

Synthetic Routes to Coumarin(Benzopyrone)-Fused Five-Membered Aromatic Heterocycles Built on the α-Pyrone Moiety. Part 1: Five-Membered Aromatic Rings with One Heteroatom

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HAL Id: hal-03372689

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Review

Synthetic Routes to Coumarin(Benzopyrone)-Fused Five-Membered Aromatic Heterocycles Built on the α-Pyrone Moiety. Part 1: Five-Membered Aromatic Rings with One Heteroatom

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Abstract: This review gives an up-to-date overview of the different ways (routes) to the synthesis of coumarin (benzopyrone)-fused, five-membered aromatic heterocycles with one heteroatom, built on the pyrone moiety. Covering 1966 to 2020.

Keywords: coumarins; benzopyrones; five-membered aromatic heterocycles; furan; pyrrole; thiophene; selenophen

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Citation: El-Sawy, E.R.; Abdelwahab, A.B.; Kirsch, G. Synthetic Routes to Coumarin(Benzopyrone)-Fused Five-Membered Aromatic Heterocycles Built on the α-Pyrone Moiety. Part 1: Five-Membered Aromatic Rings with One Heteroatom. *Molecules* **2021**, *26*, 483. https://doi.org/10.3390/molecules26020483

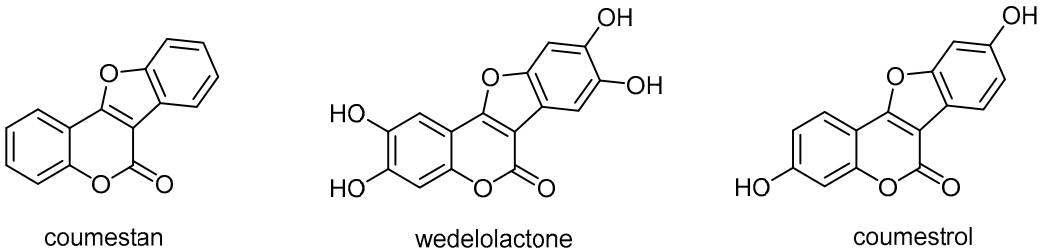
Academic Editor: Maria João Matos
Received: 26 December 2020
Accepted: 13 January 2021
Published: 18 January 2021

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1. Introduction

Coumarins are a family of benzopyrones (1,2-benzopyrones or 2*H*-[1]benzopyran-2-ones), which represent an important family of oxygen-containing heterocycles, widely distributed in nature [1–4]. Coumarins display a broad range of biological and pharmacological activities, [5,6] such as antiviral [7–10], anticancer [11–13], antimicrobial [14,15], and antioxidant [16–18] activities. On the other hand, coumarin represents an ingredient in perfumes [19], cosmetics [20], and as industrial additives [21,22]. Furthermore, coumarins play a pivotal role in science and technology as fluorescent sensors, mainly due to their interesting light-emissive characteristics, which are often responsive to the environment [23–26]. The coumarin (benzopyrane)-fused, membered aromatic heterocycles built on the α-pyrone moiety are an important scaffold. The only fused heterocycle with an α-pyrone moiety of coumarin that can be found in nature is the furan ring. One example is the naturally occurring furan 4*H*-furo[3,2-*c*]benzopyran-4-one, which provides the main core of many natural compounds of so-called coumestans. These comestans include coumestan, wedelolactone, and coumestrol. The coumestans are found in a variety of plant species that are commonly used in traditional medicine [27].



Naturally occurring furan, so-called coumestans

In order to enrich the limited versatility of the structures found in nature, synthesis of coumarin (benzopyrane)-fused, membered aromatic heterocycles has received considerable attention, including numerous reported routes.

This review gives an up-to-date overview of the different ways (routes) to the synthesis of benzopyrone-fused, five-membered aromatic heterocycles with one heteroatom, built on the pyrone moiety, from 1966 to 2020. Our main interest in this current work is to describe the components that have one heteroatom in an alicyclic-fused ring with the pyrone part of coumarin. The synthetic pathway of the investigated scaffold has provided systems containing oxygen, nitrogen, sulfur, and selenium in their core structure. The last heteroatom is less described in the output of the synthetic efforts. The fused heterocycles that contain more than one heteroatom will be detailed in the next part, which we intend to publish in the future.

Many strategies have been developed for the synthesis of the fused, five-membered aromatic heterocycle-benzopyran-4-ones. There are two main approaches to constructing these skeletons: five-membered, aromatic heterocycle construction, and pyrone-ring construction.

2. Synthesis of Benzopyrone-Fused, Five-Membered Aromatic Heterocycles

2.1. Five-Membered Aromatic Rings with One Heteroatom

2.1.1. Furans

Furobenzopyrone (or furocoumarins) comprises an important class of coumarins found in a wide variety of plants, particularly in the carrot (*Apiaceae/Umbelliferae*), legume (*Fabaceae*), and citrus families (*Rutaceae*) [27]. The chemical structure of furobenzopyrone (furocoumarins) consists of a furan ring fused with coumarin. The fusion of the furan ring to the α-pyrone moiety of coumarin forms the core structure of the three most common isomers, viz. 4*H*-furo[2,3-*c*]chromen(benzopyran)-4-one, 4*H*-furo[3,4-*c*]chromen(benzopyran)-4-one, and 4*H*-furo[3,2-*c*]chromen (benzopyran)-4-one (Figure 1).

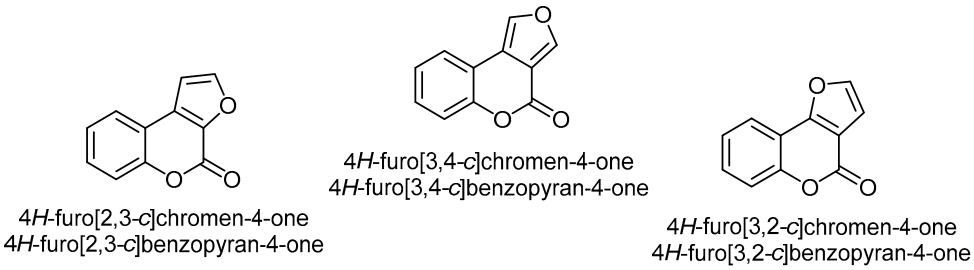
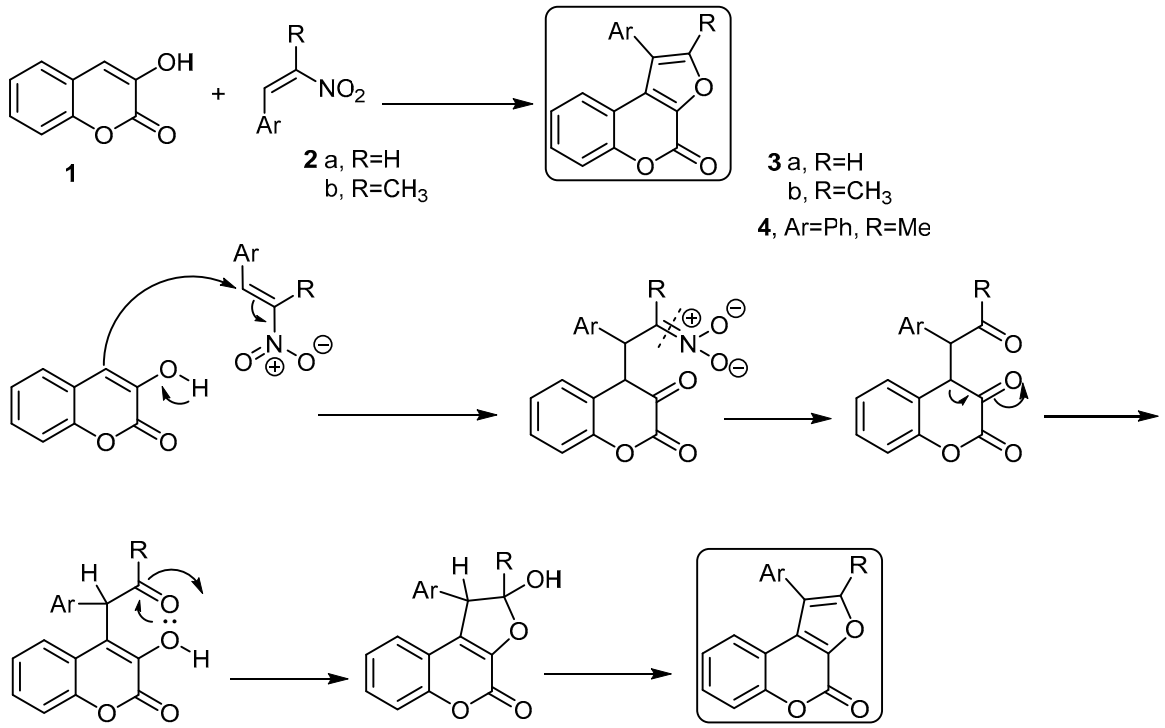


Figure 1. The three most common isomers of a furan ring fused to the α-pyrone moiety of coumarin.

4*H*-Furo[2,3-*c*]benzopyran-4-one

Furan Construction

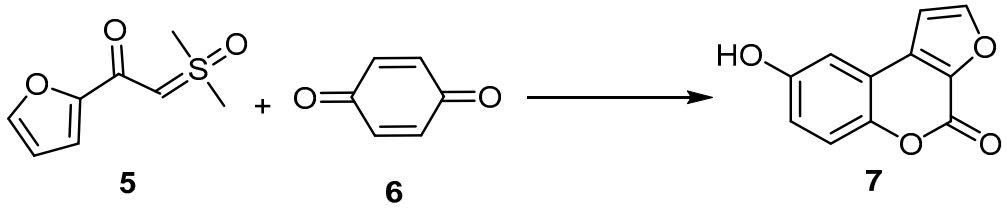
The basic building block for the formation of 4*H*-furo[2,3-*c*]benzopyran-4-one is the 3-hydroxycoumarin (**1**) [28,29]. Pandya and coworkers [30] developed a method to synthesize some 4*H*-furo[2,3-*c*]benzopyran-4-ones starting with 3-hydroxycoumarin using the Nef reaction. Thus, the reaction of 3-hydroxycoumarin (**1**) with various 2-aryl-1-nitro ethenes **2a**,**b**, in the presence of piperidine and methanol as a solvent, followed the Nef reaction condition and afforded a series of 1-aryl-furo[2,3-*c*]benzopyran-4-ones **3a**,**b** and 1-phenyl-2-methyl-furo[2,3-*c*]benzopyran-4-one (**4**), respectively (Scheme 1). The formation of these products was explained by the reaction mechanism (Scheme 1).



