CHAPTER 6.4

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

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6.4.1 INTRODUCTION

The synthesis of *O*- and *S*-6-membered heterocycles was actively pursued in 2015. Special emphasis is given to the synthesis of natural oxygen derivatives.

The chemistry of α-oxoesters in the synthesis of *O*-, *S*-, and *S*,*O*-heterocycles (15CR151) and of copper-catalyzed C–H functionalization reactions to prepare *O*-heterocycles has been discussed (15CR1622). Reviews on natural occurrence and biological properties of xanthone dimers (15NPR6); natural occurrence, synthesis, and biological activities of dihydrocoumarins (15OPP1); synthesis and structure–activity relationship of natural and synthetic peloruside analogs (15CC4750) and of coumarin derivatives (15EJM(101)476, 15NPR1472); and synthesis and bioactivities of 1,4-benzodioxane lignans (15NPR1369) and of chroman-4-ones (15EJM(93)539) have appeared. The synthesis and reactivity of 6-(trifluoromethyl)-2*H*-pyran-2-ones (15JFC36) and of furochromen-4-ones (15EJM(90)633); synthesis and physical properties of π-expanded coumarins (15JMCC1421); and isolation, biosynthesis, synthesis, and biological activities of naphthopyranones (15NPR578) were also reviewed.

An overview on unconventional terpene cyclases and their impact on biomimetic biosynthesis of terpenoids bearing pyran and chroman moieties (15AGE2604) and the chemical features, synthesis, and biological properties of mangiferin and derivatives have appeared (15MRMC582). The background and implications of natural antimalarial artemisinin in traditional Chinese medicine (15NPR1617) as well as its synthesis, biosynthesis and large-scale production (15NPR359) have been highlighted.

Multicomponent reactions as green protocols for the synthesis of polysubstituted pyrans and thiopyrans (15MD625) and the synthesis of several

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oxygen heterocycles through insertion of arynes into the C═O bond of aldehydes and formamides (15MOL12558) and through Baker–Venkataraman O→C acyl migration reactions (15S141) were disclosed.

Enantioselective organocatalyzed synthesis of 2-amino-4*H*-chromene-3-carbonitriles (15SYM1519), Achmatowicz rearrangement–oxidative ring expansion of furfuryl alcohols to prepare 6-hydroxy-2*H*-pyran-3(6*H*)-ones (15S3435), and stereoselective synthesis of 3-hydroxy-3-methylglutaryl–coenzyme A reductase inhibitors possessing chiral 4-hydroxytetrahydropyran-2-one moieties (15T8487) were surveyed. The synthesis of various oxygen six-membered derivatives is also achieved through iron-catalyzed reactions (15CR3170) and through ceric ammonium nitrate-catalyzed multicomponent reactions (15SC2399).

The literature on the total synthesis of natural compounds, involving several types of reactions to build *O*-6-membered heterocycles, was very rich in 2015. One can highlight the synthesis of various pyran derivatives, such as aspergillide A (15TA296), 11-*epi*-azadirachtin I (15OL2338), bryostatins (15TL3975), (−)-centrolobine (15JOC3315, 15TL4916), decytospolides A and B (15TA296), (2*R*,4*S*,6*R*)-2-(4-hydroxyphenethyl)-6-(4-hydroxyphenyl) tetrahydro-2*H*-pyran-4-ol (15TL1360), karlotoxin 2 (15TL4299), mandelalide A (15CEJ10416), murrayamines-O and -P (15CEJ8347), nanaomycin D (15T7137), and (+)-sorangicin A (15TL5930). Of chroman-type compounds, one can refer to (+)-machaeriol B, (+)-machaeriol D, (+)-Δ^8-THC (15AGE8547), mahanine, murrayamine D, and 7-hydroxymurrayazolinine (15OL2298); siccanochromene F, metachromin U, and siccanin (15EJO3266); and (−)-spirooliganones A and B (15OL3118), while on isochromans, deoxyactinorhodin, and deoxy-γ-actinorhodin (15CEJ4842), hemiactinorhodin and hemi-γ-actinorhodin (15EJO4931) can be included. Pyranone-type compounds (+)-altholactone and (−)-goniofupyrone (15OBC10487), crassalactone A (15HCA509), (+)-etharvendiol (15TL1344), (6*S*,1′*S*,2′*S*)-hydroxypestalotin (15TL1115, 15TL4711), ieodomycin B (15SC1321), (+) and (−)-nor-mevalonic lactones (15T7531), pectinolides A, C, D, and E (15S330), (+)-Prelog–Djerassi lactone (15JOC204), 5′-*epi*-synargentolide B (15T5472), and tarchonanthuslactone (15SL2019) were also synthesized. The synthesis of some natural compounds with a complex structure (irciniastatin A and B) includes the construction of tetrahydropyran and isocoumarin moieties (15JOC12333).

The total synthesis of polyphenolic compounds homoisoflavonoids (15EJO4964), the aglycone of IB-00208 (15OL114), aminocoumacin C (15T1992), arnottin I (15JOC3339), lamellarin D trimethyl ether and

lamellarin H (15JOC11605), proanthocyanidin A1 and A2 (15OL2306), and secalonic acid E (15CEJ16807) were accomplished.

Ring-closure metathesis (RCM) was used as the key reaction in the synthesis of several types of natural compounds, namely the 2*H*-pyrans (−)-dysiherbaine (15OL3972), (±)-centrolobine (15SL2583) and (−)-brevisamide (15TL1099), the 2*H*-pyran-2-ones hemicalide (15OL2446), (−)-callystatin A (15TL4371), synargentolide B (15TA928), (+)-phomopsolide B (15TL4112), and the 2*H*-chromene brazilin (15JOC2001). This reaction was also used in the preparation of synthetic pyran derivatives (15SC1768). Other specific transformations were also applied to the synthesis of natural products, namely the Prins cyclization in the asymmetric synthesis of ossamycin (15TL365) and in the total synthesis of (−)-exiguolide (15OL4706) and the intramolecular oxa-Michael reaction in the stereoselective total synthesis of decytospolides A and B (15HCA267), (+)-decarestrictine L (15JOC204), and curvulone B (15SL751).

Several fascinating [7]- and [11]helicene-type molecules were obtained through rhodium(I)-catalyzed intramolecular [2 + 2 + 2] cycloaddition reactions of 2-naphthol-linked triynes and hexaynes, respectively. Thus, the intermolecular [2 + 2 + 2] cycloaddition reactions of tetraynes with diynes affords [7]- and [9]helicene-type molecules (15BCSJ375).

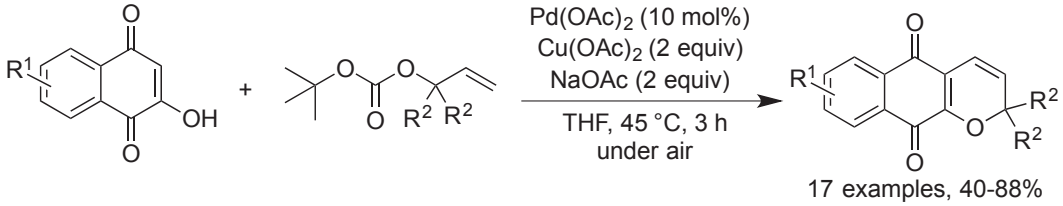
The synthesis of compounds with important photophysical properties was undertaken. Various indeno[1,2-*c*]chromenes were applied as dye-sensitized solar cells (15CEJ4065), while dilactone-bridged terphenyls with crankshaft architectures (15T283) and 5- and 6-carboxyfluoresceins (15EJO7301) are potential fluorescent probes.

Herein, we provide a personal overview of the most important developments in the synthesis of *O*- and *S*-6-membered heterocycles.

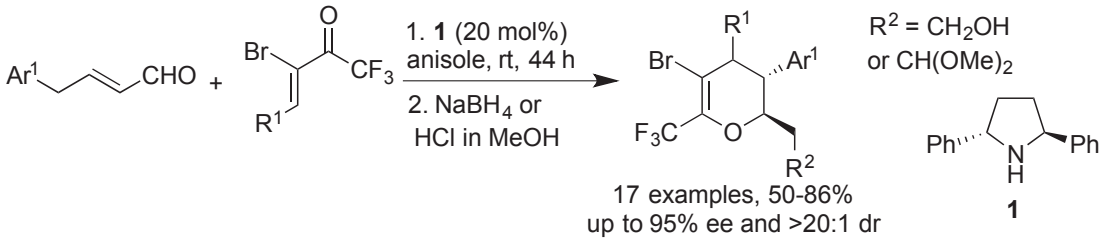
6.4.2 HETEROCYCLES CONTAINING ONE OXYGEN ATOM

6.4.2.1 Pyrans

A wide range of 3-bromo/iodo-2*H*-pyrans was synthesized through an *N*-bromo/iodosuccinimide-induced 1,4-diazabicyclo[2.2.2]octane (DABCO)-catalyzed electrophilic cyclization reaction of propargyl alcohols with dialkylacetylene dicarboxylates, in moderate-to-excellent yields (15TL401). Palladium(II)-mediated cascade scalable reaction of 2-hydroxy-1,4-naphthoquinones with *tert*-butyl-(1,1-disubstituted-prop-2-en-1-yl) carbonates carried out in the presence of $Cu(OAc)_2$, NaOAc in tetrahydrofuran (THF) at 45°C, affords naphthoquinone-fused 2*H*-pyrans (Scheme 1) (15OL3410).



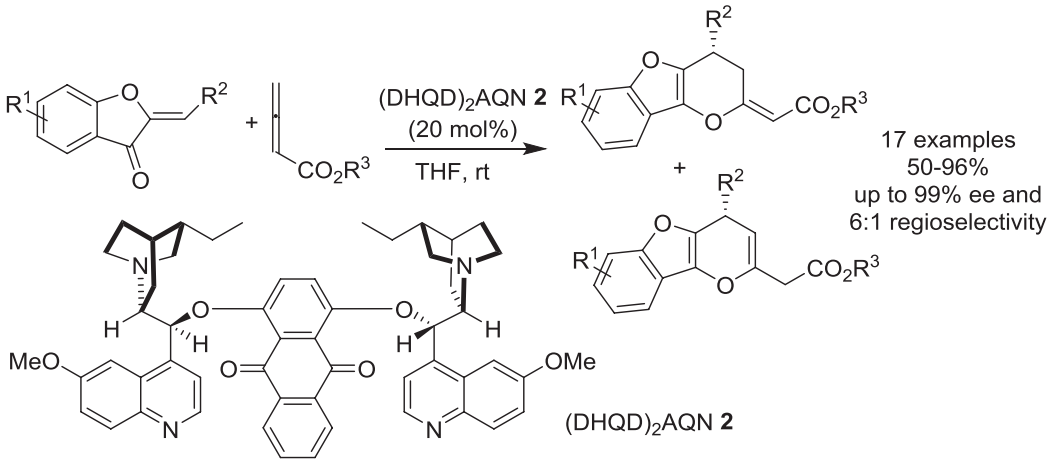
Scheme 1



Scheme 2

An L-threonine-derived bifunctional phosphine catalyzes [4 + 2] annulation of allenones with β,γ-unsaturated α-ketoesters to provide 3,4-dihydro-2*H*-pyrans in high yields and with excellent enantioselectivity (15JA54). Further 2,4,6-trisubstituted derivatives arise from zinc iodide–catalyzed diastereoselective [4 + 2] inverse electron demand hetero-Diels–Alder (IED hDA) reaction of β,γ-unsaturated α-keto thioesters with olefins (15JOC2972) and three-component radical cyclization of an aldehyde with two alkenes catalyzed by $FeCl_2$ in the presence of di-*tert*-butyl peroxide (15OL4324). DABCO-catalyzed [4 + 2] cycloaddition reactions of allenoates with enynals or enynones gives access to polysubstituted 3,4-dihydro-2*H*-pyrans in good yields (15JOC4084). Highly functionalized 6-(trifluoromethyl)-3,4-dihydro-2*H*-pyrans are obtained from the IED hDA reaction of α,β-unsaturated aldehydes with trifluoromethyl α-bromoenones catalyzed by C_2-symmetric 2,5-diphenylpyrrolidine **1** (Scheme 2) (15CC13666).

The synthesis of cycloalkanone-fused 3,4-dihydro-2*H*-pyrans occurs through organocatalytic Michael addition of cycloalkane-1,3-diones with α,β-unsaturated aldehydes in dichloromethane at 0°C (15EJO5709). A mixture of chiral benzofuran-fused 3,4-dihydro-2*H*-pyrans and 4*H*-pyrans were enantioselectively obtained through [4 + 2] cycloaddition reaction of allenoates with 2-olefinic benzofuran-3-ones catalyzed by the tertiary-amine-derived catalyst **2** (Scheme 3) (15OL338). More derivatives were obtained from [4 + 2] cycloaddition reaction of allenoates with 3-olefinic benzofuran-2-ones: using normal β-isocupreidine (β-ICD) catalyst the *R*-enantiomer results as major product; replacing the phenolic proton of the



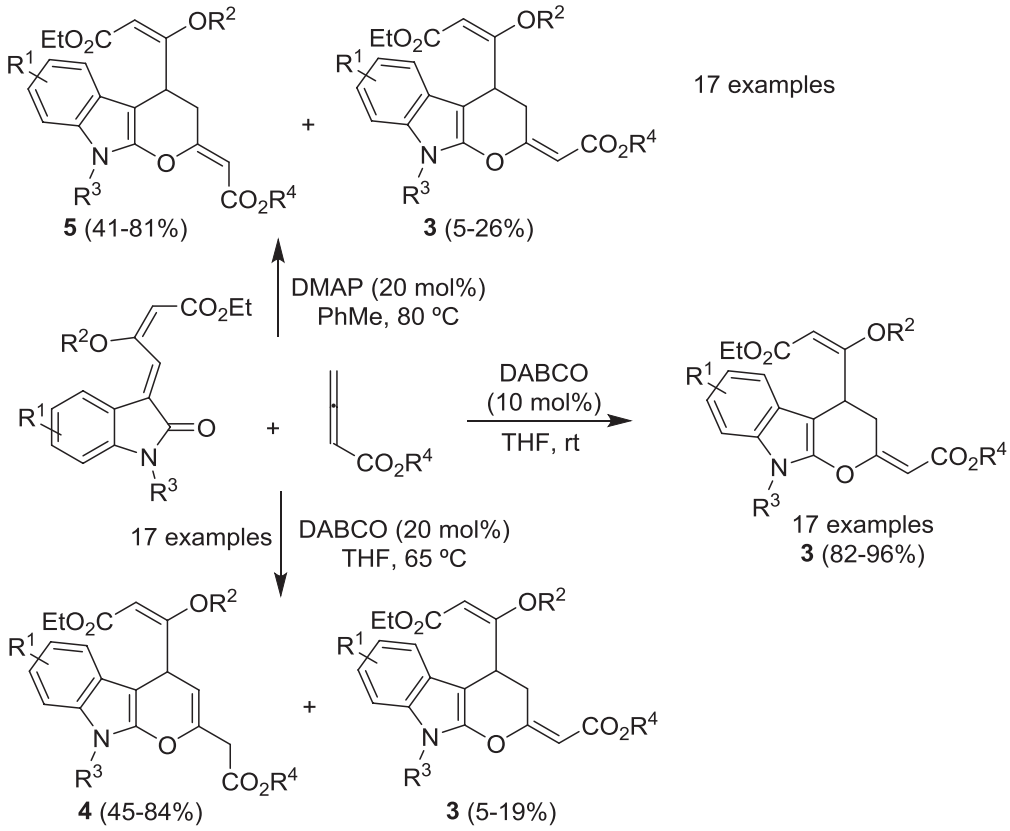
Scheme 3

catalyst by a methyl group, a chirality inversion of the cycloadduct is observed and the *S*-enantiomer appears as major product (15CEJ10443).

The β-ICD catalyst was also used in the [4 + 2] annulation reaction of allenoates with 3-olefinic oxindoles to afford indoline-fused 3,4-dihydro-2*H*-pyrans bearing an (*E*)-exocyclic double bond, with good enantioselectivity (15JOC5279). [4 + 2] Annulation reactions of isatin-derived electron-deficient alkenes with allenoates are conditions-controlled: DABCO in THF at room temperature gives indoline-fused 3,4-dihydro-2*H*-pyrans with an (*E*)-exocyclic double bond **3**, while at 65°C indoline-fused 4*H*-pyrans **4** are formed as major products; using DMAP in toluene at 80°C gives mainly indoline-fused 3,4-dihydro-2*H*-pyrans with a (*Z*)-exocyclic double bond **5** (Scheme 4) (15T7706).

Triphenylphosphine catalyzes *β′*-addition/[4 + 4] cycloaddition domino reactions of *β′*-acetoxy allenoates with 2-acyl-3-methylacrylonitriles in toluene at room temperature giving access to 2-oxabicyclo[3.3.1]nonanes (structure bearing a 3,4-dihydro-2*H*-pyran) (15JA6400). Further oxabicyclic and oxatricyclic compounds arise from enynols via gold(I)-catalyzed oxonium/Prins-type cyclization (15CC12435). Three-component reactions of isoquinolinium salts, acetone, and cyclic 1,3-diketones carried out under refluxing triethylamine for 24 h afforded a series of oxazatricyclic 3,4-dihydro-2*H*-pyran derivatives (15JHC1513).

Low loading of trityl tetrafluoroborate as catalyst was applied to the synthesis of various 3,6-dihydro-2*H*-pyrans via hDA reaction of unactivated aromatic and aliphatic aldehydes with simple unactivated dienes in dichloromethane at room temperature (15EJO6610). *trans*-2,6-Disubstituted-5-methyl-3,6-dihydro-2*H*-pyrans were obtained through zinc bromide-catalyzed tandem reaction of δ-hydroxy-α-methyl-α,β-unsaturated aldehydes

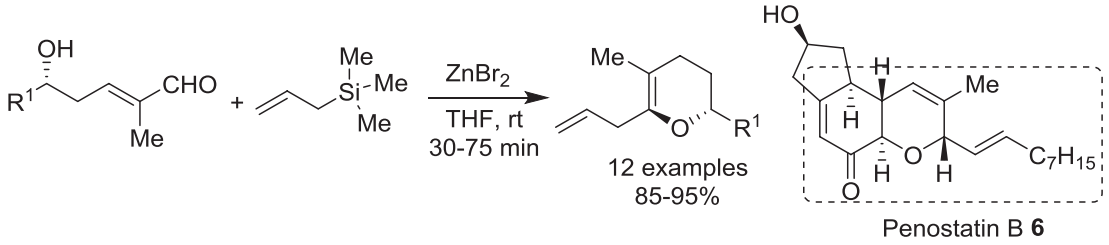


Scheme 4

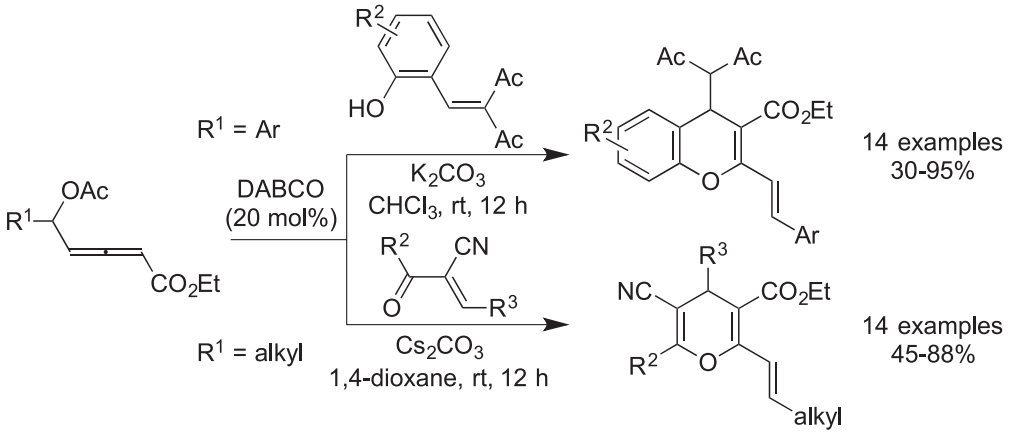
with allyltrimethylsilane (Scheme 5). This diastereoselective strategy was used to build the bicyclic core of penostatin B **6** (15JOC1365).

