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Thiochroman-4-ones: synthesis and reactions

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Thiochroman-4-ones: synthesis and reactions

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The aim of this paper is to present the synthesis and reactions of thiochroman-4-ones. These compounds are used as precursors for the synthesis of many heterocyclic rings. The reactions of thiochroman-4-ones are subdivided into groups that cover reactions yielding heterocycles such as pyrazoles, imidazoles, thiazoles, indoles, pyridines, pyrimidines, and thiazepines.

Keywords: thiochroman-4-ones; thiochromones; heterocycles

1. Introduction

Thiochroman-4-ones are versatile reagents that have been extensively utilized in heterocyclic synthesis. In spite of an enormous number of reports on the utility of these compounds in the synthesis of heterocycles, to the best of our knowledge, this subject has never been surveyed. This paper demonstrates the synthesis and reactions of thiochroman-4-ones and shows the importance of thiochroman-4-ones as versatile reagents and intermediate in heterocyclic synthesis. This would be of value for both researchers and instructors of heterocyclic chemistry. The most important isomers of thiochromanones and thiochromones are listed. We will focus on the synthesis and reactions of thiochroman-4-ones.

2. Synthesis

2.1. *Synthesis of thiochroman-4-ones*

The palladium-catalyzed carbonylative ring-forming reactions of 2-iodothiophenol **1** with allene and carbon monoxide was described by Alper and coworker. The reaction afforded thiochroman-4-one **2** in good to excellent yield with quite high regioselectivity. The catalytic heteroannulation may involve regioselective addition of the sulfur moiety of thiol on the terminal site of allene, leading to

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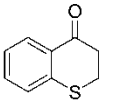
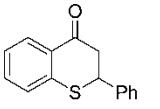
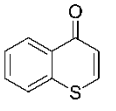


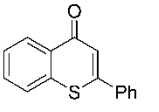
Thiochroman-4-one
(2,3-dihydro-4*H*-1-benzothiopyran-4-one)



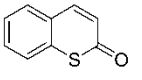
Thioflavanone
(2,3-dihydro-2-phenyl-4*H*-1-benzothiopyran-4-one)



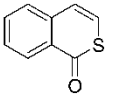
Thiochromone
(4*H*-1-benzothiopyran-4-one)



Thioflavone
(2-phenyl-4*H*-1-benzothiopyran-4-one)



Thiocoumarin
(2*H*-1-benzothiopyran-2-one)



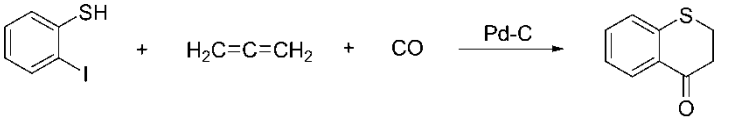
Isothiocoumarin
(1*H*-2-benzothiopyran-1-one)

arylpalladium formation followed by carbon monoxide insertion and subsequent intramolecular cyclization and then reductive elimination. The regioselectivity is probably governed by electronic factors (*1*) (Scheme 1).

Thiochroman-4-ones **5** were prepared in quantitative yields by the microwave irradiation-assisted cyclization of β-arylthiopropanoic acids **4**, which were prepared by the base-catalyzed addition of arylthiols **3** to β-chloropropanoic acid (*2, 3*) (Scheme 2).

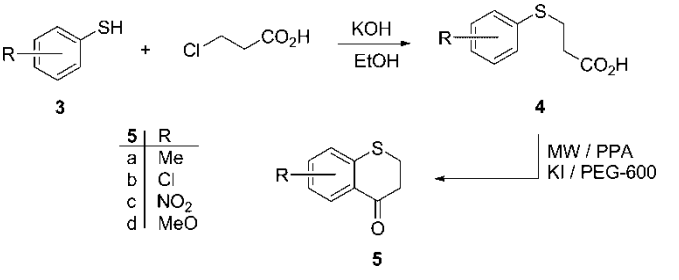
Treatment of thiophenols **6** with β-bromopropionic acid in ethanol containing 10% aqueous KOH under reflux gave 3-arylthiopropionic acids **7**. Cyclization of **7** to thiochroman-4-ones **8** was achieved when heated with concentrated sulfuric acid containing a catalytic amount of P_2O_5 (*4*) (Scheme 3).

The base-catalyzed condensation of β-propiolactone with 2-ethylthiophenol **9** gave 80% of arylthiocarboxylic acid derivative **10**. Cyclization of **10** with 98% sulfuric acid gave 8-ethylthiochromanone **11** in 55% yields (*5, 6*) (Scheme 4).



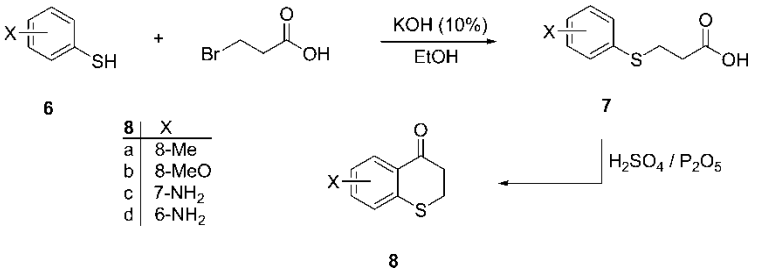
1 **2**

Scheme 1.

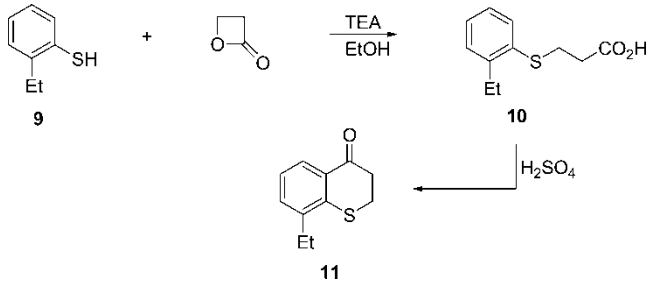


3 **4** **5**

Scheme 2.



Scheme 3.



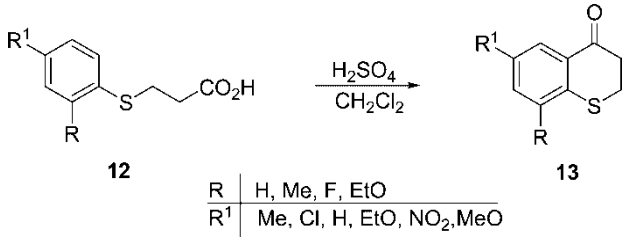
Scheme 4.

Thiochroman-4-ones **13** were prepared in excellent yields by treating β-arylthiopropanoic acids **12** with fuming sulfuric acid in methylene chloride at room temperature (*7*) (Scheme 5).

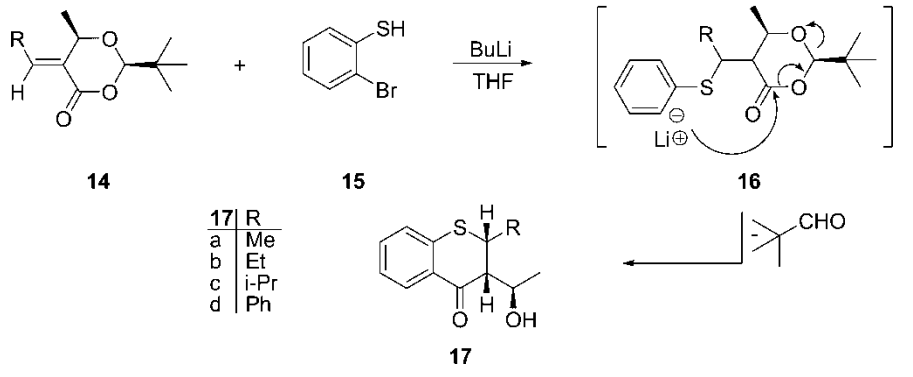
Liebscher and coworkers have recently reported the stereoselective synthesis of thiochroman-4-ones **17** by ring transformation of chiral 5-ylidene-1,3-dioxan-4-ones **14** with 2-bromothiophenol **15** via bromo-lithium exchange. The formation of thiochroman-4-ones **17** can be rationalized via stereoselective conjugate addition of thiophenol to α, β-unsaturated enone to form the non-isolable 5-(1-phenylthioalkyl)-1,3-dioxan-4-ones **16**, which undergo ring transformation to form thiochroman-4-one by the attack of the lithiated phenyl ring on the dioxanone carbonyl carbon atom with the cleavage of pivalaldehyde (*8*) (Scheme 6).

Thiochromanone **19** was efficiently synthesized by the intramolecular Friedel–Crafts acylation reaction of 3-methyl-4-(4′-chlorophenyl)thiobutyric acid **18** using catalytic amounts of Lewis acids such as $Bi(NTf_2)_3$ and $M(OTf)_3$ (M=Bi, Ga, In, and rare-earth metals) (*9*) (Scheme 7).

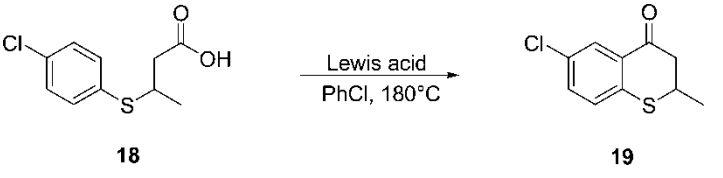
The reaction of thiophenols **3** with 3-methylbut-2-enoic acid in the presence of methane sulfonic acid afforded thiochromanones **20**. The reaction mechanism involved the *t*-butyl alkylation of the aromatic ring (*10*) (Scheme 8).



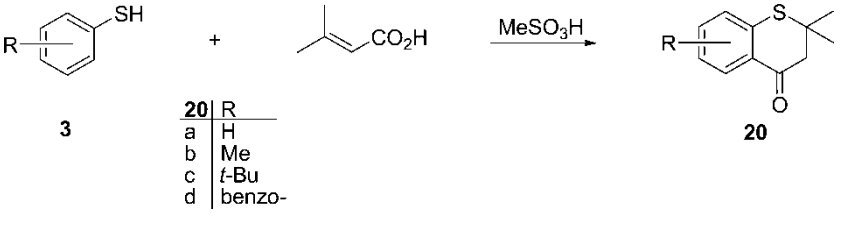
Scheme 5.



Scheme 6.



Scheme 7.



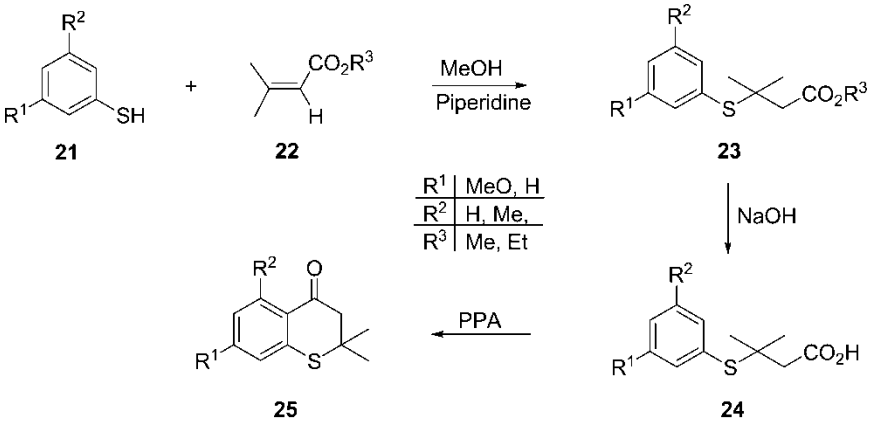
Scheme 8.

(Phenylthio)isovalerates **23** could be obtained via the base-catalyzed addition of thiophenols **21** to acrylates **22** in boiling methanol. Alkaline saponification of compounds **23** produced carboxylic acids **24**. Heating **24** with polyphosphoric acid (PPA) gave 2,2-dimethylthiochromanones **25** in good yields (*11*) (Scheme 9).