Scheme 1. The Nef reaction to synthesize furo[2,3-*c*]benzopyran-4-ones **3a**,**b** and **4**. *Reagents and conditions*: MeOH, piperidine, reflux, five outputs in 55%–61% yield.

Pyrone Construction

Dong et al., 2020 developed a novel and facile rhodium(III)-catalyzed process of sulfoxonium ylide (**5**) with hydroquinone (**6**). The carbonyl in the sulfoxonium ylide assisted the ortho-C–H functionalization of the sulfoxonium ylide, followed by intramolecular annulation with hydroquinone to afford 8-hydroxy-4*H*-furo[2,3-*c*]benzopyran-4-one (**7**) (Scheme 2) [31].

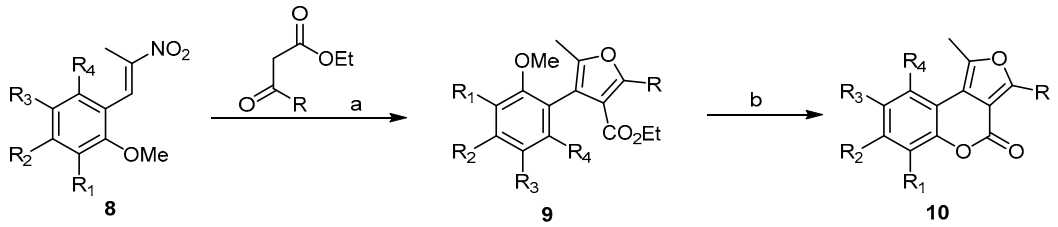


Scheme 2. Rhodium(III)-catalyzed sequential ortho-C–H oxidative arylation/cyclization of sulfoxonium ylide to afford 4*H*-furo[2,3-*c*]benzopyran-4-one (**7**). *Reagents and conditions*: $[Cp^*RhCl_2]_2$ (5 mol %), $AgBF_4$ (20 mol %), $Zn(OAc)_2$ (0.225 mmol), AcOH (0.3 mmol), and acetone (2 mL), 12 h, in a sealed Schlenk tube under N_2 at 100 °C, 25% yield.

4*H*-Furo[3,4-*c*]benzopyran-4-one

Furan and Pyrone Construction

In the literature, a large number of reports described the synthesis of 4*H*-furo[2,3-*c*] and 4*H*-furo[3,2-*c*]benzopyran-4-ones, while synthesis of the 4*H*-furo[3,4-*c*]benzopyran-4-one was reported by only one study, that of Brahmbhatt and his coworkers [32]. The first 4*H*-furo[3,4-*c*]benzopyran-4-ones (**10**) was synthesized by the demethylation–cyclization reaction of intermediates, 3-substituted-4-ethoxycarbonyl furans **9** (Scheme 3). For the demethylation and in situ lactonization steps, several reagents were tried, of which pyridine hydrochloride and HBr in acetic acid were found to be the most promising.



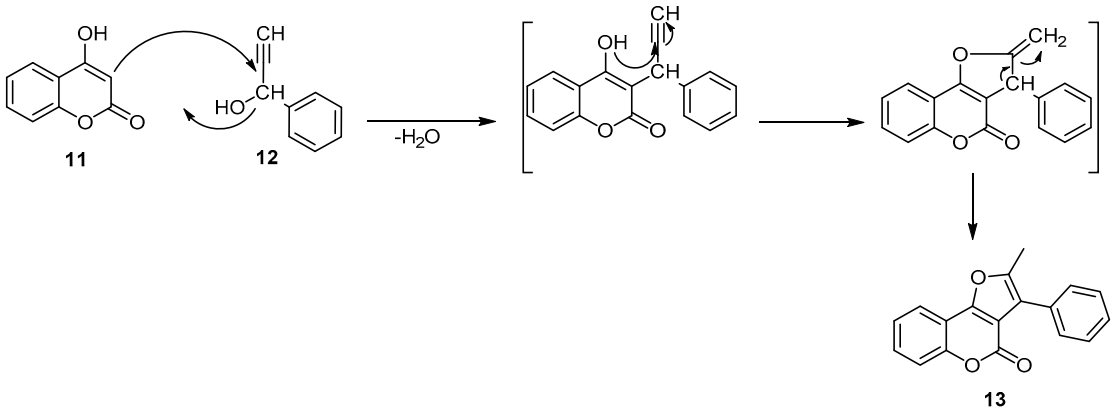
Scheme 3. Demethylation and in situ lactonization steps to prepare the first 4*H*-furo[3,4-*c*]benzopyran-4-one **10**. *Reagents and conditions*: (a) ethyl acetoacetate or ethyl benzoylacetate, piperidine, and MeOH (the Nef reaction condition); (b) HBr, AcOH concentration, 130 °C, 4 h, 16 outputs with 50%–65% yield.

4*H*-Furo[3,2-*c*]benzopyran-4-one

Furan Construction

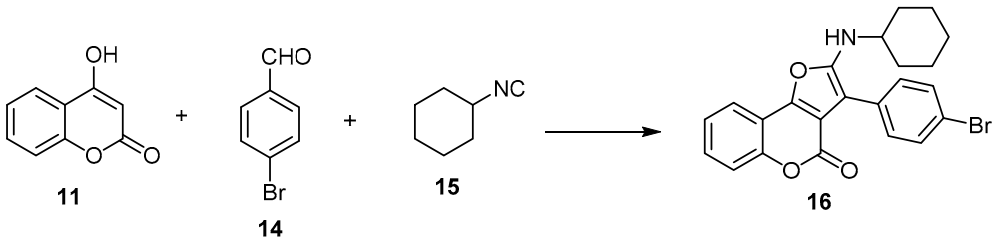
A wide range of research has demonstrated that 4-hydroxycoumarin is the key compound for the synthesis of 4*H*-furo[3,2-*c*]benzopyran-4-ones, which can readily react with the C=C bond of the alkene, or the C≡C bond of the alkyne [33–37].

Reisch reported the condensation of 4-hydroxycoumarin (**11**) with 1-phenyl-2-propyn-1-ol (**12**) under acidic conditions (a mixture of glacial acetic and concentrated sulfuric acid) to deliver the corresponding 2-methyl-3-phenylfuro[3,2-*c*]benzopyran-4-one (**13**) (Scheme 4) [38].



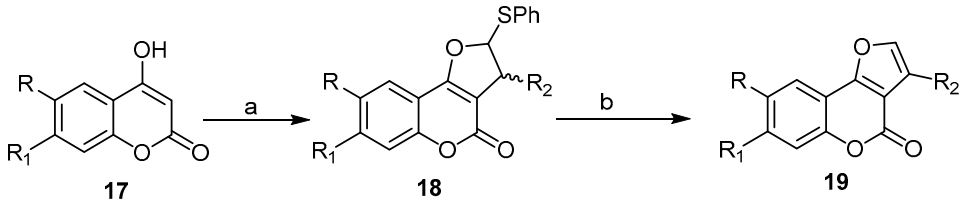
Scheme 4. Synthesis of 2-methyl-3-phenylfuro[3,2-*c*]benzopyran-4-one (**13**). *Reagents and conditions*: AcOH, conc. H_2SO_4, 110 °C, 1 h, 70% yield.

A few studies employed the aliphatic aldehydes as building blocks with 4-hydroxycoumarin (**11**) to synthesize 4*H*-furo[3,2-*c*]benzopyran-4-ones [25,39]. This method was ineffective as it gave a poor yield as well as a mixture of 2,3-dihydrofuran, 4*H*-furo[3,2-*c*]benzopyran-4-ones, and 4*H*-furo[3,2-*c*]benzopyran-4-ones [39]. Conversely, in the case of using the aromatic aldehyde as a building block, the 4*H*-furo[3,2-*c*]benzopyran-4-one was obtained [40]. Kadam et al. developed atom-efficient multicomponent reactions (MCRs) and step-efficient, one-pot synthesis of 3-(4-bromophenyl)-2-(cyclohexylamino)-4*H*-furo[3,2-*c*]benzopyran-4-one (**16**) using 4-hydroxycoumarin (**11**) with 4-bromobenzaldehyde (**14**) and cyclohexyl isocyanide (**15**) as an alkylene source (Scheme 5) [40].



Scheme 5. Atom-efficient multicomponent reactions (MCRs) and step-efficient, one-pot synthesis of 4*H*-furo[3,2-*c*]benzopyran-4-one (**16**). *Reagents and conditions*: DMF or toluene, μw, 80 °C, 20 min, 97% yield.

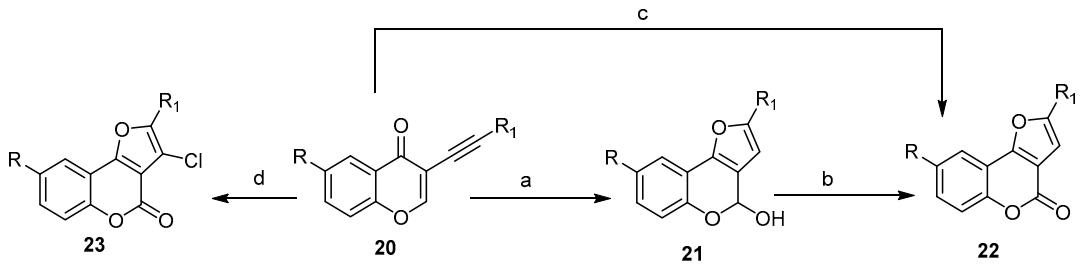
4-Hydroxycoumarin derivatives have received significant attention from researchers, as these derivatives possess 1,3-dicarbonyl systems. It allows for the easy generation of α,α′-dicarbonyl radicals, which can be readily added to the C=C bond of the alkene [41]. The first example of this reaction was described in 1998, by Lee and his coworkers. They reported an efficient way to prepare 4*H*-furo[3,2-*c*]benzopyran-4-ones **19** by Ag_2CO_3/celite (Fetizon's reagent)-mediated oxidative cycloaddition of 4-hydroxycoumarin **17** to olefins, such as vinyl sulfide and phenyl propenyl sulfide. The resulting dihydrofuro[3,2-*c*]benzopyran-4-ones **18** was treated by sodium periodate in aqueous methanol to form the corresponding sulfoxides, which, upon refluxing with pyridine in carbon tetrachloride, directly delivered the 4*H*-furo[3,2-*c*]benzopyran-4-one **19** in good yields (Scheme 6) [41].



