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Salicylaldehydes as privileged synthons in multicomponent reactions

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Salicylaldehyde (2-hydroxybenzaldehyde) bearing two different active functional groups, namely, a hydroxy group and an aldehyde group, finds wide application as a key chemical in a variety of industrial processes, especially in the large-scale production of pharmaceuticals. Salicylaldehyde and most of its derivatives are commercially available or readily accessible, and hence are ideal starting materials for multicomponent reactions (MCRs), mostly in *pseudo*-three and four-component ones, giving rise to a plethora of heterocyclic systems. The importance of salicylaldehyde and an impressive amount of studies concerning its applications in MCRs prompted us to highlight in this review the important role of this compound as a privileged synthon in the synthesis of heterocycles.
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1. Introduction

A multicomponent reaction (MCR) is a synthetic approach in which three or more commercially available or easily accessible starting materials are reacted in a one-pot fashion to produce a compound where almost all the parent entities contribute to this newly formed compound. This strategy provides many advantages over the traditional multi-step reactions such as shorter reaction times, higher yields as well as a wide scope for molecular diversity and atom economy.[1] On the other hand, a MCR is a domino or cascade reaction. A cascade reaction is a chemical process involving at least two consecutive reactions wherein each subsequent reaction takes place only in virtue of the chemical functionality generated in the previous step.[2, 3] MCRs are currently on the top of the most valuable synthetic processes since they provide facile and rapid access to large combinatorial libraries of organic molecules, what is of particular importance in drug design. The most advantageous and promising drug nominees are small organic molecules, since common peptides and standard oligonucleotides have certain restrictions in terms of bioavailability. Having a number of commercially available or easily accessible starting materials in hand, a large libraries of small organic molecules can be readily synthesized *via* MCRs. However, despite the obvious synthetic convenience and advantages of MCRs, and their availability for construction of a wide range of chemical structures, their wide applications have been overlooked over the years. Fortunately, during the last decade, the significance of MCRs, particularly those involving salicylaldehyde, for drug design has been well-recognized and substantial attempts have been made in this field, both in academia and industry.[4]

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Salicylaldehyde and its derivatives are commonly used as preservatives in essential oils, cosmetics and fragrances.[5] Salicylaldoximes containing branched alkyl chains are frequently used as extracting agents in the processes of separation and concentration in the copper recovery.[6]

There are several different approaches to the preparation of salicylaldehyde. One of them comprises formylation of phenol with formaldehyde in the presence of $Mg(OMe)_2$ in anhydrous media.[7] Although salicylaldehyde is a simple molecule, it is an important and versatile precursor for a variety of useful compounds, particularly for complex heterocyclic systems. Salicylaldehyde and its derivatives can be effectively applied in MCRs, particularly, in (*pseudo*)-three and four-component reactions. There is a plethora of studies reporting the synthesis of various heterocycles *via* MCR involving salicylaldehyde as a suitable starting material.[8,9] However, a literature survey showed no comprehensive review covering these data.

In continuation of our interest in the chemistry of heterocyclic compounds[10–14] and their synthesis *via* MCRs,[15–23] in this review we will try to highlight the applications of salicylaldehyde as a privileged synthon for the synthesis of various heterocycles. Here, we decided to restrict our consideration to reactions involving both hydroxyl and aldehyde groups of salicylaldehydes in the MCRs.

2. Multi-component reactions of salicylaldehyde

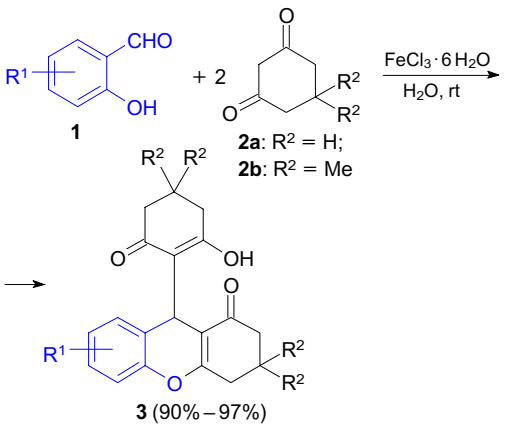
2.1. *Pseudo*-three-component reactions

Pseudo-multicomponent reaction is a kind of MCRs wherein at least one of the reactants participates two or more times in the reaction, and the reaction product contains two or more molecules of this reactant.

Among the most commonly used starting materials in both multicomponent and *pseudo*-multicomponent reactions involving salicylaldehyde, there are active methylene compounds, such as 1,3-dicarbonyl compounds, and various derivatives of malonic acid. Such reactions provide a general approach to a variety of xanthene and chromene derivatives, representing 'privileged medicinal scaffolds' and displaying a wide spectrum of pharmacological activities.[24,25]

Thus, Tajbakhsh *et al.* performed *pseudo*-three component iron(III) chloride-mediated reaction *via* condensation

Scheme 1



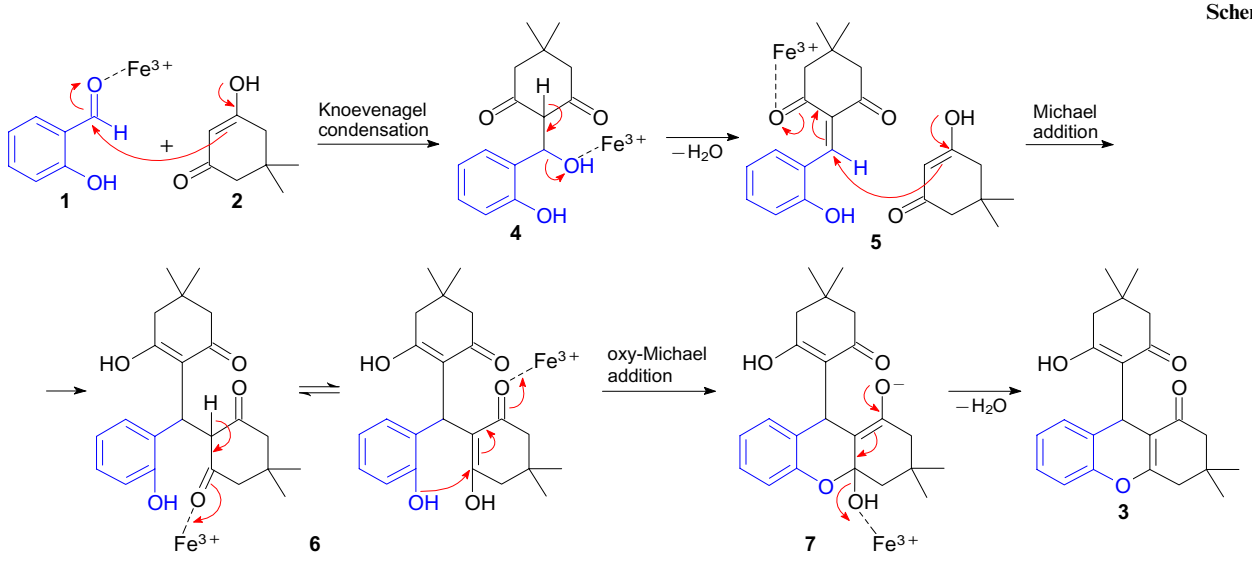
R^1 = H, 3-Br, 3-Cl, 5-OMe, 3,5-Cl_2; R^2 = H, Me

of salicylaldehydes **1** with two moles of cyclic 1,3-diketones **2** in water at ambient temperature to obtain the corresponding 1-oxo-tetrahydro-1*H*-xanthen-1-ones **3** (Scheme 1).[26]

A possible mechanism for this reaction is illustrated in Scheme **2**. First, the Knoevenagel coupling is catalyzed by $FeCl_3 \cdot 6H_2O$ *via* coordination of the Lewis acid sites (Fe^{3+}) to the oxygen atom of the carbonyl group in salicylaldehyde, generating intermediate **5**. Then, a nucleophilic attack of intermediate **5** on the electrophilic carbon during a Michael addition takes place affording intermediate **6**. Next, the phenolic oxygen atom attacks the enone *via* the 'oxy-Michael' reaction to yield intermediate **7**, which can also exist as an enolate. Elimination of water from the above intermediate results in transformation of the latter into the target product **3** (Scheme 2).

It should be mentioned that, apart from ferric trichloride, other homogeneous and heterogeneous catalysts were reported to be effective in this reaction, *e.g.*, $CeCl_3 \cdot 7H_2O$,[27] triethylbenzylammonium chloride (TEBA),[28] L-proline,[29] *para*-toluenesulfonic acid,[30] nano-$ZnAl_2O_4$,[31] nano-Fe/NaY,[32] AcOH–H_2O,[33] diethylamine,[34] cellulose sulfuric acid,[35] 2,4,6-trichloro-1,3,5-triazine (TCT, cyanuric chloride),[36] Brønsted acid ionic liquid $[(CH_2)_4SO_3HMIM][HSO_4]$,[37] lemon extract as a natural Brønsted acid-type biosurfactant,[38] 1,4-diazabicyclo[2.2.2]octane (DABCO),[39] polyvinylpyrrolidone

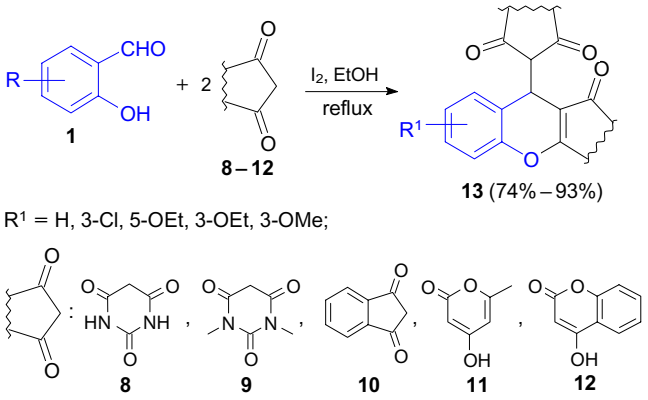
Scheme 2



(PVP) stabilized Ni(0) nanoparticles,[40] sodium acetate,[41] Preyssler acid,[42] piperidine,[43] ferric triflate[44] and cesium fluoride.[45] Moreover, catalyst-free conditions were also reported.[46] Most of these catalysts provide high yields, simple experimentation and easy isolation procedure.

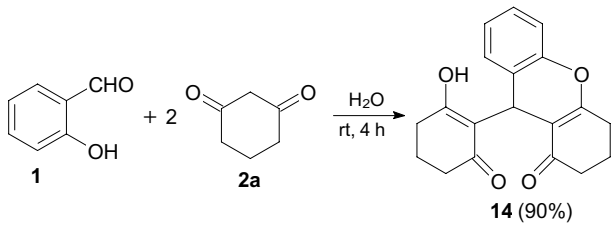
Zeng *et al.* has performed a more general reaction using a series of dicarbonyl and monocarbonyl compounds such as barbituric acids (**8**, **9**), 1*H*-indene-1,3(2*H*)-dione (**10**), 4-hydroxy-6-methylpyran-2-one (**11**) and 4-hydroxycoumarin (**12**) in the presence of I_2 to afford chromene derivatives **13** (Scheme 3).[47] Salicylaldehydes bearing both electron-donating and electron-withdrawing substituents showed similar reactivity producing the corresponding products in high yields.

Scheme 3



An interesting example of a tandem Knoevenagel condensation and Michael addition was discovered by Yu *et al.* when studying the reaction between aldehydes and 1,3-diketones.[48] It was shown that, contrary to benzaldehydes producing tetraketones, salicylaldehyde **1** reacted with cyclohexane-1,3-dione (**2a**) to afford 2-(1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)cyclohexane-1,3-dione **14** in almost quantitative yield (Scheme 4). The reaction proceeded in water at room temperature without any catalyst.

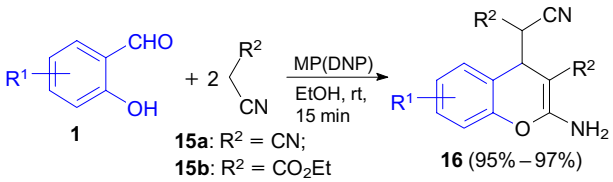
Scheme 4



A *pseudo*-three component reaction between salicylaldehyde derivatives **1** and 2 moles of malononitrile or ethylcyanoacetate **15a**,**b** produced 2-amino-4*H*-chromenes **16** (Scheme 5).[49] The molecular complex of 1-methylpiperidine (MP) and 2,4-dinitrophenol (DNP) was found to be a highly effective organo-catalyst for this reaction.

It should be noted that a variety of catalysts such as NaOAc or KF,[50] poly(*N*,*N*′-dibromo-*N*-ethylbenzene-1,3-disulfonamide) [PBBS] or *N*,*N*,*N*′,*N*′-tetrabromobenzene-1,3-disulfonamide [TBBDA],[51] potassium fluoride doped with natural phosphate,[52] sodium hydrogen carbonate,[53] lipase from *Bacillus subtilis*,[54] piperidine or acetic acid,[55] lithium nitrate/natural phosphate[56] and aluminium oxide[57] were also successfully applied in the aforementioned reaction.

Scheme 5



R^1 = H, 3-CO_2Et, 5-Br, 5-NO_2; R^2 = CN, CO_2Et;
MP(DNP) is a molecular complex of 1-methylpiperidine (MP) and 2,4-dinitrophenol (DNP)

2.2. Three-component reactions

Three-component reactions constitute the most numerous part of the MCRs of salycylaldehyde providing an access to functionalized chromene, coumarin, xanthene derivatives, *etc.*, most of which relating to medicinally privileged scaffolds.

For example, 2-aminochromenes represent a very important class of chemical compounds as they are the main constituents of many natural products and also find a wide application as pigments, cosmetics, agrochemicals, *etc.*[58] However, their biological activities are of particular importance.[59] Three-component reactions between salicylaldehyde, malononitrile and various nucleophiles proved to be a powerfool tool to obtain these compounds.

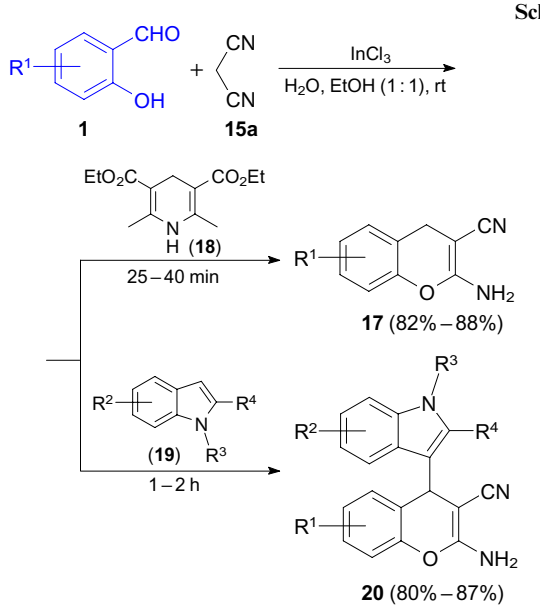
In 2007, Shanthi and Perumal developed a facile and efficient approach to the synthesis of 2-amino-3-cyanochromene derivatives **17** *via* the reaction between substituted salicylaldehydes **1**, malononitrile **15a** and Hantzsch dihydropyridine ester **18** (Ref. 60) catalyzed by indium trichloride.[61] Using indoles **19** in place of ester **18**, indolyl chromenes **20** were obtained (Scheme 6). Salicylaldehydes **1** bearing both electron-donating and electron-withdrawing substituents are suitable for this procedure, resulting in the formation of the corresponding chromenes **17**, **20** in relatively short reaction times.

The reaction between salicylaldehydes **1**, either malononitrile **15a** or cyanoacetamide **15c**, and trimethylsilylcyanide (TMSCN) **21** catalyzed by $LiClO_4$ in EtOH at ambient temperature afforded the corresponding 2-amino-4-cyano-4*H*-chromenes **22** (Scheme 7).[62] It should be noted that in the case of malononitrile **15a** the yields of the cyano-substituted chromenes **22** are significantly higher (73%–87%) compared to cyanoacetamide-substituted ones (41%–47%).[51]

The same catalytic system in the reaction of salicylaldehyde **1**, 2-imino-2*H*-chromene-3-carbonitrile **23** and various secondary amines **24** produced 2-(chromeno[2,3-*d*]-pyrimidin-2-yl)phenols **25** in satisfactory yields (Scheme 8).[62]

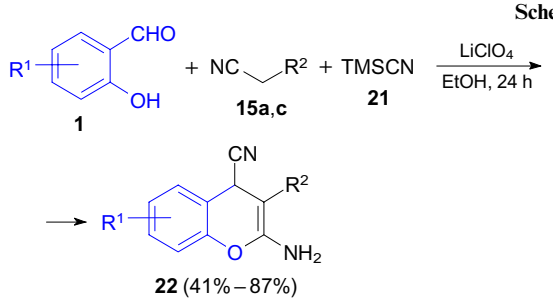
A probable mechanism for the synthesis of products **25** is shown in Scheme 9. The reaction is initiated by the nucleophilic attack of amines **24** on the nitrile group of **23**

Scheme 6



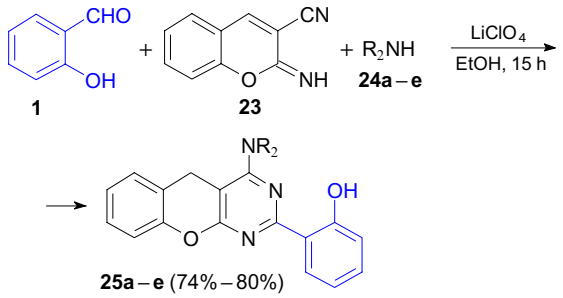
R^1 = Me, OMe, Br, Cl; R^2 = H, OMe, Br, Cl; R^3, R^4 = H, Me

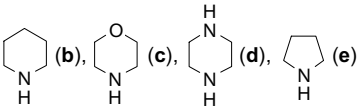
Scheme 7



R^1 = H, OMe, Me, Br, NO_2; R^2 = CN (73% – 87%);
R^2 = $CONH_2$ (41% – 51%); **15c**: R = $CONH_2$

Scheme 8



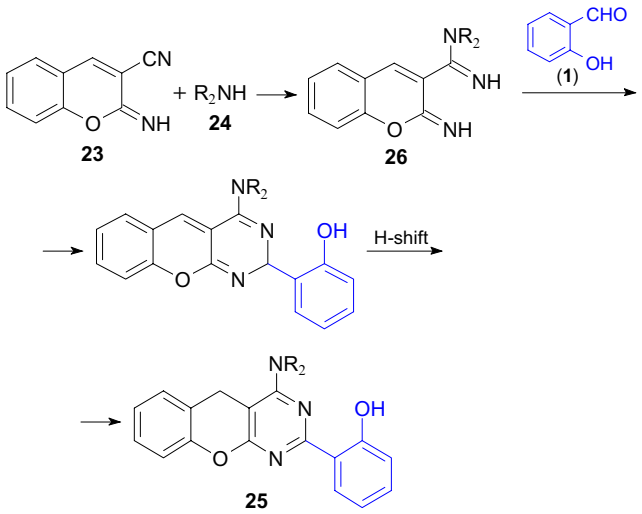
R_2NH = Me_2NH (**a**),  (**b**), (**c**), (**d**), (**e**)

to generate **26**. The latter then reacts with salicylaldehyde **1**, and undergoes isomerization to give the desired products **25**.

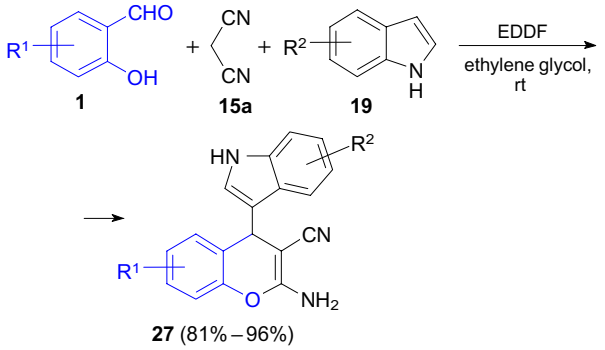
Indoles possessing a variety of important biological functions are considered to be a privileged scaffold in drug discovery,[63] therefore they are among the most popular starting materials in the MCRs.