Palladium(II)-catalyzed domino reaction of 5-cinnamyloxypent-3-yn-2-ols with iodobenzenes leads to 5-aryl-3-benzylidene-4-(1-hydroxyethyl)-3,6-dihydro-2*H*-pyrans, in moderate-to-good yields (15EJO6278). Chemo-, regio-, and diastereoselective calcium triflimide–promoted formal intermolecular [2 + 2 + 2] cycloaddition reactions of a couple of enynols with aliphatic and aromatic aldehydes provided various cyclopentane-fused 3,6-dihydro-2*H*-pyrans (15CEJ6371).

Highly functionalized monofluorinated 4*H*-pyrans result from the cascade reaction of terminal or internal trifluoromethylated alkenes with 1,3-dicarbonyl compounds mediated by potassium carbonate and molecular sieves in DMF at room temperature (15CC8326). A wide range of 2-amino-4-aryl-4*H*-pyrans were attained through multicomponent reactions of aromatic aldehydes and active methylene compounds with acetoacetanilide derivatives in ethanol using a catalytic amount of triethylamine (15CPB1055), with ethyl acetoacetate in the presence of aqueous sodium hydroxide (15JHC1226) or sodium ethoxide in ethanol under ultrasound irradiation (15AJC273), and with methyl acetoacetate or ethyl benzoylacetate promoted by dibutylamine, in solvent-free conditions (15TL717).



Scheme 5

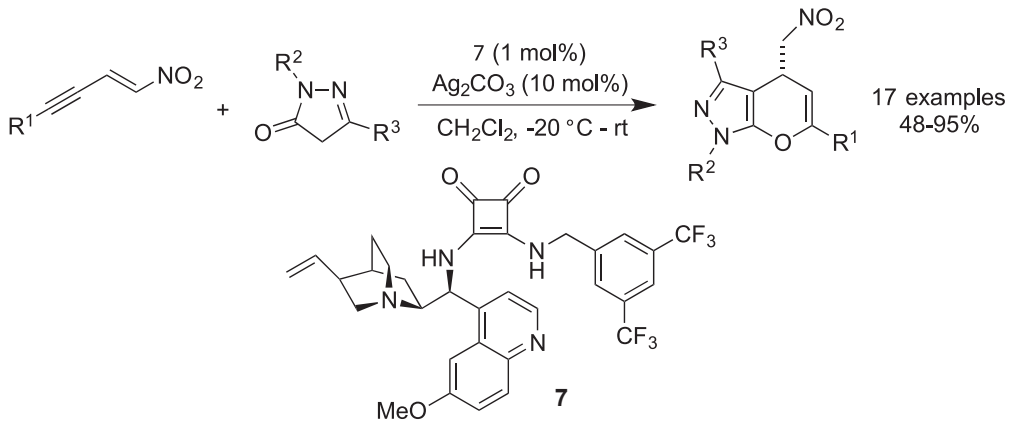


Scheme 6

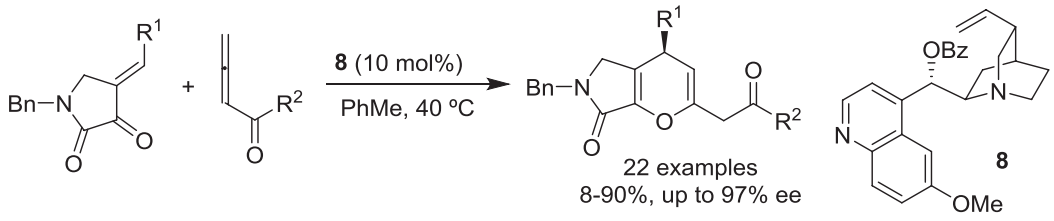
DABCO-mediated [4 + 2] annulation reactions of δ-acetoxy allenoates with 2-acyl-3-alkylacrylonitriles using cesium carbonate in 1,4-dioxane affords polysubstituted 4*H*-pyrans while with 3-(2-hydroxybenzylidene) pentane-2,4-diones in the presence of potassium carbonate in chloroform, 4*H*-chromenes were produced (Scheme 6) (15OL1106).

A cationic cyclopentadienyl (Cp) ruthenium(II) complex is involved in the Trost's cyclization of non-2-en-7-yn-1-ones to give cyclopentane-fused 4*H*-pyrans. Similarly, using esters or amides leads to the corresponding 3,4-dihydro-2*H*-pyran-2-ones(15JA12478). One-pot solvent-free calcium triflate and tetrabutyl hexafluoroammonium phosphate-mediated cascade reactions of chalcones with 4-hydroxycoumarin or cyclic 1,3-diketones provides, respectively, coumarin-fused or cyclohexanone-fused 4*H*-pyrans in high yields (15TL1649). Under dual catalysis of silver carbonate and cinchona-derived squaramide **7**, a series of pyrazole-fused 4*H*-pyrans result from the one-pot Michael addition of alkyne-tethered nitroolefins with pyrazolinones followed by a 6-*endo*-*dig* cyclization reaction (Scheme 7) (15CC2266).

High yields of pyrrolin-2-one-fused 4*H*-pyrans were achieved through asymmetric [4 + 2] cyclization reactions of allene ketones with 4-arylidene-2,3-dioxopyrrolidine derivatives in toluene at 40°C, promoted by the cinchona alkaloid–derived amine catalyst **8** (Scheme 8) (15JOC7288). A



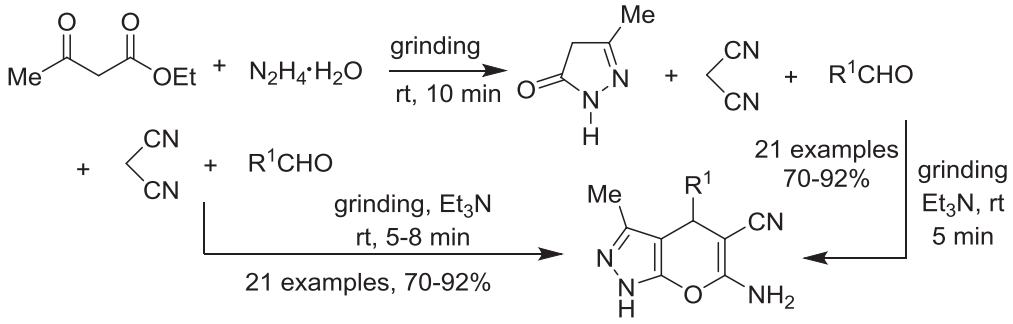
Scheme 7



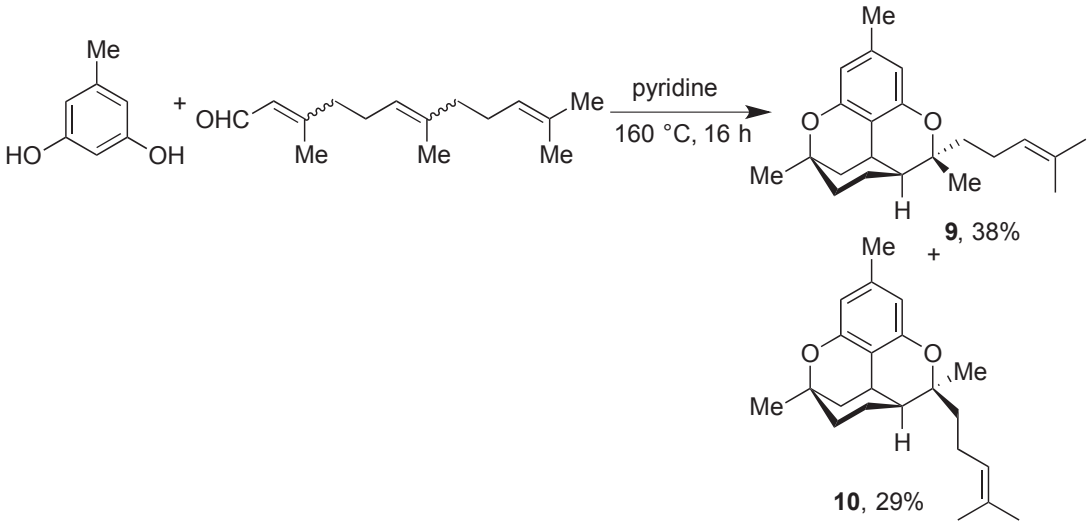
Scheme 8

bifunctional chiral bis-squaramide catalyzes the conjugate addition of 2-hydroxy-1,4-naphthoquinone to 2-enoylpyridines providing naphthoquinone-fused 4*H*-pyrans (15OBC5243). A wide variety of pyrimidine-fused 4*H*-pyrans results from copper(II)-promoted one-pot three-component tandem reaction of barbituric acid, aldehydes, and terminal alkynes carried out in the presence of potassium *t*-butoxide in 1,2-dichloroethane (DCE) (15OBC4668). Three-component reactions of benzaldehydes with malononitrile and 4-hydroxycoumarin mediated by 1,8-diazabicycloundec-7-ene (DBU) or with 4-hydroxybenzo[*h*]coumarin promoted by DABCO, give access, respectively, to coumarin-fused (15SC2311) or benzo[*h*]coumarin-fused (15JHC97) 2-amino-4-aryl-4*H*-pyran-3-carbonitriles. The synthesis of quinoline-fused 2-amino-4-aryl-4*H*-pyran-3-carbonitriles/carboxylates occurs via microwave-assisted three-component reactions of 8-hydroxyquinoline with aromatic aldehydes and malononitrile/ethyl cyanoacetate mediated by indium trichloride in ethanol (15JHC926).

A 3-min vigorous stirring of the emulsion of salicylaldehydes, malononitrile, and 4-hydroxy-1-methylquinolin-2(1*H*)-one carried out in the presence of a catalytic amount of sodium acetate in ethanol forms quinolinone-fused 2-amino-4-aryl-4*H*-pyran-3-carbonitriles in excellent yields (15HCA1104). Grinding methodologies were developed for the synthesis of pyrazole-fused 2-amino-4-aryl/alkyl-4*H*-pyran-3-carbonitriles.These solvent-free approaches may occur in two steps, reacting ethyl acetoacetate with hydrazine, and then



Scheme 9



Scheme 10

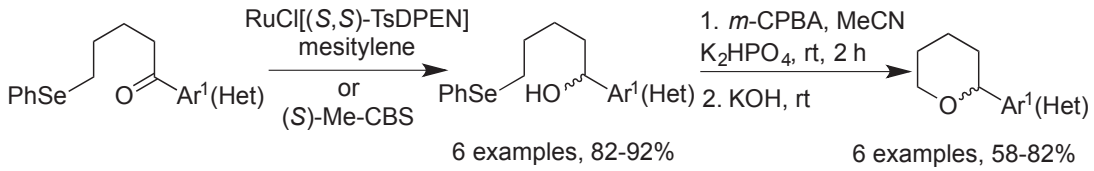
the resulting pyrazolone is ground with aldehydes and malononitrile in the presence of triethylamine or in one step where all four reactants are ground together with triethylamine (Scheme 9) (15H(91)1615). Further derivatives are available when the one-pot four-component reaction is carried out in a (9:1) mixture of water/ethanol at 80°C using β-cyclodextrin as catalyst. Replacing aldehydes for isatins, a range of related spirooxindole derivatives are obtained (15TL2441). One-pot five-component reaction of hydrazine hydrate, active methylene compounds, malononitrile, propargyloxy aldehydes, and azides provides several pyrazole-fused 2-amino-4-aryl-4*H*-pyran-3-carbonitriles bearing a 1,2,3-triazole group, in good yields (15HCA633).

Organocatalyzed three-component cascade reactions of isatins and malononitrile with 5,7-dihydroxy-4-methylcoumarin or 2-hydroxy-1,4-naphthoquinones yield 4-spirooxindole coumarin–fused (15TL359) or naphthoquinone-fused (15EJO3320) 2-amino-4*H*-pyran-3-carbonitriles, respectively. Tandem pericyclic reactions of 5-methylbenzene-1,3-diol with a (*Z*/*E*)-mixture of farnesal in refluxing pyridine gives 6*H*-dibenzo[*b*,*d*]pyran **9** and its diastereoisomer **10** (Scheme 10). This biomimetic one-step approach involves aldol-type addition, 6π electrocyclization, and hDA reactions (15SL927).

The synthesis of the tetrahydropyran ring of natural (+)-neopeltolide was achieved through enantioselective ring-opening/cross-metathesis of an oxabicyclic alkene with *n*-butyl vinyl ether mediated by a molybdenum monoaryloxide pyrrolide complex (15AGE215). The (4-methylamino)tetrahydropyranyl moiety of the antimitotic agent Tuv *N*-methyl tubulysin resulted from the hDA reaction of the Danishefsky's diene with a thiazole aldehyde, followed by catalytic hydrogenation and reductive amination reactions (15SL1063).

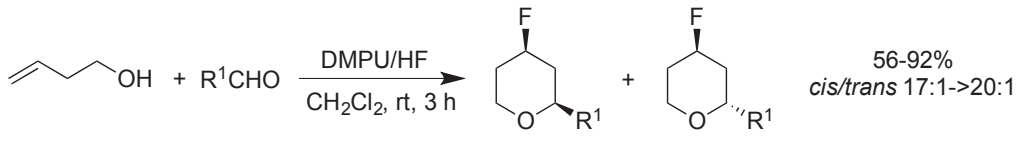
Stereoselective synthesis of 2-substituted tetrahydropyrans can be accomplished via catalytic asymmetric reduction of δ-phenylseleno ketones to give the corresponding alcohols and subsequent oxidation/cyclization reactions conducted in acetonitrile with an excess of *m*-chloroperoxybenzoic acid (*m*-CPBA) and potassium hydrogen phosphate (Scheme 11). This selenium-promoted methodology is extended to the synthesis of various 1-substituted, 4-substituted, and 1,1-disubstituted isochromans (15JOC8102).

A few examples were reported of 2-alkenyltetrahydropyran-3-carboxylates arising from the asymmetric intramolecular 1,6-C–H insertion reaction of methyl/ethyl 5-alkyloxy-2-diazopentanoates mediated by a chiral dirhodium(II) carboxylate complex (15TL1397). High yields and diastereoselectivity are prompted from fluoro-Prins reaction of but-3-en-1-ol with aromatic and aliphatic aldehydes mediated by 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone (DMPU)/HF to give 4-fluoro-2-substituted tetrahydropyrans (Scheme 12) (15OL3975).



RuCl[(*S*,*S*)-TsDPEN]mesitylene = [*N*-[(1*S*,2*S*)-2-(amino-κN)-1,2-diphenylethyl]-4-methylbenzenesulfonamidato-κ*N*]chloro[(1,2,3,4,5,6-η)-1,3,5-trimethylbenzene]ruthenium
(*S*)-Me-CBS = (*S*)-2-methyl-CBS-oxazaborolidine
m-CPBA = *meta*-chloroperoxybenzoic acid

Scheme 11



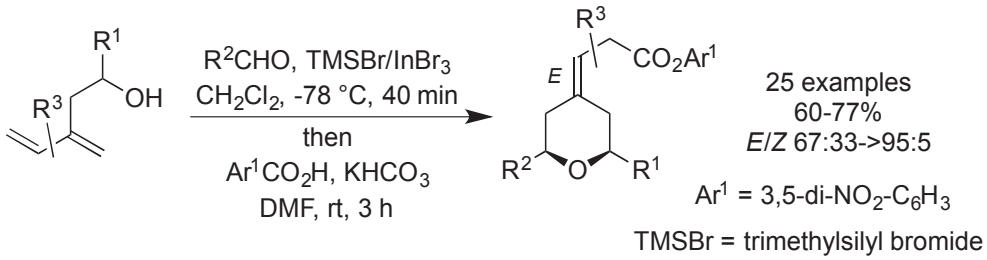
DMPU = 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone

Scheme 12

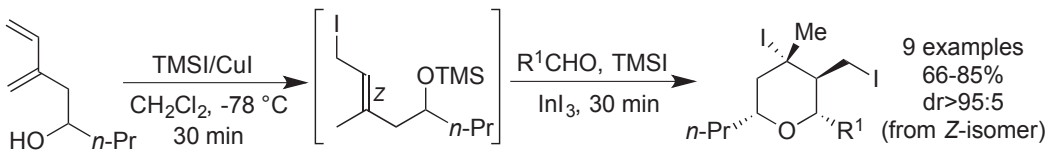
N-Tosyl alkenamides undergo a catalytic asymmetric iodocyclization reaction using an aminoiminophenoxy copper(II) carboxylate complex and *N*-iodosuccinimide (NIS) to deliver 2-*N*-tosyl-6-(iodomethyl)tetrahydropyran-2-imines (15AGE12767). Powdered $FeCl_3$•$6H_2O$-catalyzed cyclization of hydroxy allylic acetates in dichloromethane at room temperature leads to 2,6-disubstituted and 2,4,6-trisubstituted tetrahydropyrans with a high diastereoselectivity in favor of the more stable isomer (15JOC12509). A series of 2,6-disubstituted tetrahydropyrans bearing a (4*E*)-exocyclic double bond are readily formed by the trimethylsilyl bromide (TMSBr)/$InBr_3$-catalyzed reaction of dienyl alcohols with aldehydes via Prins cyclization/homobromination reactions (Scheme 13) (15CC14925).

A three-step route was applied for the synthesis of various 2-aryl-3-hydroxy-6-phenyl-5-sulfonyl tetrahydropyrans. It involved a base-assisted α-cinnamylation of β-keto sulfones, stereoselective reduction of the keto group with $NaBH_4$, and stereoselective *m*-CPBA-mediated epoxidation/intramolecular S_N2 reactions (15T1192). Several polysubstituted 4-iodo-3-(iodomethyl)tetrahydropyrans are attained from 1,4-hydroiodination of dienyl secondary alcohols performed in the presence of TMSI and CuI and subsequent Prins cyclization/iodination reactions of the TMS-protected (*Z*)-homoallylic alcohols with aldehydes using TMSI and InI_3 (Scheme 14) (15OL1846).

Chiral β-nitro alcohols, derived from the C_1-symmetric chiral diamine copper(II)-mediated asymmetric Henry reaction of aliphatic aldehydes with nitromethane, undergo an organocatalyzed Michael addition/hemiacetalization cascade with α,β-unsaturated aldehydes to give polysubstituted



Scheme 13



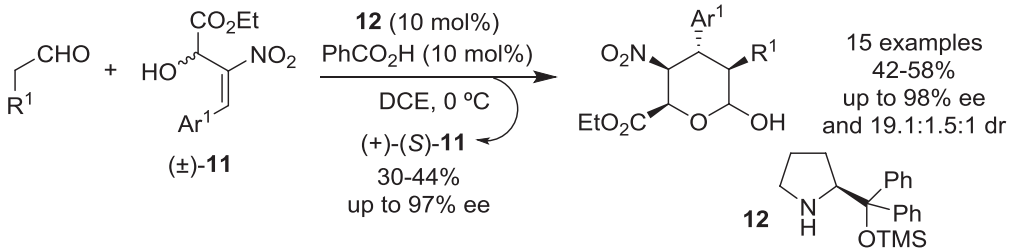
Scheme 14

3-nitrotetrahydropyrans in high yields, diastereo- and enantioselectivities (15JOC1446). Fully substituted tetrahydropyranols are achieved from organocatalytic Michael addition–acetalization reactions of simple aliphatic aldehydes with racemic secondary nitroallylic alcohols in the presence of benzoic acid in DCE at 0°C. The less reactive (*S*)-nitroallylic alcohols **11** were recovered in moderate yields (Scheme 15) (15OL430.

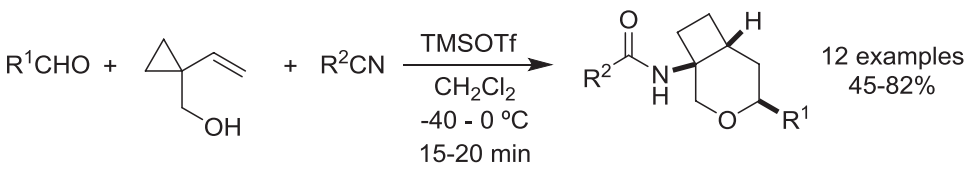
A chiral imidodiphosphoric acid catalyzes asymmetric Prins cyclization of salicylaldehydes with 3-methyl-3-buten-1-ol to prepare 2-substituted 4-methylenetetrahydropyrans in moderate-to-good yields (15AGE7703).

A wide range of spiroquinolinedione 2-substituted tetrahydropyrans were obtained through a domino Prins/pinacol cascade of 3-hydroxy-3-(4-hydroxybut-1-en-2-yl)-1-methylindolin-2-ones with aliphatic and aromatic aldehydes promoted by BF_3•OEt_2 in dichloromethane at 0°C (15OBC8729). Three-component reactions of aldehydes with vinylcyclopropyl carbinols and nitriles promoted by TMSOTf afforded cyclobutane-fused tetrahydropyran amides in moderate-to-good yields (Scheme 16) (15OBC5532).

