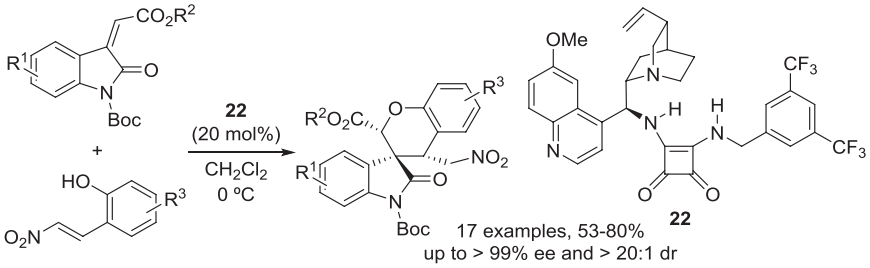
Scheme 33

endo-diastereomers occur as major products except for *trans*-β-methylstyrene, which affords *exo*-isomers (13JOC1404). The synthesis of octahydro-2*H*-chromans occurs via Prins cyclization of (−)-isopulegol with various aldehydes in the presence of acid-treated montmorillonite K10, under microwave irradiation and solvent-free conditions (Scheme 32) (13SL1137).

Enantioselective synthesis of [3.3.1]-bicyclic ketals can be achieved by palladium(II)-catalyzed 1,4-conjugate addition of 2-hydroxyphenylboronic to enones (Scheme 33). The reaction involves an in situ transmetalation of the boronic acid, that acts as bis(nucleophile) (13CC3360). Similar structures are obtained via a sequential Michael addition–bicyclization reactions



Scheme 34



Scheme 35

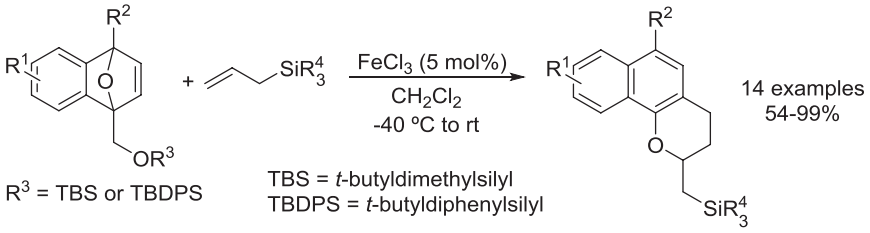
involving α,β-unsaturated carbonyl systems and 1,3-dicarbonyl compounds (13JOC3132).

Enantiopure polycyclic chromans arise from an asymmetric cascade annulation reaction of 2-hydroxystyrenes with *o*-alkynyl benzaldehydes or ketones (Scheme 34) (13JA11402).

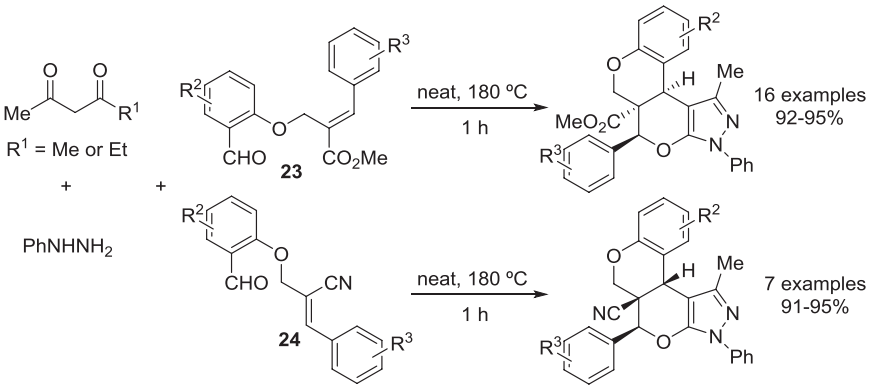
A squaramide-tertiary amine catalyst is used in the oxa-Michael–Michael cascade reaction of *N*-protected 3-methyleneindolin-2-ones with 2-(*E*)-(2-nitrovinyl)phenols to give spiro-indolinone chromans, with high stereoselectivity (Scheme 35) (13OL4062).

The one-pot three-component reaction of 2-hydroxynaphthoquinone, aromatic aldehydes and ethyl 4,4,4-trifluoro-3-oxobutanoate in the presence of ammonium acetate and acetic acid affords a series of 2-trifluoromethylated benzo[*g*]chroman derivatives (13S2193). Various allyl silanes are suitable for an annulation reaction with 1-naphthoquinone-2-methide, formed through an $FeCl_3$-mediated transformation of 1,4-epoxy-1,4-dihydronaphthalenes, to prepare benzo[*h*]chromans, in moderate to good yields (Scheme 36) (13AGE1515).

Multicomponent cascade reactions of methyl/ethyl acetoacetate, phenyl hydrazine, and Baylis–Hillman adducts **23** and **24** give access to tetracyclic



Scheme 36

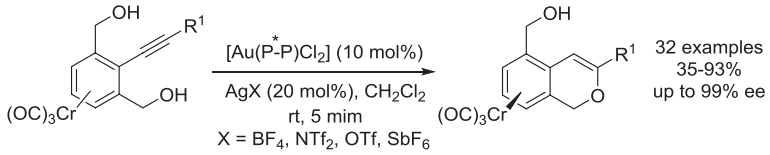


Scheme 37

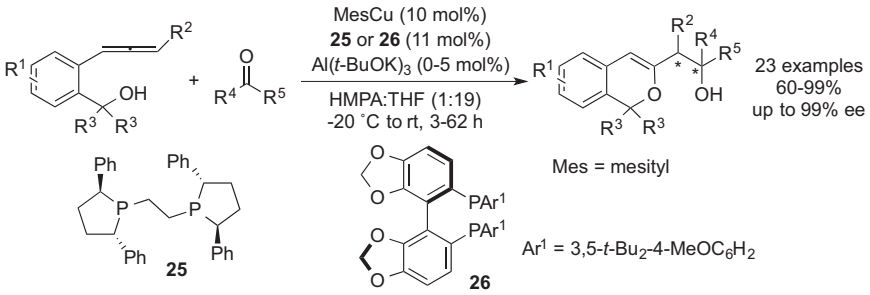
chromanopyranpyrazoles in excellent yields (13CC10947). This stereoselective reaction involves hydrazone and cyclic amide formation, Knoevenagel condensation, and intramolecular hDA reactions (Scheme 37). Tri- and tetracyclic fused chroman pyrrole derivatives are obtained by intramolecular [3 + 2] cycloaddition reactions of azomethine ylides derived from secondary amino acids with *O*-allylated salicylaldehydes prepared from Morita–Baylis–Hillman carbonates of β-lactam aldehyde (13SL2107). Other tetracyclic fused chromans are formed through domino Knoevenagel–hDA reactions of *O*-propargyloxy benzaldehydes with active methylene compounds in the presence of CuI in ionic liquid [Bmim][NO_3] (13SC1787) and from a four-step domino Knoevenagel–hDA–elimination–oxidation reaction of 2-(3-aryl-3-chloro-2-propenyloxy)benzaldehydes with 4-thioxo-1,3-thiazolidin-2-one in the presence of sodium acetate in refluxing acetic acid (13TL5667)

6.4.2.3 [2]Benzopyrans and Dihydro[2]benzopyrans (Isochromenes and Isochromans)

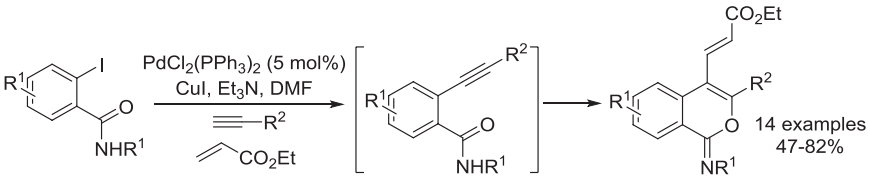
Gold(I)-catalyzed asymmetric intramolecular cyclization of prochiral 1,3-bis(hydroxymethyl)-2-alkynylbenzene tricarbonylchromium complexes



Scheme 38



Scheme 39

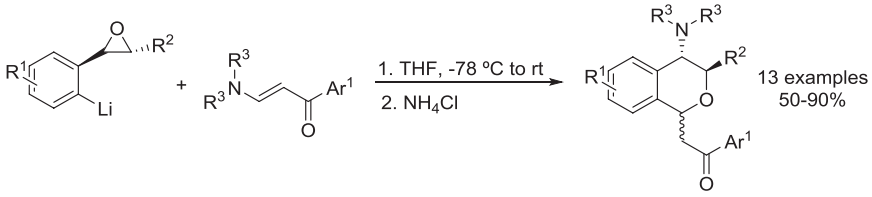


Scheme 40

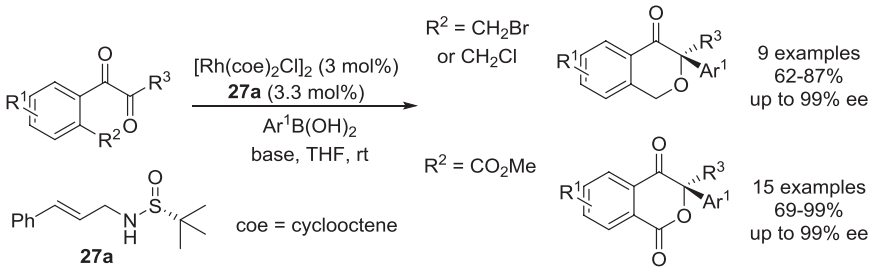
provides planar chiral (1*H*-isochromene)chromium complexes. The high enantioselectivity results from the combination of axially chiral diphosphine(AuCl)$_2$ precatalysts and silver salt cocatalysts (Scheme 38) (13JOC10986). A gold(III) catalyst promotes the annulation of 2-alkynyl benzaldehydes with ethyl vinyl ether in the presence of an alcohol to afford a range of 1*H*-isochromenes (13CEJ4043).

High yields of 1*H*-isochromenes result from the intramolecular oxycupration of allenes and subsequent asymmetric addition of the in situ-generated allylcopper species to carbonyl compounds, with excellent enantioselectivity (Scheme 39) (13AGE7177). 4-Iodo-1-nitromethyl-1*H*-isochromenes are prepared by condensation of 2-alkynylbenzaldehydes with nitromethane followed by an electrophilic iodocyclization (13JOC10476).

One-pot, stepwise Sonogashira–cascade oxycyclization–Heck coupling from 2-iodobenzamides, terminal alkynes, and ethyl acrylate yields 1-imino-1*H*-isochromenes in moderate to good yields (Scheme 40) (13S2009).