Thus, Thakur *et al.*[64] reported the synthesis of 3-indolochromenes **27** using ethylenediammonium diformate

Scheme 9



Scheme 10



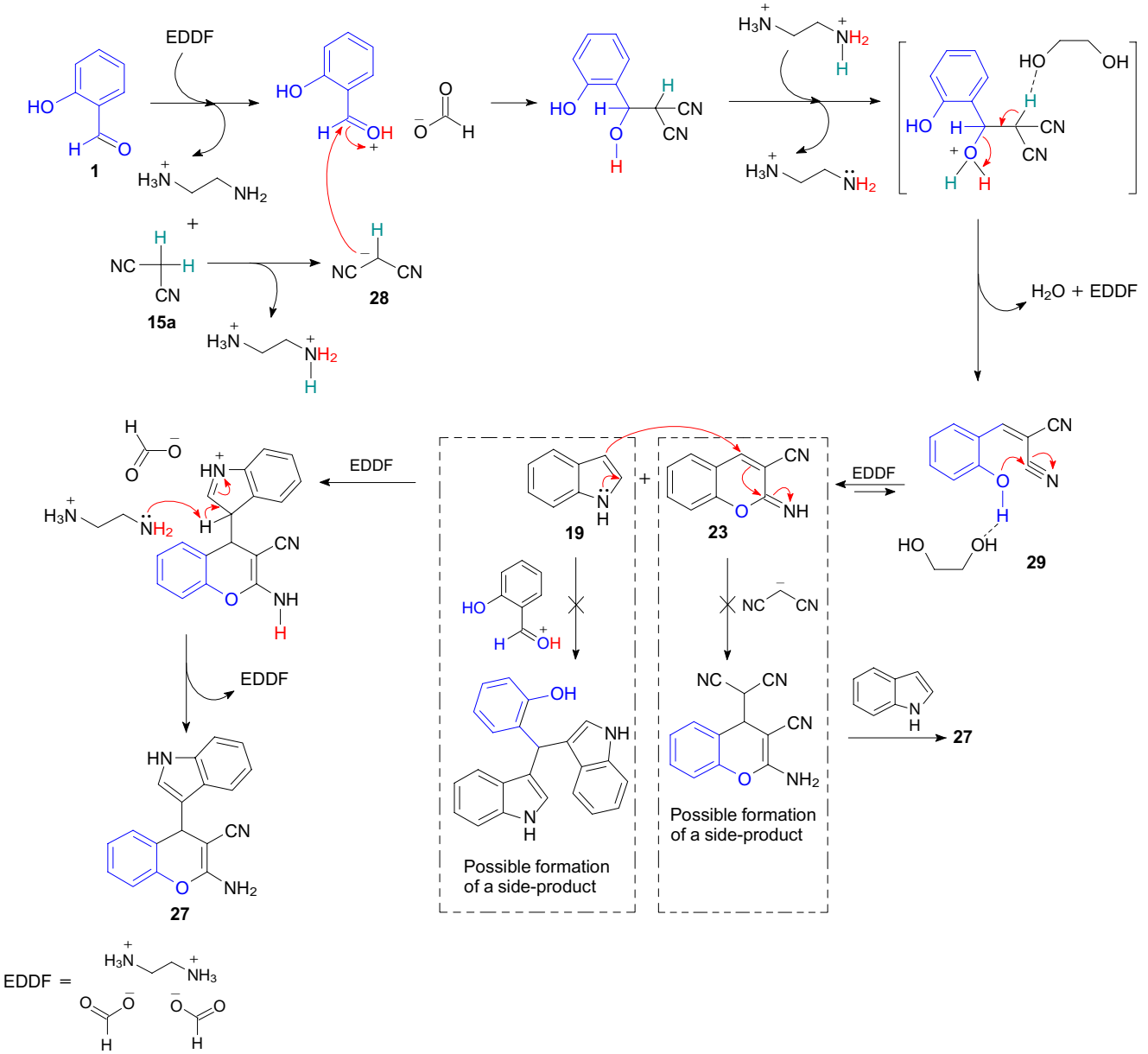
R^1 = H, 3-OMe, 4-OH; R^2 = H, 2-Me, 1-Me, 2-Br, 5-Br, 5-OMe

(EDDF) as a catalyst and ethylene glycol acting both as a co-catalyst and a solvent (Scheme 10).

A probable mechanism demonstrating the role of ethylene glycol as a co-catalyst is shown in Scheme 11. EDDF is a salt and, therefore, it can be applied as an ambiphilic catalyst in which both the anion and cation act in combination as a nucleophile and electrophile. On the one hand, the acidic portion improved the electrophilicity of the carbonyl group of **1**, while on the other hand, the immediately produced amine promotes an attack of the malonate ion **28**. Following the protonation and elimination of the water molecule, the first Knoevenagel adduct **29** is generated undergoing cyclization to afford intermediate 2-iminochromene **23** *via* the Pinner reaction.[65]

The diversity of catalysts for MCRs affording 3-indolopyrans is really impressive. In addition to an EDDF-ethylene glycol catalytic system, a plethora of heterogeneous and homogeneous catalytic systems have also been applied. Their examples include copper sulfonato salen,[66] Zn(salphen),[67] β-cyclodextrin,[68] 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU),[69] tetrabutylammonium bromide (TBAB),[70] nanocomposite consisting of the reduced graphene oxide and zinc oxide nanoparticles (RGO/ZnO),[71] polystyrene-supported *p*-toluenesulfonic acid,[72] L-cysteine functionalized magnetic nanoparticles (LCMNP),[73] tetrabutylammonium valinate supported on 3-chloropropyltriethoxysilane-grafted superparamagnetic Fe_3O_4 nanopar-

Scheme 11



ticles (VSF-nano),[74] Gly-tetra(*n*-butyl)ammonium salt,[75] potassium dihydrogenphosphate[76] and L-proline.[77]

In recent times, using environmentally benign solvents and reagents is among the most attractive trends in MCRs.

A new versatile tool for the synthesis of diversely substituted 4*H*-chromene scaffolds with a predefined arrangement of functional groups based on the electrocatalytic chain transformations of salicylaldehydes and CH-acids was proposed by Elinson *et al.*[78] Reactions were carried out in an individual cell in an alcohol medium using sodium bromide as an electrolyte.

Thus, electrochemically induced MCR between salicylaldehydes **1** and two different CH-acids (**15** and **30**) afforded functionalized 2-amino-4*H*-chromenes **31** in 65% – 86% yields (Scheme 12). It should be noted that this is a rare example of a selective one-pot reaction with different CH-acids where a distinction is made according to their reactivity. Here, more acidic cyano derivative **15a** serve as a source for the 2-amino-3-cyano-4*H*-chromene framework, while the less acidic CH-acid **30** contributes to the corresponding 4-substituent in 2-amino-4*H*-chromene **31**.

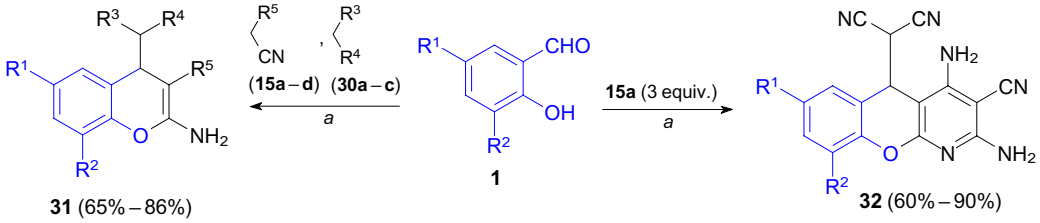
With three moles of malononitrile **15a** under the optimized conditions, the reaction led to the formation of chromeno[2,3-*b*]pyridine **32** with a fused dicyanomethyl-substituted 4*H*-chromene moiety.[79]

As for salicylaldehydes **1**, MCRs proceed smoothly with substrates containing both electron-withdrawing and electron-donating substituents. However, nitroalkanes gave only moderate yields in this reaction, probably due to the undesired oxidation on the cathode under the reaction conditions.

Electrocatalytic MCRs are very promising in view of the further development of 2-amino-4*H*-chromene chemistry as they allow the selective and one-step introduction of a wide range of medicinally significant functionalitites into the 2-amino-4*H*-chromene framework and also have obvious advantages over the traditional procedures as being simple, environmentally friendly and easy to scale-up.

Moreover, the same authors developed one more general approach to 4-functionalized 2-amino-4*H*-chromene

Scheme 12

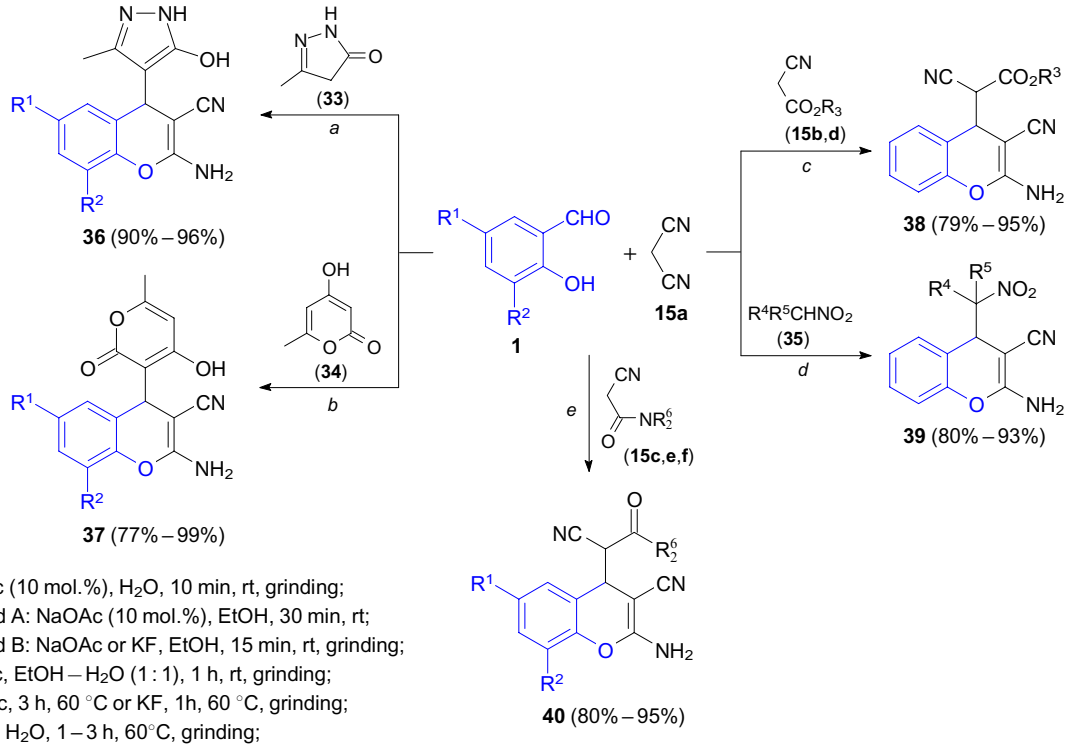


(*a*) Electrolysis, NaBr, EtOH, 78 °C, 10 mA cm^{-2}, 0.1 Fmol^{-1} passed; R^1 = H, Me, Br; R^2 = H, OMe, OEt; **15**: R^5 = CN (**a**), CO_2Et (**b**), $CONH_2$ (**c**), CO_2Me (**d**); **30**: R^3 = H, R^4 = NO_2 (**a**), R^3 = R^4 = CO_2Me (**b**), R^3 = R^4 = CO_2Et (**c**)

derivatives **31** applying solvent-free or 'on-solvent' strategies.[80–84] According to these methods, MCRs between salicylaldehyde, malononitrile and a number of carbon nucleophiles **15**, **33**–**35** were performed either by grinding the starting materials substantially without any solvent or under 'on-solvent' conditions, *i.e.* in a minimum amount of a solvent, using commercially available and inexpensive catalysts such as sodium acetate, potassium fluoride or sodium hydroxide (Scheme 13).

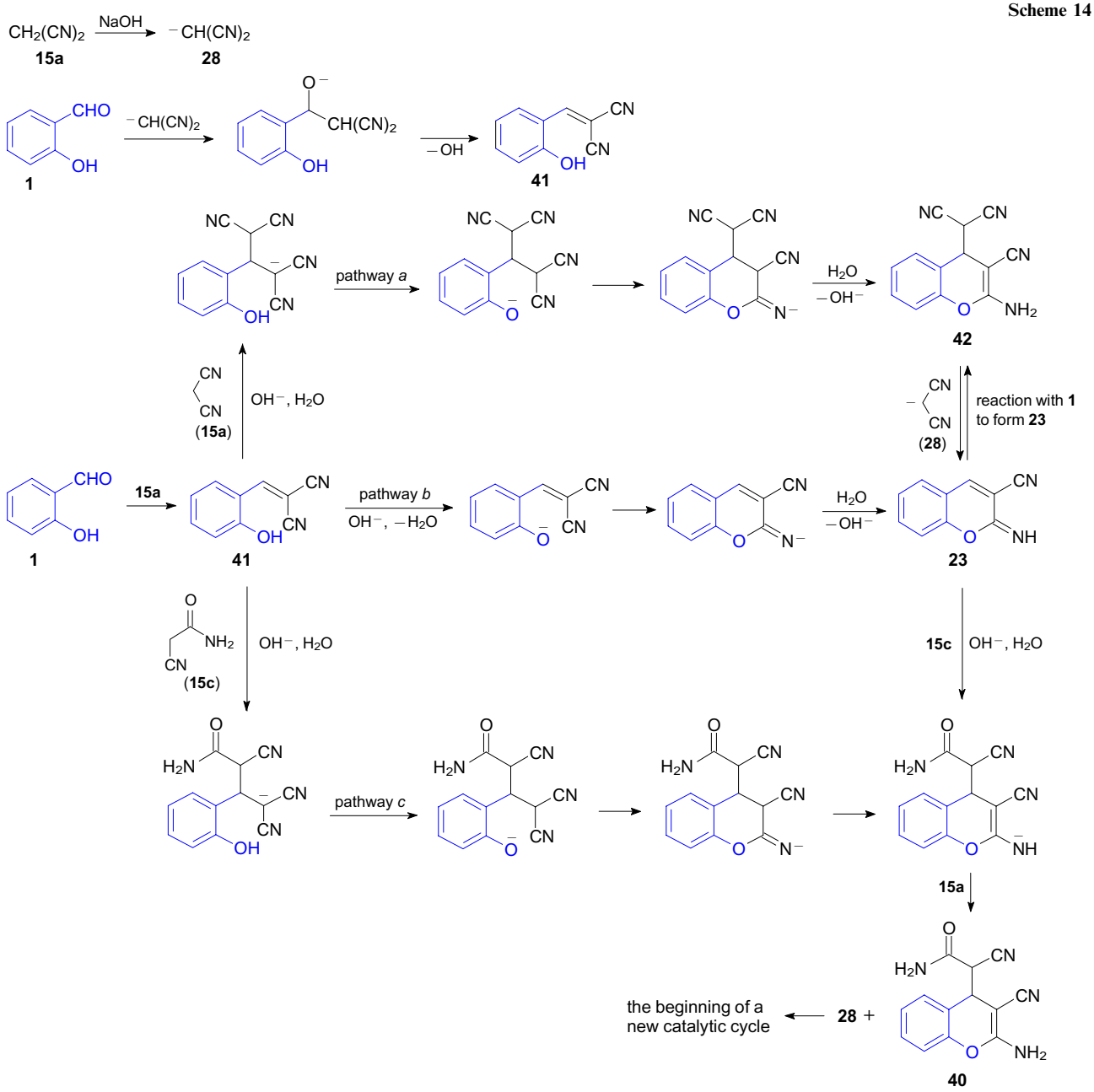
Depending on the nature of a carbon nucleophile, certain reaction parameters (catalyst, temperature, reaction time) were varied. Thus, the reaction with 3-methyl-2-pyrazolin-5-one **33** proceeded in 10 min just upon grinding the reactants in a mortar (see Scheme 13).[80] It was shown that the desired products **36** were obtained even in the absence of any solvent, but only in satisfactory yields (55%). However, addition of 1 ml of water had a significant effect on the reaction rate, and the yields increased by more than 20%. For the reaction with 4-hydroxy-6-methyl-2*H*-pyran-2-one **34**, two convenient procedures were proposed, one of them comprised stirring with NaOAc in EtOH for 30 minutes at room temperature (method A), and the second one involved grinding with NaOAc or KF under 'on-alcohol' conditions for 15 min at room temperature (method B) (see Scheme 13).[81] Both methods gave comparable yields of products **37**. Cyanoacetates **15b**,**d** reacted under similar 'on-solvent' conditions in a (1 : 1) water-alcohol mixture, but it took these compounds about an hour to produce the corresponding products **38** in high yields.[82] At the same time, CH-acids such as cyanoacetamides **15c**,**e**,**f** and nitroalkanes **35** required somewhat different reaction conditions. Thus, the reaction with nitroalkanes **35** proceeded under solvent-free conditions at 60 °C with both catalysts; however, KF proved to be more effective providing shorter reaction times (1 h *vs* 3 h with NaOAc) (see Scheme 13).[83] As it was mentioned above, application of nitroalkanes in the electrocatalytic method by Elinson *et al.*[78] was not especially successful because of the undesirable oxidation of the substrate. On the contrary, the proposed solvent-free procedure can be considered to be the most effective approach to 4-nitroalkyl-substituted 4*H*-chromenes **39** for the moment. As for cyanoacetamides

Scheme 13



(*a*) NaOAc (10 mol.%), H_2O, 10 min, rt, grinding;
(*b*) method A: NaOAc (10 mol.%), EtOH, 30 min, rt;
method B: NaOAc or KF, EtOH, 15 min, rt, grinding;
(*c*) NaOAc, EtOH – H_2O (1 : 1), 1 h, rt, grinding;
(*d*) NaOAc, 3 h, 60 °C or KF, 1h, 60 °C, grinding;
(*e*) NaOH, H_2O, 1 – 3 h, 60°C, grinding;
R^1, R^2 = H, Me, Cl, Br, OMe, OEt, NO_2; R^3 = Me, Et; R^4 = H, Me; R^5 = H, Me, Et, Ph, CO_2Me, $(CH_2)_2COMe$, $(CH_2)_2CO_2Me$;
$R^4 + R^5$ = $(CH_2)_5$; **15**: NR^6_2 = NH_2 (**c**), N⬠ (**e**), N⬡O (**f**)

Scheme 14



15c,**e**,**f**, a stronger base (NaOH) and higher temperatures were required for the reaction to be accomplished under 'on-water' conditions (see Scheme 13).[84]

The probable mechanism for the reaction with cyanoacetamide is illustrated in Scheme 14.

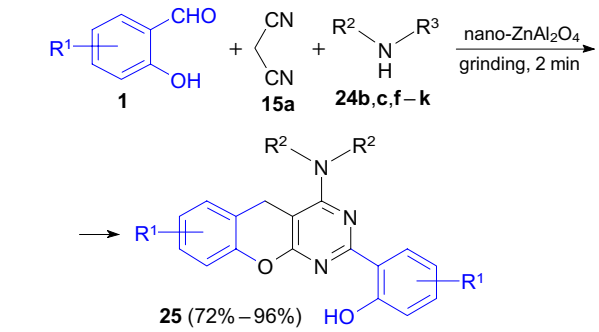
First, sodium hydroxide deprotonates malononitrile **15a** generating the anion **28**, which undergoes the Knoevenagel condensation with salicylaldehyde **1** proceeding with the removal of the hydroxide anion to afford benzylidenemalononitrile **41**.[85] In fact, the Knoevenagel adduct **41** can give rise to three reaction routes. The Michael addition of malononitrile to adduct **41** followed by an intramolecular cyclization yields (2-amino-3-cyano-4*H*-chromen-4-yl)-malononitrile **42** (pathway *a*). Compound **42** was detected in the reaction mixture when the solvent-free reaction of salicylaldehyde **1**, malononitrile **15a** and cyanoacetamide **15c** was performed in the presence of sodium hydroxide in shorter reaction times. (2-Amino-3-cyano-4*H*-chromen-4-yl)malononitrile **42** could exist in equilibrium with 2-imino-2*H*-chromene-3-carbonitrile **23** and malononitrile **15a** under certain reaction conditions.[55] If such an equilibrium takes place, the uptake of malononitrile from the equilibrium process by salicylaldehyde **1** could promote the base-stimulated addition of a weaker CH acid such as cyanoacetamide **15c** to 2-imino-2*H*-chromene **42**, resulting in the conversion of **42** into the corresponding 2-amino-4*H*-chromene **40** (see Scheme 14).

Despite the fact that every new substrate requires the tuning of the reaction conditions, the proposed solvent-free or 'on-solvent' methods gave remarkable results and are characterized by high yields, operational simplicity and extremely simple isolation of the resulting functionalized 4*H*-chromene derivatives.

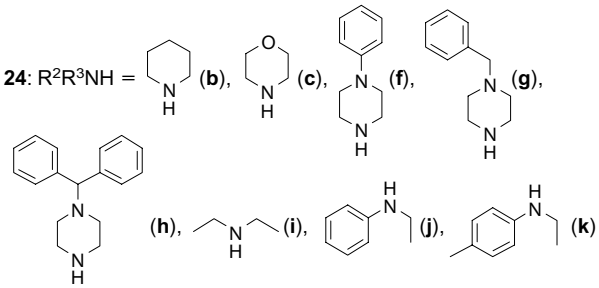
An alternative procedure for similar reactions with two different CH-acids was developed by Wang *et al.* using basic-functionalized ionic liquids such as [bmim]OAc, [bmim]OH, *etc.*[86]

One more solvent-free procedure based on grinding the starting materials was developed to obtain fluorescent chromeno[2,3-*d*]pyrimidines **25** (Scheme 15).[87] The reaction of substituted salicylaldehydes **1**, malononitrile **15a** and secondary amines **24** proceeded in the presence of a catalytic amount of $ZnAl_2O_4$ nanoparticles at ambient temperature upon grinding in a mortar and was accomplished in two minutes, so it can be considered as the most rapid reaction to obtain the compounds of such type. Among other advantages, the chemical stability of the catalyst, its recyclability, environmentally benign and cost effectiveness are worth mentioning. As for the scope of the reaction, the substituents in salicylaldehyde **1** have no significant effect on the product yields. The amine component **24** is limited to only secondary amines; both cyclic and acyclic ones such as diethylamine reacted smoothly in high yields. However alkylarylamines were not reactive at all and could not be used in this reaction.