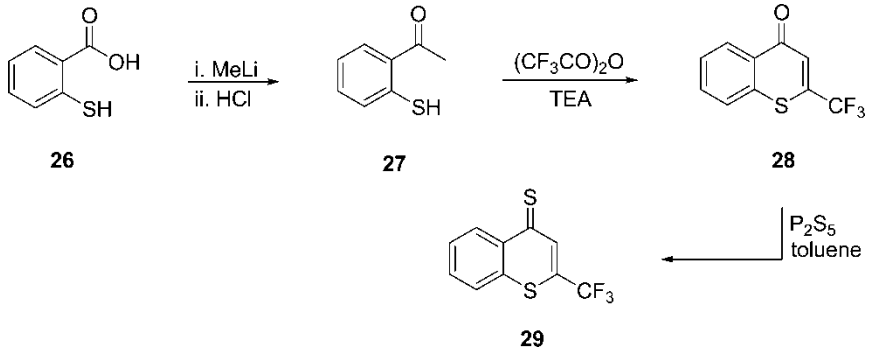
2.2. *Synthesis of thiochromones*

Sosnovskikh and coworkers have developed a simpler and more convenient route to 2-trifluoromethyl thiochromone **28** by treating 2-mercaptoacetophenone **27** (synthesized from thiosalicyclic acid **26** and methyl lithium (*12*) with trifluoroacetic anhydride in the presence of triethylamine in THF. When **28** refluxed with P_2S_5 in toluene, it afforded 2-trifluoromethyl-dithiochromone **29** in 66% yield (*12, 13*) (Scheme 10).

Thiosalicyclic acid **26** was converted into its *S*-acyl derivatives **30** by reaction with corresponding acid chlorides. Treatment of **30** with *t*-butyl-dimethylsilyl chloride (TBDMS-Cl) in the presence of imidazole gave the corresponding silyl ester **31** in good yields. When a mixture of **31** and (trimethylsilyl)methylene-triphenylphosphorane was heated in refluxing THF, the 2-substituted, 4*H*-1-benzothiopyran-4-ones **34** were obtained in 58–90% yields. The plausible

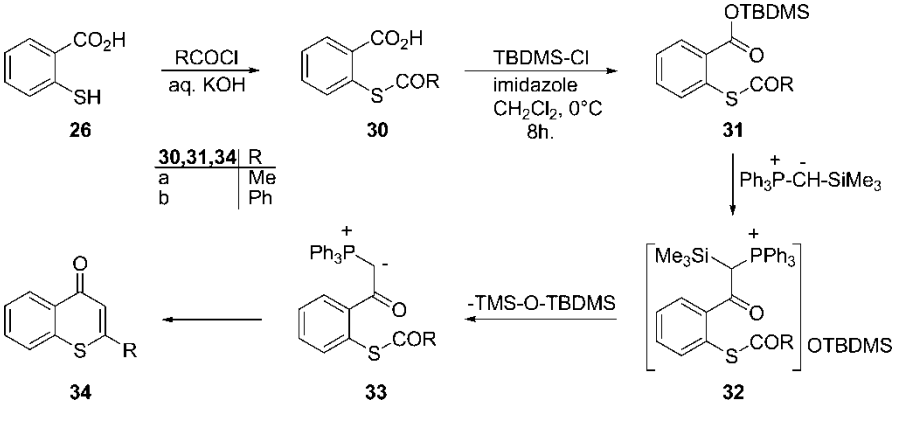


Scheme 9.



Scheme 10.

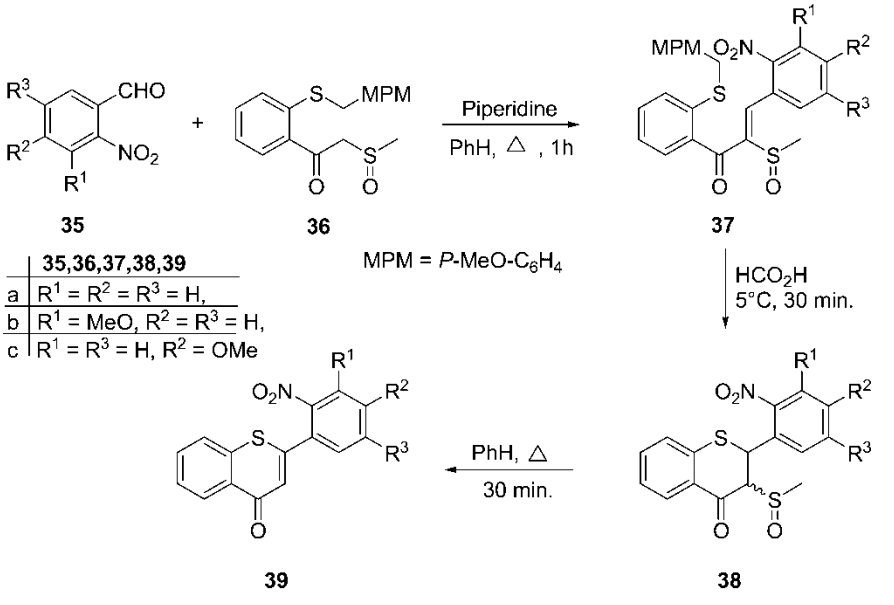
mechanism for formation of **34** can be visualized as initial acylation of (trimethylsilyl)methylene-triphenylphosphorane by **31** to the resulting phosphonium salt **32**. There is then migration of the trimethylsilyl group from C to O followed by the extrusion of silyl ether leading to the acylphosphorane **33**, which subsequently undergoes ring closure via the intramolecular Wittig reaction on the thiolester carbonyl to afford the desired thiochromones **34** (*14*) (Scheme 11).



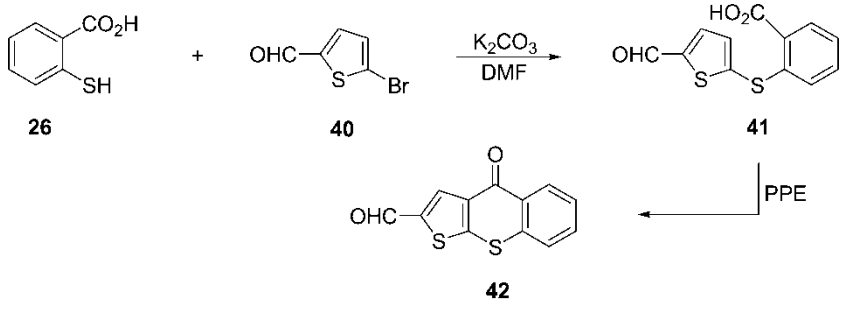
Scheme 11.

Condensation of benzaldehyde derivatives **35** with α-benzoylsulfoxide **36** in benzene containing a catalytic amount of piperidine gave α-sulfinyl enones **37** in good yields. Cyclization of **37** followed by debenzylation was performed by treatment with formic acid at 5 °C to give 3-(methylsulfinyl)-2,3-dihydro-4*H*-benzothiopyran-4-ones **38** as a mixture of diastereoisomers. Refluxing the diastereomer mixtures of **38** in benzene caused the elimination of methanesulfenic acid to form thioflavones **39** (*15*) (Scheme 12).

2-Formyl-4*H*-thieno[2,3-*b*][1]benzothiopyran-4-one **42** was prepared by the interaction of 5-bromo-2-thienaldehyde **40** and thiosalicylic acid **26** in DMF in the presence of potassium carbonate to furnish 2-[(5-formyl-2-thienyl)thio]benzoic acid **41**, which was cyclized by the action of polyphosphoric acid ethyl ester (PPE) to yield **42** (*16–18*) (Scheme 13).



Scheme 12.



Scheme 13.

3. Reactions

3.1. *Oxidation reactions*

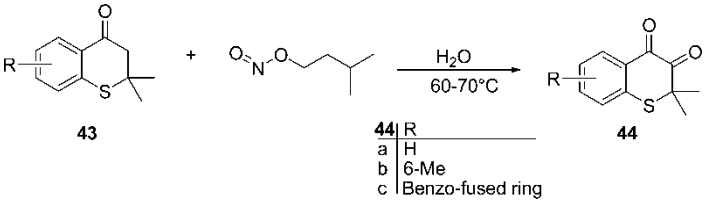
Oxidation of thiochroman-4-ones **43** with isoamyl nitrite led to the formation of thiochroman-3,4-diones **44** (*19*) (Scheme 14).

The oxidation of thiochroman-4-ones **45** by dimethyldioxirane (DMD) produced the corresponding sulfoxides **46** and/or sulfones **47**; their relative amounts depended on the amount of oxidant used. A low diastereoselectivity was observed in the sulfoxidation of the 2-substituted 1-thiochromanone **45** due to the small steric differentiation during the DMD attack (*20*) (Scheme 15).

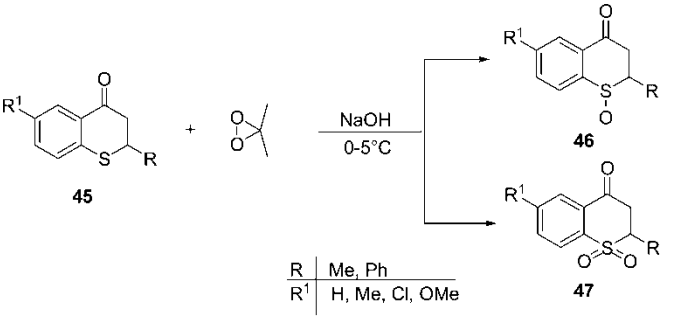
An unusual reactivity pattern was found in the DMD oxidation of the 1-thiochromones **48** in that the sulfoxides **49** were more reactive toward the electrophilic oxidizing agent than the corresponding sulfides. The observed abnormality may be explained in terms of the transannular stabilization of the transition structure for sulfone formation, promoted through favorable conformational effects in the sulfoxide. Higher sulfoxide/sulfone ratios were found in solvents of greater hydrogen bond donor capacity, which is in accordance with the postulated stabilizing effect (*20*) (Scheme 16).

Adam and coworkers have reported that the oxidation of (*E*)-3-arylidene-1-thiochroman-4-ones **50** with DMD afforded the corresponding sulfones **51** in good yields. Excess of DMD gave the sulfones chemoselectivity without the formation of epoxides. The epoxidation of sulfones **51** to spiroepoxides **52** required the more reactive methyl (trifluoromethyl)dioxirane as an oxidizing agent (*21*) (Scheme 17).

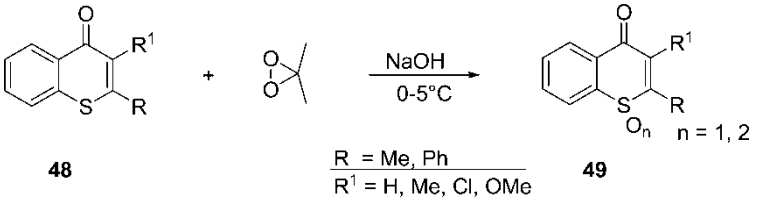
Oxidation of compounds **53** with hydrogen peroxide in glacial acetic acid delivered 3-benzyl-4H-1-thiochromen-4-one-1,1-dioxides **54** (*22*) (Scheme 18).



Scheme 14.

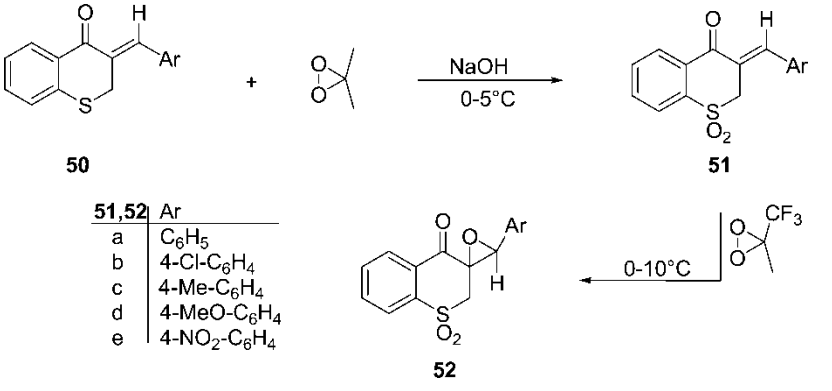


Scheme 15.



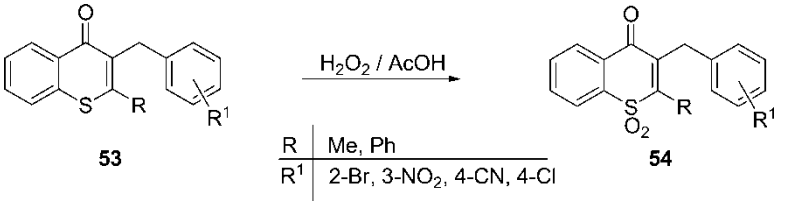
48 **49**

Scheme 16.



50 **51** **52**

Scheme 17.



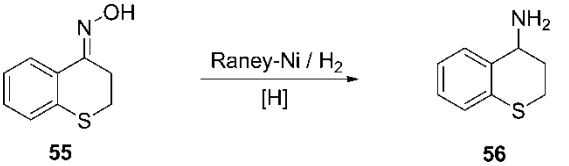
53 **54**

Scheme 18.

