PROGRESS IN HETEROCYCLIC CHEMISTRY

VOLUME 32

EDITORS
Gordon W. Gribble & John A. Joule

ELSEVIER

Progress in Heterocyclic Chemistry

VOLUME 32

EDITORIAL ADVISORY BOARD MEMBERS PROGRESS IN HETEROCYCLIC CHEMISTRY

2019-2020

Progress in Heterocyclic Chemistry

VOLUME 32

Edited by

Gordon W. Gribble
Department of Chemistry, Dartmouth College
Hanover, NH, USA

John A. Joule
Department of Chemistry, The University of Manchester
Manchester, UK

ELSEVIER

Elsevier
Radarweg 29, PO Box 211, 1000 AE Amsterdam, Netherlands
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, United Kingdom
50 Hampshire Street, 5th Floor, Cambridge, MA 02139, United States

Notices
Knowledge and best practice in this field are constantly changing. As new research and experience broaden our understanding, changes in research methods, professional practices, or medical treatment may become necessary.

Practitioners and researchers must always rely on their own experience and knowledge in evaluating and using any information, methods, compounds, or experiments described herein. In using such information or methods they should be mindful of their own safety and the safety of others, including parties for whom they have a professional responsibility.

To the fullest extent of the law, neither the Publisher nor the authors, contributors, or editors, assume any liability for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions, or ideas contained in the material herein.

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library

ISBN: 978-0-323-89812-6

ISSN: 0959-6380

For information on all Elsevier publications visit our website at
https://www.elsevier.com/books-and-journals

Publisher: Susan Dennis
Acquisition Editor: Emily McCloskey
Editorial Project Manager: Allison Hill
Production Project Manager: Bharatwaj Varatharajan
Cover Designer: Matthew Limbert

Typeset by TNQ Technologies

Contents

Six-membered ring systems: with *O* and/or *S* atoms

6.4

Clementina M.M. Santos [1,*], *Artur M.S. Silva* [2,*]
[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Bragança, Portugal; [2]QOPNA & LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, Aveiro, Portugal
*Corresponding authors. E-mails: clems@ipb.pt; artur.silva@ua.pt

6.4.1 Introduction

This chapter is dedicated to the synthesis of *O*- and *S*-6-membered heterocycles, covering the literature published during 2019. Highlights include the most interesting chemistry dedicated of these heterocyclic ring systems, from our personal point of view, with special emphasis to the synthesis of natural oxygen derivatives.

Reviews on the isolation, biological properties, biosynthesis, and total synthesis of benzannulated spiroketal natural products (19OBC8272) and of diterpene pyran-2-ones (19OBC8943), on the natural occurrence, pharmacological properties, and structure−activity relationships of quassinoids, a kind of triterpenoid bearing a tetrahydropyran bridge (19CPB654), on the biosynthesis of *Monascus* azaphilone pigment congeners containing chromene frameworks (19NPR561), and on naturally occurring 3-aryl-4*H*-chromen-4-ones isolated after 2012 (19NPR1156), have appeared.

Transition metal vinylidene- and allenylidene-mediated catalysis in the synthesis of various *O*-6-membered compounds (19CR4293), domino transformations using *o*-alkene/alkyne-tethered aryl aldehydes/ketones for the synthesis of *O*-6-membered compounds such as chromans, chromen-4-ones, xanthones, thiochromans, and related fused derivatives (19CEJ15710), and on enzyme-catalyzed cascade reactions for the total synthesis of natural compounds possessing tetrahydropyran, tetrahydroisochromene, and pyran-2-one frameworks (19AGE6846) were also reviewed.

Minireviews on the palladium-catalyzed carbopalladation-initiated cascade processes for the synthesis of chromans and isochromans (19AGE1562), palladium-catalyzed carbonylative coupling reaction for the synthesis of chromans, pyran-2-ones, coumarins, isocoumarins, and chromones (19EJO4626), and palladium-catalyzed double cyclization reactions for the synthesis of heterocycle-fused dihydropyrans, tetrahydropyrans, chromenes, and isocoumarins (19EJO5073) have been disclosed. Other minireviews cover transition metal−catalyzed C−H functionalization reactions in sustainable medium for the synthesis of chromene, isochromene, benzo[*c*]coumarin, and isocoumarin derivatives (19CEJ9366), in-depth discussion of comparative approaches for the synthesis of the natural tetrahydropyran-containing derivatives gelsemine and gelsedine (19AGE681), and 5-*exo* versus 6-*endo*

Progress in Heterocyclic Chemistry. https://doi.org/10.1016/B978-0-323-89812-6.00015-8

thiyl-radical cyclization reactions for the synthesis of dihydrothiopyrans, tetrahydrothiopyrans, and dihydropyran-2-thiones (19HCA1900162).

Recent advances in the synthesis of various *O*-6-membered natural derivatives via carbonylative cyclization reactions (19NPR174), on the synthesis of oxaspirolactones and their application in the total synthesis of related natural compounds (19OBC7270), on polyketide biosynthesis via Michael addition strategies (19NPR531), on α-nitroketones as useful bidentate reagents for the synthesis of chromans, pyran-2-ones, and chroman-4-ones (19OBC5190), on arenediazonium salts as building blocks in transition metal−catalyzed cross-coupling, C-H-arylation, and annulation reactions for the synthesis of benzo[*c*]chromenes and benzo[*c*]coumarins (19CSR1150), on ionic liquids as solvents, catalysts, and reaction media for the synthesis of fused *O*-6-membered heterocycles such as pyrans, chromenes, and xanthenes (19SC1679), on coumarin-based small molecules as fluorescent chemosensors (19CR10403), and on spiropyrans as versatile photochromes (19CSR3406) have all been overviewed.

The literature concerning the total synthesis of natural *O*-6-membered compounds was very rich in 2019. Thus, biomimetic and biocatalytic total synthesis of meroterpenoid bruceol (19AGE1427), biomimetic total synthesis of five meroterpenoid austalides: (±)-17*S*-dihydroaustalide K, (±)-austalide K, (±)-13-deacetoxyaustalide I, (±)-austalide P, and (±)-13-deoxyaustalide Q acid (19JOC4961), biomimetic hetero-Diels−Alder (hDA) reactions for the synthesis of the dihydropyran core of xenovulene A and sterhirsutins A and B (19OL998), biomimetic Knoevenagel/hDA reaction cascades for the total synthesis of chromans, (±)-pestalachloride C, and (±)-pestalachloride D (19OL1755), of psiguajanones A−D and psiguajanol A and subsequent radical dimerization to obtain psiguajdianone (19OL8700), biomimetic total synthesis of isochromen furoerioaustralasine and their structure revision (19OL8776), and biomimetic synthesis of meroterpenoids, including its xanthene moiety, from dimethyl orsellinic acid and farnesyl pyrophosphate (19AGE16141), have all been accomplished.

Several strategies have been developed to build *O*-6-membered heterocycles in the total synthesis of various natural compounds and their analogues, namely pyrans anhydrofusarubin and 8-*O*-methylanhydrofusarubin (19OBC7078), dihydropyrans actinorhodin (19AGE4264), (−)-secologanin, (−)-5-carboxystrictosidine and (−)-rubenine (19CEJ8996), fusarubin and 8-*O*-methylfusarubin (19OBC7078); tetrahydropyrans applanatumol B (19OL6199), aspergillide A (19JOC11848), (−)-englerin A and (−)-englerin B (19AGE8346) and putative structure of scholarein A (19OBC6831), chromenes cannabinol (19OL1212, 19OL6122), fontanesine B and its isomer (19HCA1900116), chromans-revised guignardones H and I (19OL3008), meroterpenoid azamerone (19JA2867), (−)-phomoarcherin C (19JOC14053), wikstrol A and wikstrol B (19OBC8206), isochromenes naphterpin, naphterpin B, naphterpin C, 7-demethylnaphterpin, debromomarinone, and isomarinone (19OL8312), 5,6-dihydropyran-2-ones cryptofolione and (+)-strictifolione (19SC1031), putative structure of diplopyrone (19JOC666), (+)-goniotriol (19TL151039), 5-hydroxy gonithalamin (19S780), parvistone C (19JHC815) and phosdiecin A (19JA13778), tetrahydropyran-2-ones (±)-boschnialactone, (±)-7-*epi*-boschnialactone, (±)-teucrium lactone, (±)-iridomyrmecin, (±)-isoboonein, (±)-7-*epi*-argyol, (±)-scabrol A, (±)-7-*epi*-scabrol A and (±)-patriscabrol (19OBC6831), constanolactone

A (19OBC4572), (+)-goniopypyrone (19TL151039) and (±)-pentalenolactone A (19JOC10172); coumarins dipetalolactone (19JHC99), goniothaline A and goniothaline B (19S552), lamellarin G trimethyl ether, lamellarin D trimethyl ether, lamellarin H, lamellarin η, dihydrolamellarin η, and lamellarin U (19JOC11596), myxocoumarin B (19OBC1966), palodesangren B trimethyl ether and palodesangren D dimethyl ether (19JOC13410), isocoumarins dehydroxanthomegnin and 9-*O*-methylpaepalantine (19EJO1145) and neonectrolides B, C, D and E (19JA15135), dihydroisocoumarins cladosporin (19TL831), (+)-monocerin (19JOC6191) and dihydro eurotiumide B (19JOC16329), and finally, chromen-4-ones integrin and (±)-oxyisocyclointegrin (19EJO1571).

Total synthesis and stereochemical assignment of natural derivatives such as tetrahydropyran cryptoconcatone H with a revised structure (19SL178), 5,6-dihydropyran-2-one tuscoron D (19AGE13019), isochromans (+)-eurotiumide F and (+)-eurotiumide G (19CPB953), tetrahydropyran-2-one tuscoron E (19AGE13019), dihydroisocoumarins granulactone, (±)-radulactone, echinolactone A (19CC4250, 19OL6879) and (±)-calomelanolactone (19CC4250), and chromen-4-ones diaportheone A (19TL52)and parimycin (19OL7665), were also obtained.

Reductive Heck cyclization for the construction of the DEF-benzoxocin ring system of nogalamycin and menogaril (19JOC173), construction of ABCDEF-ring system in the total synthesis of nogalamycin (19JOC760), synthesis of difluorinated tetrahydropyran moieties for the synthesis of various 20,20-difluorinated C17−C27 fragments of natural bryostatin (19OBC1487), synthesis of tetrahydropyran-containing GHIJKL fragment of gymnocin-B (19OL6864), and synthesis of tetrahydropyran unit in the macrolactone core of neopeltolide (19TL432) have all been surveyed.

Discussion on specific reactions such as palladium-catalyzed cyclization reactions for the formation of tetrahydropyran core in the total synthesis of the putative cryptoconcatone H and structural revision of cryptoconcatones K and L (19S1545), organosilane-mediated reactions for the total synthesis of natural tetrahydropyrans bryostatin 8 and (−)-exiguolide (19SL753), palladium-catalyzed oxidative cyclization reaction cascade for the synthesis of benzofuran-fused tetrahydropyrans (19CC7013), tandem allylic oxidation/oxaconjugate addition and macrocyclization reactions for the synthesis of tetrahydropyran-containing macrocycles (19CEJ6500), 1,2-rearrangement and S_NAr oxycyclizations of aryl fluorides to build the chromene unit in the total synthesis of (−)-rotenone and (−)-deguelin and its conversion into (−)-tephrosin and (+)-12a-*epi*-tephrosin (19S1139), annulation reactions for the total synthesis of chromans procyanidins A1 and A2 (19OBC9129), tandem radical cyclization reactions for the synthesis of heterocycle-fused chroman bisabosqual A and some analogues (19T4255), and *O*-annulation strategies through C−H cleavage for the synthesis of xanthenes and xanthones (19S3588), were all accomplished.

Development of specific reagents include a new axially chiral ligand, 6-(2-chloronaphthalen-1-yl)-5-methylpyridine-2-carboxylic acid) for the CpRu-catalyzed dehydrative cyclization of (*E*)-hept-2-ene-1,7-diol to form 2-vinyltetrahydro-2*H*-pyran (19BCSJ1707) and the synthesis and characterization of Pheox- and Phebox−aluminum complexes as tunable Lewis acid catalysts in the competitive hDA reaction of electron-rich with electron-deficient aldehydes for the synthesis of dihydropyran-4-ones (19CEJ10792).

A series of *C*-alkyl coumarin[4]arenes and various derivatives have been synthesized and their fluorescent properties studied (19EJO7787). The importance of the solvent and charge of the xanthene moiety on their photophysical properties was studied in pyridyl and *N*-methylpyridinium analogues of rosamines (19CEJ15073). The synthesis of angular-fused dithioxanthones and their application in organic optoelectronic devices was also undertaken (19OL8832).

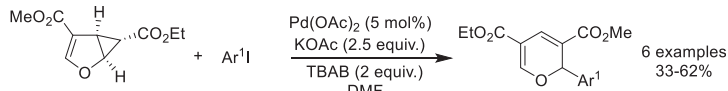
Some biologically important molecules and other complex examples deserve attention. Optically active hexahydro-4*H*-furopyranols were synthesized in a multistep approach from furan and 3-(tetrahydropyranyloxy)propanal (19JOC9801), while the 4*H*-pyran-4-one kojic acid was prepared through a chemo-enzymatic three-step protocol from D-glucose (19CC14737). The enantioselective synthesis and epimerization of highly emissive chiral *S*-shaped [11]helicene-like compounds bearing benzo[*c*]chromene moieties is achieved through intramolecular double [2 + 2 + 2] cycloaddition reactions of a naphth-2-ol-linked hexayne promoted by a rhodium(I)/(*R*)-difluorphos complex (19EJO1390).

Herein, we will provide a broad overview of the most important achievements in the synthesis of *O*- and *S*-6-membered heterocycles based on a personal selection.

6.4.2 Heterocycles containing one oxygen atom

6.4.2.1 Pyrans

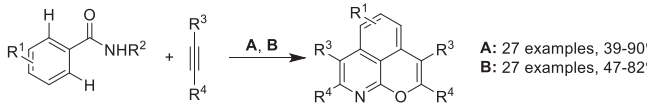
The synthesis of 3,5-disubstituted 2-aryl-2*H*-pyrans is accomplished through a palladium-catalyzed Heck coupling reaction and ring-opening sequence of cyclopropano[*b*]dihydrofurans with aryl iodides using potassium carbonate and tetrabutylammonium bromide (TBAB) in dimethylformamide (DMF) at 40°C for 66 h (Scheme 1) (19AGE3594). Diversely functionalized 2*H*-pyrans result from propargyl Claisen rearrangement/[1,3]H-shift/oxa-6π electrocyclization reaction of tertiary propargyl vinyl ethers in the presence of imidazole in refluxing toluene (19EJO1784).



Scheme 1

Regioselective gold−catalyzed intramolecular hydroarylation of 7-(prop-2-yn-1-yloxy)coumarins in dichloromethane is controlled by the ligand on the gold complex: using JohnPhosAu(MeCN)SbF_6 complex affords mainly coumarino[7,8-*b*]pyrans, although being sensitive in some extent to electronic and steric effects of the arene, while using $Ph_3PAuCl/AgSbF_6$ catalytic system, coumarino[7,6-*b*]pyrans are formed as major products. In addition, intramolecular hydroarylation of 8-iodo-7-(prop-2-yn-1-yloxy)coumarins promoted by JohnPhosAu(MeCN)SbF_6 leads solely

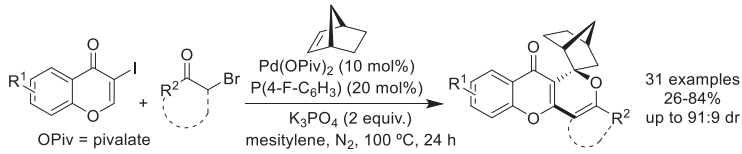
to iodinated coumarino[7,6-*b*]pyrans (19OBC10065). Polysubstituted coumarino [4,5,6-*bc*]pyrans or benzo[*de*]chromenes are provided via cobalt(III)-catalyzed oxidative annulation reactions of 4-hydroxycoumarins or 1-naphthol with alkynes using copper(II) oxide, sodium acetate in 2,2,2-trifluoroethanol (TFE) (19JOC1176). One-pot three-component reaction of 5,7-dihydroxy-4-methylcoumarin with dialkyl acetylenedicarboxylates and aromatic aldehydes mediated by sodium carbonate in refluxing ethyl acetate gives coumarino[7,8-*b*]pyrans (19TL557). The synthesis of pyridino[3,2-*c*]pyrans or quinolono[3,2-*c*]pyrans is accomplished via 6-*endo-dig* iodocyclization and nucleophilic addition reactions of 2-ethynylpyridine-3-carbaldehyde or 2-ethynylquinoline-3-carbaldehyde with sodium azide, molecular iodine, and potassium carbonate in acetonitrile (19TL1854). Double annulation reactions of benzamides without *o*-substitution with unactivated alkynes mediated by ruthenium(II) (19JOC13033) or rhodium(III) (19JOC15697) catalysts provide a wide variety of isoquinoline-fused pyrans (Scheme 2).



A: $[RuCl_2(p\text{-cymene})]_2$ (10 mol%), $AgSbF_6$ (40 mol%), $Cu(OAc)_2{\cdot}H_2O$ (1.5 equiv.), DCE, 120 °C, 24 h
B: $[Cp^*RhCl_2]_2$ (5 mol %), AgTFA (30 mol %), Ag_2O (1 equiv.), $Mg(OAc)_2{\cdot}4H_2O$ (1 equiv.), 1-methylcyclohexane-1-carboxylic acid (1 equiv.), DCE, N_2, 85 °C, 12 h

Scheme 2

Palladium(II)-catalyzed three-component [2 + 3 + 1] domino annulation of 3-iodochromones with α-bromoacetophenones and norbornene leads to spironorbornene chromen-4-ono[3,2-*c*]pyrans in moderate to good yields and with high diastereoselectivity (Scheme 3) (19OL8857).

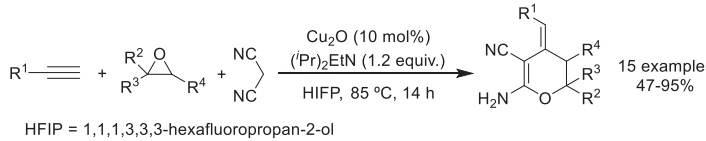


OPiv = pivalate

Scheme 3

A large variety of chiral polysubstituted 3,4-dihydro-2*H*-pyrans were obtained through inverse-electron-demand hetero-Diels−Alder (IED-hDA) reactions, via dienolate catalysis, of β,γ-unsaturated α-keto esters with β,γ-unsaturated amides promoted by a bifunctional thiourea catalyst (19OL7337), with 3-styrylindoles mediated by an imidodiphosphoric acid (19OL5438), and with α,β-unsaturated hydrazones catalyzed by $Eu(hfc)_3$ (19OL4245), and of allyl ketones with alkenyl 1,2-diketones using a bifunctional thiourea catalyst (19OL1979). Copper(I)-catalyzed reaction of terminal

alkynes with oxiranes and malononitrile proceeded in the presence of $(i\text{-Pr})_2$EtN and 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) to afford 4-alkylidene/4-arylidene-6-amino-3,4-dihydro-2*H*-pyran-5-carbonitriles (Scheme 4) (19JHC1850).

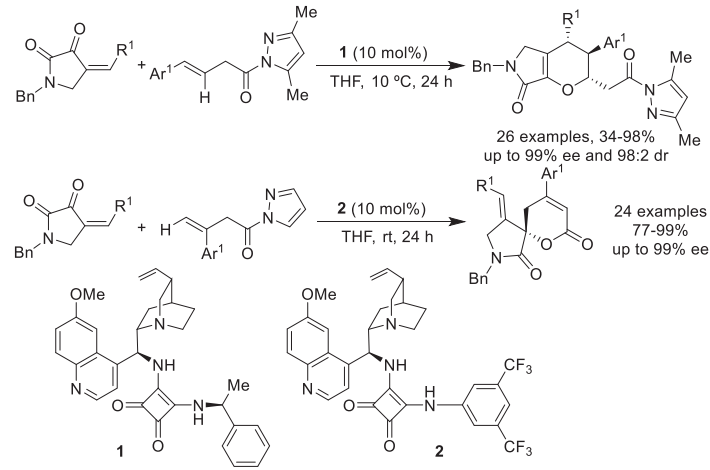


Scheme 4

Palladium-catalyzed intermolecular [4 + 2] formal cycloaddition reaction of allenamides with (*Z*)-3-iodoprop-2-en-1-ols using DMAP in 1,4-dioxane provides 2-amino-substituted 3-methylene-3,6-dihydro-2*H*-pyrans in moderate to good yields (19OBC2651).

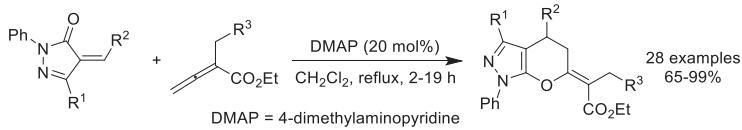
It is through 6-*endo-dig* iodocyclization reaction that (2-alkynylcyclobutyl)methanols in the presence of molecular iodine and sodium bicarbonate in acetonitrile give a series of cyclobutane-fused 5-iodo-3,4-dihydro-2*H*-pyrans (19JOC5712).

Organo-catalyzed regiodivergent vinylogous addition−cyclization reactions of cyclic α-amide enones with *N*-(4-arylbut-3-en-1-yl)acylpyrazoles led to pyrrolidin-2-one-fused 3,4-dihydro-2*H*-pyrans via 1,4-selective γ-addition, while *N*-(3-arylbut-3-en-1-yl)acylpyrazoles via 1,2-selective γ-addition provide spiropyrrolidin-2-one 5,6-dihydro-2*H*-pyran-2-ones (Scheme 5) (19OL10069).



Scheme 5

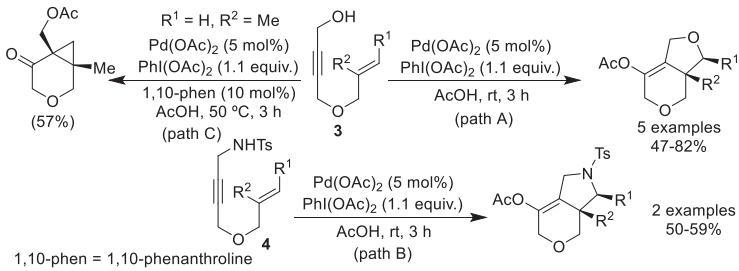
Regiodivergent annulation reactions of 4-hydroxycoumarins with isoprene were promoted by different acids: Brønsted acid [2,4-$(NO_2)_2C_6H_3SO_3H$] in 1,4-dioxane leads to coumarino[4,3-*b*]dihydropyrans, while in the presence of Lewis acid $Sm(OTf)_3$ in 1,2-dichloroethane (DCE), several chromen-4-ono[2,3-*b*]dihydropyrans are obtained (19EJO6510). High yields of 4-alkyl/4-aryl-2-alkylidene pyrazolo[5,4-*b*]dihydropyrans are produced from annulation reactions of alkylidene/arylidene pyrazolones with allenoates mediated by 4-dimethylaminopyridine (DMAP) in dichloromethane (Scheme 6) (19T3609) and by a quinidine catalyst in toluene (19TL703). Domino Knoevenagel/hDA reaction of pyrazolone derivatives with *N*-acrylated anthranilic aldehydes promoted by zinc bromide in refluxing ethanol furnishes tetracyclic tetrahydropyrazolo[4′,3′:5,6]pyrano[3,4-*c*]quinolones, in good yields (19SL1782).



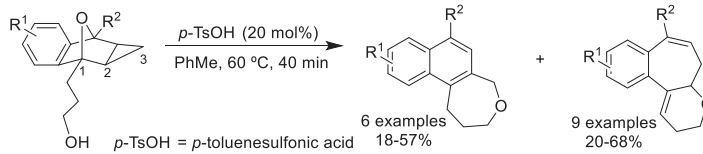
Scheme 6

Palladium(II)-catalyzed intramolecular and selective acetoxylative [3 + 2] annulation reactions of propargyloxy alcohols bearing allyl units, **3**, carried out in the presence of $PhI(OAc)_2$ in acetic acid provide dihydrofurano[3,4-*c*]dihydropyrans (path A), while propargyloxy amines **4** afford pyrrolidino[3,4-*c*]dihydropyrans (path B). The addition of 1,10-phenanthroline to the reaction with **3** led to the synthesis of a single cyclopropane-fused dihydropyran-3-one via oxidative cyclopropanation of the enyne (path C, Scheme 7) (19OL5368). Intramolecular ring-opening reactions of various cyclopropanated oxabenzonorbornadienes bearing an alcohol aliphatic chain promoted by *p*-toluenesulfonic acid (*p*-TsOH) in toluene form two regioisomeric products: attack at C-3 delivers naphthalene[*c*]oxepans, while attack at C-2 results in benzo[3,4]cyclohepta[1,2-*b*]dihydropyrans (Scheme 8) (19TL151228).

Various 2-spirocyclohexanone 4,6-diaryl-3,4-dihydro-2*H*-pyran-5-carbonitriles are prepared via cascade reactions of 2-cyanoacetophenones with 3-styrylcyclohex-2-en-1-ones under dual catalysis of a cinchona alkaloid−derived bifunctional primary amine and *N*-Boc-(L)-*t*-leucine in toluene at 0°C for 5 days (19OBC7849).

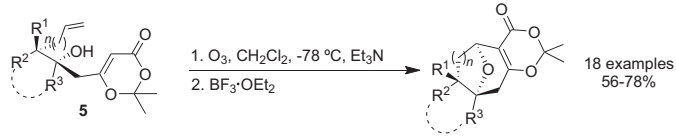


Scheme 7



Scheme 8

Palladium(0)-catalyzed reaction of 4-hydroxy-2*H*-pyran-2-ones with allylic bisacetates carried out in the presence of 1,4-bis(diphenylphosphino)butane and *i*-Pr_2NEt in refluxing 1,4-dioxane provides pyran-2-one-annulated 2-oxabicyclo[3.3.1]nonane derivatives, in good yields (19TL151262). Tandem heterocyclization/[4 + 3] cycloaddition reaction of 2-(1-alkynyl)-2-alken-1-ones with 1,3-diphenylbenzo[*c*]furan promoted by a gold(I)/Ming−Phos complex and $AgBF_4$ in toluene produces chiral tricylic seven-membered oxa-bridged rings (19OL3018). The synthesis of other oxa-bridged bicyclics is achieved via gold(I)-catalyzed tandem rearrangement reactions of 5-aryl-1-(2-propargylaryl)dihydrofurans in the presence of $AgSbF_6$ in DCE (19CEJ9405) and via intramolecular Prins cyclization reactions of dioxinones **5** with ozone in dichloromethane followed by treatment with BF_3•Et_2O (Scheme 9) (19OL1881).

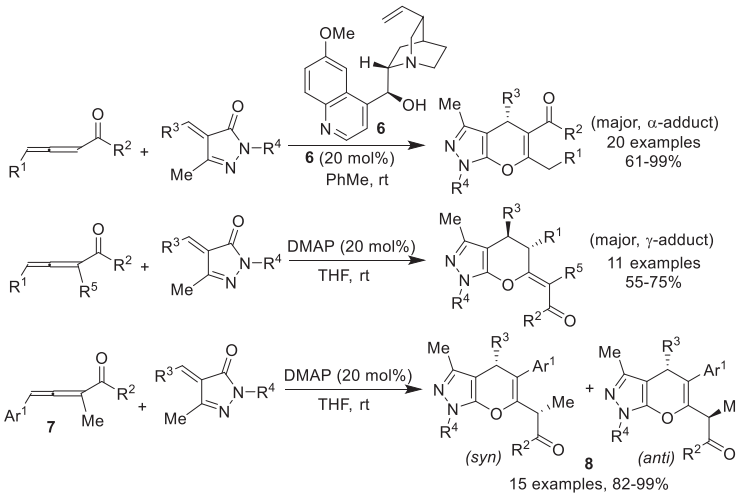


Scheme 9

One-pot three-component reaction of aromatic aldehydes with (*E*)-*N*-methyl-1-(methylthio)-2-nitroethenamine and β-keto esters in the presence of anhydrous $ZnCl_2$ under neat conditions gives 4-aryl-2-(methylamino)-3-nitro-4*H*-pyran-3-carboxylates (19JHC1020). More examples can be prepared by replacing β-keto esters by *t*-butyl 2,4-dioxopiperidine-1-carboxylate using ionic liquid [BMIM]BF_4 in triethylamine (19JHC1393).