Scheme 41

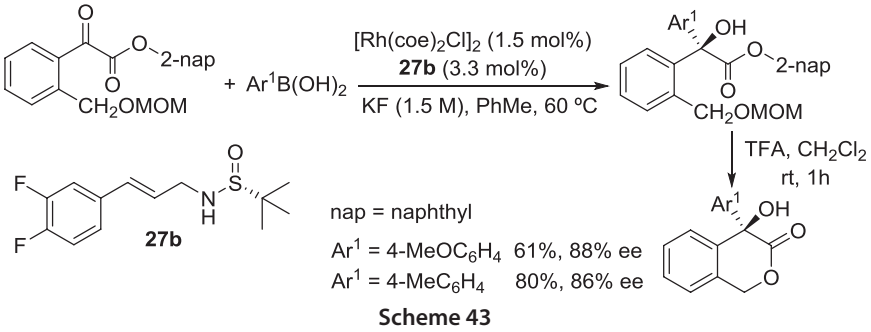


Scheme 42

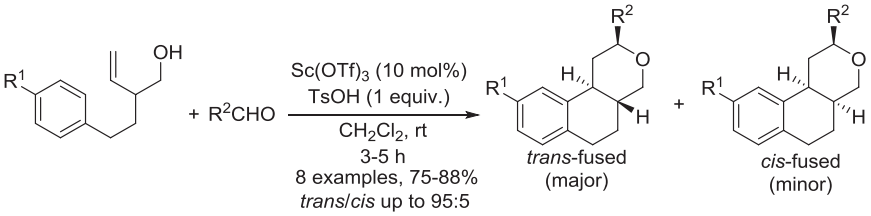
A photoredox catalysis approach can be used for the direct benzylic C–H activation for the C–O bond formation of isochromans. These cycloetherification reactions require neither a metal catalyst nor a chemical oxidant (13AGE5146). Several isochromans can be prepared in good yields by an oxa-Pictet–Spengler cyclization of a 2-aryl-1-ethanol with various arylacetaldehydes (13T8914). A diastereoselective version was used to construct the benzoisochroman scaffold of the natural (+)-frenolicin A and *epi*-(+)-frenolicin B as well as several frenolicin analogs (13OL5566).

A mixture of two epimeric stereoisomers of polysubstituted isochromans are obtained from the addition reaction of *o*-lithiated aryloxiranes to enaminones (Scheme 41) (13JOC11059).

A range of 4-isochromanones are prepared by a $AuCl_3$-catalyzed cascade reaction of allyl 1-(2-hydroxymethylphenyl)propargyl ethers, which involves a tandem intramolecular *exo-dig* heterocyclization–enol isomerization–Claisen rearrangement sequence (13OL2778). High yields are achieved in a regio- and enantioselective 1,2-addition of aryl boronic acids to asymmetric α-diketones followed by etherification or heterocyclization to give the corresponding 4-isochromanones and 1,4-isochromandiones, catalyzed by a rhodium/sulfur–olefin complex (Scheme 42) (13CEJ865). Using the same catalyst, two 3-isochromanones were prepared starting from α-ketoesters (Scheme 43) (13CC11659).



Scheme 43



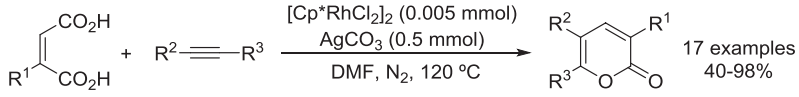
Scheme 44

6-Methyl-1-phenylhept-3-yne-2,6-diol undergoes a one-pot three-step cascade reaction with alkyl and aryl aldehydes to provide 2,4-dihydro-1*H*-benzo[*f*]isochromans. This two-component cascade reaction promoted by $BF_3{\cdot}OEt_2$ involves an alkynyl-Prins cyclization, Friedel–Crafts arylation, and dehydrative aromatization (13OL4070). Other Prins cascade cyclizations of 2-arylethylbut-3-en-1-ol with aliphatic and aromatic aldehydes occur in the presence of $Sc(OTf)_3$ and *p*-TsOH to prepare *trans*-fused hexahydro-1*H*-benzo[*f*]isochromans in good yields and excellent selectivity (Scheme 44) (13EJO1993).

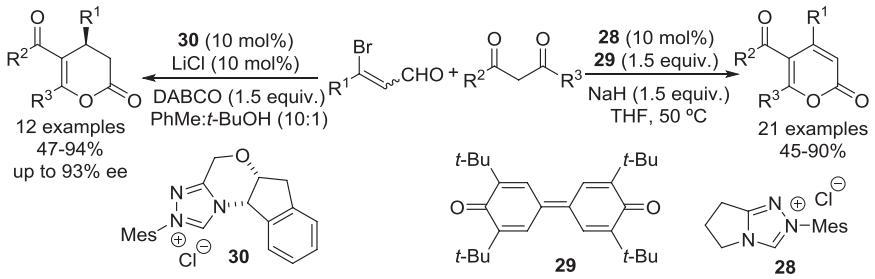
6.4.2.4 Pyranones

Polysubstituted 2*H*-pyran-2-ones are available through rhodium(III)-mediated decarboxylative and dehydrogenative coupling reactions of maleic acid derivatives with alkynes, in moderate to excellent yields (Scheme 45) (13JOC11427).

3-Bromoenals and 1,3-dicarbonyl compounds undergo a controlled and divergent NHC (**28**)-catalyzed oxidative transformation: treatment with an external oxidant provides 2*H*-pyran-2-ones, while in the absence of an external oxidant, chiral 3,4-dihydro-2*H*-pyran-2-ones are obtained in moderate to good yields and with good enantioselectivity (Scheme 46)



Scheme 45

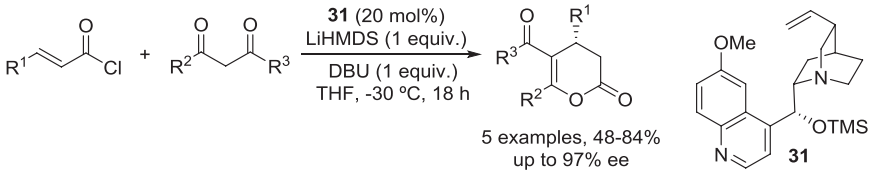


Scheme 46

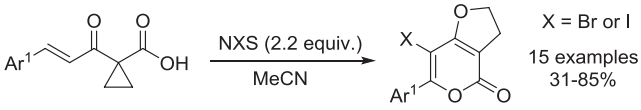
(13JOC6223). Other 3,4-dihydro-2*H*-pyran-2-ones are stereoselectively synthesized through NHC-catalyzed addition reactions of saturated aldehydes with 1,3-dicarbonyl compounds in the presence of oxidant **29** (13AGE8588), of enals with chalcones using acetic acid as cocatalyst (13CC261), of modified enals with enolizable aldehydes (13OL5202), of α-aroyloxyaldehydes with β-trifluoromethyl enones (13JOC9243), and of alkylarylketenes with β,γ-unsaturated α-ketocarboxylic esters and amides (13OBC3230), or with β,γ-unsaturated α-ketophosphonates (13SL1243). High enantioselectivity is achieved in the NHC-promoted [4 + 2] cycloaddition reactions of ketenes with 3-aroylcoumarins (13OBC158) and of heteroaryl aldehydes with trifluoromethyl ketones and isatins (13AGE11134) to give heteroaryl-fused dihydro-2*H*-pyran-2-ones. The organocatalytic Michael–Michael–lactonization cascade reaction of 1-methyl-3-(pent-2-en-4-on-yl)oxindoles and alkynyl aldehydes mediated by an NHC affords spirooxindole-fused 3,4-dihydro-2*H*-pyran-2-ones (13CEJ4428).

Enantioselective organocatalytic synthesis of 3,4-dihydro-2*H*-pyran-2-ones can be accomplished through a nucleophile-catalyzed Michael addition–proton transfer–enol lactonization of α,β-unsaturated acyl chlorides and 1,3-dicarbonyl compounds (Scheme 47) (13AGE13688).

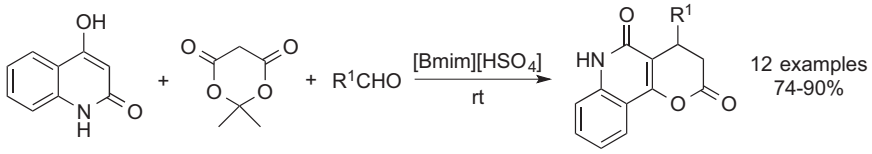
3-Hydroxypent-4-ynoic acids, prepared in good yields by a BF_3•OEt_2-promoted nucleophilic addition of bis(trimethylsilyl) ketene acetals to acetylenic ketones and aldehydes, undergo an intramolecular electrophilic annulation in the presence of NBS to afford 5-bromo-3,4-dihydro-2*H*-pyran-2-ones (13T7365). Heating a mixture of 1-alkenoylcyclopropane



Scheme 47



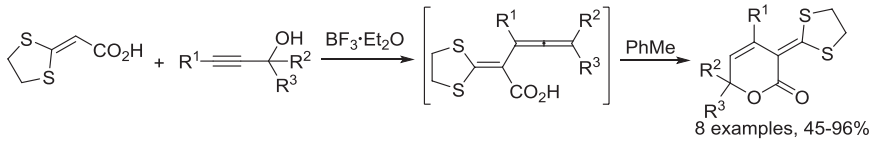
Scheme 48



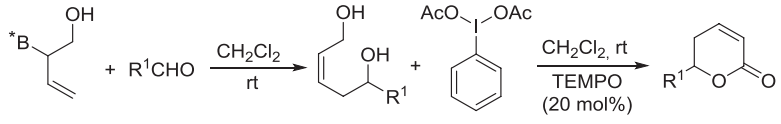
Scheme 49

carboxylic acids with NBS or NIS produces a range of halogenated furan-fused 2*H*-pyran-2-ones (Scheme 48). The mechanism involves a halo-oxacyclization, HBr elimination, cyclopropane ring opening and recyclization (intramolecular oxacyclization) and bromination cascade reaction (13OBC7212). A gold(I)-catalyzed tandem C-1–C-5 cyclization reaction of enediynes bearing a pendant carboxy group affords indene-fused 2*H*-pyran-2-ones or indene-fused 1*H*-isocoumarins through a C–C and C–O bonds formation (13CC695).