3.2. *Reduction reactions*

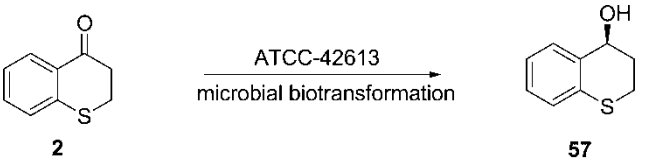
Reduction of 4-thiochromanone oxime **55** with Raney-Ni/H_2 was proved to be practically useful for the selective production of 4-aminothiochromane **56** (*23*) (Scheme 19).

Reduction of the carbonyl group of thiochroman-4-one **2** by *Mortierella isabellina* ATCC-42613 proceeds with high yield and enantiomeric excess (ee > 98%) to give (*S*)-3,4-dihydro-2*H*-thiochromen-4-ol **57** (*24*) (Scheme 20).



55 **56**

Scheme 19.



2 **57**

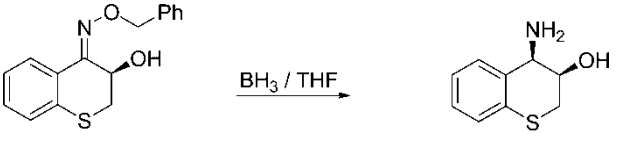
Scheme 20.

Stereoselective reduction of (*R*, *Z*)-2,3-dihydro-3-hydroxythiochromen-4-one O^4-benzyl oxime **58** with borohydride in THF gave an excellent yield (>90%) of (3*R*, 4*R*)-4-amino-3,4-dihydro-2*H*-thiochromen-3-ol **59** (*25*) (Scheme 21).

3.3. *Halogenation reactions*

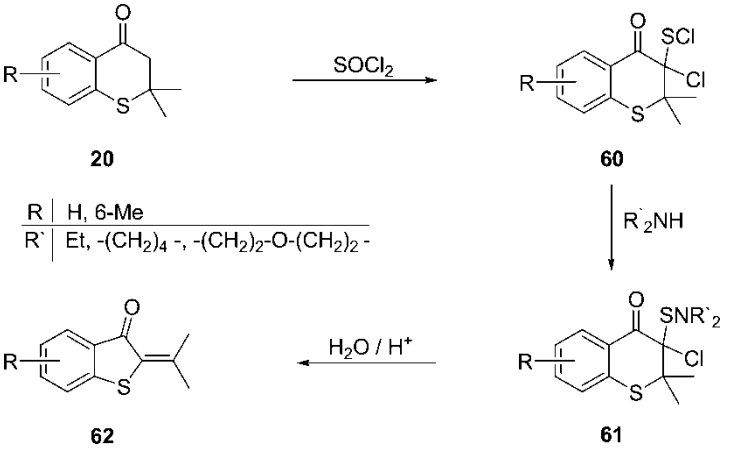
Gabbutt and coworkers have reported that 3-chloro-3-sulfenylchroman-4-ones **60** are efficiently obtained from the treatment of thiochroman-4-ones **20** with excess of thionyl chloride. Treatment of **60** with secondary amine gave sulfenamides **61**, which underwent acid-catalyzed hydrolytic cleavage to give benzo[*b*]thiophen-3-ones **62** (*26, 27*) (Scheme 22).

Treatment of 3-(hydroxymethylene)thiochroman-4-one **63** with *N*-chlorosuccinimide in carbon tetrachloride afforded a mixture of 3-chlorothiochroman-4-one **64**, 3-chlorothiochromone **65**, and 2,3-dichlorothiochromone **66**. The products obtained are rationalized in terms C-chlorination, in contrast to the action of *N*-chlorosuccinimide on thiochromanone, for which S-chlorination is postulated (*28*) (Scheme 23).



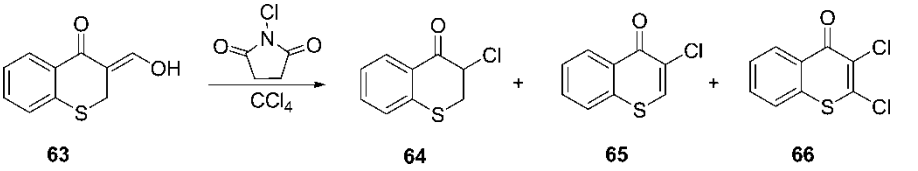
58 **59**

Scheme 21.



20 **60** **62** **61**

Scheme 22.



Scheme 23.

3.4. *Cyanoethylation reactions*

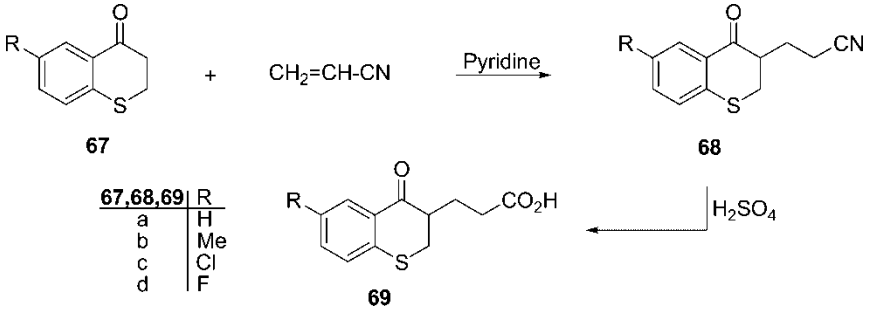
Cyanoethylation of thiochroman-4-ones **67** with acrylonitrile gave 4-cyanoethylthiochromanones **68**, which hydrolyzed to give carboxylic acid derivatives **69** (*29*) (Scheme 24).

3.5. *Mannich reactions*

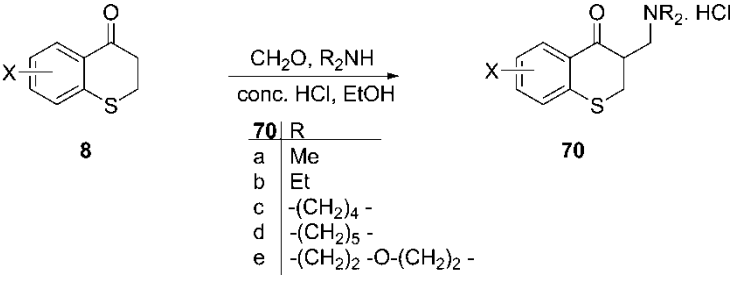
Warming of compound **8** with formaline and secondary amine in ethanol containing a catalytic amount of concentrated hydrochloric acid produced 3-alkylaminomethylthiochroman-4-ones **70** in good yields (*4*) (Scheme 25).

Condensation of 8-ethylthiochroman-4-one **11** with *p*-formaldehyde and secondary amine in dry benzene containing few drops of concentrated hydrochloric acid gave the corresponding Mannich bases **71**. The Mannich bases **71** showed antiamebic activity (*5, 6*) (Scheme 26).

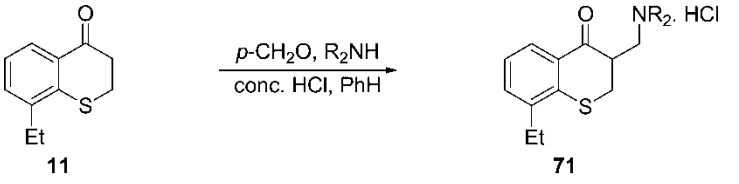
Treatment of 6-fluorothiochroman-4-one **67d** with *p*-formaldehyde and secondary amine with few drops of acetic acid in boiling ethanol afforded the corresponding Mannich bases **72**. The Mannich bases showed high antifungal activities (*30, 31*) (Scheme 27).



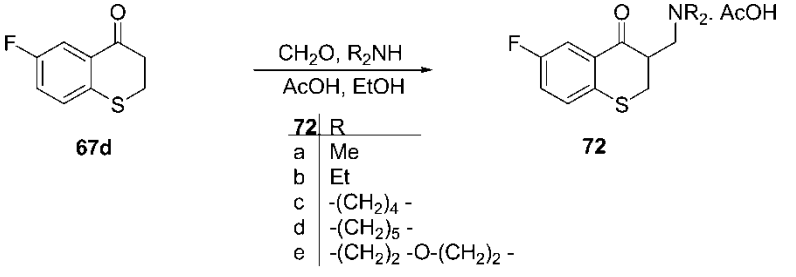
Scheme 24.



Scheme 25.



Scheme 26.



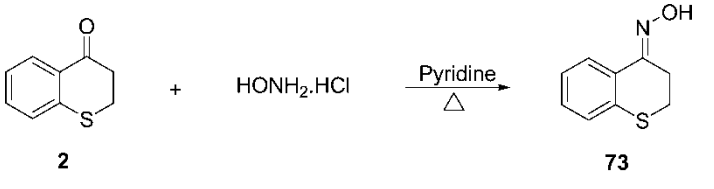
Scheme 27.

3.6. *Oxime formation*

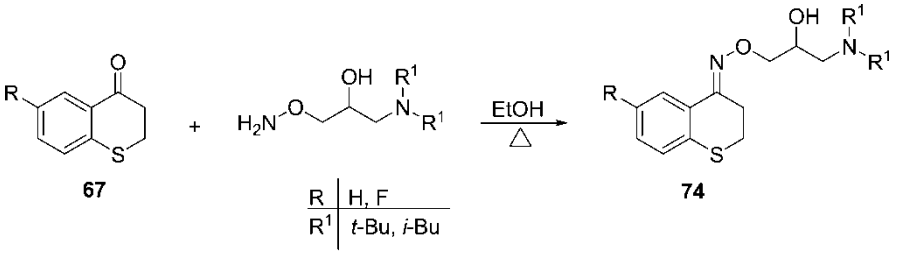
4-Thiochromanone oxime **73** was formed through heating of thiochroman-4-one **2** with hydroxylamine in boiling ethanol containing pyridine as a basic catalyst (*32*) (Scheme 28).

Thiochromanone oximes **74** were prepared via refluxing of thiochroman-4-ones **67** with hydroxylamine derivatives in ethanol. The oximes were applied as adrenergic β-blocking agents. Compound **74** (R=F, R^1=*t*-Bu) showed good activity in the in vitro experiments on the isolated atria of guinea pigs stimulated with isoprenaline (*33*) (Scheme 29).

The condensation of *o*-phenylhydroxylamine with thiochroman-4-one **2** in boiling ethanol gave thiochromanone oxime **75**. Heating of thiochromanone oxime **75** in acidic medium gave 6*H*-benzo[*d*]thiochromeno[4,3-*b*]furan **78** in good yields. The plausible mechanism for the formation



Scheme 28.



Scheme 29.

of compound **78** was the initial [3,3] sigmatropic rearrangement of oxime **75** to form the non-isolable intermediate **76**, which underwent intramolecular cyclization to form **77** followed by deamination to give the desired product **78** (*34, 35*) (Scheme 30).

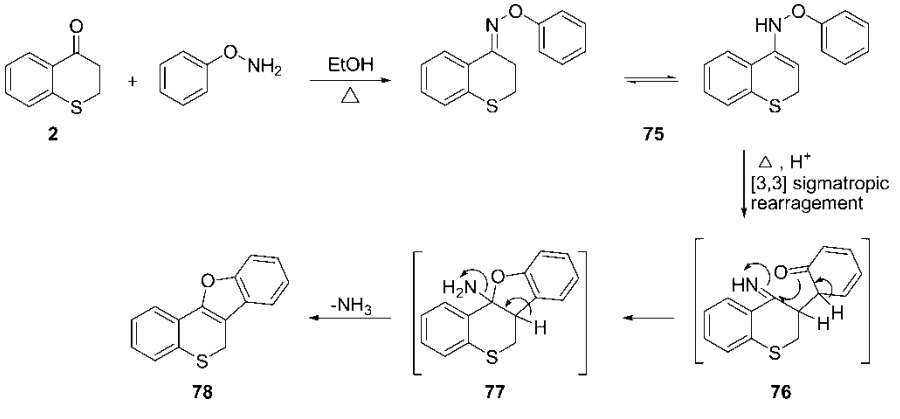
3.7. *Reaction with aldehydes*

3-Benzyl-4*H*-1-thiochromones **53** have been synthesized by the piperidine catalyzed reaction of thiochroman-4-ones **34** with aromatic aldehydes. Thiation of compound **53** with the Lawesson reagent in dry xylene afforded 3-benzyl-4*H*-1-thiochromen-4-thiones **79** (*22*) (Scheme 31).