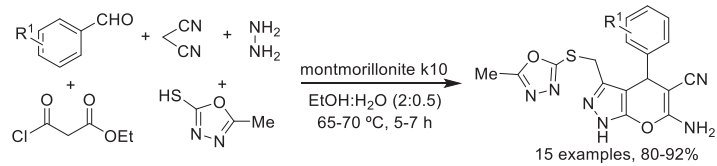
Cyclopentane-1,2-dione undergoes Michael addition reaction with alkylidene malononitriles promoted by a thiourea catalyst followed by intramolecular cyclization to provide cyclopentanone-fused 2-amino-4*H*-pyran-3-carbonitriles, in moderate to good yields (19S4198). Annulative etherification reaction of 2-(3-alkyl/3-arylprop-2-yn-1-yl)cyclopentane-1,3-diones and of 2-(3-arylprop-2-yn-1-yl)cyclohexane-1,3-diones mediated by silver triflate in dry methanol at room temperature provides cyclopentanone-fused and cyclohexanone-fused 2-alkyl/2-aryl-4*H*-pyrans, respectively (19JOC15399). High yields and enantioselectivity is accomplished via [4 + 2] annulation reaction of 2-ylideneoxindole with malononitrile using a cinchonine catalyst in toluene to afford indole-fused 2-amino-4*H*-pyran-3-carbonitriles (19JOC5450). A wide range of pyrazole-fused polysubstituted 4*H*-pyrans are

produced through α- and γ-[4 + 2] formal cycloaddition of allene ketones with 4-arylidenepyrazolones catalyzed by quinine **6** and DMAP, respectively. In the case of α-methyl allene ketones bearing different aryl groups **7**, the reaction afforded the double bond−migrated γ-adducts **8** (Scheme 10) (19OBC3232).



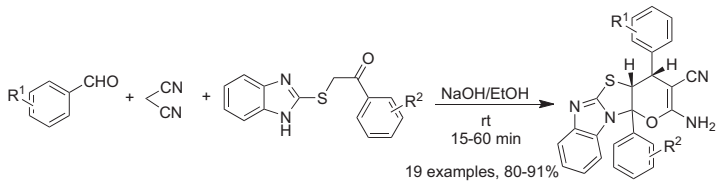
Scheme 10

Under ultrasound irradiation, three-component reactions of 1-aryl-1*H*-1,2,3-triazole-4-carbaldehydes with malononitrile and 5-methyl-2,4-dihydro-3*H*-pyrazol-3-one carried out in the presence of sodium bicarbonate in water produce pyrazole-fused 2-amino-4-(1-aryl-1*H*-1,2,3-triazol-4-yl)-4*H*-pyran-3-carbonitriles, in excellent yields (19SC2521). One-pot multicomponent synthesis of diversely substituted pyrazole-fused 2-amino-4-(hetero)aryl-4*H*-pyran-3-carbonitriles is achieved by reacting benzaldehydes with ethyl acetoacetates, malononitrile, and: i) isoniazid using 2-aminoethanesulfonic acid (taurine) as biocatalyst in water (19SC2244); ii) hydrazine derivatives using water extract of *Agave americana* (century plant) leaf ash as catalyst (19JHC1898); iii) hydrazine hydrate and 5-methyl-2-thiolyl-1,3,4-oxadiazole using montmorillonite k10 as catalyst (Scheme 11) (19JHC1806).



Scheme 11

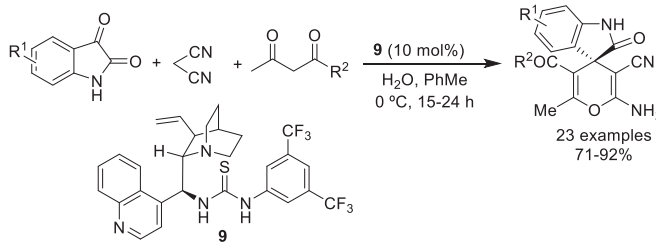
Three-component reaction of benzaldehydes with malononitrile and barbituric acid mediated by 1,4-diazabicyclo[2.2.2]octane (DABCO) in ethanol provides pyrimidine-2,4-dione-fused 2-amino-4-aryl-4*H*-pyran-3-carbonitriles (19JHC3008). Replacing barbituric acid by 3*H*-pyrido[1,2-*a*]pyrimidine-2,4-dione and using ZnO nanoparticles, a series of pyridopyrimidine-fused 2-amino-4-aryl-4*H*-pyran-3-carbonitriles are obtained via a microwave-assisted protocol (19JHC1820). Several thiazolo[3,2-*c*]benzimidazole-fused 2-amino-4-aryl-4*H*-pyran-3-carbonitriles are synthesized through condensation reactions of aromatic aldehydes with malononitrile and 1-aryl 2-[(1*H*-benzo[*d*]imidazole-2-yl)thio]ethan-1-one in the presence of sodium hydroxide in ethanol (Scheme 12) (19OBC4196).



Scheme 12

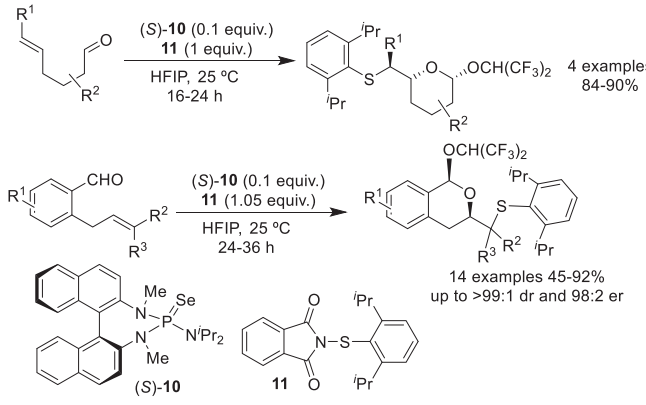
One-pot two-step four-component reactions of 4-hydroxy-6-methyl-2*H*-pyran-2-one with aliphatic amines using solid acid as catalyst in water and with subsequent addition of aromatic aldehydes and malononitrile lead to the synthesis of polysubstituted pyridone-fused 2-amino-4-aryl-4*H*-pyran-3-carbonitriles. Replacing aldehydes by various isatins, various 4-spiroxindolinone derivatives are obtained (19JHC2517). The synthesis of coumarin-fused 4-aryl-3-benzoyl-2-(trifluoromethyl)-4*H*-pyrans is readily available via three-component reaction of benzaldehydes with 4,4,4-trifluoro-1-phenylbutane-1,3-dione and 4-hydroxycoumarin using a catalytic amount of the metal−organic framework TMU-8 and potassium carbonate in ethanol (19JHC1413). Examples of quinolone-fused 2-amino-4-aroyl-4*H*-pyran-3-carboxylates arise from three-component reaction of 4-hydroxyquinolin-2(1*H*)-one with substituted arylglyoxals and ethyl cyanoacetate in the presence of tetrapropylammonium bromide as catalyst in a 1:1 mixture of water:ethanol, at reflux (19JHC268).

Asymmetric addition reactions of 2-(2-oxindolin-3-ylidene)malononitriles with 1,3-dicarbonyl compounds proceeded using barium (*S*)-prolinate as catalyst in difluoroethanol at −20°C to afford 4-spiroxindolinone 2-amino-4*H*-pyran-3-carbonitriles in excellent yields and moderate enantioselectivity (19SL1241). A wide variety of 4-spiroxindolinone 2-amino-4*H*-pyran-3-carbonitrile/3-carboxylates were synthesized through one-pot three-component reactions of isatins with malononitrile/ethyl cyanoacetate and 1,3-dicarbonyl compounds in the presence of sodium carbonate in a 1:1 mixture of water:methanol (19JHC2008) or using a cinchonidine-derived thiourea **9** and water as catalysts in toluene (Scheme 13) (19SC2971).



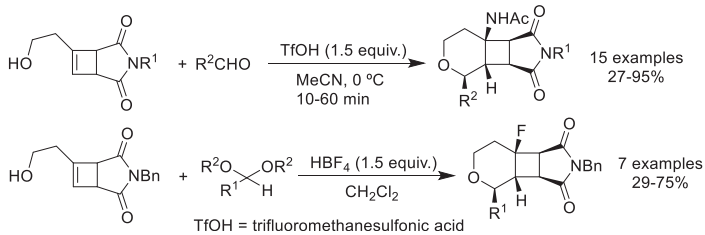
Scheme 13

A four-step protocol was developed for the synthesis of 2,4,5-trisubstituted tetrahydropyrans: i) peptide-catalyzed asymmetric Michael addition reaction of α,β-unsaturated ketones with dimethyl malonate and benzoic acid in THF; ii) transformation of the 1,4-addition products into the corresponding ketals using 2,2-dimethylpropane-1,3-diol and *p*-TsOH in refluxing benzene; iii) reduction of the methyl esters units with lithium aluminum hydride in THF, and finally iv) Kishi's reductive cyclization of the diols formed (19H(99)989). Intramolecular hydroalkoxylation reactions of hepta-5-en-2-ols can be catalyzed by a hexameric resorcin[4]arene capsule and using trace amounts of hydrochloric acid in $CDCl_3$ to furnish 2,2,6,6-tetrasubstituted tetrahydropyrans (19CC3573). Several hex-5-enals underwent cascade sulfenoacetalization reactions in the presence of a Lewis acid and 2,6-diisopropylphenyl-substituted sulfenylating agent in HFIP to give polyfunctionalized tetrahydropyrans via intramolecular capture of thiiranium ion and intermolecular capture of oxocarbenium ion. The reaction was extended to the synthesis of isochroman derivatives starting from 2-(prop-2-en-1-yl)benzaldehydes (Scheme 14) (19AGE12486). Various examples of highly substituted tetrahydropyrans are formed through asymmetric cycloetherification of phenyl (*E*)-5-(di-2-oxoethanyl)pent-2-enoates with acetone cyanohydrin mediated by a thiourea catalyst and molecular sieves as additive in chloroform at room temperature (19OL2156).



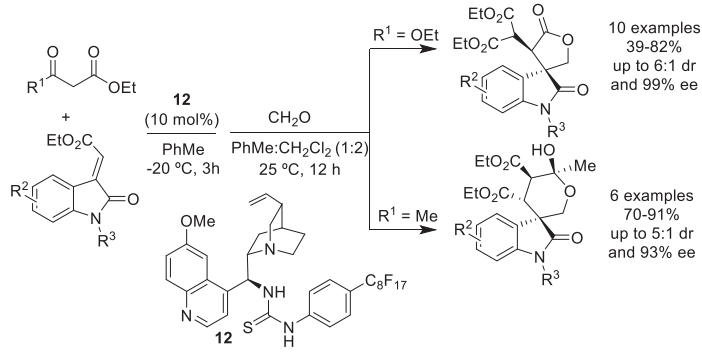
Scheme 14

Diastereoselective synthesis of tricyclic cyclobutane−fused tetrahydropyrans bearing an amide moiety can be achieved through Prins−Ritter cyclization reactions of (2-hydroxyethyl)cyclobutene-type compounds with various aldehydes promoted by trifluoromethanesulfonic (triflic) acid (TfOH) in acetonitrile at room temperature. Using a series of acetals catalyzed by HBF_4 in dichloromethane produces similar tricyclic compounds with a tertiary fluoride (Scheme 15) (19AGE9095). Palladium(0)-catalyzed decarboxylative heterocyclization reaction of [60]fullerene with 2-alkylidenetrimethylene carbonates in 1,2-dichlorobenzene produces [60] fullerene-fused 3-methylenetetrahydrofurans (19CC14498).



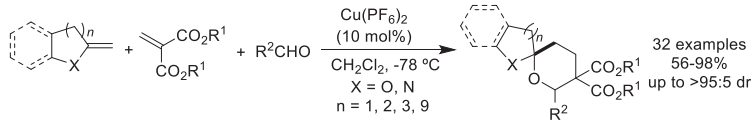
Scheme 15

It is through allylic alcohol transposition, oxocarbenium ion formation, and Prins cyclization that 12-hydroxydodeca-1,10-dien-6-ones in the presence of Re_2O_7 in dichloromethane provide 2-spirocyclohexane 6-vinyltetrahydropyrans, in good yields (19OL5064). Regioselective formal [4 + 2] cycloaddition reactions of nitrostyrene-derived Morita−Baylis−Hillman alcohols with 2-arylideneindane-1,3-dione carried out in the presence of cesium carbonate in chloroform result in 3-spiroindane-1,3-dione 2,4-diaryl-5-nitrotetrahydropyrans (19EJO2234). Bifunctional cinchona alkaloid-thiourea catalyst **12** promotes Michael addition/aldol reaction/cyclization sequence of olefinic oxindoles with diethyl malonate and formaldehyde to give 4-spiroxindolin-2-one 4,5-dihydrofuran-2-one, while replacing diethyl malonate by ethyl 3-oxobutanoate, a series of 5-spiroxindolin-2-one polysubstituted tetrahydropyrans are obtained (Scheme 16) (19EJO150).



Scheme 16

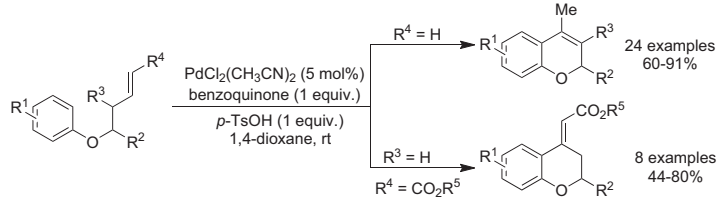
6-Spiroheterocyclic 2,3,3-trisubstituted tetrahydropyrans arise from copper(II)-catalyzed multicomponent reactions of exocyclic enol ethers/enamines with methylene malonates and aldehydes in dichloromethane (Scheme 17) (19AGE15016).



Scheme 17

6.4.2.2 [1]Benzopyrans and Dihydro[1]benzopyrans (chromenes and chromans)

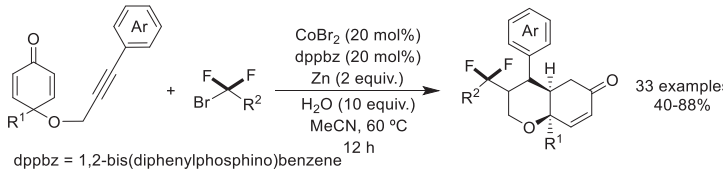
2-(3,3-Diaryl-3-hydroxyprop-1-ynyl)phenols undergo cascade cyclization reactions using *p*-TsOH as promoter and a sulfonate source to give 2,2-diaryl-4-tosyloxy-2*H*-chromenes (19TL331) and using potassium thiocyanate and trifluoroacetic acid (TFA) in nitromethane to afford 2,2-diaryl-4-thiocyanato-2*H*-chromenes (19TL1248). In the last reaction conditions, secondary propargylic alcohols provide 2-aryl-4-thiocyanato-2*H*-chromenes (19TL1248). Palladium(II)-catalyzed C−H alkenylation reactions of 1-(but-3-en-1-yloxy)benzenes or 5-aryloxypent-2-enoates carried out in the presence of benzoquinone and *p*-TsOH in 1,4-dioxane at room temperature furnish 2,3-disubstituted 4-methyl-2*H*-chromenes or 2-(chroman-4-ylidene)acetates (Scheme 18) (19JOC2048).



Scheme 18

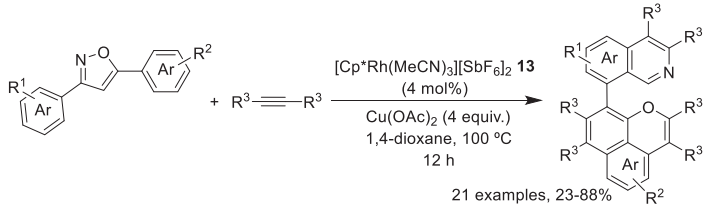
The synthesis of 3-(arylsulfonyl)-2-methyl-2*H*-chromen-2-ols is accomplished via cascade three-component coupling reactions of *o*-silyl aryltriflates with (2-bromoallylsulfonyl)benzenes and DMF using cesium fluoride, at room temperature (19OBC333). Several 4-aryl-2-trifluoromethyl-2*H*-chromenes arise from the reaction of 2-alkyl/2-aryl-1,1,1-trifluoro-4-(2-hydroxyaryl)but-3-yn-2-ols with benzenes using a catalytic amount of TfOH in HFIP at 50°C (19JOC15926). A wide variety of 2-aryl-4-butoxy-3-sulfonyl-2*H*-chromenes were made by a one-pot two-step protocol involving copper(II) acetate/benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP)-mediated intermolecular [4 + 2] annulation reaction of substituted salicylic acids with β-sulfonyl styrenes in the presence of DMAP in refluxing

DMF and subsequent *O*-alkylation of the resulting sulfonyl flavanones with *n*-butyl bromide (19S3419). Rhenium-catalyzed regioselective *o*-alkenylation of phenols, involving a [3 + 2 + 1] cycloaddition reaction of phenols with two equivalents of internal alkynes in chlorobenzene, produces polysubstituted 2*H*-chromenes (19OL3441). Further examples were synthesized via direct nucleophilic substitution of tertiary propargylic alcohols with methoxyphenols in the presence of *p*-TsOH in acetonitrile (19T4071). Diversely substituted 4-aryl-3-difluoroalkyl-2*H*-chromene-type compounds are available through cobalt(II)-catalyzed difluoroalkylation/Giese radical conjugate cyclization reaction of alkyne-*O*-tethered cyclohexadienones with halogenated fluorinating reagents using 1,2-bis(diphenylphosphino)benzene, zinc dust, and water as a catalytic system in acetonitrile (Scheme 19) (19OL5387). Similar starting cyclohexadienones undergo thioarylative radical cyclization with arylthiols mediated by *N*-hydroxyphthalimide in dichloromethane to obtain 4-aryl-3-thioaryl 2*H*-chromene-type compounds (19JOC10509).



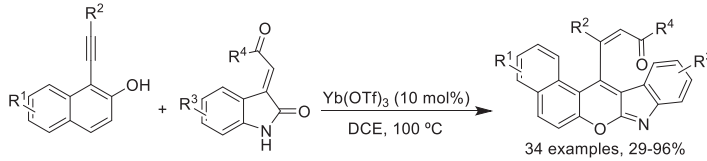
Scheme 19

It is through a thermal-assisted intramolecular benzannulation reaction that diazoacetoacetate enones tethered with *O*-propargylated phenols in xylenes under nitrogen provides substituted 6*H*-benzo[*c*]chromenes, in moderate to good yields (19S4165). Further derivatives are obtained via benzoyl peroxide (BPO)-promoted free radical–based cascade reactions of biaryl vinyl ethers with unactivated alkanes under argon. This protocol was extended to the synthesis of 6*H*-benzo[*c*]thiochromenes starting from the corresponding biaryl vinyl thioethers (19OBC7715). Cascade annulative coupling reaction of 3,5-diarylisoxazoles with three equivalents of internal alkynes occurs in the presence of rhodium complex **13** and copper(II) acetate in 1,4-dioxane to deliver benzo[*de*]chromenes-bearing isoquinoline units (Scheme 20) (19S258). Isoquinolin-8-ones, formed via silver(I)-catalyzed cycloisomerization of *o*-alkynylsalicylaldimines formed in situ, react with one equivalent of acetylenedicarboxylates to provide pyridino[2,3-*de*]chromenes, while when reacted with two equivalents of the alkyne, complex benzo[*de*]chromene-type compounds are obtained (19JOC3184).



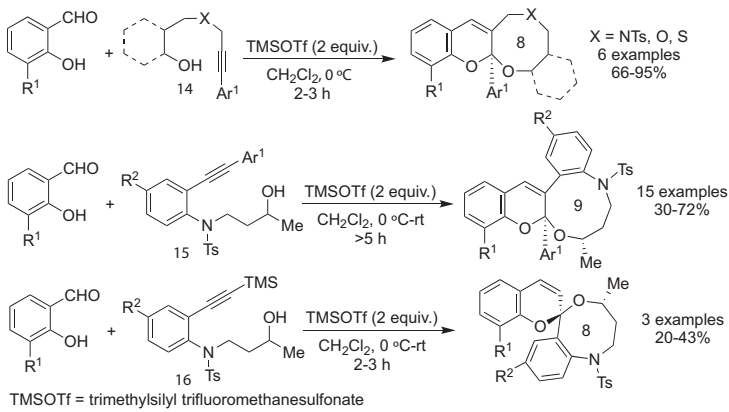
Scheme 20

The palladium(0)-catalyzed [3 + 3] cycloaddition reaction of naphth-1- or 2-ols with vinylethylene carbonates is regioselectively promoted by the 1,3-bis(diphenylphosphino)propane (dppp) ligand and potassium carbonate in trifluoromethylbenzene to provide benzo[*h*]chromenes or benzo[*f*]chromenes, respectively (19CC4675). Tetracyclic 6*H*-naphtho[2,1-*c*]chromenes are obtained in moderate to good yields through three-step cascade reactions of phenol-derived alkynyl substrates with activated aldehydes mediated by BF_3•OEt_2 in dichloromethane. The sequence involves alkyne-Prins cyclization, Friedel−Crafts, and elimination reactions (19JOC15633). Under dual catalysis of a gold(I) complex and zinc(II) triflate, annulation reaction of anthranils with propargyloxy phenols in DCE leads to quinolino[2,3-*c*]chromenes (19OBC4452). A wide variety of pentacyclic indole−fused benzo[*f*]chromenes were synthesized via ytterbium(III) triflate−catalyzed intermolecular [2 + 2] cycloaddition−retroelectrocyclization annulation reactions of *o*-alkynylnaphth-2-ols with 3-methyleneindolin-2-ones in DCE (Scheme 21) (19CC14757).



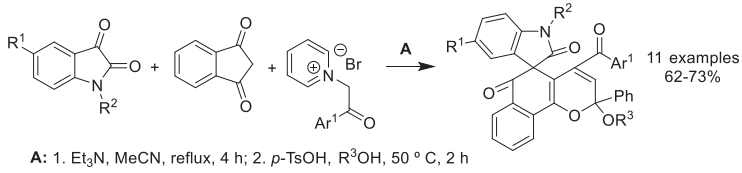
Scheme 21

Structurally diverse eight- and nine-membered heterocycle-fused chromenes can be diastereoselectively prepared through tandem 8-*endo-dig* or 9-*endo-dig* hydroalkoxylation-formal [4 + 2] cycloaddition reactions of X-tethered alkynols **14** (X = NTs, O, S) or **15** (X = NTs) with salicylaldehydes using trimethylsilyl trifluoromethanesulfonate (TMSOTf) as catalyst in dichloromethane. TMS-alkynols **16** underwent an 8-*exo-dig* hydroalkoxylation cascade reaction to give spirocyclic chromenes (Scheme 22) (19OBC8806).



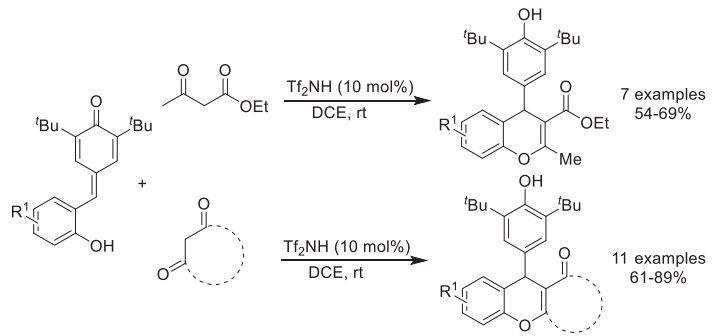
Scheme 22

Oxa-Michael−aldol condensation reactions of salicylaldehydes with sugar-derived 3-*C*-vinyl sugar nitro olefins carried out in the presence of triethylamine under neat conditions afford (2*S*)-2-*C*-spiroglycosyl-3-nitrochromenes, in moderate to good yields (19OBC74). Two-step syntheses of spiroindolinone benzo[*h*]chromene derivatives are accomplished via three-component reactions of *N*-alkylisatins with indane-1,3-dione and two equivalents of *N*-phenacylpyridinium salts in the presence of triethylamine in refluxing acetonitrile, subsequent purification followed by treatment of the obtained residue dissolved in alcohol with *p*-TsOH (Scheme 23) (19OBC3978).



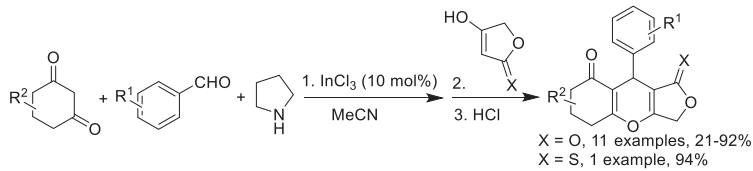
Scheme 23

Three-component reactions of aromatic aldehydes with malononitrile and orcinol derivatives using a catalytic amount of triethylamine in dichloromethane at room temperature afford various 2-amino-4-aryl-4*H*-chromene-3-carbonitriles (19JHC1812). One-pot synthesis of 2-amino-4-aryl-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbonitriles is achieved via a cascade enzymatic reaction of 4-hydroxycoumarin with malononitrile and benzyl alcohols using (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and laccase immobilized on the surface of KCC-1 functionalized magnetic nanoparticles in citrate buffer (19EJO1741). Examples of 2-amino-4-(2-furanone)-4*H*-chromene-3-carbonitriles arise through tandem Knoevenagel/Pinner/vinylogous Michael condensation reactions of salicylaldehydes with malononitrile and butenolides in the presence of sodium *t*-butoxide in 1,4-dioxane (19OBC8853). 1,6-Conjugate addition reactions of 2-hydroxy-*p*-quinone methides with ethyl acetoacetate mediated by Brönsted acid Tf_2NH in DCE lead to ethyl 4-aryl-2-methyl-4*H*-chromene-3-carboxylates. Using cyclic 1,3-diketones instead of ethyl acetoacetate, a series of 2,3,4,9-tetrahydro-1*H*-xanthenone derivatives are obtained (Scheme 24) (19EJO3127).



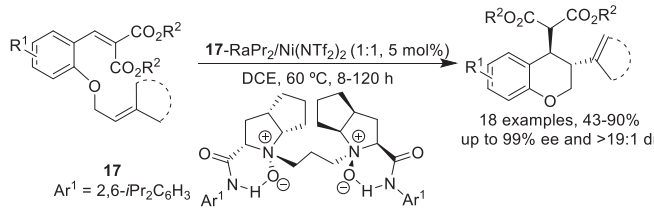
Scheme 24

A one-pot three-step approach was developed for the synthesis of functionalized furanone-fused 4*H*-chromene-type derivatives involving i) reaction of dimedone or cyclohexane-1,3-dione with benzaldehydes and pyrrolidine promoted by indium(III) chloride in acetonitrile at room temperature; ii) addition of tetronic acid derivatives; and finally iii) addition of hydrochloric acid to promote cyclization (Scheme 25) (19T130606). It is through a cascade conjugate addition/ketalization/dehydration process that oxindole-embedded *o*-quinone methides react with 1,3-dicarbonyls using TfOH as catalyst in DCE to provide spiroxindole 4*H*-chromenes (19JOC3990).