Scheme 15



R^1 = H, 5-OMe, 5-OEt, 3-NO_2, 3-Br, C_4H_4;

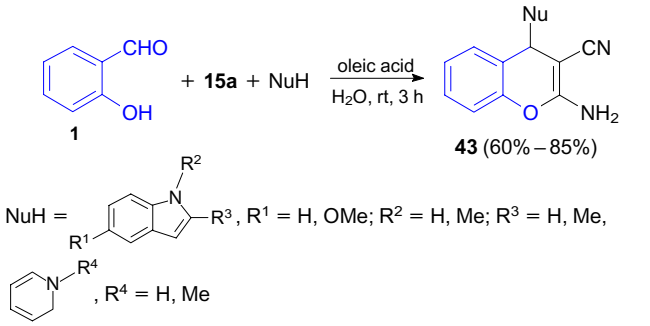


The authors assumed that $ZnAl_2O_4$ nanoparticles promoted both the Knoevenagel condensation of salicylaldehyde with malononitrile and nucleophilic attack of a secondary amine due to the presence of the acidic Zn^{2+} and Al^{3+} sites.

The synthesis of chromeno[2,3-*d*]pyrimidines **25** *via* the tandem reaction of salicylaldehydes **1**, malononitrile **15a** and appropriate secondary amines in a one-pot fashion has also been performed using other catalysts such as [Bmim]BF_4 ionic liquid,[88] Fe_3O_4/SiO_2/Salen/Mn magnetic nanoparticles (MNP),[89] silica nanoparticles supported on benzoylthiourea ferrous complex,[90] lithium perchlorate,[91] Brøensted acidic ionic liquids,[92] sodium molybdate dehydrate,[93] covalently anchored 1-(aminoethyl)-3-propylimidazolium bromide on SBA-15,[94] 3-aminopropyltriethoxysilane immobilized on SBA-15,[95] 1-butyl-3-methylimidazolium tetrafluoroborate,[96] zirconium(IV) oxychloride octahydrate,[97] as well as under microwave irradiation (MWI)[98] and catalyst-free conditions.[99]

Among reactions combining the application of eco-friendly catalysts and reaction media, the ones using easily accessible, non-toxic and biodegradable oleic acid as an effective catalyst for the formation of 4*H*-chromenes **43** in an aqueous media cannot but be mentioned (Scheme 16).[100] The scope of this domino reaction is rather wide and includes also *pseudo*-three-, three- and four-component reactions. Remarkably, the oleic acid-mediated three-component reaction afforded the desired indole-tethered 4*H*-chromenes **43** at ambient temperature in high yields.

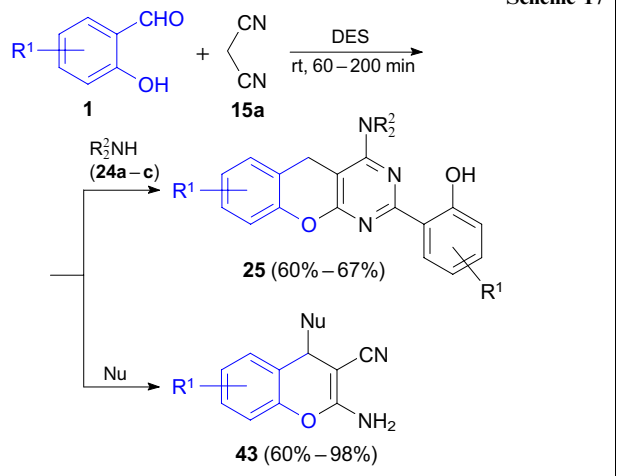
Scheme 16



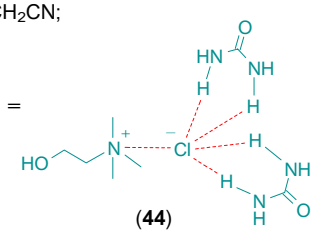
, R^1 = H, OMe; R^2 = H, Me; R^3 = H, Me, R^4 = H, Me

A promising alternative to conventional harmful organic solvents in MRCs was found to be a choline chloride based deep eutectic solvent (DES, **44**) used as a reaction medium in the reaction of salicylaldehyde **1**, malononitrile **15a** and a wide range of various nucleophiles to provide the corresponding 2-amino-3-cyano-4*H*-chromenes **43** (Scheme 17).[101] The required solvent **44** was obtained by the reaction of choline chloride and urea.[102]

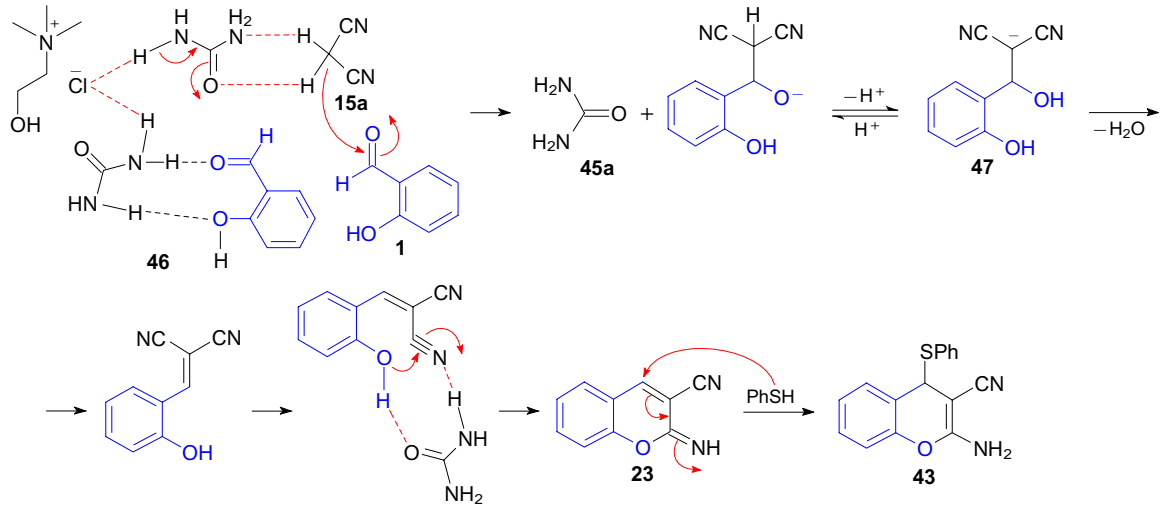
Scheme 17



R^1 = H, Br, MeO; R^2_2NH = Me_2NH (**24a**), NH (**24b**), O NH (**24c**), $BnNH_2$; Nu = R^3SH; R^3 = C_6H_5, p-MeC_6H_4, p-Cl-C_6H_4, p-$MeOC_6H_4$, Naph, cyclohexyl, isobutyl; TMSCN, NaCN, indole, $NCCH_2CN$;



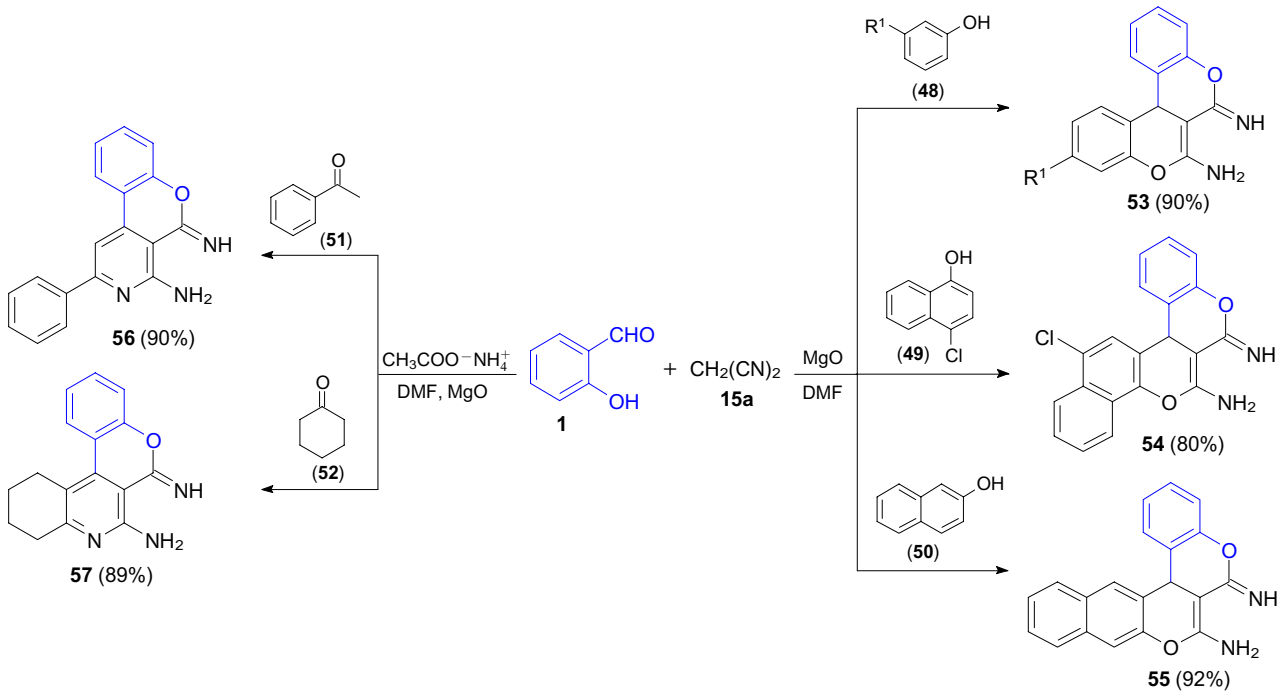
Scheme 18



Deep eutectic solvent is easily recovered from the reaction mixture and can be effectively reused at least three times without noticeable loss of activity. Remarkably, salicylaldehydes **1** bearing both electron-donating (*e.g.*, MeO) and electron-withdrawing groups (*e.g.*, Br) showed almost similar reactivity giving 4*H*-chromenes in 65% – 98% yields. As for thiols, aromatic compounds like 2-naphthylthiol and a number of functionalized thiophenol derivatives produced the corresponding chromenes **43** in 80% – 98% yields, while aliphatic ones (cyclohexylthiol and *iso*-butylthiol) were significantly less reactive (28% and 45%, respectively). At the same time, secondary amines **24a** – **c** provided benzopyrano[2,3-*d*]pyrimidines **25** under similar conditions. It was shown that the scope of this reaction is limited to secondary amines, with cyclic ones such as piperidine **24b** and morpholine **24c** being much more reactive compared to acyclic dimethylamine **24a**, whereas primary amines, *e.g.*, benzylamine, did not react at all. Nevertheless, this method provides an easy access to a variety of chromenes **43** and benzopyrano[2,3-*d*]pyrimidines **25** and is very attractive from the viewpoint of green chemistry since it requires mild conditions, no catalyst and recyclable non-toxic reaction medium.

A plausible mechanism for the synthesis of 2-amino-2-chromenes **43** in DES **44** as exemplified by the reaction with thiophenol is shown in Scheme 18. First, the urea part of DES **44** assists the Knoevenagel condensation *via* hydrogen bonding between the urea hydrogen atom and the oxygen atom of the carbonyl group of salicylaldehyde **1**. At the same time, urea **45a** can activate deprotonation of malononitrile **15a** using its Lewis basic sites, providing intermediate **46**. Next, the higher reactivity of salicyldehyde **1** and malononitrile **15a** facilitates the Knoevenagel reaction generating intermediate **47**, and then nucleophilic attack of

Scheme 19

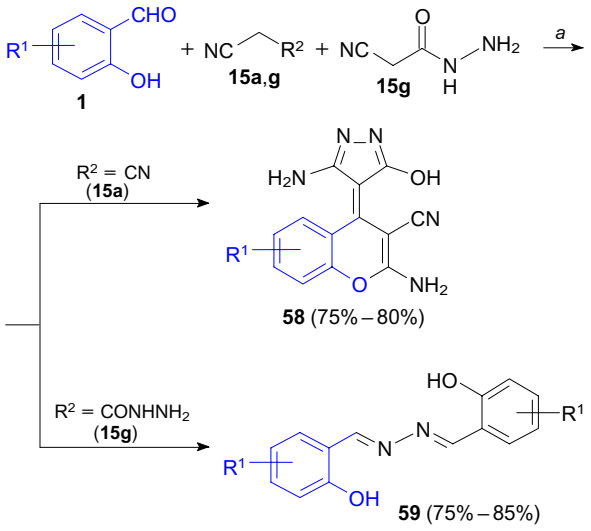


thiophenol on the electrophilic carbon–carbon double bond in **23** affords 2-amino-2-chromenes **43**.[101]

Mohammadzadeh *et al.* demonstrated that high surface area magnesium oxide in DMF represents a highly effective heterogeneous catalytic system for the reaction of salicylaldehyde **1**, malononitrile **15a** and aryl alcohols **48**–**50** or ketones **51**, **52** to produce chromeno[3,4-*c*]chromenes **53**–**55** and chromeno[3,4-*c*]pyridines **56**, **57**, respectively (Scheme 19).[103] The reaction proceeds very rapidly and provides the corresponding heterocycles in high yields. The catalyst is easily prepared by dehydration of $Mg(OH)_2$ at about 450 °C for 2 hours. Unfortunately, the authors gave poor information about the scope of the reaction, but nevertheless, this method represents a very attractive approach to such polycyclic compounds.

An interesting result was obtained for MCRs between salicylaldehydes and hydrazide derivatives. Thus, the reaction of salicylaldehydes **1**, malononitrile **15a** and 2-cyanoacetohydrazide **15g** was found to produce 2-amino-4-(3-amino-5-hydroxy-4*H*-pyrazol-4-ylidene)-4*H*-chromene-3-carbonitrile derivatives **58** under catalysis with potassium phosphate in ethanol (Scheme 20).[104] Surprisingly, under the same conditions, the reaction with two equivalents of 2-cyanoacetohydrazide **15g** produced linear salicylaldehyde azine derivatives **59** instead of the expected analogue of **58**, providing an alternative approach to salicylaldehyde azines.

Scheme 20

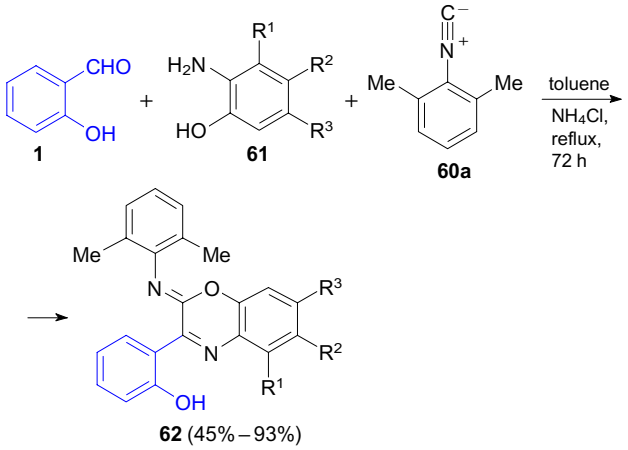


(*a*) K_3PO_4, EtOH, Δ, 1 h; R^1 = H, 5-Cl, 5-Br, 5-OEt

Using isonitriles **60** as nucleophiles in MCRs between salicylaldehyde and *ortho*-aminophenols **61** gives rise to 2-imino-1,4-benzoxazine derivatives **62** (Scheme 21).[105] Here, the hydroxy group of salicylaldehyde **1** is not involved in the reaction, whereas its presence in aminophenol **61** is of key importance for the formation of compounds **62**.

A probable mechanism for the synthesis of compounds **62** is shown in Scheme 22. Initially, condensation of salicylaldehyde **1** and an appropriate aminophenol **61** gives Schiff base **63**, which then reacts with isonitrile **60** to generate nitrilium intermediate **64**. Nucleophilic attack by the oxygen of *ortho*-aminophenol **61** on the electrophilic carbon atom affords 2-imino-3,4-dihydroxybenzoxazine **65** undergoing successive oxidation to produce benzoxazine **62** (pathway *a*). An alternative cyclization pathway involving

Scheme 21



$R^1 = R^2 = H$; R^3 = H, Me, NO_2; $R^1 = R^3$ = H; R^2 = H, Cl

the salicylaldehyde hydroxyl group and subsequent oxidation that would result in the formation of imino-1-benzofuran **67** was not observed (pathway *b*). Probably, the NH precursor of **67** (**66**) is in equilibrium with **64**, and the formation of **65** and **62** is thermodynamically favoured, driving the reaction to benzoxazine derivatives **62**.

Apart from using carbon, nitrogen or sulfur nucleophiles in the three-component reactions of salicylaldehyde and cyanoacetic acid derivatives, application of phosphorus nucleophiles has also been reported. Thus, condensation of salicylaldehyde **1**, malononitrile **15a** and trialkyl phosphites **68** proceeds *via* the phospha-Michael addition and affords (2-amino-4*H*-chromen-4-yl)phosphonates **69**. This reaction has attracted a special attention of researchers and was accomplished by a plenty of procedures using catalysts such as, *e.g.*, K_3PO_4,[106] ethylene diaminediacetate,[107] iodine,[108] indium trichloride[109] and polyethylene glycol 400[110] (Scheme 23).

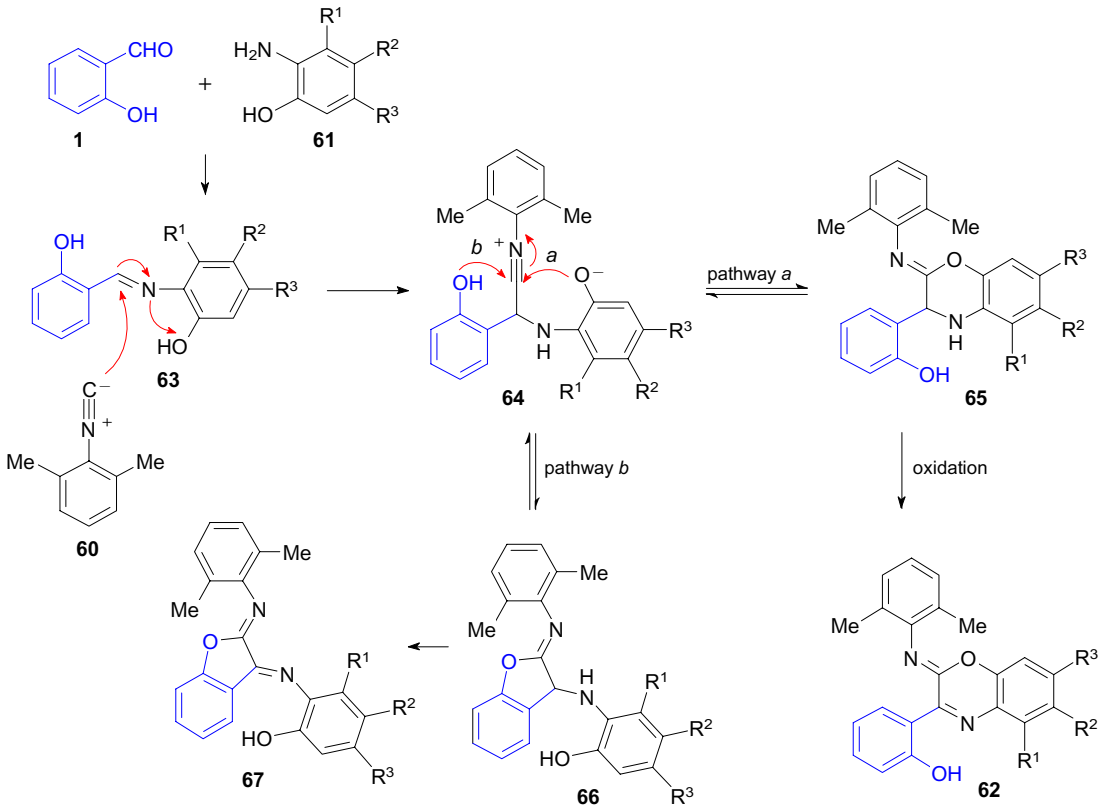
Other catalysts include tetramethylguanidine,[111] 5-hydroxypentylammonium acetate,[112] silica-bonded 2-hydroxyethylammonium acetate (HEAA),[113] sulfochitosan-incapsulated nano-Fe_3O_4,[114] nano-MgO,[115] ZnO nanorods,[116] 4-dimethylaminopyridine (DMAP) under MWI,[117] β-cyclodextrin,[118] diethylamine,[119] dibutylamine[120] and LiOH.[121] Some reactions were performed under solvent-free and catalyst-free conditions.[122] Most of these procedures propose simple experimentation, easy isolation and high yields of the reaction products, so the choice of a particular procedure is a matter of preference of a researcher.

Metal complex catalysis, both hetero- and homogeneous, has also become an indispensable tool for MCRs involving salicylaldehydes as allowing the synthesis of a variety of useful heterocycles.

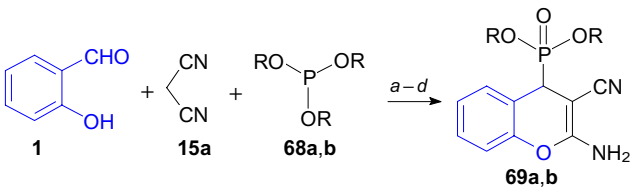
Copper(I)-catalyzed three-component reactions of salicylaldehyde, an alkyne and an amine (sometimes referred to as A^3 coupling reaction) provides a reliable approach to 2,3-disubstituted benzo[*b*]furan derivatives.