Stereoselective synthesis of cycloheptanone-fused tetrahydropyrans occurs through a Prins/alkynylation/hydration reactions sequence involving (*E*/*Z*)-non-3-en-8-yn-1-ol and aromatic or aliphatic aldehydes carried out in the presence of CuCl and BF_3•OEt_2 (Scheme 17) (15OBC10212). Intramolecular Prins cascade cyclization of (*E*/*Z*)-8-methylnona-3,8-dien-1-ols and (*E*/*Z*)-9-methyldeca-3,8-dien-1-ols with aromatic aldehydes promoted by $AgSbF_6$ led to cyclopentene/cyclohexene-fused tetrahydropyrans in good yields with excellent selectivity (15OBC2669). Several examples of complex pentacyclic tetrahydropyrans were shown to arise



Scheme 15



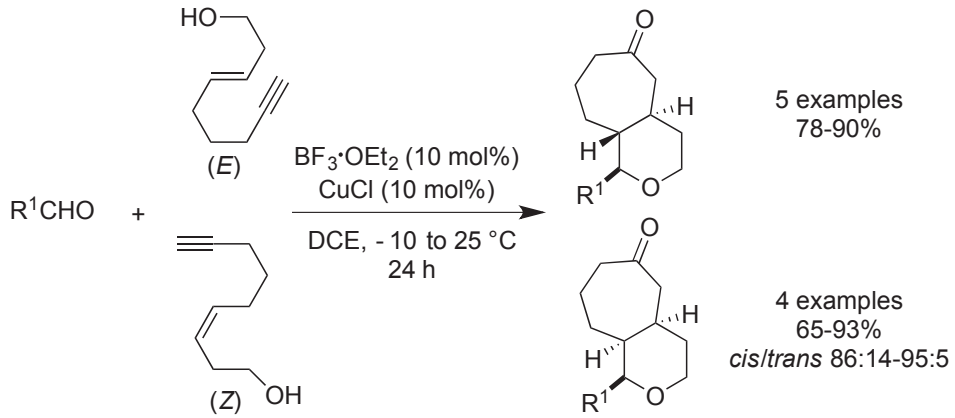
Scheme 16

from intramolecular DA reaction of various pendant aromatic groups to trap thermally generated benzynes. The most electron-rich arenes were more reactive dienes toward the electrophile benzyne partner (15OL856).

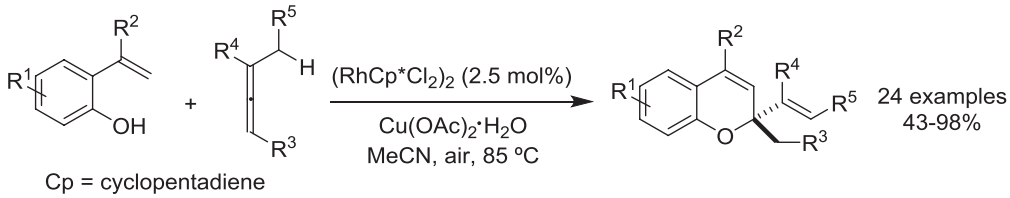
6.4.2.2 [1]Benzopyrans and Dihydro[1]benzopyrans (Chromenes and Chromans)

A series of 2*H*-chromenes result from an oxa-[3 + 3] annulation reaction of vinyliminium salts, formed in situ from α,β-unsaturated aldehydes and piperidine, with resorcinols. One of these 2*H*-chromenes is the intermediate in the total synthesis of natural (±)-rhododaurichromanic acid A (15S2713). One-pot synthesis of 2-allyl-2*H*-chromenes occurs through Wittig reactions of salicylaldehydes with (triphenylphosphoranylidene) acetaldehyde in THF to afford the corresponding *o*-hydroxycinnamaldehydes followed by trimethylsilyl iodide–promoted reaction with allyltrimethylsilane (15EJO542). Palladium(II)-catalyzed coupling and SiO_2-mediated condensation reactions of 2-halophenols with 2-methylbut-3-en-2-ol give access to 2,2-dimethyl-2*H*-chromenes in moderate-to-good yields (15SC1920). Other 2,2-disubstituted 2*H*-chromenes were produced from the rhodium(III)-catalyzed addition reaction of 2-alkenylphenols with allenes followed by [1,7] sigmatropic hydrogen shift and 6π-electron electrocyclic ring closure (Scheme 18) (15AGE2374).

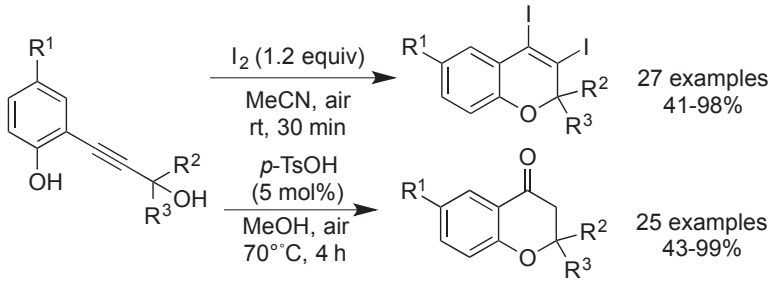
Baylis–Hillman adducts, derived from the DABCO-mediated reaction of salicylaldehydes with *t*-butyl acrylate, undergo potassium hydroxide–catalyzed tandem reactions to form 2*H*-chromene-3-carboxylic acids (15T4868). Highly functionalized 2-amino-2*H*-chromene-3-carboxylates result from the reaction of salicylaldehydes with β-aminoacrylates, under microwave irradiation and catalyst-free conditions (15T6894). A wide range



Scheme 17



Scheme 18

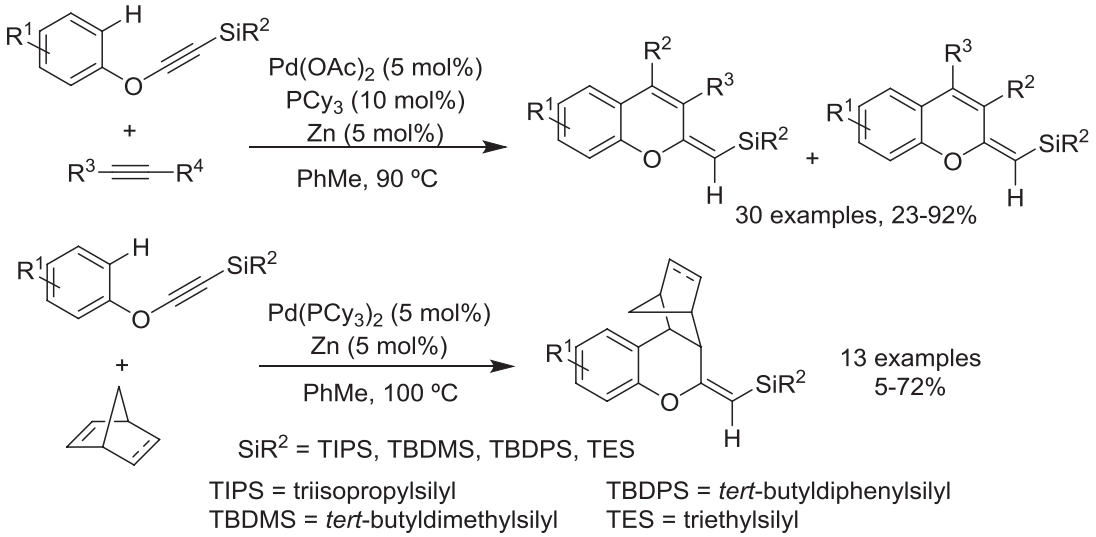


Scheme 19

of 3-(2-hydroxyaryl)propynols underwent iodine-mediated cascade cyclization in acetonitrile at room temperature to provide 3,4-diiodo-2*H*-chromenes whereas *p*-TsOH-mediated cascade cyclization in methanol at 70°C led to 4*H*-chroman-4-ones (Scheme 19) (15CEJ3480).

A microwave-assisted formal allenic carbocyclization reaction of 2-(buta-2,3-dienyloxy)benzaldehydes in water provides 4-methyl-2*H*-chromenes while NHC-promoted allenic hydroacylation reaction of 2-(propa-2,3-dienyloxy)benzaldehydes in the presence of DBU in 1,4-dioxane affords 3-methyl-4*H*-chromen-4-ones (15CEJ1533). Intramolecular hydroarylation of *p*-substituted aryl propargyl ethers catalyzed by indium(III) halides gives access to 4,6-disubstituted 2*H*-chromenes, via a 6-*endo*-*dig* cyclization process. The reaction proceeds with terminal and internal alkynes bearing electron-rich and electron-deficient substituents in the arenes and alkynes (15OBC379). A ruthenium complex catalyzes oxidative C–H acylation and dehydrative annulation reactions of phenols with α,β-unsaturated aldehydes to achieve polysubstituted 2*H*-chromenes (15EJO1899). Other polysubstituted 2-silylmethylidene-2*H*-chromenes arise from the palladium(0)-mediated insertion/annulation reactions of silylethynyl aryl ethers with internal alkynes. Replacing internal alkynes by norbornene and norbornadiene, $Pd(PCy_3)_2$-promoted double insertion/annulation reactions take place, and thus a series of cyclic-fused 2-silylmethylidenechromans can be formed (Scheme 20) (15BCSJ1388).

One-pot three-component reaction of salicylaldehydes, methyl/ethyl acetoacetate and methanol/ethanol carried out in the presence of a catalytic

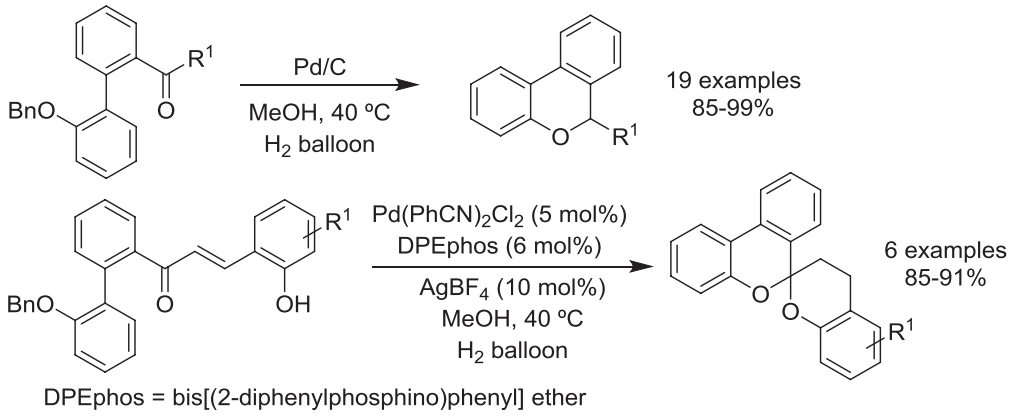


Scheme 20

amount of L-proline produces 2-alkoxy-2-methyl-2*H*-chromene-3-carboxylates, in good yields (15HCA978). The same catalyst was used for the one-pot three-component reactions of salicylaldehydes with methanol/ethanol and propiolates to afford 2-alkoxy-2*H*-chromene-3-carboxylates or with acetylenedicarboxylates to give 2-hydroxy-2*H*-chromene-2,3-dicarboxylates (15EJO5212).

2′-(2-Benzyloxyphenyl)acetophenone-type compounds undergo domino hydrogenation reactions catalyzed by Pd/C to provide 6*H*-benzo[*c*]chromenes or mediated by $Pd(PhCN)_2Cl_2$/DPEphos/$AgBF_4$ to give rise to chroman-spiro 6*H*-benzo[*c*]chromens (Scheme 21) (15TL2393). More examples of 6*H*-benzo[*c*]chromenes are prompted through palladium(II)/norbornene-catalyzed reaction of 2-substituted aryl iodides with primary and secondary 2-bromobenzyl alcohols carried out in the presence of potassium carbonate in DMF and using trifurylphosphine as ligand. The reaction occurs efficiently without ligands when tertiary 2-bromobenzyl alcohols are used (15T6389). Under dual catalysis of palladium(II)/norbornene and cinchona alkaloid catalyst, a wide range of chiral 6*H*-benzo[*c*]chromenes are achieved by one-pot reaction of 2-substituted aryl iodides with 2-bromophenols and electron-deficient terminal alkenes in the presence of potassium carbonate in DMF (15OBC2260).

High yields of thiophene-linked bisbenzo[*h*]chromenes are obtained from the reaction of symmetric and nonsymmetric bispropargyl alcohols with 2-naphthol with the aid of a catalytic amount of pyridinium *p*-toluenesulfonate (PPTS) and trimethyl orthoformate in refluxing DCE (15T4061). Intramolecular direct C–H functionalization of



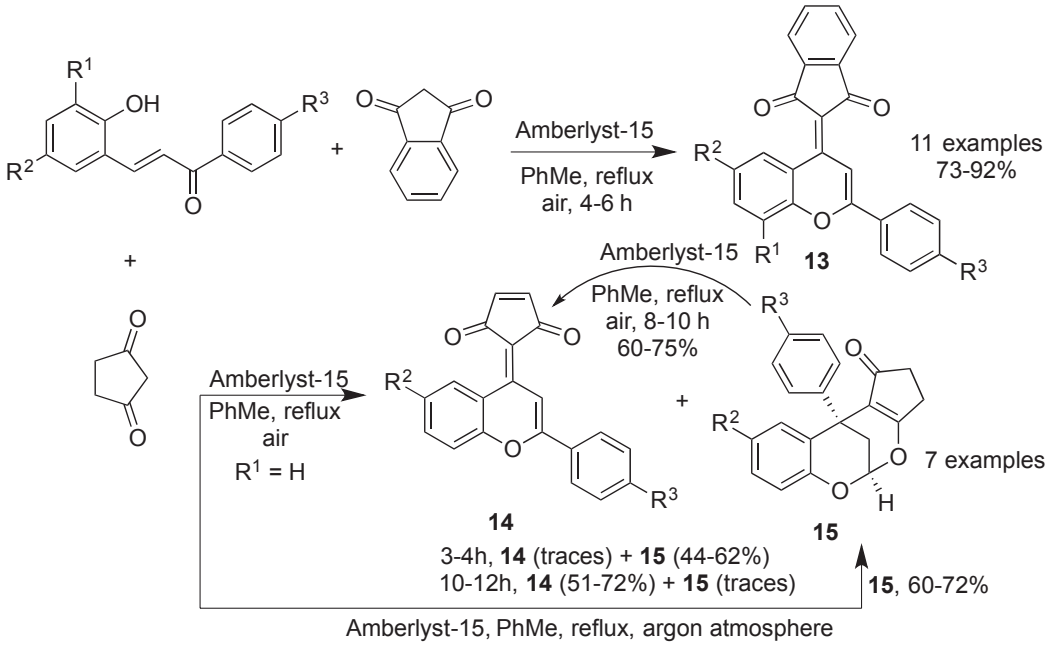
Scheme 21

1-substituted-4-[(2-halophenoxy)methyl]-1*H*-1,2,3-triazoles using potassium *t*-butoxide and a catalytic amount of isopropanol leads to 1,2,3-triazole-fused chromenes (15TL6123).

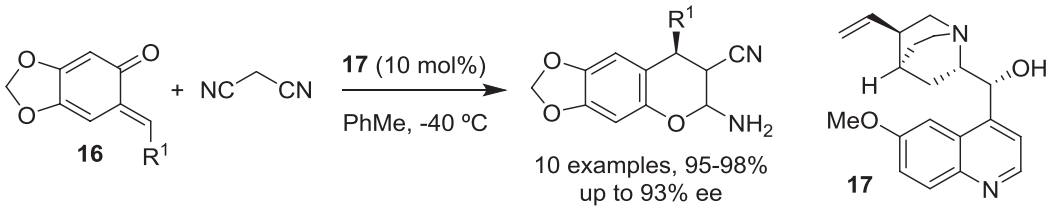
Microwave-assisted one-pot three-component reaction of cyclic 1,2-diketones with 2-naphthol and acetophenones or barbituric acids in aqueous media provides 4-spiro benzo[*f*]chromenes or pyrimidine-fused benzo[*f*]chromenes, in good-to-excellent yields (15JHC1639). A wide range of spirooxindole pyrazole–fused benzo[*h*]chromene derivatives result from the one-pot four-component reaction of hydrazine hydrate, β-ketoesters, isatins, and 2-hydroxy-1,4-naphthoquinone promoted by magnesium chloride in ethanol (15TL1072).

Treating 2-hydroxychalcones with indane-1-3-dione in the presence of Amberlist-15 in refluxing toluene affords 4-ylidene-4*H*-chromenes **13**, in air. Using the same conditions, the reaction with cyclopentane-1,3-dione gives the corresponding 4-ylidene-4*H*-chromenes **14** and 2,8-dioxabicyclo[3.3.1]nonanes **15**, in different rates according to the reaction time. However, these tetracyclic compounds **15** are converted to the 4-ylidene-4*H*-chromenes **14** under the same reaction conditions (Scheme 22) (15TL4954).

o-Quinone methides, photochemically generated from 2-(hydroxymethyl)/2-(dimethylaminomethyl)phenols, react with malononitrile in acetonitrile/water (1:1) solution to give a series of 2-amino-4*H*-chromene-3-carbonitrile derivatives (15JHC59). Enantioselective synthesis of 4-substituted 2-amino-4*H*-chromenes involves manganese dioxide–promoted C–H oxidation of 2-alkyl-substituted phenols, to generate the *o*-quinone methides, and a bifunctional squaramide-mediated Michael addition with active methylene compounds bearing a cyano group and subsequent cyclization (15OL6134). A similar strategy uses *o*-quinone



Scheme 22



Scheme 23

methides derived from 2-(1-tosylalkyl)phenols (15TL4334). More derivatives arise from the cycloannulation reaction of other *o*-quinone methides **16** with malononitrile, using the quinine-based catalyst **17** (Scheme 23) (15OBC2247).

A wide range of 2-amino-4*H*-chromene-3-carbonitriles were achieved from a one-pot three-component reaction of aromatic aldehydes, malononitrile, and phenols mediated by sodium carbonate (15SC1546) and a CuO-ZnO nanocatalyst (15SC485), in water. Further examples result from the three-component reactions of aliphatic/aromatic aldehydes, malononitrile, and indoles carried out in the presence of L-cysteine-functionalized magnetic nanoparticles in water (15OBC7772) or tetrabutylammonium glycinate [TBA][Gly] ionic liquid (IL), under solvent-free conditions (15TL1790). Using a catalytic amount of triethylamine, the reaction of aromatic aldehydes with malononitrile/ethyl cyanoacetate and 4-hydroxycarbazole affords indole-fused 2-amino-4*H*-chromene-3-carbonitriles/carboxylates (15OBC1404). Pseudo four-component reactions of salicylaldehydes,

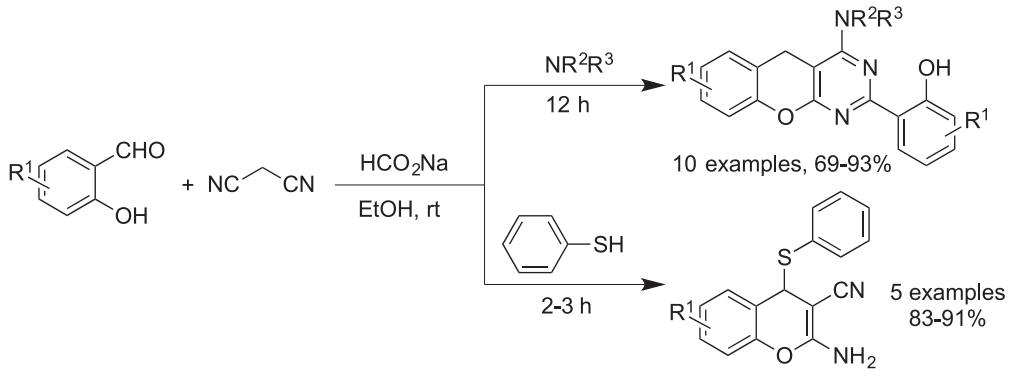
malononitrile, and secondary amines in the presence of sodium formate provide pyrimidine-fused 4*H*-chromenes. Replacing secondary amines by thiophenol furnishes 2-amino-4-arylsulfanyl-4*H*-chromene-3-carbonitriles (Scheme 24) (15JHC653). Various 4-spirooxindole 2-amino-4*H*-chromene-3-carbonitriles are obtained in excellent yields from three-component reaction of isatins, malononitrile, and 2,3-dihydro-5*H*-[1,3]thiazolo[3,2-*a*]pyrimidine-5,7(6*H*)-dione with the aid of diisopropylethylamine in refluxing ethanol (15T2458).