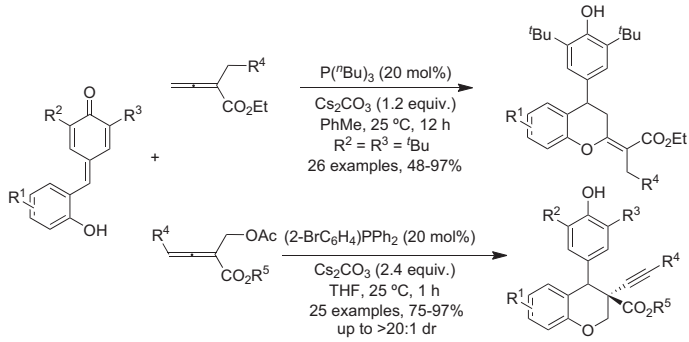
Scheme 25

A one-pot ionic hydrogenation cascade cyclization reaction of 2-hydroxychalcones with Et_3SiH and indium(III) chloride in acetonitrile at room temperature produces 2-arylchromans in moderate to excellent yields. This protocol was extended to 1,5-diarylpentano-1,5-diones to afford 1,6-diaryltetrahydropyrans and to 2-(2-hydroxyaryl)aceto/benzophenones in refluxing conditions to give 6*H*-benzo[*c*] chromenes (19JOC5141). Copper(I)-catalyzed intramolecular asymmetric desymmetrization of 2,2-bis(2-bromoaryl)-3-hydroxypropanenitrile derivatives using a chiral cyclohexane-1,2-diamine as ligand and cesium carbonate as base in 1,4-dioxane furnishes 3-(arylmethyl)chroman-3-carbonitrile-type compounds (19OL8852). A wide variety of 3,4-disubstituted chromans are diastereo- and enantioselectively prepared via intramolecular Alder−ene reaction of 1,7-dienes bearing an oxygen-incorporated tether using a chiral *N*,*N*′-dioxide/nickel(II) complex as catalyst in DCE (Scheme 26). A single example of thiochroman was also prepared in 71% yield, after 10 days of reaction (19CC4479). Reductive chlorination of substituted (3-phenylsulfinyl)propoxybenzenes using $(COCl)_2$ in dichloromethane at 0°C affords *o*-chlorophenol sulfides which underwent Pummerer−Friedel−Crafts cyclization in the presence of $BF_3{\bullet}Et_2O$ to give 4-thiophenylchromans (19OL6903). Various 4-methyl-4-thiophenylmethylchromans are synthesized via palladium-catalyzed carbothiolation of 1-iodo-2-(3-methylbut-3-en-1-yloxy)benzenes with triisopropylsilyl thioethers in the presence of cesium carbonate in toluene at 100°C (19OL8280).



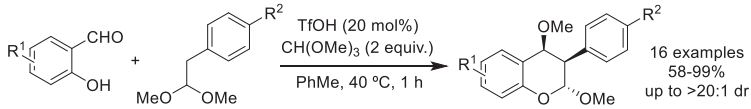
Scheme 26

[4 + 2] Annulation reactions of *p*-quinone methides with α-substituted allenoates via phosphine catalysis and using cesium carbonate as base in toluene provide 2-substituted 4-arylchromans (19OBC2361), while in THF, a series of 3-substituted 4-arylchromans were produced in high yields (19OL908) (Scheme 27).



Scheme 27

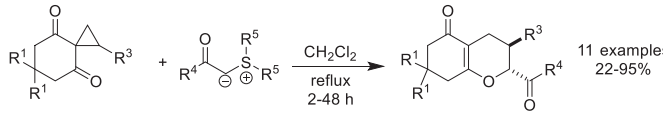
Diversely substituted chromans are readily available through [4 + 2] regioselective cycloaddition reactions using various *o*-quinone methides as starting materials: i) formed from 2-[hydroxy(aryl)methyl]phenols with silver oxide and further reaction with terminal alkenes in ethyl acetate promoted by a thioxanthylium photoredox catalyst under green light LED irradiation (19JOC10669); ii) reaction of salicylaldehydes with terminal alkenes or acetophenones (19JOC13858) or with arylacetaldehyde dimethyl acetals (Scheme 28) (19SL189), TfOH, and trimethyl orthoformate in dry toluene; iii) formed in situ from 2-[hydroxy(aryl)methyl]phenols with 1-styrylnaphth-1-ols in the presence of H_8-BINOL-type chiral imidodiphosphoric acids as catalyst and molecular sieves in toluene (19EJO7264); iv) formed in situ from 2-[hydroxy(alkyl/aryl)methyl]phenols with methyl (*S*,*E*)-3-[dimethyl(phenyl)silyl]hex-4-enoate mediated by anhydrous iron(III) chloride in the presence of 2,6-lutidine in chloroform (19OL32); and v) formed from chemoenzymatic transformation of *o*-cresols into benzylic alcohols, followed by the loss of water and subsequent reaction with terminal alkenes (19JA20269).



Scheme 28

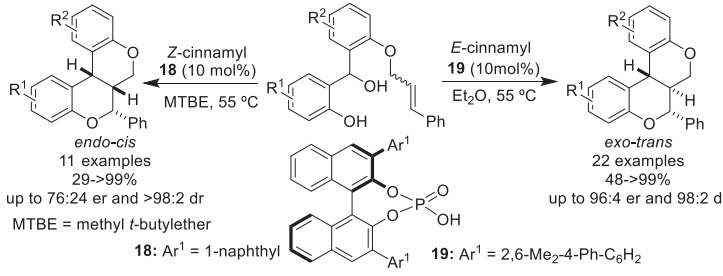
Regioselective ring-opening cyclization of cyclohexane-1,3-dione-2-spirocyclopropanes with stabilized sulfonium ylides in refluxing dichloromethane leads to 2,3-*trans*-disubstituted chromans (Scheme 29) (19CC6539). The synthesis of 3,4-*trans*-disubstituted chroman-type derivatives can be accomplished through

rhodium(I)-catalyzed diastereoselective arylative cyclization of enone-tethered cyclohexadienones with boronic acids carried out in the presence of 2,2′-bis(diphenylphosphino)-1,1′-binaphthalene, potassium *t*-butoxide, and water in 1,4-dioxane (19OBC1937).



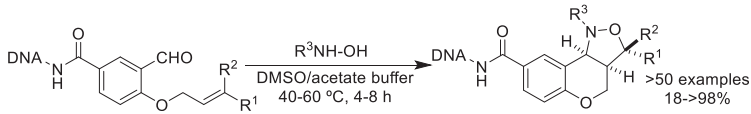
Scheme 29

Polysubstituted benzo[*h*]chromans are available through silver(I)-catalyzed cyclization of 2-alkenylphenyl alkynyl ketones, as *o*-naphthoquinone methides intermediates, with styrenes in pentane, in moderate to excellent yields (19OL1488). Electrophilic aromatic substitution of phloroglucinol with (−)-verbenol followed by cyclization is promoted by TfOH in dichloromethane (19EJO2289) or TMSOTf in a 4:1 mixture of nitromethane:THF (19OL563) to afford the corresponding benzo[*c*]chroman-type derivative. Replacing phloroglucinol by resorcinol halides, halide regioisomers of benzo[*c*]chromans are obtained (19EJO2289). Intramolecular hDA reaction of *o*-quinone methide precursors tethered by a simple phenoxy linker with unactivated dienophiles is diastero- and enantioselectively achieved depending on the dienophile configuration and catalyst used to obtain *endo*- or *exo*-stereoisomers of chromanochromans (Scheme 30) (19JOC7175).



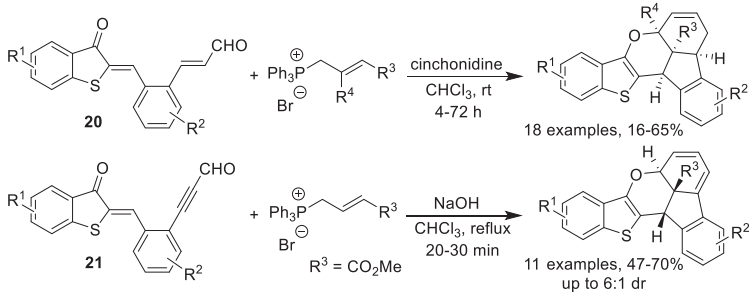
Scheme 30

[3 + 2] Nitrone−olefin cycloaddition reactions of DNA-linked 2-(prop-2-en-1-yloxy)salicylaldehydes with various hydroxyamines in acetate buffer led to a large library of DNA-conjugated isoxazolidine-fused chromans (Scheme 31) (19OL1325). Other isoxazolidine-fused chromans arise from visible light (LED)-promoted intramolecular cycloaddition reactions of salicylic nitrones bearing an *o*-prop-2-en-1-yloxy group in the presence of catalytic amounts of $Ru(bpy)_3Cl_2$ in acetonitrile (19OL1388).



Scheme 31

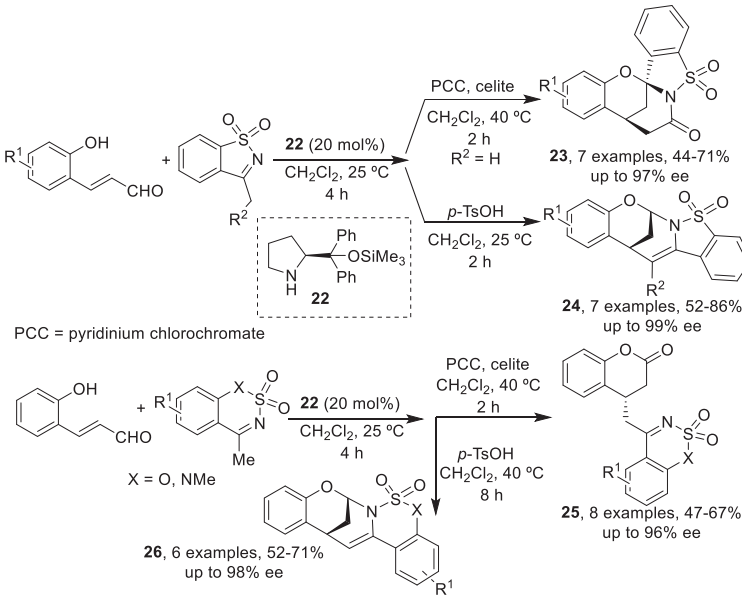
A range of spiroindolinone-furan−fused chromans are synthesized through tandem reaction of diazoindolinones with *O*-propargyl salicylaldehydes in the presence of copper(I) thiophene-2-carboxylate in refluxing DCE (19OBC8088) and of 3-cinnamyl-3-hydroxyindolinones with salicylaldehydes mediated by copper(II) triflate and acetic acid in refluxing dichloromethane (19JOC879). One-pot multicomponent cascade reactions of hydroxyketones with 2-hydroxychalcones proceed in the presence of bismuth triflate in ethyl acetate to form pentacyclic chromanfuran−fused chromans in moderate to good yields (19CC5207). Hexacyclic benzothiophene-fused indane-fused chromans are obtained from quadruple domino reactions of thioaurones bearing an α,β-unsaturated aldehyde as substituent **20** with allylic phosphonium salts and using cinchonidine in chloroform. Similar derivatives are obtained using thioaurones containing a propargyl aldehyde group **21** and sodium hydroxide as catalyst (Scheme 32) (19CEJ9665).



Scheme 32

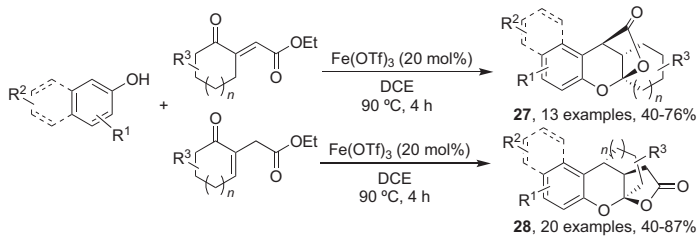
The synthesis of complex 2,8-oxabicyclo[3.3.1]nonane derivatives can be achieved through cascade reactions of 2-hydroxycinnamaldehydes with i) β-oxo aldehydes mediated by multiple organocatalysts (19OL6750); ii) with keto esters organocatalyzed by prolinol derivatives. If the reaction contains *m*-chloroperoxybenzoic acid (*m*-CPBA), 2,7-dioxabicylco[3.2.1]octane derivatives are obtained instead (19OL190). 2-Oxabicyclo[3.3.1]nonanes can be synthesized via domino Knoevenagel−hDA reactions of 2-allylbenzaldehydes with 1,3-diketones promoted by iron(III) chloride (19OBC5684). Similar compounds were obtained from organocatalytic asymmetric reaction of *o*-hydroxybenzylidene acetones with 3-hydroxyindolin-2-ones (19EJO2552). Under neat conditions, multicomponent quadruple domino reactions of 3-(2-formylphenoxy)acrylates with acetylenedicarboxylates and phenyl hydrazine furnish pyrazole annulated 2,8-oxabicyclo[3.3.1]nonanes (19OBC3884). Asymmetric

organo-catalyzed reaction of 2-hydroxycinnamaldehydes with five-membered cyclic *N*-sulfonyl ketimines using aminocatalyst **22** followed by oxidation with pyridinium chlorochromate (PCC) provides pentacyclic-bridged aminals **23** while dehydration catalyzed by *p*-TsOH leads to bridged aminals **24**. Using six-membered cyclic *N*-sulfonyl ketimines, oxidation with PCC affords dihydrocoumarins **25** while dehydration with *p*-TsOH gives pentacyclic-bridged aminals **26** (Scheme 33) (19OL5556).



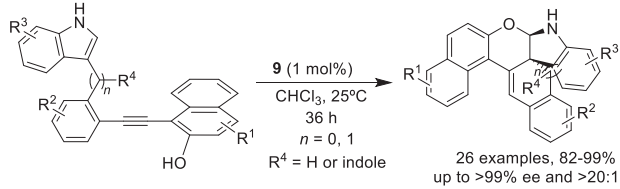
Scheme 33

Iron(III)-catalyzed Friedel−Crafts alkylation−hemiketalization−lactonization cascade reactions of electron-rich hydroxyarenes with functionalized unsaturated 4-keto esters in DCE produce polycyclic doubly bridged chromanol lactones **27** and **28**, in moderate to good yields (Scheme 34) (19OL2629).



Scheme 34

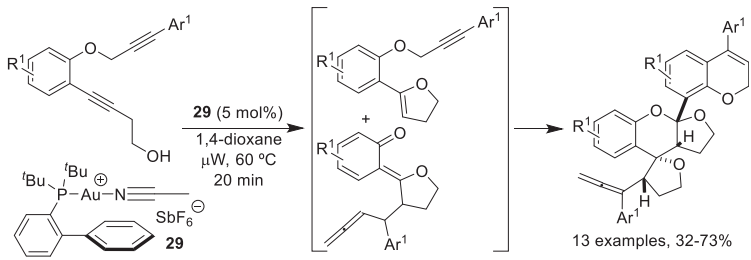
Under low loading of cinchonidine-derived thiourea catalyst **9**, a large variety of complex indole-fused benzo[*f*]chroman derivatives were prepared through one-step desymmetrizing dearomatization reaction of indoles with vinylidene *o*-quinone methides derived from 1-(phenylethynyl)naphth-2-ol in chloroform at 25°C (Scheme 35) (19AGE216).



Scheme 35

Treating 5-(2-allyloxyaryl)-3-oxopentanoates or 6-(2-allyloxyaryl)-4-oxobuta-2-ones with *trans*-1,4-dibromobut-2-ene and potassium carbonate in DMSO and subsequent addition of $Pd(PPh_3)_4$ and potassium carbonate in ethanol affords spirotetrahydrofuran chromans (19OL2872). A variety of spiroisoxazolone chromans are readily available via domino oxa-Michael/1,6-addition reactions of *o*-hydroxyphenyl-substituted *p*-quinone methides with unsaturated isoxazolones carried out in the presence of triethylamine in ethanol (19T682). Replacing isoxazolones by barbiturates, various spirobarbiturate chromans are obtained (19T130752). Asymmetric synthesis of spironaphthalenone benzo[*f*]chromans is accomplished through dearomatization of (*S*)-1,1′-bisnaphth-2-ols [(*S*)-BINOLs] with α-alkyl/arylpropargyl carbonates using a palladium complex in DCE at 50°C (19OL9188).

Microwave-assisted hDA cascade reactions of 2-(4-hydroxybut-1-en-1-yl)-1-propargyloxybenzenes promoted by gold(I) complex **29** deliver complex spirotetrahydrofuran tetrahydrofuran−fused chromans (Scheme 36) (19OL6084).

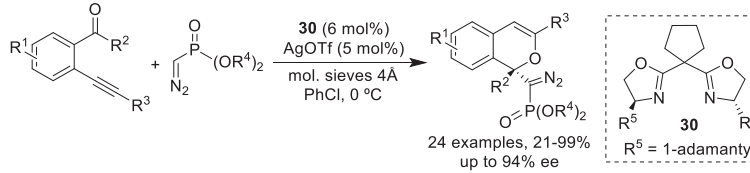


Scheme 36

6.4.2.3 [2]Benzopyrans and Dihydro[2]benzopyrans

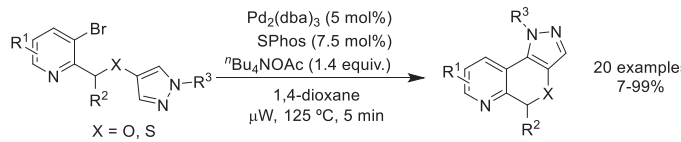
(**Isochromenes and Isochromans**).

2-(But-3-en-1-yn-1-yl)benzamides undergo copper(II)-catalyzed regioselective 6-*endo-dig* *O*-cyclization reactions in refluxing toluene to provide *N*-substituted 3-vinyl-1*H*-isochromen-1-imines (19S4058). High enantioselectivity is achieved in the asymmetric cyclization/nucleophilic tandem reaction of *o*-alkynylacetophenones with (diazomethyl) phosphonates promoted by a chiral bis(oxazoline) ligand **30** and silver triflate in chlorobenzene, giving access to a variety of isochromenes bearing a tetra-substituted stereocenter and (diazomethyl) phosphonate at C-1 (Scheme 37) (19OL7597).



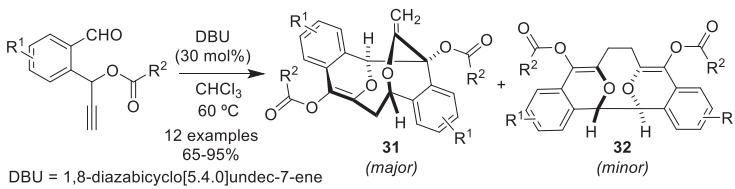
Scheme 37

One-pot synthesis of 1,5-dihydropyrazolo[3′,4′:5,6](thio)pyrano[3,4-*b*]pyridines is accomplished through microwave-assisted, palladium(0)-catalyzed regioselective C−H heteroarylation of 3-bromo-2-{[(1-alkyl/1-aryl-1*H*-pyrazol-4-yl)(thio)oxy]methyl}pyridines carried out in the presence of SPhos ligand and Bu_4NOAc in 1,4-dioxane (Scheme 38) (19JOC5855).



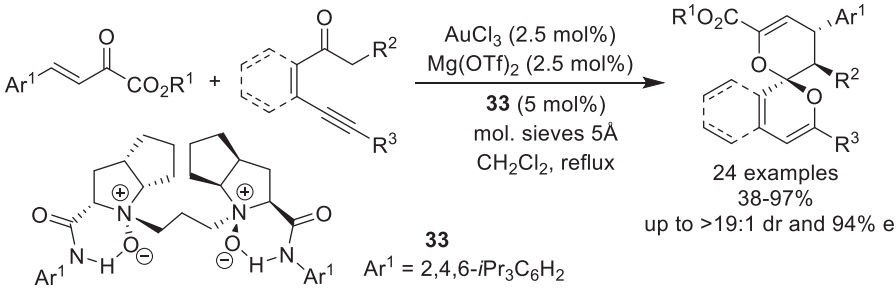
Scheme 38

o-[1-(Acyloxy)propargyl]benzaldehydes undergo selective dimerization reactions promoted by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in chloroform in air, to produce a mixture of complex bischromene-bridged products **31** and **32** (Scheme 39). A couple of heteraldehyde derivatives were also used and only the major product was obtained (19JOC11114).



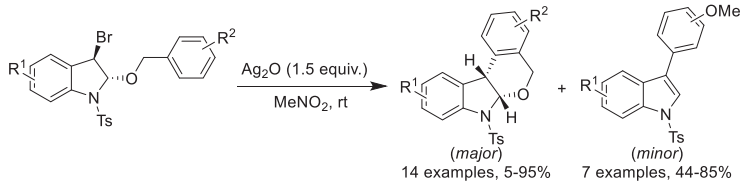
Scheme 39

Rhodium(III)-catalyzed dehydrogenative cyclization of 2-aryl-1-(2-hydroxyaryl) ethane-1,2-diones with diarylacetylenes proceeded using $AgSbF_6$ and copper(II) acetate in DCE at 130°C to provide spirobenzofuranone isochromenes (19AGE2660). A wide variety of spirodihydropyran isochromenes were synthesized under dual catalysis of an achiral gold(III) salt and chiral *N*,*N*′-dioxide-magnesium(II) complex via enantioselective tandem reaction of β,γ-unsaturated α-keto esters with β-alkynyl ketones in refluxing dichloromethane. It involves cycloisomerization and intermolecular [4 + 2] cycloaddition reactions (Scheme 40) (19AGE4017).



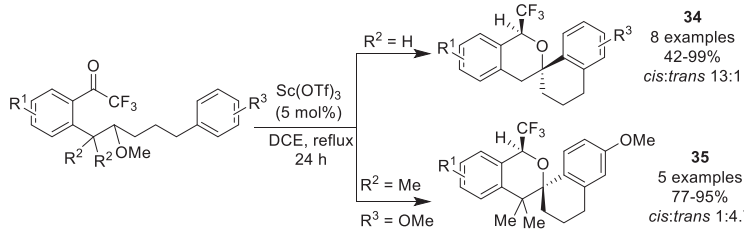
Scheme 40

A huge variety of multifunctional 1-arylisochroman-3-ones arise from one-pot carboxy-Pictet–Spengler reaction of arylacetic acids with arylaldehydes or ketones in acetonitrile at room temperature (19JOC11687). Dirhodium(II)-catalyzed [3 + 3] annulation reactions of diazocarbonyl compounds with cyclopropane dicarboxylates carried out in the presence of scandium triflate and ytterbium triflate in toluene produce cyclohexane-fused isochroman-4-ones (19AGE6225). Treating ninhydrin with *N*-methyl-*C*-aryl nitrones and secondary amines in anhydrous THF results in the synthesis of 3,3-disubstituted isochroman-1,4-diones, in good yields (19JHC2333). Tandem Friedel–Crafts reactions and stereoselective acetalization of β-arylaldehydes with aliphatic or aromatic keto acids mediated by TfOH in toluene provided a series of 1,3-(epoxymethanone)isochromans (19SL2091). The synthesis of dihydropyrano [4,3,2-*ij*]isochromans occurs through a multistep strategy involving cascade reactions of aryl iodides without *o*-substitution with chiral epoxides as the alkylating reagents and terminal alkynes to form C_2-symmetrical bis-alkylated phenylacetylenes and subsequent bicyclization using $Pd(PhCN)_2Cl_2$ as catalyst. When using (*S*)-glycidol instead of 2-alkyloxiranes, novel (1,3-epoxymethyl)isochromans are obtained (19OL8938). Tetrahydro-1*H*-4a,8a-(epoxyethano)isochromans are prepared in high yields and with excellent diastereoselectivity from 3-ene-1,6-diols and aromatic and aliphatic aldehydes through a Prins bicyclic annulation reaction (19EJO3567). Intramolecular Friedel–Crafts-type cyclization of 2-benzyloxy-3-bromo-*N*-tosylindolines mediated by Ag_2O in nitromethane delivers mainly indolino[2,3-*c*]isochromans. Moreover, when a methoxy group is present in the benzyl moiety, deformylative arylation takes place to afford 3-arylindoles (Scheme 41) (19SL2247).



Scheme 41

It is through [1,5]-hydride shift/cyclization/intramolecular Friedel−Crafts reaction strategy that 2′-(5-aryl-2-methoxypent-1-yl)-2-trifluoromethylacetophenones in the presence of scandium triflate in refluxing DCE produce spirotetrahydronaphtho-1-trifluoromethylisochromans, in moderate to excellent yields. The absence of substituents in the benzylic position ($R^2 = H$) favors the formation of the *cis*-isomer **34**, while the presence of substituents in that position ($R^2 = Me$) favors the formation of the *trans*-isomer **35** (Scheme 42) (19OL2383).

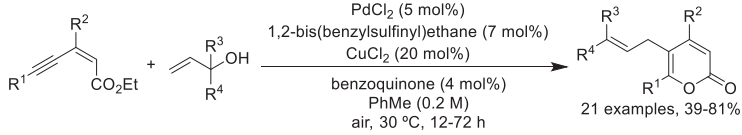


Scheme 42

6.4.2.4 Pyranones

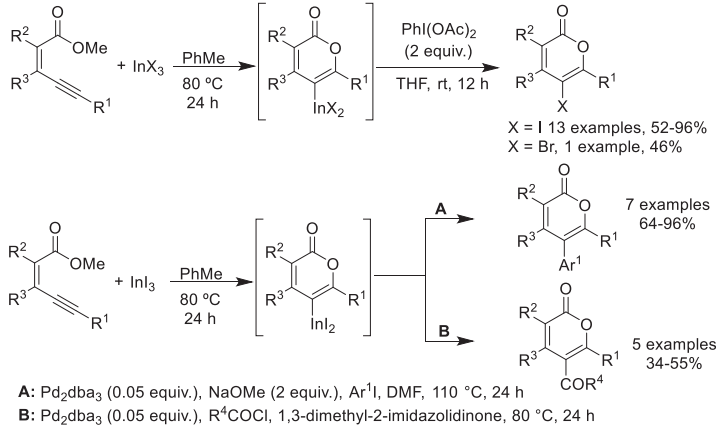
Various 4-*O*-glycosylated 6-substituted-2*H*-pyran-2-ones are prepared from gold(I)-catalyzed rearrangement reaction of glycosyl 3-oxopent-4-ynoate derivatives in dichloromethane at room temperature (19JOC14141).

The synthesis of 4-pyrrolo-substituted 3,6-disubstiuted 2*H*-pyran-2-ones is achieved through [4 + 2] cycloaddition reaction of 3-pyrrolosubstituted 1-arylprop-2-ynones with diethyl malonate using potassium hydroxide in acetonitrile (19TL151126). $PdCl_2$-catalyzed cascade intramolecular cyclization and allylation reactions of ethyl (*Z*)-pent-2-en-4-ynoates with allylic alcohols carried out in the presence of 1,2-bis(benzylsulfinyl)ethane, copper(II) chloride, benzoquinone, and toluene under air furnish 6-substituted 5-allyl-2*H*-pyran-2-ones, in moderate to good yields (Scheme 43) (19JOC6729).