Indole-fused 2*H*-pyran-2-ones are synthesized by three different metal-free approaches starting from 1-substituted 3-acetyl-1*H*-indol-2-ols and phenylacetic acids using DCC in DMSO at 110 °C, 1,1′-carbonyldiimidazole in the presence of DBU in dichloromethane at room temperature and using Mukaiyama's reagent (2-chloro-1-methylpyridinium iodide) with an excess of triethylamine in refluxing acetonitrile (13S1235). The organocatalytic three-component reaction of 4-hydroxycoumarin, aromatic aldehydes, and 3-bromo-4-hydroxycoumarin using a DBU/acetic acid system provides coumarin-fused 3,4-dihydro-2*H*-pyran-2-ones, in good yields and diastereoselectivity (13OBC279). High yields of quinoline-fused 3,4-dihydro-2*H*-pyran-2-ones are accessible from the three-component reaction of 4-hydroxyquinolin-2-one, Meldrum's acid and aliphatic and aromatic aldehydes using an acidic ionic liquid as catalyst (Scheme 49) (13TL4633).



Scheme 50

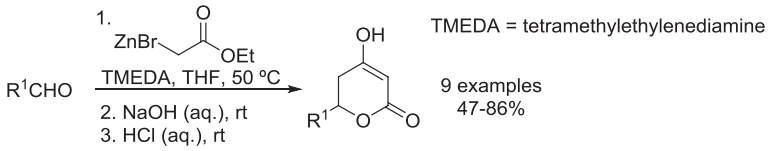


Scheme 51

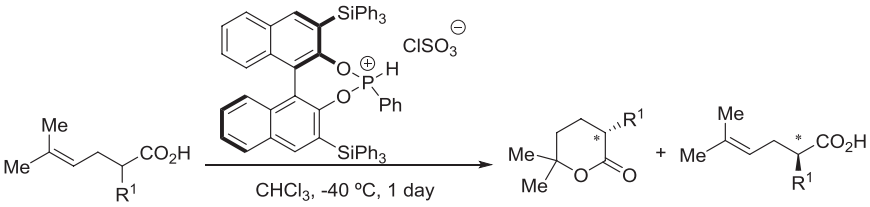
A range of 3-(1,3-dithiolan-2-ylidene)-2*H*-pyran-2-ones are obtained through a regiospecific 6-*endo*-annulation of the in situ formed 2-(1,3-dithiolan-2-ylidene)-3,4-dienacids from the dehydrative coupling of 2-(1,3-dithiolan-2-ylidene)acetic acid with tertiary propargyl alcohols mediated by $BF_3{\cdot}OEt_2$ (Scheme 50) (13OL2608).

The total synthesis of synargentolide B involves a Wittig–Horner reaction of a chiral phosphonate derived from (*S*)-lactic acid and a ring-closing metathesis for the construction of the 5,6-dihydro-2*H*-pyran-2-one motif, as key steps (13JOC3313). Another approach for the synthesis of this natural product and some of their stereoisomers uses diethyl tartrates as starting materials and a tandem ring-closing–cross metathesis reaction in which lactone formation and fragment coupling occurs in one-pot (13EJO4870). Similar ring-closing metathesis is used in the total synthesis of cryptocaryol A (13EJO1051, 13JA9334) and B (13JA9334), (+)-7-epigoniodiol and (−)-8-epigoniodiol (13HCA1366), passifloricin A (13HCA505), synparvolide C (13EJO6702), and the tubulin inhibitor WF-1360F (13AGE5866). The synthesis of the natural 5,6-dihydro-2*H*-pyran-2-ones goniothalamin, parasorbic acid, and massoia lactone are accomplished by allyl addition of enantiomerically pure allylboronic esters to various aldehydes and selective oxidation of the obtained 2-ene-1,5-diols with (diacetoxyiodo)benzene and a catalytic amount of TEMPO (2,2,6,6-tetramethylpyrrolidin-1-oxyl) (Scheme 51) (13S1106).

The synthesis of 6-substituted-4-hydroxy-5,6-dihydro-2*H*-pyran-2-ones is accomplished through a double Reformatsky reaction of aldehydes with ethyl bromozincacetate, followed by lactonization (Scheme 52). This synthetic protocol is applied to the synthesis of naturally occurring



Scheme 52



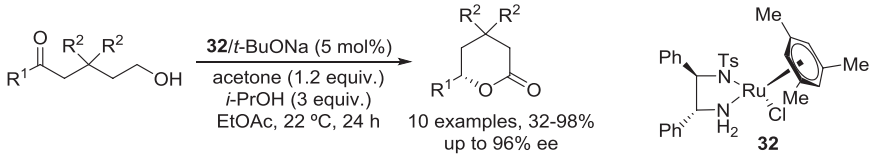
Scheme 53

yangonin (13T10921). An intramolecular Pinner reaction of 5-hydroxypent-2-enenitriles provides a wide range of substituted 5,6-dihydro-2*H*-pyran-2-ones, in moderate to good yields (13T5374). Few examples are also formed from AgOTf-mediated intramolecular cyclization of phenoxyethynyl α,γ-diols having tertiary alcohol moieties (13OL4150).

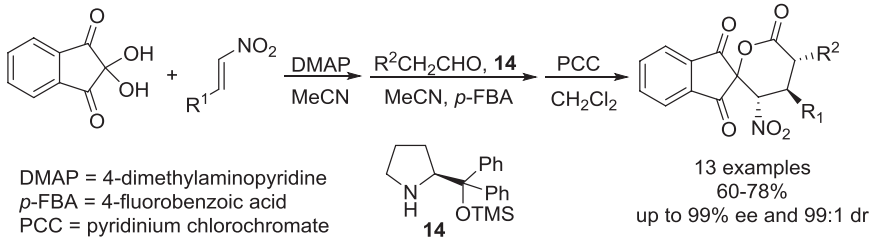
Chiral phosphonous acid diester induces the kinetic resolution of racemic α-substituted γ-unsaturated carboxylic acids through asymmetric protolactonization (Scheme 53) (13OL2838). Dinamic kinetic resolution with *Candida antartica* lipase B and the ruthenium catalyst [$RuCl(CO)_2(\eta^5\text{-}C_5Ph_5)$] of several homoallylic alcohols is applied in the key step to the synthesis of enantiomerically pure 5,6-dihydro-2*H*-pyran-2-ones ([13CEJ13859]).

Extensive NMR and reactivity studies elucidate a γ-*C*-alkylation mechanism involved in the preparation of 6-phenyl-2,4-dioxytetrahydropyrans via potassium carbonate-mediated condensation of benzaldehyde and acetoacetate esters (13JOC4563). 6-Aryl analogs undergo further sequential condensation with α,β-unsaturated aldehydes and 6π-electrocyclization to give pyran-2-one-fused 2*H*-pyrans under classic heating conditions and microwave irradiation (13BCSJ870).

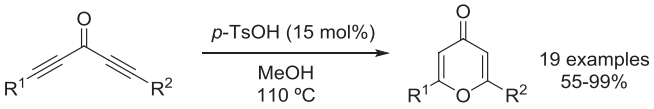
Enantioselective hydroacylation of 1,5-ketoalcohols using Noyori's transfer hydrogenation catalyst **32** provides a series of tetrahydro-2*H*-pyran-2-ones (Scheme 54) (13JA5553). 6-Iodomethyltetrahydro-2*H*-pyran-2-ones are achieved by asymmetric iodolactonization of 5-arylhex-5-enoic acid with a catalytic amount of iodine using a PyBidine-$Ni(OAc)_2$ complex as catalyst (13SL2045). A similar iodolactonization is the key step in the



Scheme 54



Scheme 55



Scheme 56

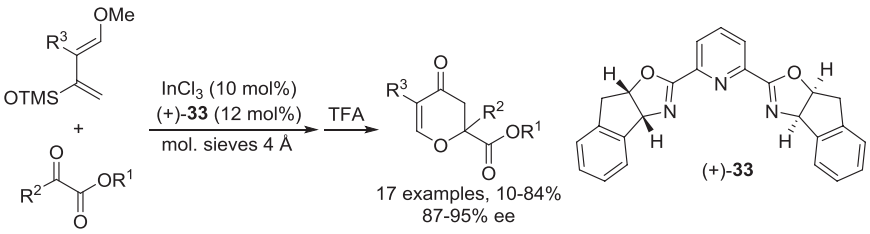
synthesis of natural isochroman derivatives, eleutherin and isoeleutherin (13SL185).

An organocatalytic cascade reaction involving a Morita–Baylis–Hillman–Michael cascade reaction of ninhidrin, nitroalkenes, and saturated aldehydes resulted in a series of spiroindanone δ-tetrahydro-2*H*-pyran-2-ones, with high chemo-, regio-, enantio-, and diastereoselectivities (Scheme 55) (13CC8692).

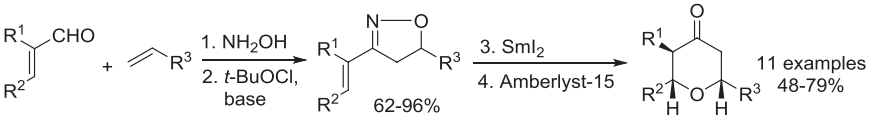
A series of symmetrical and asymmetrical diynones undergo a *p*-TsOH-promoted electrophilic cyclization reaction to give access to 4*H*-pyran-4-ones, in moderate to good yields (Scheme 56) (13JOC12018).

Asymmetric hDA reaction of Danishefsky's dienes with α-carbonyl esters catalyzed by an indium(III)-pybox complex affords 2,3-dihydro-4*H*-pyran-4-ones with good to excellent enantioselectivity (Scheme 57) (13OL2914).