Thus, in 2008, Sakai *et al.* found that a combination of Cu^I and Cu^{II} catalysts and DMAP was very effective in catalysis of the reaction between salicylaldehydes **1**, secondary amines **24** and alkynylsilanes **70** to produce 2,3-disubstituted benzo[*b*]furans **71** in satisfactory to high yields (Scheme 24).[123] However, the scope of this reaction is rather limited. The alkyne component **70** is limited to

Scheme 22

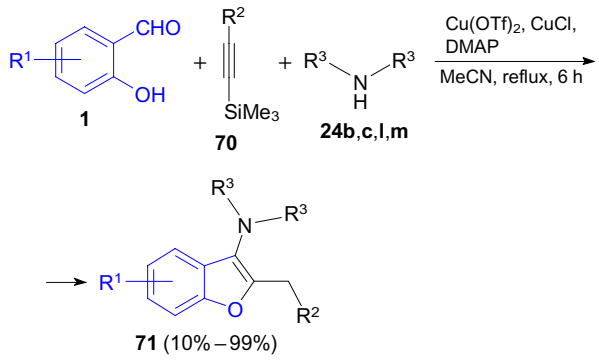


Scheme 23

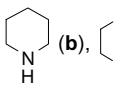
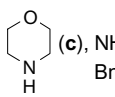


(*a*) I_2, H_2O, rt, (77%–91% yields); (*b*) $InCl_3$, EtOH, rt (70%–86%); (*c*) PEG-400, 80 °C (81%–91%); (*d*) K_3PO_4, EtOH, rt (79%–94%); **68**: R = Me (**a**), Et (**b**)

Scheme 24



R^1 = H, 3-Me, 3-NO_2, 3-Br; R^2 = H, Me, Ph, hexyl;

24: R^3_2NH =  (**b**),  (**c**), $NH(CH_2CH{=}CH_2)_2$ (**l**), Bn_2NH (**m**)

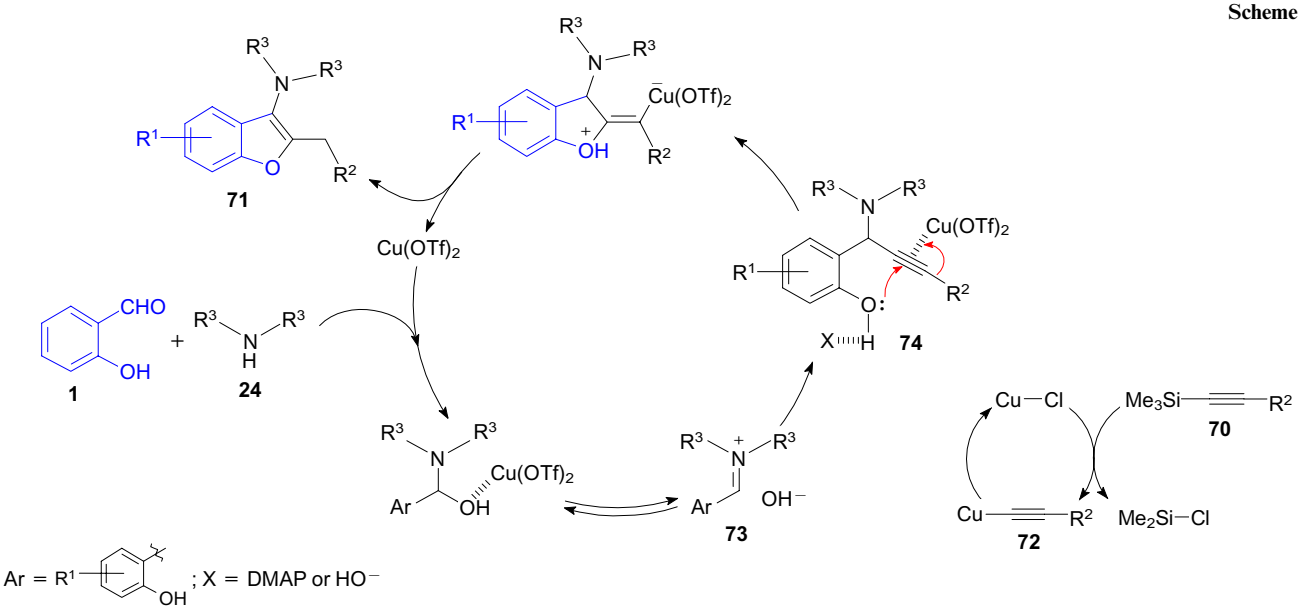
silylalkynes, where only phenyl and hexyl substituents gave high yields, whereas the introduction of the methyl group decreased the yields to as low as 22%–28%. As for an amine component, the lowest yield was observed for diallylamine **24l** (27%–30% yields). At the same time, for piperidine **24b**, morpholine **24c** or dibenzylamine **24m**, the desired benzofurans **71** were formed in moderate to high yields (50%–99%), with the lowest yield (50%) obtained for a nitro-substituted compound.

A probable mechanism for the synthesis of benzofurans **71** is illustrated in Scheme 25. The authors assumed that the reaction proceeds through an intramolecular 5-*exo*-*dig* cyclization. Copper(I) chloride forms copper acetylide **72** with an alkynylsilane **70**.[124] At the same time, copper(II) triflate plays a dual role: (a) it acts as a Lewis acid for the *in situ* generation of iminium intermediate **73** from aldehyde **1** and amine **24**; and (b) activates the alkyne moiety to assist the intramolecular nucleophilic attack by a hydroxy group *via* 5-*exo*-*dig* cyclization in **74**.

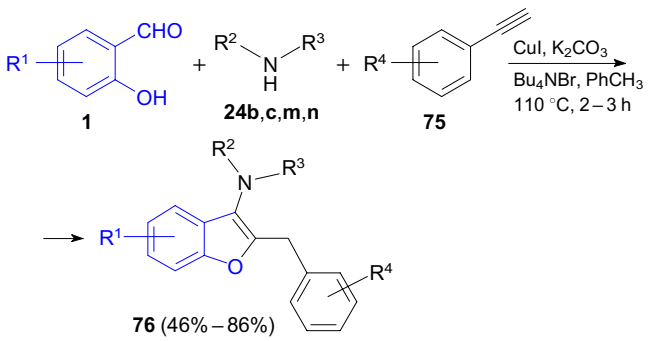
Later, Li *et al.* developed the CuI-catalyzed A^3 coupling reaction between salicylaldehydes **1**, secondary amines **24**, and arylacetylenes **75** followed by the base-assisted O-annulation reaction to obtain benzo[*b*]furan derivatives **76** (Scheme 26).[125] It was found that the final closure of the benzofuran ring requires the presence of a base, and the system K_2CO_3/Bu_4NBr turned out to be optimal. Here, the yields of products **76** were influenced mainly by the structure of amine component **24** (the presence of at least one alkyl substituent decreased the yield by 19%), and the nature of a substituent in alkyne **75** (those substituted with electron-donating groups were more reactive).

It should be noted that the majority of other metal catalysts tested in the above-mentioned reaction, *e.g.*, *N*,*N*′-ethylenebis(salicylideneiminato)copper(II),[126] Ni^{2+} exchanged Y-zeolite,[127] nano-copper(I) oxide-zinc oxide,[128]

Scheme 25

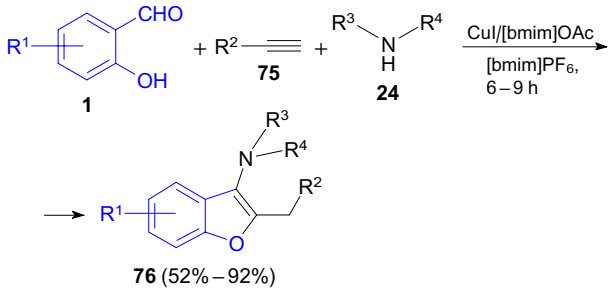


Scheme 26



R^1 = H, 3-Cl, 3-Br, 3-NO_2, C_4H_4; **24**: R^2R^3NH = **(b)**, **(c)**, Bn_2NH (**m**), Bn(Bu^n)NH (**n**); R^4 = H, 4-Cl, 4-OMe

Scheme 27



R^1 = H, Cl, Br; R^2 = Ph, n-MeC_6H_4, Pr^n;

24: R^3R^4NH = **(b)**, **(c)**, Bn_2NH (**m**), Bn(Ph)NH (**o**), Ph(Me)NH (**p**)

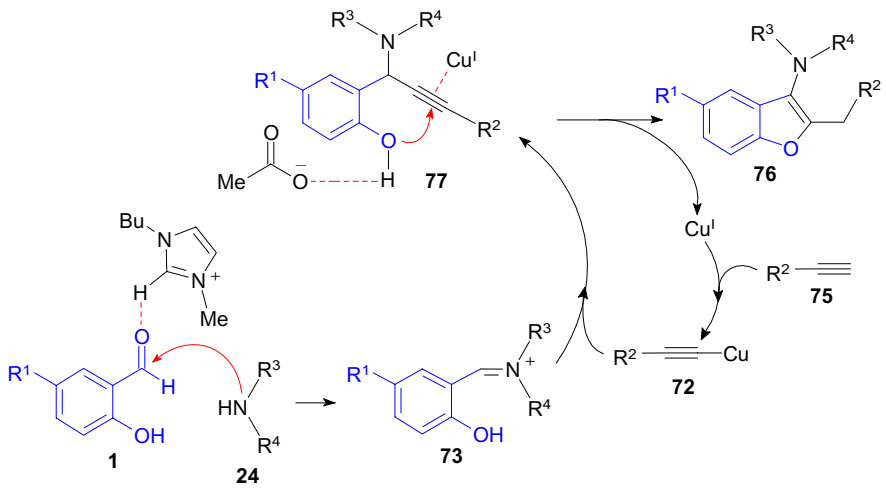
zinc(II) oxide,[129] Zn^{II} anchored onto the magnetic natural hydroxyapatite [130] and a copper(II) Schiff base complex immobilized on graphene oxide [131] produced only the corresponding intermediate propargylamine derivatives of type **74**, whereas the $AgNO_3$/DMF system was reported to catalyze the tandem 5-*exo*-*dig* cyclization and allylic rearrangement to afford 2-substituted benzofurans **71** under rather drastic conditions.[132]

In contrast to the above-mentioned procedures utilizing volatile and toxic organic solvents, a catalytic system consisting of CuI and [bmim]OAc (1-butyl-3-methylimidazolium acetate) in [bmim]PF_6 proved to be an effective and 'green' heterogeneous catalytic system for the synthesis of 2,3-disubstituted benzo[*b*]furan derivatives **76** (Scheme 27).[133] A particular advantage of this procedure is that this catalytic system is easily recoverable and can be reused at least five times without loss in its efficiency. The amine component **24** is limited to aliphatic secondary amines **24** such as piperidine **24b**, morpholine **24c** and dibenzylamine **24m**, whereas both secondary aralkyl amines (**24o**,**p**) and aromatic primary amines ($PhNH_2$) gave no desired benzo[*b*]furan products, probably due to the reduced nucleophilicity of the NH scaffold conjugated to the aromatic ring. Also, aromatic alkyne substrates **75** were found to be more reactive than aliphatic ones.

A plausible mechanism for the synthesis of 2,3-disubstituted benzo[*b*]furans **76** is similar to that for the synthesis of compounds **71** and is shown in Scheme 28. First, the condensation of salicylaldehyde **1** with amine **24** generates active iminium intermediate **73**. At the same time, CuI reacts with terminal alkyne **75** to form copper-alkynyl complex **72**, which subsequently reacts with **73** yielding propargylamine **77**. At this step, the AcO^- anion of [bmim]OAc acts as a base inducing the polarization of the O–H bond in **77** and increasing the nucleophilicity of the oxygen atom, thus facilitating the intramolecular hydroaryloxylation of the coordinated carbon–carbon triple bond with copper(I) to afford the desired 2,3-disubstituted benzo[*b*]furan **76**. According to the authors opinion, [bmim]PF_6 or [bmim]OAc plays a key role in condensation of **1** and **24** through hydrogen bonding between the hydrogen atom in the position 2 of the imidazolium cation in [bmim]PF_6 or [bmim]OAc and the oxygen atom of the aldehyde group.

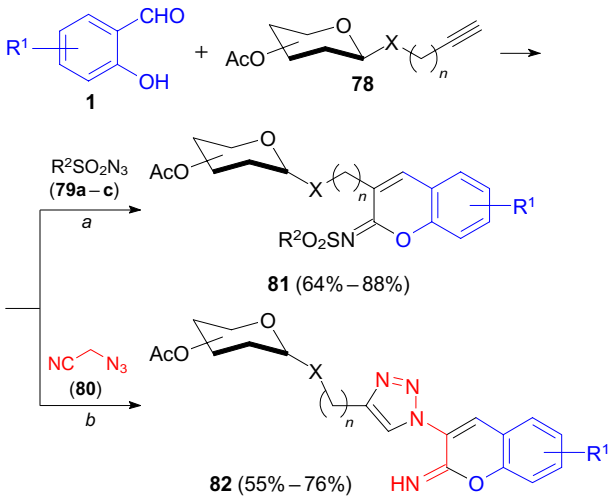
Application of Cu-catalyzed click reactions in MCRs between salicylaldehydes **1**, sugar alkynes **78** and azides **79**, **80** provides a highly useful approach to functionalized glycosylated iminocoumarins **81**, **82**.[134] Depending on the nature of an azide component, various types of iminocoumarins are formed. In the case of sulfonyl azides **79** the

Scheme 28



reaction proceeds *via* the ketenimine intermediate and affords glycosylated iminocoumarins **81**. With 2-azidoacetonitrile **80**, a tandem 'CuAAC-aldol-cyclization-dehydration' reaction sequence takes place furnishing the corresponding glycosyl 3-triazolyl-2-iminocoumarin derivatives **82** (Scheme 29). In this case, a Cu-mediated cycloaddition between 2-azidoacetonitrile **80** and sugar alkynes **78** provided a triazole derivative *in situ* and activated the adjacent methylene group, inducing an aldol-cyclization-dehydration sequence involving salicylaldehyde **1**. The most remarkable is that two rings and four bonds of different types (one C–C, one C–O and two C–N bonds) are formed in this reaction, and all four bonds are formed with 2-azidoacetonitrile **80**.

Scheme 29

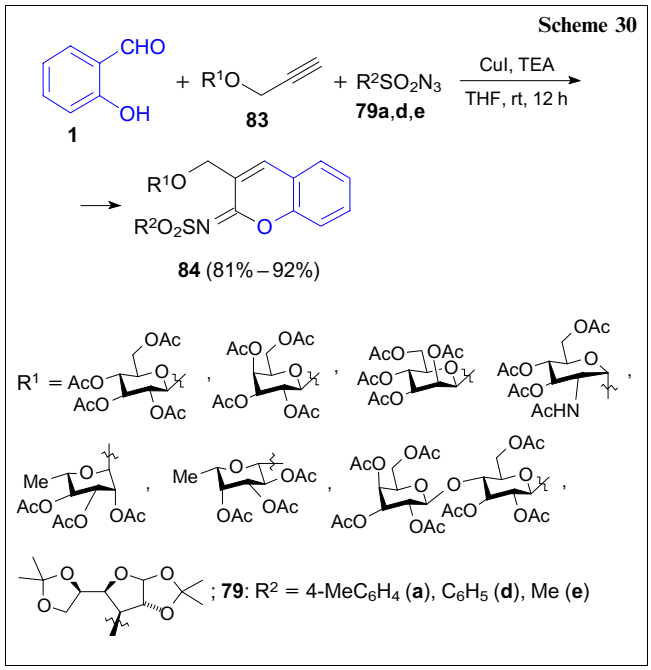


(*a*) CuI, Et_3N, THF, rt, 2–4 h; (*b*) CuI, Et_3N, THF, rt, 6–10 h; X = O, S, SO_2, *n* = 1, 2; R^1 = H, NO_2, Br, OMe, C_4H_4; **79**: R^2 = p-MeC_6H_4 (**a**), p-$MeOC_6H_4$ (**b**), Naph (**c**)

Salicylaldehydes bearing both electron-withdrawing and electron-donating substituents reacted smoothly and in high yields in both types of reactions. In the synthesis of glycosylated iminocoumarins **81**, the most reactive were propargyl glycosides (X = O, *n* = 1, reaction time 2 h), whereas for *S*-propynyl and sulfonyl glycoside derivatives it took 4 hours for the reaction to proceed.

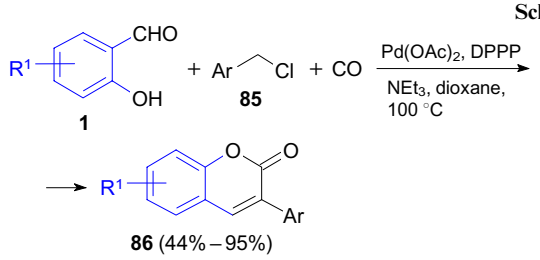
The above-mentioned reaction between salicylaldehyde **1**, sugar alkynes **83** and sulfonyl azides **79a**,**d**,**e** was independently performed by Rajput *et al.* under the same conditions.[135] However, in this case the authors used only propargyl ethers of carbohydrates **83** as an alkyne component (Scheme 30). Glycosides **83** containing 6-deoxy, 2-deoxy-2-acetamido and disaccharide moieties as well as carbohydrates linked to other positions rather than anomeric afforded high yields of iminocoumarins **84**. Also, sulfonylazides bearing different substituents showed virtually equal reactivity. Iminocoumarins **84** with deprotected acetoxy groups were subsequently tested as galectine antagonists and demonstrated high activity.

Scheme 30



In 2013, Wu *et al.*[136] developed a straightforward procedure for the Pd-catalyzed carbonylation of salicylaldehydes **1** and substituted benzyl chlorides **85** to obtain chromenone derivatives **86** (Scheme 31). The scope of the reaction is rather wide; benzyl chlorides with both electron-donating and electron-withdrawing substituents were tolerated under the reaction conditions; however, the former substituents provided higher product yields (69%–99%) compared to the latter ones (71%–76%). As for salicylal-

Scheme 31

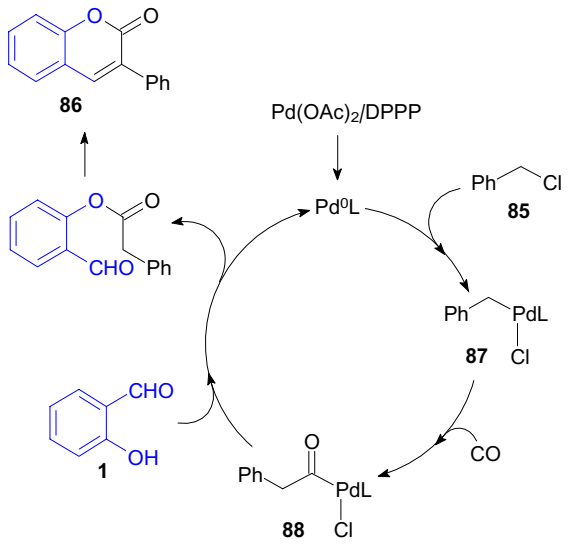


R^1 = H, 2-Me, 4-CO_2Me, 4-Bu^t, 4-Cl, 4-OMe, NO_2; Ar = C_6H_5, 3-MeC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$; DPPP is 1,3-bis(diphenylphospino)propane

dehydes **1**, substrates with different functionalities gave the desired product in moderate to high yields (44%–95%). The only one exception were nitro-substituted substrates, which proved to be unstable under reaction conditions and underwent the reduction of the nitro group to the amino one followed by self-polymerization.

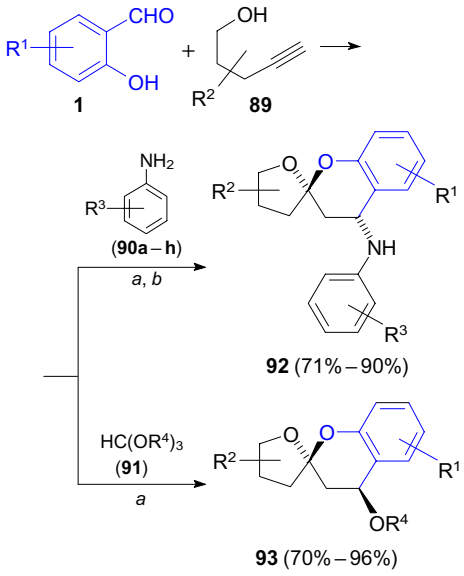
A probable reaction mechanism is depicted in Scheme 32. The catalytic cycle is initiated by palladium(0) generated from palladium(II) by the action of the phosphine ligand. Then, the oxidative addition of benzyl chloride **85** to palladium(0) occurs to afford organopalladium species **87**. After the coordination and insertion of CO, the key intermediate acyl-palladium complex **88** is formed. Nucleophilic attack of the salicylaldehyde on complex **88** results in the elimination of 2-formylphenyl 2-phenylacetate affording final product **86** after the intramolecular condensation.[137] Palladium(0) can be regenerated by treatment with a base and used directly in the next catalytic cycle.