Bromodimethylsulfonium bromide catalyzes the one-pot pseudo three-component reaction of salicylaldehydes with acetophenones in acetonitrile giving rise to 4-phenacylidene 4*H*-chromenes (15TL2412). High yields of polysubstituted 4*H*-chromenes are obtained from the three-component reaction of 3,5-dimethoxyphenol, methyl acetoacetate, and benzaldehydes catalyzed by $NbCl_5$ in dichloromethane at room temperature (15TL4476).

Morita–Baylis–Hillman carbonates of 2-cyclohexenone and isatylidene malononitriles undergo divergent cyclization reactions: *N*-methyl electrophiles under the catalysis of β-ICD **18** afford spirooxindoles containing a bridged bicyclo[2.2.2] octane moiety while *N*-MOM electrophiles using α-isocupreine **19** as catalyst leads to spirooxindoles bearing a chromene skeleton (Scheme 25) (15OL4490).

Ruthenium(II)-promoted annulation reactions of 2-arylquinolones with internal alkynes provide benzo[*d*]chromene-type compounds and of 2-arylbenzoxazinones with alkynes produce isocoumarins. In this substrate-controlled transformation, the weaker carbonyl oxygen in the presence of a stronger nitrogen directing group dictates the annulation pathway (Scheme 26) (15OL5678).

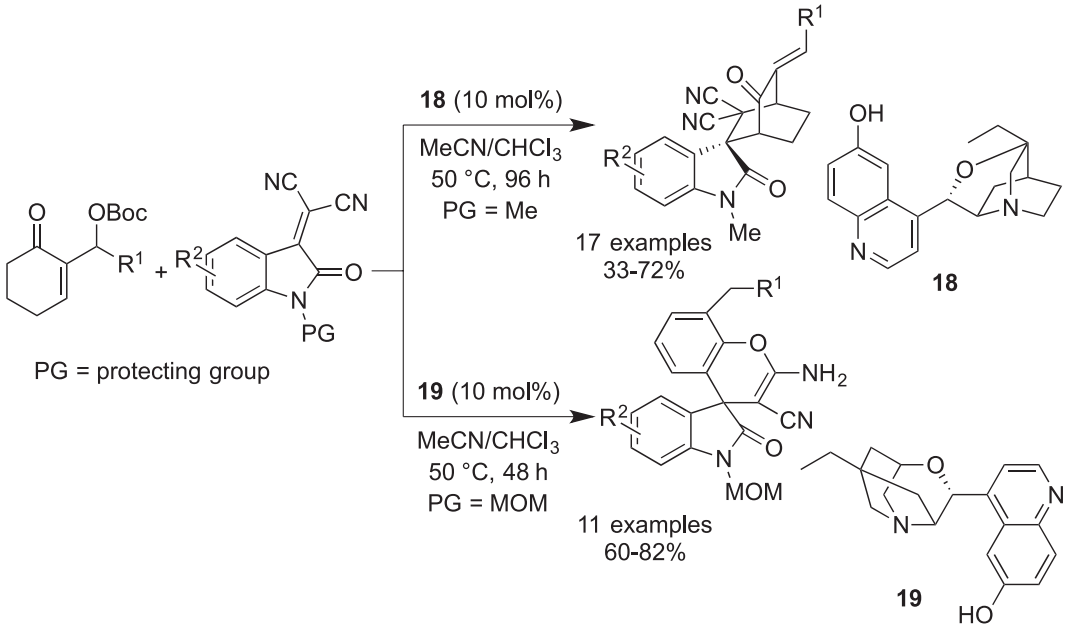
One-pot three-component reactions of benzaldehydes, cyclohexane-1,3-diones, and 2-aryl-5-(trifluoromethyl)-2,4-dihydro-3*H*-pyrazol-3-ones using a catalytic amount of *p*-TsOH produce pyrazolone-fused



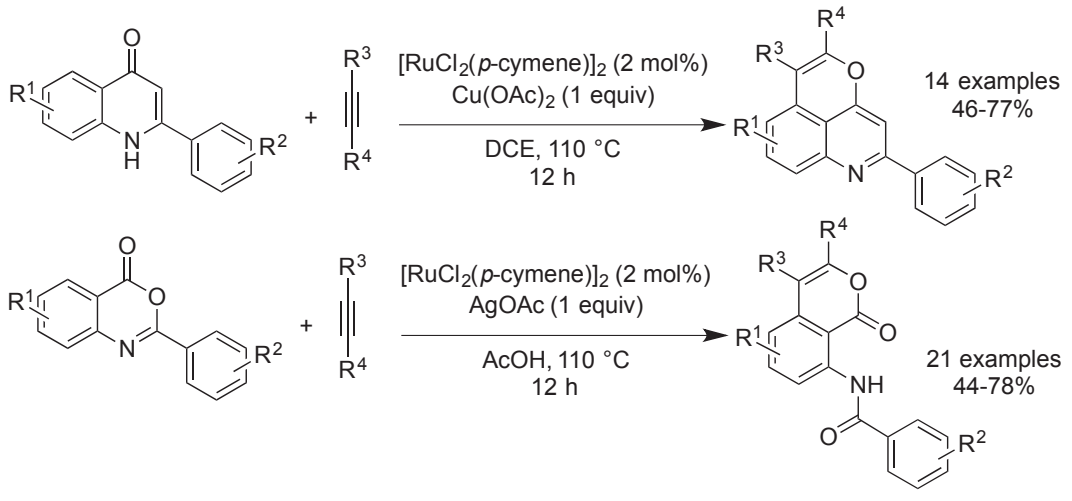
Scheme 24

tetrahydrochroman-type compounds (15S2073). Tetracyclic 1,8-dioxapyrenes and pentacyclic 1,12-dioxaperylenes arise from Rh-promoted direct cyclization of 1,4-naphthoquinones and 9,10-phenanthraquinones, respectively, with internal alkynes (15CC6337). The syntheses of natural (±)-deguelin and (±)-munduserone, 4*H*-chroman-4-one-fused chroman derivatives, involves an alkyne carbonyl metathesis to construct the 4-acyl-2*H*-chromene key intermediate (15JOC11460).

One-pot tosylhydrazine-promoted conjugate reduction of 2-hydroxychalcones followed by reductive coupling cyclization in refluxing 1,4-dioxane leads to various 2-arylchromans (15T8187). A wide range of



Scheme 25

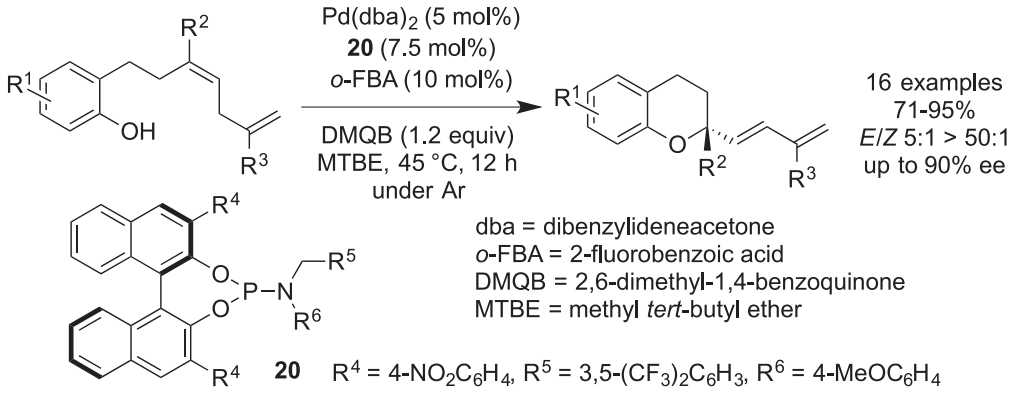


Scheme 26

2-CF_3-3-nitrochromans were synthesized in excellent yields through an enantioselective cascade of 2-hydroxychalcones with β-CF_3-nitroalkenes promoted by a squaramide catalyst (15OL3826). Under dual catalysis of 2-fluorobenzoic acid and a palladium complex of chiral phosphoramidite ligand, asymmetric allylic C–H oxidation of 2-(hepta-3,6-dien-1-yl)-phenols furnishes 2-alkyl-2-(buta-1,3-dien-1-yl)chromans in high yields and enantioselectivity (Scheme 27) (15JA12732).

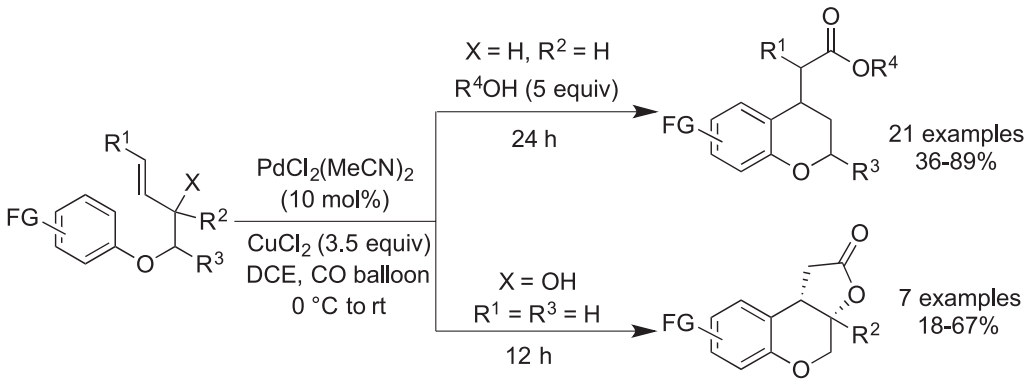
A series of 2-alkenyl-4-alkynylchromans were obtained from one-pot $ZnMe_2$-mediated nucleophilic addition of salicylaldehydes with alkynes and subsequent $ZnCl_2$-promoted [4 + 2] cycloaddition reaction with functionalized 1,3-butadienes (15SL827). Multicomponent reaction of sesamol, benzaldehydes, and styrenyl boronates mediated by chiral 3,3′-diiodo-BINOL led to chiral 2,4-diarylchromans in good yields and enantioselectivities (15OL5812).A novel cyclopentadienyl ligand enables enantioselective rhodium(III)-mediated C–H functionalization of *N*-isopropoxy-3-(3-oxopropoxy)benzamides to prepare 4-hydroxy-*N*-isopropoxychroman-5-carboxamides (15SL1490). Aryl alkenes and aryl alkenols readily undergo palladium(II)-catalyzed intramolecular carbonylative cyclization reactions to prepare diverse polysubstituted chromans in moderate-to-good yields (Scheme 28) (15OL1240).

Highly substituted chromans are produced through cross-coupling reactions of benzylic with aliphatic alcohols using the $NaHSO_4/SiO_2$ reagent system in DCE at 80°C (15SL1875). Chiral BINOL-based phosphoric acid catalyzes asymmetric hDA reactions of *o*-quinone methides, generated in situ from *o*-hydroxybenzyl alcohols, with 3-methyl-2-vinylindoles (15AGE5460) and unactivated alkenes (15AGE5762) to prepare polyfunctionalized chromans. Other chiral derivatives arise from the organocatalytic asymmetric cascade reactions of hydroxyarenes with 2,4-dienals

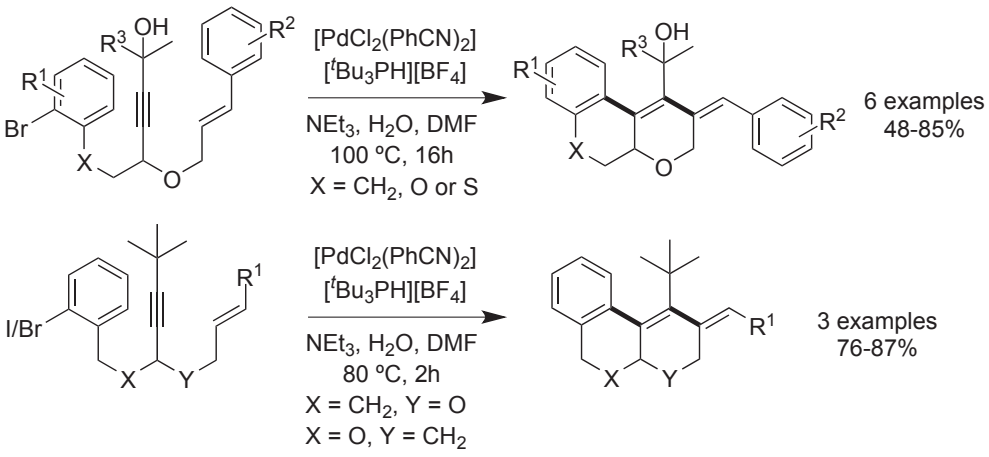


Scheme 27

(15AGE8203) and of 2-hydroxychalcone-type compounds with *trans*-nitroalkenes (15JOC11115) in high yields, diastereo- and enantioselectivities. Enynes bearing an aryl halide and a tertiary alcohol capping the alkyne undergo intramolecular formal *anti*-carbopalladation/Heck reactions to achieve benzodihydrochroman-type compounds (15CEJ12303). Replacing tertiary alcohol by a *t*-butyl group, lower temperature and reaction time is required for full conversion of substrates (Scheme 29) (15CEJ12303).γ,δ-Unsaturated alcohols, derived from 1,4-addition of phenylboronic acid to 2-hydroxycinnamaldehyde followed by reduction, undergo TMSOTf-promoted reaction with aldehydes to provide a series of pyranochromans (15OL3884). Tandem Prins bicyclization of (*E*)-3-[2-(4-methoxybenzyloxy)phenyl]-5-phenylpent-4-en-1-ol with aliphatic/aromatic aldehydes carried out in the presence of TMSOTf provides a mixture of *trans*-fused tetrahydropyran[3,4-*c*]chromans, one bearing the 4-methoxybenzyl substituent and the other unsubstituted in the aromatic ring. Using benzyloxy derivatives, only nonalkylated products are formed when the reaction is performed in the presence of BCl_3 (15EJO3103). Polyfunctionalized chiral



Scheme 28

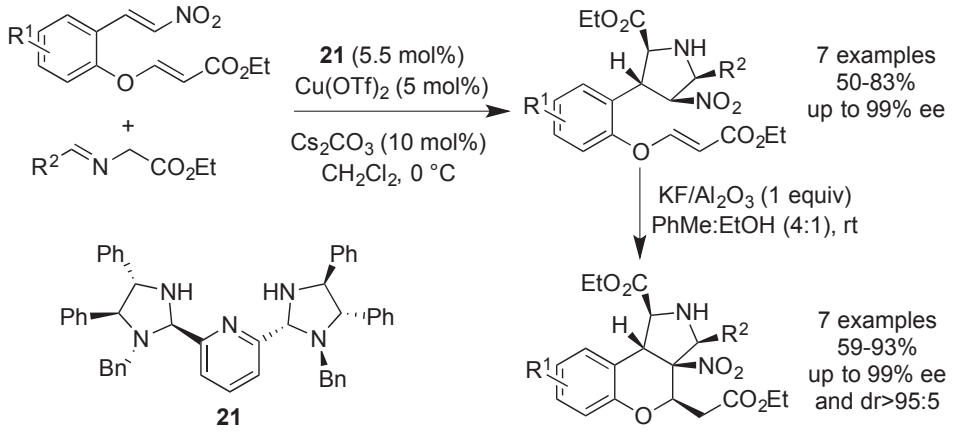


Scheme 29

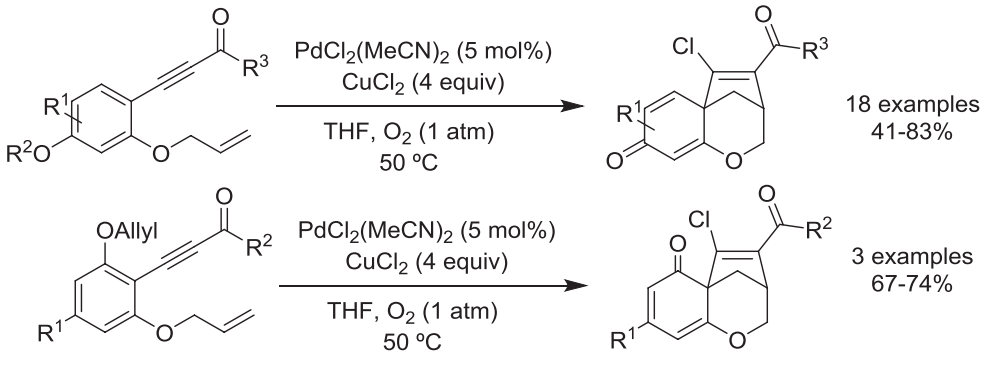
pyrrolidine–fused chromans arise from $Zn(OTf)_2$-mediated reaction of tertiary enamides with imines of salicylaldehydes in DCE at room temperature (15T523) and from asymmetric [3 + 2] cycloaddition reactions of α,β-unsaturated esters bearing a nitroalkene moiety with imino esters catalyzed by the chiral bis(imidazolidine)pyridine-Cu(II) complex and subsequent intramolecular diastereoselective cyclization with KF/Al_2O_3 (Scheme 30) (15JOC10346).

Organocatalytic multicomponent cascade reaction of 2-nitrovinyl phenols with β,β-disubstituted enals and olefinic oxoindoles gives spirooxindole cyclohexane-fused chromans in moderate-to-good yields and with high diastereo- and enantioselectivities (15CC13113).

Palladium(II)-catalyzed tandem chloropalladation/cyclization and dearomative cyclization reactions of several enynes provide a series of structurally diverse tricyclic bridged [3.2.1] skeletons (Scheme 31) (15OL4110). The total syntheses of pterocarpans, (−)-medicarpin, (−)-sophoracarpan A, and (±)-kushecarpin A, involved *o*-quinone methide chemistry to diastereoselectively build the chroman moiety (15AGE1864).



Scheme 30



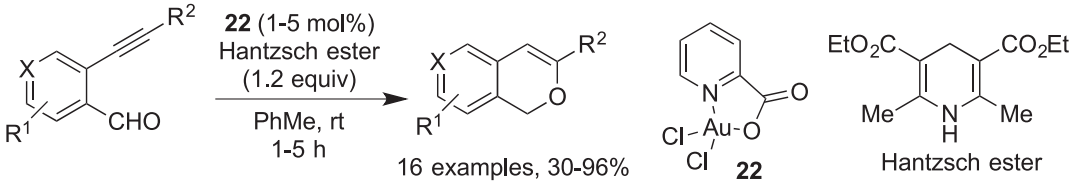
Scheme 31

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

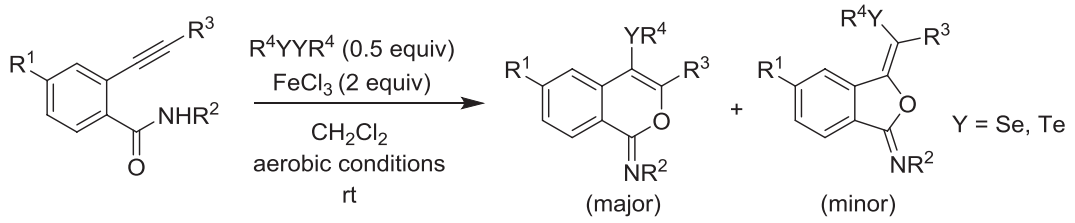
A wide variety of 1*H*-isochromenes were prepared through domino cycloisomerization/reduction of *o*-alkynylbenzaldehyde derivatives catalyzed by the commercially available dichloro(2-pyridinecarboxylato)gold(III) [$AuCl_2$(Pic)] complex and using the Hantzsch ester as hydride source (Scheme 32) (15OL6126). Another gold(I) catalyst was used in the asymmetric desymmetrization of *meso*-alkynylbenzenediols in the presence of silver salts to give 1*H*-isochromenes in high yields and enantioselectivity. The kinetic resolution of the corresponding (±)-2-alkynylbenzenediols to afford isochromene derivatives along with the recovery of highly optically enriched diols occurred under similar conditions (15CEJ4398).