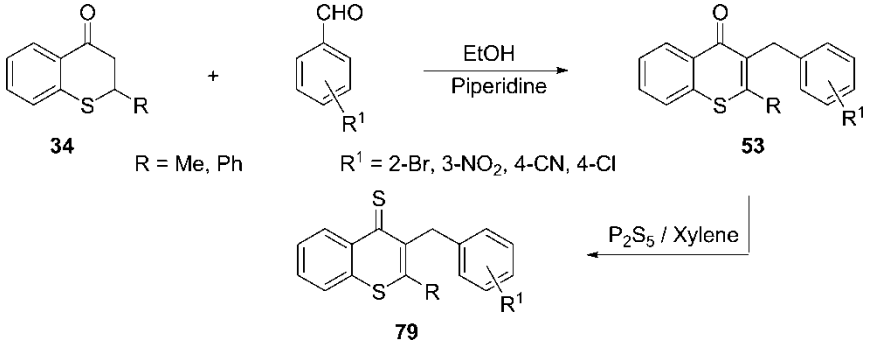
3.8. *Claisen condensation*

The Claisen condensation of thiochroman-4-one **2** with ethylformate in sodium methoxide gave 2-hydroxymethylenethiochroman-4-one **80**. Treatment of **80** with hydroxylamine followed by basification with sodium hydroxide delivered 3-cyano-thiochroman-4-one **81** (*36*) (Scheme 32).

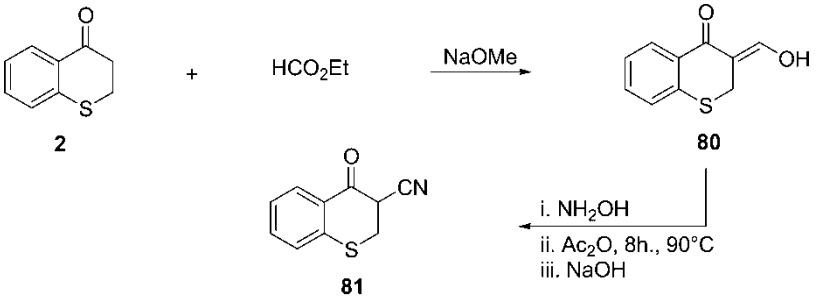
The Claisen condensation of thiochroman-4-one **82** with diethyl oxalate in sodium ethoxide solution gave ethyl 2-(3,4-dihydro-4-oxo-2*H*-thiochromen-3-yl)-2-oxoacetate **83**, which underwent heterocyclization upon heating with phenyl hydrazine in glacial acetic acid to



Scheme 30.



Scheme 31.



Scheme 32.

produce ethyl 1,4-dihydro-1-phenyl[1]benzothiopyrano[4,3-*c*]pyrazole-3-carboxylate **84**. Heating of **84** with acetonitrile in the presence of sodium hydride gave 3-(1,4-dihydro-1-phenyl-[1]benzothiopyrano[4,3-*c*]pyrazol-3-yl)-3-oxopropanenitrile **85**, which upon stirring with phenylisocyante afforded 2-cyano-3-(1,4-dihydro-1-phenyl-[1]benzothiopyrano[4,3-*c*]pyrazol-3-yl)-3-oxo-*N*-phenylpropanamide **86** (*37*) (Scheme 33).

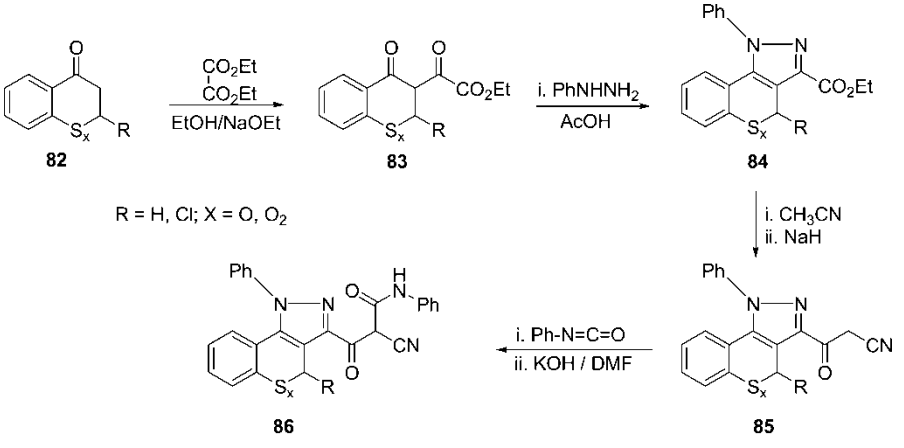
3.9. *Arylidene formation*

The base-catalyzed (*e.g.* NaOH, piperidine) Aldol condensation of thiochroman-4-one **2** with aromatic aldehydes in ethanol gave 3-arylidene-1-thiochroman-4-ones **50** in high yields. The compounds **50** showed potent antimycotic activity (*38, 39*) (Scheme 34).

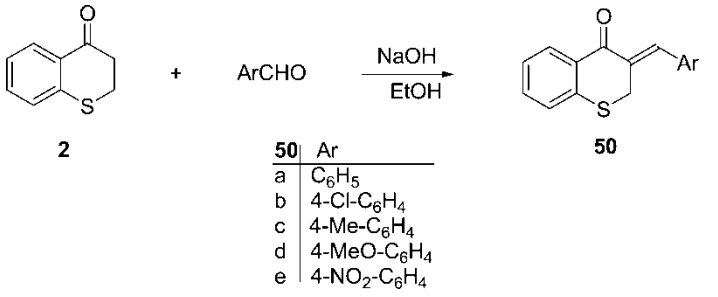
The UV-induced photoisomerization of (*E*)-3-arylidene-1-thiochromanones **50** led to the formation of (*Z*)-3-arylidene-1-thiochromanones **87** (*40*) (Scheme 35).

3.10. *Vilsmeier reaction*

Treatment of thiochroman-4-one **2** with Vilsmeier–Haack reagent (DMF-$POCl_3$) at 20 °C gave β-chlorovinyl aldehyde **88**. However, with excess of DMF-$POCl_3$ at 100 °C, thiochroman-4-one **2** gave 4-oxo-4*H*-thiochromene-3-carbaldehyde **89** (*41, 42*) (Scheme 36).

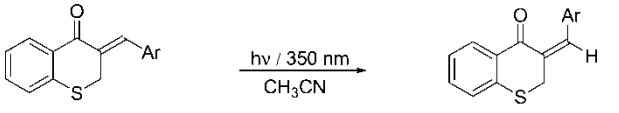


Scheme 33.



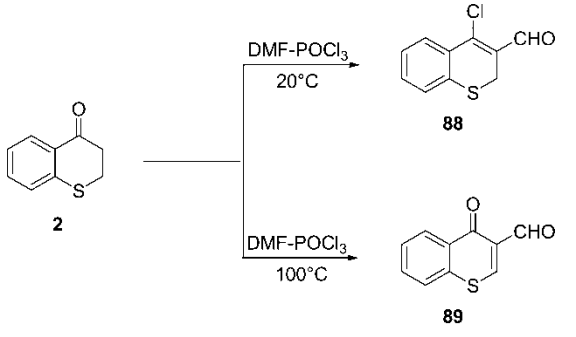
50	Ar
a	C_6H_5
b	4-Cl-C_6H_4
c	4-Me-C_6H_4
d	4-MeO-C_6H_4
e	4-NO_2-C_6H_4

Scheme 34.



89	Ar
a	C_6H_5
b	4-Cl-C_6H_4
c	4-Me-C_6H_4
d	4-MeO-C_6H_4
e	4-NO_2-C_6H_4

Scheme 35.



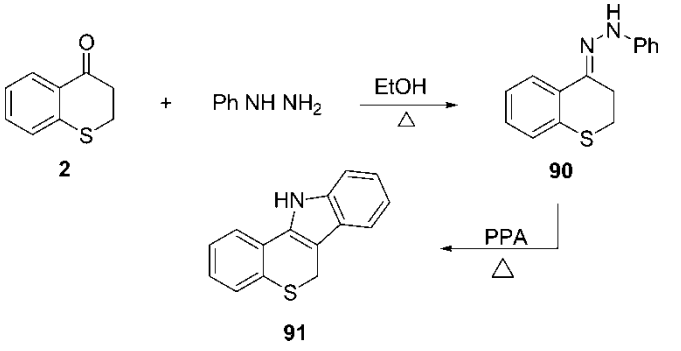
Scheme 36.

3.11. *Fischer indole synthesis*

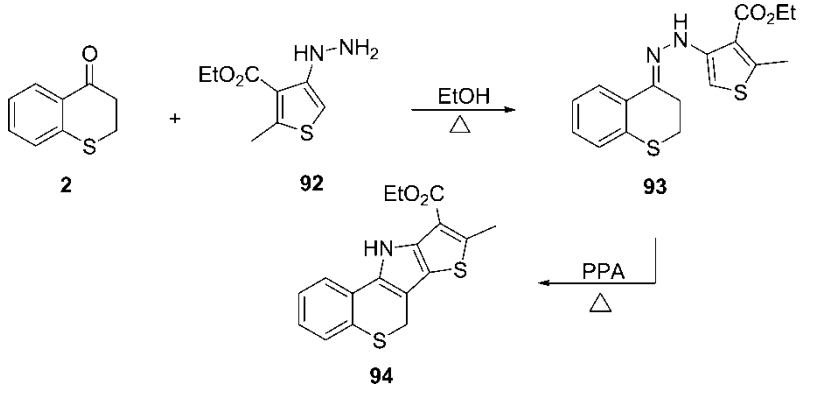
Condensation of thiochroman-4-one **2** with phenyl hydrazine in boiling ethanol produced phenylhydrazonothiochroman-4-one **90**. The Fischer indolization of compound **90** with polyphosphoric acid (PPA) led to the formation of 6,11-dihydrothiochromeno[4,3-*b*]indole **91**, which showed potential biological interest as potential carcinogens or enzyme-inducers (*43*) (Scheme 37).

Condensation of thiochroman-4-one **2** with 2-methyl-3-ethoxycarbonyl-4-thienylhydrazine **92** in boiling ethanol afforded thienylhydrazonothiochromanone **93**. The Fischer indolization of compound **93** produced 8-methyl-9-carboethyl-10*H*-5,6-dihydrothieno[2,3-*d*]thiochromeno[4,3-*b*]pyrrole **94** (*44*) (Scheme 38).

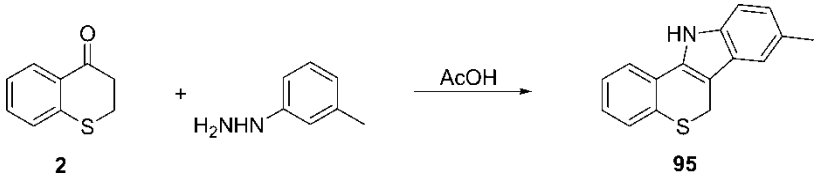
6,11-Dihydro-8-methylthiochromeno[4,3-*b*]indole **95** was synthesized through heating of thiochroman-4-one **2** with 3-methylphenylhydrazine in glacial acetic acid. Compound **95** was used in agriculture and horticulture (*45*) (Scheme 39).



Scheme 37.



Scheme 38.



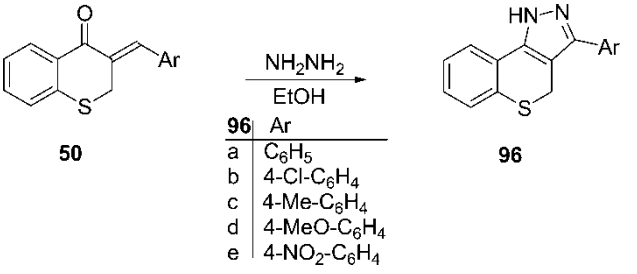
Scheme 39.

3.12. *Pyrazoles formation*

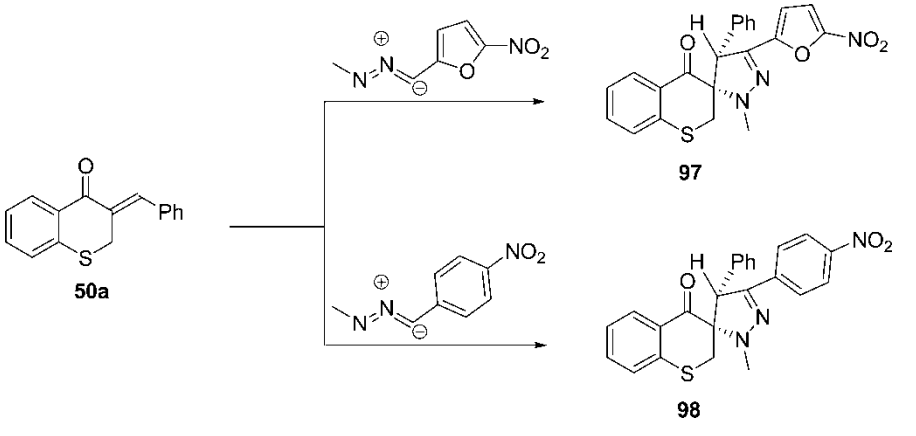
The basic catalyzed cyclocondensation of 3-arylidenethiochromanones **50** with hydrazine gave the corresponding thiochromeno[4,3-*c*]pyrazole **96** (*46*) (Scheme 40).