Scheme 32



Pd^{II}-Catalyzed three-component coupling reaction between salicylaldehydes **1**, alkynols **89** and anilines **90** or orthoesters **91** represents a straightforward diastereoselective synthetic route to chromane spiroacetals **92**, **93**, respectively (Scheme 33).[138] Previously, such compounds were obtained, *e.g.*, by the hetero-Diels–Alder reactions requiring tedious experimentation.[139–141] In contrast, the proposed Pd^{II}-catalyzed MCR is a convenient one-pot procedure performed under ambient temperature from

Scheme 33



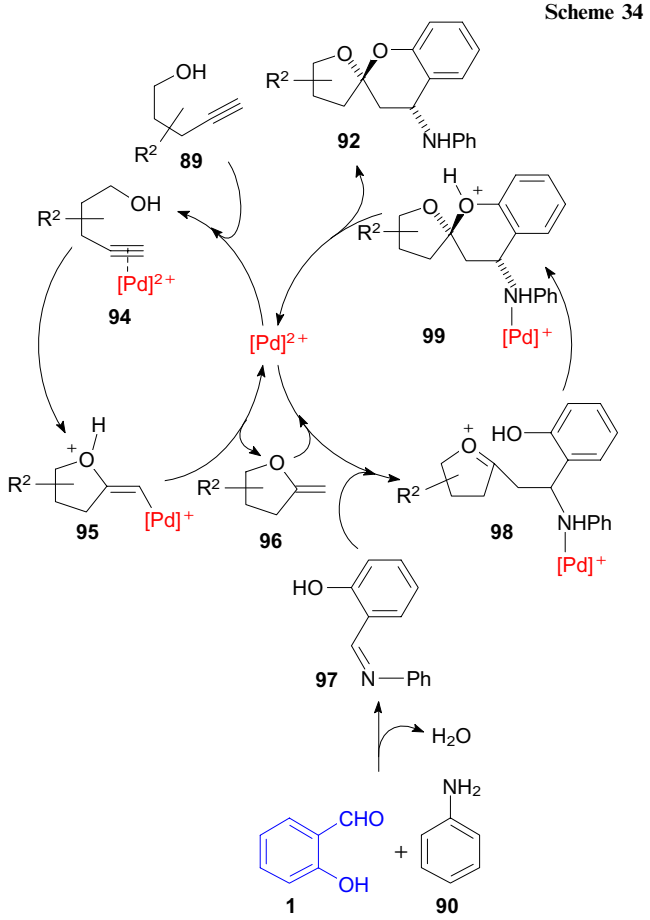
(*a*) $[Pd(MeCN)_4](BF_4)_2$, MeCN, rt; (*b*) $Mg(ClO_4)_2$, $HClO_4$; CH_2Cl_2/MeCN (10 : 0), rt; R^1 = H, 5-Br, 3,5-Me_2; R^2 = H, 3,3-Me_2, 3,3-Ph_2, 3-C_6H_{11}; **90**: R^3 = 4-Me (**a**), 4-Bu^t (**b**), 2-OMe (**c**), 4-OMe (**d**), 4-F (**e**), 4-Cl (**f**), 2-Br (**g**), 3-Br (**h**); **91**: R^4 = Me, Et

easily available starting materials. In both cases, spiroacetals **92**, **93** are produced stereospecifically and in high yields.

A plausible mechanism for the formation of spiroacetals **92** proposed by the authors is illustrated in Scheme 34. The reaction is initiated by coordination of the cationic Pd complex to the triple bond of the starting alkynol **89** to generate intermediate **94**. Then, intramolecular addition of the hydroxy group to the internal carbon atom of the triple bond affords **95**. Protodemetalation of the latter gives enol ether **96** and releases the catalytic species.[142–151] Being generated, **96** enters the second catalytic cycle where it reacts with imine **97** produced through condensation of aldehyde **1** with amine **90**. Thus, the coordination of the nitrogen atom of imine **97** by the Pd catalyst favours the addition of **96** to produce oxonium intermediate **98** *via* the Mannich-type reaction.[152, 153] Intramolecular nucleophilic addition of the hydroxy group to the oxonium ion affords **99**, which undergoes a protodemetalation reaction to yield the desired product **92**, thus terminating the second catalytic cycle.

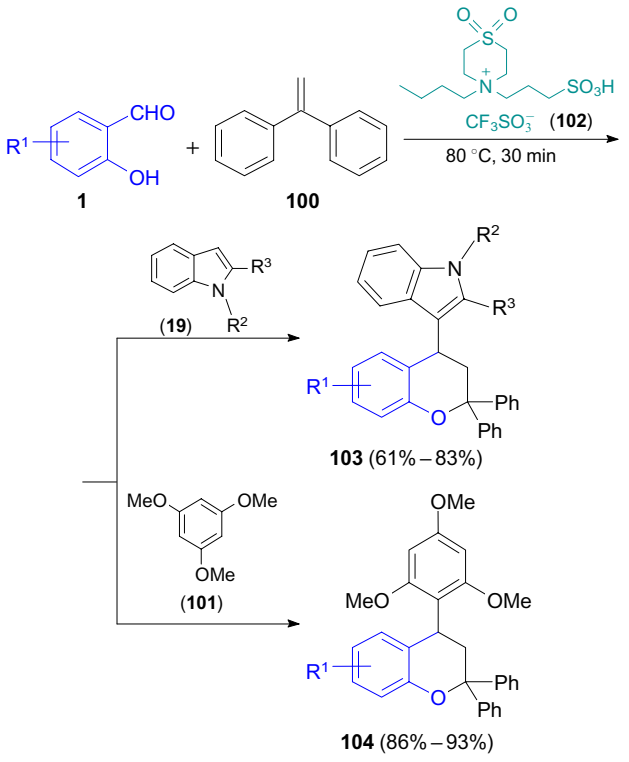
Another general approach to densely substituted chromanes was elaborated by Taheri *et al.* by using diarylethylene **100** as the starting material in MCRs involving salicylaldehyde and carbon nucleophiles.[154] Three-component reaction of salicylaldehyde **1**, 1,1-diphenylethylene **100** and indoles **19** or trimethoxybenzene **101** was accomplished in the presence of a sulfonyl-containing Brønsted acid ionic liquid **102** serving both as a catalyst and as a solvent at 80 °C to provide the desired chromanes **103**, **104** in high yields (Scheme 35). The first reaction step comprises an intermolecular hydroalkoxylation of the carbon–carbon double bond of **100**. It was shown that the scope of the olefinic component is limited to 1,1-diphenylethylene **100** only, since other styrene derivatives such as methylstyrene have insufficient nucleophilicity to enter this reaction. Substituents in indoles **19** have almost no effect on the yield of chromanes **103**. This method represents a convenient

Scheme 34



$[Pd]^{2+}$ = $[Pd(MeCN)_4]^{2+}$

Scheme 35



R^1 = H, 3-Cl, 3-Br, 5-OEt, 2Cl–5Br, 5-NO_2; R^2 = H, Me, Et; R^3 = H, Ph, Me

approach to chromanes of such type and provides usual advantages of utilizing ionic liquids, namely, a simple reaction procedure, easy isolation of the desired compounds and possibility to reuse the ionic liquid several times with the same efficiency.

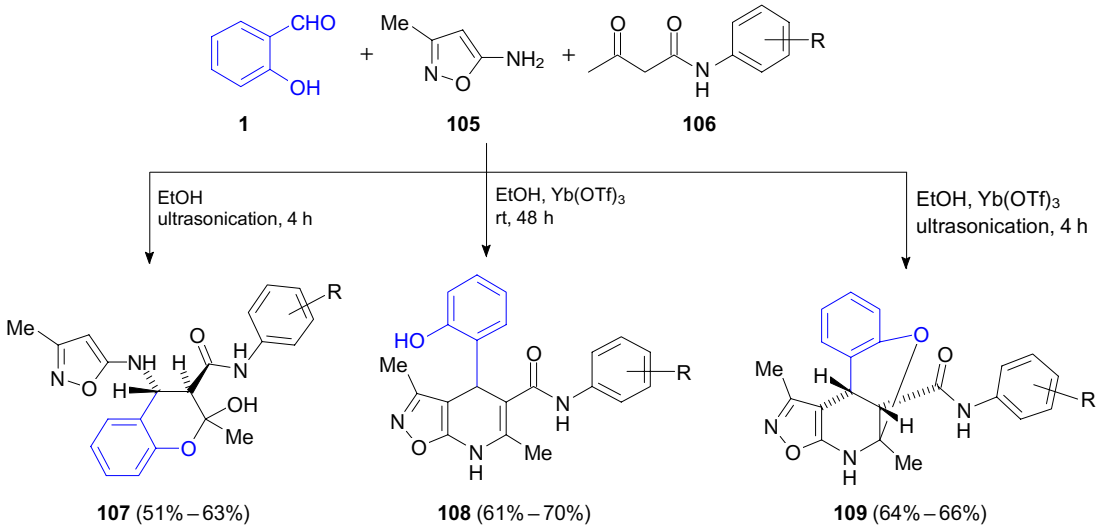
In recent times, application of ultrasonic or microwave assistance in MCRs occupies a special place.

An unusual switchable three-component reaction between salicylaldehyde **1**, 5-amino-3-methylisoxazole **105** and *N*-aryl-3-oxobutanamides **106** was reported in 2014 by Chebanov *et al.*[155] Applying either ultrasonication, or Lewis acid [$Yb(OTf)_3$] catalysis, or both, one can change the direction of the reaction and selectively obtain one of three kinds of heterocyclic scaffolds **107**–**109** depending on the group in the *N*-aryl moiety (Scheme 36).

A plausible mechanism for such transformation is shown in Scheme 37. First, it should be mentioned that the formation of any of the products **107**–**109** through intermediate **110** (pathway *a*) as for cyclic 1,3-diketones[156] was excluded as intermediate **110** did not react with amide **106** under any comparable conditions. Probably, the synthesis of chromane-3-carboxamide **107** proceeds *via* generation of imine **111** (pathway *b*) since ultrasonication of **111** and **106** at ambient temperature provided the desired compound **107** during the same reaction time. Expectedly, the Lewis acid activates the carbonyl group in salicylaldehyde **1**. As a result, this active species can interact not only with the exocyclic NH_2 group but also with the 4-CH nucleophilic centre of aminoisoxazole **105**.[157] When treated with carboxamide **106**, adduct **112** (pathway *c*) generated from intermediate **113** can lose a water molecule *via* two different routes: either by elimination at ambient temperature resulting in the formation of dihydroisoxazolo[5,4-*b*]pyridine **108** or by nucleophilic substitution involving the phenolic OH group under ultrasonication providing oxygen-bridged compound **109**. Presumably, in this case the main effect of ultrasound is the energy transfer to the reaction mixture required for the intramolecular heterocyclization, which cannot be provided by heating under conventional magnetic or even mechanical stirring. However, the possibility of the Lewis acid-mediated route cannot be completely excluded since it has been reported for the similar three-component reactions.[158, 159] This route involves an initial attack of the exocyclic NH_2 moiety of aminoisoxazole on the acid-activated β-carbonyl substituent of acetoacetamide and subsequent reaction with salicylaldehyde.

The same tendency to form oxygen-bridged structures under MWI was also observed in the three-component reaction of salicylaldehyde **1**, 5-amino-3-arylpyrazole **114** and pyruvic acid **115** (Scheme 38).[160] Refluxing the reaction mixture in acetic acid results in the formation of 3-aryl-6-(2-hydroxyphenyl)pyrazolo[3,4-*b*]pyridine-4-carboxylic acid derivatives **116**. The same result was also obtained by applying MWI at 150 °C, allowing one to gain a four-fold reduction in the reaction time due to the higher reaction temperature. Reaction of the starting materials in AcOH at ambient temperature by using ultrasonic irradiation produced oxygen-bridged 3-aryl-10,11-dihydro-4,10-methanopyrazolo[4,3-*c*][1,5]benzoxazocine-4-carboxylic acid derivatives **117**. Heterocycles **117** are rather stable and tolerated refluxing in a number of solvents (AcOH, MeOH, EtOH and BuOH). Also, treatment with NaOH in ethanol resulted in removal of the bridged moiety, oxidation, and transformation into compounds **116** in 90% yield.

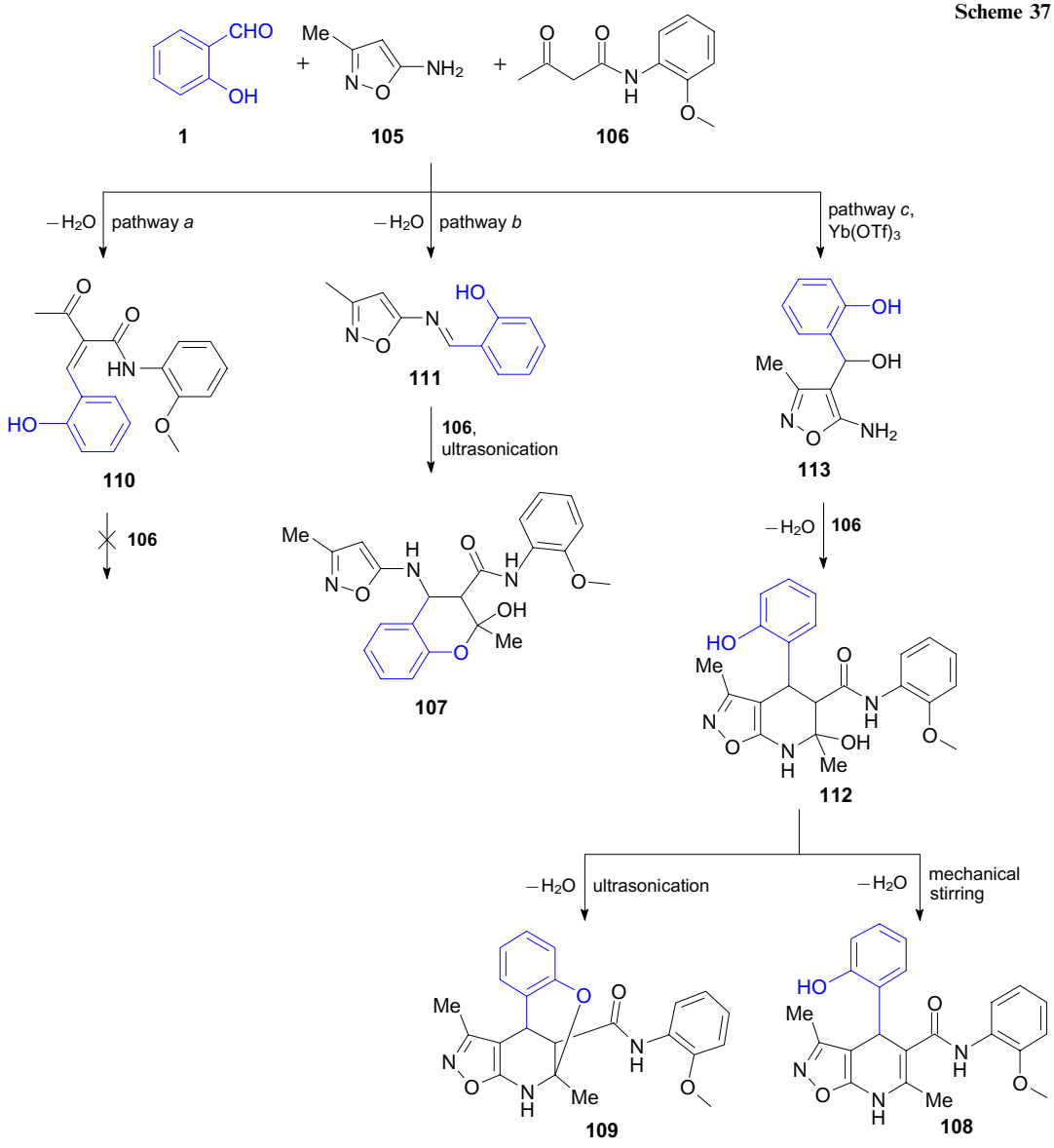
Scheme 36



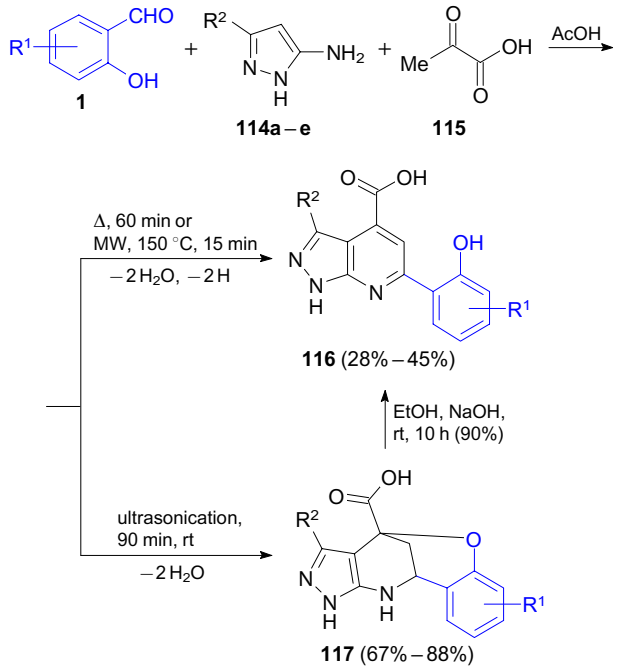
107 (51% – 63%) **108** (61% – 70%) **109** (64% – 66%)

R = H, 2-OMe, 2-OEt, 2-Cl, 2-Me, 2-OH, 3-Cl, 2,4-Me

Scheme 37



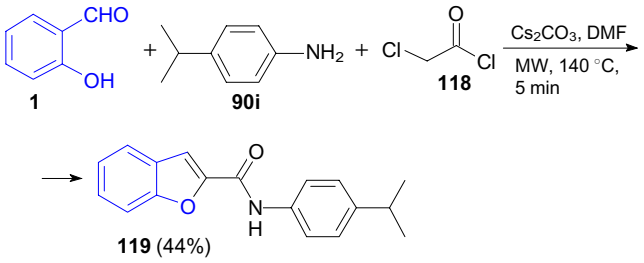
Scheme 38



R^1 = H, 3-OMe, 5-Cl, 5-NO_2, 5-OMe;
114: R^2 = C_6H_5 (**a**), 4-$MeOC_6H_4$ (**b**), 4-BrC_6H_4 (**c**), 4-ClC_6H_4 (**d**), 4-EtC_6H_4 (**e**)

MW-Promoted MCR between salicylaldehyde, *p*-isopropylaniline **90i** and α-chloroacetyl chloride **118** gives rise to benzofuran-2-carboxamide **119** (Scheme 39).[161] In place of salicylaldehyde, acetophenones can also be used. This approach allows producing highly functionalized 3-alkylbenzofurans, 3-aminobenzofurans and 3-unfunctionalized benzofurans, however in only satisfactory yields.

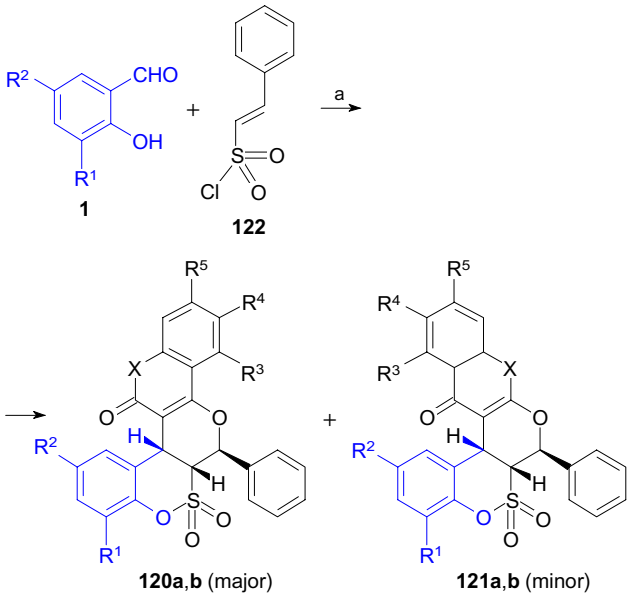
Scheme 39

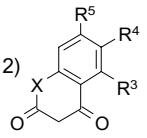


A unique *o*-sulfonylation/Knoevenagel condensation/hetero-Diels-Alder reaction cascade affording pentacyclic fused pyranochromenone **120a** and pyranoquinolinone benzosultones **120b** was found for the reaction of salicylaldehydes **1**, (*E*)-2-phenylethenesulfonyl chloride **122** and 4-hydroxycoumarins **123a** or 4-hydroxyquinolinones **123b**, respectively (Scheme 40).[162] The reactions were catalyzed by ethylenediamine-*N*,*N*′-diacetic acid (EDDA) and proceeded smoothly under prolonged reflux in water. The condensation is regioselective, and the corresponding pyranochromenes **121a** and pyranoquinolines **121b** are formed as minor products.