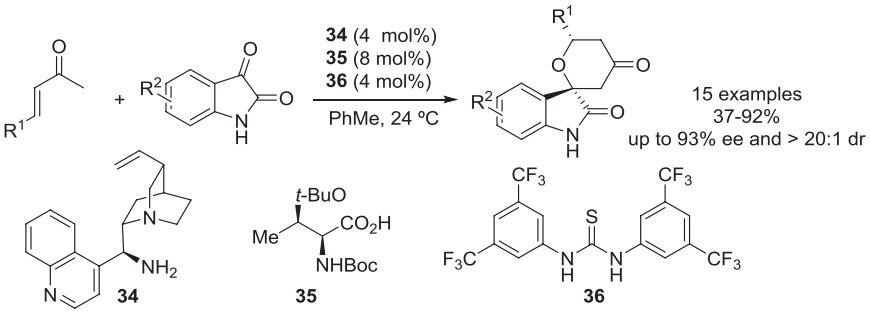
$BF_3{\cdot}OEt_2$ promotes the condensation of hydroxyl silyl enol ethers with various aldehydes to give *cis*-2,6-disubstituted 3,3-dimethyltetrahydro-4*H*-pyran-4-ones. The tetrahydro-4*H*-pyran-4-one moiety of the natural compound cyanolide A is enantioselectively prepared using this method



Scheme 57



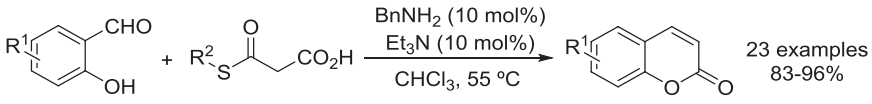
Scheme 58



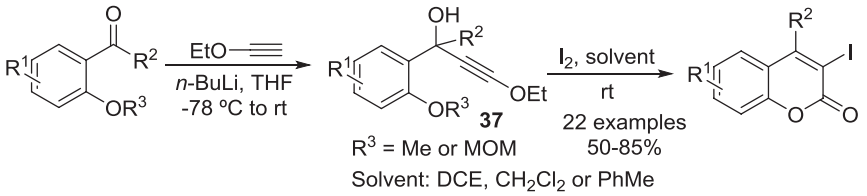
Scheme 59

(13OL4536). Further tetrahydro-4*H*-pyran-4-ones are achieved by [3 + 2] cycloaddition reaction of α,β-unsaturated nitrile oxides with alkenes and further chemoselective redutive isoxazoline's ring opening and 6-*endo*-*trig* oxa-Michael cyclization (Scheme 58). This strategy is also applied to the diasteroselective total synthesis of (±)-diospongin A (13CC193).

Indole-fused pyran-4-ones are prepared in one-pot two-step synthesis. In the first there is the acylation of 1-substituted 3-acetyl-1*H*-indol-2-ols with acid chlorides using triethylamine as base, in dichloromethane at room temperature. The second consists in the 4*H*-pyran-4-one ring formation from the in situ-obtained 3-acetyl-2-acyloxy-1*H*-indole derivatives (13S1235). A highly diastereo- and enantioselective organocatalytic formal hDA reaction of enones with isatins occurs in the presence of amine **34**, acid **35**, and thiourea **36** to produce spirooxindole tetrahydro-4*H*-pyran-4-ones (Scheme 59) (13CEJ6213).



Scheme 60



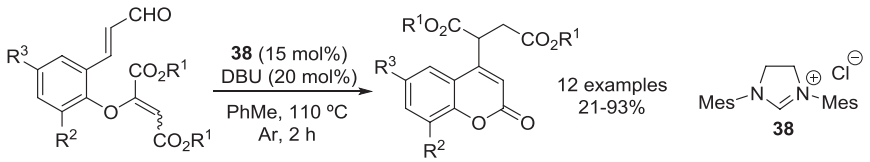
Scheme 61

6.4.2.5 Coumarins

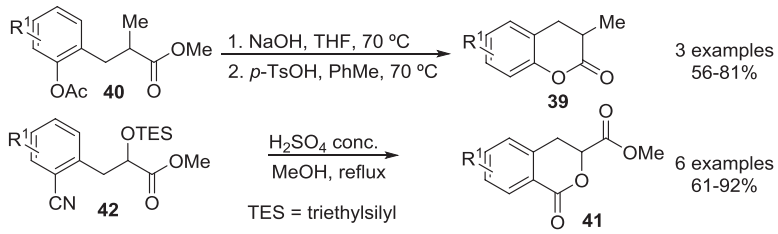
3,4-Diunsubstituted coumarins are available from the palladium(II)-catalyzed intermolecular annulation reaction of phenols with methyl acrylate (13AGE12669) and from an organocatalytic cascade reaction of salicylaldehydes with malonic acid half-thioesters mediated by a combination of benzylamine and triethylamine (Scheme 60) (13EJO4499).

Palladium(II)-catalyzed carbonylative reaction of salicylaldehydes with benzyl chlorides leads to a range of 3-arylcoumarins in good to excellent yields (13CEJ12245). Further derivatives are obtained from the NHC-catalyzed condensation and annulation reaction of 2-aryl-2-chloroacetaldehydes and salicylaldehydes (13T3669) and from the Perkin condensation of salicylaldehydes and 2-(4,5-dimethoxy-2-nitrophenyl)acetonitrile (13TL5734). In the latest case, subsequent microwave-assisted Cadogan cyclization gives the corresponding indole-fused coumarins (13TL5734). 3-Aryl-4-hydroxycoumarins are available by intramolecular Claisen condensation reaction of methyl 2-(2-arylacetoxy)benzoates carried out in the presence of Cs_2CO_3 in acetone (13CPB1166). The synthesis of 4-substituted 3-iodocoumarins occurs through a 6-*endo*-*dig* iodocyclization of 3-ethoxy-1-(2-alkoxyphenyl)-2-yne-1-ols **37** using iodine at room temperature (Scheme 61) (13JOC5878).

A range of 3,5,8-trisubstituted coumarins is obtained through the reaction of salicylaldehydes, derived from propargyl vinyl ethers, with three different carbonyl compounds: ethyl acetoacetate, Meldrum's acid, and ethyl cyanoacetate. This strategy involves a Knoevenagel condensation followed by lactonization and the corresponding coumarins armed with an ester, acid, or nitrile group at C-3 are obtained in moderate to good yields (13JOC8853).



Scheme 62

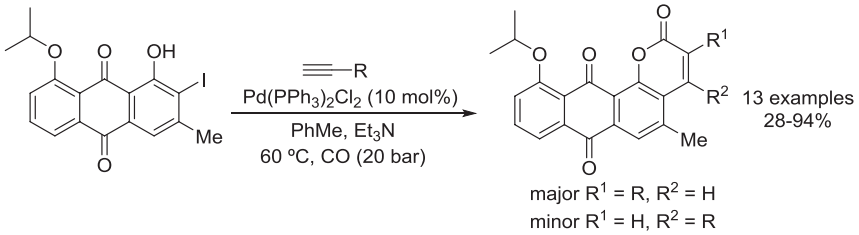


Scheme 63

Under solvent-free conditions, the Pechmann reaction of methyl acetoacetate with various phenols catalyzed by $H_3PW_{12}O_{40}$ supported in silica, titania, and carbon affords 4-methylcoumarins in high yields (13JHC1121). NHC catalyzes the intramolecular addition of enals to α,β-unsaturated esters to provide 4-alkyl substituted coumarins (Scheme 62). This cascade reaction involves an intramolecular Michael addition of homoenolate, alkene transfer fragmentation, and intramolecular cyclization (13OL68). Under atmospheric pressure of CO_2, other 4-substituted coumarins are synthetized in good yields by palladium(II)-catalyzed direct carboxylation of α-substituted 2-hydroxystyrenes using Cs_2CO_3 as base (13JA10954). Palladium(II) also promotes a one-pot dehydrogenation–oxidative Heck–cyclization cascade reaction involving cyclohexanones and electron-deficient alkenes to give 3,4-diunsubstituted, or 3- and 4-aryl substituted coumarins (13CC4021).

A general method for the synthesis of a large number of coumarin derivatives and 2*H*-pyran-2-ones include a carbanion-induced ring transformation of lactones with methylene carbonyl compounds followed by DDQ-mediated unprecedented oxidative cleavage of oxaylidene intermediates (13OBC5239).

A few examples of 3,4-dihydrocoumarins **39** are achieved after hydrolysis and cyclization of the *o*-acetoxylated β-arylated lactates **40**. 3,4-Dihydroisocoumarins **41** are obtained using *o*-cyano β-arylated lactates **42** (Scheme 63) (13OL5056).



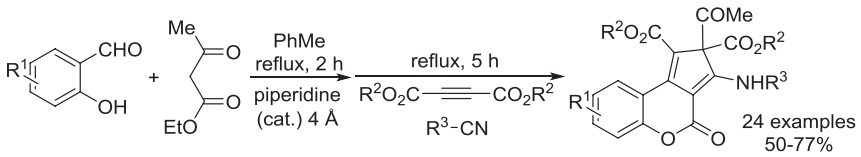
Scheme 64

A range of benzo[*c*]coumarins were synthesized from the tandem C–H activation–carbonylation reaction of 2-arylphenols using either palladium(II) (13AGE10598) or ruthenium(II) catalysts (13OL3962), C–H activation–lactonization of 2-arylbenzoic acids mediated by palladium(II)/(IV) species (13OL2574), and copper(II) or $K_2S_2O_8$ catalysts (13CEJ15836). Other derivatives are also obtained from copper(I)-catalyzed and microwave-assisted C–O lactonization of 2-halobiarylcarboxylates in subcritical water (13T9277), intramolecular nucleophilic substitution of triazene esters promoted by $BF_3{\cdot}OEt_2$ (13EJO5475), and palladium(II)-catalyzed one-pot Suzuki–Miyaura coupling of 2-hydroxyphenylboronic acid and *o*-halobenzaldehydes followed by oxidative lactonization (13TL657). The synthesis of natural benzo[*c*]coumarin derivatives lysilactone A (13T10322) and alternariol derivatives (13T2093) involves palladium(II) C–H activation and Suzuki coupling reactions as key steps, respectively. In the case of the natural nigricanin, the synthesis of the benzo[*c*]coumarin skeleton involves a palladium(II)-catalyzed intramolecular coupling of activated aryl iodobenzoates (13H2555).

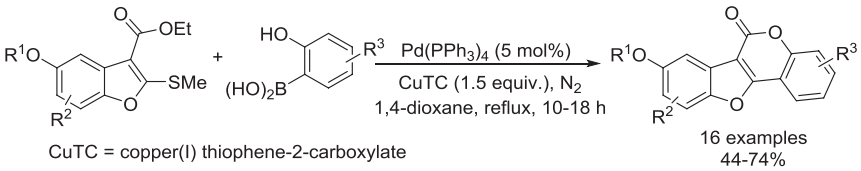
High yields of coumarin derivatives can be achieved when *o*-iodo phenolic compounds react with alkynes via domino alkyne addition–CO insertion–nucleophilic acylation reaction (Scheme 64) (13OL4834).

NHC-catalyzed diastereoselective annulation of enals with 2′-hydroxychalcones give access to cyclopentane-fused coumarins in good to excellent yields (13OL1756). Highly functionalized cyclopentadiene-fused coumarins are prepared by the one-pot multicomponent reaction of salicylaldehydes and ethyl acetoacetate with 1:1 acetylenecarboxylates-isocyanides in toluene (Scheme 65) (13JOC2611). One-pot three-component reaction of salicylaldehydes with β-ketoesters and isocyanides leads to a range of pyrrole-fused coumarins (13SL2124, 13T3054).