The regio- and stereoselective synthesis of spiropyrazolines **97** and **98** was obtained by the 1,3-dioplar cycloaddition of (*E*)-3-benzylidenethiochromanone **50a** to *C*-2-(5-nitrofuryl)-*N*-methylnitrile-imine and *C*-(4-nitrophenyl)-*N*-methylnitrile-imine, respectively (*47–50*) (Scheme 41).

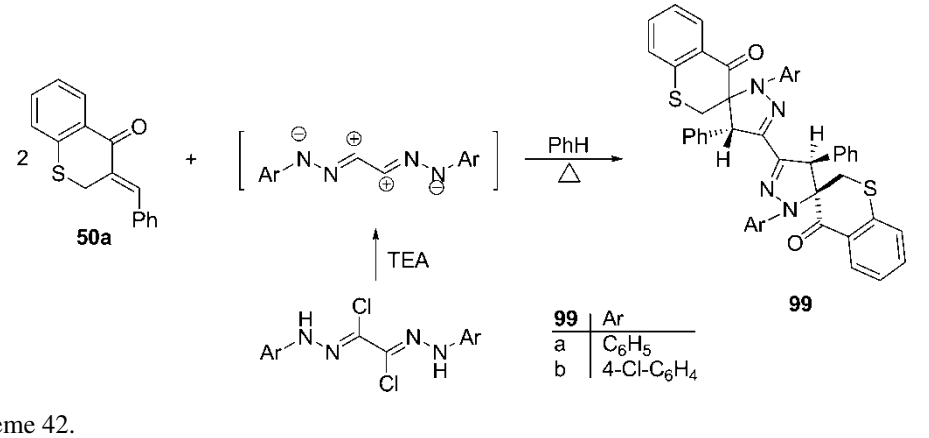
Dawood *et al.* reported the regio- and stereoselective synthesis of *bis*-spiropyrazoline-5,3′-thiochroman-4-one derivatives **99** via the 1,3-dipolar cycloaddition of *bis*-nitrilimines (obtained *in situ* from the reaction of *bis*-hydrazonoyl chlorides with triethylamine) with 3-benzylidene thiochroman-4-one **50a** (*51*) (Scheme 42).



Scheme 40.



Scheme 41.

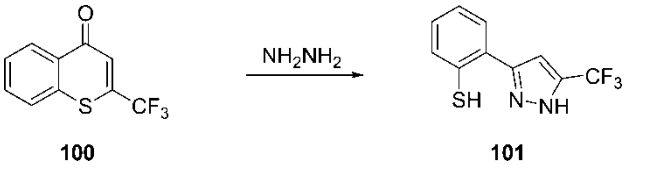


Scheme 42.

Treatment of thiochromone **100** with hydrazine hydrate at 20 °C gave 3-(2-mercaptophenyl)-5-trifluoromethylpyrazole **101** (*52*) (Scheme 43).

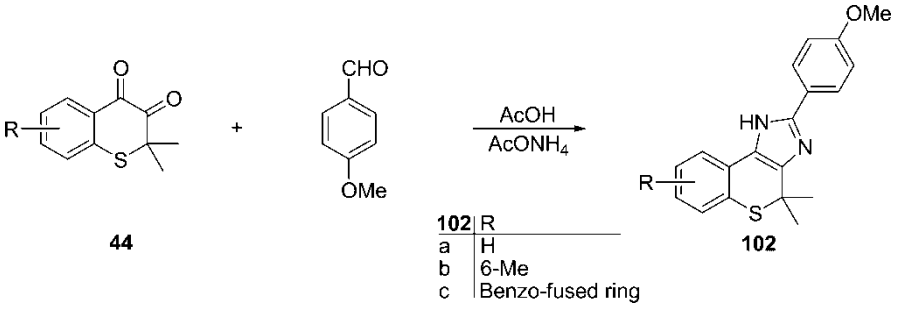
3.13. *Imidazoles formation*

Heterocyclization of thiochroman-3,4-diones **44** with *p*-anisaldehyde and ammonium acetate in glacial acetic acid at reflux gave the corresponding 1,4-dihydrothiochromeno[4,3-*d*]imidazoles **102** (*19*) (Scheme 44).



100 **101**

Scheme 43.



44 **102**

102	R
a	H
b	6-Me
c	Benzo-fused ring

Scheme 44.

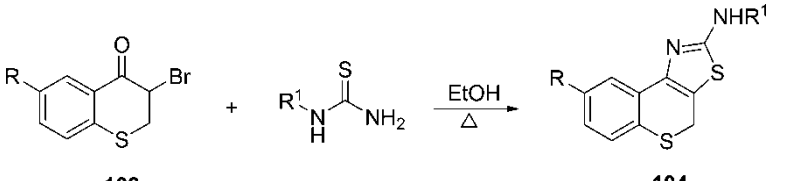
3.14. *Thiazoles formation*

2-Amino-4*H*-benzothiopyrano[4,3-*d*]thiazoles **104** were synthesized by the interaction of 3-bromothiochroman-4-ones **103** with substituted thioureas in boiling ethanol. Compounds **104** showed high antimicrobial, analgesic, and anti-inflammatory activities (*53*) (Scheme 45).

9-Methyl-6*H*,11*H*-benzothiopyrano[4′, 3′ : 4, 5]thiazolo[3,2-*a*]pyrimidin-11-one **105** could be achieved via the reaction of 3-bromothiochroman-4-one **103** with 2-mercapto-6-methyl-pyrimidin-4-one in boiling ethanol containing a catalytic amount of triethylamine (*54*) (Scheme 46).

3.15. *Isoxazole formation*

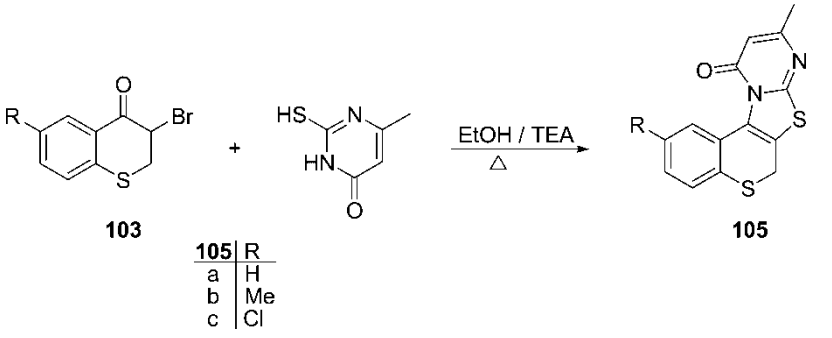
The 1,3-dipolar cycloaddition of (*E*)-3-benzylidenethiochroman-4-one **50a** to 4-nitrobenzonitrile oxide proceeded with high regio- and stereoselectivity and gave spiroisoxazole **106** (*47–49*) (Scheme 47).



103 **104**

R	H, Me, Cl
R^1	H, Ph, 4-MeC_6H_4, 4-MeO-C_6H_4, 4-ClC_6H_4, 4-Br-C_6H_4, 1-naphthyl

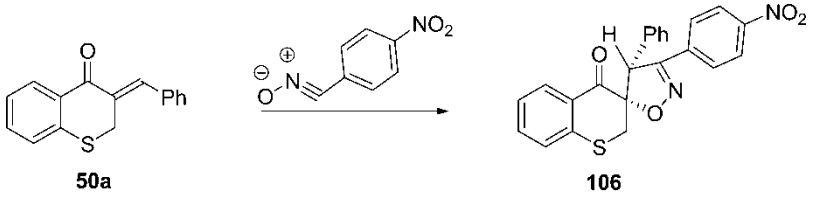
Scheme 45.



103 105

105	R
a	H
b	Me
c	Cl

Scheme 46.



50a 106

Scheme 47.

3.16. *Pyridines formation*

3-Aminothiochromone **108** was easily prepared by the reaction of 3-bromothiochromone **107** with sodium azide in aqueous methanol. Condensation of **108** with diethyl ethoxymethylenemalonate and dimethyl acetylene dicarboxylate gave intermediates **109** and **111**, which were thermally cyclized to give 4,10-dihydro-4,10-dioxo-1*H*-[1]benzothiopyrano[3,2-*b*]pyridine carboxylates **110** and **112**, respectively (*55*) (Scheme 48).

The Micheal addition of malononitrile to 3-arylidene thiochroman-4-ones **50** in glacial acetic acid containing ammonium acetate afforded the corresponding thiochromeno[4,3-*b*]pyridines **113** (*46*) (Scheme 49).

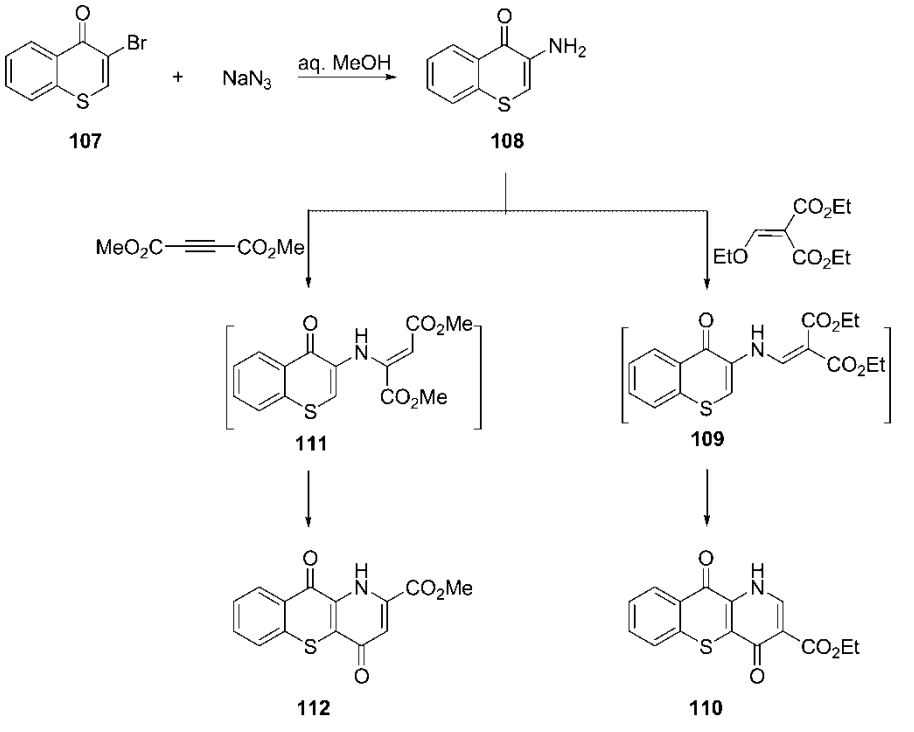
3.17. *Pyran formation*

The Micheal addition of malononitrile to 3-arylidene thiochroman-4-ones **50** in boiling methanol containing a catalytic amount of piperidine afforded the corresponding thiochromeno[4,3-*b*]pyran **114** (*46*) (Scheme 50).

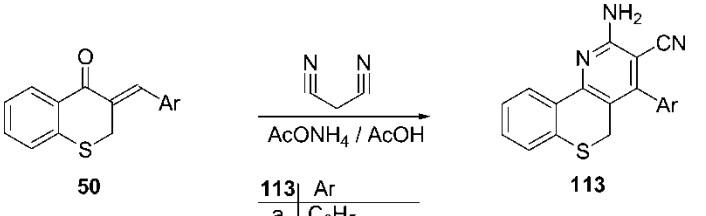
3.18. *Pyrimidines formation*

The basic catalyzed cyclocondensation of 3-arylidenethiochroman-4-ones **50** with guanidine and thiourea gave the corresponding thiochromeno[4,3-*d*]pyrimidine **115** and thiochromeno[4,3-*d*]pyrimidine-2(5*H*)thione **116** derivatives, respectively (*46, 56*) (Scheme 51).

Metwally *et al.* reported that the acid-catalyzed cyclocondensation one-pot reactions of thiochroman-4-one **2** with *p*-anisaldehyde and urea/or 5-aminotetrazole in *n*-butanol afforded the corresponding 3,4-dihydro-1*H*-thiochromeno[4,3-*d*]pyrimidinone **117** and tetrazolo[1,5-*a*]thiochromeno[4,3-*d*]pyrimidine **118**, respectively (*57*) (Scheme 52).