A large group of MCRs involving salisylaldehyde comprises reactions with 1,3-dicarbonyl compounds. These

Scheme 40



(*a*) 1) K_2CO_3, H_2O, rt, 2 h; 2)  , EDDA, reflux, 16 h;

X = O: R = H, Me, Bu^t, Cl; X = NH: R = H

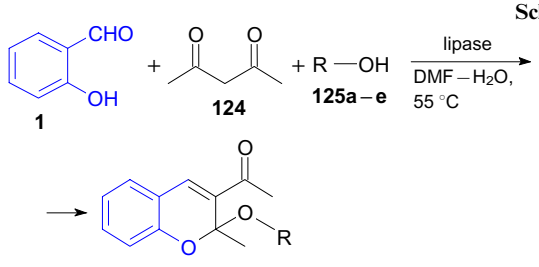
(**123a**,**b**)

EDDA is ethylenediamine-*N*,*N*′-diacetic acid; X = O (**120a**, **121a**, **123a**), NH (**120b**, **121b**, **123b**); R^1 = H, OMe; R^2 = H, NO_2, Br; R^3 = H, Me; R^4 = H, Me, Bu^t, Cl; R^5 = H, Me

reactions give rise to another very important privileged medicinal scaffold, namely, 2*H*-chromenes representing an ubiquitous structural motif in a variety of compounds displaying a wide range of biological activities.[163]

Yang *et al.* pioneered to demonstrate that lipase can catalyze MCRs between salicylaldehyde, acetoacetone **124** and alcohols **125** to afford functionalized 2*H*-chromenes **126** in satisfactory yields (Scheme 41).[164] The scope of alcoholic substrates is limited to aliphatic alcohols, where the linear ones with a longer alkyl moiety are less reactive, and branched-chain alcohols do not react at all. The proposed procedure cannot be considered to be practically valuable; however, this study extends the utility of lipase in organic synthesis.

Scheme 41

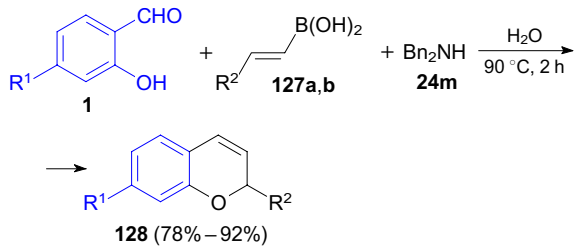


R = Me (**a**), Et (**b**), Pr^i (**c**), Bu^n (**d**), Bn (**e**)

A more convenient approach to 2*H*-chromenes **126** comprises catalysis with L-proline (rt, 6–8 h) providing higher yields of the products (52%–90%) for a wider range of alcohols.[165]

Petasis-borono-Mannich reaction represents an efficient synthetic route to 2*H*-chromenes proceeding without participation of 1,3-dicarbonyl compounds. Candeias *et al.*[166] and, independently, Petasis *et al.*[167] have shown that the reaction between salicylaldehyde **1**, amine **24** and vinylboronic acids **127** can be successfully performed using water as a reaction medium to produce substituted 2*H*-chromenes **128** in high yields (Scheme 42).

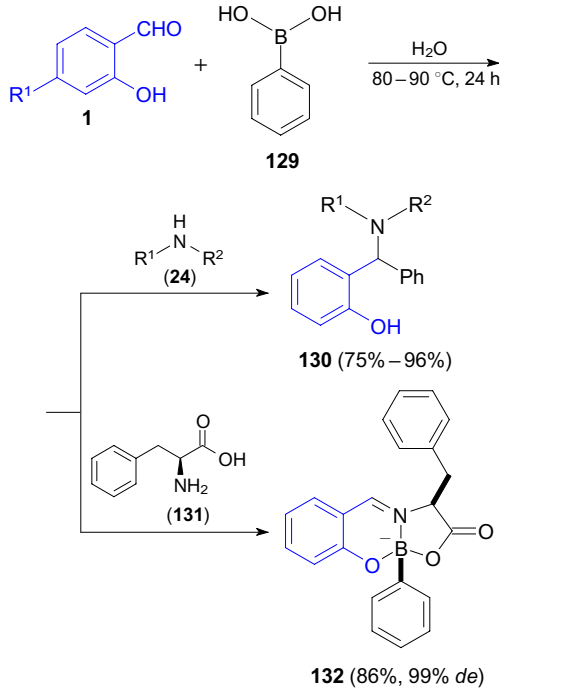
Scheme 42



R^1 = H, Me; **127**: R^2 = Ph (**a**), Bn (**b**)

Changing one of the starting materials in this reaction results in changing the reaction pathway. For example, using phenylboronic acid **129** in the above-mentioned reaction led to the formation of alkylaminophenols **130** in yields up to 96%. At the same time, with an amino acid, *e.g.* L-phenylalanine **131**, as an amino component, boron complex **132** was obtained in 85% yield with 99% *de* (Scheme 43).

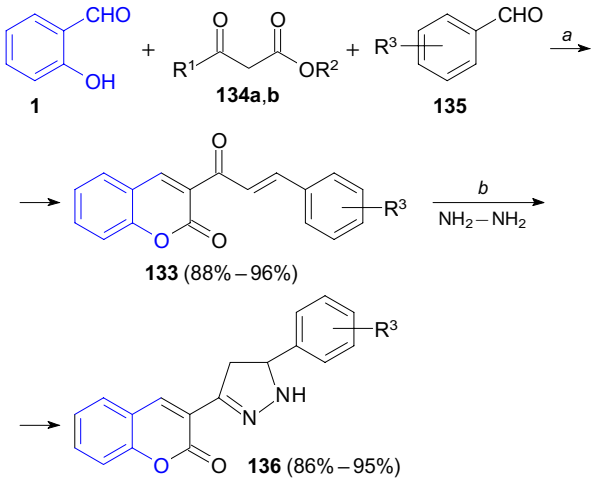
Scheme 43



In all cases the resulting products required no laborious isolation or purification since they precipitated from the reaction mixture.

A convenient approach to 3-cinnamoylcoumarins **133** represents the three-component reaction between salicylaldehyde **1**, β-keto esters **134** and aromatic aldehydes **135** catalyzed by bismuth(III) trifluoromethanesulfonate (Scheme 44).[168] Interestingly, addition of hydrazine turns this reaction into the four-component one, affording pyrazolyl-coumarins **136** in high yields under the same reaction conditions. This efficient and selective methodology characterized by using a 'green' catalyst, low costs, short reaction times and an easy work-up procedure provides a useful approach to coumarin derivatives, a structural scaffold realized in a range of naturally occurring products and pharmaceuticals.

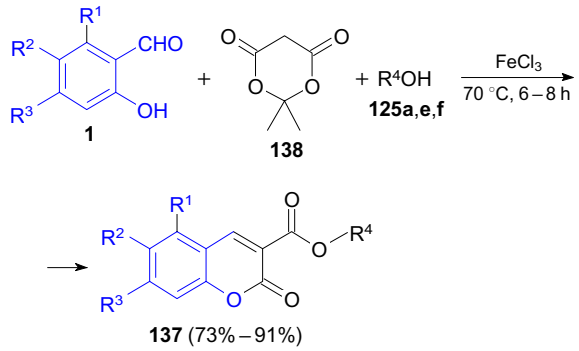
Scheme 44



(*a*) $Bi(OTf)_3$ (5 mol.%), DCM, 50 °C, 15–30 min;
(*b*) $Bi(OTf)_3$ (5 mol.%), DCM, 50 °C, 2–4 h;
R^3 = H, 4-Cl, 3-Cl, 4-F, 4-Br, 4-OH, 2-OH, 4-NO_2, 3-NO_2, *etc.*;
134: R^1 = Me; R^2 = Me (**a**), Et (**b**)

An approach to coumarin-3-carboxylic esters **137** comprises the reaction of salicylaldehydes **1**, cyclic 1,3-dicarbonyl compound, such as 2,2-dimethyl-1,3-dioxane-4,6-dione **138** (Meldrum's acid), and alcohols **125** under catalysis with ferric chloride (Scheme 45).[169] Here, alcohols **125** act both as a reagent and a solvent.

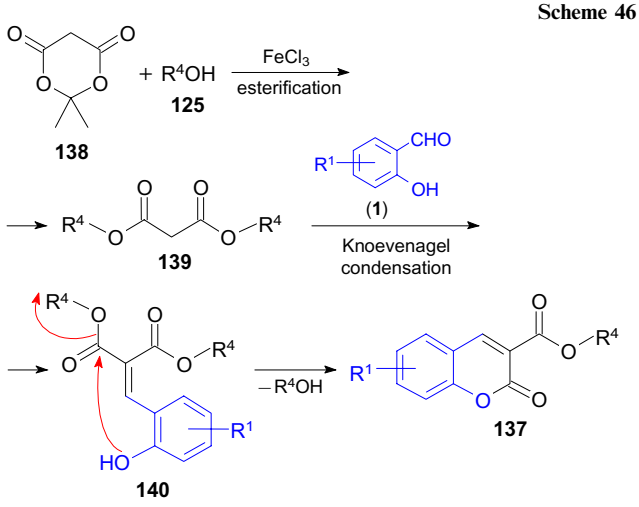
Scheme 45



R^1 = H, Bu^t, CH=CH–CH=CH; R^2 = H, Me, Bu^t, Cl, Br, NO_2; R^3 = H, OMe, NEt_2, Bu^t; **125**: R^4 = Me (**a**), Bn (**e**), CH_2–CH=CH_2 (**f**)

A probable mechanism of this process is illustrated in Scheme 46. First, $FeCl_3$-catalyzed reaction of Meldrum's acid **138** with alcohol **125** yields esterification product **139**, and then the Knoevenagel condensation of the latter with salicylaldehydes **1** provides intermediate **140**, which is easily

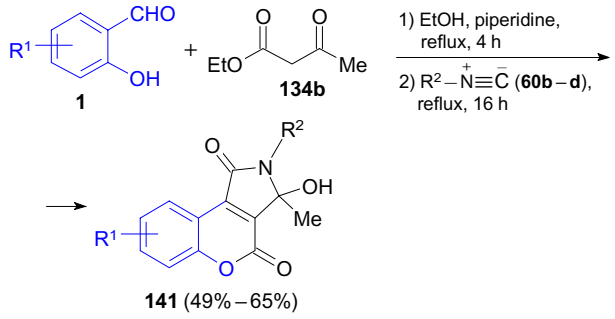
Scheme 46



transformed into the corresponding products **137** through an intramolecular transesterification.

Amines proved to be effective catalysts for the synthesis of coumarin derivatives. Among them, piperidine is one of the most commonly used. Thus, in 2013 Ghandi *et al.* performed piperidine-catalyzed condensation of salicylaldehydes **1** and ethyl acetoacetate **134b** with isocyanides **60** to obtain substituted pyrrole-fused coumarins **141** in good yields (Scheme 47).[170] The target compounds are probably formed through a reaction of *in situ* produced 3-acetyl-2*H*-chromen-2-one intermediates with isocyanides **60** *via* Michael addition/intramolecular cyclization/oxidation tandem reactions. Both strong electron-withdrawing and electron-donating substituents in salicylaldehydes **1** decrease the product yields (49% – 59%), while the modest electron-withdrawing substituents have less pronounced effect. The highest yields were achieved with unsubstituted salicylaldehyde.

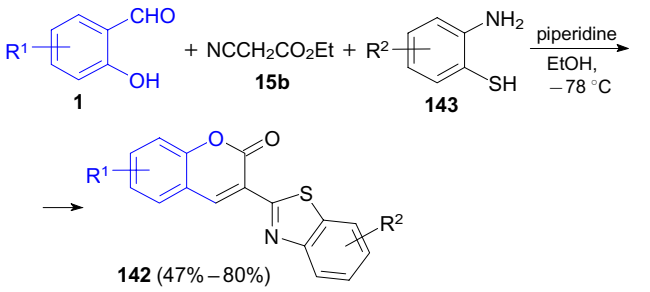
Scheme 47



R^1 = H, 5-Br, 5-NO_2, 3-OMe;
60: R^2 = C_6H_{11} (**b**), Bu^t (**c**), $C(Me)_2CH_2C(Me)_3$ (**d**)

Fluorescent 3-(2′-benzothiazolyl)coumarins **142** were obtained by a convenient piperidine-mediated reaction between salicylaldehydes **1**, ethyl cyanoacetate **15b** and *o*-aminobenzenethiols **143** (Scheme 48).[171] This reaction proceeded smoothly for salicylaldehydes containing both electron-withdrawing and electron-donating substituents; however, the product yields in the latter case were higher, and the highest yield was obtained for the methoxy substituent (80%). At the same time, the diethylamino substituent provided lower yield, probably due to a facile oxidation under reaction conditions. However, the scope of this reaction is limited to only one type of a substrate, namely, ethyl cyanoacetate **15b**, since attempts to use malonic acid, malononitrile or diethyl malonate failed. Later, it was shown that this reaction can also be performed not only under basic catalysis conditions, but also under acidic ones ($PhCO_2H$, BuOH, reflux, 8 – 24 h).[172, 173]

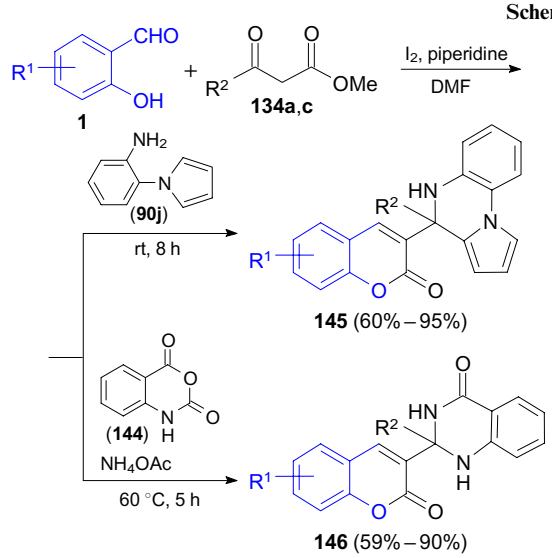
Scheme 48



R^1 = H, 4-Cl, 4-Br, 5-OMe, 5-NEt_2; R^2 = H, 5-Cl

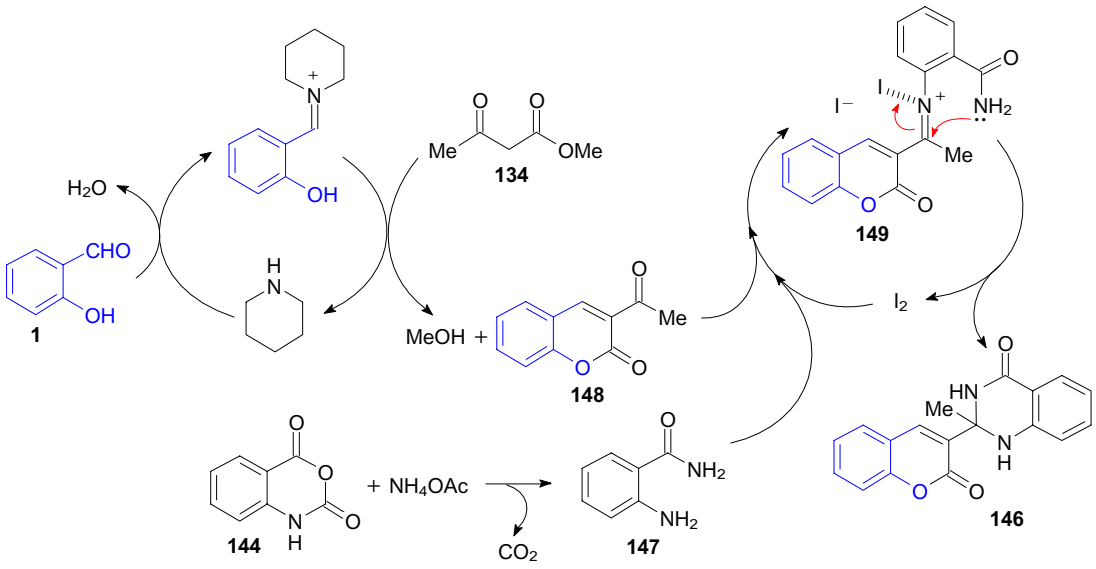
Alizadeh *et al.* demonstrated that the piperidine-iodine dual catalyst system showed excellent results in the synthesis of coumarins bearing a heterocyclic moiety. Reactions between salicylaldehyde **1**, β-keto esters **134** and 1-(2-aminophenyl)pyrrole **90j** or isatoic anhydride **144** provided pyrrolo[1,2-*a*]quinoxaline- **145** or quinazolinone-substituted coumarins **146** respectively (Scheme 49).[174, 175] In the case of coumarin **146** the reaction requires the presence of ammonium acetate and thus is considered to be the four-component process.[175] The highest yields of the heterocycles **145**, **146** were attained with salicylaldehydes **1** having electron-withdrawing substituents (NO_2, Cl), whereas the presence of electron-donating substituents (MeO) reduces the yields by on average 30%. The same tendency is observed with the elongation of the alkyl radical R^2 in

Scheme 49



R^1 = H, 5-Me, 3-OMe, 5-OMe, 5-NO_2, 3,5-Cl_2, 3,5-Br_2;
134: R^2 = Me (**a**), Pr^n (**c**)

Scheme 50



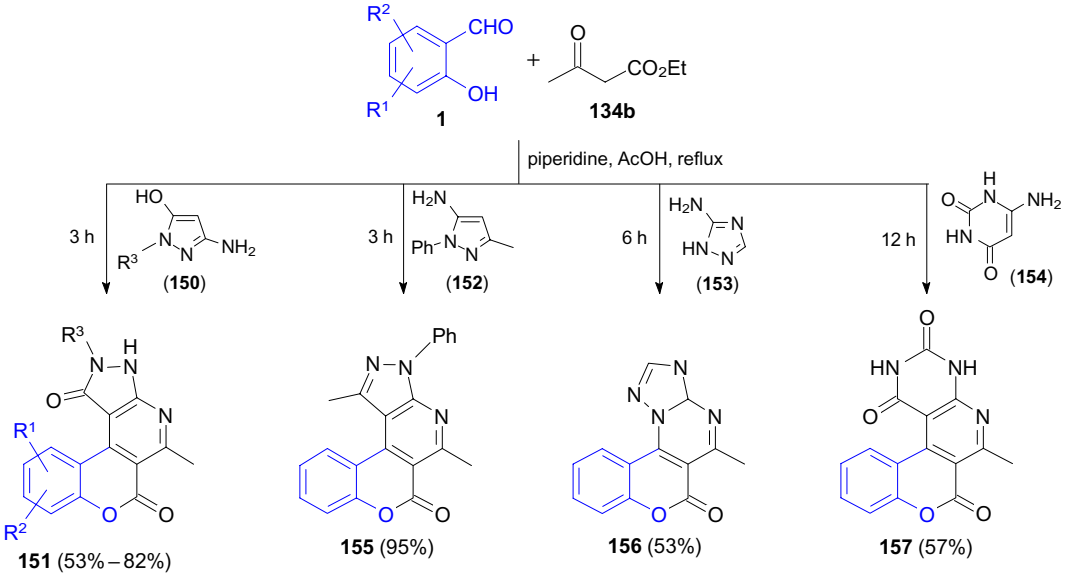
β-keto ester **134**. Undoubtful advantages of this procedure are mild reaction conditions and easy isolation of the resulting compounds.

A probable mechanism for the formation of **146** is illustrated in Scheme 50. First, isatoic anhydride **144** transforms into 2-aminobenzamide **147**. Next, the piperidine-catalyzed Knoevenagel reaction and cyclization of salicylaldehyde **1** and β-keto ester **134a** provides 3-acetylcoumarin **148**. Then, I_2-catalyzed condensation reaction of 2-aminobenzamide **147** and 3-acetylcoumarin **148** generates intermediate **149**. Subsequently, an intramolecular nucleophilic attack of the amide NH_2 on the imine group in compound **149** provides the anticipated product **146**. It appears that I_2 plays two essential roles in this reaction, a) the construction of imine **149**, potentially *via* coordination to the carbonyl group, and b) activation of the imine group to promote its reaction with nucleophiles.

MCRs of salicylaldehydes **1**, acetylacetic ester **134b** and 3-aminopyrazol-5-ones **150** under catalysis with piperidine in acidic medium gives rise to 2,3-dihydrochromeno[4,3-*d*]-pyrazolo[3,4-*b*]pyridine-1,6-diones **151** possessing antibacterial activity against certain Gram-(+) strains.[176] The authors demonstrated that this reaction proceeds stepwise through an initial condensation of salicylaldehyde **1** with acetylacetic ester **134b** to form 3-acetylcoumarins followed by condensation of the latter with pyrazolones. As for the scope of this method, it turned out that acetylacetic ester **134b** seems to provide optimal electronic and steric environment of the carbonyl group, since attempts to replace it with, *e.g.*, ethyl benzoylacetate were unsuccessful. At the same time, the range of aminoheterocyclic components is rather wide and includes also 5-amino-3-methyl-1-phenylpyrazole (**152**), 3-amino-1,2,4-triazole (**153**), and 6-aminouracil (**154**), so these MCRs can be used as a general approach to coumarin-based polyheterocycles **151**, **155** – **157** (Scheme 51).

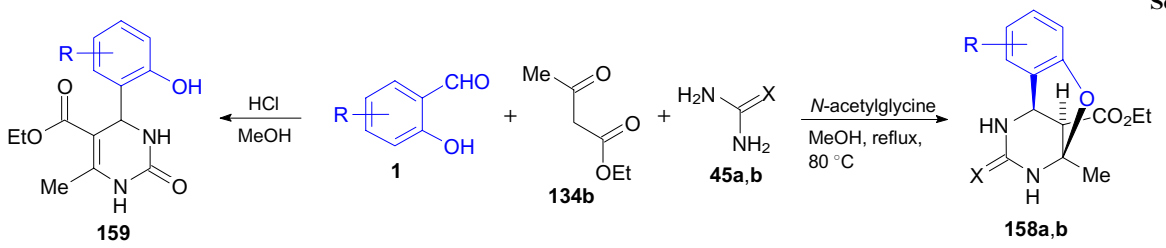
Among amine catalysts used in the MCRs involving salicylaldehyde and 1,3-dicarbonyl derivatives, amino acids occupy a special place.