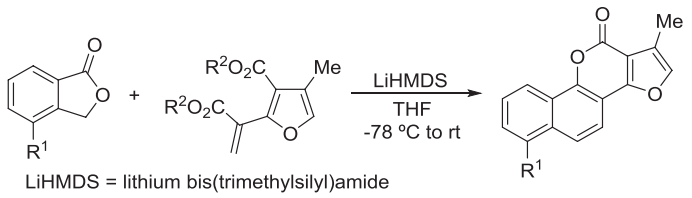
2-(Methylthio-3-ester)benzofurans undergo a palladium(0)-catalyzed C–S activation for [3 + 3] annulation reaction with 2-hydroxyphenylboronic



Scheme 65



Scheme 66



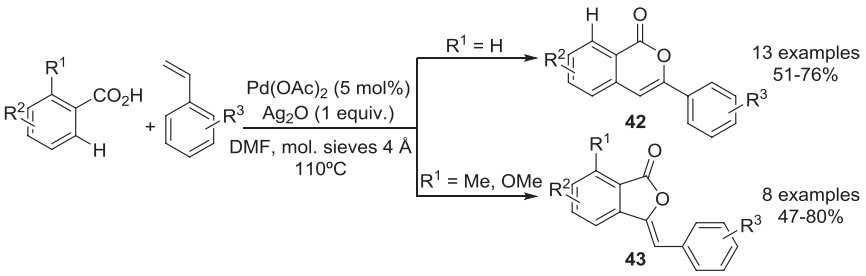
Scheme 67

acids to provide substituted coumestans in fairly good yields (Scheme 66) (13JOC7293). Iron-based cross-dehydrogenative coupling of β-(*o*-methoxyaryl)-β-ketoesters with phenols gives benzofurans, which after demethylation and lactonization affords a range of hydroxycoumestans. This strategy is used in a gram-scale total synthesis of coumestrol (13CEJ13575).

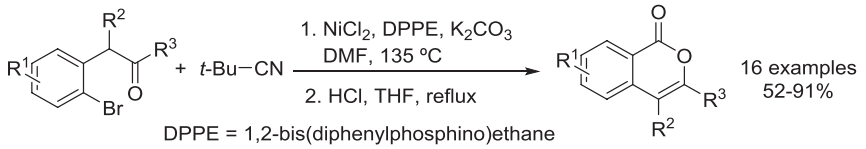
A cascade benzoannulation–lactonization reaction features in the total synthesis of neo-tanshinlactones using phthalides and α-carboxyfurylacrylates in the presence of lithium bis(trimethylsilyl)amide (LiHMDS) (Scheme 67) (13EJO4037).

The asymmetric total synthesis of fusarentin 6-methyl ether, a natural isocoumarin derivative, is achieved in nine steps with 20.5% overall yield. This compound is also the key intermediate in the total synthesis of fusarentin 6,7-dimethyl ether, 7-*O*-demethylmonocerin and monocerin with 16.5, 12.9% and 12.5% overall yields, respectively (13JOC6338).

High yields of 3-substituted isocoumarins **42** result from the reaction of 2-(4-hydroxybut-1-ynyl)benzaldehydes with an excess of Jones reagent (13JOC10178) and of ligandless palladium(II)-catalyzed oxidative coupling



Scheme 68



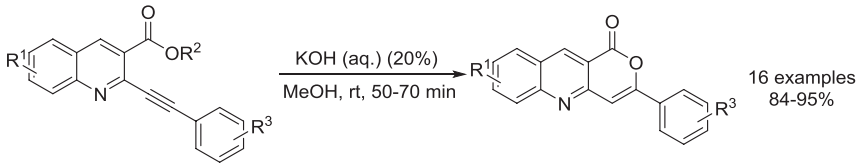
Scheme 69

reaction of benzoic acids with styrenes (13JOC3445). In addition, the presence of substituents in the *ortho* position of the benzoic acid affords 3-benzylidenephthalides **43** (Scheme 68) (13JOC3445).

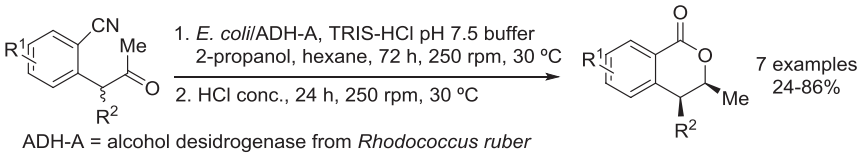
3,4-Disubstituted isocoumarins arise from the copper(II)-catalyzed addition of *o*-halobenzoic acids to active internal alkynes (13JOC1660), rhodium(III)-mediated oxidative coupling of benzoic acids with disubstituted alkynes (13T4454), palladium(II)-catalyzed tandem annulation reaction of *o*-alkynylbenzoates with methyl vinyl ketone (13T8626), and nickel(II)-promoted *t*-butyl isocyanide insertion in 2-(*o*-bromophenyl)-1-ethanones followed by hydrolysis (Scheme 69) (13SC3262). Ruthenium(II)-mediated oxidative annulation reaction of benzoic acids and cyclopropylarylethynes furnishes a mixture of 3- and 4-cyclopropyl substituted isocoumarins (13OBC142). A facile one-pot synthesis of 4-aryl-isocoumarins involves an acidic hydrolysis of (*Z*)-2-(1-aryl-2-methoxy-ethenyl)benzaldehydes with HBr and subsequent oxidation with PCC (13HCA2173).

Excellent yields of isocoumarin-type compounds are obtained via 6-*endo*-*dig* cyclization of 2-(2-arylalkynyl)quinoline-3-carboxylates using KOH in MeOH at room temperature (Scheme 70) (13T1822).

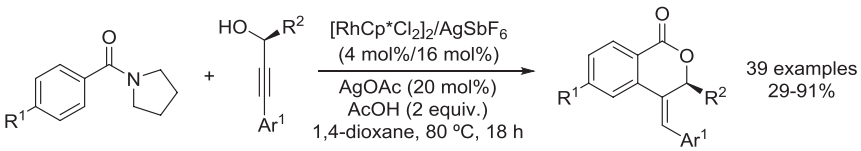
Novel *trans*-3-acetyl-4-hydroxy-3,4-dihydroisocoumarins occurs through an organocatalytic intramolecular *trans*-selective 6-*eno*/*exo*-*exo*-*trig* aldol reaction of 2-oxopropyl 2-formyl benzoate derivatives in good yields with high diastereo- and enantioselectivity (13S1708).



Scheme 70



Scheme 71



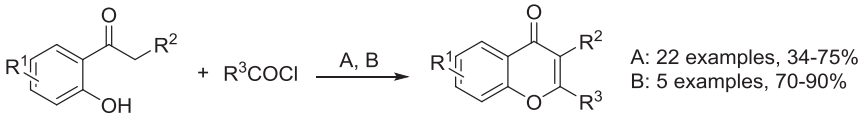
Scheme 72

3-Alkyl-4-oxy-3,4-dihydroisocoumarins are enantioselectively prepared by oxylactonization of *o*-(alk-1-enyl)benzoates promoted by the in situ-generated chiral lactate-based hypervalent iodine(III) catalysts (13EJO7128). Chemoenzymatic synthesis of 3,4-dialkyl-3,4-dihydroisocoumarins involves one-pot dynamic kinetic reductive resolution processes catalyzed by *E. coli*/alcohol desidrogenase. This strategy consists in the bioreduction of various racemic ketones to the corresponding enantiopure alcohols followed by intramolecular acidic cyclization (Scheme 71) (13OL3872).

4-Benzylideneisocoumarins are accessible from rhodium(III)-catalyzed C–H activation and annulation of 1-benzoylpyrrolidines with propargyl alcohols (Scheme 72) (13OL6290).

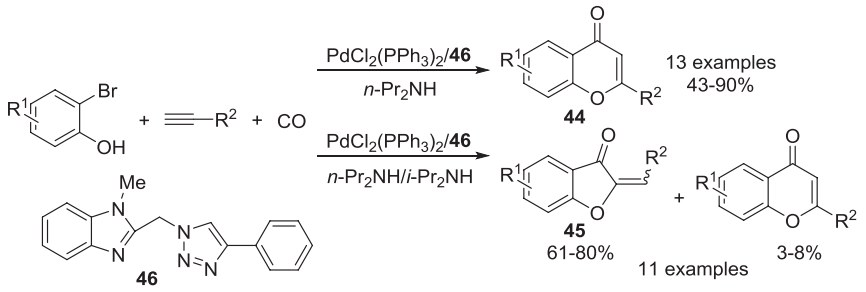
6.4.2.6 Chromones and Chromanones

The total synthesis of the natural chromone pestalotiopsone A includes a microwave-promoted aldol condensation and oxa-Michael cyclization to construct the chromanone core, followed by 2-iodoxybenzoic acid (IBX)-induced dehydrogenation to afford the desired chromone. The synthesis of pestalotiopsones B, C, and F is also accomplished using similar approaches (13OBC1109). 1,3,5-Trimethoxybenzene is the starting material for the



A: R^2 = H, R^3 = alkyl or aryl, (i) *t*-BuOK, THF, 0-80 ºC; (ii) H_2SO_4, reflux
B: R^1 = H, R^2 = Me, R^3 = aryl, (i) LiHMDS, PhMe, rt; (ii) HCl conc., rt

Scheme 73



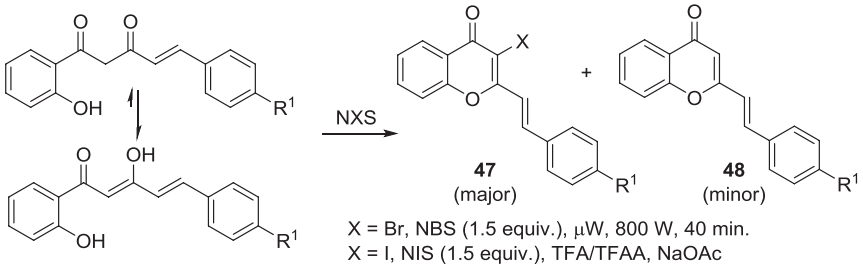
Scheme 74

synthesis of the natural prenylated flavones norartocarpin and artocarpin, in 14% and 3.5% overall yields, respectively (13T5850).