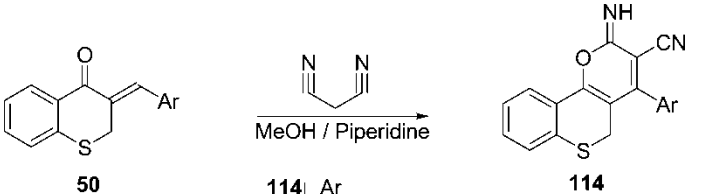


Scheme 48.



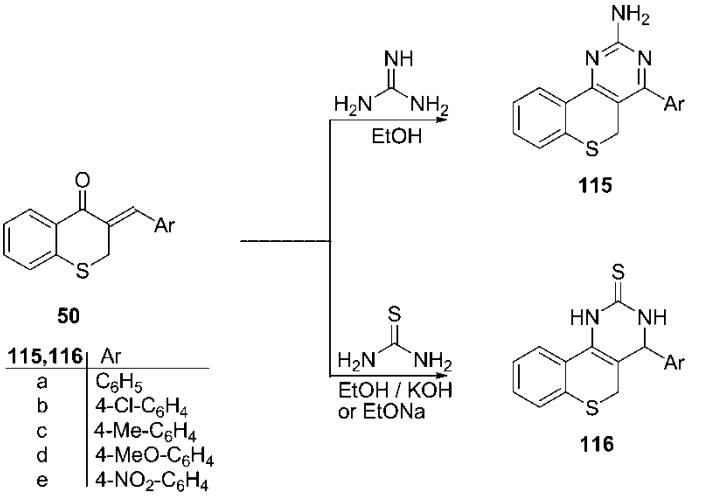
113	Ar
a	C_6H_5
b	4-Cl-C_6H_4
c	4-Me-C_6H_4
d	4-MeO-C_6H_4
e	4-NO_2-C_6H_4

Scheme 49.



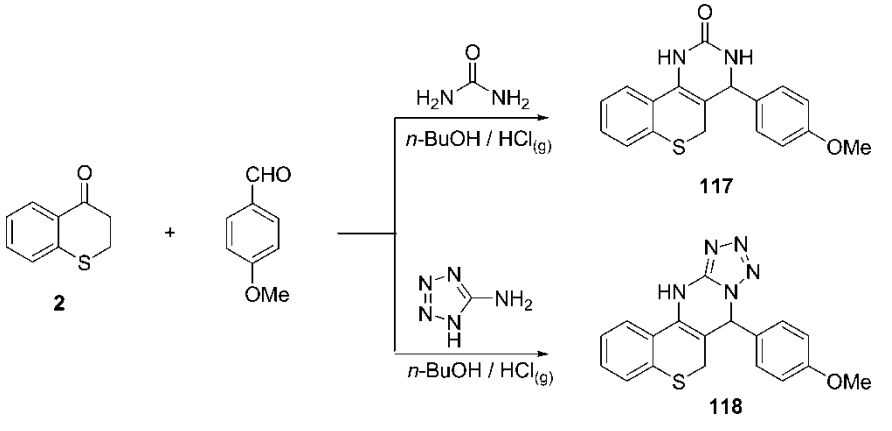
114	Ar
a	C_6H_5
b	4-Cl-C_6H_4
c	4-Me-C_6H_4
d	4-MeO-C_6H_4
e	4-NO_2-C_6H_4

Scheme 50.

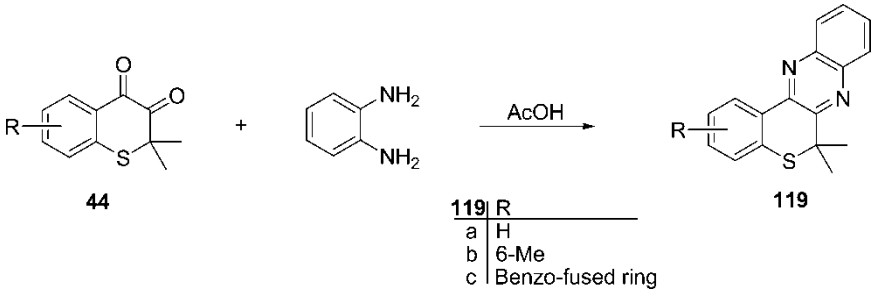


115,116	Ar
a	C_6H_5
b	4-Cl-C_6H_4
c	4-Me-C_6H_4
d	4-MeO-C_6H_4
e	4-NO_2-C_6H_4

Scheme 51.



Scheme 52.

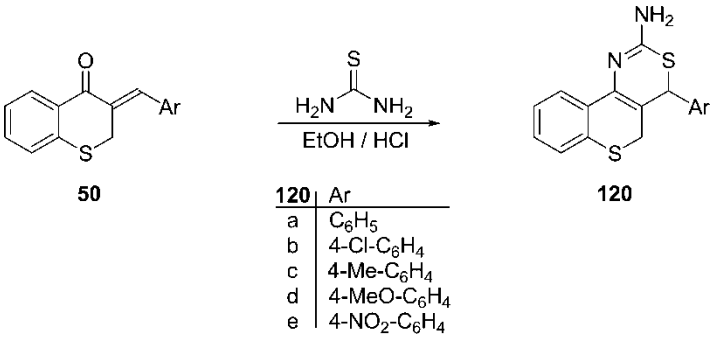


119	R
a	H
b	6-Me
c	Benzo-fused ring

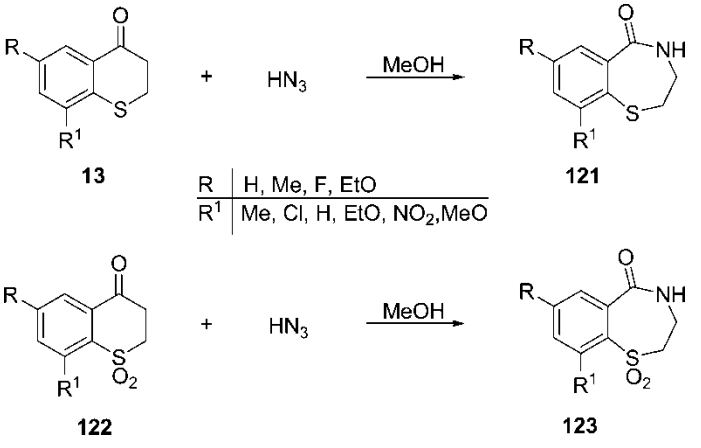
Scheme 53.

3.19. *Quinoxaline formation*

Heterocyclization of thiochroman-3,4-diones **44** with *o*-phenylenediamine in glacial acetic acid at reflux gave the corresponding 6*H*-thiochromeno[3,4-*b*]quinoxalines **119** (*19*) (Scheme 53).



Scheme 54.



Scheme 55.

3.20. *Thiazine formation*

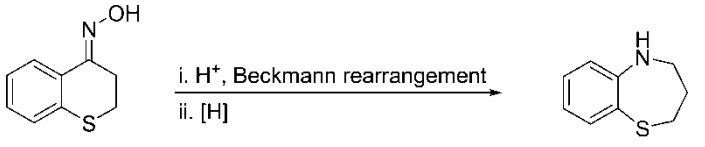
When 3-arylidenethiochroman-4-ones **50** were allowed to react with thiourea in hot ethanol in the presence of concentrated hydrochloric acid, [1]benzothiopyrano[4,3-*d*]-3,1-thiazines **120** were obtained as the only products (*56*) (Scheme 54).

3.21. *Thiazepines formation*

The Schmidt rearrangement reaction of 6,8-disubstituted-1-thiochroman-4-ones **13** with hydrazoic acid afforded 7,9-disubstituted-5-oxo-2,3,4,5-tetrahydro-1,4-benzothiazepine **121** in 3–29% yields. However, the Schmidt reaction of 1-thiochromanone 1,1-dioxides **122** under the same experimental condition gave only 1,5-benzothiazepine 5,5-dioxides **123** in 15–65% yields (*58, 59*) (Scheme 55).

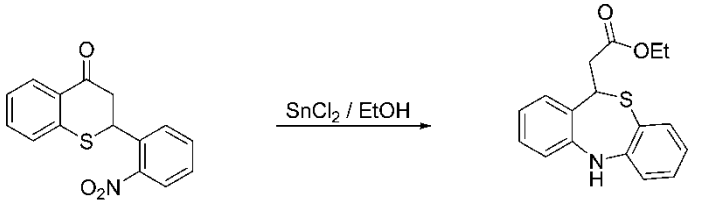
Orlova *et al.* [32] reported a preparative method for the synthesis of 2,3,4,5-tetrahydro-1,5-benzothiazepine **124** by the Beckmann rearrangement of 4-thiochromanone oxime **73** (Scheme 56).

2-(2-Nitrophenyl)thiochroman-4-one **125** on treatment with $SnCl_2$ in ethanol produced ethyl 5,11-dihydrodibenzo[*b*, *e*][1,4]thiazepin-11-ylacetate **126**. The formation of **126** was rationalized on the basis of the semipinacol rearrangement (*60*) (Scheme 57).



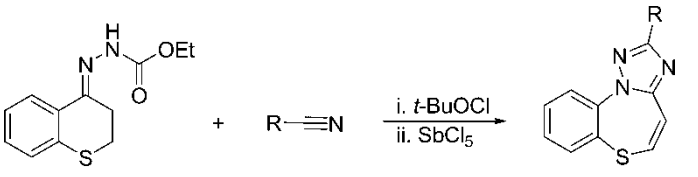
73 124

Scheme 56.



125 126

Scheme 57.



127

128	R
a	Me
b	Ph

128

Scheme 58.

A facial synthesis of the neutral 1,2,4-triazolo[3,2-*d*][1,5]benzothiazepines **128** was accomplished via cycloaddition of the allene-like cations, generated sequentially by the action of thiochroman-4-one ethoxycarbonylhydrazone **127** with *t*-butoxy chloride and $SbCl_5$ on the triple bond of nitriles, ensuing ring expansion annulation and hydrolytic removal of the *N*(1)-ethoxycarbonyl group (*61, 62*) (Scheme 58).

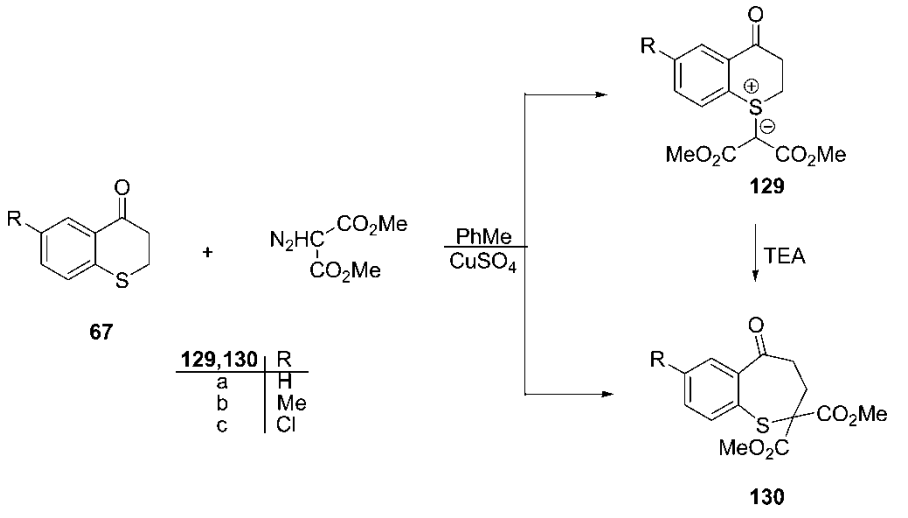
3.22. *Miscellaneous reactions*

Heating of thiochroman-4-ones **67** with dimethyldiazomalonate in refluxing toluene in the presence of copper sulfate gave the corresponding *bis*-methoxycarbonylmethanides **129** and the ring expansion product benzothienpin-5-ones **130**. Treatment of **129** with triethylamine gave compounds **130** (*63, 64*) (Scheme 59).

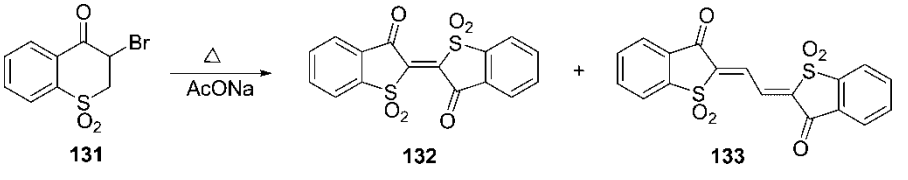
Heating of 3-bromothiochroman-4-one 1,1-dioxide **131** in the presence of sodium acetate led to the formation of a mixture of thioindigo **132** and ethanediylidenethioindigo **133** via a ring contraction (*65*) (Scheme 60).