Scheme 6. A facile synthesis of 4*H*-furo[3,2-*c*]benzopyran-4-ones **19** by silver(I)/celite promoted an oxidative cycloaddition reaction. *Reagents and conditions*: (a) CH_2=CHSPh and/or CH_3CH=CHSPh, Ag_2CO_3/celite, acetonitrile, reflux, 3 h; (b) $NaIO_4$, MeOH, CCl_4, pyridine, Al_2O_3, four outputs with 71%–82% yield.

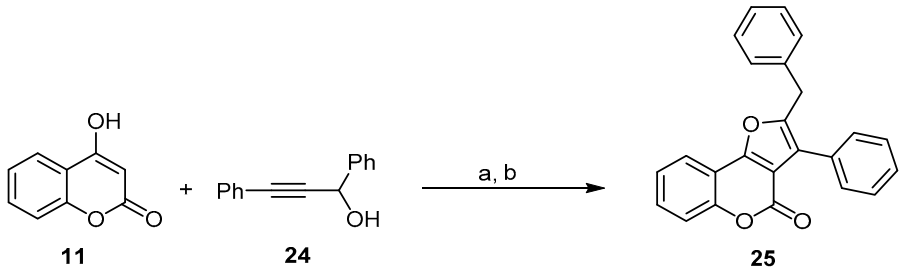
Recently, different catalytic methodologies have been developed for the synthesis of 2*H*-chromenes, and they are based on three main approaches: catalysis with (transition) metals, metal-free Brønsted catalysis, and Lewis acid/base catalysis, which includes examples of nonenantioselective organocatalysis and enantioselective organocatalysis [42–44]. Alkynes have been widely employed as building blocks for this reaction in most cases.

To date, different transition metal (Au, Pt, and Cu) catalyzed/mediated methodologies for benzopyrane synthesis have been reported [27,42,45,46]. Cheng and Hu described a one-pot cascade of an addition/cyclization/oxidation sequence using $CuCl_2$ as the oxidant and CH_3SO_3H as the acid for regioselective synthesis of 2-substituted-4*H*-furo[3,2-*c*]benzopyran-4-ones **22** from the substituted 3-alkynyl-4*H*-benzopyran-4-one **20** (Scheme 7) [47]. This strategy included the CH_3SO_3H-acid-catalyzed construction of the furan ring, followed by oxidation of **21** with $CuCl_2$ (Scheme 7) [47]. When the reaction was carried out in the presence of a catalytic amount of CuCl as a Lewis acid and atmospheric oxygen as an oxidative reagent, compound **22** was provided directly. On the other hand, the presence of 10% CuBr and an excess of $CuCl_2$ as the oxidant afforded the corresponding 3-chloro-2-substituted- 4*H*-furo[3,2-*c*]benzopyran-4-ones **23** (Scheme 7) [48].



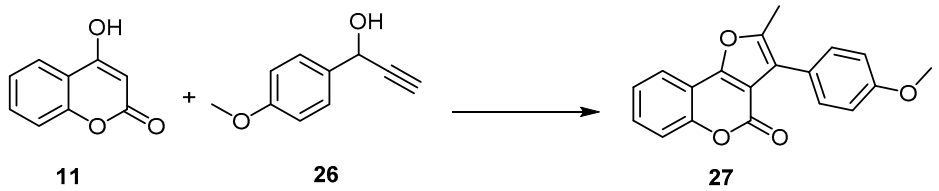
Scheme 7. Transition metal Cu catalyzed/mediated methodologies for synthesis of the 4*H*-furo[3,2-*c*]benzopyran-4-ones **22** and **23**. *Reagents and conditions*: (a) CH_3SO_3H, H_2O, DMF, 90 °C, 1–3 h; (a) $CuCl_2$, 90 °C, 20 h; (c) CuCl, O_2, DMF, H_2O, 90 °C, 10–20 h, 10 outputs with 37%–88% yield; (d) CuBr, $CuCl_2$, DMF, H_2O, 75 °C, 10 h, 13 outputs with 45%–81% yield.

Brønsted-acid-catalyzed propargylations of several organic substrates, including 1,3-dicarbonyl compounds, with alkynols have been reported [49]. In most cases, the acid catalyst is required to promote the propargylation process efficiently. Zhou and coworkers developed a one-pot $Yb(OTf)_3$ propargylation–cycloisomerization sequence of 4-hydroxy coumarin (**11**) with the propargylic alcohol (**24**) for the synthesis of a 2-benzyl-3- phenyl-4*H*-furo[3,2-*c*]chromen-4-one (**25**) skeleton using $Yb(OTf)_3$ as a Lewis acid (Scheme 8) [50].



Scheme 8. One-pot synthesis of 4*H*-furo[3,2-*c*]chromen-4-one (**25**) using a $Yb(OTf)_3$-catalyzed propargylation and allenylation reaction. *Reagents and conditions*: (a) 5 mol % $Yb(OTf)_3$, CH_3NO_2, dioxane, 50 °C; (b) K_2CO_3, 70 °C, 37% yield.

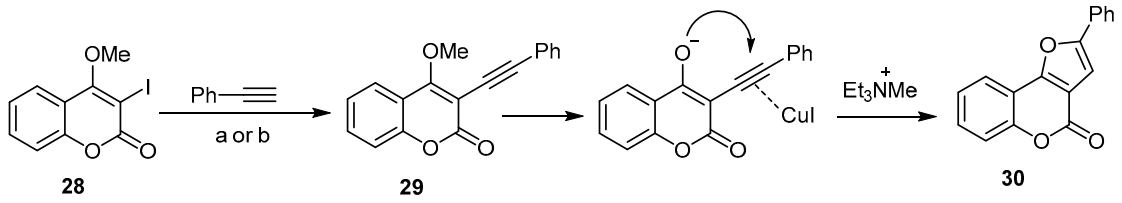
Similarly, 4*H*-furo[3,2-*c*] benzopyran-4-one formation reactions proceeded in higher yields and in a one-pot manner, employing a catalytic system composed of the 16-electron allyl–ruthenium(II) complex [Ru(η3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (dppf=1,1′-bis(diphenyl phosphino)ferrocene) and trifluoroacetic acid (TFA) in the reaction of 4-hydroxycoumarin (**11**), with 1-(4-methoxyphenyl)-2-propyn-1-ol (**26**) as an example. The 4*H*-furo[3,2-*c*]benzo pyran-4-one (**27**) was synthesized with a 72% yield (Scheme 9) [50–52].



Scheme 9. The 16-electron allyl–ruthenium(II) complex in preparation of 4*H*-furo[3,2-*c*]benzopyran-4-one (**27**). *Reagents and conditions*: 16-electron allyl–ruthenium(II) complex [Ru(η3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (5 mol %), trifluoroacetic acid (TFA) (50 mol %), THF, 75 °C, 5 h, 72% yield.

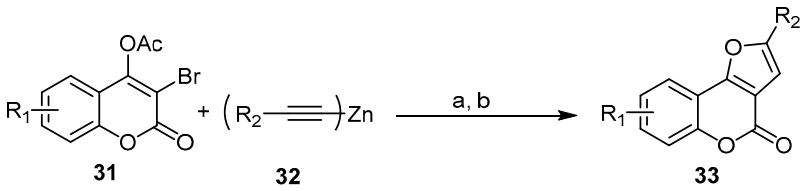
Extensive work has been done to investigate the utility of an aryl alkynyl ether as a furan substrate, instead of arylalkynol, in the synthesis of 4*H*-furo[3,2-*c*]benzopyran-4-one [29,35]. The treatment of 3-iodo-4-methoxycoumarin (**28**) with phenylacetylene by means of sequential Sonogashira C–C coupling conditions resulted in a high-yield formation of the 4*H*-furo[3,2-*c*]benzopyran-4-one (**30**) (Scheme 10) [53]. In this reaction, the triethylamine was used as a base to induce the S_N2-type demethylation of the Sono-

gashira coupling product, followed by an intramolecular attack of the enolate onto the cuprohalide π-complex of the triple bond (Scheme 10).



Scheme 10. Et_3N-induced demethylation–annulation of an aryl alkynyl ether in the synthesis of 4*H*-furo[3,2-*c*]benzopyran-4-one (**30**). *Reagents and conditions*: (a) alkyne (3 equiv.), 8 mol % $PdCl_2(PPh_3)_2$, 8 mol % CuI, Et_3N/DMF, 80 °C, 48 h, 82% yield; (b) alkyne (3 equiv.), 8 mol % $PdCl_2(PPh_3)_2$, 8 mol % CuI, Et_3N/MeCN, 60 °C, 15 h, 70% yield.