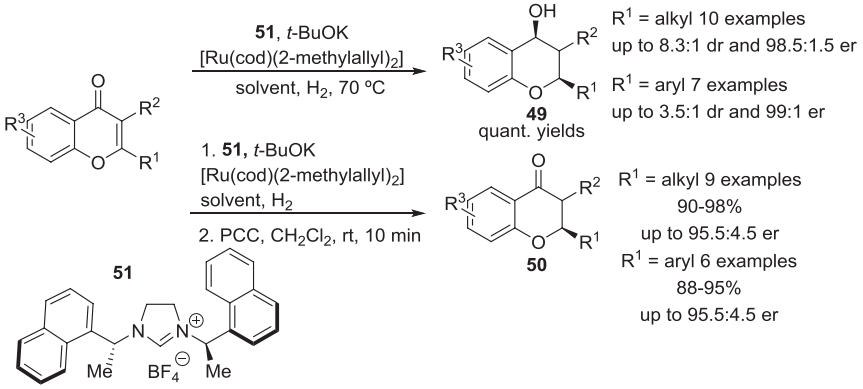
Regioselective oxidative cyclization of *o*-hydroxyphenyl propargyl carbinols using *t*-BuOLi as mediator and air as oxidant provides 2-substituted chomones in good yields (13EJO2080). Highly substituted chromones are prepared through a DBU-promoted regioselective intramolecular 6-*exo*-*trig* cyclization–dehydration of *o*-diketophenoxyethers (13T9335). Further derivatives are obtained from the one-pot reaction of 2′-hydroxyacetophenones with aliphatic or aromatic acid chlorides, in moderate to good yields (Scheme 73) (13SC1549, 13SL2683).

The one-pot synthesis of 2-substituted-3-carboxychromones is readily attained by the reaction of 3-oxo-3-(2,6-difluorophenyl)propanoates and acyl chlorides (13CC5313) and of 3-[2-(methoxymethoxy)phenyl]propiolates and aldehydes followed by DDQ oxidation of the formed chromanones (13T647), via transition metal-free approaches. Palladium(II)-catalyzed cascade carbonylative cyclization of 2-bromophenols and terminal alkenes gives chromones **44** in moderate to good yields. Variation on the amine used in the catalytic system led to aurones **45** as major products (Scheme 74) (13TL1802).

2′-(Mesyloxy)epoxychalcones, obtained after epoxidation in alkaline hydrogen peroxide of the corresponding chalcones, led to a series of flavonols when irradiated with microwaves in the presence of montmorillonite KSF



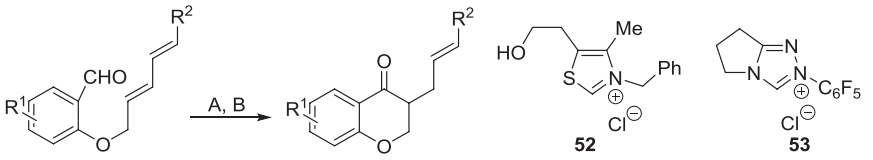
Scheme 75



Scheme 76

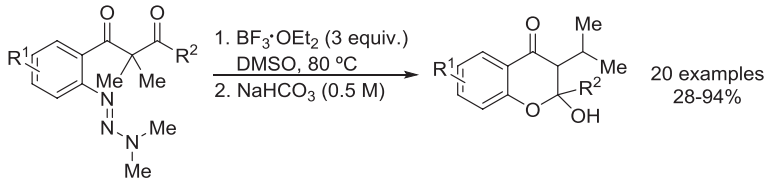
clay, under solvent-free conditions (13HCA1269). A series of flavone-type compounds are prepared by the three-step Baker–Venkataraman (BV) method from substituted 2′-hydroxyacetophenones and 5-methyl-3-phenylisoxazole-4-carboxylic acid (13JHC999) and of nicotinic acid under ultrasound irradiation (13JHC149). The synthesis of naturally occurring pyranoflavones occurs through the BV method using 2′,4′-dihydroxyacetophenones as starting materials and the formation of the pyran-fused 2′-hydroxyacetophenones as the key step (13HCA644). (*E*)-3-Bromo-2-styrylchromones **47** (X = Br) are available through 2-bromination of 5-aryl-1-(2-hydroxyphenyl)pent-4-ene-1,3-diones with NBS under microwave irradiation and solvent-free conditions, while 3-iododerivatives **47** (X = I) are obtained using NIS in the presence of TFA/TFAA and NaOAc. The corresponding (*E*)-2-styrylchromones **48** are also isolated as minor products (Scheme 75) (13T9701).

A chiral ruthenium(II)–NHC complex catalyzes the asymmetric hydrogenation of chromones and flavones to prepare enantiomerically enriched chromanols and flavanols **49**, chromanones, and flavanones **50** (Scheme 76) (13AGE8454). Chiral 2-alkylchromanones are prepared in good yields and



A: **52** (10 mol%), Cs_2CO_3 (30 mol%), PhMe, 70 °C
B: **53** (10 mol%), DBU (10 mol%), PhMe, rt

Scheme 77

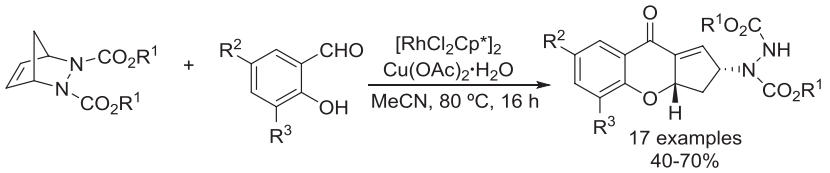


Scheme 78

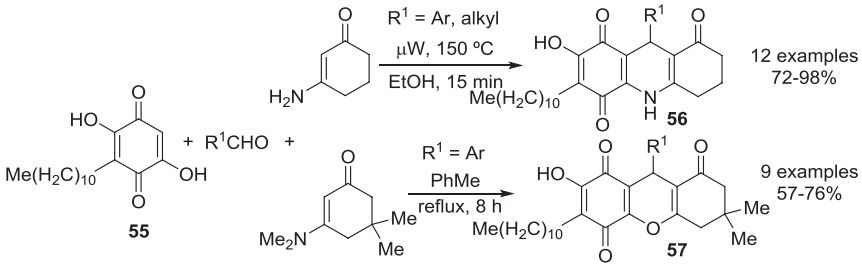
high enantioselectivity through a copper(I)-catalyzed conjugate addition of Grignard reagents to chromones, using the ferrocenyl-based bisphosphine ligand [(*R*,*S*)-Rev-Josiphos] (13CC5933).

Chiral azolium salts **52** and **53** have been used in the intramolecular vinylogous Stetter reaction of oxygen substrates **54** to provide 3-substituted chromanones (Scheme 77) (13CEJ15852). Other examples are obtained from the free-radical cascade reaction of *O*-allyl acylphosphonate with various functionalized β-ketoxanthates in the presence of dilauroyl peroxide, with moderate to good yields (13OL4818). A series of 2,3-disubstituted chromanones are synthesized from the reaction of acrylic acids with arynes in the presence of CsF (13T2789).

2′-Hydroxychalcones are cyclized to flavanones using potassium hydroxide and piperidine in water at room temperature (13SC1023) and sodium perborate tetrahydrate in warm aqueous acetonitrile medium (13SC1351). In the later case, some flavones are also obtained when warm acetic acid is used as solvent and 6,8-diiodoflavone is obtained using a catalytic amount of diacetoxyiodobenzene ([13SC1351]). A large variety of 2-hydroxyflavanone-type compounds are accessible by $BF_3{\cdot}OEt_2$-promoted tandem *O*-arylation–hydroxylation of dimethyltriazenyl-substituted 1,3-diketones (Scheme 78) (13EJO7411). Other flavanones are obtained through the conjugate addition of arylboronic acids to chromones using a palladium(II) catalyst formed in situ from palladium(II) trifluoroacetate and a chiral pyridinooxazoline ligand, in moderate to excellent yields and high enantioselectivity (13CEJ74).



Scheme 79



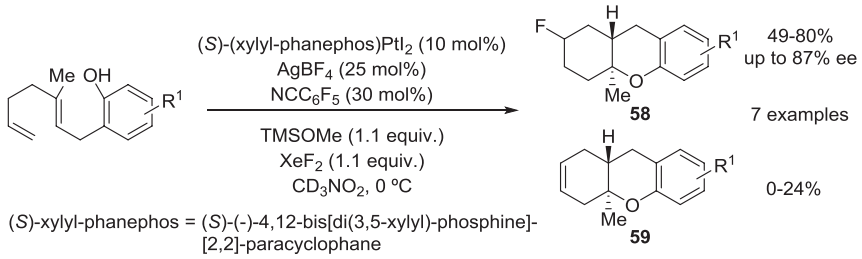
Scheme 80

Cyclopentene-fused chromanones are obtained through a direct oxidative coupling of salicylaldehydes with diazabicyclic olefins in the presence of rhodium(II)/copper(II) catalyst system, in moderate to good yields (Scheme 79) (13CC7349).

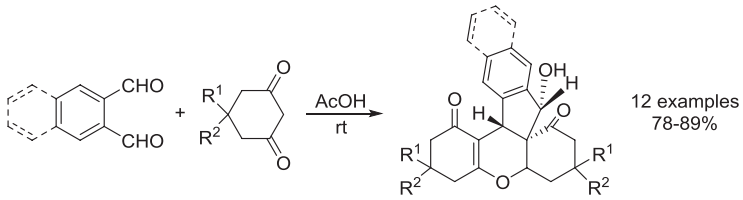
6.4.2.7 Xanthenes and Xanthones

A facile one-pot synthesis of 4-tosylaminoxanthenes involves an addition–cyclization cascade reaction of salicyl *N*-tosylimines with arenes, formed by treatment 2-(trimethylsilylaryl) triflates with CsF (13SL640). Tetrasubstituted alkenes containing a xanthene motif are prepared through the palladium(II)-catalyzed domino process, involving Sonogashira, carbopalladation, and C–H functionalization reactions, of aryl iodides and alkynes (13AGE3668). A similar protocol uses *N*-benzyl-*N*-(2-bromobenzyl)-*N*-[1-aryl-3-(2-phenoxyphenyl)]propargylamines (13OL382). The one-pot three-component reaction of embelin **55**, benzaldehydes, and cyclic enaminones are substrate controlled: an enaminone containing a primary amine substituent affords acridine derivatives **56** while that bearing a disubstituted amine provides xanthene derivatives **57**. In addition, the reaction with aliphatic aldehydes only occurs in the case of primary amine enaminone (Scheme 80) (13JOC7977).