The regio- and chemoselective cascade reaction of 2-alkynylarylcarboxamides with methyl vinyl ketone or acrylaldehyde proceeds efficiently using the system $PdCl_2$/KI or solely PdI_2 to prepare 1*H*-isochromen-1-imines (15EJO6298). A range of 4-organochalcogenyl-1*H*-isochromen-1-imines were obtained as major products of the nucleophilic cyclization (via a 6-*endo*-*dig* process) of 2-alkynylbenzamides mediated by iron(III) chloride and diorganyl dichalcogenides at room temperature under aerobic conditions (Scheme 33) (15EJO1583).

Intramolecular direct arylation of 4-(2-halobenzyloxy)-2*H*-pyran-2-ones, -coumarins, -pyridin-2-ones, and -quinolin-2-ones promoted by a palladium(II) catalyst and pivalic acid as additive led to the corresponding heterocycle-fused 1*H*-isochromenes (15EJO3540). Tandem polycyclization of internal 2-alkynylbenzyl alcohols with vinyl azides promoted by $In(OTf)_3$ affords a series of indeno[1,2-*c*]isochromenes through a cycloisomerization,



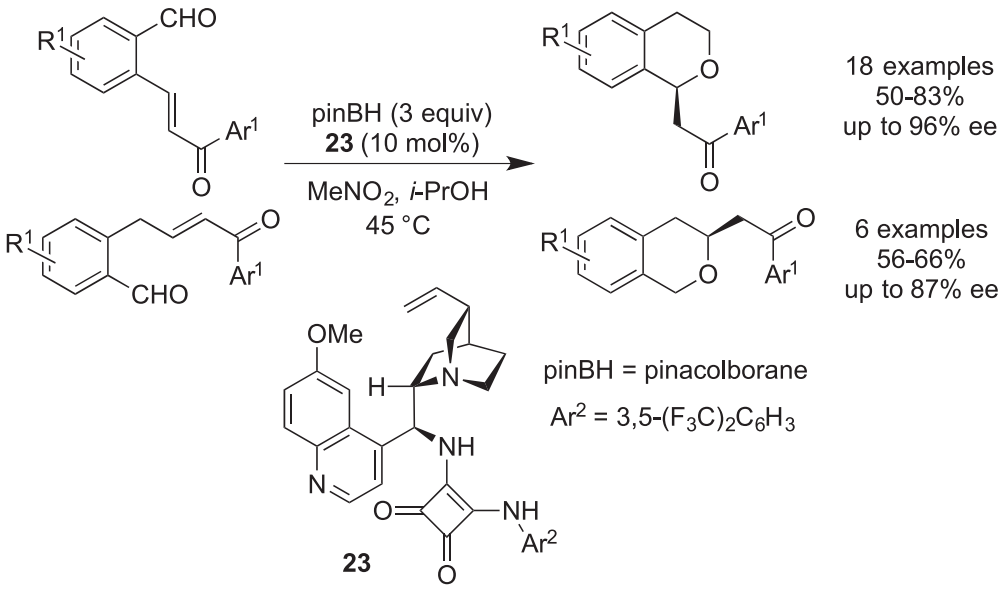
Scheme 32



Scheme 33

formal [4 + 2] cycloaddition, and elimination processes (15OL5220). Alkoxyboronate activation of (*E*)-2-[2-(3-oxo-3-arylprop-1-en-1-yl)aryl]acetaldehydes and (*E*)-2-(4-oxo-4-arylbut-2-en-1-yl)benzaldehydes with pinacolborane in the presence of the cinchona alkaloid-based bifunctional organocatalyst **23** led to the enantioselective synthesis of 1-substituted and 3-substituted isochromans, respectively (Scheme 34). This strategy was applied to the enantioselective synthesis of 1-substituted isochroman (+)-sonepiprazole (15JOC7008).

A few examples of dihydroisochromans resulted from the NHC-nickel(0)-catalyzed [2 + 2 + 2] cycloaddition reaction of terminal enynes with branched allyl and homoallyl ethers (15T4426). $AgSbF_6$-promoted stereoselective intramolecular Prins/yne cyclization of (*E*/*Z*)-octa-3-en-7-yn-1-ols and 2-vinylhexa-5-yn-1-ols with aldehydes leading to tetrahydro-1*H*-isochromans. Similarly, (*E*/*Z*)-nona-3-en-8-yn-1-ols or 2-vinylhepta-6-yn-1-ols with aldehydes afforded cycloheptene-fused tetrahydropyrans (15EJO5389). The same type of chemistry was used to prepare hexahydro-1*H*-isochromans and cyclopentane-fused tetrahydropyrans (15OBC2669). Weinreb amides, prepared from alkylation of 2-bromobenzyl alcohols with 2-bromo-*N*-methoxy-*N*-methylaceta/propanamides, undergo Parhan-type cyclization using *n*-BuLi as lithium reagent to yield isochroman-4-ones. The reaction occurs in 1 min with good-to-excellent yields (Scheme 35). This strategy was applied to the synthesis of natural isochroman-4-one (±)-XJP in six steps and overall yield up to 54% (15T8172).

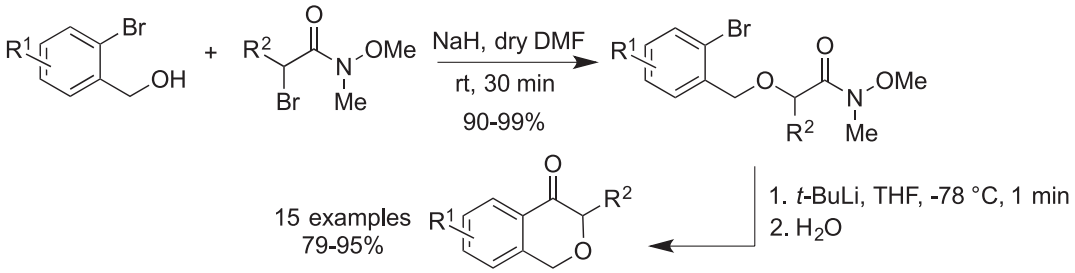


Scheme 34

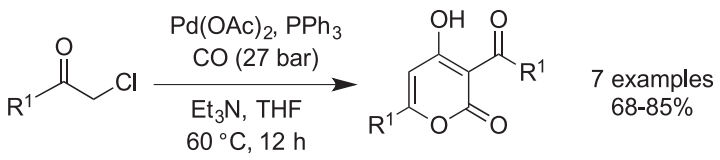
6.4.2.4 Pyranones

Soft α-vinyl enolization of β-chlorovinyl ketones occurs in the presence of triethylamine. Further reaction with one equivalent of methyl cyanoacetate promotes cyclization to afford 2*H*-pyran-2-ones, in a one-pot synthesis (15OL6254). A few 3-acyl-4-hydroxy-2*H*-pyran-2-ones were obtained by palladium(II)-catalyzed carbonylation of aliphatic and aromatic α-chloroketones, through the formation of an acylketene and dimerization by a [4 + 2] cycloaddition reaction (Scheme 36) (15TL2773).

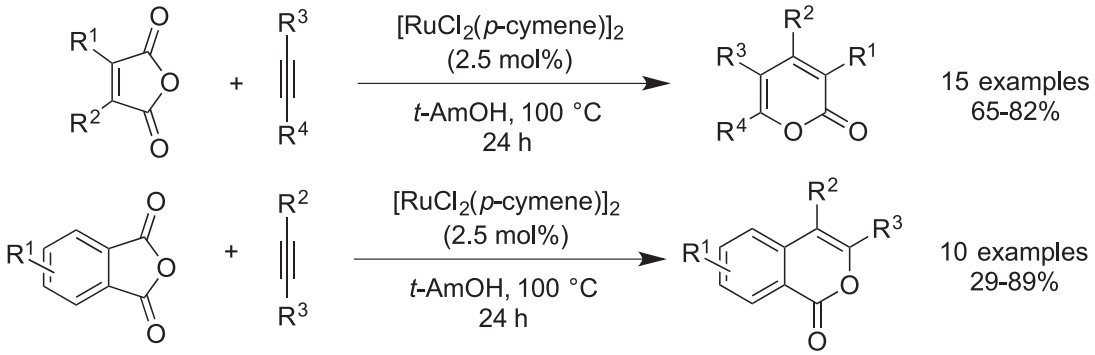
Under microwave irradiation, copper powder–promoted reaction of β-bromo-α,β-unsaturated carboxylic acids with 1,3-diketones affords a range of 2*H*-pyran-2-ones (15S216) while enamines, derived from ylidene-cyanoacetates, undergo cyclization with an excess of organohalides to produce 3-cyano-2*H*-pyran-2-ones (15JOC8583). Polysubstituted 2*H*-pyran-2-ones are available by oxidative annulation of alkynes and cinnamic acid derivatives catalyzed by an inexpensive ruthenium(II) complex (15OL5264). The same ruthenium complex catalyzes the decarbonylative addition of various cyclic acid anhydrides with symmetrical and unsymmetrical alkynes to give 2*H*-pyran-2-ones or isocoumarins (Scheme 37) (15CC9972). Other polysubstituted 5-vinyl-2*H*-pyran-2-ones arise in moderate-to-good yields from palladium(II)-mediated reaction of enynoates with electron-deficient alkenes via a selective 6-*endo* cyclization and alkenylation processes (15OL1636). A range of indole-fused 2*H*-pyran-2-ones result from the reaction of aromatic/aliphatic 2-alkynyl indoles with five equivalent of CO_2 carried out in the presence of a catalytic amount of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (15AGE6862).



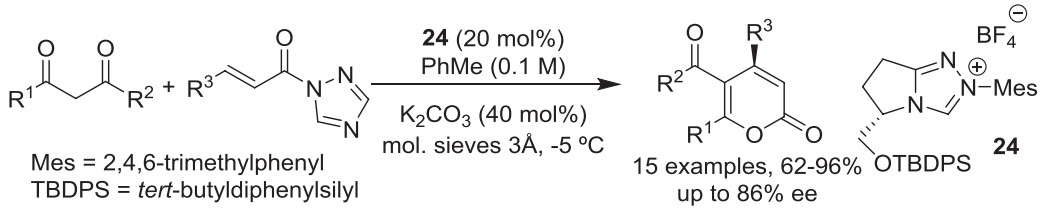
Scheme 35



Scheme 36



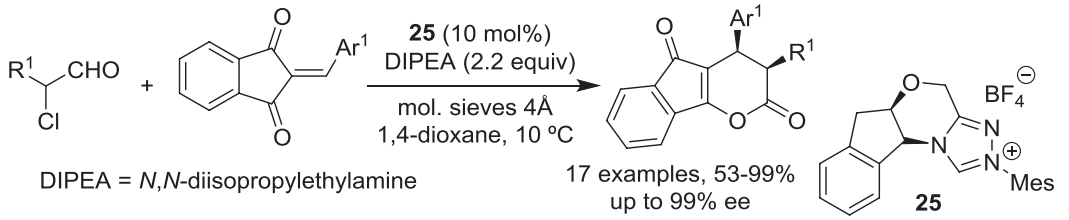
Scheme 37



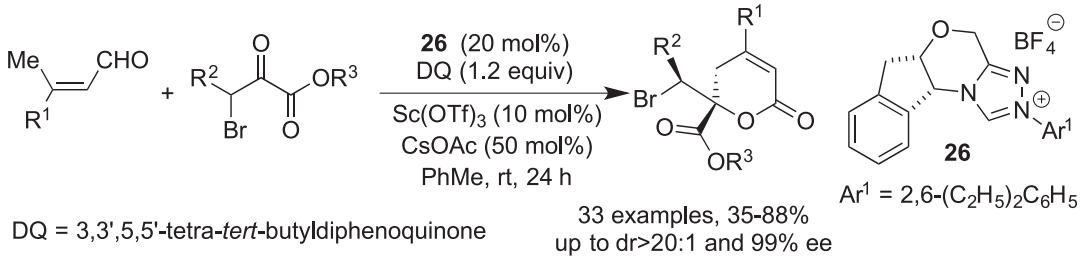
Scheme 38

NHC-promoted redox [4 + 2] hDA reactions of α-aroyloxyaldehydes with α,β-unsaturated trichloromethyl ketones (15JOC9728) and of 2-aryl carboxylic acids with enones (15OBC1313) provide 3,4-dihydro-2*H*-pyran-2-ones in moderate-to-excellent yields with high diastereo- and enantioselectivities. Further polyfunctionalized derivatives were achieved through enantioselective formal [3 + 3] cycloaddition reaction of α,β-unsaturated *N*-acyltriazoles with 1,3-diketones (Scheme 38) (15CC14628) and asymmetric Michael addition of α,β-disubstituted enals with 1,3-diketones (15CC4473), mediated by NHC catalysts.

NHC-catalyzed cascade reactions of enals with malonates gives access to cyclopentane- and cyclohexane-fused 3,4-dihydro-2*H*-pyran-2-ones in moderate-to-good yields with high diastereo- and enantioselectivities (15OL4940, 15OL5140). NHC catalysts are also used in the annulation reaction of enals with pyrazolones to prepare pyrazole-fused 3,4-dihydro-2*H*-pyran-2-ones (15OL1417) and of [4 + 2] cyclization of 1-chloroaldehydes with 2-arylidene indane-1,3-diones to afford indenone-fused 3,4-dihydro-2*H*-pyran-2-ones (Scheme 39) (15OBC6694). Treating indoline-2,3-diones with stabilized phosphonium ylides in boiling THF gives the corresponding propylidenes which react by a [4 + 2] cycloaddition reaction with a (2-oxovinylidene)triphenylphosphorane giving 4-spirooxindole 3,4-dihydro-2*H*-pyran-2-ones. In a similar procedure, starting from a naphthofuran-1,2-dione, a couple of naphthofuran-fused 2*H*-pyran-2-ones were achieved (15JHC15).



Scheme 39

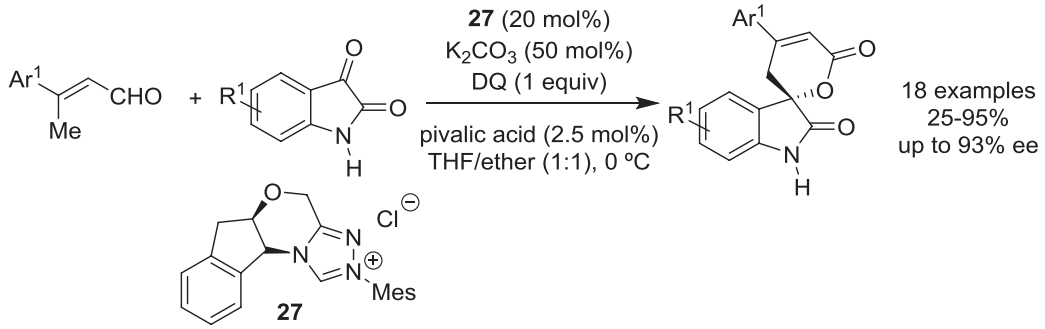


Scheme 40

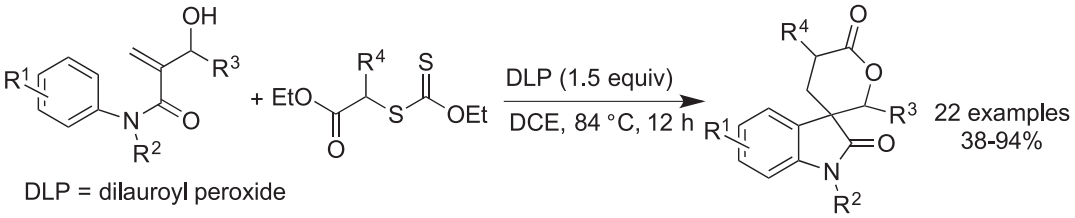
RCM of allylic alkenoates was used to construct the 5,6-dihydro-2*H*-pyran-2-one core in a total synthesis of (+)-cryptorigidifoliol A (15TL5474). A wide range of 5,6-dihydro-2*H*-pyran-2-ones were diastereo- and enantioselectively obtained through the reaction of enals with β-bromo-α-ketoesters involving an intermolecular dynamic kinetic resolution under dual catalysis by the NHC **26** and $Sc(OTf)_3$ (Scheme 40) (15AGE1629). Migita–Stille coupling reaction of (*Z*)-β-iodoacrylates with (*E*)-α-stannyl allylic alcohols mediated by palladium black in DMF provides 4-substituted 5-alkylidene-5,6-dihydro-2*H*-pyran-2-ones in good yields (15OL520).

Dual-oxidative dehydrogenative tandem annulation reactions of glycine derivatives with tetrahydrofurans using a Fe(II)/HCl/TBHP catalytic system in acetonitrile at room temperature produce quinoline-fused 5,6-dihydro-2*H*-pyran-2-ones (15OL5028). An unsubstituted dienolate, generated from the reaction of an NHC catalyst and methyl (*E*)-(4-oxobut-2-en-1-yl)carbonate, undergoes a subsequent [4 + 2] annulation reaction with isatins to afford spirooxindole 5,6-dihydro-2*H*-pyran-2-ones in moderate-to-good yields with moderate-to-good enantioselectivity (15EJO1047). More examples were obtained in high yields through a formal [4 + 2] cycloaddition reaction of α,β-unsaturated aldehydes with isatins promoted by NHC catalyst **27** and pivalic acid (Scheme 41) (15CC8330).

One-pot Michael-cyclization cascade reactions of α,β-unsaturated aldehydes with pyrazole amides mediated by a proline-derived organocatalyst provided polysubstituted tetrahydropyran-2-ones in good yields with excellent diastereo- and enantioselectivities (15CC9793). A wide range of



Scheme 41



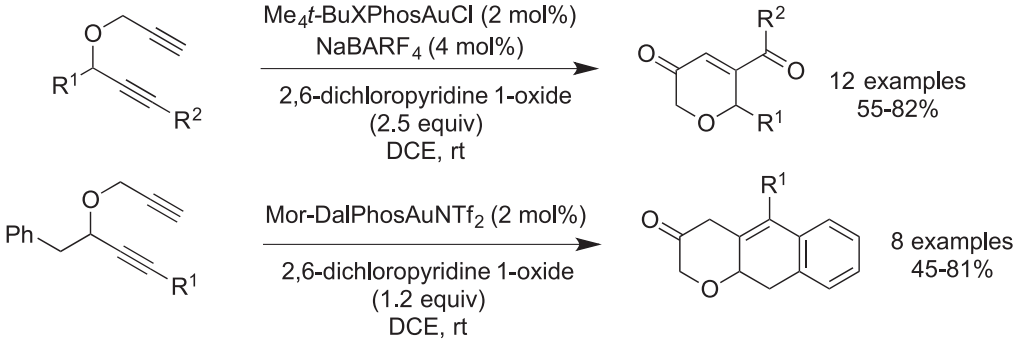
Scheme 42

spirooxindole tetrahydropyran-2-ones were formed in good yields from tandem radical addition/cyclization and ester exchange processes of *N*-aryl hydroxymethylacrylamides with xanthates carried out in the presence of dilauroyl peroxide (Scheme 42) (15T8117).

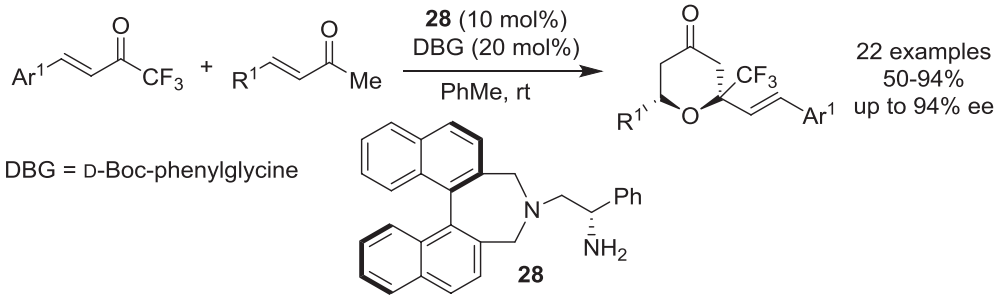
Gold-mediated selective oxidation of 4-oxahepta-1,6-diynes leads to 2*H*-pyran-3(6*H*)-ones and dihydro-2*H*-benzo[*g*]chromen-3(4*H*)-ones, through α-oxo gold carbene intermediates generated in situ and β-C-gold vinyl cation intermediates, which can be trapped by the external *N*-oxide and the internal aryl ring system (Scheme 43) (15CC10318).

The synthesis of 2,3,6-trisubstituted-5,6-dihydro-4*H*-pyran-4-ones can proceed through Maitland–Japp reaction of δ-hydroxy-β-ketoesters with dimethyl acetals of *N*,*N*-dimethylamides or with their orthoester counterparts. Subsequent treatment with L-Selectride gives tetrahydropyran-4-ones with excellent 2,6-*cis*-diasteroselectivity (15OBC4743).