Scheme 43

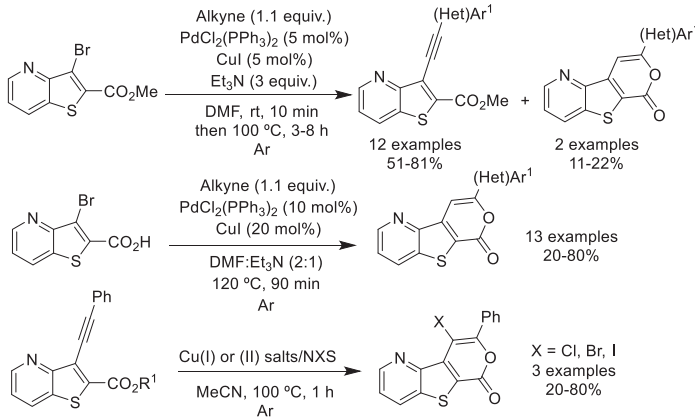
One-pot palladium(II)-catalyzed Sonogashira coupling reactions of ethyl (*Z*)-4-aminosubstituted-3-iodobut-2-enoates with terminal alkynes afford the corresponding 3-ethynyl esters which undergo intramolecular iodocyclization in the presence of ICl at room temperature to provide a series of 4-aminomethyl-substituted-5-iodo-6-substituted 2*H*-pyran-2-ones (19TL151087). Tandem palladium(II)-catalyzed Sonogashira coupling reactions of (*Z*)-4-aminosubstituted-3-iodobut-2-enoic acids with terminal alkynes are dependent on the nature of the alkyne: aryl-substituted alkynes underwent 5-*exo-dig* cyclization at 55°C to give *N*-amino-substituted γ-alkylidenebutenolides; linear aliphatic or cyclohexyl-substituted alkynes at 55°C undergo 5-*exo-dig* and 6-*endo-dig* cyclization to give a mixture of *N*-amino-substituted γ-alkylidenebutenolides and 6-substituted 2*H*-pyran-2-ones, while at 35°C only 6-*endo-dig* cyclization occurs to form *N*-amino-substituted-6-substituted 2*H*-pyran-2-ones (19EJO7439). Highly functionalized 2*H*-pyran-2-ones arise from electrochemical vinylic C−H functionalization reaction of acrylic acids with alkynes catalyzed by an iridium(III) complex in the presence of *n*-Bu_4NOAc in methanol (19JA18970). Other derivatives were synthesized through intramolecular oxymetalation of methyl pent-2-en-4-ynoates using indium trihalides in toluene to afford 5-metalated 2*H*-pyran-2-ones that underwent subsequent halogenation or palladium-mediated cross-coupling with aryl iodides or acid chlorides (Scheme 44) (19JOC14330).



Scheme 44

Oxidative [4 + 2] annulation reactions of isoxazole-4-carboxylic acids with internal alkynes using $[Cp^*RhCl_2]_2$ as catalyst, silver carbonate as base in DMF at 100°C delivers isoxazolo[4,5-*c*]pyran-2-ones (19CC8382). High yields of 6-phenyl-5-selanyl-substituted quinolino[3,2-*c*]pyran-2-ones are obtained from the seleno-cyclization reaction of methyl 2-phenylethynylquinoline-3-carboxylates with molecular iodine and diorganyl diselenides in refluxing dichloromethane (19OBC9039). Domino double C−H activation reactions of *N*-substituted 1*H*-indole-3-carboxylic acids with acrylates proceed in the presence of $Pd(OAc)_2$ catalyst,

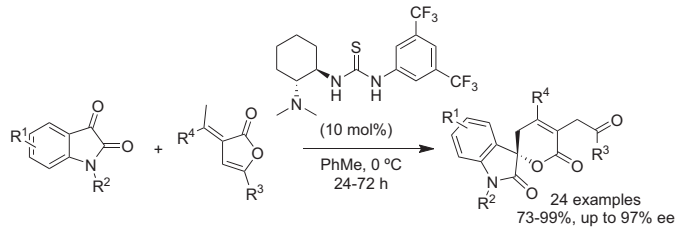
an *N*-monoprotected amino acid−derived ligand, and a benzoquinone derivative in acetonitrile to provide *N*-substituted indolo[3,2-*c*]pyran-2-ones (19OL2847). Highly substituted coumarino[3,4-*f*]pyran-2-ones arise from molecular iodine−mediated tandem cyclization reactions of aryl methyl ketones with 4-hydroxycoumarins in DMSO, in moderate to good yields (19T130756). Tandem Sonogashira coupling reactions of methyl 3-bromothieno[3,2-*b*]pyridine-2-carboxylate with (het)arylalkynes led to methyl 3-[(het)arylethynyl]thieno[3,2-*b*]pyridine-2-carboxylates as major products along with the 6-*endo-dig* lactonization product 8-(het)aryl-6*H*-pyrano[4′,3′:4,5]thieno[3,2-*b*]pyridines, in minor amounts. Moreover, replacing the ester by the corresponding carboxylic acid, tandem Sonogashira coupling and 6-*endo-dig* lactonization occurs to obtain solely 8-(het)aryl-6*H*-pyrano[4′,3′:4,5]thieno[3,2-*b*]pyridines. In addition, halolactonizations of 3-(arylethynyl)thieno[3,2-*b*]pyridine-2-carboxylic acid or carboxylate using copper(I) or copper(II) salts/*N*-halosuccinimides afforded the 9-halogenated lactones (Scheme 45) (19T1387).



Scheme 45

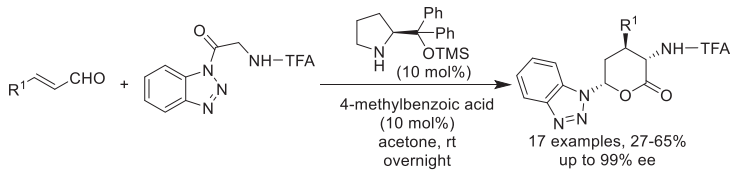
Enantioselective tandem reaction of α,β-unsaturated Meldrum's acid derivatives with terminal alkynes promoted by CuI, AgOAc, and (*S*)-MeStackPhos in dichloromethane provides 4,6-disubstituted 3,4-dihydro-2*H*-pyran-2-ones (19AGE9485). Various 4,5,6-trisubstituted 3,4-dihydro-2*H*-pyran-2-ones can be prepared from *N*-heterocyclic carbene (NHC)-catalyzed annulation reactions of propanoyl chloride derivatives with 1,3-dicarbonyl compounds in the presence of cesium carbonate, 3,3′,5,5′-tetra-*t*-butyl-[1,10-bi(cyclohexylidene)]-2,2′,5,5′-tetraene-4,4′-dione in a 4:1 mixture of dichloromethane:toluene at room temperature (19CC298). Other NHCs catalyze [4 + 2] reactions of 1-benzyl-4-ylidenepyrrolidine-2,3-diones with azlactones in chloroform to give 2-oxopyrrolidino[4,3-*e*]dihydro-2*H*-pyran-2-ones (19OBC3945). α,β-Unsaturated ketones derived from thioisatin underwent IED−hDA reactions with azlactones under *N*-methylmorpholine catalysis in dichloromethane to form benzothiophene-fused 3,4-dihydro-2*H*-pyran-2-ones. The enantioselective version

was also developed by applying quinine-derived catalysts (19EJO6592). Organocatalyzed sequential vinylogous aldol reaction/transesterification of isatins with methyl-substituted olefinic butyrolactones led to a series of 6-spiroxindolin-2-one 5,6-dihydro-2*H*-pyran-2-ones, in high yields and enantioselectivities (Scheme 46) (19CC9327).



Scheme 46

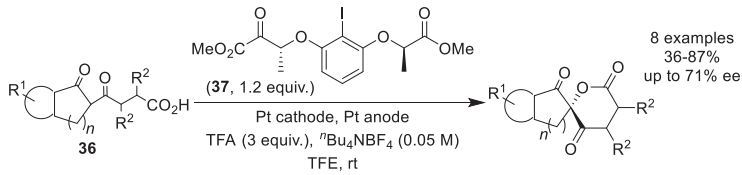
Synthesis of a wide range of 6-alkyl/aryl-6-(bromomethyl)tetrahydro-2*H*-pyran-2-ones was accomplished via regioselective bromolactonization reactions of δ-unsaturated carboxylic acids under low loading of the organoselenium compound di(*endo*-3-camphoryl) diselenide catalyst in the presence of NBS in acetonitrile (19JOC11373). Regio- and enantioselective thiolactonization reaction of (*E*)-5-alkyl/5-arylpent-4-enoic acids with *N*-phenylthiosaccharin as sulfenylating agent is cocatalyzed by chiral Lewis base BINAM−derived selenide and Brønsted acid $EtSO_3H$ in dichloromethane at −10°C to deliver 6-substituted 5-thiophenyltetrahydropyran-2-ones (19CEJ15411). Under the same conditions, a couple of 6-[aryl(phenylthio)methyl]tetrahydropyran-2-ones were obtained when reacting (*E*)-6-arylhex-5-enoic acids with 2-(phenylthio)isoindoline-1,3-dione as sulfenylating agent (19CC9367). Chiral 6-benzotriazolo-3-*N*-TFA-4-substituted tetrahydro-2*H*-pyran-2-ones are obtained via organocatalyzed cascade reactions of *N*-TFA-protected glycine-benzotriazole derivatives with α,β-unsaturated aldehydes in the presence of 4-methylbenzoic acid in acetone at room temperature (Scheme 47) (19JOC10526).



Scheme 47

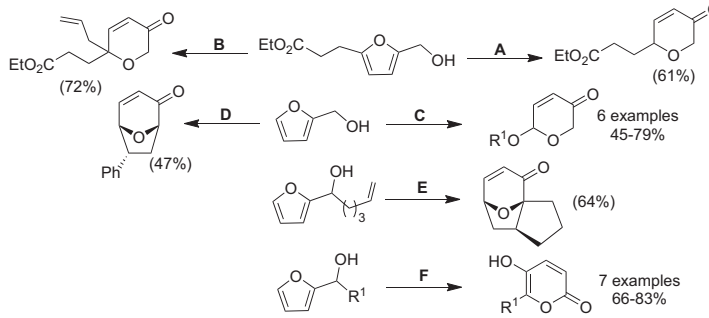
Under dual catalysis of NHC and copper salts, asymmetric [3 + 3] annulation reactions of isatin-derived enals with ethynylethylene carbonates proceeded in triethylamine and fluorobenzene at 10°C to produce spiroindolin-2-one 3-ethynyltetrahydro-2*H*-pyran-2-ones (19AGE12190). Enantioselective electrochemical spirolactonization of

4,6-dioxoacid derivatives **36** using chiral iodoarene **37** as redox mediator in TFE delivers spiro tetrahydropyran-2,5-diones (Scheme 48) (19S276).



Scheme 48

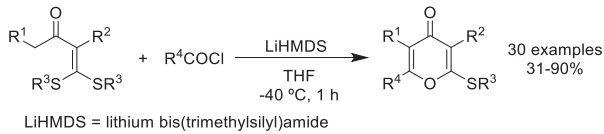
Several one-pot strategies were developed to promote Achmatowicz rearrangement (AchR) of furfuryl alcohol derivatives in the presence of silica gel and KBr/oxone under near anhydrous conditions (Scheme 49): i) AchR−Kishi reduction using BF_3•Et_2O and Et_3SiH to give 2,6-dihydropyran-3-one (path A); ii) AchR−Ferrier allylation using BF_3•Et_2O and allyl silane to give 6-allyl-2,6-dihydropyran-3-one (path B); iii) AchR-acylation/palladium(0)-catalyzed *O*-glycosylation using $(Boc)_2O$ and DMAP to give 6-*O*-substituted 3,6-dihydropyran-3-ones (path C); iv) AchR--acylation-[5 + 2]-cycloaddition reaction using acetic anhydride, Et_3N, and styrene (path D) or using acetic anhydride and DABCO (path E) to give cycloalkane-fused 3,6-dihydropyran-3-ones; and v) AchR-TEMPO oxidation to give 5-hydroxypyran-2-ones (path F, Scheme 49) (19T1669). High yields and diastereoselectivity is accomplished via dirhodium(II)-catalyzed oxonium ylide formation-[2,3]-sigmatropic rearrangement reaction of 6-alkyl/6-aryl-substituted 6-allyloxy-2-diazo-3-keto esters in dichloromethane at room temperature to provide 6-substituted 2-allyl-3-oxotetrahydropyran-2-carboxylates (19T2436).



A: 1. KBr, oxone, silica gel, $NaHCO_3$, CH_2Cl_2, rt; 2. BF_3·OEt_2, Et_3SiH, rt
B: 1. KBr, oxone, silica gel, $NaHCO_3$, CH_2Cl_2, rt; 2. BF_3·OEt_2, allylSiMe_3, rt
C: 1. KBr, oxone, silica gel, $NaHCO_3$, CH_2Cl_2, rt; 2. DMAP, Boc_2O; 3. alcohol, $Pd(PPh_3)_4$, PPh_3, rt
D: 1. KBr, oxone, silica gel, $NaHCO_3$, DMF, rt; 2. Et_3N, Ac_2O, styrene, rt
E: 1. KBr, oxone, silica gel, $NaHCO_3$, DMF, rt; 2. Ac_2O, DABCO, rt
F: 1. KBr, oxone, silica gel, $NaHCO_3$, MeCN:DMF (10:1), rt; 2. TEMPO, rt
TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl

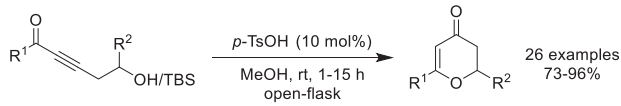
Scheme 49

The synthesis of 2-(1,3-dioxolan-4-yl)-4*H*-pyran-4-ones occurs through $AgSbF_6$/$Rh_2(OAc)_4$-promoted tandem 6-*endo-dig* cyclization/cycloaddition reaction of 2-diazo-3,5-dioxo-6-ynoates/ynamides/ynones with two equivalents of aldehydes in dichloromethane under nitrogen (19EJO3979). Replacing aldehydes by *N*-phenyl-*N*,*N*-disubstituted amines, various 2-[4-disubstituted aminophenyl(acyl) methyl]-4*H*-pyran-4-ones are formed (19EJO6871), while using alkenes, 2-(cyclopropyl)-4*H*-pyran-4-ones are obtained (19T855). Formal [4 + 2] cyclization reactions of ketene dithioacetals with acyl chlorides promoted by lithium bis(trimethylsilyl)amide (LiHMDS) in THF furnishes a series of polysubstituted 4*H*-pyran-4-ones, in moderate to good yields (Scheme 50) (19JOC9603).



Scheme 50

In open-air conditions, intramolecular rearrangement reactions of δ-hydroxyalkynones promoted by *p*-TsOH in methanol give access to 6-substituted ($R^2 = H$) or 2,6-disubstituted ($R^2 \neq H$) 2,3-dihydro-4*H*-pyran-4-ones (Scheme 51) (19JOC3537).

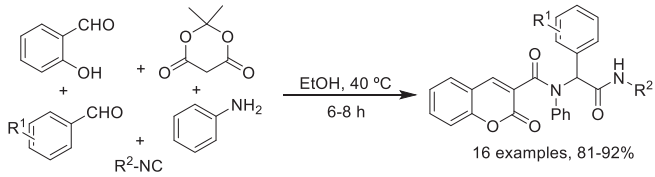


Scheme 51

6.4.2.5 Coumarins

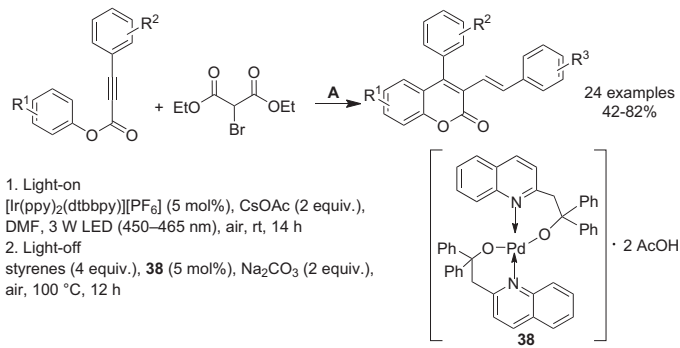
Regioselective synthesis of 3-arylcoumarins is readily achieved via visible light irradiation (blue LEDs) copper(I)-catalyzed aerobic oxidative cascade from salicylaldehyde *N*-tosylhydrazones with terminal arylalkynes, conducted in the presence of KO*t*-Bu in acetonitrile at room temperature (19CC5151). Few 3-trifluoromethylcoumarins are obtained in moderate to good yields via one-step Mizoroki−Heck reaction of α-trifluoromethylacrylates with 2-iodophenols using $Pd(TFA)_2$ as catalyst and AgOTf as additive in 1,4-dioxane (19JOC2072). Under visible light (blue LEDs) catalysis, cascade reaction of ethyl *o*-hydroxycinnamate with various bromo/iodo fluoroalkylation reagents ($BrCF_2COR$, R_FX) promoted by an Ir(III) complex and potassium carbonate in acetonitrile gives 3-fluoroalkylated coumarins (19JOC7480). Various *N*-aryl-3-substituted-2-iminocoumarins are achieved via one-pot two steps involving the reaction of salicylaldehydes with malononitrile in triethylamine to give 2-imino-2*H*-chromene-3-carbonitriles which undergo copper(II)-catalyzed reaction with aryl boronic acids in a biomass-derived green solvent 2-methylTHF at room temperature (19TL150940). The synthesis of various

3-amidosubstituted coumarins is accomplished via stepwise one-pot five-component reactions of salicylaldehyde with Meldrum's acid in ethanol at 40°C, sequential addition of benzaldehydes and aniline followed by the addition of isocyanides (Scheme 52) (19TL8). Zinc(II)-catalyzed one-pot synthesis of 3-substituted coumarins is accomplished through the reaction of salicylaldehydes with ynamides in refluxing toluene. Replacing salicylaldehydes by α-hydroxyaryl ketones, a series of 3,4-disubstituted coumarins are formed (19OL3422).



Scheme 52

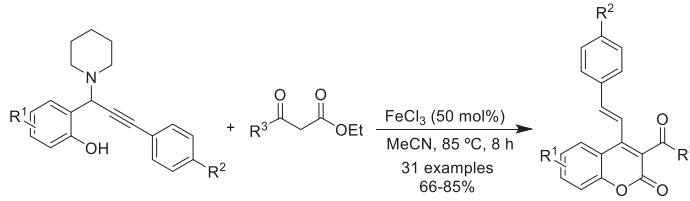
High yields of 3,4-diarylcoumarins arise from base-mediated *O*-alkylation of 2-hydroxyaryl *p*-quinone methides with arylacetyl halides in acetone at room temperature followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (19JOC15978). One-pot sequential synthesis of 4-aryl-3-styrylcoumarins is accomplished through light-on (LED 450−465 nm) radical cyclization reaction of aryl 3-arylprop-2-ynoates with diethyl bromomalonate promoted by an iridium(III) catalyst in DMF at room temperature and subsequent light-off palladium-catalyzed cross-coupling with styrenes at 100°C (Scheme 53) (19OBC4621). Other aryl 3-alkyl/3-arylprop-2-ynoates underwent silver-mediated domino radical addition/cyclization reactions with diarylphosphine oxides in acetonitrile under argon atmosphere to produce 3-phosphorylated 4-alkyl/4-arylcoumarins (19OBC8175).



Scheme 53

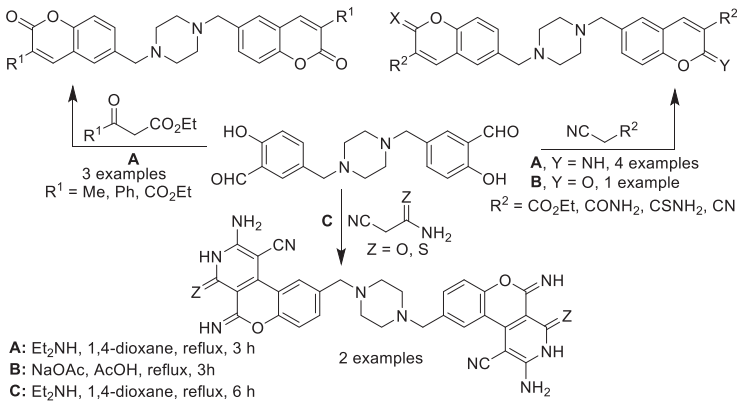
Rhodium(I)-catalyzed domino synthesis of 4-hydroxy-3-methylcoumarins occurs through the reaction of salicylaldehydes with alkyl acrylates using sodium carbonate as base in DMF at 120°C, as well as reacting salicylaldehydes with ethyl acrylate or

N,*N*-dimethylacrylamide in the presence of cesium carbonate in DMF at 80°C (19OBC9275). Regioselective tandem reactions of alkynyl *o*-quinone methides, generated in situ from 2-[3-aryl-1-(piperidin-1-yl)prop-2-yn-1-yl]phenols, with β-keto esters mediated by $FeCl_3$ in acetonitrile provide 3-acyl-4-styrylcoumarins (Scheme 54). The process involves an intermolecular 1,4-conjugate addition/alkyne−allene isomerization/intramolecular transesterification/isomerization cascade (19OBC4005). Under LED (380−385 nm) irradiation and metal-free conditions, a series of aryl 3-alkyl/3-(hetero)arylprop-2-ynoates in the presence of NIS (20 mol%) in THF at room temperature undergo intramolecular cyclization and ester rearrangement to give 4-alkyl/4-(hetero)arylcoumarins. Higher loading of *N*-iodosuccinimide (NIS) (1.1 equiv) or NBS (2 equiv) led to the formation of the corresponding 3-halogenated 4-arylcoumarins (19T1044).



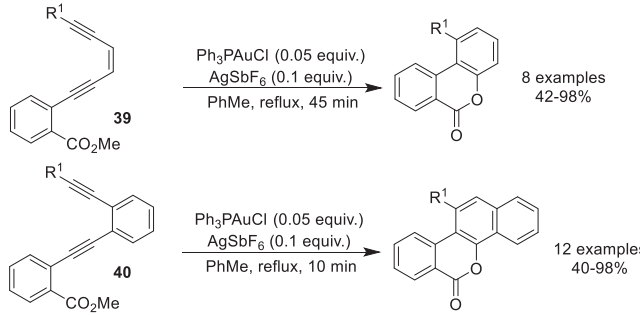
Scheme 54

Cyclocondensation reaction of bis(2-hydroxybenzaldehyde), incorporating a piperazine moiety, with two equivalents of β-keto esters or β-cyano ester/(thio)amide/malononitrile in the presence of a catalytic amount of diethylamine in refluxing 1,4-dioxane provides the corresponding bis(3-acylcoumarins) or bis(2-iminocoumarin-3-carboxylate/carbox(thio)amide/carbonitrile). The reaction with two equivalents of malononitrile in the presence of sodium acetate in acetic acid also yielded bis(coumarin-3-carbonitrile). Moreover, the reaction with four equivalents of 2-cyanoacetamide or 2-cyanoethanethioamide in the presence of a catalytic amount of diethylamine in refluxing 1,4-dioxane affords the corresponding bis[4-(thio)oxo-3*H*-2-iminochromeno[3,4-*c*]pyridine] derivatives (Scheme 55) (19SC1385).



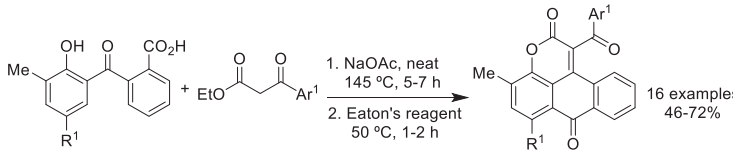
Scheme 55

Various benzo[*c*]coumarins were made from visible light−irradiated oxidative lactonization reaction of 2-methyl-1,1′-biaryls with molecular oxygen as oxidant, [Acr-Mes]ClO_4 as photocatalyst, and hydrochloric acid as cocatalyst in a 2:1 mixture of acetonitrile:water, at room temperature (19OBC4212). The synthesis of benzo[*c*]coumarins and dibenzo[*c*,*h*]coumarins is readily achieved by treating, respectively, enediynes **39** and arenediynes **40** with Ph_3PAuCl and $AgSbF_6$ in refluxing toluene (Scheme 56) (19T1034). Different benzo[*c*]coumarin-type compounds are obtained from the reaction of 2-bromobenzoic acids with cyclohexane-1,3-diones mediated by copper(I) iodide/L-proline in the presence of cesium carbonate when the reaction occurs under argon or oxygen atmosphere, being in the last case even dependent on the substituents of the ketone unit for the regioselective oxidation (19JHC2822).



Scheme 56

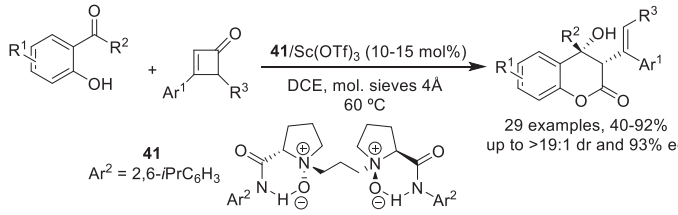
Direct lactonization reactions of isoflavone-2-carboxylic acids carried out in the presence of silver nitrate and potassium persulfate in a 1:1 mixture of acetonitrile: water at 60°C deliver polysubstituted chromono[2,3-*c*]coumarins (19EJO2971). The synthesis of naphtha-fused coumarins occurs in two steps in the presence of sodium acetate under neat conditions at 145°C via Knoevenagel-transesterification reaction of 2-(2-hydroxyaroyl)benzoic acid derivatives with an ethyl aroylacetate and subsequent intramolecular Friedel−Crafts acylation using Eaton's reagent (Scheme 57) (19JOC4451).



Scheme 57

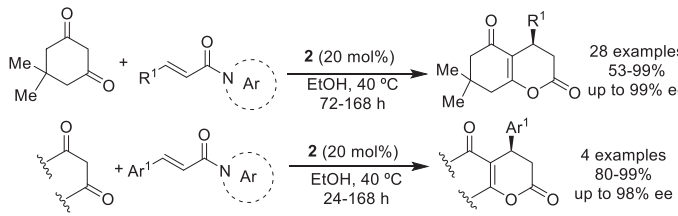
High yields, enantioselectivity, and diastereoselectivity are achieved in an NHC-catalyzed formal [4 + 2] annulation reaction of α,β-unsaturated carboxylic acids bearing a γ-H with *o*-quinone methides carried out in the presence of 2-(7-azabenzotriazol-1-yl)-*N*,*N*,*N*′,*N*′-tetramethyluronium hexafluorophosphate and cesium carbonate in dichloromethane at −5°C to provide 4-aryl-3-vinylsubstituted

3,4-dihydrocoumarins (19OBC4564) and through ring-opening/cycloaddition reaction of 2′-hydroxyacetophenone derivatives or salicylaldehyde with cyclobutenones promoted by a chiral *N*,*N*′-dioxide-scandium(III) complex in DCE to afford 3-(1-arylvinyl)-4-hydroxy-3,4-dihydrocoumarins (Scheme 58) (19OL2388).



Scheme 58

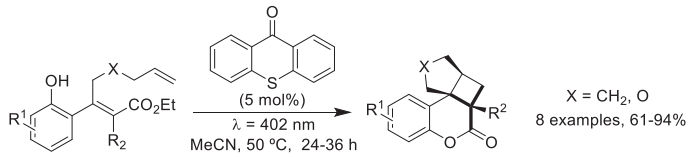
A range of 3-substituted or 3,3-disubstituted 4-(nitromethyl)-3,4-dihydrocoumarins were stereoselectively synthesized via domino Michael/hemiacetalization reaction of aliphatic aldehydes with (*E*)-2-(2-nitrovinyl)phenols mediated by a quinidine thiourea and L-proline and subsequent oxidation with PCC and dihydroxylation (19OBC151). Diversely substituted 4-aryl-3,4-dihydrocoumarins are prepared via annulative partial dimerization of two molecules of ethyl 3-aryloxyacrylates promoted by BF_3•OEt_2 in DCE, with loss of one propiolate molecule (19CC2313). It is through an organocatalyzed Michael addition/lactonization cascade strategy that dimedone reacts with various β-alkyl/β-aryl-α,β-unsaturated *N*-acyl heterocycles to form 4-alkyl/4-aryl-3,4-dihydrocoumarins, after a long time reaction (48−168 h). Replacing dimedone by other cyclic or acyclic β-diketones gave a few 4-aryl-3,4-dihydropyran-2-one derivatives (Scheme 59) (19T2350).