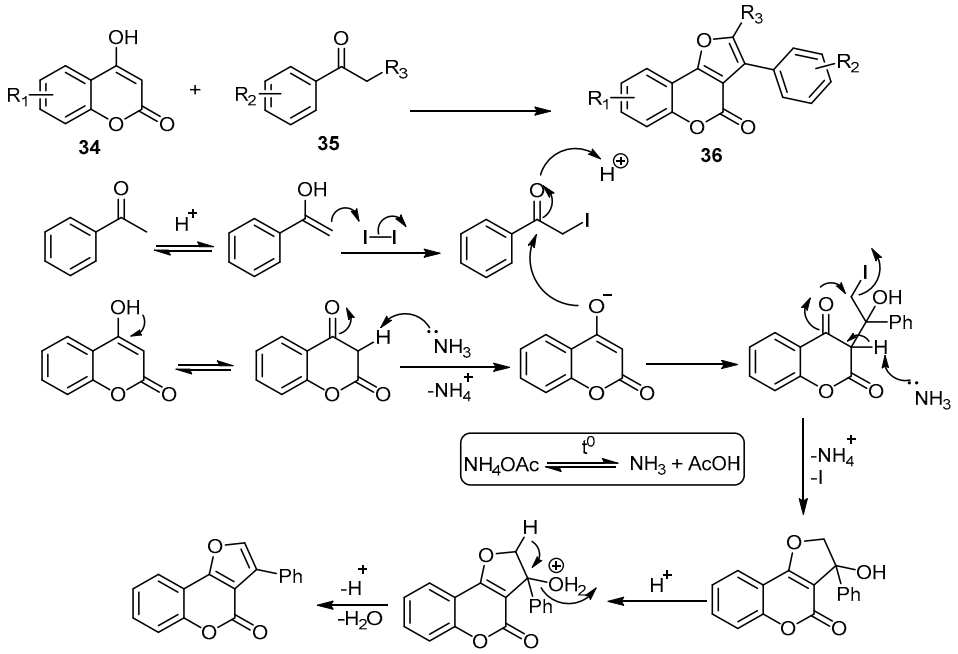
As a follow-up to this type of reaction, a novel and rapid assembly of an interesting class of 4*H*-furo[3,2-*c*]benzopyran-4-ones, **33**, was successfully achieved using a one-pot sequential coupling/cyclization strategy with 3-bromo-4-acetoxycoumarins **31** and dialkynlzincs **32** prepared in situ as reactive acetylides in transition-metal-catalyzed crosscoupling. The cascade transformation relies on palladium/copper-catalyzed alkynylation and intramolecular hydroalkoxylation (Scheme 11) [54].



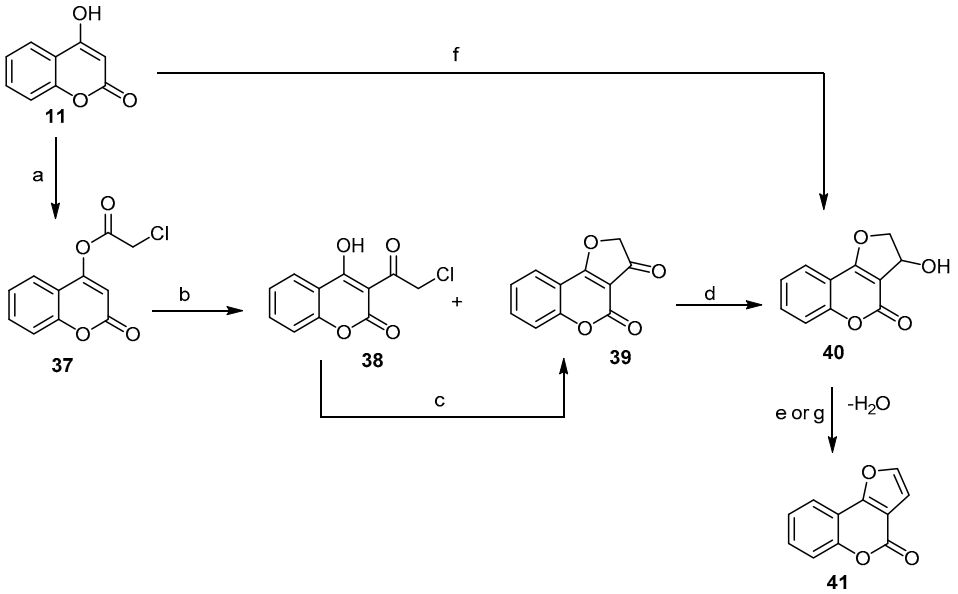
Scheme 11. A one-pot sequential coupling/cyclization strategy in the synthesis of 4*H*-furo[3,2-*c*]-benzopyran-4-ones **33**. *Reagents and conditions*: (a) $Pd(PPh_3)_2$, CuI, THF, 60 °C; (b) K_2CO_3, H_2O, 13 outputs with 51%–96% yield.

A transition-metal-free approach was developed to achieve 4-*H*-furo[3,2-*c*]benzopyran-4-ones via an iodine-promoted one-pot cyclization between 4-hydroxycoumarins **34** and acetophenones **35**. The transformation spontaneously proceeded to produce (**36**) in the presence of NH_4OAc. The possible reaction mechanism suggested for the iodine-promoted one-pot cyclization is depicted (Scheme 12) [55].

Additionally, Traven et al. [56] provided a new short way for the synthesis of 4*H*-furo-[3,2-*c*]benzopyran-4-one, employing the Fries rearrangement of 4-chloroacetoxycoumarin (**37**) to yield two products, namely 3-chloroacetyl4-hydroxycoumarin (**38**) and dihydrofuro [2,3-*c*]coumarin-3-one (**39**), in the ratio of 2:1. Compound (**38**), which underwent cyclization, led to the formation of (**39**). The latter, under reduction and dehydration conditions, afforded 4*H*-furo[3,2-*c*]chromen-4-one (**41**) (Scheme 13). A closely related reaction that allowed for the preparation of (**41**) was developed by Majumdar and Bhattacharyya [57], following a similar procedure but using chloroacetaldehyde instead of chloroactylchloride in the presence of aqueous potassium carbonate to give 3-hydroxy-2,3- dihydrofuro[3,2-*c*]benzopyran-4-one (**40**), which upon treatment with aqueous hydrochloric acid provided 4*H*-furo[3,2-*c*]benzopyran-4-one (**41**) with 72% yield (Scheme 13).



Scheme 12. Metal-free synthesis of 4-*H*-furo[3,2-*c*]benzopyran-4-ones **36**. *Reagents and conditions*: I_2, NH_4OAc, PhCl, 120 °C, 18 outputs with 28%–90% yield.

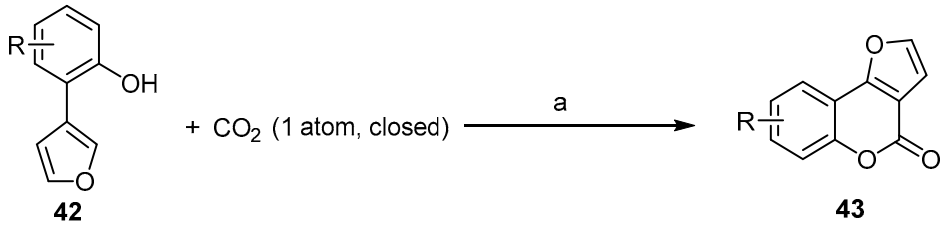


Scheme 13. Regioselective synthesis of 4*H*-furo[3,2-*c*]chromen-4-one (**41**). *Reagents and conditions*: (a) $ClCH_2COCl$, dry pyridine, 40 min, reflux, 85% yield; (b) $AlCl_3$, 140–150 °C, 60% yield; (c) $AlCl_3$, 140–150 °C, 30–40 min or K_2CO_3, acetone, 10 min, stirring, r.t., 50% yield; (d) $NaBH_4$, 85% yield; (e) H_2SO_4 (30%), EtOH, heat, 30 min, 80% yield; (f) $COCH_2Cl$, K_2CO_3, 73% yield; (g) HCl, 72% yield.

Pyrone Construction

Recently, much effort has been devoted to the development of oxidative intramolecular C–O bond-forming cyclization reactions for the synthesis of bioactive benzopyranones. These methods are limited to being used with arenes building blocks [58–60]. Fu et al. reported a ligand-enabled, site-selective carboxylation of 2-(furan-3-yl)phenols **42** under the atmospheric pressure of CO_2. It was performed through an Rh(ii)-catalyzed C–H bond activation, assisted by the ligand chelation of the phenolic hydroxyl group to afford 4*H*-furo[3,2-*c*]benzopyran-4-ones **43** (Scheme 14) [61]. This reaction indicates the role of

phosphine ligands in combination with $Rh_2(OAc)_4$ in promoting the reactivity and the selectivity during C–H carboxylation. The right choice of a suitable basic catalyst is an additional critical point.

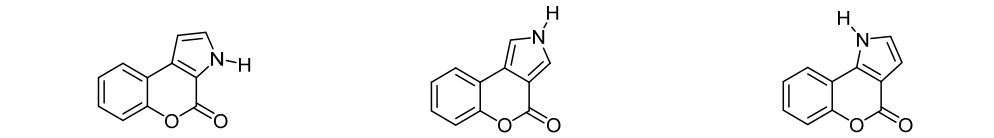


42 **43**

Scheme 14. Rhodium(II)-catalyzed aryl C–H carboxylation with CO_2 in the synthesis of 4*H*-furo[3,2-*c*] benzopyran-4-ones **43**. *Reagents and conditions*: (a) $Rh_2(OAc)_4$ (1 mol %), tricyclohexylphosphine PCy_3 (2 mol %), t-BuOK (4.5 equiv.), diglyme, 100 °C, 48 h, six outputs with 70%–86% yield.