Various dialkyl 2-(1,3-diaryl-3-oxopropyl)malonates undergo a Barbier-type zinc-promoted allylation/cyclohexenylation followed by intramolecular lactonization/transesterification reactions to achieve highly substituted tetrahydropyran-4-ones (15SL2121). Further derivatives arise through formal hDA reaction of trifluoromethylated enones with enolizable acyclic aliphatic enones in good-to-excellent yields and with high enantioselectivity (Scheme 44) (15CEJ11773). High yields of pyrazole-fused 4*H*-pyran-4-ones result from tandem cyclization of 2-diazo-3,5-dioxo-6-ynoates performed in the presence of triethylamine and using ethanol as solvent (15OL4651).



Scheme 43



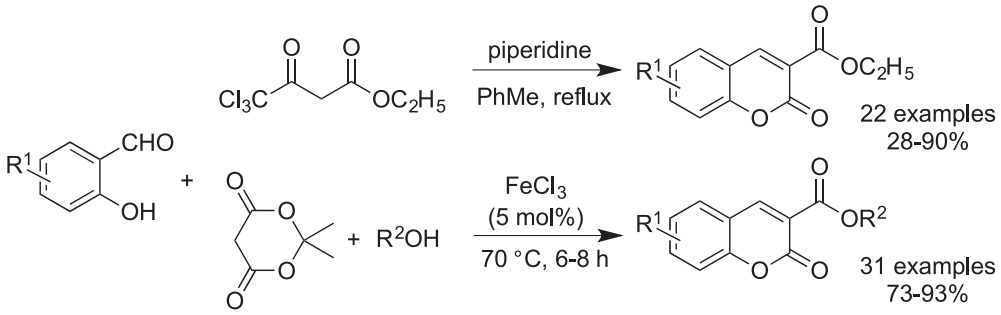
Scheme 44

6.4.2.5 Coumarins

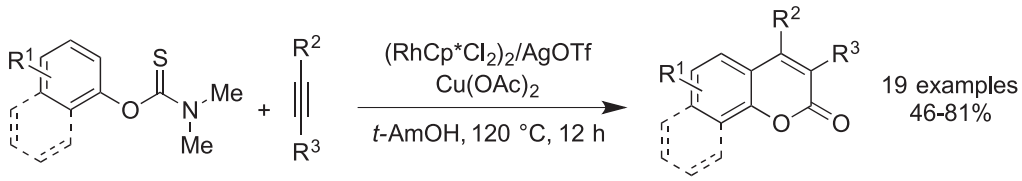
A series of 2*H*-coumarins were prepared via tandem nucleophilic addition of salicylaldehydes to ketene, generated in situ by the reaction of acetyl chloride and triethylamine, in good yields. The reaction only occurs in the presence of molecular sieves, which trap the by-product, water (15SC232).

Under solvent-free conditions, a wide range of 3-aryl-2*H*-coumarins arise from the condensation of salicylaldehydes with arylacetic acids carried out in the presence of DABCO at 180°C (15SC741). Microwave-assisted synthesis of coumarin-3-carboxylic acids occurs through condensation of Meldrum's acid with salicylaldehydes/2′-hydroxyacetophenones promoted by ytterbium triflate under solvent-free conditions (15TL2434). A wide range of 2*H*-coumarin-3-carboxylates were prepared by condensation of salicylaldehydes with ethyl 4,4,4-trichloro-3-oxobutanoate using piperidine in refluxing toluene (15TL1338) and $FeCl_3$-catalyzed three-component reaction of salicylaldehydes, Meldrum's acid, and alcohols (15T863) (Scheme 45).

Metal-free arylsulfonylation of phenyl propiolates with sulfonylhydrazides using TBAI as catalyst and TBHP as oxidant (15CC768) and with sulfinic acids using eosin Y as photocatalyst and TBHP as oxidant (15CC7520) delivers 3-sulfonated 2*H*-coumarins. The synthesis of 3-*N*-sulfonylamidine derivatives can proceed through a microwave-assisted



Scheme 45

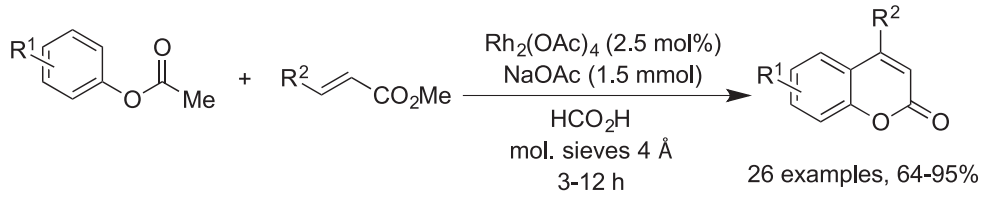


Scheme 46

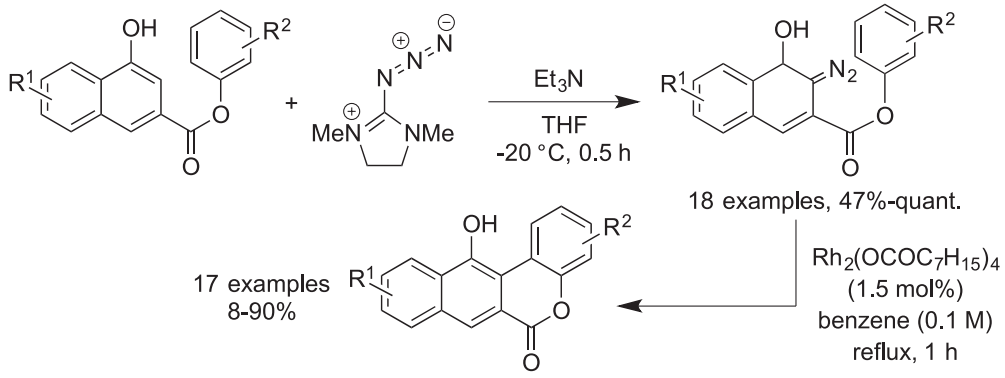
four-component tandem reaction of salicylaldehydes, propiolates, sulfonyl azides, and secondary amines promoted by CuI in alkaline medium (15JOC6291). Other 4-substituted-2*H*-coumarins are readily accessible through the Cp*Co(III)-catalyzed annulation reaction of 2-alkenylphenols with CO under mild reaction conditions (15OL5404). A Cp*Rh(III) catalyst promotes oxidative annulation reaction of aryl thiocarbamates with internal alkynes to furnish 3,4-disubstituted-2*H*-coumarins (Scheme 46) (15OL1477). Other 3-acyl-4-arylated derivatives were attained through silver-catalyzed radical cyclization of aryl alkynoates with α-keto acids (15JOC1550) and metal-free tandem oxidative acylation/cyclization of aryl alkynoates with aliphatic and aromatic aldehydes mediated by TBAB and $K_2S_2O_8$ (15JOC148). Examples of 3,4-disubstituted-2*H*-coumarins containing a 3-difluoroacetyl moiety were prepared from a visible light–promoted tandem radical cyclization of aryl alkynoates with ethyl bromodifluoroacetate using *fac*-Ir(ppy)$_3$ as photocatalyst (15JOC4766).

Under solvent-free conditions, a variety of 4-substituted 2*H*-coumarins arise from Pechmann condensation of phenols with β-ketoesters promoted by the sulfonic acid nanocomposite Fe_3O_4@SiO_2@Et-$PhSO_3H$ (15SL1263) and rhodium(II)-mediated annulation reaction of aryl acetates with acrylates, using formic acid as reducing agent (Scheme 47) (15JOC11544). Palladium(II)-catalyzed arylation/cyclization reactions of ethyl *o*-hydroxycinnamates with diaryliodonium salts produce 4-aryl-2*H*-coumarins in good-to-excellent yields (15TL3809).

The synthesis of 4,3′-bicoumarins can be achieved through the reactions of coumarin-4-acetates with salicylaldehydes using piperidine in ethanol



Scheme 47



Scheme 48

and of coumarin-4-acetic acids with salicylaldehydes in the presence of sodium hydride and acetic anhydride (15SC2043).

A range of benzo[*c*]coumarins were synthesized through lactonization reactions of 2-arylbenzoic acids mediated by silver nitrate (15JOC911) or 9-mesityl-10-methylacridinium perchlorate as photocatalyst (15OL4550) using both methods $(NH_4)_2S_2O_8$ as oxidant and through rhodium(III)-mediated cascade reaction of *N*-methoxyarylamides with hydroquinones in the presence of iodosylbenzene as oxidant (15CC661). Various 3-aryloxycarbonyldiazonaphthoquinones, synthesized from the diazo-transfer reaction of 2-azido-1,3-dimethylimidazolinium chloride to aryl naphthoic acids, undergo a rhodium-catalyzed cyclization to give naphtho[*c*]coumarins (Scheme 48) (15JOC8406).

Gold-promoted intramolecular hydroarylation of aryl alkynoates bearing a pyrroloquinoxaline-fused moiety gives access to the corresponding pyrroloquinoxaline-fused 4-aryl-2*H*-coumarins in high yields (15EJO4860). A large variety of pyrrolo-fused 2*H*-coumarins arise from a one-pot reaction sequence starting from *N*-substituted Boc-glycine *O*-aryl esters including an *o*-alkyne substituent. It involves *N*-Boc deprotection, azomethide ylide generation with an aromatic aldehyde, intramolecular 1,3-cycloaddition, and oxidative aromatization reactions (15TL3358).

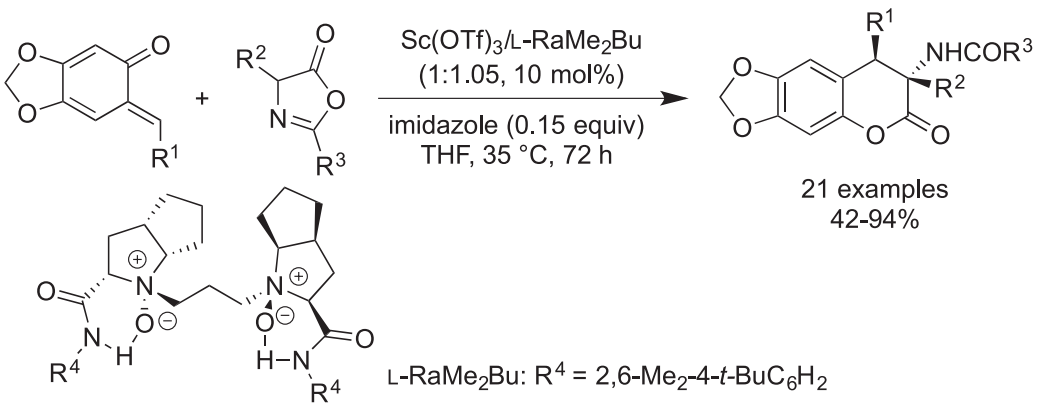
Various 4-(2-aryl-2-oxoethyl)-3-methylidene-3,4-dihydrocoumarins were formed by enantioselective intramolecular Rauhut–Currier reaction of acrylates, derived from 2-hydroxychalcones mediated by a chiral phosphine (15SL2679) or by a bifunctional dipeptidic phosphane catalyst

(15OL2462). Palladium-catalyzed hydroesterification of 2-alkenylphenols with phenyl formate as CO source produces polysubstituted 3,4-dihydrocoumarins, generally in high yields and enantioselectivity (15OBC10341). Asymmetric IED hDA reaction of *o*-quinone methides with azlactones catalyzed by a chiral scandium(III) complex provides various 3-amino-3,4-dihydrocoumarins (Scheme 49) (15CC3835).

It was through an electrophilic Claisen rearrangement and subsequent oxidation of allyloxyamides bearing an aromatic ring carried out in the presence of triflic anhydride and 2,4,6-collidine that a series of 3-allylated 3,4-dihydrocoumarins were prepared (15T5994). Further 3-alkyl/benzyl 3,4-dihydrocoumarins were attained from NHC-promoted enantioselective formal [4 + 2] annulation reactions of alkyl/benzyl-substituted acyl imidazoles with *o*-(*O*-TBS)benzyl bromides (15CC3407). NHC catalysts also promote the cascade reaction of enals with nitroalkenes to chemo- and enantioselectively give 3,4-disubstituted 3,4-dihydrocoumarins in moderate-to-good yields (15OL3588).

o-Quinone methides, generated in situ by sulfinic acid elimination of 2-(arylsulfonyl)alkyl phenols under basic conditions, underwent squaramide-catalyzed addition reactions with Meldrum's acid to give 4-aryl-3,4-dihydrocoumarins or with malononitrile and 1,3-dicarbonyl compounds to afford 4-aryl-4*H*-chromenes (15CEJ6037).

Niobium pentachloride–mediated multicomponent reactions of 2-naphthol, dimethyl malonate, and an aromatic aldehyde give mainly 4-aryl-3,4-dihydrobenzo[*f*]coumarin-3-carboxylates with a small amount of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes (15SC1114). A series of 3-alkyl/benzyl-tetrahydrobenzo[*h*]coumarin-type compounds arise from the NHC-catalyzed annulation reaction of aliphatic/aromatic enals with α-methylene cycloalkanones/chromanones using DBU in

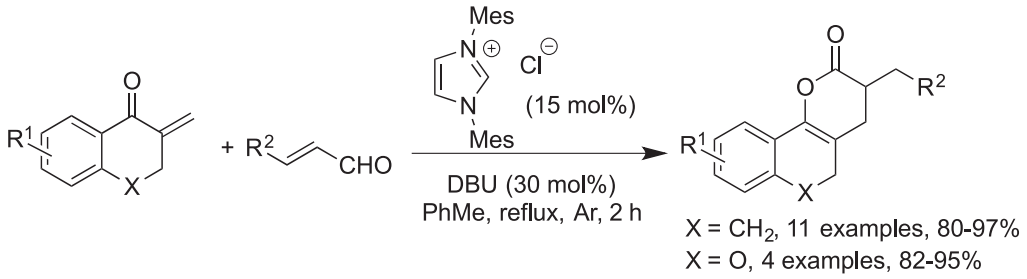


Scheme 49

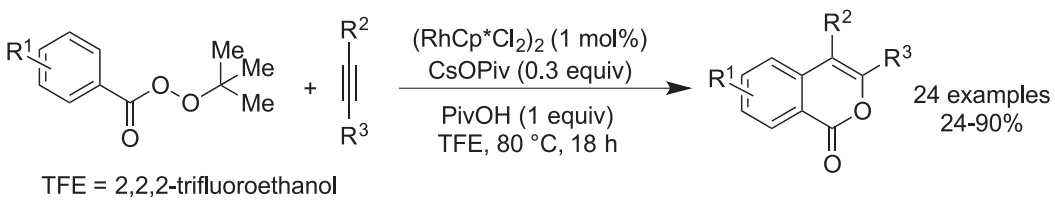
refluxing toluene (Scheme 50) (15T9022). Stereoselective synthesis of tetra/pentacyclic 3,4-dihydrocoumarin-type compounds involves a solid-state melt reaction of various 2-formylaryl cinnamate or crotonate derivatives with *N*,*N*-dimethylbarbituric acid, 5,5-dimethylcyclohexane-1,3-dione, 1-phenyl-1*H*-pyrazol-5(4*H*)-ones, or 4-hydroxycoumarin (15OBC5597).

A wide range of isocoumarins can be prepared through oxidative C–H activation and alkyne annulation reactions with perester as the internal oxidizing directing group promoted by a rhodium(III) catalyst (Scheme 51) (15OL4960) or benzoic acids and molecular oxygen or air as sole oxidant, catalyzed by a ruthenium(II) biscarboxylate complex (15AGE5513). The same rhodium(III) catalyst was used in the C–H α-acylalkylation/deaminative cyclization reactions of pyrrolidine amides with cyclic alkenyl carbonates for the synthesis of several 3-substituted isocoumarins (15OL4850).

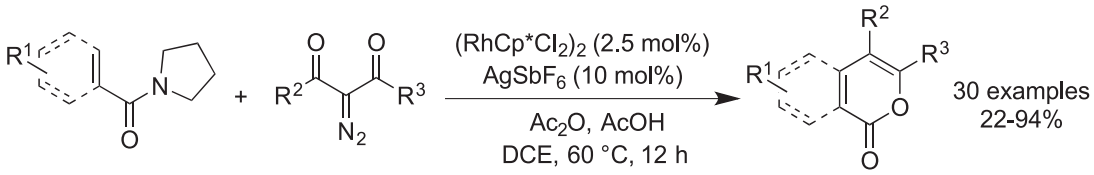
Treating 2-ethynylbenzoic acids with a catalytic amount of a rhenium(I) complex led to 3-arylisocoumarins as major products, via a 6-*endo* cyclization (15H(91)2172). Further derivatives arise from a multistep approach involving alkylation of α-amino-α-arylnitriles with methyl 2-(bromomethyl)benzoate, hydrolysis to afford the corresponding δ-keto esters and an annulation reaction in the presence of DBU. Replacing the benzyl bromide component with 5-(bromomethyl)-2,2-dimethyl-4*H*-benzo[*d*][1,3]dioxin-4-one led to a series of 8-hydroxy-3-arylisocoumarins. This strategy was applied to the synthesis of natural 3-aryl-8-hydroxyisocoumarins, thunberginol A and cajanolactone A (15EJO1797).



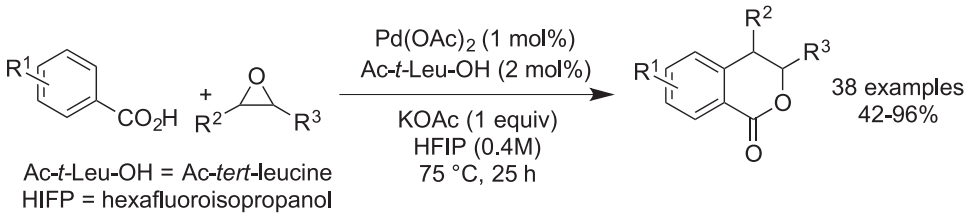
Scheme 50



Scheme 51



Scheme 52



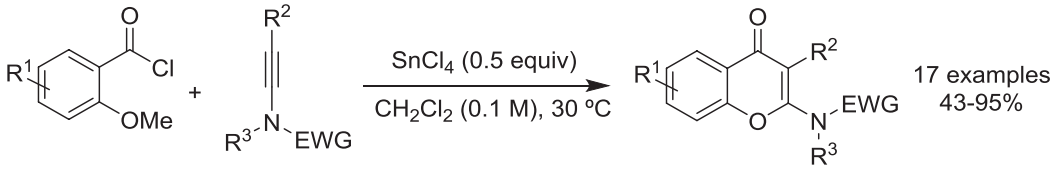
Scheme 53

Microwave-assisted domino reactions of 2-carboxybenzaldehydes with 2-bromoacetophenones mediated by potassium carbonate afforded 3-benzoylisocoumarins in moderate-to-good yields (15SC857). Various isocoumarins/2*H*-pyran-2-ones resulted from rhodium(III)-catalyzed C–H activation/cyclization reactions of benzamide-type compounds with 2-diazo-1,3-dicarbonyl compounds (Scheme 52) (15CC2380). Other polysubstituted isocoumarins were obtained in good yields through ruthenium-mediated decarboxylative annulation reactions of α-keto acids with internal alkynes; the carboxylic acid acts as both directing and leaving group (15CEJ1904).

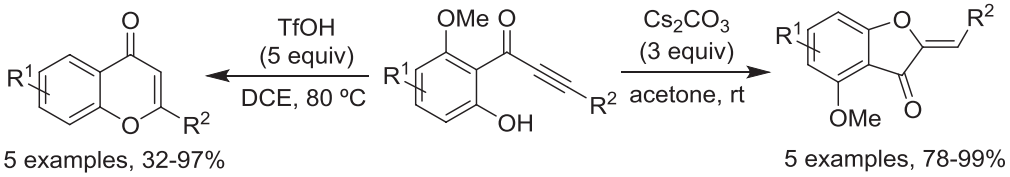
Palladium(II)-catalyzed C(sp^2)–H alkylation of benzoic acids with both terminal and internal epoxides provides 3,4-dihydroisocoumarins. The presence of the potassium cation is crucial for the reaction, and monoprotected amino acid ligands enable the use of a low loading of catalyst (Scheme 53) (15JA10950). Natural cytosporone derivatives were prepared from benzoic acids and involved their homologation to phenyl acetates, followed by acylation, selective reduction, and biomimetic lactonization (15AJC1583).