Scheme 59

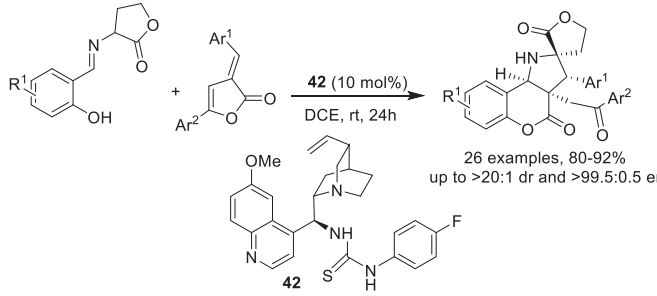
Domino Michael/Michael/hemiacetalization reactions of *trans*-2-hydroxy-β-nitrostyrenes with *trans*-7-oxohept-5-enals under dual catalysis of amino acids and cinchona alkaloid derivatives, followed by oxidation with PCC, deliver hexahydrobenzo[*c*]coumarins with high diastereo- and enantioselectivities (19CEJ7515). An NHC catalyzes formal [3 + 3] annulation reaction of α-bromocinnamaldehydes with β-tetralones using potassium carbonate in THF under nitrogen to afford benzo[*f*]-3,4,7,8-tetrahydrocoumarins (19OBC268). Under violet LED irradiation, ethyl *o*-hydroxy-β-(pent-4-en-1-yl)cinnamates in the presence of thioxanthen-

9-one underwent a sequential energy transfer catalysis for the cascade synthesis of angularly fused 3,4-dihydrocoumarins (Scheme 60) (19OL9724).

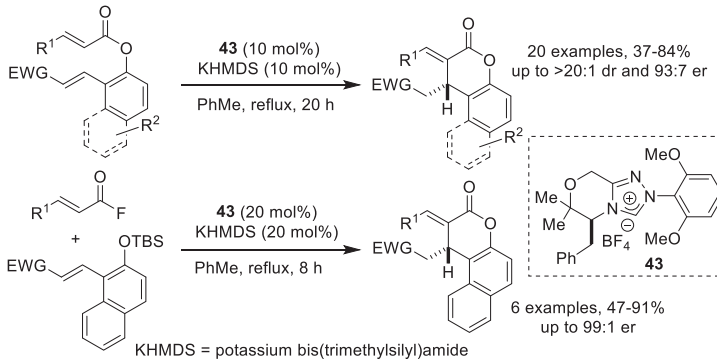


Scheme 60

A wide variety of spirofuranone pyrrolidine−fused 3,4-dihydrocoumarins are obtained in good yields through initial [3 + 2]-dipolar cycloaddition reactions of salicylaldehyde imine derivatives with (*E*)-5-aryl-3-arylidenefuran-2(3*H*)-ones mediated by bifunctional thiourea catalyst **42** to construct the pyrrolidine ring followed by butenolide ring-opening reactions to form the 3,4-dihydrocoumarin unit (Scheme 61) (19OBC2624). High enantioselectivity is achieved in the NHC **43**-catalyzed intramolecular Rauhut−Currier reaction of bis(enoate) derivatives and esterification/Rauhut−Currier reaction of acroloyl fluorides with naphthol derivatives to give benzo[*f*] 3,4-dihydrocoumarins (Scheme 62) (19AGE13370).

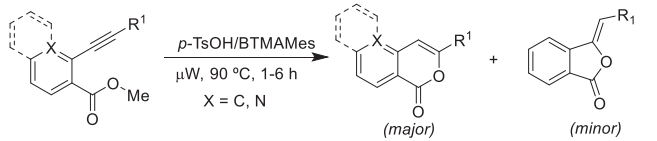


Scheme 61



Scheme 62

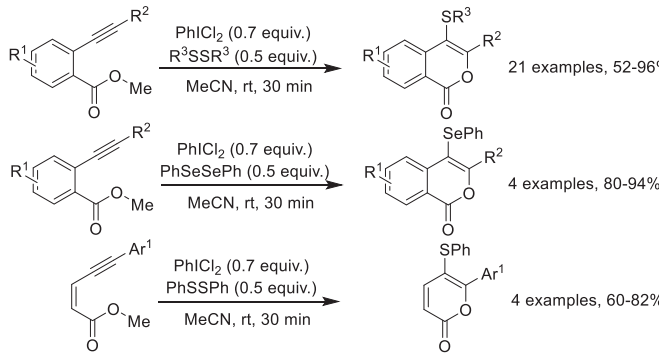
2-Alkynylbenzoic acids in the presence of TBAB and oxone in water undergo regioselective 6-*endo-dig* radical cyclization to produce 3-substituted isocoumarins, in good yields (19T3850). Using 2-alkynyl-*N*-phenylbenzamides as starting materials, a series of *N*-phenyl-3-substituted isocoumarin-1-imines are obtained. In addition, changing the *N*-phenyl protecting group to hydrogen, methyl, or benzyl, the sequence provides 3-substituted isocoumarins (19OBC4335). Under microwave irradiation, cyclization reactions of 2-alkynyl-(hetero)arylcarboxylates mediated by *p*-TsOH-based deep eutectic solvent lead mainly to 3-substituted isocoumarins; in some cases, 3-arylideneisobenzofuran-1-ones are formed as minor products (Scheme 63) (19EJO1904). More derivatives arise from BF_3•Et_2O-mediated 6-*endo-dig* cyclization reaction of 2-alkynylbenzoates in DCE at 80°C. Moreover, under these conditions, the reaction of 2-(arylethynyl)benzoates with acyl chlorides proceeds via a lactonization/acylation cascade to form 4-acyl-3-arylisocoumarins (19JOC10402).



p-TsOH/BTMAMes = *p*-toluensulfonic acid/benzyl-trimethylammonium mesylate

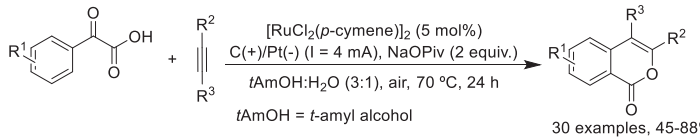
Scheme 63

3-Substituted 4-chloroisocoumarins are obtained via metal-free intramolecular halolactonization reactions of 2-alkynylbenzoates using $PhICl_2$ as oxidant and chlorine source (19OL1989), and using *N*-chlorosuccinimide in the presence of trimethylsilyl chloride (19JOC16222), in acetonitrile. Other 2-alkynylbenzoates undergo regioselective intramolecular cyclization with organosulfenyl chlorides or selenenyl chlorides, generated in situ from unactivated disulfides or diselenides and $PhICl_2$, leading to the formation of 4-sulfenyl- and 4-selenenylisocoumarins, respectively. Using methyl (*Z*)-5-arylpent-2-en-4-ynoates as starting materials in the presence of diphenyl disulfide and $PhICl_2$, a few 5-sulfenyl-2*H*-pyran-2-ones were obtained (Scheme 64) (19OL3620).



Scheme 64

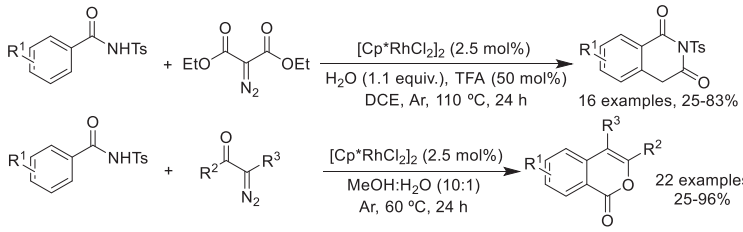
Polyfunctionalized 3,4-disubstituted isocoumarins can be synthesized through cobalt(III)-catalyzed oxidative annulation reactions of benzaldehydes with internal alkynes in the presence of copper(I) oxide in poly(ethylene glycol) (19JOC6807) and through ruthenium(II)-mediated electrochemical [4 + 2] annulation reactions of benzylic alcohols (19CC1124) or arylglyoxylic acids (Scheme 65) (19CC7251) with internal alkynes. Regioselective annulation reaction of benzoic acids with trifluoromethylated alkynes promoted by an iridium(III) complex and silver acetate as oxidant in TFE affords 3-trifluoromethyl-4-substituted isocoumarins as major products along with small amounts of 3-substituted 4-trifluoromethylisocoumarins (19OL3043). The same iridium complex catalyzes regioselective oxidative cyclization of benzoic acids with propargyl alcohols carried out in the presence of lithium acetate and silver carbonate in DCE to give 3,4-disubstituted isocoumarins (19JOC2699).



Scheme 65

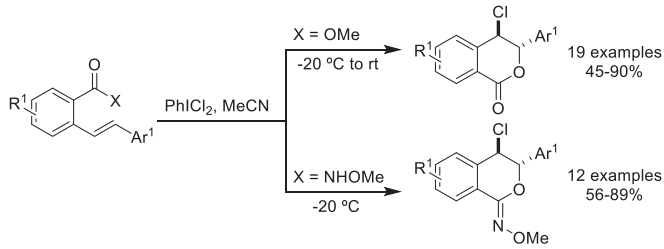
Microwave-assisted tandem cyclization reaction of (*E*)-2-styrylbenzoic acids in the presence of Selectfluor and potassium iodide in a 2:1 mixture of acetonitrile:water provides 3-arylisocoumarins, while in the absence of potassium iodide, a series of 3-aryl-4-fluoro-3,4-dihydroisocoumarins are obtained (19OBC5038).

Rhodium(III)-catalyzed C−H annulation reactions of *N*-tosylbenzamides with diazo compounds are dependent on the reaction conditions: using TFA and water in DCE at 110°C furnishes isoquinolinediones, while reacting in a 10:1 mixture of methanol:water at 60°C leads to 3,4-disubstituted isocoumarins (Scheme 66) (19OBC8768). The same rhodium catalyst is used in the annulation reaction of benzoic acids with *N*-vinyl acetamide using silver acetate and sodium bisulfite in acetonitrile to give 3-acetamido-3,4-dihydroisocoumarins; using *N*-vinyl formamide carried out in the presence of silver acetate and potassium bicarbonate in benzonitrile affords isoquinolones (19OL9425).



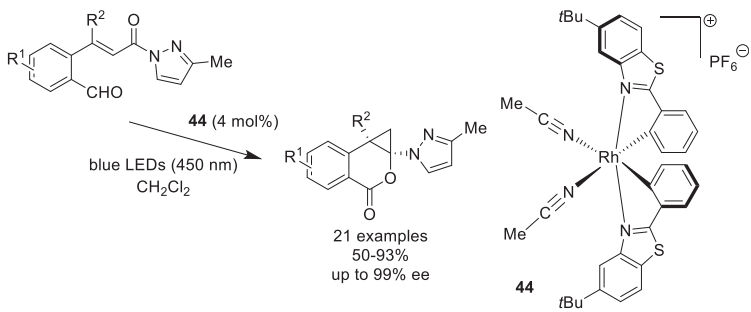
Scheme 66

Enantioselective intramolecular bromolactonization reactions of *o*-(2-methylene-3-oxoprop-1-yl)benzoic acids are accomplished by using an amino−urea catalyst and NBS in toluene to provide 3-acyl-3-bromomethyl-3,4-dihydroisocoumarins, in excellent yields (19SL1474). Metal-free regioselective intramolecular chlorolactonization reactions of methyl 2-styrylbenzoates in the presence of $PhICl_2$ in acetonitrile provide 3-aryl-4-chloro-3,4-dihydroisocoumarins, while using 2-styrylbenzamides as starting materials affords 3-aryl-4-chloro-3,4-dihydroisocoumarin-1-imines (Scheme 67) (19JOC13832).



Scheme 67

Various 4-methylene-3,4-dihydroisocoumarins were synthesized via ruthenium(II)-mediated C−H allylation of aryl oxazolines and allylic alcohols in the presence of copper(II) acetate and potassium acetate in methanol at 80°C, in moderate to good yields (19JOC12881). High enantioselectivity is achieved in the visible light (blue LEDs)-promoted asymmetric photorearrangement of 3-(2-formylaryl)-1-(3-methylpyrazol-1-yl)prop-2-en-1-ones in the presence of bis-cyclometalated rhodium catalyst **44** to give cyclopropa[*c*]3,4-dihydroisocoumarins bearing the pyrazole substituent (Scheme 68) (19AGE14462).

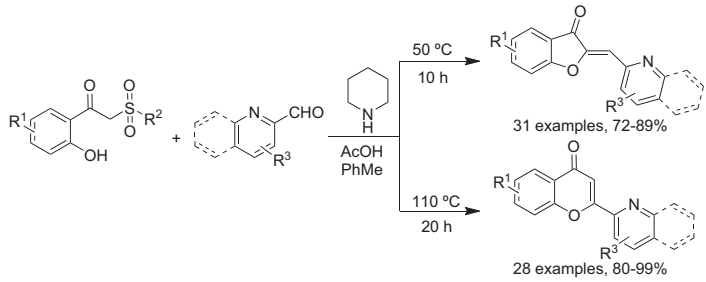


Scheme 68

6.4.2.6 Chromones and chromanones

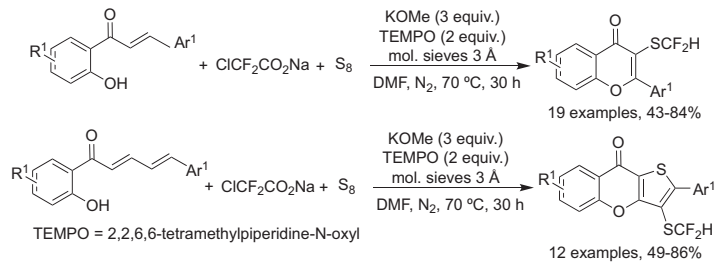
Using one equivalent of $POCl_3$−water, 2′-hydroxychalcones undergo cyclization at 70−75°C to give the corresponding 2-aryl-4*H*-chroman-4-ones, while using three equivalents of $POCl_3$−water at 90−95°C, cyclization and oxidative dehydrogenation

reactions occur to produce 2-aryl-4*H*-chromen-4-ones (19SC2805). Further examples of 2-aryl-4*H*-chromen-4-ones were synthesized through tandem reactions of *o*-bromoaryl ynones with benzaldehyde oxime using cesium carbonate as base, in DMF. This transition metal−free approach involves Michael addition and Ullmann-type *O*-arylation reactions (19OBC7461). Intermolecular desulfonylative condensation reactions of α-sulfonyl 2′-hydroxyacetophenones with 2-formyl azaarenes (pyridines and quinolones) in toluene are temperature controlled: at 50°C provides azaaryl (pyridyl and quinolyl) aurones, while at reflux, various 2-azaaryl (pyridyl and quinolyl) 4*H*-chromen-4-ones are obtained (Scheme 69) (19JOC326).



Scheme 69

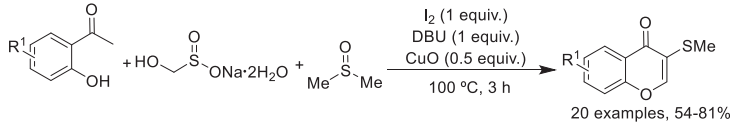
Tandem oxa-Michael addition and oxidative difluoromethylthiolation reactions of 3-aryl-1-(2-hydroxyaryl)prop-2-en-1-ones (2′-hydroxychalcones) with sodium chlorodifluoroacetate and sulfur under basic conditions using TEMPO as oxidant afforded 2-substituted 3-(difluoromethylthio)-4*H*-chromen-4-ones, while using 5-aryl-1-(2-hydroxyaryl)penta-2,4-dien-1-ones (2′-hydroxycinnamylideneacetophenones) as starting materials, various 9*H*-thieno[3,2-*b*]chromen-9-ones were obtained (Scheme 70) (19OL9326). A wide range of 3-alkyl/3-aryl-1-(2-hydroxyaryl)propane-1,3-diones underwent intramolecular trifluoromethylthiolation/cyclization in the presence of R_FSOCl and pyridine in dichloromethane at room temperature to give 2-alkyl/2-aryl-3-(perfluorinated substituent thio)-4*H*-chromen-4-ones (19CEJ10797). The synthesis of 2-substituted 3-(iso)quinolinyl-4*H*-chromen-4-ones is achieved via metal-free reaction of 2-(hydroxyaryl)prop-2-yn-1-ones with (iso)quinoline *N*-oxides carried out in the presence of hydrochloric acid and DMF at 140°C (19OL9995).



Scheme 70

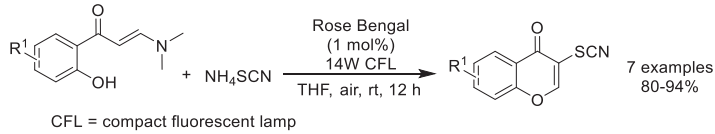
2,3-Disubstituted 4*H*-chromen-4-ones arise from iridium(III)-catalyzed C−H/O−H functionalization of salicylaldehydes with α-diazocarbonyl compounds using PivOH as additive in methanol (19JOC9188) or water (19JOC6207), as solvents.

The synthesis of 3-fluoro-4*H*-chromen-4-ones is accomplished through tandem cyclization reactions of enaminones, prepared from the reaction of 2′-hydroxyacetophenones with *N*,*N*-dimethyl formamide dimethyl acetal (DMF-DMA) in refluxing toluene, promoted by Selectfluor in DCE at room temperature (19SL2295). It is through DDQ-promoted tandem oxidative−coupling/annulation reactions that enaminones react with 1,3-diarylpropenes in DCE to afford 3-(1,3-diarylprop-2-en-1-yl)-4*H*-chromen-4-ones, in moderate to good yields (19EJO4589). A range of 3-methylthio-4*H*-chromen-4-ones are produced from iodine-promoted multicomponent reaction of 2′-hydroxyacetophenones with rongalite and DMSO carried out in the presence of DBU and copper(II) oxide at 100°C (Scheme 71) (19OBC1535).



Scheme 71

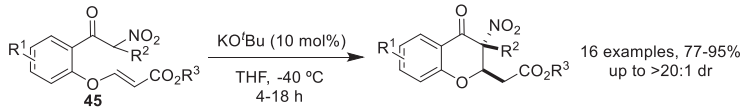
One-pot synthesis of 3-substituted 4*H*-chromen-4-ones is accomplished through oxa-Diels−Alder reaction of *o*-quinone methides, generated from aryl/hetaryl-substituted *o*-(*N*,*N*-dimethylaminomethyl) phenols, with (2*E*)-3-(*N*,*N*-dimethylamino)-1-(2-hydroxyaryl)prop-2-en-1-ones and subsequent cascade of reactions, carried out in various solvents (DMF, DMA, or diglyme) at reflux (19JOC7138). Further derivatives are formed from palladium(0)-catalyzed domino reactions of other *o*-hydroxyarylenaminones with aryl boronic acids in the presence of catalytic potassium iodide, BPO, and sodium carbonate in ethanol (19CEJ6907). More examples are synthesized from the reaction of similar *o*-hydroxyarylenaminones with various 3-diazoindolin-2-imines mediated by copper(II) (19JOC6395) and with α-diazoacetates/amides/ketones promoted by gold(I) (19OL335) catalysts. Under metal-free and aerobic atmospheric conditions, a series of *o*-hydroxyarylenaminones in the presence of Rose Bengal in THF undergo light-promoted thiocyanation using NH_4SCN as thiocyano source to provide 3-thiocyanato-4*H*-chromen-4-ones (Scheme 72) (19JOC2243).



Scheme 72

A chemoselective intramolecular Wittig approach is involved in the reaction of 2′-aroyloxy-α-chloroacetophenone oximes with acyl chlorides in the presence of

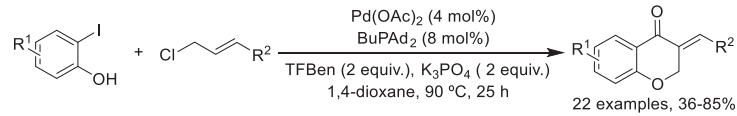
7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene and are solvent dependent: in THF, isoxazoles are formed, while in dichloromethane, chromenone-oximes result (19OL4219). A wide range of 2-arylfurano[3,2-*g*]chroman-4-ones were synthesized in moderate to good yields through cycloisomerization reaction of 2′-hydroxyfuranochalcones mediated by sulfuric acid in refluxing ethanol (19S3431). Diastereoselective intramolecular Michael-type cyclization reaction of α-nitro aryl ketones bearing unsaturated ether units **45** in the presence of a catalytic amount of potassium *t*-butoxide in THF delivers 2,3-disubstituted 3-nitro-4*H*-chroman-4-ones in good to excellent yields (Scheme 73) (19OBC1062).



45

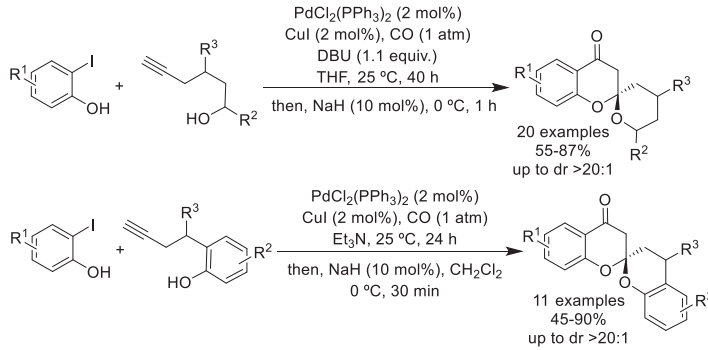
Scheme 73

Some 3-substituted 4*H*-chroman-4-ones are obtained from organopalladium-catalyzed cyclization reactions of 3-bromo-2-methoxyalkan-1-ones in refluxing toluene, involving a 1,4-palladium shift for the formation of two C−C bonds from two C−H bonds (19AGE14625). Other polyfunctionalized derivatives are obtained via a silver-promoted radical ring-opening/coupling/cyclization cascade of cyclopropanols with alkenyl benzaldehydes and using potassium persulfate as oxidant in a 1:1 mixture of DMSO:water (19T130490). High yields of (*E*)-3-benzylidene-4*H*-chroman-4-ones are obtained through palladium(II)-catalyzed carbonylation reactions of 2-iodophenols with allyl chlorides using benzene-1,3,5-triyl triformate (TFBen) as a solid CO source in 1,4-dioxane (Scheme 74) (19CEJ3521).



Scheme 74

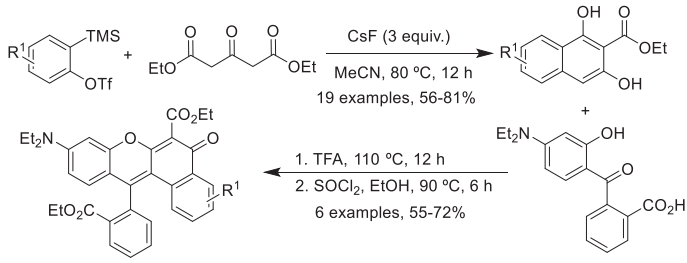
The synthesis of pyran- and chroman-2-spiro-4*H*-chroman-4-ones occurs via one-pot palladium(II)-catalyzed carbonylative Sonogashira coupling/double annulation reaction of 2-iodophenols with terminal alkynols or alkynyl phenols carried out in the presence of copper(I) iodide and DBU or triethylamine under balloon pressure CO, followed by the addition of sodium hydride (Scheme 75) (19OL412).



Scheme 75

6.4.2.7 Xanthenes and xanthones

Various ethyl 1,3-dihydroxynaphth-2-carboxylates, prepared through benzoannulation reaction of 2-(trimethylsilyl)aryl triflates with diethyl 3-oxopentanedioate using CsF as a fluoride source in acetonitrile at room temperature, reacted with 2-(4-diethylamino-2-hydroxybenzoyl)benzoic acid in the presence of TFA followed by esterification to give ethyl 9-(diethylamino)-12-[2-(ethoxycarbonyl)phenyl]-5-oxo-5*H*-benzo[*a*]xanthene-6-carboxylates (Scheme 76) (19JOC2269).



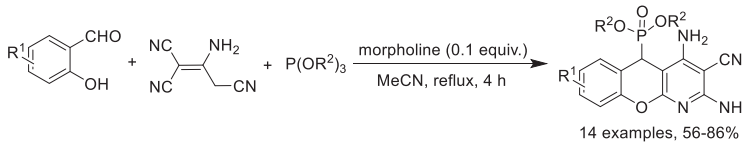
Scheme 76

High yields, diastereo- and enantioselectivity is accomplished in the cycloaddition reaction of *o*-hydroxyaryl *p*-quinone methides with enamides promoted by a BINOL-based chiral phosphoric acid catalyst (19JOC7883) or by *p*-TsOH hydrate (19T3456) in dichloromethane at room temperature to give 1a-acetamido tetrahydroxanthenes.

Substituted naphth-2-ols in the presence of copper(II) acetate undergo self-coupling or cross-coupling reactions via solid-phase carbon-bath microwave irradiation to deliver *peri*-xanthenoxanthenes, in good yields (19CPB690).

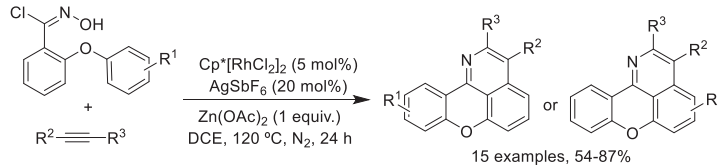
Depending on the position of the substituents of 2-hydroxybenzophenones, their oxidation promoted by ceric ammonium sulfate provided a series of xanthones, 9*H*-xanthen-2,9(4a*H*)-diones, 3*H*-spiro[benzofuran-2,1′-cyclohexa[2,5]-diene]-3,4′-diones,

or biaryl compounds. In addition, xanthen-2,9(4a*H*)-diones are converted to xanthones by treatment with sodium dithionite in a 1:1 mixture of THF:water (19JOC150). Cascade reactions of 2-arylimidazo[1,2-*a*]pyridine-3-carbaldehydes with cyclohexane-1,3-diones mediated by gluconic acid in ethanol provide 9-(2-arylimidazo[1,2-*a*]pyridin-3-yl)hexahydroxanthene-1,8-dione derivatives, in good yields (19SC1836). Under solvent-free conditions, three-component reactions of aromatic aldehydes with cyclohexane-1,3-diones and barbituric acid using scandium(III) triflate as catalyst (19SC431) and with dimedone and kijoic acid mediated by tris(pentafluorophenyl)borane (19SC1143) afford 9-arylxanthenes. Other functionalized 9-arylxanthene-type compounds arise via ultrasound-assisted tandem reactions of aromatic aldehydes with 4-hydroxycoumarin and (thio)barbituric acid in the presence of trisodium citrate dihydrate in aqueous ethanol (19TL1904). Multicomponent reactions of salicylaldehydes with 2-aminoprop-1-ene-1,1,3-tricarbonitrile (malononitrile dimer) and trialkyl phosphites using morpholine in refluxing acetonitrile lead to 9-phosphonated xanthenes (Scheme 77) (19EJO4171).



Scheme 77

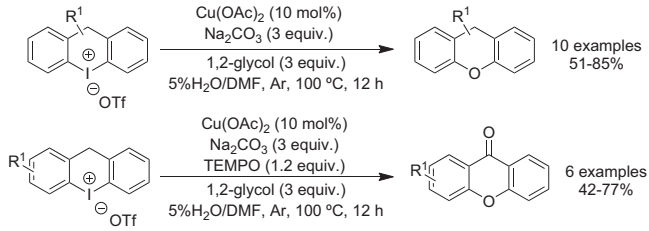
Various spiroxindolinone xanthene-type derivative are readily available through pseudo-multicomponent reactions of isatin with barbituric acid/dimedone/4-hydroxycoumarin/indene-1,3-dione by using the deep eutectic solvent (zinc chloride+urea) at 80°C (19SC2342). One-pot synthesis of pyridine-fused xanthenes is accomplished via cascade intramolecular imidoylation and C−H activation/annulation reactions of *N*-hydroxy-2-phenoxybenzimidoyl chlorides with internal alkynes promoted by a rhodium(III) catalyst in DCE (Scheme 78) (19CC7097).