Scheme 51



R^1 = H, R^2 = 5-Cl, 5-Br, 5-Me, 5-NO_2, 3-OMe, 4-OH; R^1 = 3-Cl, R^2 = 5-Cl; R^3 = H, Ph, 2,5-$Cl_2C_6H_3$

Scheme 52



R = H, 5-OMe, 4-Cl, 4-Me, 4-OMe; **45**: X = O (**a**), S (**b**); **158**: X = O, 3 h (**a**, 40% yield); S, 8 h (**b**, 58%)

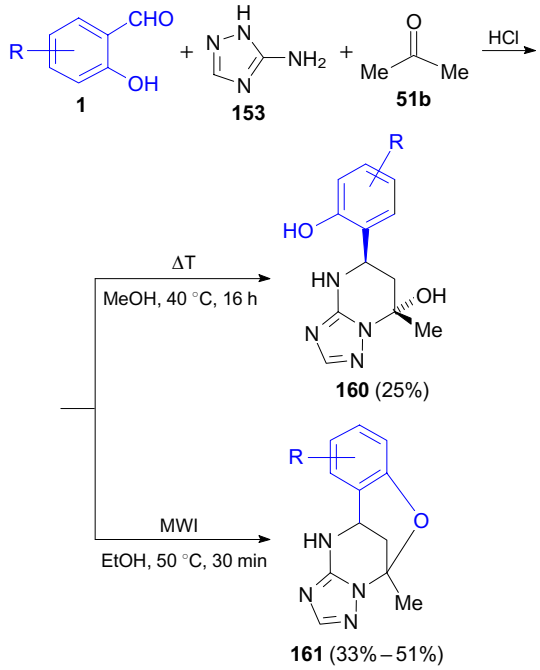
Application of *N*-acetylglycine as an inexpensive catalyst in the Biginelli reaction between salicylaldehyde, ethyl acetoacetate **134b** and urea/thiourea **45a**,**b** gave a surprising result.[177] It was found that salicylaldehyde reacts to form unexpected bicyclic oxygen-bridged pyrimidines **158a**,**b** under refluxing in methanol in the presence of *N*-acetylglycine, whereas under traditional reaction conditions (MeOH, HCl) in the absence of the catalyst the expected dihydropyrimidine **159** was obtained (Scheme 52).

One more example of an unusual course of the Biginelli-like MCRs was discovered by Gorobets *et al*. when studying the reaction between salicylaldehydes **1**, 3-amino-1,2,4-triazole **153** and acetone **51b** (Scheme 53).[178] The aldehyde component reacted with the exocyclic amino substituent rather than with the endocyclic nitrogen atom of triazole **153** resulting in the formation of tetrahydropyrimidine **160**. Depending on the reaction conditions, condensation afforded various products. Thus, under refluxing in methanol with a catalytic amount of 4 N HCl, compound **160** was produced; however, the microwave irradiation (170 °C) of the reaction mixture led to the formation of oxygen-bridged compound **161**, in both cases in moderate yields.

It should be noted that a great deal of other catalytic systems were applied to obtain dihydropyrimidine derivatives including hydrogen chloride in water,[179] α-$Zr(O_3PCH_3)_{1.2}(O_3PC_6H_4SO_3H)_{0.8}$,[180] ytterbium picrate under solvent-free conditions,[181] Wells-Dawson heteropolyacid catalyst,[182] poly(4-acetylmethyl)pyridinium chloride-supported $H_3Mo_{12}O_{40}$,[183] guanidine,[184] tin(IV) chloride pentahydrate,[185] nano-γ-$Fe_2O_3-SO_3$,[186] copper(II) choride dihydrate,[187] $[Cu(2,2'\text{-bipy})]_2[Cu(2,2'\text{-bipy})_2]_2[Pmo_8V_6O_{42}]\cdot 1.5\,H_2O$,[188] aluminium oxide-supported sulfuric acid,[189] yttria–zirconia-based Lewis acid catalyst,[190] 1-methylimidazole hydrogen sulfate,[191] chromic(III) sulfamate,[192] [DMEA][HSO_4],[193] titanium grafted polyamidoamine second generation dendritic benzene mesoporous silica,[194] indium(III) chloride,[195] $Ce(SO_4)_2-SiO_2$,[196] sodium hydrogen sulfate,[197] aminosulfonic acid,[198] [cmmim][BF_4],[199] magnesia in acetonitrile,[200] γ-AlOOH,[201] Li(glycine).(CF_3SO_3),[202] molybdenum(V) chloride in acetonitrile,[203] zeolite supported molybdophosphoric acid in acetonitrile,[204] [1-((3-sulfonic acid)propyl)pyridin-1-ium]$_3\cdot PW_{12}O_{40}$,[205] polyphosphoric acid,[206] copper-ethylenediamine tetracarboxylate modified core-shell magnetic $(Fe_3O_4-SiO_2-(CH_2)_3-NH-EDTA-Cu)$,[207] poly(ethylene glycol)/sulfonated montmorillonite nanocomposite,[208] imidazol-1-ylacetic acid,[209] organosilane sulfonated graphene oxide nanocatalyst,[210] sodium tetrafluoroborate,[211] aluminosilicate AlKIT-5,[212] copper diacetate,[213] 3-butyl-1,3-thiazolidinium-2-thione *p*-toluenesulfonate,[214] silica-supported fluoroboric acid,[215] nano-silica supported tin(II) chloride,[216] triethyl(sulfopropyl)ammonium dihydrogen phosphomolybdate,[217] borax/sulfuric acid,[218] 3-butyl-1-methyl-1*H*-imidazol-3-ium hexafluorophosphate,[219] zinc(II) perchlorate,[220] $H_2O_9S_2Si$,[221] silica-gel-supported sulfuric acid,[222] imidazolium-tagged iron,[223] silica-supported ionic liquid Si[SbSipim][PF_6],[224] brominated Amberlyst 15,[225] phosphorus pentoxide,[226] phenylacetic acid coated Fe_3O_4,[227] 4-aminobenzamido-functionalized polymer triflic acid salt,[228] hydrogen chloride,[229] copper methanesulfonate,[230] dodecatungstophosphoric acid/KSF montmorillonite,[231] triphenyl bismuth(V) bisperfluorooctanesulfonate,[232] dimethylbromosulfonium bromide,[233] $MgAlCO_3$ hydrotalcite,[234] nano-zirconia sulfuric acid,[235] zinc tetrafluoroborate,[236] large pore H-BEA zeolite,[237] boric acid tributyl ester,[238] pyridinium p-toluenesulfonate,[239] titanium tetrachloride,[240] catalyst free, in ethanol,[241] hydrogen chloride, aluminium(III) chloride in methanol,[242] 1-methylimidazolium hydrogen sulphate [Hmim]HSO_4 (Ref. 243) most of which provide the Biginelli products in high yields and with high purity.

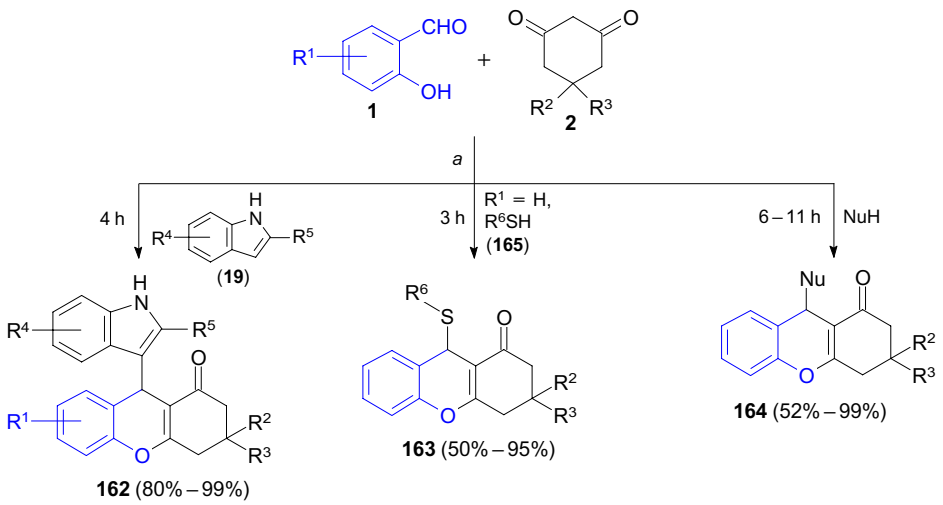
Multicomponent reactions involving salicylaldehyde, 1,3-cyclohexanediones and various nucleophiles open an access to functionalized tetrahydro-1*H*-xanthen-1-one derivatives.

Scheme 53

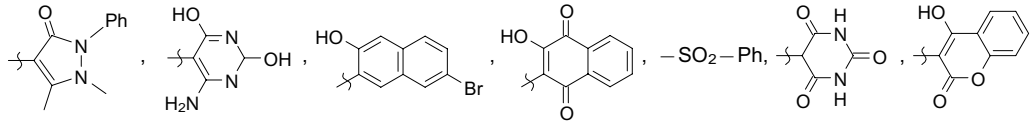


R = H, 5-OMe, 5-OEt, 4-OMe, 3-Me, 3-Cl, 3-Br

Scheme 54



(*a*) L-proline (10 mol.%), ethanol, 80 °C; R^1 = H, 5-Br, 3-OMe; R^2 = R^3 = H, Me; R^2 = H, R^3 = Me, Ph, Pr^i; R^4 = H, 6-Me, 6-F, 5-Br; R^5 = H, Ph; **165**: R^6 = Ph (**a**), Bn (**b**), 2-MeC_6H_4 (**c**), 2-MeOC_6H_4 (**d**), 3,5-$Me_2C_6H_3$ (**e**), 2,4-$Me_2C_6H_4$ (**f**), 4-ClC_6H_4 (**g**),Cy (**h**), 2-furyl (**i**)

Nu = 

In 2012, Li *et al.* reported on the MCRs between salicylaldehydes **1**, 1,3-cyclohexanediones **2** and a variety of carbon-, sulfur-, and nitrogen-based nucleophiles, which were successfully performed in the presence of L-proline to afford densely functionalized 4*H*-chromenes **162** – **164** (Scheme 54).[244] Interestingly, none of other catalysts tested in this reaction (*e.g.*, TsOH, $FeCl_3$, H_3BO_3, NaOH, K_2CO_3, DABCO, *etc.*) was effective in generating the desired heterocycles. Instead, by-products in variable ratio were formed. However, later Bhattacharjee *et al.* have independently demonstrated that such MCRs using various thiols can be successfully catalyzed by NH_4Cl in aqueous medium.[245] The nature of substituents in salicylaldehyde **1** has no significant effect on the yields of compounds **162** – **164**. At the same time, sterical hindrance in the position 5 of 1,3-cyclohexanediones **2** favours the reaction, and the corresponding 5,5-dimethyl and 5-isopropyl derivatives being the most reactive.

A probable mechanism for the synthesis of 4*H*-chromenes **163** by the example of the reaction between salicylaldehyde **1**, dimedone **2b** and thiophenol **165a** is depicted in Scheme 55. The process is induced by the formation of imine intermediate **166** by the reaction of salicylaldehyde **1** with L-proline.[246 – 248] Next, **166** undergoes nucleophilic addition of thiophenol **165** (pathway *a*) or dimedone **2b** (pathway *b*) to yield the corresponding Mannich-type intermediate **167** or **168**, respectively, which are susceptible towards nucleophilic attack of the other nucleophile, providing the desired product **163** following an intramolecular dehydration. Although pathway *a* and pathway *b* are both able to generate **163**, the authors believed that the reaction proceeds predominantly *via* the pathway *b*.

It should be noted that among MCRs of salicylaldehyde, those involving 1,3-dicarbonyl compounds and indoles always attracted a special attention, since the resulting 9-(1*H*-indol-3-yl)-xanthen-1-(9*H*)-ones have versatile biological activities.[249]

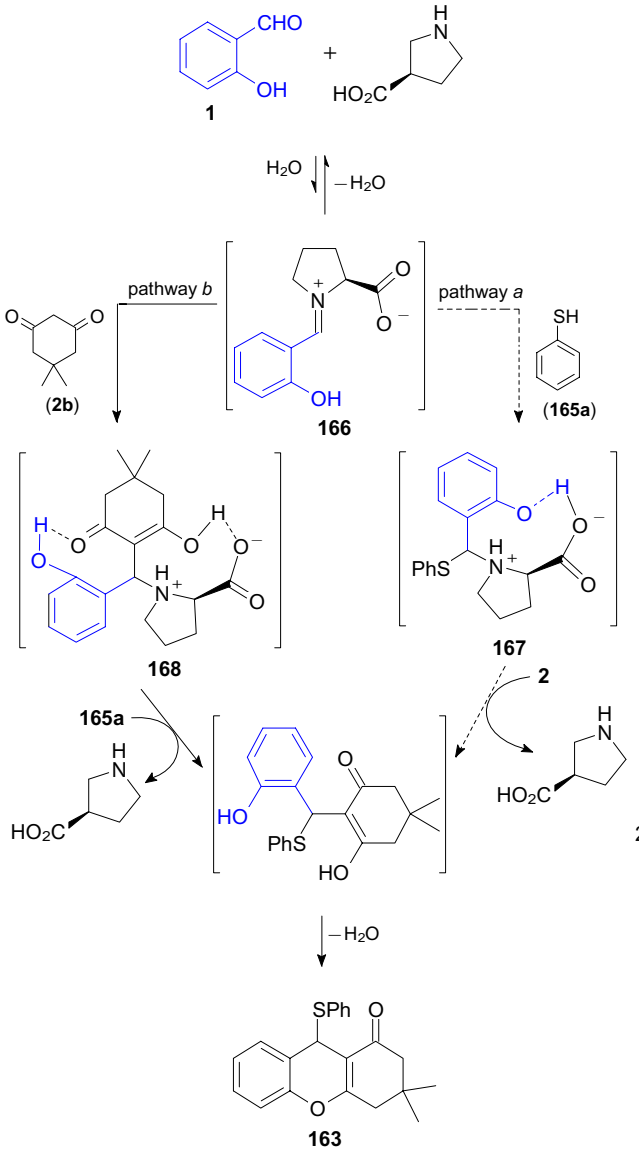
In 2015, Kasralikar *et al.* studied the reaction of salicylaldehyde with 4-hydroxycoumarin **169** using indole **19** and barbituric acid **170a** as nucleophiles, and in search for optimal reaction conditions L-proline was confirmed to be the most effective catalyst compared to various metal chlorides ($ZnCl_2$, $SnCl_2$, $InCl_3$ and $Sc(OTf)_3$). The above reaction gives rise to a series of 7-(1*H*-indol-3-yl)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one **171** and 5-(6-hydroxy-6-oxo-6*H*,7*H*-chromeno[4,3-*b*]chromen-7-yl)-6-hydroxypyrimidine-2,4(1*H*,3*H*)-dione derivatives **172** having potential anti-HIV activity (Scheme 56).[250]

A useful inexpensive catalyst for the synthesis of coumarins and chromenes was found to be an acid hydrolysate of bovine tendons (TH), which is a renewable source of amino acids such as proline and hydroxyproline. As depicted in Scheme 57, the treatment of salicylaldehydes **1**, 1,3-hexanediones **2** and various nucleophiles with TH in ethanol afforded chromene derivatives **164** in moderate to excellent yields (43% – 95%).[251] It should be noted that this reaction has also been performed by using different catalysts such as Amberlite IRA-400 Cl,[252] oleic acid[253] and ZnO nanoparticles;[254] however, the above TH-catalyzed procedure has obvious advantages such as using an inexpensive catalyst, simple isolation of the products and possibility to be scaled-up to multigram amounts.

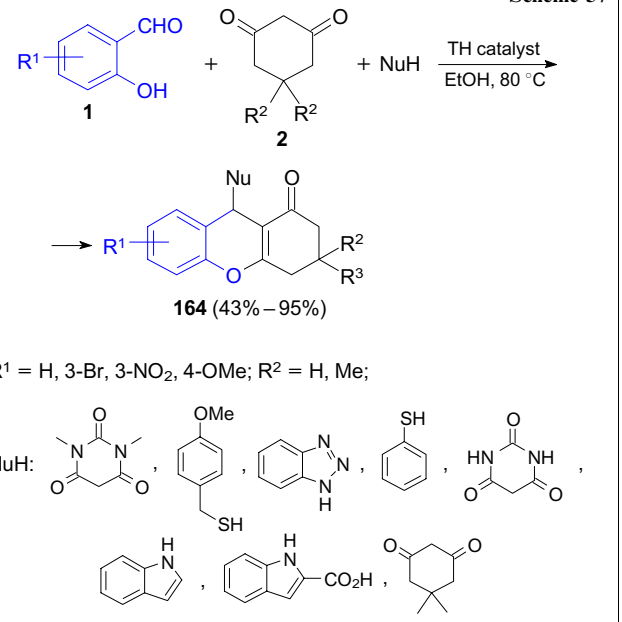
L-Cysteine-functionalized magnetic nanoparticles (LCMNP) were applied as an effective and magnetically separable organocatalyst for the reaction of salicylaldehyde **1**, dimedone **2b** and indole **19** producing 9-(1*H*-indol-3-yl)-xanthen-4-(9*H*)-ones **173** from high to excellent yields.[255] Using barbituric or thiobarbituric acids **170a**,**b** in place of dimedone **2b** gives rise to a variety of 5-(1*H*-indol-3-yl)-chromeno[2,3-*d*]pyrimidines **174** (Scheme 58).

The authors proposed the reaction mechanism for the formation of 9-(1*H*-indol-3-yl)xanthen-1-(9*H*)-ones **173**. LCMNP can probably activate salicylaldehyde **1** *via* formation of imine **175**. Both carboxylic and amino moieties of the amino acid participate in activating the aldehyde for

Scheme 55



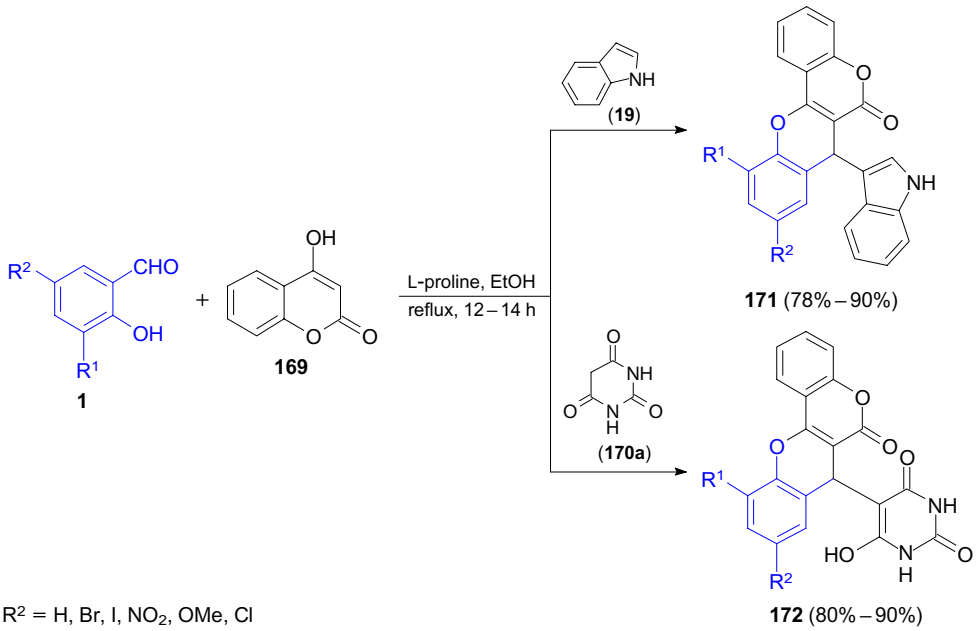
Scheme 57



addition of diketone or indole components.[256, 257] Therefore, at this step, two reaction routes were possible (*a* and *b*). According to the route *a*, which is more probable, intermediate **175** reacts with diketone **2b** to form the corresponding Knoevenagel condensation adduct **176**. Addition of indole **19** to this adduct generates intermediate **177** undergoing a cyclization to afford the desired product **173**. This reaction route has been confirmed by isolation of a Knoevenagel adduct without an indole component. The alternative reaction route b comprises the addition of indole **19** to intermediate **175** to generate intermediate **178**, which subsequently undergoes the addition of diketone **2b** to yield **177** transforming into the desired product **173** (Scheme 59).