6.4.2.6 Chromones and Chromanones

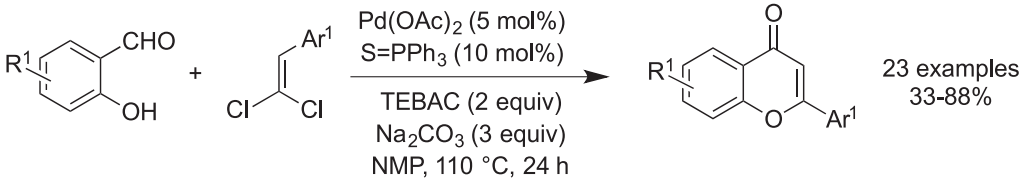
Two-component one-pot cascade reactions of diethyl acetylenedicarboxylate with phenols using pyridine and polyphosphoric acid as catalysts give ethyl 4*H*-chromen-4-one-2-carboxylates, in good yields (15H(91)1212). A wide range of 3-substituted 2-amino-4*H*-chromen-4-ones is readily available through tin(IV) chloride–mediated annulation reaction of ynamines with 2-methoxyaroyl chlorides. This procotol involves a tandem Friedel–Crafts acylation, oxo-Michael addition, and elimination reactions (Scheme 54) (15OL4472).



Scheme 54



Scheme 55



Scheme 56

Microwave-assisted tandem Claisen rearrangement/6-*endo* cyclization reactions of *O*-allylated/prenylated *o*-alkynoylphenols occur in the presence of *N*,*N*-diethylaniline to provide 8-allylated or 6-prenylated 4*H*-chromen-4-ones. A similar strategy was applied to the synthesis of the natural 8-prenyl-4*H*-chroman-4-one pestaloficiol J (15EJO7602). Microwave-assisted tandem Claisen rearrangement was also the key step in the synthesis of the natural pyran-fused 2-aryl-4*H*-chromen-4-ones, sophoflavescenol, flavenochromane C, and citrusinol. The sequences involved the formation of an 8-prenylated flavone from a 5-*O*-prenylflavone in refluxing *N*,*N*-diethylaniline and further pyran ring formation (15EJO2297). *o*-Alkynoylphenols undergo cesium carbonate–promoted 5-*exo* cyclization reactions to afford aurone derivatives while TfOH mediates regioselective 6-*endo* cyclization to form 2-aryl-4*H*-chromen-4-one derivatives (Scheme 55) (15TL4392).

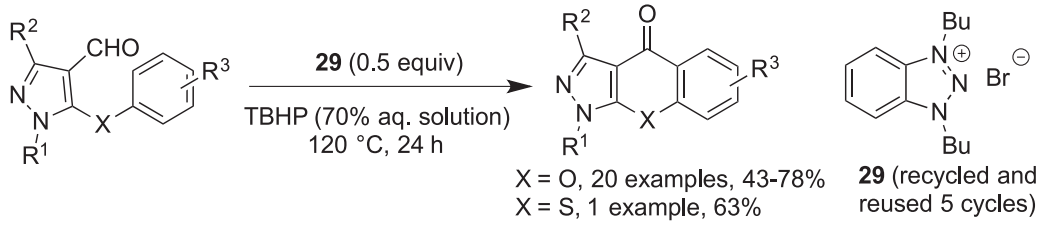
The synthesis of various 2-aryl-4*H*-chromen-4-ones can be achieved through one-pot reaction of 2′-hydroxyacetophenones with benzaldehydes carried out in the presence of gold nanoparticles supported on a Mg-Al layered double hydroxide (15AGE13302) and regioselective intramolecular nucleophilic substitution of *gem*-dichloroarylalkenes with salicylaldehydes promoted by the $Pd(OAc)_2$/triphenylphosphine sulfide reagent system (Scheme 56) (15CC17576).

Algar–Flynn–Oyamada reaction under a phase transfer catalyst improved the yields obtained in the synthesis of 2-aryl-3-hydroxy-4*H*-chromen-4-ones starting from 4′-benzyloxy-2′-hydroxychalcones (15AJC1102). The total synthesis of the naturally occurring 2-aryl-5-deoxy-4*H*-chromen-4-ones diplotrins A-C involves Algar–Flynn–Oyamada oxidation of chalcones as the key step (15T4557). (*E*)-2-aryl-8-iodo-4*H*-chromen-4-ones, precursors of 8-styryl derivatives, arise from a regioselective one-pot oxidative cyclization–iodination reactions of (*E*)-2′-hydroxychalcones with iodine in refluxing dimethyl sulfoxide (15SL1379).

A green oxidative protocol is applied to the synthesis of pyrazole-fused 4*H*-chromen-4-ones via intramolecular annulation of 5-(aryloxy)-1*H*-pyrazole-4-carbaldehydes in aqueous media, in moderate-to-good yields, promoted by the heterocyclic IL, 1,3-dibutyl-1*H*-benzo[*d*][1,2,3]triazol-3-ium bromide **29**. This IL can be recycled and reused at least five cycles with the same efficacy (Scheme 57) (15OL932). The natural furan-fused 2-aryl-4*H*-chromen-4-ones, lanceolatin B and pongaglabrone, were obtained by treatment of furano-hydroxychalcones with potassium carbonate in DMF, through base-promoted intramolecular tandem *O*-arylation and C–O bond cleavage processes (15OBC10461).

Chiral 4*H*-chroman-4-one-2-carboxylates were synthesized through intramolecular Mitsunobu etherification of methyl (*S*)-2-hydroxy-4-oxo-4-(2′-hydroxy)phenylbutanoates, derived from L-malic acid. The corresponding chroman-2-carboxylates were obtained after catalytic hydrogenation (15TA912). The asymmetric total synthesis of (−)-isosilybin A was accomplished in 16 steps. It involved a late-stage biomimetic cyclization of a 2′-hydroxychalcone to synthesize the 4*H*-chroman-4-one core and asymmetric Sharpless dihydroxylation and Mitsunobu inversion reactions to construct the benzodioxane ring (15OL98).

Enantioselective intramolecular crossed-benzoin reaction of 2-(2-aryl-2-oxoethoxy)benzaldehydes promoted by (1*R*)-camphor-derived NHC **30** gave access to 3-aryl-3-hydroxy-4*H*-chroman-4-ones in high yields and enantioselectivity (Scheme 58). This method was also applied to the



Scheme 57

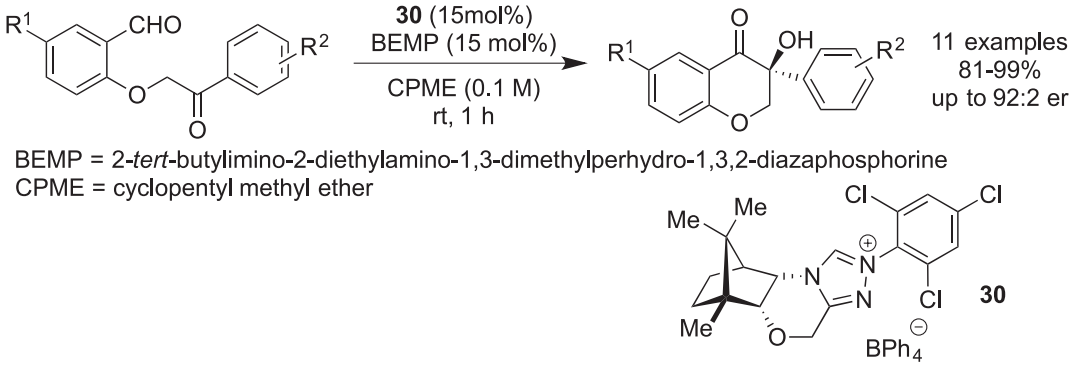
enantioselective synthesis of ethyl 2-(4*H*-chroman-4-one-2-yl)acetate (15JOC7468).

High yields of 2,3-disubstituted 4*H*-chroman-4-ones were obtained through one-pot diastereoselective rhodium(I)-catalyzed hydroacylation reactions of internal alkynes with salicylaldehydes followed by intramolecular oxo-Michael addition (15OL3276). Sonogashira coupling of 2-iodophenols with terminal alkynes and subsequent gold(I)-mediated intramolecular domino cyclizations provided cyclopentene/cyclohexene-fused 4*H*-chroman-4-ones in moderate-to-good yields (Scheme 59) (15SL1461).

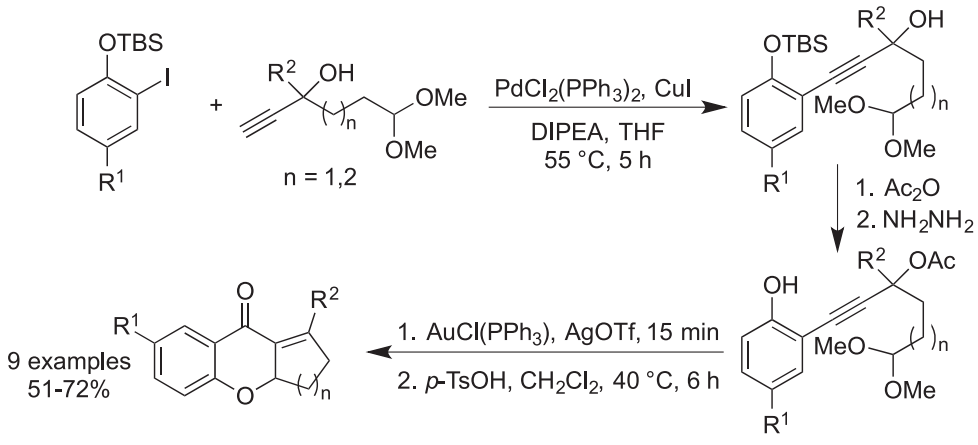
6.4.2.7 Xanthenes and Xanthones

Spirocyclopropene xanthenes were obtained via formal [2 + 2] cycloaddition reactions of arynes with cyclopropenones followed by electrocyclic ring opening and [4 + 2] cycloaddition of the formed *o*-quinone methides with a second aryne unit (15JOC3730).

The synthesis of xanthene dyes possessing bulky groups at C-3′ and C-7′ involves nucleophilic addition of a 2,6-disubstituted aryllithium



Scheme 58

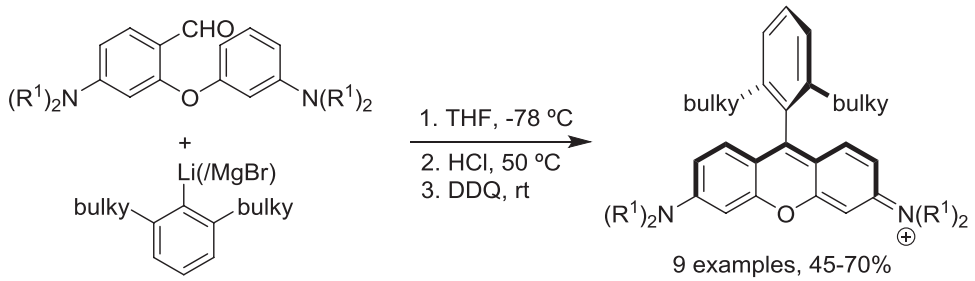


Scheme 59

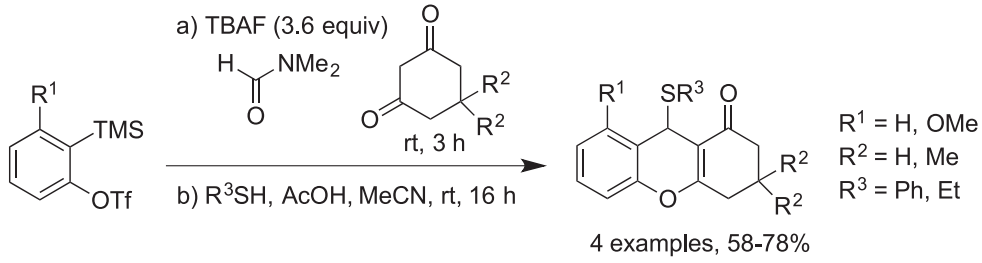
(or magnesium bromide) to 2-aroyloxybenzaldehydes, intramolecular electrophilic aromatic substitution, and oxidation reactions (Scheme 60) (15JOC11538).

A chiral BINOL-derived phosphoric acid catalyzes the chemo- and enantioselective C1,2 cyclization of 2-hydroxybenzyl alcohols with dimedone-derived enaminones to prepare *N*-aryl-1-iminotetrahydroxanthenes (15JOC10016). One-pot four-component reactions of arynes, formed in situ, cyclic 1,3-diketones, DMF, and thiols in the presence of TBAF afford 9-*S*-substituted tetrahydro-1*H*-xanthen-1-ones in good yields (Scheme 61) (15JOC8464). The natural antibiotic rhodomyrtone **31** was obtained by two alternative routes. In the first, an *o*-quinone methide, generated from a dioxaborinine, reacted with syncarpic acid to construct the tetrahydroxanthene-1,3-dione core (Route A). The second approach involved a Knoevenagel condensation of syncarpic acid with a benzaldehyde to form a hemiacetal precursor of the tetrahydroxanthene-1,3-dione moiety (Route B) (Scheme 62) (15T9662).

1-(2-Hydroxyaryl)octa-2,6-dienes undergo a visible light–promoted radical cascade using eosin Y as photocatalyst and hexafluoro-2-propanol as solvent to achieve hexahydroxanthenes in moderate-to-excellent yields (15CEJ14723). The synthesis of several polysubstituted xanthene-type compounds occurs through sulfamic acid–promoted condensation of salicylaldehydes with barbituric acid using a 20:80 mixture of ethanol/water as solvent (15SC868), and a four-component reaction of salicylaldehydes,



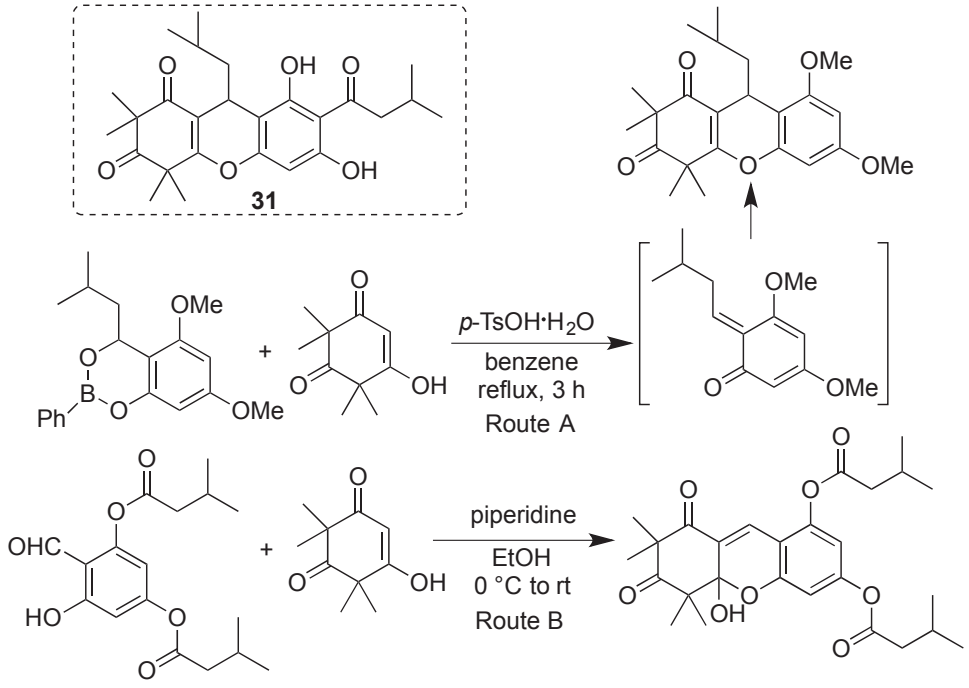
Scheme 60



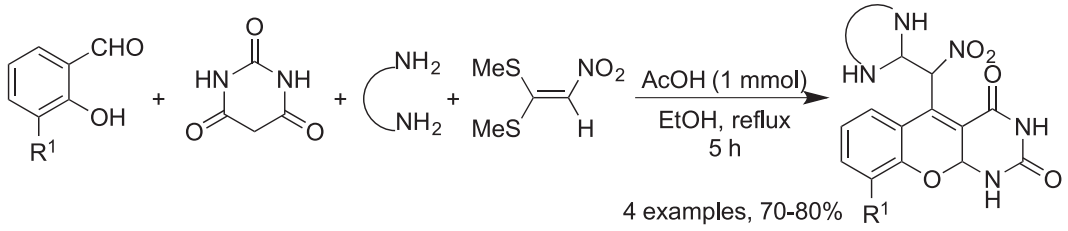
Scheme 61

barbituric acid, diamines, and 1,1-bis(methylsulfanyl)-2-nitroethene in the presence of acetic acid in ethanol (Scheme 63) (15HCA663).

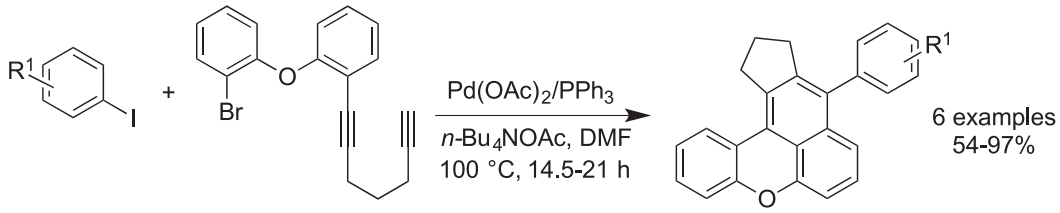
Solvent-free ultrasound-promoted condensation of salicylaldehydes, malononitrile, and secondary amines carried out in the presence of polystyrene-supported *p*-toluenesulfonic acid (*p*-TsOH) gives access to polysubstituted xanthenes (15T2168). The one-pot three-component synthesis of benzo[*c*]xanthene-type derivatives occurs through double heteroannulation of 1-naphthol with alkyl- and arylmethylidenes of malononitrile dimer and aliphatic and aromatic aldehydes in refluxing ethanol (15TL1830). Under solvent-free conditions, one-pot three-component reactions of aromatic aldehydes, dimedone, and naphthols using mesoporous Zr-MCM-41 nanoreactors as catalyst (15SC94), and of 2-hydroxy-1-naphthaldehyde, 1,3-diketones, and various nucleophiles (e.g., indole, naphthols) catalyzed by Amberlite IRA-400 Cl resin (15TL150), delivers a wide range of 12-aryl/heteroaryl-tetrahydrobenzo[*a*]xanthen-11-ones.



Scheme 62



Scheme 63



Scheme 64

A series of indane-fused xanthenes were produced via palladium(II)-catalyzed domino Sonogashira/double carbopalladation/C–H activation reactions of aryl iodides with 1-bromo-2-[2-(hepta-1,6-diyn-1-yl)phenoxy]benzene (Scheme 64) (15H(90)919).

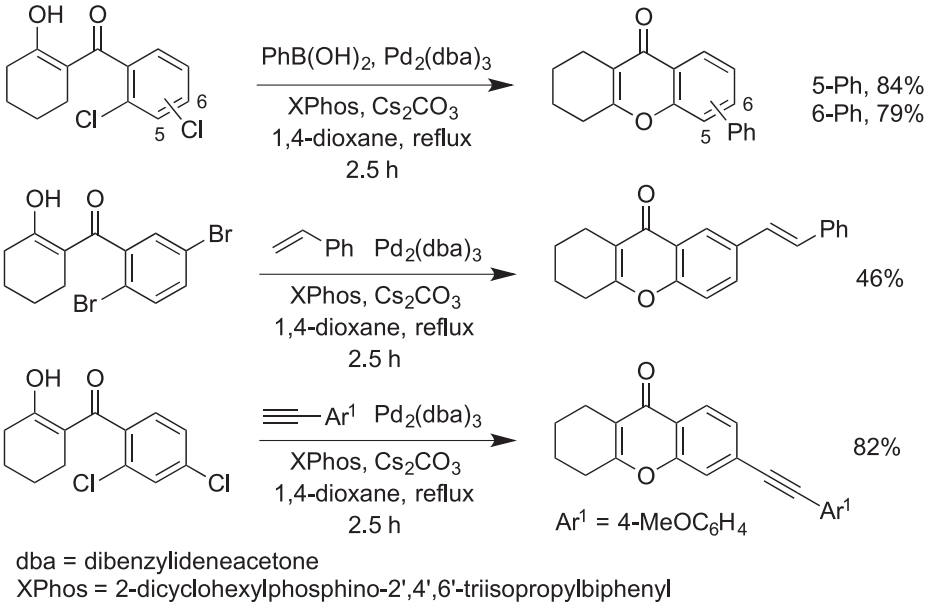
A chiral BINOL-based phosphoric acid catalyst promotes the one-pot reactions of 1-(2-hydroxyphenyl)propargylic alcohols (15OL648) or 1-(2-hydroxyaryl)benzyl alcohols (15CEJ2348) with enamides in dichloromethane at room temperature to prepare polysubstituted acetamidotetrahydrobenzo[*c*]xanthenes with excellent diastereo- and enantioselectivities. Several examples of dibenzoxanthenes arise from the ring opening of 2-(2-hydroxynaphthalen-1-yl) pyrrolidine-1-carboxamides under the action of trifluoroacetic acid and 2-naphthol, in moderate-to-good yields (15T445).