2.1.2. Pyrroles

Fusion of the pyrrole ring with the pyrone ring of coumarin (benzopyrane) leads to three structural isomers, viz. chromeno[3,4-*b*]pyrrol-4(*3H*)-one, chromeno[3,4-*c*]pyrrol-4(*2H*)-one, and chromeno[4,3-*b*]pyrrol-4(*1H*)-one (Figure 2).



chromeno[3,4-*b*]pyrrol-4(3*H*)-one
3*H*,4*H*[1]benzopyrano[3,4-*b*]pyrrol-4-one

chromeno[3,4-*c*]pyrrol-4(2*H*)-one
[1]benzopyrano[3,4-*c*]pyrrol-4-one

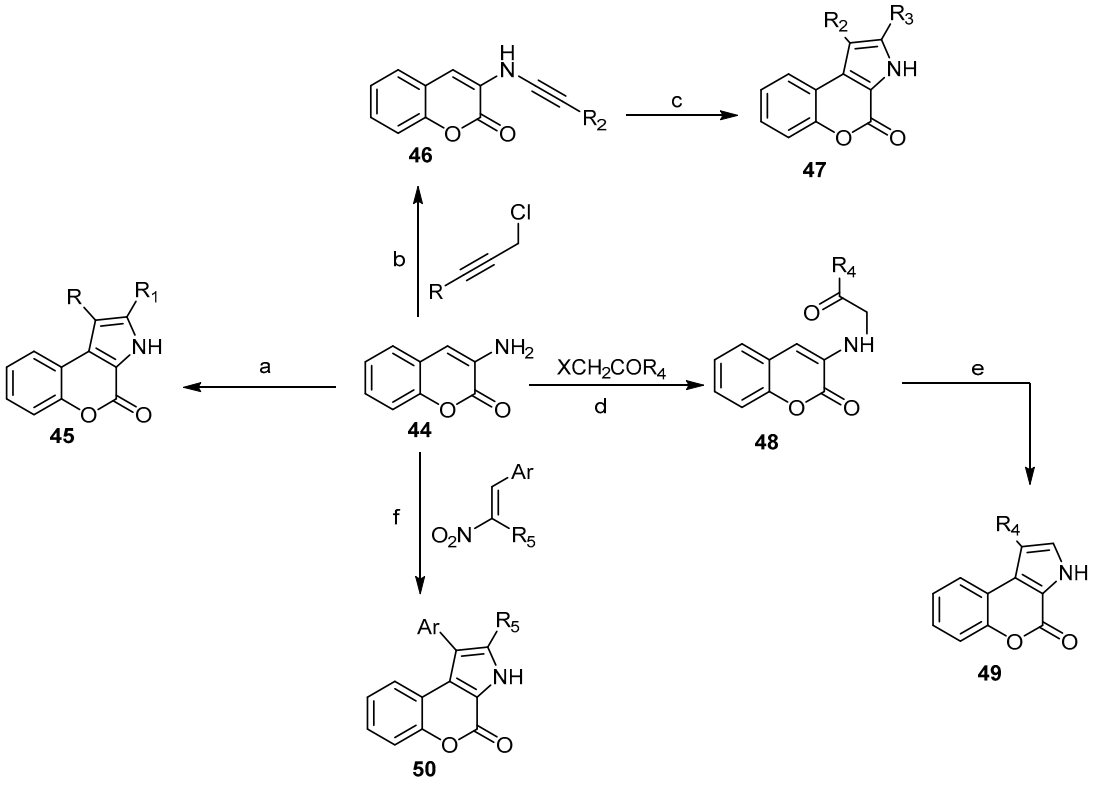
chromeno[4,3-*b*]pyrrol-4(1*H*)-one
[1]benzopyrano[4,3-*b*]pyrrol-4-one

Figure 2. The three common isomers of the pyrrole ring fused to the α-pyrone moiety of coumarin.

3*H*,4*H*[1]Benzopyrano[3,4-*b*]pyrrol-4-one

Pyrrole Construction

The 3-Aminocoumarin (**44**) is considered the starting compound for the preparation of fused *3H,4H*[1]benzopyrano[3,4-*b*]pyrrol-4-ones. The amino group represents the key moiety of this cyclization process in the reaction with different reagents [30,62–64]. Compound **45** was prepared by the reaction of 3-aminocoumarin (**44**) with different carbonyls via Fischer indole synthesis after being diazotized and reduced to coumarin-3-yl-hydrazine [62]. The compound 1-Aryloxy-4-chlorobut-2-ynes reacted with 3-aminocoumarin (**44**) to afford **47** through amino-Claisen rearrangement [64]. Condensation of (**44**) with α-halo ketones, followed by cyclization catalyzed by TFA, led to the formation of **49** [63], while **50** was prepared under Nef conditions using 2-aryl-1- nitro ethenes [30] (Scheme 15).

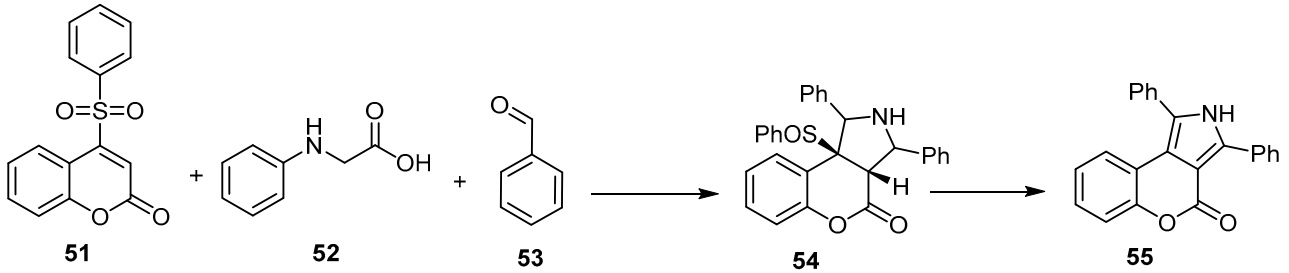


Scheme 15. Different pathways to synthesize *3H,4H*[1]benzo- pyrano[3,4-*b*]pyrrol-4-ones **45**, **47**, **49**, and **50** via 3-aminocoumarin. *Reagents and conditions*: (a) i: $NaNO_2$, HCl, −30 °C, ii: $SnCl_2$, −10 °C, HCl, 2 h, iii: carbonyl compounds, polyphosphoric acid, 1 h, 130 °C, seven outputs with 33%–51% yield; (b) anhydride ethyl methyl ketone, K_2CO_3, NaI, reflux, 24–30 h, five outputs with 51%–63% yield; (c) *N*,*N*-dimethylaniline, reflux, 6–9 h, five outputs with 90%–94% yield; (d) KI (cat.), reflux, 5 h; (e) TFA (cat.), AcOH, 12 h, reflux, four outputs with 28%–86% yield; (f) MeOH, piperidine, reflux, five outputs with 55%–61% yield.

3*H*,4*H*[1]Benzopyrano[3,4-*e*]pyrrol-4-one

Pyrrole Construction

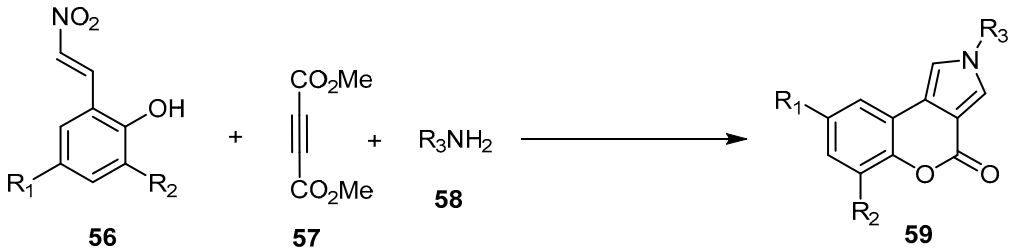
A one-pot, three-component reaction of phenylsulphinyl-2*H*-benzopyran-2-one (**51**), phenylglycine (**52**), and benzaldehyde (**53**) led to the formation of 1,3-diphenyl[l]benzopyrano[3,4-*e*]pyrrol-4-one (**55**) (Scheme 16) [65].



Scheme 16. Synthesis of 1,3-diphenyl[l]benzopyrano[3,4-*e*]pyrrol-4-one (**55**). *Reagents and conditions*: DMF, stirring, 120 °C, 24 h, 51% yield.

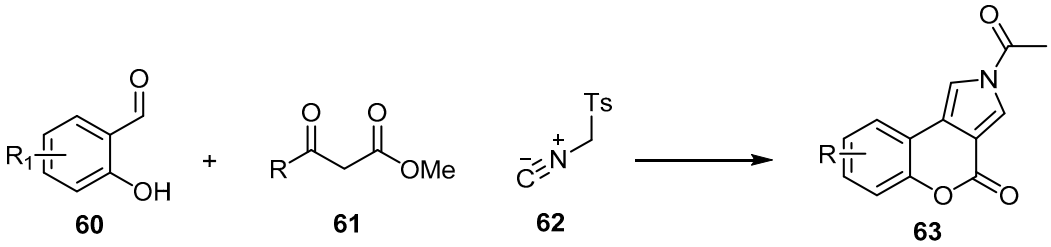
Xue et al. developed an efficient and straightforward synthetic protocol for the preparation of [1]benzopyrano[3,4-*e*]pyrrol-4-ones **59** through $FeCl_3$-promoted, three-component reactions between substituted 2-(2-nitrovinyl)phenols **58**, acetylene dicarboxylate (**57**), and amines **58** (Scheme 17) [66]. This reaction involved the sequential $FeCl_3$-mediated

nucleophilic addition of acetylenedicarboxylates, amines, and 2-(2-nitrovinyl)phenols, following intramolecular transesterifcation to form a coumarin core. This strategy offers a complementary approach to substituted pyrrolo[3,4-*c*]coumarin compounds, with advantages that include a variety of cheap and readily available reactants and a wide range of substrates with dense or flexible substitution patterns [66].



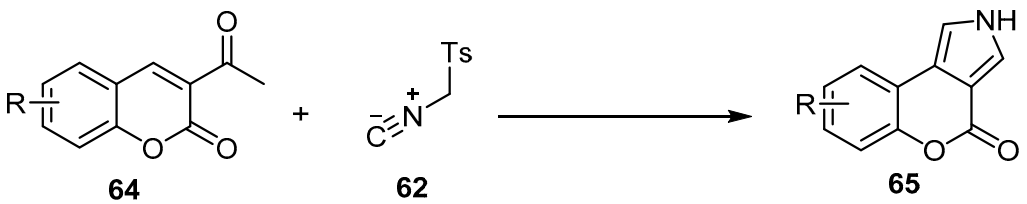
Scheme 17. Synthesis of [1]benzopyrano[3,4-*e*]pyrrol-4-ones **59** by a $FeCl_3$-promoted, three-component reaction. *Reagents and conditions*: $FeCl_3$, toluene, 110 °C, 6 h, 17 outputs with 62%–92% yield.

Alizadeh et al. reported a sequential three-component reaction of salicylaldehydes **60**, β-keto esters 61, and *p*-toluenesulfonylmethyl isocyanide (TosMIC) (**62**) via [1,3] acyl shift to give 2-acyl[1] benzopyrano[3,4-*e*]pyrrol-4-ones **63** (Scheme 18) [67]. A simple workup procedure, mild reaction conditions, lack of side products, and good yields of 62%–95% are the main aspects of this method.