The reaction of thiochroman-4-ones **134** with sodium chloro-*p*-toluene sulfonamide in methanol gave the corresponding *N*-tolylsulfonylsulfimides **135**. When compounds **135** were heated with triethylamine in chloroform, they gave the corresponding ring opening adduct sulfenamides **136** (R=Me) and benzothiazepinones **137** (R=H) (*66*) (Scheme 61).

The anodic fluorination of spiropyrazole-5,3′-thiochroman-4-ones **138** in dimethoxyethane containing tetra-ethyl ammonium fluoride resulted in ring opening of spiroheterocycles, which



Scheme 59.



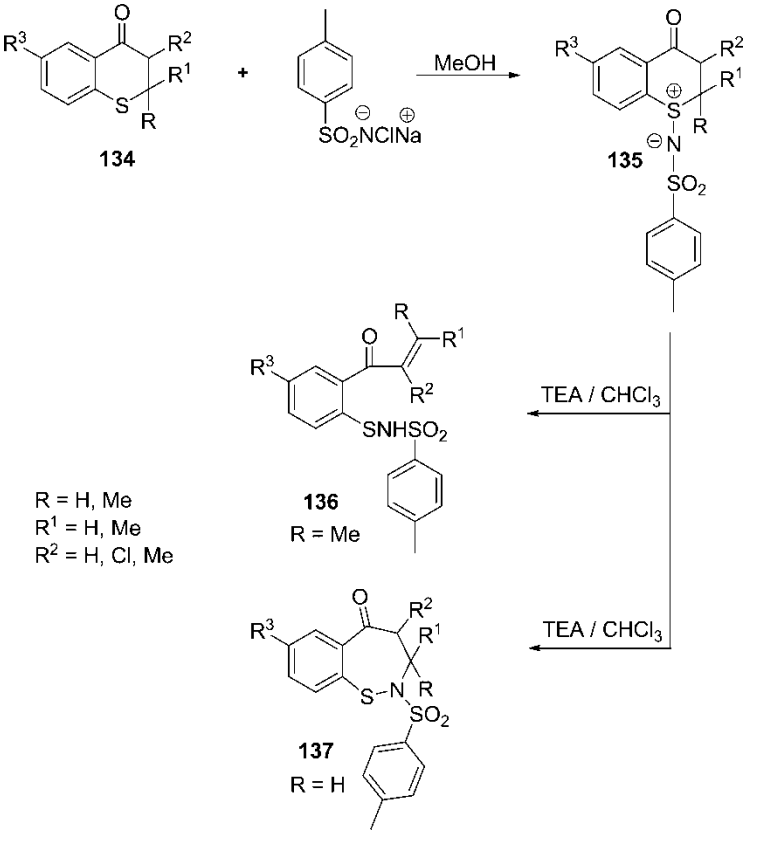
Scheme 60.

led to the formation of (5-pyrazolyl)methyl *o*-fluorocarbonyl-phenylthioethers **139**, which further converted to 1,3-diphenylpyrazole-5-carboxaldehyde derivatives **140** (*50*) (Scheme 62).

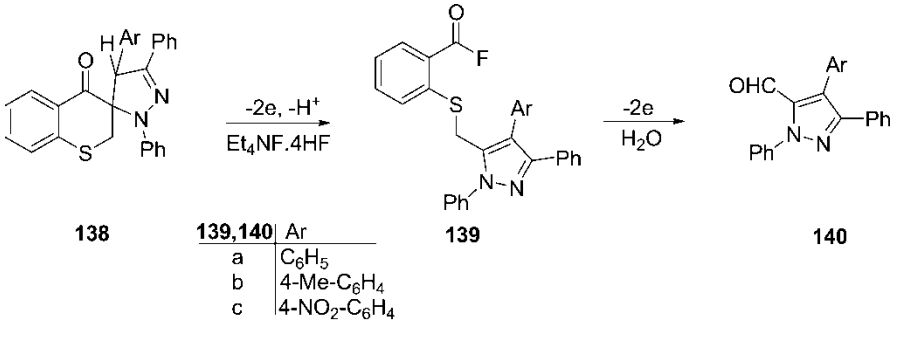
Treatment of (3*R**, αR*)-3-bromo-3-(α-bromobenzyl)-1-thiochromanones **141** with sodium azide in the DMF solution led to the formation of 3-(α-azido-4-substituted benzyl)thiochromones **142** in good yields (75–92%). A small amount (0.7–3.6%) of the parent (*E*)-3-benzylidene thiochroman-4-ones **50** was also obtained. Incorporation of a phenyl substituent into the 2-position of 1-thiochromanone skeleton resulted in a dramatic change in product distribution. The reaction of compounds **143** with sodium azide gave the debrominated parent compound **144** as major (71–76%) products as well as some minor compounds **145**. The appearance of these thermodynamically less stable diastereoisomers in the product could be rationalized in terms of either incomplete diastereoselectivity in the debromination step or a subsequent photoisomerization of α, β-enones during column chromatography (*67*) (Scheme 63).

Heating of thiochroman-4-one **2** with formaldehyde in aqueous methanol containing potassium carbonate afforded 63% yield of 3,3-*bis*-(hydroxymethyl)thiochroman-4-one **146**. Treatment of **146** with phenylisocyanate in tetrahydrofuran and in the presence of triethyl amine yielded 60% of 3,3-*bis*-(phenylcarbamoyloxymethyl)thiochromanone **147** (*68*) (Scheme 64).

When **28** refluxed with excess of $NaBH_4$ in isopropanol, it is reduced to *cis*-2-(trifluoromethyl)thiochroman-4-ol **148** in 53% yield. The formation of *cis*-product is due to the fact that the hydrogenation of the enone fragment proceeds on one side because of steric hindrances. Reduction of **28** under milder conditions (0 °C) with a smaller excess of $NaBH_4$ gave 2-trifluoromethyl-4*H*-thiochromen-4-ol **149**, its formation suggests that the C(4) atom in compound **28** is more reactive than the C(2) atom (*54*) (Scheme 65).



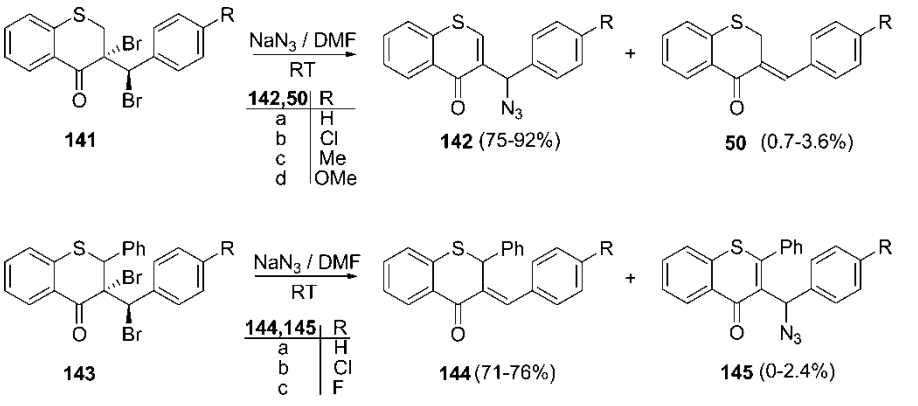
Scheme 61.



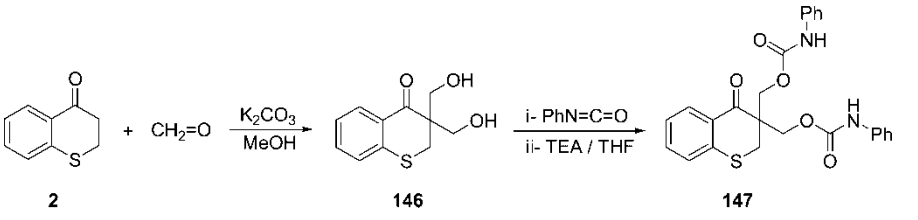
Scheme 62.

Refluxing of thiochroman-4-one **2** with benzoic anhydride in carbon tetrachloride and in the presence of a trace of 60% perchloric acid yielded the expected enolbenzoate **150** (27%) and the unexpected novel 3,3′-dichloro-3-methylene-4-thiochromane **151** (22%) (*69*) (Scheme 66).

Treatment of 7-methoxy-2-methyl-4*H*-1-benzothiopyran-4-one **152** with lithium diisopropylamide (LDA) in THF followed by benzaldehyde gave 2-(2-hydroxy-2-phenylethyl)-7-methoxy-4*H*-thiochromomen-4-one **153**. Compound **153** showed potential analgesic and anti-inflammatory activities (*70*) (Scheme 67).



Scheme 63.



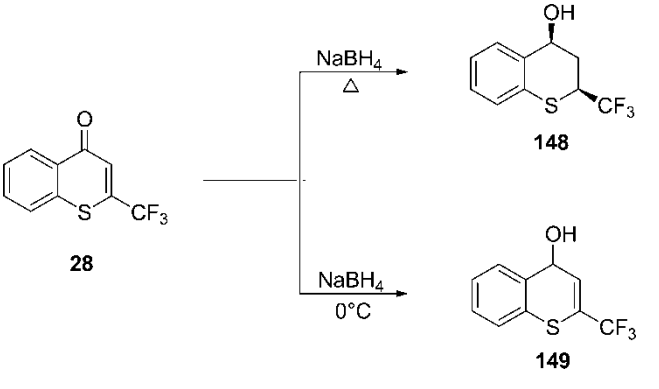
Scheme 64.

Ram and coworkers [71–73] reported an innovative approach to the synthesis of highly functionalized 6*H*-benzo[*c*]thiochromenes **155** via the reaction of a suitably functionalized 6-aryl-4-substituted-2*H*-pyran-2-one-3-carbonitriles **154** with thiochroman-4-one **2** in DMF containing KOH through ring transformation reactions (Scheme 68).

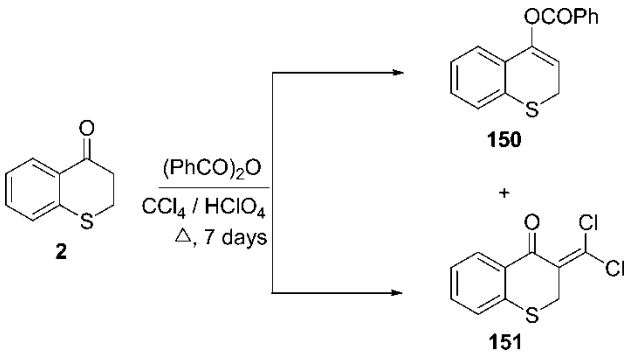
However, treatment of **127** with ferrous sulfate followed by $SnCl_2$ in ethanol led to the formation of 12-ethoxy-11,12-dihydro-6*H*-6,12-methanodibenzo[*bf*][1,5]thiazocine **156** (*62*) (Scheme 69).

Surprisingly, the reaction of compound **2** with *p*-anisaldehyde in *n*-butanol catalyzed by $HCl_{(g)}$ resulted in the formation of 3-(4-oxo-4*H*-thiochromen-3-yl)-4*H*-thiochromen-4-one **157** (*59*) (Scheme 70).

Treatment of thiochroman-4-one 1,1-dioxide **84** with ethylene glycol in the presence of *p*-TsOH yielded 3,4-dihydro-2H-1-benzothiopyran-4-spiro-2′-(1′,3′-dioxolane)1,1-dioxide **158**.



Scheme 65.



Scheme 66.

The reaction of **158** with 1-bromo-3-chloropropane gave 2-chloropropylthiochromone **159**, which upon treatment with 1-phenylpiperazine afforded compound **160**. Compound **160** showed anti-serotonin action (*74*) (Scheme 71).

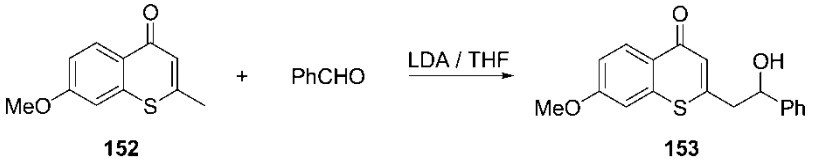
The base-induced cyclization of benzoylthiochromanone **161**, prepared in a two-step sequence from thiochroman-3-one, affords 6*H*,12*H*-[1]benzothiopyrano[3,4-*b*][1]benzopyran-12-ones **162**. Reduction of **162** with diisobutylaluminium hydride affords a separable mixture of *cis*- and *trans*-5-thiorotenoids **163** (*75*) (Scheme 72).