A microwave-assisted thermolysis of methyl 4-(2-allylphenoxy)penta-2,4-dienoates in toluene leads to a few dihydroxanthenes (13CEJ6566). A platinum(II) complex [(*S*)-(xylyl-phanephos)PtI_2] in combination with



Scheme 81

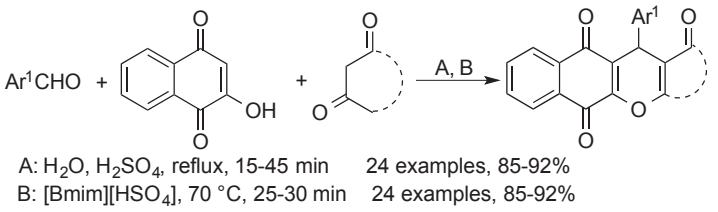


Scheme 82

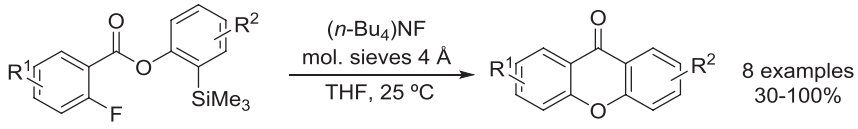
XeF_2 catalyzes the enantioselective cyclization and C3-fluorination of various phenol terminated dienes to prepare 3-fluorotetrahydro-1*H*-xanthenes **58** along with a small amount of the β-H eliminated product **59** (Scheme 81) (13JA628).

Under microwave irradiation, the condensation of *N*-phenyl-*N*-arylmethylidenamine oxides with dimedone occurs in the presence of polyethylene glycol under solvent-free conditions to afford a range of 1,8-dioxo-octahydroxanthenes (13SC2739). An efficient one-pot synthesis of xanthene-type compounds involves a Michael reaction of dimedone with α,α′-bis(substituted-benzylidene)cycloalkanones using a catalytic amount of *p*-TsOH (13SC1188). Further derivatives are obtained from the one-pot three-component reactions of salicylaldehydes, barbituric acid, and isocyanides (13T8511), of dimedones, barbituric acids, and isatins in gluconic acid aqueous solution (13T2056), and of salicylaldehydes, active methylene compounds, and carbon-based nucleophiles catalyzed by ZnO nanoparticles in water (13JOC6170). Other derivatives are prepared from a pseudo four-component reaction of salicylaldehydes, naphthols, and two molecules of malononitrile, under solvent-free and catalyst-free conditions (13TL1963).

The multicomponent reaction of *o*-dialdehydes with two molecules of cyclic 1,3-dicarbonyls in acetic acid involves a stereoselective [4 + 1]/[3 + 2 + 1] biscyclizations to give indeno-fused xanthenes (Scheme 82) (13TL6341).



Scheme 83



Scheme 84

A range of 12-aryltetrahydrobenzoxanthene-11-ones were synthesized from aliphatic and aromatic aldehydes, β-naphthol, and dimedone promoted by thiamine hydrochloride in aqueous micellar medium (13TL6732) and from benzaldehydes, 2-hydroxy-1,4-naphthoquinone, and cyclic 1,3-dicarbonyl compounds using a catalytic amount of sulfuric acid in water or in the presence of the acidic ionic liquid [Bmim][HSO_4] (Scheme 83) (13SC2147).

The stereocontrolled synthesis of the natural trichodermatide A, an oxygenated pentacyclic structure, is accomplished in a short sequence starting with L-tartaric acid. The strategy involves a diastereoselective intramolecular ketal formation to afford the pentacyclic core and a chemo-, regio-, and stereoselective cobalt(II)-promoted hydration of an enol ether for a specific functionalization of this core (13AGE3646). Studies in the total synthesis of natural compounds containing a xanthone motif include (−)-simaomicin α (13AGE10796), xanthofulvin, and vinaxanthone (13AGE3421).

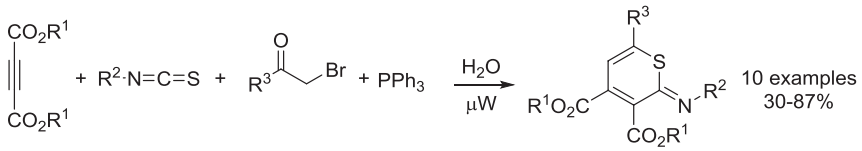
A cross dehydrogenative coupling reaction of *o*-formyl biaryl ethers produces a range of xanthones through a base-mediated homolytic aromatic substitution (13OL928). Similar derivatives are obtained when 2-(trimethylsilyl)aryl 2-fluorobenzoates are treated with tetrabutylammonium fluoride and undergo a Fries-type rearrangement followed by an intramolecular nucleophilic aromatic substitution (Scheme 84) (13SL2575). Several xanthones were also formed when *o*-halobenzoic acids reacted with benzyne precursors [2-(trimethylsilyl)aryl triflates] in the presence of CsF (13T2789). Intramolecular dehydration of 2,2′-dihydroxybenzophenones using a catalytic amount of K_2CO_3, in water at 150 °C, affords (di)benzoxanthones in good to excellent yields (13T1694).

6.4.3 HETEROCYCLES CONTAINING ONE SULFUR ATOM

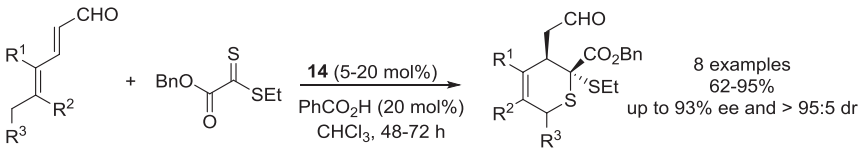
6.4.3.1 Thiopyrans and Analogues

One-pot multicomponent reaction of dialkyl acetylenedicarboxylates, aryl-isothiocyanates, and α-bromoketones in the presence of triphenylphosphine in water produces a series of 2-imino substituted 2*H*-thiopyrans (Scheme 85) (13SL2137).

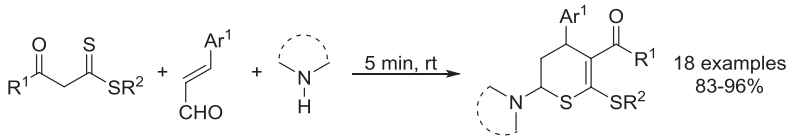
Chiral 3,4-dihydro-2*H*-thiopyrans are accessible through the formal thio [3 + 3] cycloaddition reactions of binucleophilic bisketone thioethers with enals, catalyzed by a diphenyl pyrrolidine silyl ether (13OL5570). A similar organocatalyst **14** is used in the asymmetric thio-Diels–Alder reaction of dienals with dithioesters to afford 3,6-dihydro-2*H*-thiopyrans in good yields and excellent diastereo- and enantioselectivities (Scheme 86) (13JA5200). Other derivatives are obtained from the hDA reaction of trifluoromethyl- and polyfluoroalkylthioamides with various electron-rich 1,3-dienes (cyclic or acyclic, symmetrical or non-symmetrical) (13T1322). Under catalyst-free and solvent-free conditions, the one-pot three-component reaction of β-oxodithioesters, α,β-unsaturated aldehydes, and cyclic aliphatic secondary amines provides 4-aryl-5,6-dihydro-4*H*-thiopyrans in excellent yields (Scheme 87) (13T8013).



Scheme 85



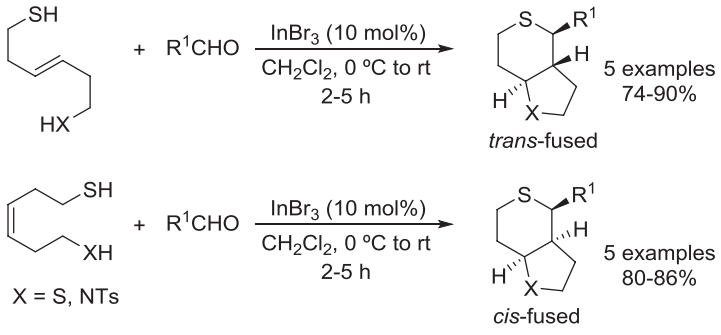
Scheme 86



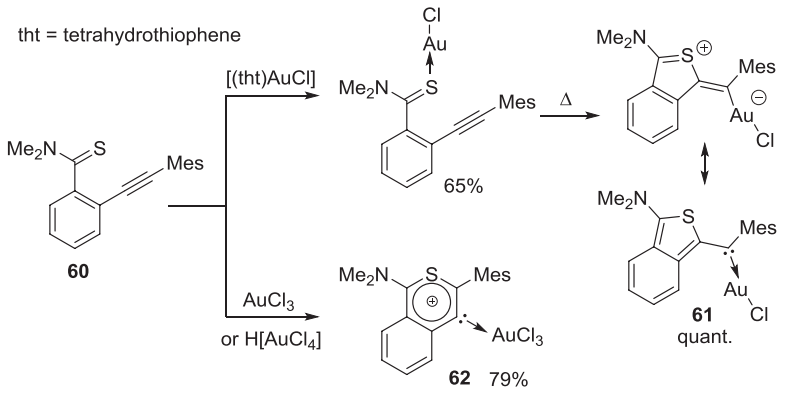
Scheme 87

A stereoselective Michael addition of nitromethane to (*Z*,*Z*)-2,2′-thiobis(1,3-diarylprop-2-en-1-ones) features in the asymmetric synthesis of 4-nitrotetrahydro-2*H*-thiopyrans. Under thermal heating the reaction leads to a diastereomeric mixture of products, while under microwave irradiation only one isomer is obtained (13SC1964). Several tetrahydro-2*H*-thiopyran derivatives are obtained by a thia-Prins biscyclization of homoallylic mercaptans with various aldehydes. This reaction is stereoselective and affords *trans*- and *cis*-fused thia-bicycles from the corresponding (*E*)- and (*Z*)-homoallylic mercaptans (Scheme 88) (13JOC6303). The photolysis of polyethylene glycol (PEG)–phenacyl sulfides affords quantitatively PEG–thioaldehydes, which can be trapped by different dienes in hDA reactions to give the corresponding 2*H*-thiopyran derivatives (13CC633).

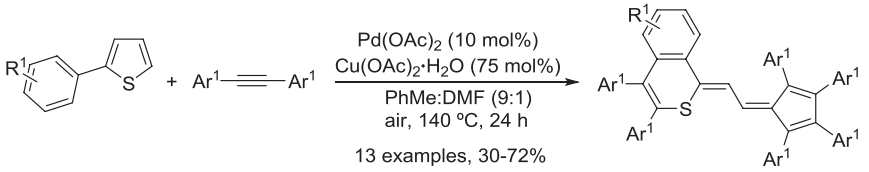
Synthesis of a range of 2*H*-thiochromenes is accomplished when 2,2′-dithiodibenzaldehyde reacts with electron-deficient alkenes in the presence of DBU or triphenylphosphine, but when used together as a dual-catalyst system, the overall yields are improved and the reaction time consistently reduced (13SC1837). The formation of other 2*H*-thiochromenes by a three-component reaction of *o*-substituted (halo and nitro groups) benzaldehydes, carbon disulfide, and electron-deficient vinyl compounds is efficiently catalyzed by DABCO (13EJO4816). The regioselectivity of the gold-catalyzed cyclization of the *o*-alkynyl benzothioamide **60** is controlled by the oxidation state of the metal: an Au(I) promoter led to an unusual 5-*exo*-*dig* cyclization to afford a rare example of an acyclic (aryl)(heteroaryl) carbene gold complex **61**; an Au(III) catalyst induced a 6-*endo*-*dig* ring closure for the preparation of a cyclic 6-membered mesoionic carbene gold complex **62** (Scheme 89) (13AGE758).