A series of 9*H*-xanthen-9-ones were prepared through microwave-assisted condensation of salicylaldehydes with phenols mediated by ytterbium triflate, under solvent-free conditions (15TL847). Different cross-coupling partners (aryl, alkenyl, and alkynyl) were used in palladium-catalyzed reactions with halogenated 2-haloaryl-(2-hydroxycyclohex-1-enyl)methanones to give tetrahydro-9*H*-xanthen-9-ones substituted at C-5, C-6, or C-7 (Scheme 65) (15T9433). Various *N*-methylmaleimide-fused tetrahydro-9*H*-xanthen-9-ones arise from microwave-assisted DA reactions of 2-(4-arylbut-1-en-3-yn-1-yl)-4*H*-chromen-4-ones and of related 1,2,3-triazole derivatives with *N*-methylmaleimide followed by oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (Scheme 66) (15EJO4732).

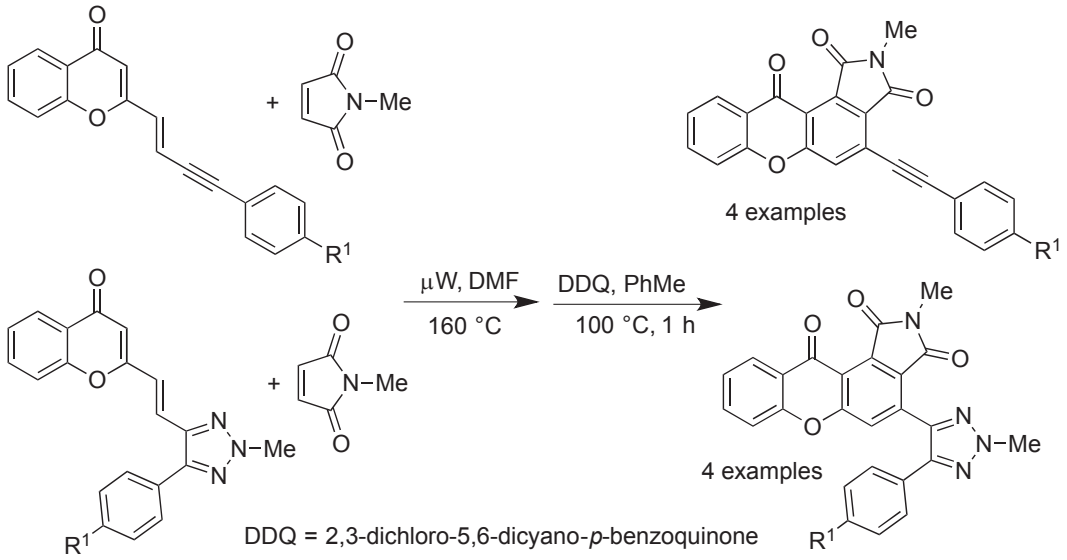
6.4.3 HETEROCYCLES CONTAINING ONE OR TWO SULFUR ATOMS

6.4.3.1 Thiopyrans and Analogs

High yields of a diastereomeric mixture of tetrahydrothiopyranols are obtained from the [3 + 3] annulation reaction of cyclopropane 1,1-diesters with in situ generated mercaptoacetaldehyde promoted by $Sc(OTf)_3$.



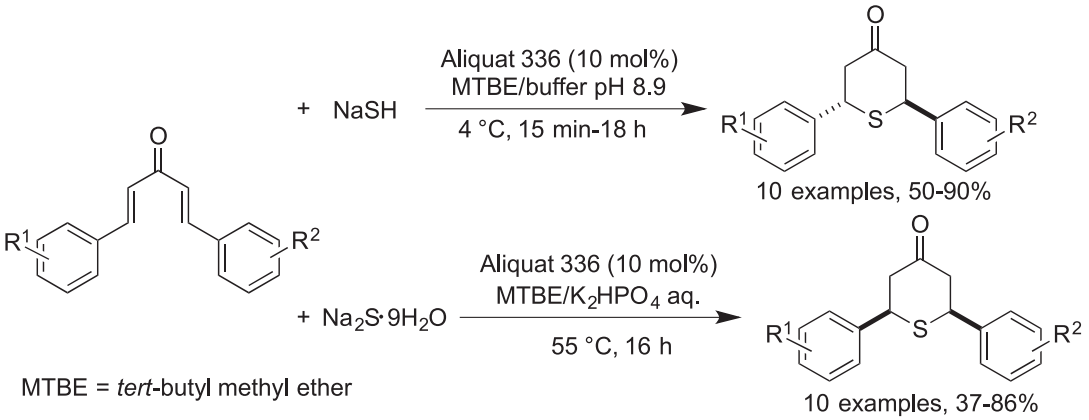
Scheme 65



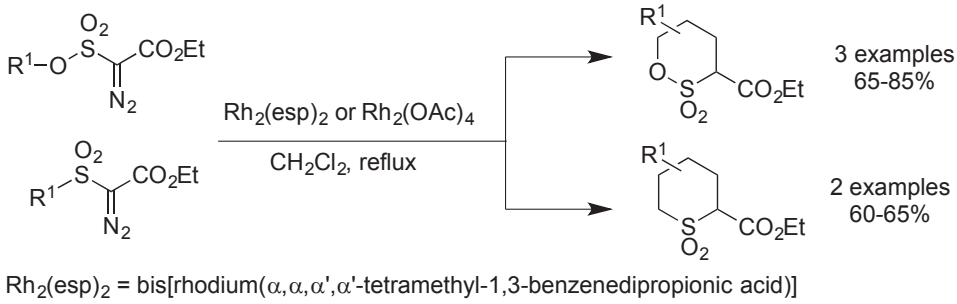
Scheme 66

(15EJO3486). Two diastereoselective strategies under phase-transfer catalysis were applied in the synthesis of 2,6-diaryltetrahydrothiopyran-4-ones. Starting from diarylideneacetones in the presence of Aliquat 336 and using carbonate buffer pH 8.9, NaSH, and MTBE (*tert*-butyl methyl ether) at 4°C gives the *trans*-isomer, while using K_2HPO_4, $Na_2S•9H_2O$ in a mixture of water and MTBE at 55°C affords the *cis*-isomers (Scheme 67) (15EJO1790).

Regioselective $BF_3•Et_2O$-mediated reaction of indoline-2-thiones with unsaturated alcohols and subsequent gold(III)-catalyzed hydroarylation of the formed 2-(pent-2-en-4-yn-1-ylthio)indoles led to a series of indole-fused



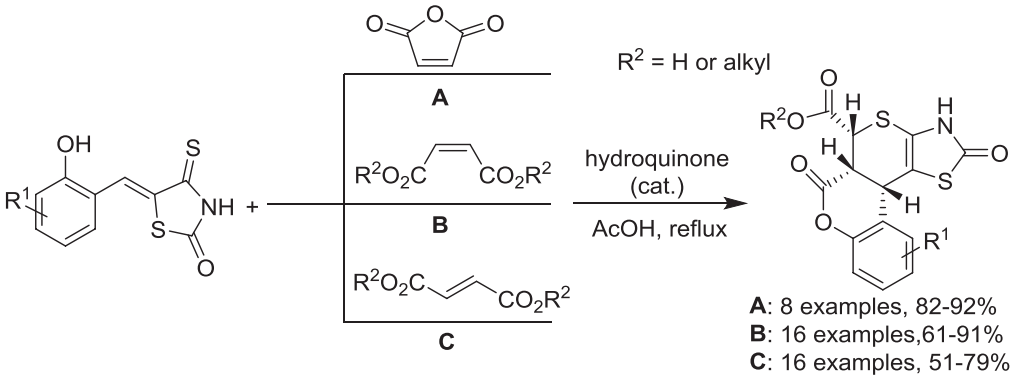
Scheme 67



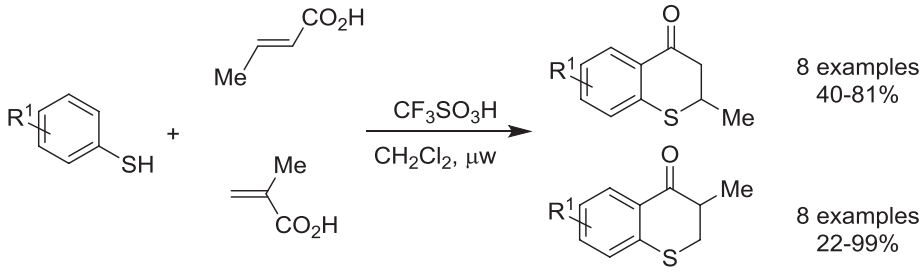
Scheme 68

dihydrothiopyrans (15JOC5272). Enantioselective formal thio [3 + 3] cyclization of indoline-2-thiones with 2-benzylidenemalononitriles catalyzed by a (1*R*,2*R*)-1,2-diphenylethane-1,2-diamine (DPEN)-derived chiral thiourea gives access to thiopyrano[2,3-*b*]indole-3-carbonitriles (15OL42). Rhodium catalysts promote intramolecular C–H insertion of diazosulfones and diazosulfonates to achieve thiane 1,1-dioxides and sultones, respectively (Scheme 68) (15SC226). 4,5-Disubstituted 2*H*-thiopyran 1,1-dioxides are achieved via 6π-electrocyclization reaction of propargyl alkenyl sulfones induced by sodium hydride in a cold solution of DMSO for 10 min (15EJO6017).

A few examples of chroman-fused thiopyran-type compounds came from tandem hDA hemiacetal reaction of 5-(2-hydroxybenzylidene)-4-thioxo-2-thiazolidinones with arylidene pyruvic acids using a catalytic amount of hydroquinone in glacial acetic acid (15SC2266). With the same experimental conditions, other 5-(2-hydroxybenzylidene)-4-thioxo-2-thiazolidinones react with maleic anhydride or maleic and fumaric acid derivatives to afford various dihydrocoumarin-fused dihydrothiopyran-type compounds (Scheme 69). Structurally related derivatives arise from domino reactions of isorhodanine with (2*E*)-4-(2-formylphenoxy)but-2-enoates (15T9501). 5-Hetarylmethylene-4-thioxo-2-thiazolidinones, synthesized by Knoevenagel



Scheme 69



Scheme 70

condensation of 3-phenyl-4-thioxo-2-thiazolidine with 3-aryl-1-phenyl-1*H*-pyrazole-4-carbaldehydes, undergo [4 + 2] cycloaddition reactions with *N*-arylmaleimides, acrylonitrile, or ethyl acrylate to give a variety of functionalized thiopyrano[2,3-*d*]thiazoles bearing a pyrazole unit (15CPB495).

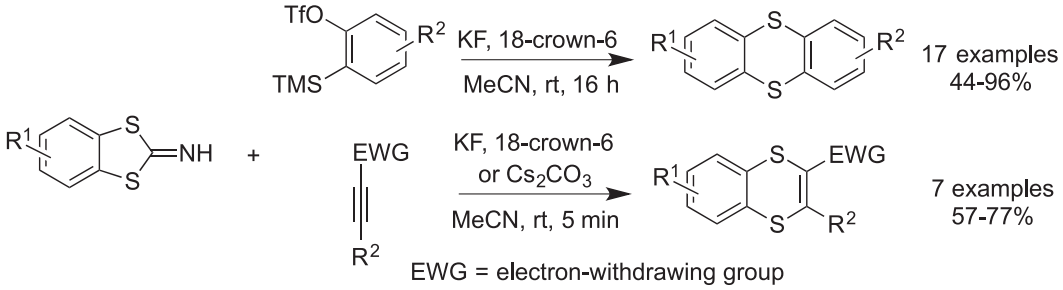
Microwave-promoted one-pot reaction of benzenethiols and crotonic/methacrylic acid carried out in the presence of triflic acid provides 2-/3-methylthiochroman-4-ones in good yields and selectivity (Scheme 70) (15OL6170). A series of 2-arylthiochroman-4-ones were achieved in high yields through copper(II)-catalyzed domino reaction of 2′-iodo/bromochalcones with potassium ethyl xanthogenate, an odorless sulfur source (15OL6006).

Benzodithioloimines react with arynes or alkynes bearing electron-withdrawing groups to give thianthrenes or benzo[*b*][1,4]dithiines, respectively. This metal-free approach was carried out in the presence of KF and 18-crown-6 in acetonitrile (Scheme 71) (15CC9165).

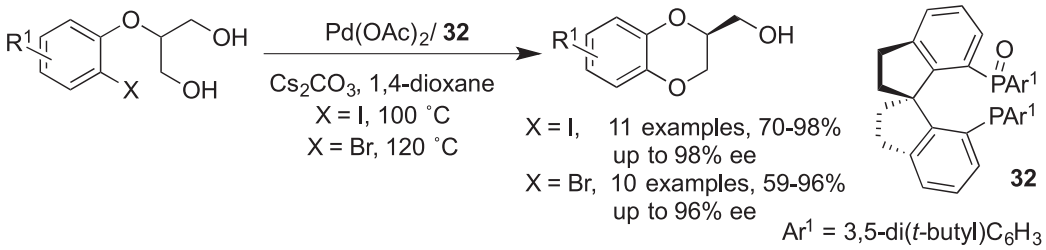
6.4.4 HETEROCYCLES CONTAINING TWO OR MORE OXYGEN ATOMS

6.4.4.1 Dioxanes

A couple of 1,2-dioxanes were obtained through formal [2 + 2 + 2] cycloaddition reactions of a 1,3-dione, an olefin and molecular oxygen, promoted



Scheme 71



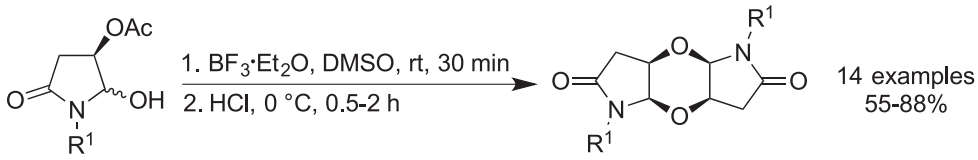
Scheme 72

by light (15OL5420). High yields and enantioselectivity were achieved in the palladium(II)-catalyzed intramolecular reaction of 2-(2-halophenoxy) propane-1,3-diols using a chiral spirodiphosphine monoxide ligand **32**, to prepare functionalized 1,4-benzodioxanes (Scheme 72) (15OL840). Enantioselective synthesis of *cis*- and *trans*-rodgersinine A and B, four natural 1,4-benzodioxane neolignans, were prepared from catechol in six- and eight-step strategies, respectively. These syntheses were essential to assign their absolute configurations and correct those previously described (15OL1046).

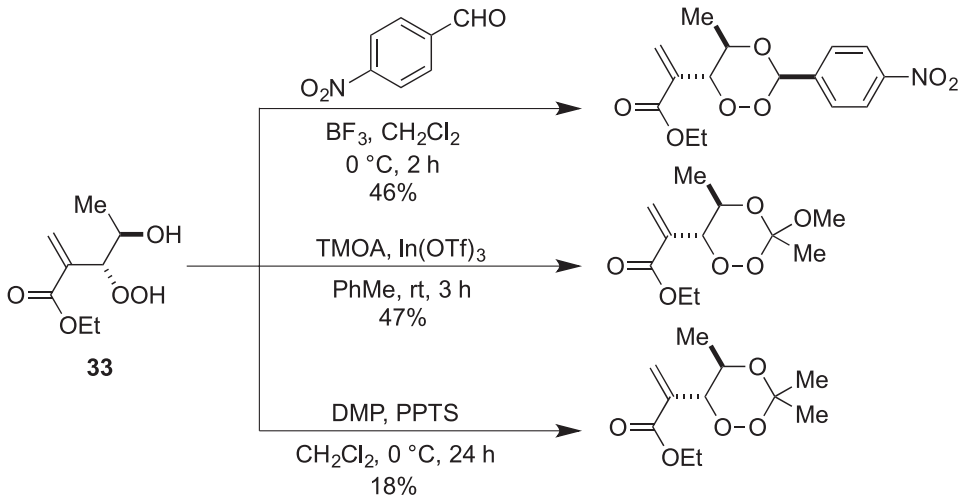
Cyclodimerization of *N*-substituted 4-acetoxy-5-hydroxypyrrolidones mediated by BF_3•Et_2O and HCl affords symmetrical 1,4-dioxanes in moderate-to-good yields (Scheme 73) (15TL1153).

6.4.4.2 Trioxanes and Tetraoxanes

The synthesis of a few enantiomerically pure 1,2,4-trioxepanes occurs in a multistep approach starting from D-glucose. These compounds present interesting antimalarial activity in a micromolar range (15OL4074). Three 1,2,4-trioxanes arise via peroxy(trans)acetalization of allylic hydroperoxide **33** with 4-nitrobenzaldehyde carried out in the presence of BF_3 in dichloromethane, with trimethyl orthoacetate (TMOA) catalyzed by $In(OTf)_3$ in toluene, and with 2,2-dimethoxypropane (DMP) promoted by PPTS in dichloromethane (Scheme 74) (15EJO4349).



Scheme 73



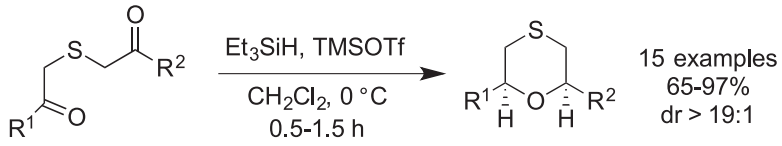
Scheme 74

6.4.5 HETEROCYCLES CONTAINING BOTH OXYGEN AND SULFUR IN THE SAME RING

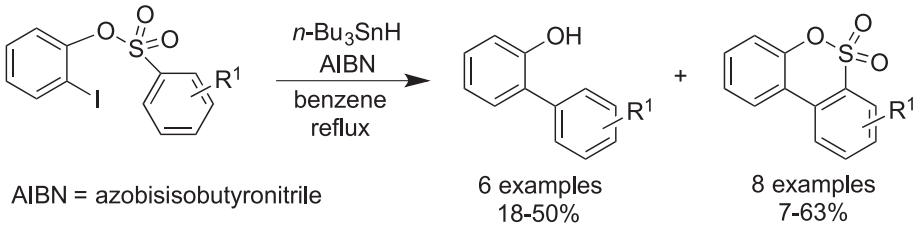
6.4.5.1 Oxathianes

Treating 3-*S*-1,5-diketones with triethylsilane and TMSOTf in dichloromethane at 0°C leads to *cis*-2,6-disubstituted 1,4-oxathianes in good yields, through an intramolecular reductive etherification mechanism (Scheme 75) (15EJO86). A couple of benzobis[1,3]oxathiins were reported from the hDA reaction of the open isomers of benzobisthietes with diethyl mesoxylate in refluxing toluene. A different approach for the synthesis of a simple angular derivative uses the twofold formation of *O*,*S*-acetals from a dihydroxydisulfanyl compound and acetone (15HCA1061). The reaction of *O*-(2-iodophenyl)arylsulfonates with *n*-Bu_3SnH and AIBN in refluxing benzene affords the 1,5-*ipso*-substitution product, 2-arylphenols, or dibenzo[*c*,*e*][1,2]oxathiin 6,6-dioxides, via a 1,6-addition process. The regioselectivity is determined by the position of the substituents on the aromatic acceptor ring (Scheme 76) (15T6701).

A series of functionalized δ-sultones arise from the NHC-catalyzed reaction of trimethylsilyl enol ethers with α,β-unsaturated sulfonyl fluorides, in moderate-to-good yields (15AGE11780).



Scheme 75



Scheme 76

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