Scheme 78

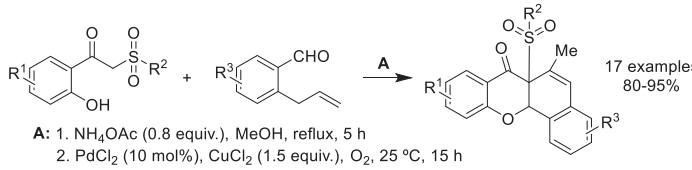
Structurally diverse xanthenes can be prepared by a copper(II)-mediated cyclization of cyclic diaryl iodoniums using sodium carbonate and 1,2-glycol in a mixture of 5% water/DMF, under argon atmosphere. Moreover, the addition of TEMPO led to the synthesis of xanthen-9-ones (Scheme 79) (19EJO4566). A wide range of polysubstituted 9*H*-xanthen-9-ones were prepared via cross-dehydrogenative intramolecular

coupling reactions of 2-aryloxybenzaldehydes, under dual catalysis of copper powder and Selectfluor in acetonitrile (19T130533).



Scheme 79

One-pot domino double cyclocondensation of α-sulfonyl 2′-hydroxyacetophenones with 2-allylbenzaldehydes occurs under multicatalysis of ammonium acetate followed by palladium(II) chloride and copper(II) chloride to provide tetracyclic sulfonyl dihydrobenzo[*c*]xanthen-7-ones. The route involves Knoevenagel condensation, Wacker aerobic oxidation, and aldol condensation reactions (Scheme 80) (19JOC15915).

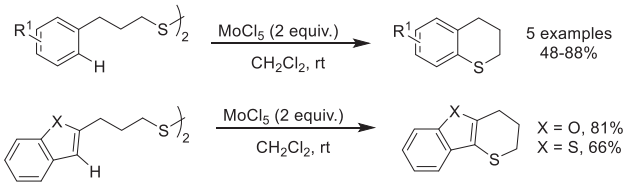


Scheme 80

6.4.3 Heterocycles containing one or two sulfur atoms

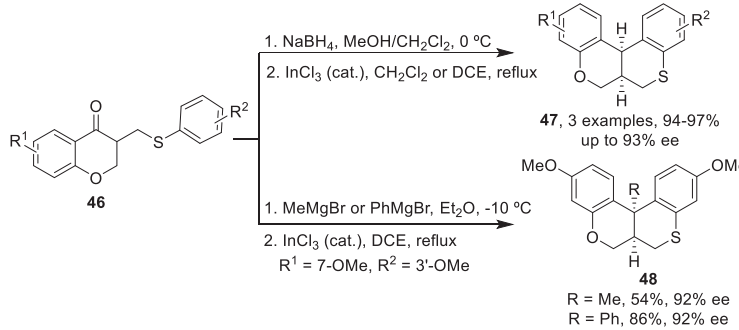
6.4.3.1 Thiopyrans and analogues

A metal-free protocol has been developed for the synthesis of 2-aryl-3-nitro-2*H*-thiochromenes, involving a cascade reaction of 2-bromobenzaldehydes with β-nitrostyrenes and using sodium sulfide nonahydrate as sulfur source (19OBC6355). A large variety of indeno[1,2-*c*]thiochromene 5,5-dioxides are readily available from three-component bicyclization cascade reactions of 2-alkynyl aryldiazonium tetrafluoroborates with a sulfur dioxide surrogate DABCO•$(SO_2)_2$ and 3-aryl-1-haloethynes in DCE at room temperature (19CC3227). Intramolecular oxidative cyclization of bis[2-(aryl/heteroaryl)ethyl]disulfides using molybdenum pentachloride as oxidizer in dichloromethane at room temperature led to thiochroman-type compounds (Scheme 81) (19CEJ1936).



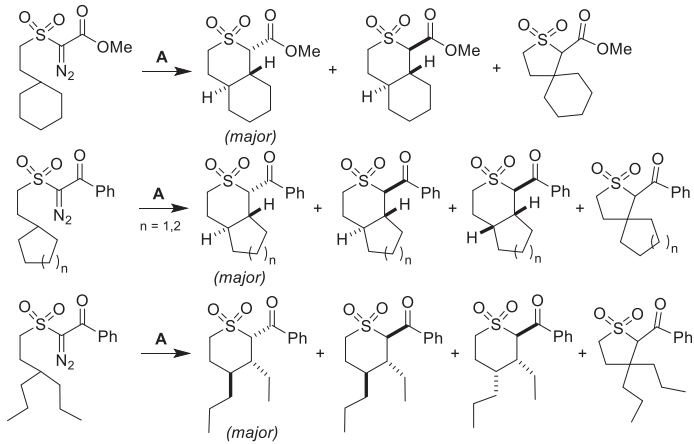
Scheme 81

Under low loading of a cinchonidine-derived bifunctional squaramide catalyst, Michael/aldol cascade reactions of 2-mercaptobenzaldehyde with α,β-unsaturated 7-azaindoline amides provide 2-substituted thiochroman-4-ols, in high yields and with high diastereo- and enantioselectivity (19JOC7984). Various 2-trifluoromethylthiochroman-4-ols are readily available through Michael/aldol cascade reactions of 2-mercaptobenzaldehyde with β-CF_3 enones promoted by a quinine squaramide catalyst in chlorobenzene at −20°C (19S3327). Reduction of sulfides bearing a 3-methylchromanone unit **46** followed by Friedel−Crafts-type cyclization furnishes chroman-fused thiochromans **47**, while the addition of Grignard reagents to **46** followed by a Friedel−Crafts-type cyclization affords substituted chroman-fused thiochromans **48** (Scheme 82) (19OL9391). The synthesis of benzo[*de*]thiochromans is accomplished in moderate to good yields via sulfhydryl-directed iridium(III)-catalyzed tandem reaction of naphthalene-1-thiols with 2-diazo-1,3-diones in 1,4-dioxane at 130°C (19OL7000). Various 1*H*-isothiochromenes were synthesized via ruthenium(II)-promoted oxidative coupling reactions of benzyl *t*-butyl thioethers with internal alkynes carried out in the presence of copper(II) acetate and potassium hexafluorophosphate in HFIP at 60°C. The process involves *S*-directed C−H activation at the *o*-position of the aryl ring, migratory insertion of the alkyne, 1,2-thio-Wittig rearrangement of the *t*-butyl group, and reductive elimination (19OBC2542).



Scheme 82

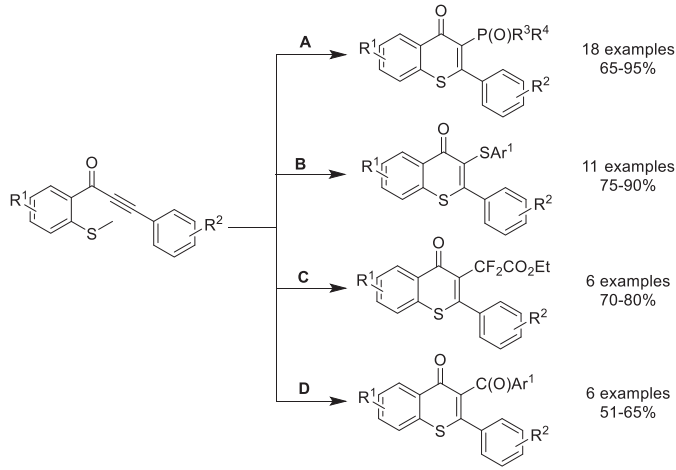
Bis(oxazoline) ligands were used in the rhodium(II)- or copper(II)-catalyzed asymmetric intramolecular C−H insertion reactions of α-diazo-β-oxosulfones for the synthesis of a mixture of fused thiopyran dioxides (Scheme 83) (19JOC7543). A series of thioesters, prepared through acyl thiol−ene reaction of γ-unsaturated esters and thioacetic acid, undergo deprotection under basic conditions followed by Steglich thiolactonization of the formed 5-mercaptopentanoic acids to produce polysubstituted thiopyran-2-ones, in good yields (19OL3460).



A: $Rh_2(OAc)_4$ or $Cu(OTf)_2$ or $CuCl_2$, bis(oxaxoline) ligands, CH_2Cl_2, reflux, N_2

Scheme 83

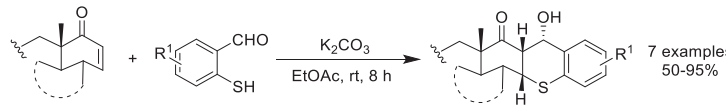
Various thiochromones arise from one-pot reactions of 2′-iodo/2′-bromochalcones with xanthate promoted by copper(II) acetate in DMSO to give thiochromanones that are oxidized in the same pot in the presence of sulfuric acid and using the waste by-product (KI) that is converted into molecular iodine, a powerful oxidant. In addition, using the same protocol with higher temperature and longer time reaction, some 3,3′-methylenebisthiochromones are formed, in which DMSO acts also as methylene source (19OL75). Highly functionalized thiochromones are formed from nickel-catalyzed cycloaddition reaction of 2-sulfobenzoic anhydrides with internal alkynes carried out in the presence of tri-*n*-butylphosphine as additive in refluxing toluene (19OL6280). Various radical promoters are used in the cyclization of 1-[2-(thiomethyl)aryl]alkynones leading to the synthesis of 3-phosphoryl-, 3-sulfenyl-, 3-EtO_2CCF_2-, and 3-acyl-containing thiochromones, in high yields (Scheme 84) (19OL1112).



Scheme 84

Regioselective copper(II)-catalyzed intramolecular ring opening of a donor–acceptor cyclopropane of substituted cyclopropyl(2-haloaryl)methanones using xanthate as a sulfur surrogate in the presence of sodium thiosulfate in DMSO delivers 3-substituted thioflavones, while in the presence of acetic acid in DMF, it affords 3-substituted thioflavothiones (19OL6648).

A few examples of arene-fused thioxanthenes arising from oxidation of 8-aryl(thiomethyl)naphthalenes with *m*-CPBA followed by treatment with TfOH and pyridine of the corresponding sulfoxides were described (19OL233). Other xanthene-type derivatives can be stereoselectively synthesized through sulfa-Michael/aldol reaction of platensimycin and platencin derivatives (two cyclohexanone-containing compounds) with 2-mercaptobenzaldehydes in the presence of potassium carbonate in ethyl acetate at room temperature (Scheme 85) (19OBC4261).



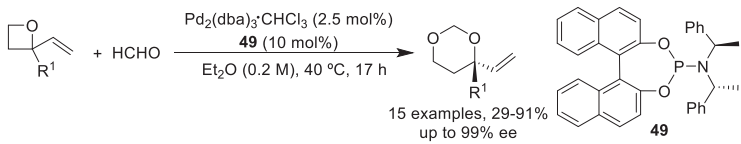
Scheme 85

1,4[Dithiino[2,3-*d*]pyrimidine-6-carbonitrile derivatives are prepared through the reaction of 2-[(4-chloropyrimidin-5-yl)sulfanyl]acetonitriles, obtained from 4,6-dichloro-2-(methylsulfanyl)pyrimidine (DCSMP), with carbon disulfide in the presence of sodium hydride followed by the addition of alkyl halides (19H(98)105).

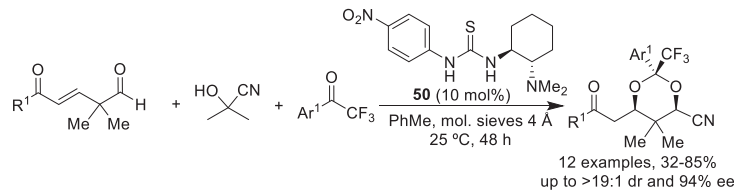
6.4.4 Heterocycles containing two or more oxygen atoms

6.4.4.1 Dioxanes and trioxanes

A palladium complex generated in situ from $Pd_2(dba)_3$•$CHCl_3$ and phosphoramidite **49** promotes asymmetric allylic cycloaddition reactions of vinyloxetanes with formaldehyde to afford a variety of 1,3-dioxanes, in moderate to excellent yields (Scheme 86) (19OL214). Further, *syn*-1,3-dioxanes can be obtained through hemiacetalization and subsequent intramolecular oxa-Michael addition reactions of δ-hydroxy-α,β-unsaturated ketones with aldehydes promoted by camphorsulfonic acid in toluene at room temperature and through olefin cross-metathesis, hemiacetalization, and intramolecular oxa-Michael addition reaction of homoallylic alcohols with α,β-unsaturated ketones and aldehydes (19OL3730). Enantio- and diastereoselective synthesis of cyano-1,3-dioxanes is achieved via cascade reactions of δ-oxo-α,β-unsaturated ketones with acetone cyanohydrin and trifluoromethyl ketones promoted by chiral bifunctional thiourea organocatalyst **50** (Scheme 87) (19OL2688).

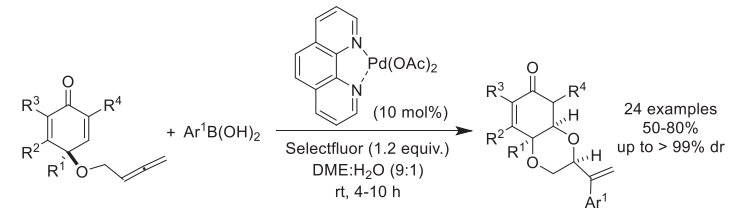


Scheme 86



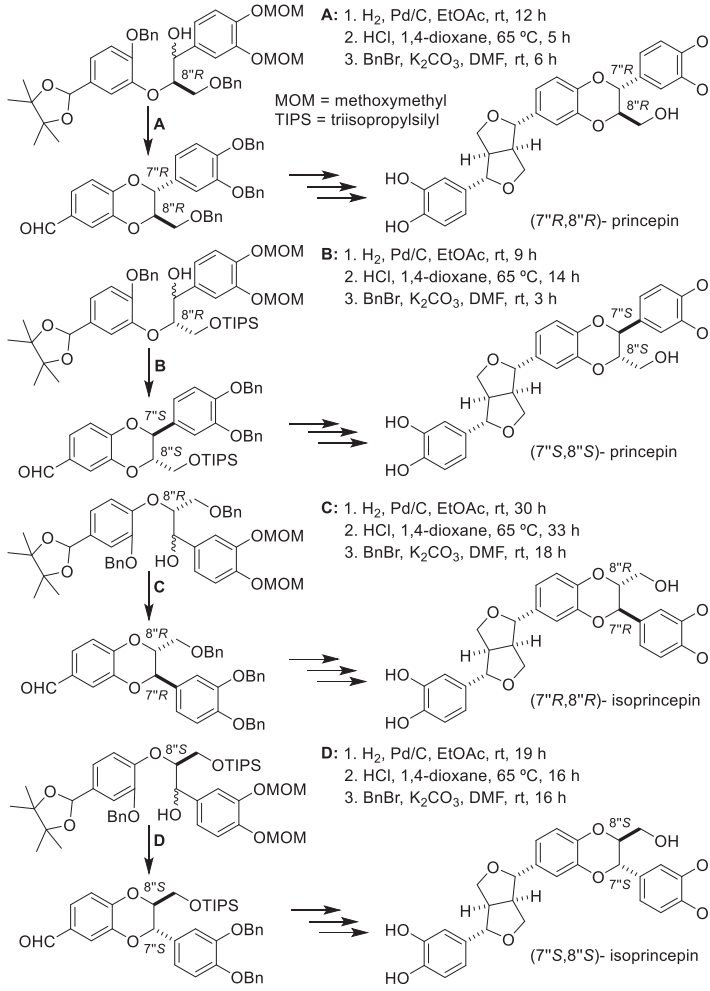
Scheme 87

Under dual catalysis of palladium(II)-bipyridine catalyst and fluorinating agent Selectfluor, arylative cascade cyclization of allene-tethered cyclohexadienones with aryl boronic acids in a 9:1 mixture of DME:water furnishes *cis*-bicyclic 1,4-dioxanes, in moderate to good yields (Scheme 88) (19OL6300).



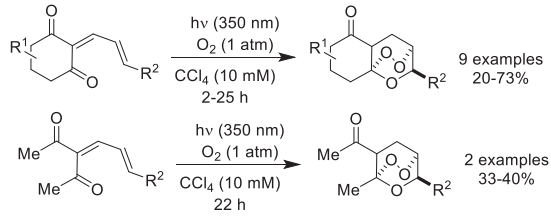
Scheme 88

The construction of the 1,4-benzodioxane ring of natural princepin and isoprincepin was accomplished in a highly stereoselective manner, involving treatment of a benzyl alcohol under acidic conditions, generation of the quinone methide intermediate, and further cyclization (Scheme 89) (19JOC14227).



Scheme 89

Under irradiation, 2-allylidene-1,3-cycloalkanedione-type compounds, prepared via Knoevenagel-type condensation reaction of 1,3-dicarbonyl compounds with α,β-unsaturated aldehydes, underwent photooxygenation in the presence of carbon tetrachloride to afford 1,2,4-trioxane derivatives (Scheme 90) (19JOC3671).

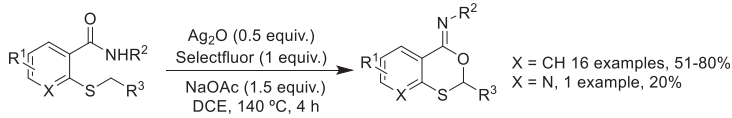


Scheme 90

6.4.5 Heterocycles containing both oxygen and sulfur in the same ring

6.4.5.1 Oxathianes

The synthesis of benzoxathiin-4-imines can be achieved by silver-mediated selective intramolecular cyclization of 2-methylthiobenzamides carried out in the presence of Selectfluor and sodium acetate in DCE (Scheme 91) (19JOC14045).

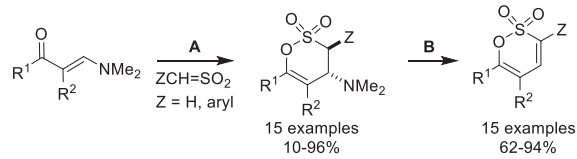


Scheme 91

Continuous-flow electrosynthesis of 1,4-benzoxathiins is achieved through intramolecular dehydrogenative C−S coupling reactions of α-aryloxythioamides promoted by $Sc(OTf)_3$ in a 9:1 mixture of acetonitrile/TFA at room temperature (19AGE6650). It is through a heterogenous catalysis, carried out in the presence of copper supported on manganese oxide−based octahedral molecular sieves, that 2-[(2-haloaryl)thio]phenols underwent intramolecular cyclization to give phenoxathiinan derivatives (19TL151259). A two-step transformation involving the reaction of DCSMP with lithium diisopropylamide and phenacyl bromide derivatives affords 1-(het)aryl-2-{[4,6-dichloro-2-(methylsulfanyl)pyrimidin-5-yl]sulfanyl}ethanones that undergo ring closure to deliver 7-(het)aryl[1,4]oxathiino[2,3-*d*]pyrimidine derivatives, upon treatment with triethylamine (19H(98)564).

Enaminoketones, formed from the reaction of ketones with DMF-DMA at reflux conditions, undergo reaction with (aryl)sulfenes, generated in situ by the action of triethylamine on (aryl)methanesulfonyl chlorides, to afford 4-dimethylamino-3,4-dihydro-1,2-oxathiine 2,2-dioxides. A Cope elimination strategy was used for dimethylamine group elimination providing 1,2-oxathiine 2,2-dioxides (Scheme 92) (19OBC9578, 19OBC9585). Various ethyl benzo[*e*][1,2]oxathiine-3-carboxylate

2,2-dioxides arise from tandem sulfonylation and Knoevenagel condensation reaction of salicylaldehydes or 2′-hydroxyacetophenones with ethyl chlorosulfonylacetate using pyridine as base in DCE (19S1809).



Scheme 92

References

19AGE216 L. Peng, D. Xu, X. Yang, J. Tang, X. Feng, S.-L. Zhang, H. Yan, *Angew. Chem. Int. Ed.* **2019**, *58,* 216.

19AGE681 A. Ghosh, R.G. Carter, *Angew. Chem. Int. Ed.* **2019**, *58,* 681.

19AGE1427 A.J. Day, J.H.Z. Lee, Q.D. Phan, H.C. Lam, A. Ametovski, C.J. Sumby, S.G. Bell, J.H. George, *Angew. Chem. Int. Ed.* **2019**, *58,* 1427.

19AGE1562 Y. Ping, Y. Li, J. Zhu, W. Kong, *Angew. Chem. Int. Ed.* **2019**, *58,* 1562.

19AGE2660 X. Si, Y. Jia, X. Luan, L. Yang, Y. Pei, W. Zhou, *Angew. Chem. Int. Ed.* **2019**, *58,* 2660.

19AGE3594 J. Yedoyan, N. Wurzer, U. Klimczak, T. Ertl, O. Reiser, *Angew. Chem. Int. Ed.* **2019**, *58,* 3594.

19AGE4017 S. Ge, W. Cao, T. Kang, B. Hu, H. Zhang, Z. Su, X. Liu, X. Feng, *Angew. Chem. Int. Ed.* **2019**, *58,* 4017.

19AGE4264 M. Ninomiya, Y. Ando, F. Kudo, K. Ohmori, K. Suzuki, *Angew. Chem. Int. Ed.* **2019**, *58,* 4264.

19AGE6225 M. Petzold, P.G. Jones, D.B. Werz, *Angew. Chem. Int. Ed.* **2019**, *58,* 6225.

19AGE6650 C. Huang, X.-Y. Qian, H.-C. Xu, *Angew. Chem. Int. Ed.* **2019**, *58,* 6650.

19AGE6846 C.T. Walsh, B.S. Moore, *Angew. Chem. Int. Ed.* **2019**, *58,* 6846.

19AGE8346 L. Guo, B. Plietker, *Angew. Chem. Int. Ed.* **2019**, *58,* 8346.

19AGE9095 B.L. Donnelly, L.D. Elliott, C.L. Willis, K.I. Booker-Milburn, *Angew. Chem. Int. Ed.* **2019**, *58,* 9095.

19AGE9485 S. Mishra, A. Aponick, *Angew. Chem. Int. Ed.* **2019**, *58,* 9485.

19AGE12190 Z.-J. Zhang, L. Zhang, R.-L. Geng, J. Song, X.-H. Chen, L.-Z. Gong, *Angew. Chem. Int. Ed.* **2019**, *58,* 12190.

19AGE12486 A. Matviitsuk, S.E. Denmark, *Angew. Chem. Int. Ed.* **2019**, *58,* 12486.

19AGE13019 B. Gçricke, M.F. Bieber, K.E. Mohr, D. Menche, *Angew. Chem. Int. Ed.* **2019**, *58,* 13019.

19AGE13370 S. Bae, C. Zhang, R.M. Gillard, D.W. Lupton, *Angew. Chem. Int. Ed.* **2019**, *58,* 13370.

19AGE14462 C. Zhang, S. Chen, C.-X. Ye, K. Harms, L. Zhang, K.N. Houk, E. Meggers, *Angew. Chem. Int. Ed.* **2019**, *58,* 14462.

19AGE14625 R. Rocaboy, I. Anastasiou, O. Baudoin, *Angew. Chem. Int. Ed.* **2019**, *58,* 14625.
19AGE15016 L. Zhou, S.-Y. Yu, Y. Tang, L. Wang, *Angew. Chem. Int. Ed.* **2019**, *58,* 15016.
19AGE16141 Z. Powers, A. Scharf, A. Cheng, F. Yang, M. Himmelbauer, T. Mitsuhashi, L. Barra, Y. Taniguchi, T. Kikuchi, M. Fujita, I. Abe, J.A. Porco Jr., *Angew. Chem. Int. Ed.* **2019**, *58,* 16141.
19BCSJ1707 S. Tanaka, Y. Suzuki, T. Kimura, M. Kitamura, *Bull. Chem. Soc. Jpn.* **2019**, *92,* 1707.
19CC298 S.-Y. Zhu, H. Zhang, Q.-W. Ma, D. Liu, X.-P. Hui, *Chem. Commun.* **2019**, *55,* 298.
19CC1124 M.-J. Luo, M. Hu, R.-J. Song, D.-L. He, J.-H. Li, *Chem. Commun.* **2019**, *55,* 1124.
19CC2313 R.A. Kunkalkar, R.A. Fernandes, *Chem. Commun.* **2019**, *55,* 2313.
19CC3227 X.-Y. Qin, L. He, J. Li, W.-J. Hao, S.-J. Tu, B. Jiang, *Chem. Commun.* **2019**, *55,* 3227.
19CC3573 Y. Zhu, J. Rebek Jr., Y. Yu, *Chem. Commun.* **2019**, *55,* 3573.
19CC4250 Z. Zeng, Y. Zhao, Y. Zhang, *Chem. Commun.* **2019**, *55,* 4250.
19CC4479 W. Liu, P. Zhou, J. Lang, S. Dong, X. Liu, X. Feng, *Chem. Commun.* **2019**, *55,* 4479.
19CC4675 Y. Xia, Q.-F. Bao, Y. Li, L.-J. Wang, B.-S. Zhang, H.-C. Liu, Y.-M. Liang, *Chem. Commun.* **2019**, *55,* 4675.
19CC5151 A. Ragupathi, A. Sagadevan, V.P. Charpe, C.-C. Lin, J.-R. Hwu, K.C. Hwang, *Chem. Commun.* **2019**, *55,* 5151.
19CC5207 J. Guo, H. Miao, Y. Zhao, X. Bai, Y. Zhu, Q. Wang, Z. Bu, *Chem. Commun.* **2019**, *55,* 5207.
19CC6539 H. Nambu, Y. Onuki, N. Ono, K. Tsuge, T. Yakura, *Chem. Commun.* **2019**, *55,* 6539.
19CC7013 M.C. Lux, M.L. Boby, J.L. Brooks, D.S. Tan, *Chem. Commun.* **2019**, *55,* 7013.
19CC7097 J. Liu, H. Fang, R. Cheng, Z. Wang, Y. Yang, J. You, *Chem. Commun.* **2019**, *55,* 7097.
19CC7251 M.-J. Luo, T.-T. Zhang, F.-J. Cai, J.-H. Li, D.-L. He, *Chem. Commun.* **2019**, *55,* 7251.
19CC8382 S. Yugandar, H. Nakamura, *Chem. Commun.* **2019**, *55,* 8382.
19CC9327 Z.-H. Wang, X.-Y. Zhang, C.-W. Lei, J.-Q. Zhao, Y. You, W.-C. Yuan, *Chem. Commun.* **2019**, *55,* 9327.
19CC9367 H.-Y. Luo, Y.-Y. Xie, X.-F. Song, J.-W. Dong, D. Zhu, Z.-M. Chen, *Chem. Commun.* **2019**, *55,* 9367.
19CC14498 Q. Liu, T.-X. Liu, Y. Ru, X. Zhu, G. Zhang, *Chem. Commun.* **2019**, *55,* 14498.
19CC14737 R. Lassfolk, A. Suonpää, K. Birikh, R. Leino, *Chem. Commun.* **2019**, *55,* 14737.
19CC14757 K. Chen, T. Xu, J. Liang, M. Zhou, J. Zhang, W.-J. Hao, J. Wang, S.-J. Tu, B. Jiang, *Chem. Commun.* **2019**, *55,* 14757.
19CEJ1936 P. Franzmann, S.B. Beil, D. Schollmeyer, S.R. Waldvogel, *Chem. Eur. J.* **2019**, *25,* 1936.
19CEJ3521 W.-F. Wang, J.-B. Peng, X. Qi, J. Ying, X.-F. Wu, *Chem. Eur. J.* **2019**, *25,* 3521.
19CEJ6500 H. Lee, K. Sylvester, E.R. Derbyshire, J. Hong, *Chem. Eur. J.* **2019**, *25,* 6500.