Scheme 18. A sequential three-component reaction to synthesize [1]benzopyrano[3,4-*e*]pyrrol-4-ones **63**. *Reagents and conditions*: TEA, piperidine, DMF, r.t., 8 h, 10 outputs with 62%–95% yield.

Recently, Khavasi and his coworkers investigated the reactivity, chemo-, region-, and diastreo-selectivity of *p*-toluenesulfonylmethyl isocyanide (TosMIC) (**62**) in Van Leusen-type [3 + 2] cycloaddition reactions with the 3-acetylcoumarins **64** to give [1]benzopyrano [3,4-*e*]pyrrol-4-ones **65** (Scheme 19) [68]. This method offers several advantages, such as being inexpensive, providing good to excellent yields, producing short reaction times, high atom economy, and ease of product isolation under catalyst-free conditions without any activation at ambient temperature.

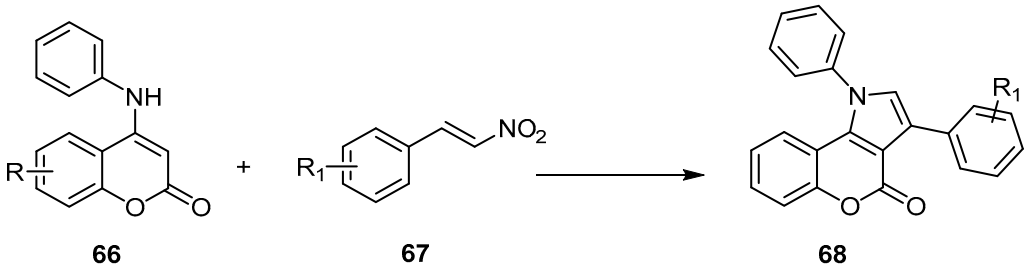


Scheme 19. The Van Leusen protocol for the synthesis of [1]benzopyrano[3,4-*e*]pyrrol-4-ones **65**. *Reagents and conditions*: K_2CO_3, EtOH, 15 min, r.t, three outputs with 72%–86% yield.

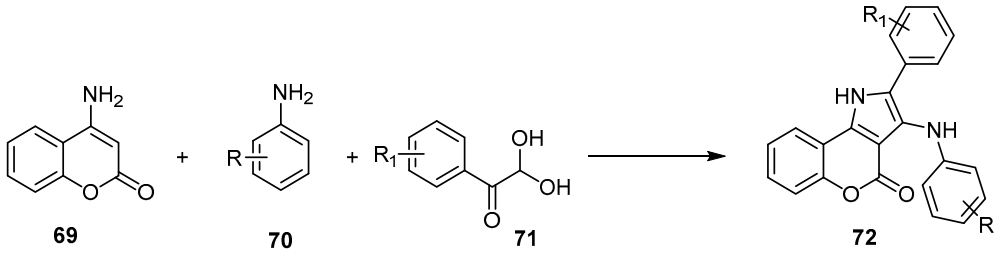
[1]Benzopyrano[4,3-*b*]pyrrol-4-one

Pyrrole Construction

Many synthetic protocols have been reported for the synthesis of [l]benzopyrano [4,3-*b*]pyrrole-4(1*H*)-ones, including the reaction of β-nitroalkenes **67** and 4-phenylamino coumarins **66** under solvent-free conditions to afford **68** (Scheme 20) [69]. Moreover, the reaction of the 4-aminocoumarin (**69**), amines **70**, and glyoxal monohydrates **71** in the presence of nanocrystalline $CuFe_2O_4$ [70], or $KHSO_4$, led to the formation of [l]benzopyrano [4,3-*b*]pyrrole-4(1*H*)-ones **72** (Scheme 21) [71]. The synthesis of 71 using nanocrystalline $CuFe_2O_4$ discloses a rapid, high-yielding, green synthetic protocol for a variety of chromeno [4,3-*b*]pyrrol-4(1*H*)-one derivatives by assembling the basic building blocks in an aqueous medium using nano $CuFe_2O_4$ as the efficient, magnetically recoverable catalyst [70].

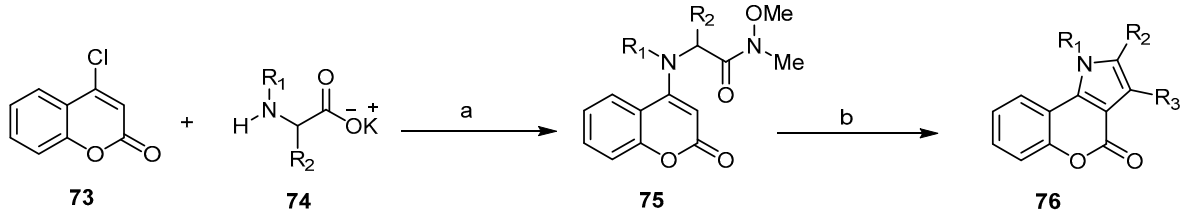


Scheme 20. Synthetic protocol to synthesize [l]benzopyrano[4,3-*b*]pyrrole-4(1*H*)-ones **68.** *Reagents and conditions*: $TsOH.H_2O$, solvent-free, 24 outputs with 6%–77% yield.



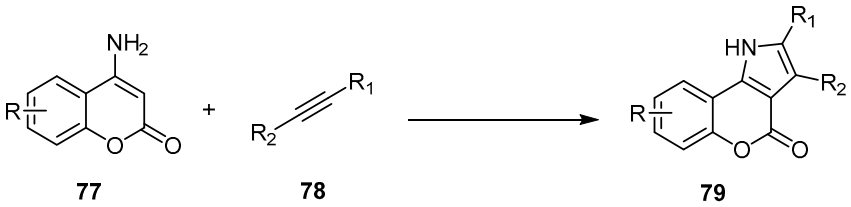
Scheme 21. Synthetic protocol to synthesize [l]benzopyrano[4,3-*b*]pyrrole-4(1*H*)-ones **72**. *Reagents and conditions*: $CuFe_2O_4$, H_2O, 70 °C, 25 outputs with 68%–94% yield; or $KHSO_4$, toluene, reflux, 23 outputs with 37%–93% yield.

Many articles have found that the 4-chlorocoumarin is the key compound for the preparation of various [l]benzopyrano[4,3-*b*]pyrrol-4-ones by Knorr- or Fischer–Fink-type reactions [72,73]. Albrola et al. indicated the preparation of N(*α*)-(2-oxo-2*H*-l-benzopyran-4-yl)Weinreb-α-aminoamides **75** from 4-chlorocoumarin (**73**) and different α-aminoacids **74**. The reaction of **75** with various organometallic compounds, followed by cyclization, led to the formation of [l]benzopyrano[4,3-*b*]pyrrol-4-ones **76** (Scheme 22) [74,75].



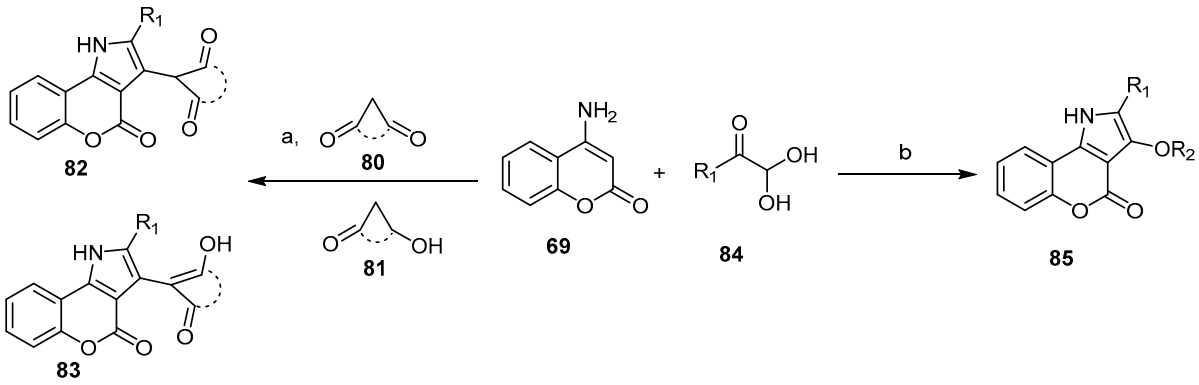
Scheme 22. Synthesis of [l]benzopyrano[4,3-*b*]pyrrol-4-ones **76** from 4-chlorocoumarin. *Reagents and conditions*: (a) i: EtOH, TEA, HCl.N(Me)OMe, ii: CH_2Cl_2, TEA, DCC; (b) i: organometallic compounds (R_3M), THF, N_2, -H_2O, ii: NaOEt, EtOH, r.t., 2 h, reflux, 1 h, nine outputs with 27%–92% yield.

On the other hand, the 4-amino-2*H*-benzopyran-2-one is employed as a key compound for the preparation of [l]benzopyrano[4,3-*b*]pyrrol-4-one [76,77]. Peng et al. synthesized a series of [l]benzopyrano[4,3-*b*]pyrrol-4-ones **79** via a palladium-catalyzed oxidative annulation reaction of 4-amino-2*H*-benzopyran-2-ones **77**, with electron-withdrawing or electron-donating groups with different alkynes **78** (Scheme 23) [76]. The method utilizes simple and readily available enamines and alkynes, and employs direct Pd(II)-catalyzed oxidative annulation to synthesize [l]benzopyrano[4,3-*b*]pyrrol-4-ones in high yields of 72%–99%.



Scheme 23. The scope of 4-aminocoumarins in the preparation of [l]benzopyrano[4,3-*b*]pyrrol-4-ones **79**. *Reagents and conditions*: $Pd(OAc)_2$, oxidant, DMSO, 100 °C, 12 outputs with 72%–99% yield.

Recently, Yang et al. reported a one-pot, two-step reaction of 4-amino-2*H*-benzopyran-2-one (**69**) with arylglyoxal monohydrates 80 and *p*-toluenesulfonates **81** to afford a series of 3-alkoxy-substituted [l]benzopyrano[4,3-*b*]pyrrol-4-ones **82** and **83**, respectively (Scheme 24) [78]. On the other hand, Yahyavi et al. described the Knoevenagle treatment of the arylglyoxals **84** with active methylene compounds and consequently an iodine-activated Michael-type reaction with 4-aminocoumarin (**69**) in a one-pot manner to afford disubstituted [l]benzopyrano[4,3-*b*]pyrrol-4-ones **85** (Scheme 24) [79].