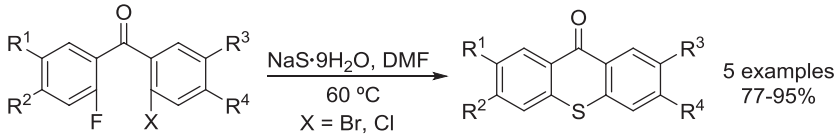
Scheme 88



Scheme 89



Scheme 90

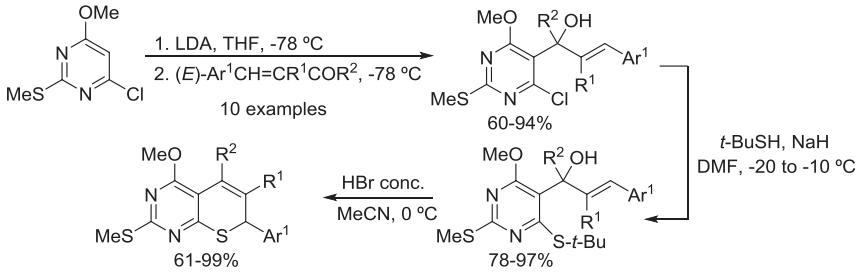


Scheme 91

Palladium(II)-promoted reaction of 2-arylthiophenes with alkynes gives access to 1*H*-isothiochromenes in moderate to good yields, via C–H and C–S bond activations (Scheme 90) (13OL282).

Transition metal-free approaches for the preparation of thiochromone derivatives are achieved by the condensation of 2′-haloacetophenones with dithioesters in the presence of sodium hydride in DMF (13TL6533) and of 2-fluoroaroyl chlorides and indole-2-thiones in the presence of potassium carbonate in DMF at 60 °C (13TL5018). A series of thioxanthones are obtained through the reaction of (2-fluorophenyl)(2-halophenyl)methanones with $Na_2S·9H_2O$ in DMF (Scheme 91) (13H2577).

Several pyrimidine-fused 2*H*-thiopyrans are accessible in a three-step sequence, reacting 4-chloro-6-methoxy-2-(methylsulfanyl)pyrimidine with



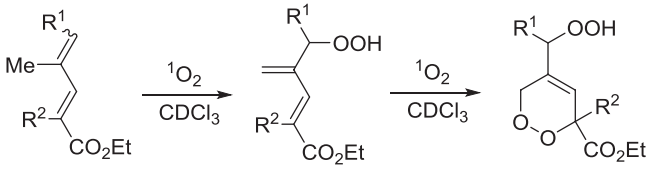
Scheme 92

α,β-unsaturated aldehydes or ketones followed by treatment with *t*-BuSH and cyclization with HBr (Scheme 92) (13H885). Pyridine-fused 2,3-dihydro-4*H*-thiopyran-4-ones are also prepared in a three-step sequence starting with the condensation of 2-chloropyridine with α,β-unsaturated aldehydes, followed by oxidation of the formed compound with MnO_2 and cyclization with NaSH (13HCA624). Using 3-aryl-2-arylimino-5-benzylidenethiazolidine-4-thiones as heterodienes, the inverse-electron-demand hDA reaction with norbornene as dienophile at room temperature affords complex hetero-fused thiopyrans (13T1337).

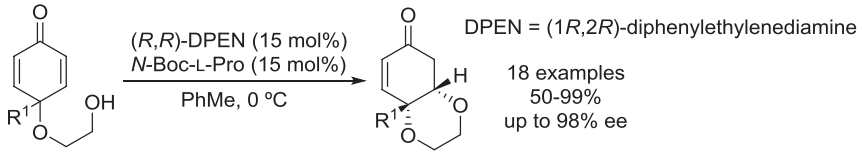
6.4.4 HETEROCYCLES CONTAINING TWO OR MORE OXYGEN ATOMS

6.4.4.1 Dioxanes

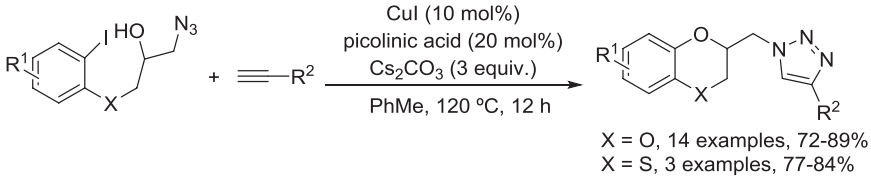
Allylic hydroperoxides **63** prepared from singlet oxygen photooxygenation of 4-methylhexa-2,4-dienoates and subsequent $^1O_2$ [4 + 2] cycloaddition delivers a diastereomeric mixture of 1,2-dioxanes **64**, in a one-pot process (Scheme 93) (13OL2073). Other trisequential singlet oxygen photooxygenations of 4,5-dimethylenecyclohex-1-ene afford a couple of tricyclic hydroperoxides, intermediates in the synthesis of isomeric carbasugars (13OL4350).



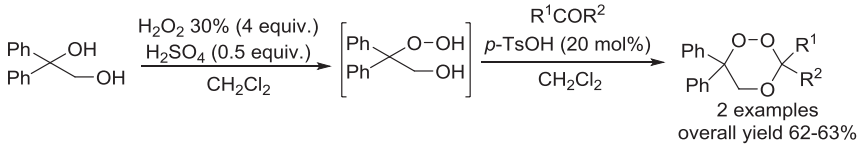
Scheme 93



Scheme 94



Scheme 95



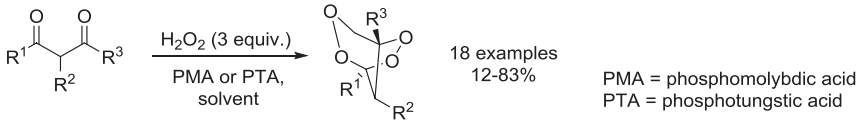
Scheme 96

A range of 1,4-dioxanes are enantioselectively achieved through an intramolecular iminium-based activation oxa-Michael reaction of cyclohexadienones (Scheme 94) (13AGE1743).

Using a copper(I) dual catalytic system, a one-pot click reaction of azides with terminal acetylenes and an intramolecular C–O bond formation (aryl iodide-secondary alcohol) provides a range of 2,3-dihydro-1,4-benzodioxines, in good yields. This strategy is extended to the synthesis of dihydrobenzoxathiines (Scheme 95) (13OBC7350). Vinyl selenones undergo a one-pot Michael addition–cyclization reactions with benzene-1,2-diols and benzene-1,2-dithiols for the synthesis of 2,3-dihydro-1,4-benzodioxins and 2,3-dihydro-1,4-benzodithiins, respectively (13T481). Other 2,3-dihydro-1,4-benzodioxins are obtained from an inverse-electron-demand hDA reaction of *o*-quinones with enamines (13TL6298).

6.4.4.2 Trioxanes and Tetraoxanes

A tertiary carbinol undergoes a H_2O_2-mediated reaction to afford β-hydroxyhydroperoxide and subsequent acid-catalyzed condensation with ketones provides 1,2,4-trioxanes (Scheme 96) (13SL173).



Scheme 97

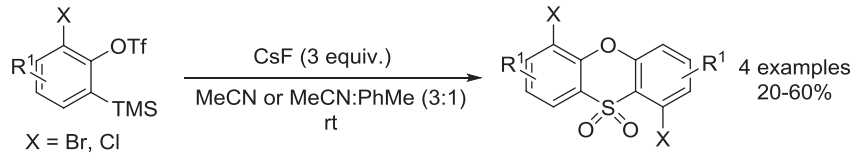
Several bridged 1,2,4,5-tetraoxanes are efficiently achieved through the addition of hydrogen peroxide to β-diketones catalyzed by phosphomolybdic acid (PMA) or phosphotungstic acid (PTA) (Scheme 97) (13OBC2613).

6.4.5 HETEROCYCLES CONTAINING BOTH OXYGEN AND SULFUR IN THE SAME RING

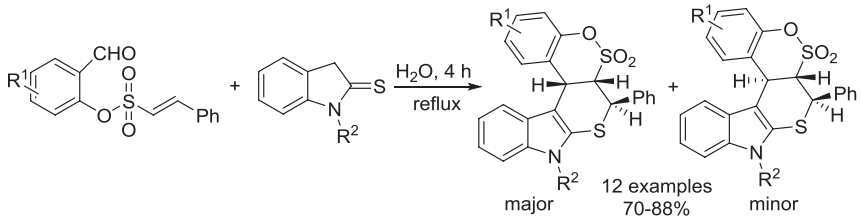
6.4.5.1 Oxathianes

The one-pot reaction of *o*-dihalogenated heterocycles with $NaS•9H_2O$ followed by nucleophilic substitution with 1-aryl-2-bromoalkan-1-ones and cyclization by treatment with NaH affords heterocyclic-fused 1,4-oxathiines in good yields (13HCA1452).

The mechanism and stereoselectivity of [2 + 2 + 2] multimolecular cycloaddition reactions of ketenes (2 molecules) and carbon disulfide (1 molecule) catalyzed by NHCs is investigated by DFT methods. The calculations indicate a four-step mechanism and an (*R*)- and (*E*)-configurations for the chiral carbon center and for the vinylic system, respectively (13JOC11849). The reaction of 1,2-dihaloarenes or 1-halo-2-nitroarenes with 2-sulfanylphenol using potassium or cesium carbonate as bases provides phenoxathiins in good to excellent yields (13S966). The synthesis of a few phenoxathiin dioxides are achieved by the treatment of 2-(trimethylsilyl)aryl triflates, benzyne precursors, with CsF at room temperature. This transformation requires an *ortho*-halogen substrate for both thia-Fries rearrangement and aryne generation followed by cyclization (Scheme 98) (13CC7602).



Scheme 98



Scheme 99

A range of pentacyclic thiopyran indole-annulated benzo-δ-sultone derivatives are obtained through a domino Knoevenagel-hDA reaction of 2-formylphenyl (*E*)-2-phenylethenyl sulfonates with indoline-2-thiones in water (Scheme 99) (13TL2685).

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