19CEJ6907 J.-P. Wan, Z. Tu, Y. Wang, *Chem. Eur. J.* **2019**, *25,* 6907.
19CEJ7515 S. Jakkampudi, R. Parella, H.D. Arman, J.C.-G. Zhao, *Chem. Eur. J.* **2019**, *25,* 7515.
19CEJ8996 K. Rakumitsu, J. Sakamoto, H. Ishikawa, *Chem. Eur. J.* **2019**, *25,* 8996.
19CEJ9366 R. Santhoshkumar, C.-H. Cheng, *Chem. Eur. J.* **2019**, *25,* 9366.
19CEJ9405 J. Zhang, Z. Liao, L. Chen, S. Zhu, *Chem. Eur. J.* **2019**, *25,* 9405.
19CEJ9665 K. Li, L. Wang, A. Yu, L. Zhu, L. Zhang, Y. Gu, X. Meng, *Chem. Eur. J.* **2019**, *25,* 9665.
19CEJ10792 Y. Nishimoto, S. Nakao, S. Machinaka, F. Hidaka, M. Yasuda, *Chem. Eur. J.* **2019**, *25,* 10792.
19CEJ10797 D.-W. Sun, M. Jiang, J.-T. Liu, *Chem. Eur. J.* **2019**, *25,* 10797.
19CEJ15073 A. Leite, L. Cunha-Silva, D. Silva, A.I.M.C.L. Ferreira, L.M.N.B.F. Santos, I.C.S. Cardoso, V.L.M. Silva, M. Rangel, A.M.G. Silva, *Chem. Eur. J.* **2019**, *25,* 15073.
19CEJ15411 H.-Y. Luo, J.-W. Dong, Y.-Y. Xie, X.-F. Song, D. Zhu, T. Ding, Y. Liu, Z.-M. Chen, *Chem. Eur. J.* **2019**, *25,* 15411.
19CEJ15710 A. Sebastian, V. Srinivasulu, I.A. Abu-Yousef, O. Gorka, T.H. Al-Tel, *Chem. Eur. J.* **2019**, *25,* 15710.
19CPB654 Z. Li, J.-Y. Ruan, F. Sun, J.-J. Yan, J.-L. Wang, Z.-X. Zhang, Y. Zhang, T. Wang, *Chem. Pharm. Bull.* **2019**, *67,* 654.
19CPB690 Y. Chen, Z.-Q. Li, Y.-Q. Deng, B.-Y. Yu, W.-L. Pan, H.-C. Song, *Chem. Pharm. Bull.* **2019**, *67,* 690.
19CPB953 A. Nakayama, H. Sato, S. Nagano, S. Karanjit, H. Imagawa, K. Namba, *Chem. Pharm. Bull.* **2019**, *67,* 953.
19CR4293 S.W. Roh, K. Choi, C. Lee, *Chem. Rev.* **2019**, *119,* 4293.
19CR10403 D. Cao, Z. Liu, P. Verwilst, S. Koo, P. Jangjili, J.S. Kim, W. Lin, *Chem. Rev.* **2019**, *119,* 10403.
19CSR1150 F.-X. Felpin, S. Sengupta, *Chem. Soc. Rev.* **2019**, *48,* 1150.
19CSR3406 L. Kortekaas, W.R. Browne, *Chem. Soc. Rev.* **2019**, *48,* 3406.
19EJO150 M. Liu, X. Zhang, X. Huang, G. Dhawan, J. Evans, M. Kaur, J.P. Jasinski, W. Zhang, *Eur. J. Org. Chem.* **2019**, 150.
19EJO1145 J.E.Y. Sumani, K.J. Ngwira, A. Lemmerer, C.B. de Koning, *Eur. J. Org. Chem.* **2019**, 1145.
19EJO1390 Y. Kimura, Y. Shibata, K. Noguchi, K. Tanaka, *Eur. J. Org. Chem.* **2019**, 1390.
19EJO1571 R.J. Smith, R.L. Bower, S.A. Ferguson, R.J. Rosengren, G.M. Cook, B.C. Hawkins, *Eur. J. Org. Chem.* **2019**, 1571.
19EJO1741 M. Mogharabi-Manzari, M.H. Ghahremani, T. Sedaghat, F. Shayan, M.A. Faramarzi, *Eur. J. Org. Chem.* **2019**, 1741.
19EJO1784 D. Tejedor, S. Delgado-Hernández, R. Diana-Rivero, A. Díaz-Díaz, F. García-Tellado, *Eur. J. Org. Chem.* **2019**, 1784.
19EJO1904 F. Curti, M. Tiecco, V. Pirovano, R. Germani, A. Caselli, E. Rossi, G. Abbiati, *Eur. J. Org. Chem.* **2019**, 1904.
19EJO2234 V.B. Gudise, P.C. Settipalli, E.K. Reddy, S. Anwar, *Eur. J. Org. Chem.* **2019**, 2234.
19EJO2289 V.R.L.J. Bloemendal, D. Sondag, H. Elferink, T.J. Boltje, J.C.M. van Hest, F.P.J.T. Rutjes, *Eur. J. Org. Chem.* **2019**, 2289.
19EJO2552 M. Balha, C. Soni, S.C. Pan, *Eur. J. Org. Chem.* **2019**, 2552.
19EJO2971 J. Boonsombat, S. Thongnest, S. Ruchirawat, *Eur. J. Org. Chem.* **2019**, 2971.

19EJO3127 S. Satbhaiya, N.S. Khonde, J. Rathod, R. Gonnade, P. Kumar, *Eur. J. Org. Chem.* **2019**, 3127.

19EJO3567 P.N. Nair, V. Swathi, G. Nishigandha, B. Sridhar, J.G. Reddy, B.V.S. Reddy, *Eur. J. Org. Chem.* **2019**, 3567.

19EJO3979 J. Zhang, G. Deng, J. Wang, *Eur. J. Org. Chem.* **2019**, 3979.

19EJO4171 M.N. Elinson, A.N. Vereshchagin, Y.E. Anisina, A.N. Fakhrutdinov, A.S. Goloveshkin, M.P. Egorov, *Eur. J. Org. Chem.* **2019**, 4171.

19EJO4566 D. Zhu, M. Li, Z. Wu, Y. Du, B. Luo, P. Huang, S. Wen, *Eur. J. Org. Chem.* **2019**, 4566.

19EJO4589 D. Cheng, M. Wang, Z. Deng, X. Yan, X. Xu, J. Yan, *Eur. J. Org. Chem.* **2019**, 4589.

19EJO4626 S. Perrone, L. Troisi, A. Salomone, *Eur. J. Org. Chem.* **2019**, 4626.

19EJO5073 B. Gabriele, R. Mancuso, L. Veltri, I. Ziccarelli, N.D. Ca, *Eur. J. Org. Chem.* **2019**, 5073.

19EJO6510 Y. Li, Y.-C. Hu, H. Zheng, D.-W. Ji, Y.-F. Cong, Q.-A. Chen, *Eur. J. Org. Chem.* **2019**, 6510.

19EJO6592 M. Saktura, B. Joachim, P. Grzelak, Ł. Albrecht, *Eur. J. Org. Chem.* **2019**, 6592.

19EJO6871 Y. Wan, H. Peng, Q. Yang, W. Liu, G. Deng, J. Wang, *Eur. J. Org. Chem.* **2019**, 6871.

19EJO7264 H. Zhang, G. Liu, X. Guan, J. Gao, X. Qin, G. Jiang, D. Sun, G. Zhang, S. Zhang, *Eur. J. Org. Chem.* **2019**, 7264.

19EJO7439 A. Mayooufi, J. Jacquemin, J. Petrignet, J. Thibonnet, *Eur. J. Org. Chem.* **2019**, 7439.

19EJO7787 P. Kumar, P. Venkatakrishnan, *Eur. J. Org. Chem.* **2019**, 7787.

19H(98)105 K. Kobayashi, K. Yamasaki, D. Fujiwara, K. Nozaki, H. Hiyoshi, K. Umezu, *Heterocycles* **2019**, *98,* 105.

19H(98)564 K. Kobayashi, K. Yamasaki, H. Hiyoshi, K. Umezu, *Heterocycles* **2019**, *98,* 564.

19H(99)989 A. Ueda, M. Higuchi, T. Umeno, M. Tanaka, *Heterocycles* **2019**, *99,* 989.

19HCA1900116 T. Abe, T. Otoh, M. Terasaki, *Helv. Chim. Acta* **2019**, *102,* e1900116.

19HCA1900162 R. McCourt, E.M. Scanlan, *Helv. Chim. Acta* **2019**, *102,* e1900162.

19JA2867 M.L. Landry, G.M. McKenna, N.Z. Burns, *J. Am. Chem. Soc.* **2019**, *141,* 2867.

19JA13778 F. Della-Felice, A.M. Sarotti, M.J. Krische, R.A. Pilli, *J. Am. Chem. Soc.* **2019**, *141,* 13778.

19JA15135 T.J. Purgett, M.W. Dyer, B. Bickel, J. McNeely, J.A. Porco Jr., *J. Am. Chem. Soc.* **2019**, *141,* 15135.

19JA18970 Q.-L. Yang, Y.-K. Xing, X.-Y. Wang, H.-X. Ma, X.-J. Weng, X. Yang, H.-M. Guo, T.-S. Mei, *J. Am. Chem. Soc.* **2019**, *141,* 18970.

19JA20269 T.J. Doyon, J.C. Perkins, S.A.B. Dockrey, E.O. Romero, K.C. Skinner, P.M. Zimmerman, A.R.H. Narayan, *J. Am. Chem. Soc.* **2019**, *141,* 20269.

19JHC99 E.-E.N. Vlachou, C. Gabriel, K.E. Litinas, *J. Heterocycl. Chem.* **2019**, *56,* 99.

19JHC268 A.P. Marjani, J. Khalafy, A. Farajollahi, *J. Heterocycl. Chem.* **2019**, *56,* 268.

19JHC815 R.R. Addada, V.R. Regalla, S.R.G. Venkata, V.N. Vema, V.R. Anna, *J. Heterocycl. Chem.* **2019**, *56,* 815.

19JHC1020 M.M. Khan, Saigal, S. Khan, *J. Heterocycl. Chem.* **2019**, *56,* 1020.

19JHC1393 Z. Pan, H. Xu, K. Mao, L. Dai, L. Zhao, L. Rong, *J. Heterocycl. Chem.* **2019**, *56,* 1393.

19JHC1413 A.M. Shahi, M. Nikpassand, H. Fallah-Bagher-Shaidaei, L.Z. Fekri, *J. Heterocycl. Chem.* **2019**, *56,* 1413.
19JHC1806 G.M. Reddy, D.Y. Chen, M.V. Subbaiah, L. Jianyou, J.-C. Wen, *J. Heterocycl. Chem.* **2019**, *56,* 1806.
19JHC1812 A. Aminkhani, M. Talati, R. Sharifi, F. Chalabian, F. Katouzian, *J. Heterocycl. Chem.* **2019**, *56,* 1812.
19JHC1820 N.F.H. Mahmoud, A.M. El-Saghier, *J. Heterocycl. Chem.* **2019**, *56,* 1820.
19JHC1850 A. Varmazyar, S. Sedaghat, A.N. Goli-Kand, M. Khalaj, S. Arab-Salmanabadi, *J. Heterocycl. Chem.* **2019**, *56,* 1850.
19JHC1898 U.P. Patil, R.C. Patil, S.S. Patil, *J. Heterocycl. Chem.* **2019**, *56,* 1898.
19JHC2008 K.N.U. Basha, S. Gnanamani, *J. Heterocycl. Chem.* **2019**, *56,* 2008.
19JHC2333 V. Sathi, A. Deepthi, N.V. Thomas, *J. Heterocycl. Chem.* **2019**, *56,* 2333.
19JHC2517 Z. Xu, Y. Du, S. Wang, Z. Wu, Y. Lou, F. Zhang, *J. Heterocycl. Chem.* **2019**, *56,* 2517.
19JHC2822 F. Dong, J.-Q. Liu, X.-S. Wang, *J. Heterocycl. Chem.* **2019**, *56,* 2822.
19JHC3008 O.S. Aremu, P. Singh, M. Singh, C. Mocktar, N.A. Koorbanally, *J. Heterocycl. Chem.* **2019**, *56,* 3008.
19JOC150 J. Dam, M.L. Bode, C.B. de Koning, *J. Org. Chem.* **2019**, *84,* 150.
19JOC173 R. Peng, M.S. VanNieuwenhze, *J. Org. Chem.* **2019**, *84,* 173.
19JOC326 M.-Y. Chang, H.-Y. Chen, Y.-L. Tsai, *J. Org. Chem.* **2019**, *84,* 326.
19JOC666 N.C. Lazzara, R.J. Rosano, P.P. Vagadia, M.T. Giovine, M.W. Bezpalko, N.A. Piro, W.S. Kassel, W.J. Boyko, D.L. Zubris, K.K. Schrader, D.E. Wedge, S.O. Duke, R.M. Giuliano, *J. Org. Chem.* **2019**, *84,* 666.
19JOC760 R. Peng, M.S. VanNieuwenhze, *J. Org. Chem.* **2019**, *84,* 760.
19JOC879 D.-F. Li, Y. Gu, J.-R. Zhang, K. Liu, L.-M. Zhao, *J. Org. Chem.* **2019**, *84,* 879.
19JOC1176 P.K. Dutta, M.K. Ravva, S. Sen, *J. Org. Chem.* **2019**, *84,* 1176.
19JOC2048 A. Carral-Menoyo, A. Misol, M. Gomez-Redondo, N. Sotomayor, E. Lete, *J. Org. Chem.* **2019**, *84,* 2048.
19JOC2072 P. Xiao, C. Schlinquer, X. Pannecoucke, J.-P. Bouillon, S. Couve-Bonnaire, *J. Org. Chem.* **2019**, *84,* 2072.
19JOC2243 Y. Gao, Y. Liu, J.-P. Wan, *J. Org. Chem.* **2019**, *84,* 2243.
19JOC2269 G.S. Ghotekar, A.C. Shaikh, M. Muthukrishnan, *J. Org. Chem.* **2019**, *84,* 2269.
19JOC2699 P. Sihag, M. Jeganmohan, *J. Org. Chem.* **2019**, *84,* 2669.
19JOC3184 P. Fernandez, C. Valdes, F.J. Fañanas, F. Rodríguez, *J. Org. Chem.* **2019**, *84,* 3184.
19JOC3537 S.P. Gholap, D. Jangid, R.A. Fernandes, *J. Org. Chem.* **2019**, *84,* 3537.
19JOC3671 M.J. Riveira, N.L. Martiren, M.P. Mischne, *J. Org. Chem.* **2019**, *84,* 3671.
19JOC3990 Y.-B. Shen, S.-S. Li, X. Liu, L. Yu, Y.-M. Sun, Q. Liu, J. Xiao, *J. Org. Chem.* **2019**, *84,* 3990.
19JOC4451 L. Qiao, Z. Duan, Y. Chen, Y. Luan, Q. Gu, Y.-K. Liu, D. Li, *J. Org. Chem.* **2019**, *84,* 4451.
19JOC4961 T.-K. Ma, P.J. Parsons, A.G.M. Barrett, *J. Org. Chem.* **2019**, *84,* 4961.
19JOC5141 W. Jia, Q. Xi, T. Liu, M. n Yang, Y. Chen, D. Yin, X. Wang, *J. Org. Chem.* **2019**, *84,* 5141.
19JOC5450 J. Zhou, B. Wang, X.-H. He, L. Liu, J. Wu, J. Lu, C. Peng, C.-L. Rao, B. Han, *J. Org. Chem.* **2019**, *84,* 5450.

19JOC5712 M.S. Garre, D. Sucunza, E. Aguilar, P. García-García, J.J. Vaquero, *J. Org. Chem.* **2019**, *84,* 5712.

19JOC5855 A.T. Garrison, E.S. Childress, D.C. Davis, C.W. Lindsley, *J. Org. Chem.* **2019**, *84,* 5855.

19JOC6191 A.K. Ghosh, D.S. Lee, *J. Org. Chem.* **2019**, *84,* 6191.

19JOC6207 S. Debbarma, M.R. Sk, B. Modak, M.S. Maji, *J. Org. Chem.* **2019**, *84,* 6207.

19JOC6395 J. Qian, Z. Lin, Z. Wang, Z. Peng, L. Wu, P. Lu, Y. Wang, *J. Org. Chem.* **2019**, *84,* 6395.

19JOC6729 S.-Q. Qiu, T. Ahmad, Y.-H. Xu, T.-P. Loh, *J. Org. Chem.* **2019**, *84,* 6729.

19JOC6807 L.-M. Tao, C.-H. Li, H. Liu, *J. Org. Chem.* **2019**, *84,* 6807.

19JOC7138 G.P. Mrug, N.V. Myshko, S.P. Bondarenko, V.M. Sviripa, M.S. Frasinyuk, *J. Org. Chem.* **2019**, *84,* 7138.

19JOC7175 R. Ukis, C. Schneider, *J. Org. Chem.* **2019**, *84,* 7175.

19JOC7480 D. Song, C.-M. Wang, Z.-P. Ye, P.-J. Xia, Z.-X. Deng, J.-A. Xiao, H.-Y. Xiang, H. Yang, *J. Org. Chem.* **2019**, *84,* 7480.

19JOC7543 T.A. Brouder, C.N. Slattery, A. Ford, U.B.R. Khandavilli, E. Skorepova, K.S. Eccles, M. Lusi, S.E. Lawrence, A.R. Maguire, *J. Org. Chem.* **2019**, *84,* 7543.

19JOC7883 G.-H. Yang, Q. Zhao, Z.-P. Zhang, H.-L. Zheng, L. Chen, X. Li, *J. Org. Chem.* **2019**, *84,* 7883.

19JOC7984 Y.-P. Zhang, Y. You, J.-Q. Zhao, X.-M. Zhang, X.-Y. Xu, W.-C. Yuan, *J. Org. Chem.* **2019**, *84,* 7984.

19JOC9188 D.M. Lade, Y.N. Aher, A.B. Pawar, *J. Org. Chem.* **2019**, *84,* 9188.

19JOC9603 M. Wang, L. Shi, Y. Li, Q. Liu, L. Pan, *J. Org. Chem.* **2019**, *84,* 9603.

19JOC9801 A.K. Ghosh, W.L. Robinson, *J. Org. Chem.* **2019**, *84,* 9801.

19JOC10172 G.-H. Niu, P.-H. Liu, W.-C. Hung, P.-Y. Tseng, G.J. Chuang, *J. Org. Chem.* **2019**, *84,* 10172.

19JOC10402 X. Zhang, X. Wan, Y. Cong, X. Zhen, Q. Li, D. Zhang-Negrerie, Y. Du, K. Zhao, *J. Org. Chem.* **2019**, *84,* 10402.

19JOC10509 R.K. Mallick, S. Dutta, R. Vanjari, A. Voituriez, A.K. Sahoo, *J. Org. Chem.* **2019**, *84,* 10509.

19JOC10526 L. Han, K. Li, H. Xu, T. Mei, Y. Sun, J. Qu, Y. Song, *J. Org. Chem.* **2019**, *84,* 10526.

19JOC10669 K. Tanaka, D. Omata, Y. Asada, Y. Hoshino, K. Honda, *J. Org. Chem.* **2019**, *84,* 10669.

19JOC11114 Y.-L. Zhao, Y. Cheng, *J. Org. Chem.* **2019**, *84,* 11114.

19JOC11373 J.E. Tungen, R. Kristianslund, A. Vik, T.V. Hansen, *J. Org. Chem.* **2019**, *84,* 11373.

19JOC11596 V. Kumar, A. Awasthi, A. Salam, T. Khan, *J. Org. Chem.* **2019**, *84,* 11596.

19JOC11687 M.-Y. Chang, S.-M. Chen, Y.-T. Hsiao, *J. Org. Chem.* **2019**, *84,* 11687.

19JOC11848 J.B. Mateus-Ruiz, A. Cordero-Vargas, *J. Org. Chem.* **2019**, *84,* 11848.

19JOC12881 D. Singh, G.S. Kumar, M. Kapur, *J. Org. Chem.* **2019**, *84,* 12881.

19JOC13033 T. Guntreddi, M. Shankar, N. Kommu, A.K. Sahoo, *J. Org. Chem.* **2019**, *84,* 13033.

19JOC13410 K. Tangdenpaisal, P. Songthammawat, K. Akkarasereenon, K. Chuayboonsong, S. Ruchirawat, P. Ploypradith, *J. Org. Chem.* **2019**, *84,* 13410.

19JOC13832 L. Xing, Y. Zhang, Y. Zhang, Z. Ai, X. Li, Y. Du, J. Deng, K. Zhao, *J. Org. Chem.* **2019**, *84,* 13832.

19JOC13858 K. Tanaka, M. Kishimoto, Y. Asada, Y. Tanaka, Y. Hoshino, K. Honda, *J. Org. Chem.* **2019**, *84,* 13858.
19JOC14045 K. Yang, B. Niu, Z. Ma, H. Wang, B. Lawrence, H. Ge, *J. Org. Chem.* **2019**, *84,* 14045.
19JOC14053 D.H. Dethe, B. VijayKumar, *J. Org. Chem.* **2019**, *84,* 14053.
19JOC14141 R. Liu, X. Li, X. Li, J. Wang, Y. Yang, *J. Org. Chem.* **2019**, *84,* 14141.
19JOC14227 M. Kobayashi, H. Ueno, N. Yoshida, H. Ouchi, T. Asakawa, F. Yoshimura, M. Inai, T. Kan, *J. Org. Chem.* **2019**, *84,* 14227.
19JOC14330 T. Yata, Y. Kita, Y. Nishimoto, M. Yasuda, *J. Org. Chem.* **2019**, *84,* 14330.
19JOC15399 M.A. Pasha, A.V. Krishna, E. Ashok, D.B. Ramachary, *J. Org. Chem.* **2019**, *84,* 15399.
19JOC15633 R.J. Hinkle, D.J. Speer, B.B. Carnell, B.L. Kanter, R.D. Pike, *J. Org. Chem.* **2019**, *84,* 15633.
19JOC15697 J. Li, J. Liu, J. Yin, Y. Zhang, W. Han, J. Lan, D. Wu, Z. Bin, J. You, *J. Org. Chem.* **2019**, *84,* 15697.
19JOC15915 N.-C. Hsueh, M.-C. Tsai, M.-Y. Chang, H.-Y. Chen, *J. Org. Chem.* **2019**, *84,* 15915.
19JOC15926 F. Noël, V.D. Vukovic, J. Yi, E. Richmond, P. Kravljanac, J. Moran, *J. Org. Chem.* **2019**, *84,* 15926.
19JOC15978 G. Singh, S. Kumar, A. Chowdhury, R.V. Anand, *J. Org. Chem.* **2019**, *84,* 15978.
19JOC16222 K. Norseeda, N. Chaisan, C. Thongsornkleeb, J. Tummatorn, S. Ruchirawat, *J. Org. Chem.* **2019**, *84,* 16222.
19JOC16329 S. Wang, G.A. Kraus, *J. Org. Chem.* **2019**, *84,* 16329.
19NPR174 K. Ma, B.S. Martin, X. Yin, M. Dai, *Nat. Prod. Rep.* **2019**, *36,* 174.
19NPR531 A. Miyanaga, *Nat. Prod. Rep.* **2019**, *36,* 531.
19NPR561 W. Chen, Y. Feng, I. Molnár, F. Chen, *Nat. Prod. Rep.* **2019**, *36,* 561.
19NPR1156 N. Al-Maharik, *Nat. Prod. Rep.* **2019**, *36,* 1156.
19OBC74 S. Nayak, P. Panda, B.P. Raiguru, S. Mohapatra, C.S. Purohit, *Org. Biomol. Chem.* **2019**, *17,* 74.
19OBC151 S. Jakkampudi, R. Parella, J.C.-G. Zhao, *Org. Biomol. Chem.* **2019**, *17,* 151.
19OBC268 S. Li, Y. Yao, Z. Tang, B. Sun, C. Yu, T. Li, C. Yao, *Org. Biomol. Chem.* **2019**, *17,* 268.
19OBC333 A. Sharma, P. Gogoi, *Org. Biomol. Chem.* **2019**, *17,* 333.
19OBC1062 H. Chen, J. Xie, D. Xing, J. Wang, J. Tang, Z. Yi, F. Xia, W.-W. Qiu, F. Yang, *Org. Biomol. Chem.* **2019**, *17,* 1062.
19OBC1487 P.R. Mears, S. Hoekman, C.E. Rye, F.P. Bailey, D.P. Byrne, P.A. Eyers, E.J. Thomas, *Org. Biomol. Chem.* **2019**, *17,* 1487.
19OBC1535 M. Wang, B.-C. Tang, J.-T. Ma, Z.-X. Wang, J.-C. Xiang, Y.-D. Wu, J.-G. Wang, A.-X. Wu, *Org. Biomol. Chem.* **2019**, *17,* 1535.
19OBC1937 S.B. Jadhav, S.B. Thopate, J.B. Nanubolu, R. Chegondi, *Org. Biomol. Chem.* **2019**, *17,* 1937.
19OBC1966 J.I. Müller, K. Kusserow, G. Hertrampf, A. Pavic, J. Nikodinovic-Runic, T.A.M. Gulder, *Org. Biomol. Chem.* **2019**, *17,* 1966.
19OBC2361 F.-R. Yuan, F. Jiang, K.-W. Chen, G.-J. Mei, Q. Wu, F. Shi, *Org. Biomol. Chem.* **2019**, *17,* 2361.
19OBC2542 E.P. Urriolabeitia, S. Ruiz, *Org. Biomol. Chem.* **2019**, *17,* 2542.
19OBC2624 D. Kowalczyk-Dworak, Ł. Albrecht, *Org. Biomol. Chem.* **2019**, *17,* 2624.