Thiochroman-4-one-1,1-dioxide **84** was successfully converted into 3-sulfinylthiochroman-4-one-1,1-dioxide **164** by the reaction with sulfonyl chloride. Reaction of compound **164** as Diels–Alder diene with 2-ethylbutene in boiling xylene yields 2,3-dihydro-5*H*-1,4-oxathinino[3,2-*c*][1]benzothiopyran **165** in 25% yield (*76*) (Scheme 73).

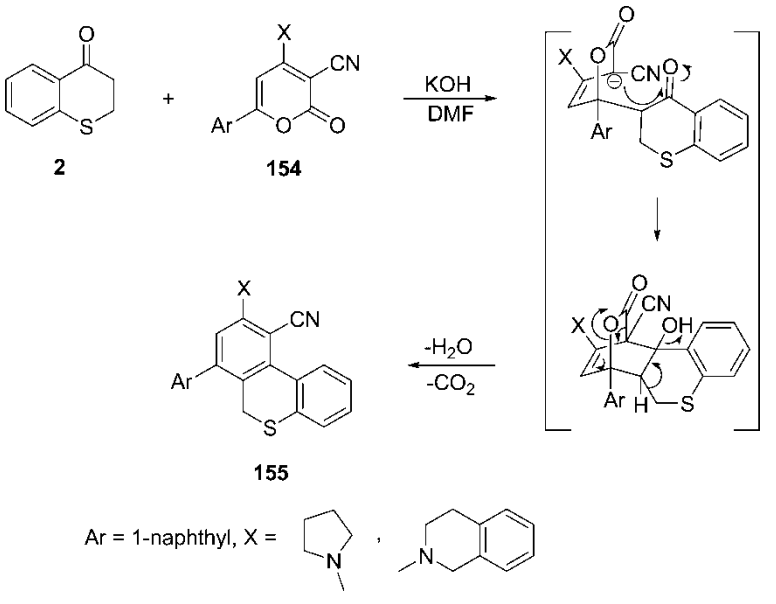
Alkylation of 4-mercaptothiocoumarin **166** with allyl bromide under phase-transfer catalyzed condition in the presence of tetra-butylammonium bromide (TBAB) or benzyl triethylammonium chloride catalyst in methylene chloride-aqueous NaOH (1%) at room temperature afforded 4-thioallylcoumarin **167**. Compound **167** underwent Claisen rearrangement when heated in chlorobenzene and quinoline to give thiopyrano[3,2-*c*][1]benzothiopyran-4-one **168** (*77, 78*) (Scheme 74).

Margaretha and coworkers [79, 80] reported that the photocycloaddition reaction of 3-cyanothiocoumarin **169** with 2,3-dimethylbut-2-ene in acetonitrile led to the selective formation of imine **170** in >75% yield. Hydrolysis of imine **170** gave cyclopenta[*c*]benzothiopyran-2,5-dione **171** [79]. However, irradiation of **169** with tertachloroethene under the same experimental condition gave the *cis*-fused cycloadduct **172** in high yields (Scheme 75).

Condensation of thiochromanones **2** with malononitrile yielded thiochroman 4-ylidenemalononitriles **173**. Treatment of **173** (R=Me) with sulfuric acid gave the three disproportionate products **174**, **175**, and **176**. From compound **173** (R=H), the sulfonated cyanoacetamide **177** was obtained (*81, 82*) (Scheme 76).

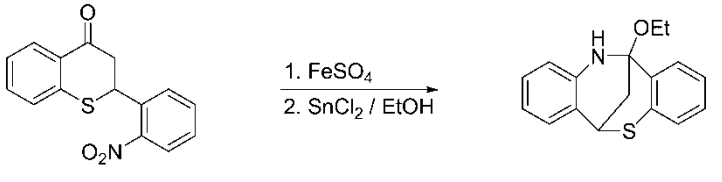


Scheme 67.



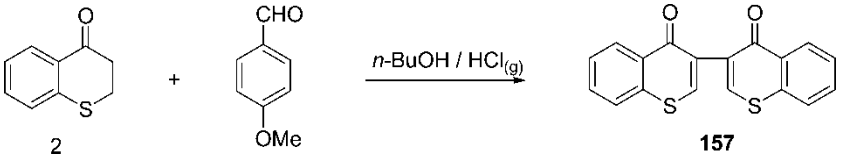
2 **154** **155**

Scheme 68.



127 **156**

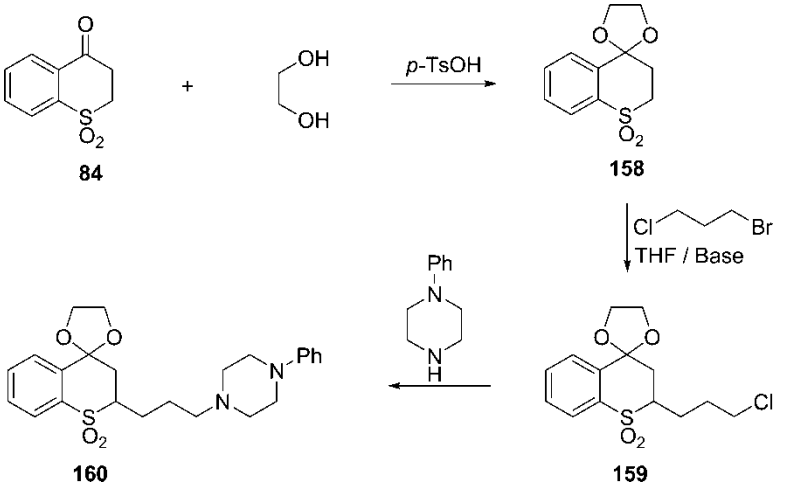
Scheme 69.



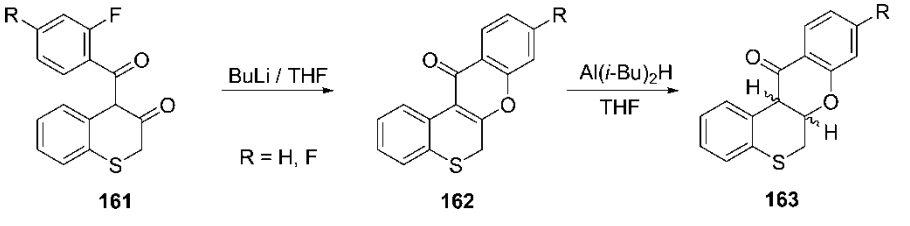
2 **157**

Scheme 70.

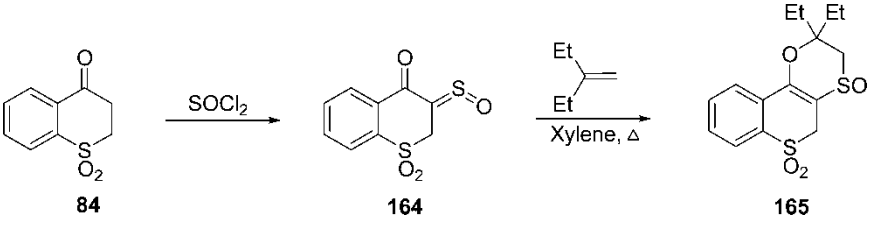
Condensation of 6-carboxy-3,3,5,8-tetramethylthiochroman-4-one-1,1-dioxide **178** with 1-ethyl-5-hydroxypyrazole using DCC in *t*-amyl alcohol at room temperature followed by heating with potassium carbonate gave 82% of 6-(3-pyrazole carbonyl)thiochromanone derivatives **179** as herbicides (*83*) (Scheme 77).



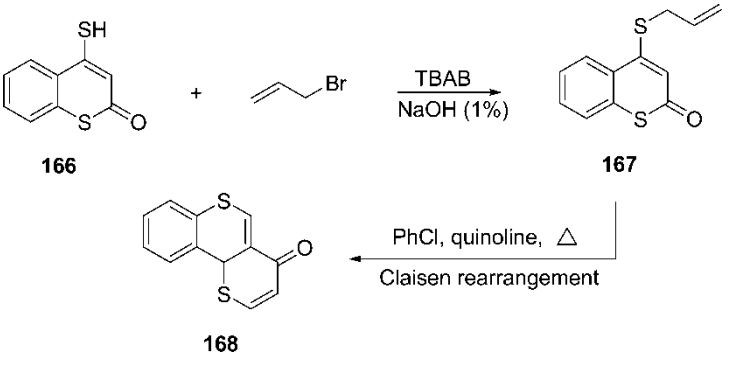
Scheme 71.



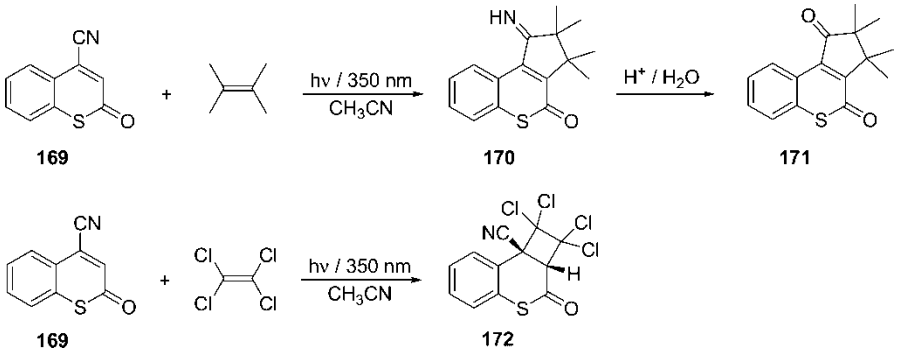
Scheme 72.



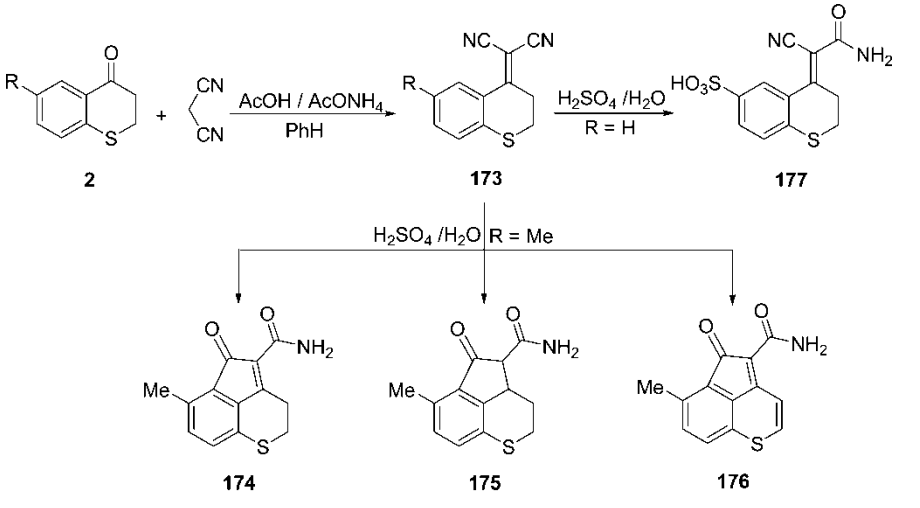
Scheme 73.



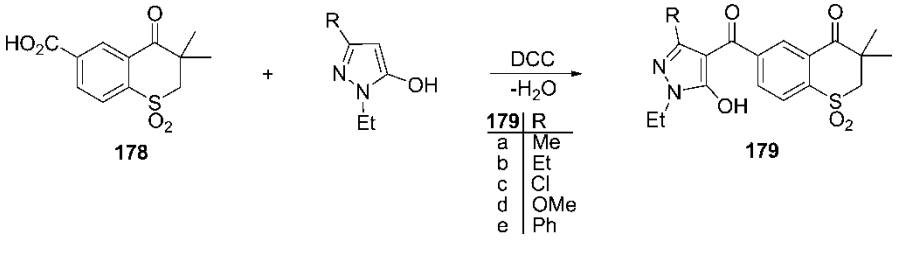
Scheme 74.



Scheme 75.



Scheme 76.



Scheme 77.

4. Conclusion

This paper outlines the progress of synthetic routes to and reactions of thiochroman-4-ones and thiochromones. The majority of these important compounds still require further exploration and applications, especially as drugs and dyestuffs. It is hoped to achieve a greater understanding of their potential in the synthesis of novel heterocycles and biologically active compounds. Finally, it is hoped that this paper will fill what was an obvious gap by providing an overview of the subject.

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