Scheme 24. Various arylglyoxals in the synthesis of [l]benzopyrano[4,3-*b*]pyrrol-4-ones **82**, **83**, and **85**. *Reagents and conditions*: (a) i: AcOH, reflux, 40 min; ii: an appropriate alkyl *p*-toluenesulfonate ($TsOR_2$), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), toluene, reflux, 1.5 h, 14 outputs with 73%–89% yield; (b) R_1=Ph, 4-$CH_3OC_6H_4$, 4-$CH_3C_6H_4$, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 2-thienyl; dimedone, 2-hydroxy-1,4-naphtoquinone barbituric acid, 1,3 dimethyl barbituric acid, I_2, DMSO, stirring, 100 °C, 7 h, 15 outputs with 15%–80% yield.

2.1.3. Thiophenes

Fusion of the thiophene ring with the pyrone ring of coumarin(benzopyrane) leads to three structural isomers, viz. *4H*-thieno[2,3-*c*]chromen(benzopyran)-4-one, *4H*-thieno[3,4-*c*]chromen(benzopyran)-4-one, and *4H*-thieno[3,2-*c*] chromen(benzopyran)-4-one (Figure 3)

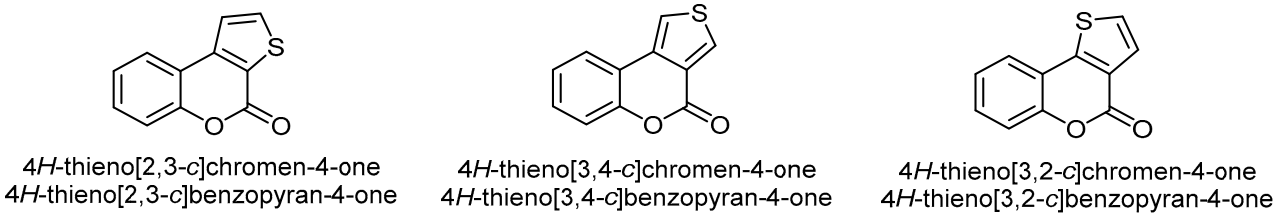
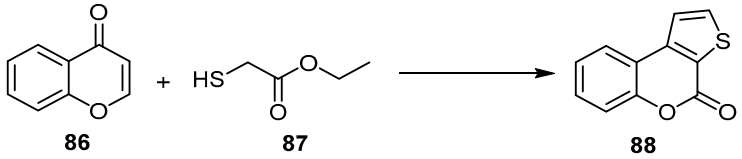


Figure 3. The three common isomers of the thiophene ring fused to the α-pyrone moiety of coumarin.

4*H*-Thieno[2,3-*c*]benzopyran-4-one

Thiophene Construction

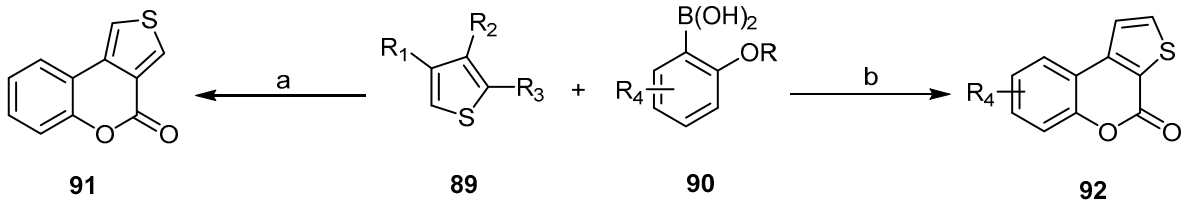
The one-pot cascade addition/condensation/intramolecular cyclization sequence of chromone (**86**) with ethyl 2-mercaptoacetate (**87**) using a complexing ligand 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) in 1,4-dioxane led to the formation of 4*H*-thieno[2,3-*c*]benzopyran-4-one (**88**) (Scheme 25) [80].



Scheme 25. Synthesis of 4*H*-thieno[2,3-*c*]benzopyran-4-one (**88**). *Reagents and conditions*: 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,4-dioxane, 60 °C, 12 h, N_2, 95% yield.

Pyrone Construction

The Suzuki–Miyaura cross coupling of bromoarylcarboxylates and *o*-hydroxy(methoxy) arylboronic acids is one of the methods that plays an important role in the preparation of 4*H*-thieno[2,3-*c*] **91** and 4*H*-thieno[3,4-*c*]benzopyran-4-ones **92** (Scheme 26) [81–83].

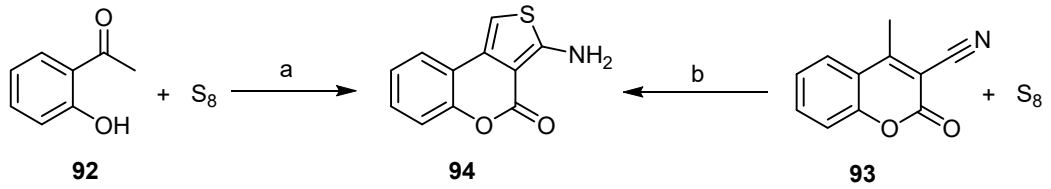


Scheme 26. 4*H*-thieno[3,4-*c*]benzopyran-4-ones **91** and **92** via a Suzuki–Miyaura cross coupling reaction. *Reagents and conditions*: (a) $Pd(PPh_3)_4$ (10 mol %), Cs_2CO_3 (4 equiv.), DME, H_2O, MW 125 °C, 15 min, 86% yield; (b) i: $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (1.5 equiv.), 1,4-dioxane, 90 °C, 4 h; ii: (a) BBr_3, CH_2Cl_2, (b) KO*t*Bu, H_2O, five outputs with 75%–81% yield [83].

4*H*-Thieno[3,4-*c*]benzopyran-4-one

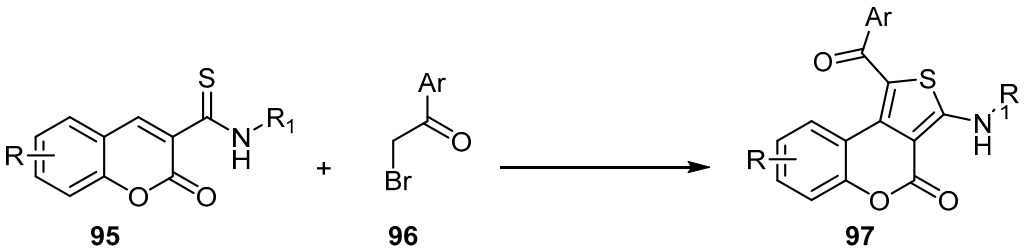
Thiophene Construction

4*H*-thieno[3,4-*c*]benzopyran-4-ones (**94**) were meanly prepared through the Gewald reaction (Scheme 27) [84–90]. Low yields of 37% and 48% were observed using these methods.



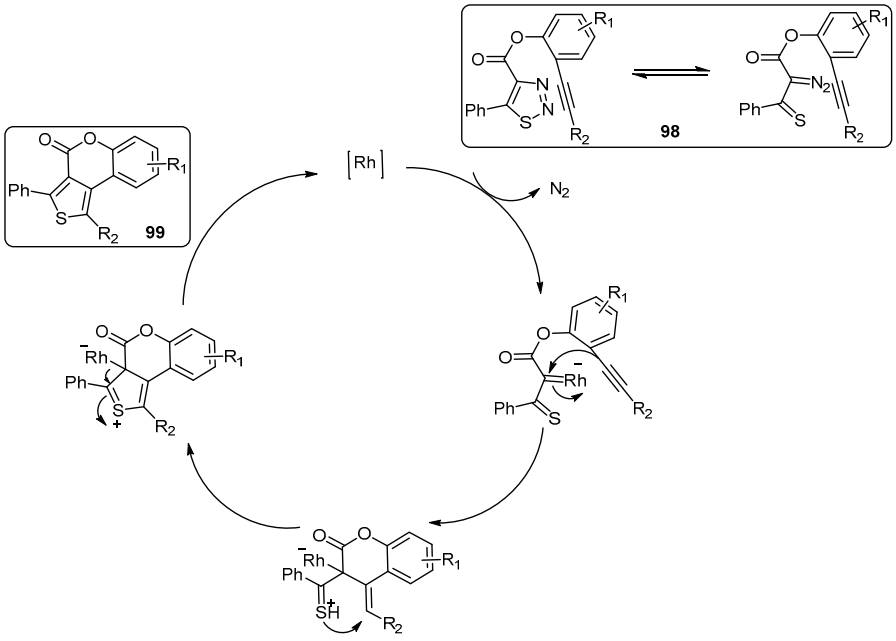
Scheme 27. The Gewald reaction to synthesize 4*H*-thieno[3,4-*c*]benzopyran-4-one (**94**). *Reagents and conditions*: (a) $CNCH_2COOEt$, base; (b) NH_3, EtOH, 48% yield [85], 37% yield [90].

Yu et al. created a new technique for the preparation of 4*H*-thieno[3,4-*c*] [1]benzopyran-4(4*H*)-ones **97** by applying a chemoselective reaction of thioamides **95** with α-bromoacetophenones **96** (Scheme 28) [91].



Scheme 28. Synthesis of 4*H*-thieno[3,4-*c*] [1]benzopyran-4(4*H*)-ones **97** via [4 + 1] annulations. *Reagents and conditions*: NaOH, diethyl azodicarboxylate (DEAD), MeCN, r.t., 20 min, 17 outputs with 68%–95% yield.

A rhodium-catalyzed intramolecular transannulation reaction of alkynyl thiadiazoles **98** provided 4*H*-thieno[3,4-*c*][1]benzopyran-4(4*H*)-ones **99**. A plausible reaction mechanism proposed for the Rh-catalyzed intramolecular transannulation of alkynyl thiadiazoles is outlined in (Scheme 29) [92].