19OBC2651 F. Yan, H. Liang, B. Ai, W. Liang, L. Jiao, S. Yao, P. Zhao, Q. Liu, Y. Dong, H. Liu, *Org. Biomol. Chem.* **2019**, *17,* 2651.
19OBC3232 C. Cheng, X. Sun, Z. Wu, Q. Liu, L. Xiong, Z. Miao, *Org. Biomol. Chem.* **2019**, *17,* 3232.
19OBC3884 M. Bakthadoss, S. Jayakumar, S. Raman, A. Devaraj, D.S. Sharada, *Org. Biomol. Chem.* **2019**, *17,* 3884.
19OBC3945 Y. Wang, Y. Chen, X. Li, Y. Mao, W. Chen, R. Zhan, H. Huang, *Org. Biomol. Chem.* **2019**, *17,* 3945.
19OBC3978 J. Sun, Y. Zhang, R.-G. Shi, C.-G. Yan, *Org. Biomol. Chem.* **2019**, *17,* 3978.
19OBC4005 L.-Q. Yan, X. Cai, X. He, H. Wang, M. Xie, Y. Zuo, Y. Shang, *Org. Biomol. Chem.* **2019**, *17,* 4005.
19OBC4196 A. Mariappan, K. Rajaguru, S. Muthusubramanian, N. Bhuvanesh, *Org. Biomol. Chem.* **2019**, *17,* 4196.
19OBC4212 Z. Luo, Z.-H. Gao, Z.-Y. Song, Y.-F. Han, S. Ye, *Org. Biomol. Chem.* **2019**, *17,* 4212.
19OBC4261 L. Qiu, Z. Wen, Y. Li, K. Tian, Y. Deng, B. Shen, Y. Duan, Y. Huang, *Org. Biomol. Chem.* **2019**, *17,* 4261.
19OBC4335 Y.-H. Wang, B. Ouyang, G. Qiu, H. Zhou, J.-B. Liu, *Org. Biomol. Chem.* **2019**, *17,* 4335.
19OBC4452 M.D. Patil, R.-S. Liu, *Org. Biomol. Chem.* **2019**, *17,* 4452.
19OBC4564 Z. Wang, H. Zhang, H. Qian, Y. Wang, C. Yu, T. Li, C. Yao, *Org. Biomol. Chem.* **2019**, *17,* 4564.
19OBC4572 R. Yalla, S. Raghavan, *Org. Biomol. Chem.* **2019**, *17,* 4572.
19OBC4621 H. Kong, Q. Li, Y. Yin, M. Huang, J.K. Kim, Y. Zhu, Y. Li, Y. Wu, *Org. Biomol. Chem.* **2019**, *17,* 4621.
19OBC5038 J. Yuan, F. Zeng, W. Mai, L. Yang, Y. Xiao, P. Mao, D. Wei, *Org. Biomol. Chem.* **2019**, *17,* 5038.
19OBC5190 C. Gharui, S.C. Pan, *Org. Biomol. Chem.* **2019**, *17,* 5190.
19OBC5684 M. Wu, J. Yang, F. Luo, C. Cheng, G. Zhu, *Org. Biomol. Chem.* **2019**, *17,* 5684.
19OBC6355 T.T.H. Le, C. Youhei, Q.H. Le, T.B. Nguyen, D.H. Mac, *Org. Biomol. Chem.* **2019**, *17,* 6355.
19OBC6831 A. Salam, S. Ray, M.A. Zaid, D. Kumar, T. Khan, *Org. Biomol. Chem.* **2019**, *17,* 6831.
19OBC7078 P. Vijitphan, V. Rukachaisirikul, C. Muanprasat, P. Iawsipo, J. Panprasert, K. Tadpetch, *Org. Biomol. Chem.* **2019**, *17,* 7078.
19OBC7270 S.S. Thorat, R. Kontham, *Org. Biomol. Chem.* **2019**, *17,* 7270.
19OBC7461 J.-W. Zhang, W.-W. Yang, L.-L. Chen, P. Chen, Y.-B. Wang, D.-Y. Chen, *Org. Biomol. Chem.* **2019**, *17,* 7461.
19OBC7715 L. Ji, Q. Deng, P. Liu, P. Sun, *Org. Biomol. Chem.* **2019**, *17,* 7715.
19OBC7849 B. Mondal, M. Balha, S.C. Pan, *Org. Biomol. Chem.* **2019**, *17,* 7849.
19OBC8088 S. Muthusamy, A. Prabu, E. Suresh, *Org. Biomol. Chem.* **2019**, *17,* 8088.
19OBC8175 H. Hou, Y. Xu, H. Yang, C. Yan, Y. Shi, S. Zhu, *Org. Biomol. Chem.* **2019**, *17,* 8175.
19OBC8206 K. Lu, M. Li, Y. Huang, Y. Sun, Z. Gong, Q. Wei, X. Zhao, Y. Zhang, P. Yu, *Org. Biomol. Chem.* **2019**, *17,* 8206.
19OBC8272 R.M. Gillard, M.A. Brimble, *Org. Biomol. Chem.* **2019**, *17,* 8272.
19OBC8768 Y. Liu, J. Wu, B. Qian, Y. Shang, *Org. Biomol. Chem.* **2019**, *17,* 8768.

19OBC8806 S.J. Gharpure, S.K. Nanda, D.J. Fartade, *Org. Biomol. Chem.* **2019**, *17,* 8806.
19OBC8853 V. Gupta, D. Sahu, S. Jain, K. Vanka, R.P. Singh, *Org. Biomol. Chem.* **2019**, *17,* 8853.
19OBC8943 A.A.Q. Al-Khdhairawi, G.A. Cordell, N.F. Thomas, N.B.S. Nagojappa, J.-F.F. Weberb, *Org. Biomol. Chem.* **2019**, *17,* 8943.
19OBC9039 K.M.N. Win, A.D. Sonawane, M. Koketsu, *Org. Biomol. Chem.* **2019**, *17,* 9039.
19OBC9129 V.V. Betkekar, M. Harachi, K. Suzuki, K. Ohmori, *Org. Biomol. Chem.* **2019**, *17,* 9129.
19OBC9275 M.L.N. Rao, B.S. Ramakrishna, S. Nand, *Org. Biomol. Chem.* **2019**, *17,* 9275.
19OBC9578 S. Aiken, C.D. Gabbutt, B.M. Heron, C.R. Rice, D. Zonidis, *Org. Biomol. Chem.* **2019**, *17,* 9578.
19OBC9585 S. Aiken, K. Anozie, O.D.C.C. de Azevedo, L. Cowen, R.J.L. Edgar, C.D. Gabbutt, B.M. Heron, P.A. Lawrence, A.J. Mills, C.R. Rice, M.W.J. Urquhart, D. Zonidis, *Org. Biomol. Chem.* **2019**, *17,* 9585.
19OBC10065 A. Arcadi, A. Ciogli, G. Fabrizi, A. Fochetti, R. Franzini, F. Ghirga, A. Goggiamani, A. Iazzetti, *Org. Biomol. Chem.* **2019**, *17,* 10065.
19OL32 C.R. Wong, G. Hummel, Y. Cai, S.E. Schaus, J.S. Panek, *Org. Lett.* **2019**, *21,* 32.
19OL75 S. Sangeetha, G. Sekar, *Org. Lett.* **2019**, *21,* 75.
19OL190 X.-J. Lv, Y.-H. Chen, Y.-K. Liu, *Org. Lett.* **2019**, *21,* 190.
19OL214 H. Xu, S. Khan, H. Li, X. Wu, Y.J. Zhang, *Org. Lett.* **2019**, *21,* 214.
19OL233 S. Moon, Y. Nishii, M. Miura, *Org. Lett.* **2019**, *21,* 233.
19OL335 P.N. Bagle, M.V. Mane, S.P. Sancheti, A.B. Gade, S.R. Shaikh, M.-H. Baik, N.T. Patil, *Org. Lett.* **2019**, *21,* 335.
19OL412 K. Xiang, P. Tong, B. Yan, L. Long, C. Zhao, Y. Zhang, Y. Li, *Org. Lett.* **2019**, *21,* 412.
19OL563 G. Hoffmann, C.G. Daniliuc, A. Studer, *Org. Lett.* **2019**, *21,* 563.
19OL908 Y. Zhu, D. Wang, Y. Huang, *Org. Lett.* **2019**, *21,* 908.
19OL998 P.-J. Li, G. Dräger, A. Kirschning, *Org. Lett.* **2019**, *21,* 998.
19OL1112 J. Xu, F. Zhang, S. Zhang, L. Zhang, X. Yu, J. Yan, Q. Song, *Org. Lett.* **2019**, *21,* 1112.
19OL1212 A. Ametovski, D.W. Lupton, *Org. Lett.* **2019**, *21,* 1212.
19OL1325 C.J. Gerry, Z. Yang, M. Stasi, S.L. Schreiber, *Org. Lett.* **2019**, *21,* 1325.
19OL1388 G. Haun, A.N. Paneque, D.W. Almond, B.E. Austin, G. Moura-Letts, *Org. Lett.* **2019**, *21,* 1388.
19OL1488 F. Wu, S. Zhu, *Org. Lett.* **2019**, *21,* 1488.
19OL1755 V. Arredondo, D.E. Roa, S. Yan, F. Liu-Smith, D.L. Van Vranken, *Org. Lett.* **2019**, *21,* 1755.
19OL1881 M.-S. Wang, Z. Wang, W. Chen, X. Yang, H. Zhang, *Org. Lett.* **2019**, *21,* 1881.
19OL1979 X. Li, X. Kong, S. Yang, M. Meng, X. Zhan, M. Zeng, X. Fang, *Org. Lett.* **2019**, *21,* 1979.
19OL1989 L. Xing, Y. Zhang, B. Li, Y. Du, *Org. Lett.* **2019**, *21,* 1989.
19OL2156 Y. Kurimoto, T. Nasu, Y. Fujii, K. Asano, S. Matsubara, *Org. Lett.* **2019**, *21,* 2156.
19OL2383 R. Tamura, E. Kitamura, R. Tsutsumi, M. Yamanaka, T. Akiyama, K. Mori, *Org. Lett.* **2019**, *21,* 2383.

19OL2388 H. Zhang, Y. Luo, D. Li, Q. Yao, S. Dong, X. Liu, X. Feng, *Org. Lett.* **2019**, *21,* 2388.
19OL2629 B.R. Borade, R. Nomula, R.G. Gonnade, R. Kontham, *Org. Lett.* **2019**, *21,* 2629.
19OL2688 A. Matsumoto, K. Asano, S. Matsubara, *Org. Lett.* **2019**, *21,* 2688.
19OL2847 H. Wang, Z.-X. Zhou, M. Kurmoo, Y.-J. Liu, M.-H. Zeng, *Org. Lett.* **2019**, *21,* 2847.
19OL2872 S. Gai, N.T. Lucas, B.C. Hawkins, *Org. Lett.* **2019**, *21,* 2872.
19OL3008 T. Kobayashi, I. Takizawa, A. Shinobe, Y. Kawamoto, H. Abe, H. Ito, *Org. Lett.* **2019**, *21,* 3008.
19OL3018 X. Di, Y. Wang, L. Wu, Z.-M. Zhang, Q. Dai, W. Li, J. Zhang, *Org. Lett.* **2019**, *21,* 3018.
19OL3043 G. Liu, G. Kuang, X. Zhang, N. Lu, Y. Fu, Y. Peng, Y. Zhou, *Org. Lett.* **2019**, *21,* 3043.
19OL3422 H.J. Yoo, S.W. Youn, *Org. Lett.* **2019**, *21,* 3422.
19OL3441 M. Murai, M. Yamamoto, K. Takai, *Org. Lett.* **2019**, *21,* 3441.
19OL3460 R.O. McCourt, E.M. Scanlan, *Org. Lett.* **2019**, *21,* 3460.
19OL3620 L. Xing, Y. Zhang, B. Li, Y. Du, *Org. Lett.* **2019**, *21,* 3620.
19OL3730 K. Murata, K. Sakamoto, H. Fuwa, *Org. Lett.* **2019**, *21,* 3730.
19OL4219 P.V. Khairnar, T.-H. Lung, Y.-J. Lin, C.-Y. Wu, S.R. Koppolu, A. Edukondalu, P. Karanam, W. Lin, *Org. Lett.* **2019**, *21,* 4219.
19OL4245 Y. Hashimoto, T. Ikeda, A. Ida, N. Morita, O. Tamura, *Org. Lett.* **2019**, *21,* 4245.
19OL5064 C. Afeke, Y. Xie, P.E. Floreancig, *Org. Lett.* **2019**, *21,* 5064.
19OL5368 T. Xu, D. Wang, X. Tong, *Org. Lett.* **2019**, *21,* 5368.
19OL5387 S. Han, S. Liu, L. Liu, L. Ackermann, J. Li, *Org. Lett.* **2019**, *21,* 5387.
19OL5438 X.-K. Guan, G.-F. Liu, D. An, H. Zhang, S.-Q. Zhang, *Org. Lett.* **2019**, *21,* 5438.
19OL5556 Y.-H. Chen, X.-J. Lv, Z.-H. You, Y.-K. Liu, *Org. Lett.* **2019**, *21,* 5556.
19OL6084 R. Pertschi, P. Wagner, N. Ghosh, V. Gandon, G. Blond, *Org. Lett.* **2019**, *21,* 6084.
19OL6122 D. Caprioglio, D. Mattoteia, A. Minassi, F. Pollastro, A. Lopatriello, E. Munoz, O. Taglialatela-Scafati, G. Appendino, *Org. Lett.* **2019**, *21,* 6122.
19OL6199 K. Uchida, Y. Kawamoto, T. Kobayashi, H. Ito, *Org. Lett.* **2019**, *21,* 6199.
19OL6280 P. Mi, L. He, T. Shen, J.Z. Sun, H. Zhao, *Org. Lett.* **2019**, *21,* 6280.
19OL6300 G. Kumaraswamy, M. Gangadhar, V. Ramesh, K. Ankamma, B. Sridhar, *Org. Lett.* **2019**, *21,* 6300.
19OL6648 N. Sundaravelu, G. Sekar, *Org. Lett.* **2019**, *21,* 6648.
19OL6750 C. Wang, Y.-H. Chen, H.-C. Wu, C. Wang, Y.-K. Liu, *Org. Lett.* **2019**, *21,* 6750.
19OL6864 T. Sakai, H. Sakakibara, Y. Omoto, M. Tsunekawa, Y. Hadano, S. Kato, Y. Mori, *Org. Lett.* **2019**, *21,* 6864.
19OL6879 M.-M. Xun, Y. Bai, Y. Wang, Z. Hu, K. Fu, W. Ma, C. Yuan, *Org. Lett.* **2019**, *21,* 6879.
19OL6903 P. Acosta-Guzmán, A. Rodríguez-López, D. Gamba-Sanchez, *Org. Lett.* **2019**, *21,* 6903.
19OL7000 K. Yan, Y. Kong, B. Li, B. Wang, *Org. Lett.* **2019**, *21,* 7000.
19OL7337 J. Qin, Y. Zhang, C. Liu, J. Zhou, R. Zhan, W. Chen, H. Huang, *Org. Lett.* **2019**, *21,* 7337.

19OL7597 L. Cai, Y. Chen, H. Cao, Q. Wei, Y. Yang, Q. Ouyang, Y. Peng, *Org. Lett.* **2019**, *21,* 7597.
19OL7665 D.-S. Hsu, J.-Y. Huang, *Org. Lett.* **2019**, *21,* 7665.
19OL8280 Y. Hosoya, I. Kobayashi, K. Mizoguchi, M. Nakada, *Org. Lett.* **2019**, *21,* 8280.
19OL8312 L.A.M. Murray, T. Fallon, C.J. Sumby, J.H. George, *Org. Lett.* **2019**, *21,* 8312.
19OL8700 S. Ning, Z. Liu, Z. Wang, M. Liao, Z. Xie, *Org. Lett.* **2019**, *21,* 8700.
19OL8776 M.A. Coleman, L. Burchill, C.J. Sumby, J.H. George, *Org. Lett.* **2019**, *21,* 8776.
19OL8832 J. Liu, Z. Li, T. Hu, X. Wei, R. Wang, X. Hu, H. Gao, G. Liu, Y. Yi, Y. Yamada-Takamura, C.-S. Lee, P. Wang, Y. Wang, *Org. Lett.* **2019**, *21,* 8832.
19OL8852 J. Cai, Z.-K. Wang, M. Usman, Z.-W. Lu, X.-D. Hu, W.-B. Liu, *Org. Lett.* **2019**, *21,* 8852.
19OL8857 S.-Y. Yang, W.-Y. Han, C. He, B.-D. Cui, N.-W. Wan, Y.-Z. Chen, *Org. Lett.* **2019**, *21,* 8857.
19OL8938 C. Wu, X. Yang, Y. Shang, H.-G. Cheng, W. Yan, Q. Zhou, *Org. Lett.* **2019**, *21,* 8938.
19OL9188 X.-L. Min, X.-R. Xu, Y. He, *Org. Lett.* **2019**, *21,* 9188.
19OL9326 P. Zhang, W. Chen, M. Liu, H. Wu, *Org. Lett.* **2019**, *21,* 9326.
19OL9391 Y.-P. Li, S.-F. Zhu, Q.-L. Zhou, *Org. Lett.* **2019**, *21,* 9391.
19OL9425 R. Sun, X. Yang, Q. Li, K. Xu, J. Tang, X. Zheng, M. Yuan, H. Fu, R. Li, H. Chen, *Org. Lett.* **2019**, *21,* 9425.
19OL9724 T. Nevesely, C.G. Daniliuc, R. Gilmour, *Org. Lett.* **2019**, *21,* 9724.
19OL9995 S. Zhang, C. Wu, Z. Zhang, T. Wang, *Org. Lett.* **2019**, *21,* 9995.
19OL10069 Y. Zhang, X. Lu, Y. Wang, H. Xu, R. Zhan, W. Chen, H. Huang, *Org. Lett.* **2019**, *21,* 10069.
19S258 T. Noguchi, Y. Nishii, M. Miura, *Synthesis* **2019**, *51,* 258.
19S276 W.-C. Gao, Z.-Y. Xiong, S. Pirhaghani, T. Wirth, *Synthesis* **2019**, *51,* 276.
19S552 S. Ahn, J.A. Yoon, Y.T. Han, *Synthesis* **2019**, *51,* 552.
19S780 S.R. Patpi, G. Jin, S. Kantevari, *Synthesis* **2019**, *51,* 780.
19S1139 S. Matsuoka, K. Nakamura, K. Ohmori, K. Suzuki, *Synthesis* **2019**, *51,* 1139.
19S1545 F. Della-Felice, F.F. de Assis, A.M. Sarotti, R.A. Pilli, *Synthesis* **2019**, *51,* 1545.
19S1809 Z. Dong, Y. Chen, Z. Yang, Z. Yang, J. Xu, *Synthesis* **2019**, *51,* 1809.
19S3327 H. Chen, C. Wang, D. Wen, Y. Deng, X. Liu, X. Liu, J. Zhang, W. Yan, *Synthesis* **2019**, *51,* 3327.
19S3419 M.-Y. Chang, Y.-H. Chen, H.-Y. Chen, *Synthesis* **2019**, *51,* 3419.
19S3431 M.J. Mphahlele, T.O. Olomola, *Synthesis* **2019**, *51,* 3431.
19S3588 A. Rossignon, D. Bonifazi, *Synthesis* **2019**, *51,* 3588.
19S4058 R.-X. Wang, Z. Fang, G. Qiu, W. Xie, J.-B. Liu, *Synthesis* **2019**, *51,* 4058.
19S4165 Y. Chen, D. Wu, J. Zhou, Y. Wang, J. Huang, X. Xu, *Synthesis* **2019**, *51,* 4165.
19S4198 E. Silm, S. Kaabel, I. Järving, T. Kanger, *Synthesis* **2019**, *51,* 4198.
19SC431 S. Kumari, D. Kumar, S. Gajaganti, V. Srivastava, S. Singh, *Synth. Commun.* **2019**, *49,* 431.
19SC1031 X. Li, G. Wang, Z. Zhang, N. Wu, Q. Yang, S. Huang, X. Wang, *Synth. Commun.* **2019**, *49,* 1031.

19SC1143 Y.P. Sarnikar, Y.D. Mane, D.O. Biradar, B.C. Khade, *Synth. Commun.* **2019**, *49,* 1143.

19SC1385 A.E.M. Mekky, S.M.H. Sanad, *Synth. Commun.* **2019**, *49,* 1385.

19SC1679 N. Kaur, *Synth. Commun.* **2019**, *49,* 1679.

19SC1836 C. Patel, A. Thakur, G. Pereira, A. Sharma, *Synth. Commun.* **2019**, *49,* 1836.

19SC2244 A.V. Chate, B.A. Shaikh, G.M. Bondle, S.M. Sangle, *Synth. Commun.* **2019**, *49,* 2244.

19SC2342 V.B. Nishtala, S. Basavoju, *Synth. Commun.* **2019**, *49,* 2342.

19SC2521 S.P. Khare, T.R. Deshmukh, J.N. Sangshetti, V.M. Khedkar, B.B. Shingate, *Synth. Commun.* **2019**, *49,* 2521.

19SC2805 M. Vimal, U. Pathak, A.K. Halve, *Synth. Commun.* **2019**, *49,* 2805.

19SC2971 S. Konda, S. Jakkampudi, H.D. Arman, J.C.-G. Zhao, *Synth. Commun.* **2019**, *49,* 2971.

19SL178 D. Csókás, R.W. Bates, *Synlett* **2019**, *30,* 178.

19SL189 K. Tanaka, M. Kishimoto, N. Ohtsuka, Y. Iwama, H. Wada, Y. Hoshino, K. Honda, *Synlett* **2019**, *30,* 189.

19SL753 Y. Zhang, J. Lu, H. Li, X. Sun, L. Gao, Z. Song, *Synlett* **2019**, *30,* 753.

19SL1241 H. Wu, H. Liu, J. Li, X. Li, H.-P. Xiao, J. Jiang, *Synlett* **2019**, *30,* 1241.

19SL1474 S. Liu, H. He, M. Gan, P. Yi, X. Jiang, *Synlett* **2019**, *30,* 1474.

19SL1782 M. Kiamehr, L. Mohammadkhani, M.R. Khodabakhshi, B. Jafari, P. Langer, *Synlett* **2019**, *30,* 1782.

19SL2091 L. Li, Y.-W. Wang, S.-Q. Zhang, X.-F. Deng, G.-X. Li, G. Zhao, Z. Tang, *Synlett* **2019**, *30,* 2091.

19SL2247 T. Yamashiro, K. Yamada, H. Yoshida, Y. Tomisaka, T. Nishi, T. Abe, *Synlett* **2019**, *30,* 2247.

19SL2295 V. Kandula, P.K. Thota, P. Mallesham, K. Raghavulu, A. Chatterjee, S. Yennam, M. Behera, *Synlett* **2019**, *30,* 2295.

19T682 Z. Ye, L. Bai, Y. Bai, Z. Gan, H. Zhou, T. Pan, Y. Yu, J. Zhou, *Tetrahedron* **2019**, *75,* 682.

19T855 W. Liu, L. Fang, Y. Wan, J. Zhang, G. Deng, J. Wang, *Tetrahedron* **2019**, *75,* 855.

19T1034 C.-C. Chen, C.-L. Hsu, M.-J. Wu, *Tetrahedron* **2019**, *75,* 1034.

19T1044 Z. Wang, X. Li, L. Wang, P. Li, *Tetrahedron* **2019**, *75,* 1044.

19T1387 J.M. Rodrigues, P. Buisson, J.M. Pereira, I.M. Pinheiro, T. Fernández-Marcelo, M.H. Vasconcelos, S. Berteina-Raboin, M.-J.R.P. Queiroz, *Tetrahedron* **2019**, *75,* 1387.

19T1669 G. Zhao, R. Tong, *Tetrahedron* **2019**, *75,* 1669.

19T2350 J. Xian, L. Chen, L. Ye, Y. Sun, Z. Shi, Z. Zhao, X. Li, *Tetrahedron* **2019**, *75,* 2350.

19T2436 H. Jinnouchi, H. Nambu, K. Takahashi, T. Fujiwara, T. Yakura, *Tetrahedron* **2019**, *75,* 2436.

19T3456 Z.-H. Wang, X.-Y. Zhang, Y. You, J.-Q. Zhao, M.-Q. Zhou, X.-M. Zhang, X.-Y. Xu, W.-C. Yuan, *Tetrahedron* **2019**, *75,* 3456.

19T3609 J. Xu, W. Yang, W. Shi, B. Mao, Y. Lin, Y. Xiao, H. Guo, *Tetrahedron* **2019**, *75,* 3609.

19T3850 Y.-H. Wang, G. Qiu, H. Zhou, W. Xie, J.-B. Liu, *Tetrahedron* **2019**, *75,* 3850.

19T4071 N. Cabrera-Lobera, N. Velasco, R. Sanz, M.A. Fernández-Rodríguez, *Tetrahedron* **2019**, *75,* 4071.

19T4255 C.W. am Ende, K.A. Parker, *Tetrahedron* **2019**, *75,* 4255.

19T130490 Q. Liu, G. Xie, Q. Wang, Z. Mo, C. Li, S. Ding, X. Wang, *Tetrahedron* **2019**, *75,* 130490.
19T130533 H. Bao, X. Hu, J. Zhang, Y. Liu, *Tetrahedron* **2019**, *75,* 130533.
19T130606 C. Shearer, O. Desaunay, S. Zorc, A.D. Richaud, S.S. Samanta, N. Jeedimalla, S.P. Roche, *Tetrahedron* **2019**, *75,* 130606.
19T130752 M. Huo, J. Zhou, L. Bai, Q. Xu, Z. Zhou, H. Zhou, G. Liang, *Tetrahedron* **2019**, *75,* 130752.
19T130756 Q. Cai, S. Zhuang, M. Yang, N. Peng, Y. Liu, A. Wu, *Tetrahedron* **2019**, *75,* 130756.
19TL8 S. Kumar, K. Mukesh, K. Harjai, V. Singh, *Tetrahedron Lett.* **2019**, *60,* 8.
19TL52 M.A. Tan, P.P. Züger, S. Roggo, *Tetrahedron Lett.* **2019**, *60,* 52.
19TL331 R. Li, F. Jin, X.-R. Song, T. Yang, H. Ding, R. Yang, Q. Xiao, Y.-M. Liang, *Tetrahedron Lett.* **2019**, *60,* 331.
19TL432 A. Meissner, N. Tanaka, H. Takamura, I. Kadota, *Tetrahedron Lett.* **2019**, *60,* 432.
19TL557 H.M. Tanuraghaj, M. Farahi, *Tetrahedron Lett.* **2019**, *60,* 557.
19TL703 R. Mutyala, V.R. Reddy, R. Donthi, V.S.R. Kallaganti, R. Chandra, *Tetrahedron Lett.* **2019**, *60,* 703.
19TL831 P. Das, Y. Mankad, D.S. Reddy, *Tetrahedron Lett.* **2019**, *60,* 831.
19TL1248 T. Yang, X.-R. Song, R. Li, F. Jin, Y. Zhang, J. Bai, R. Yang, H. Ding, Q. Xiao, *Tetrahedron Lett.* **2019**, *60,* 1248.
19TL1854 P. Kumar, V. Garg, A.K. Verma, *Tetrahedron Lett.* **2019**, *60,* 1854.
19TL1904 G. Brahmachari, K. Nurjamal, *Tetrahedron Lett.* **2019**, *60,* 1904.
19TL150940 P.S. Mandal, A.V. Kumar, *Tetrahedron Lett.* **2019**, *60,* 150940.
19TL151039 Y. Miyazawa, M. Sugimoto, A. Tanaka-Oda, H. Makabe, *Tetrahedron Lett.* **2019**, *60,* 151039.
19TL151087 A. Mayooufi, M. Romdhani-Younes, J. Jacquemin, J. Thibonnet, *Tetrahedron Lett.* **2019**, *60,* 151087.
19TL151126 M.D. Gotsko, I.V. Saliy, L.N. Sobenina, I.A. Ushakov, B.A. Trofimov, *Tetrahedron Lett.* **2019**, *60,* 151126.
19TL151228 C. Wicks, S. Koh, A. Pounder, E. Carlson, W. Tam, *Tetrahedron Lett.* **2019**, *60,* 151228.
19TL151259 N. Liu, F. Chao, Y. Huang, Y. Wang, X. Meng, L. Wang, X. Liu, *Tetrahedron Lett.* **2019**, *60,* 151259.
19TL151262 M. Yoshida, M. Shibata, S. Mukae, K. Kinoshita, K. Matsumoto, T. Hirokane, *Tetrahedron Lett.* **2019**, *60,* 151262.

PROGRESS IN HETEROCYCLIC CHEMISTRY

VOLUME 32

Progress in Heterocyclic Chemistry (PHC) is an annual series commissioned by the International Society of Heterocyclic Chemistry (ISHC). Volumes in the series contain both highlights of the previous year's literature on heterocyclic chemistry and articles on new developing topics of particular interest to heterocyclic chemists. The highlight chapters in Volume 32 are all written by leading researchers in their fields and constitute a systematic survey of the important original material reported in the literature of heterocyclic chemistry in 2019. The additional articles in this volume are "The Stereospecific and Enantiospecific Synthesis of Indole Alkaloids Which Culminated in the Ambidextrous Pictet–Spengler Reaction for the C-19 Methyl–Substituted Sarpagine Family" by M. Toufiqur Rahman, Ojas A. Namjoshi, and James M. Cook, and "Epi-3,6-dithio-2,5-diketopiperazines (ETPs): An Overview of Synthetic Approaches to the ETP Core" written by Bruno C. Sil and Stephen T. Hilton.

As with previous volumes in the series, Volume 32 will enable academic and industrial chemists, and advanced students, to keep abreast of developments in heterocyclic chemistry in a convenient way.

ISBN 978-0-323-89812-6

ELSEVIER elsevier.com/books-and-journals