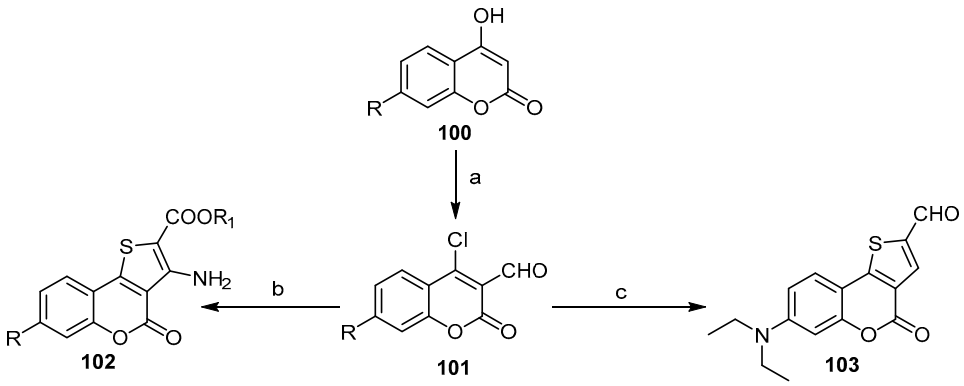


Scheme 29. A plausible reaction mechanism proposed for the preparation of 4*H*-thieno[3,4-*c*][1] benzopyran-4(4*H*)-ones **99**. *Reagents and conditions*: $[Rh(COD)Cl]_2$ (5 mol %), 1,1′-Ferrocenediyl-bis(diphenylphosphine) (DPPF) (12 mol %), PhCl, 130 °C, 30 min, three outputs with 75%–90% yield.

4*H*-Thieno[3,2-*c*][1]benzopyran-4(4H)-one

Thiophene Construction

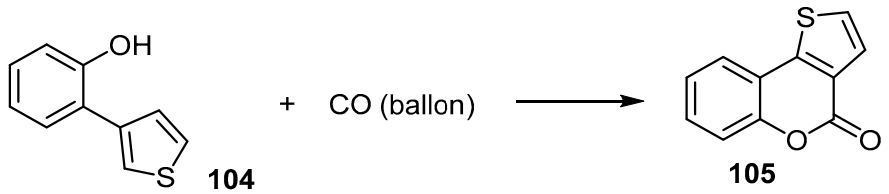
Numerous articles state the use of 4-chloro-2-*H*-benzopyran-3-carboxaldehydes **101** as a key compound in the preparation of a series of 4*H*-thieno[3,2-*c*][1]benzopyran-4(4*H*)-ones. This compound was prepared by a Vilsmeier–Haack reaction, and the cyclization process was performed through a rection with thioglycolate or dithiane to produce **102** and **103**, respectively (Scheme 30) [25,26,93,94].



Scheme 30. The synthesis of 4*H*-thieno[3,2-*c*][1]benzopyran-4(4H)-ones **102** and **103** via the cyclization of Vilsmeier–Haack products. *Reagents and conditions*: (a) $POCl_3$, DMF, 60 °C, overnight; (b) $SHCH_2COOR_1$, EtOH, base, 90% yield [25], 88% yield [94]; (c) 1,4-dithiane-2,5-diole, K_2CO_3, acetone, stirring, 1 h, r.t., 45 °C, 3 h, 85% yield.

Pyrone Construction

The palladium-catalyzed oxidative carbonylation of 2-(thiophen-3-yl)phenol (**104**) under acid-base-free and mild conditions yielded the corresponding 4*H*-thieno[3,2-*c*][1] benzopyran-4(4*H*)-one (**105**) (Scheme 31) [58].



Scheme 31. One-pot synthesis of 4*H*-thieno[3,2-*c*][1]benzopyran-4(4*H*)-one (105) by CO insertion into phenol. *Reagents and conditions*: 10 mol % $Pd(OAc)_2$, AgOAc, CH_3CN, 80 °C, 48 h, 62% yield.

2.1.4. Selenophene

The fusion of the selenophene ring with the pyrone ring of coumarin leads to two structural isomers, viz. *4H*-selenophen[2,3-*c*]chromen(benzopyran)-4-one and *4H*-selenophen[3,2-*c*]chromen(benzopyran)-4-one (Figure 4).



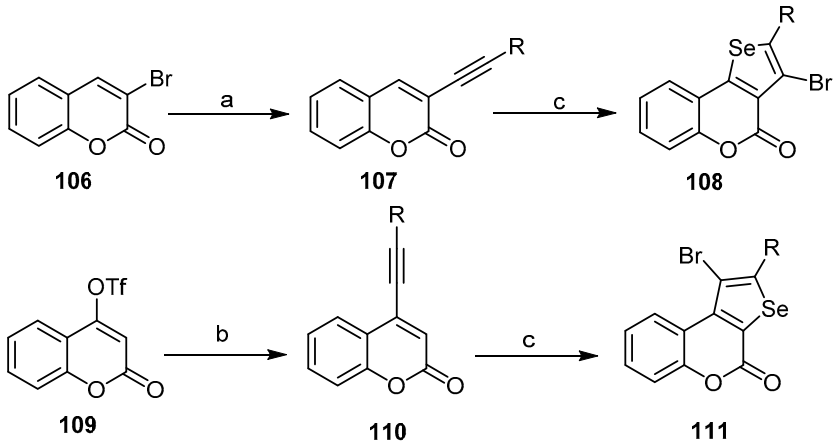
4*H*-selenophen[2,3-*c*]chromen-4-one
4*H*-selenophen[2,3-*c*]benzopyran-4-one

4*H*-selenophen[3,2-*c*]chromen-4-one
4*H*-selenophen[3,2-*c*]benzopyran-4-one

Figure 4. The two common isomers of the selenophene ring fused to the α-pyrone moiety of coumarin.

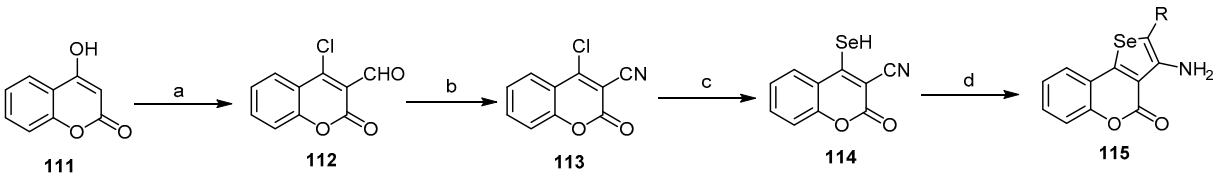
4*H*-Selenophen[2,3-*c*] and [3,2-*c*]benzopyran-4-ones

A few articles have discussed the possibility of synthesizing the fused selenophen-chromen-(benzopyran)-4-one moiety. A simple method for the synthesis of substituted 4*H*-selenopheno[2,3-*c*] benzopyran-4-ones **108** is by the treatment of 3-ethynylcoumarins **107** with selenium (IV) oxide and concentrated hydrobromic acid at room temperature [16,95]. Similarly, 4*H*-selenopheno-[3,2-*c*]benzopyran-4-ones **111** was prepared under the same conditions using 4-ethynylcoumarins **110**. The alkenyl derivatives were obtained from bromocoumarin (**106**) and 4-(trifluoromethane-sulfonyl)coumarin (**109**) by Sonogashira coupling. All the reaction steps were carried out in situ from the starting materials and until the end product (Scheme 32) [16,95].



Scheme 32. *Reagents and reaction conditions*: a: $PdCl_2$ (10 mol %), Ph_3P (20 mol %), CuI (10 mol %), terminal acetylene (1.5 equiv.), NMP, Et_3N, 55 °C, 20 h; b: $(Ph_3P)4Pd$ (5 mol %), CuI (20 mol %), terminal acetylene (1.5 equiv.), DMF, Et_3N, r.t., 20 h; **c**: SeO_2 (2 equiv.), conc. HBr, dioxane, r.t., 24–48 h, compounds **108**, four outputs with 68%–75% yield; compounds 111, four outputs with 64%–70% yield.

Additionally, Kirsch and his coworkers reported the synthesis of selenopheno[2,3-*c*]benzopyran-4-ones (**115**) via a multistep reaction. This reaction cascade started by Vilsmeier formylation of 4-hydroxycoumarine (**111**). The formylated product reacted with hydroxyl amine to afford (**113**) according to the reaction conditions, which subsequently transformed into 3-cyano-4-coumarinselenol (**114**), by refluxing with selenium and sodium-borohydride in ethanol (Scheme 33). It was the precursor of selenopheno[2,3-*c*]benzopyran-4-ones (**115**) as it was reactive towards a series of haloacids, such as chloroacetonitrile, ethyl chloroacetoacetate, and chloroacetamide [96].



Scheme 33. Synthesis of selenopheno[2,3-*c*]benzopyran-4-ones (**115**) from 4-hydroxycoumarin. *Reagents and reaction conditions*: a: $POCl_3$, DMF, 84% yield; b: $NH_2OH.HCl$, 80% yield; c: Se, $NaBH_4$, EtOH, 85% yield; d: $ClCH_2CN(R)$, DMF, stirring, r.t., 2 h, three outputs with 80%–88% yield.

In conclusion, since coumarins have versatile applications, the synthesis of different structures of the coumarin-based scaffold was attempted. Among all the heterocycles built on the α-pyrone moiety of coumarin, the furan ring is the only available structure in nature. Thus, it has inspired a lot of researchers to replace the oxygen atom with other heteroatoms. Wide varieties of heterocycles were constructed by a synthetic pathway to introduce furans, pyrroles, thiophenes, and selenophenes as a fused ring that is characterized by a single

heteroatom to the α-pyrone moiety of coumarin. The fused heterocycles that contain more than one heteroatom will be described in the next part, which we intend to publish in the future.

Author Contributions: E.R.E.-S. and G.K. collected publications and sorted them. E.R.E.-S. analyzed the literature and wrote the first draft. A.B.A. and G.K. developed the concept of the review. E.R.E.-S., A.B.A., and G.K. wrote the final draft and corrected the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: The APC was funded by MDPI.

Conflicts of Interest: The authors declare no conflict of interest.

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