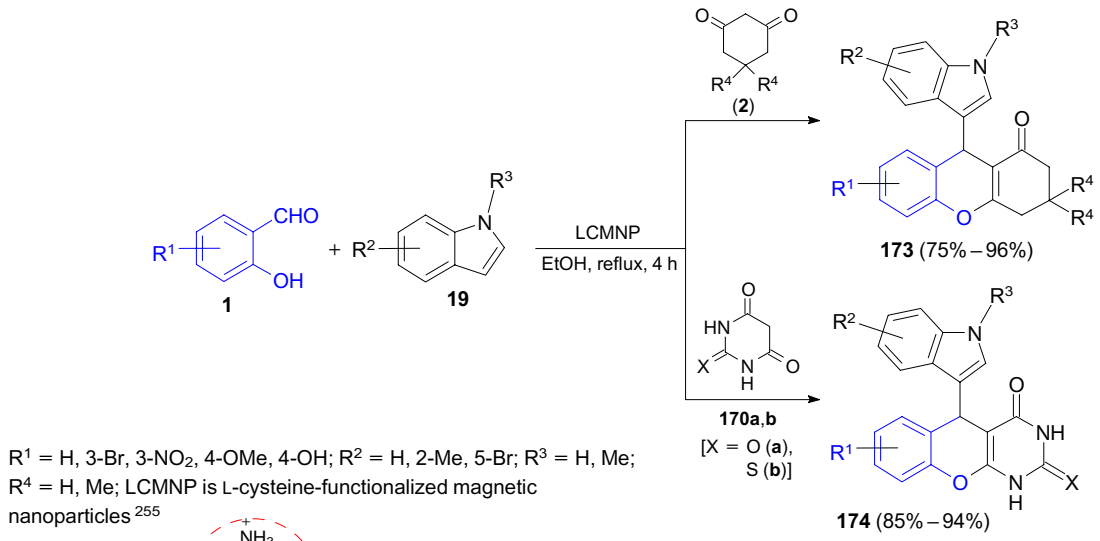
Metal-based Lewis acids are no less effective catalysts in such reactions. Three-component reactions of salicylaldehyde **1**, dimedone **2b** and various carbon-based nucleophiles

Scheme 56

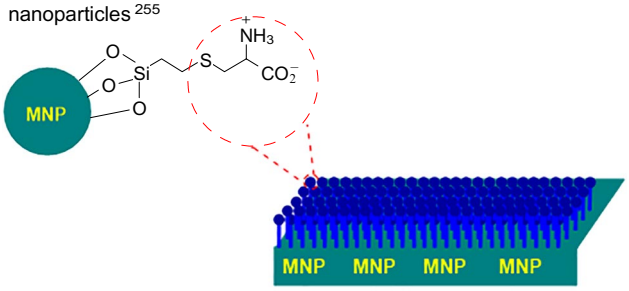


R^1 = H, Br, I; R^2 = H, Br, I, NO_2, OMe, Cl

Scheme 58

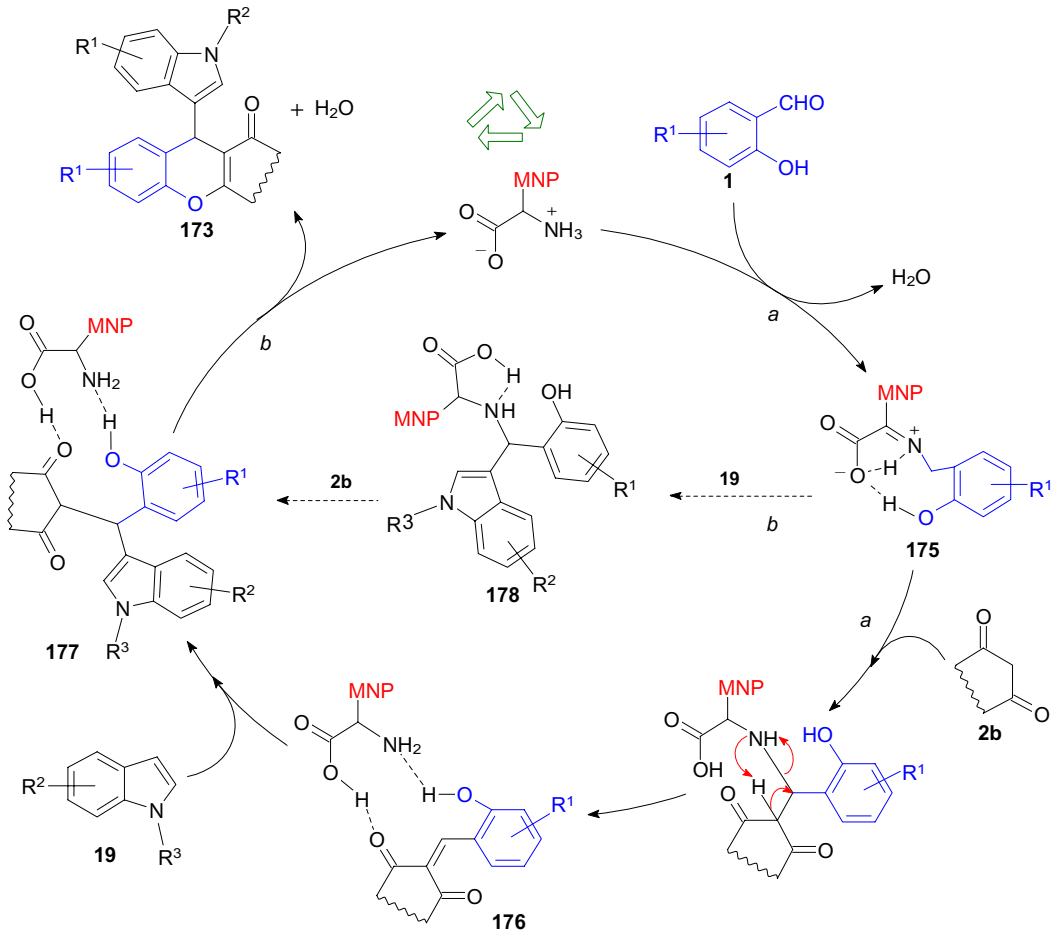


R^1 = H, 3-Br, 3-NO_2, 4-OMe, 4-OH; R^2 = H, 2-Me, 5-Br; R^3 = H, Me; R^4 = H, Me; LCMNP is L-cysteine-functionalized magnetic nanoparticles [255]

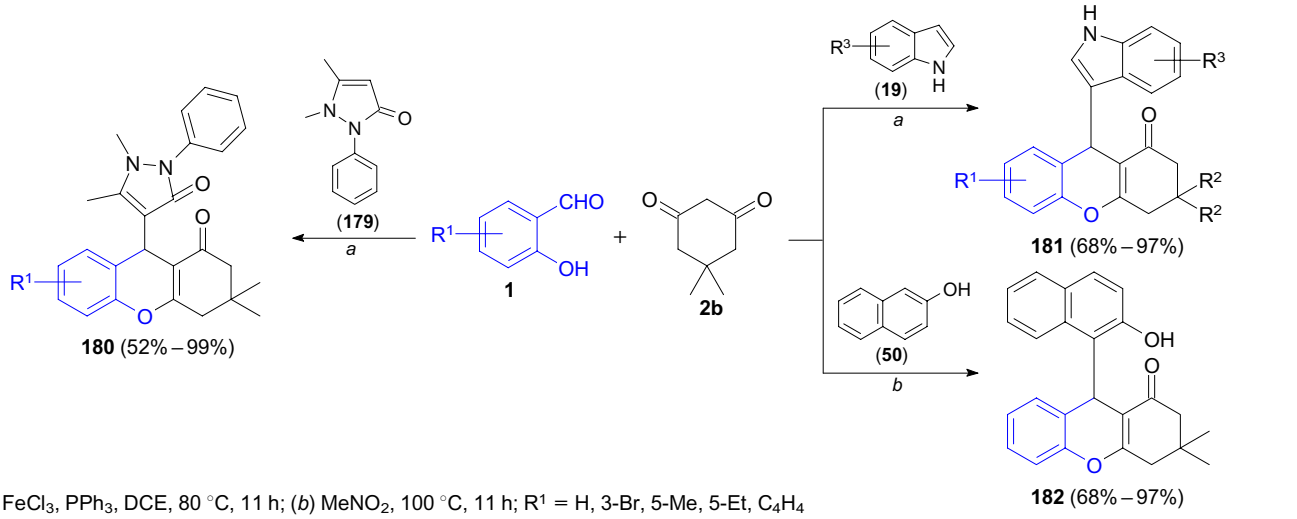


LCMNP

Scheme 59



Scheme 60

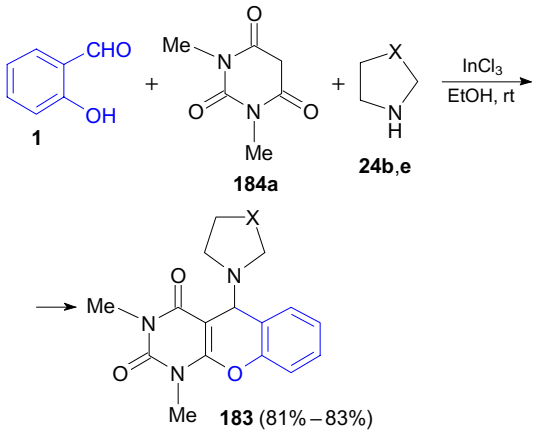


(*a*) $FeCl_3$, PPh_3, DCE, 80 °C, 11 h; (*b*) $MeNO_2$, 100 °C, 11 h; R^1 = H, 3-Br, 5-Me, 5-Et, C_4H_4

such as antipyrine **179**, as well as indoles **19** and naphthol **50**, are effectively catalyzed by an anhydrous $FeCl_3-PPh_3$ catalytic system (Scheme 60).[258] It was shown that the addition of PPh_3 significantly improved the yields of products **180**–**182**, and such effect was not observed with any other metal catalyst tested. Here, triphenylphosphine acts as the hydrogen bond acceptor weakening the intramolecular H-bond in the dimedone moiety of an intermediate product, thus facilitating the interaction of the substrate with $FeCl_3$ and subsequent transformation to the final product of the reaction. The authors have found that the key feature of the process is the reversible alkylation of dimedone with salicylaldehyde allowing one to improve the selectivity of this three-component reaction with carbon-based nucleophiles.

Barbituric acid-annulated chromenes **183** can be synthesized by a highly effective procedure comprising the $InCl_3$-catalyzed Mannich reaction between salicylaldehyde **1**, 1,3-dimethylbarbituric acid **184** and cyclic secondary amines **24** at ambient temperature (Scheme 61).[259]

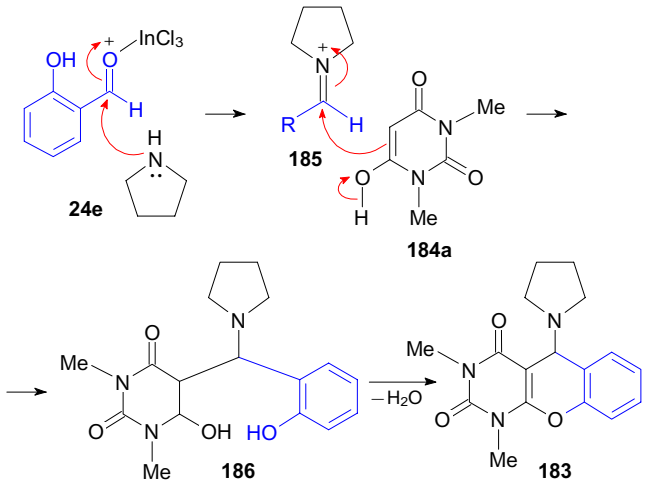
Scheme 61



24: X = $(CH_2)_2$ (**b**), CH_2O (**c**), CH_2 (**e**)

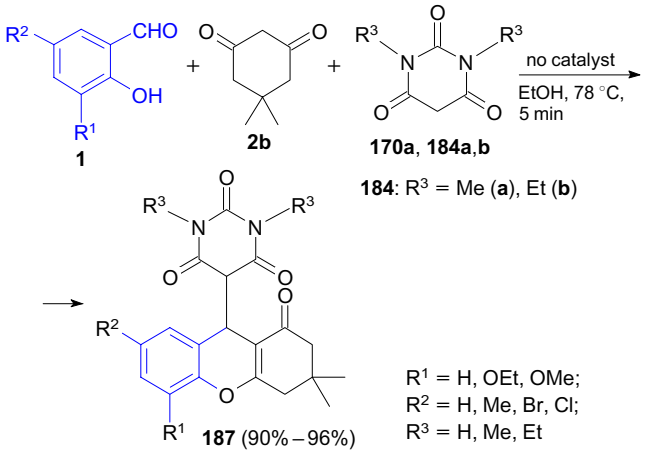
The plausible mechanism for the formation of **183** is shown in Scheme 62. Being treated with pyrrolidine **24e**, salicylaldehyde **1** generates intermediate **185** that undergoes subsequently a nucleophilic attack by **184a** forming intermediate **186**. Then, compound **186** eliminates H_2O to provide the corresponding product **183**.

Scheme 62



As was already mentioned above, the 'on-solvent' procedure proved remarkably effective in reactions of salicylaldehyde and various cyanoacetic acid derivatives.[80–84] Elinson *et al.* have demonstrated that application of this procedure to the three-component reaction involving sali-

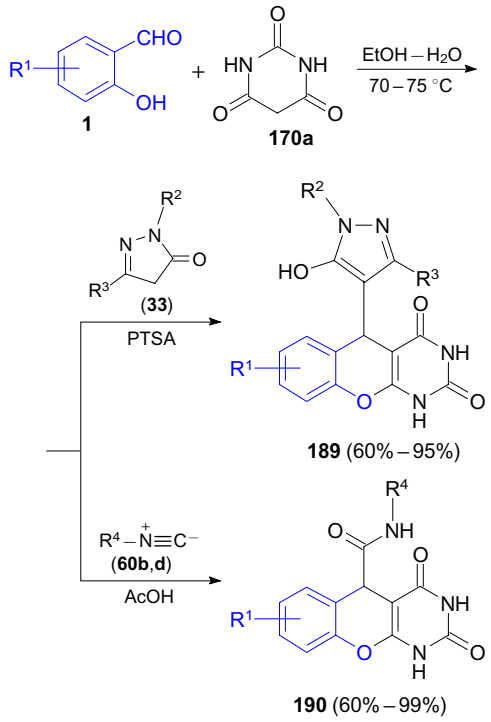
Scheme 63



cylaldehydes **1**, dimedone **2b** and barbituric acids **170a**, **184a**,**b** is no less successful.[260] Thus, functionalized tetrahydro-1*H*-xanthen-1-one derivatives **187** are formed without any catalyst under refluxing in a minimum amount of EtOH for 5 min in excellent yields (90%–95%) (Scheme 63).

Multicomponent reactions between salicylaldehyde, barbituric acid **170a** and pyrazolones **33** or isocyanides **60b**,**d** give rise to chromeno[2,3-*d*]pyrimidines **189**, **190**. Soleimani *et al.*[261,262] demonstrated that these reactions are catalyzed by organic acids such as acetic and *p*-toluenesulfonic acids in water-ethanol media (Scheme 64). In both cases the scope of the reactions is limited to only barbituric acid, and attempts to replace it with, *e.g.*, malononitrile, failed. Also, there are limitations concerning the substituents in the substrates — the presence of the 3-methoxy group in pyrazolone **33**, as well as the nitro group in salicylaldehyde **1** in the case of reaction with isocyanides **60** reduces the yields up to 60%. Apart from these exceptions, both procedures provide excellent yields of the desired heterocycles. These procedures require rather prolonged heating; however, they have such undoubtful advantages as operational simplicity and using water as a component of the reaction medium.

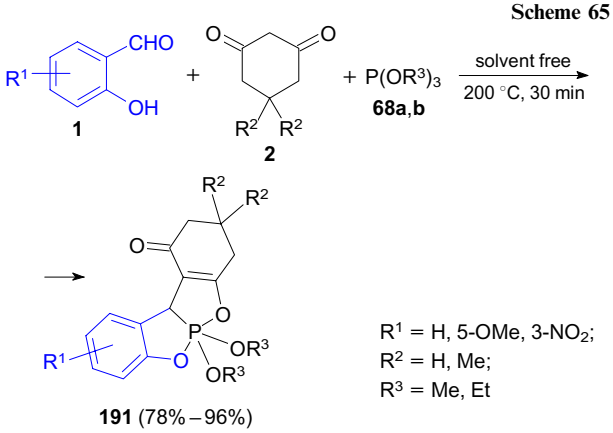
Scheme 64



R^1 = H, Ph, 4-OH, 3-OMe, 5-NO_2, 5-Me; R^2 = Me, Pr;
R^3 = H, Me, OMe, Br; **60**: R^4 = C_6H_{11} (**b**), $C(Me)_2CH_2C(Me)_3$ (**d**)

As noted above, in MCRs with salicylaldehyde and malononitrile, trialkylphosphites behave as usual nucleophiles, according to the typical reaction pattern.[107–110] At the same time, in the case of reactions involving 1,3-dicarbonyl compounds, the situation is quite different. Thus, the reaction between salicylaldehydes **1**, cyclohexane-1,3-diones **2** and trialkylphosphites **68** under solvent-free conditions and without a catalyst afforded 2,3,4,11b-tetrahydro-

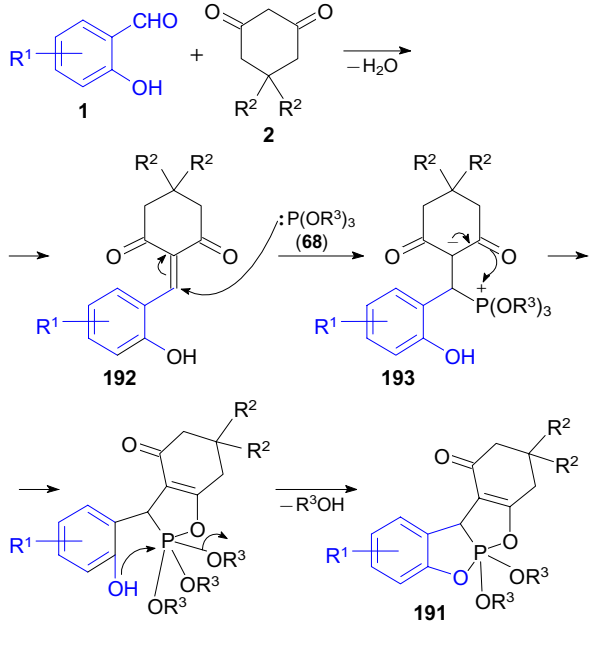
Scheme 65



1*H*,6*H*-6λ^5-[1,2]benzoxaphospholo[2,3-*b*][1,2]benzoxaphosphol-1-one derivatives **191** in high yields (Scheme 65).[263]

A probable mechanism for this reaction is demonstrated in Scheme 66. Initially, the CH-acid **2** reacts with salicylaldehyde **1** to provide α,β-unsaturated intermediate **192**. Then, nucleophilic attack of trialkylphosphite **68** on **192** generates zwitterion **193** wherein the phosphorus atom undergoes an intramolecular attack by the adjacent enolate and phenolic oxygen atoms to give the desired 1*H*,6*H*-6λ^5-[1,2]benzoxaphospholo[2,3-*b*][1,2]benzoxaphosphol-1-one derivatives **191** *via* elimination of an alcohol molecule.

Scheme 66

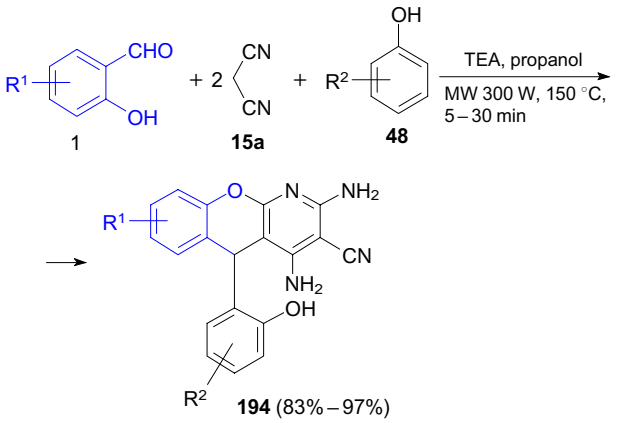


2.3. Four-component reactions

Four-component reactions of salicylaldehyde form a far less numerous pool of reactions. However, each of them provides a unique, chemo- and regioselective approach to chromene and coumarin scaffolds.

In 2016, Chung *et al.*[264] performed a *pseudo*-four component reaction of substituted salicylaldehydes **1**, functionalized phenols **48** and malononitrile **15a** in the presence of

Scheme 67



R^1 = H, OMe, C_6H_4; R^2 = NH_2, $N(Me)_2$, $N(Et)_2$, C_6H_4

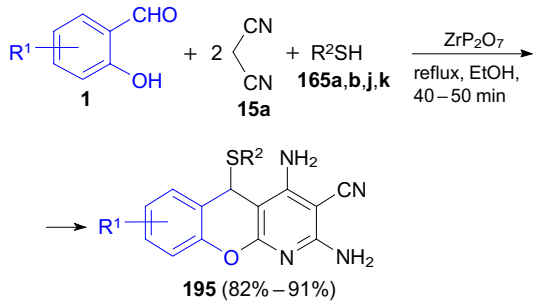
trimethylamine as a catalyst under MWI to provide a series of chromeno[2,3-*b*]pyridine derivatives **194** (Scheme 67).

An alternative procedure to obtain such type of compounds comprises a non-catalyzed variant under solvent-free conditions at 110 °C.[265] In both cases reactions are completed at most in 30 min.

Heterogeneous catalytic systems show high efficiency in four-component reactions to produce substituted chromene derivatives.

Thus, *pseudo*-four component cyclocondensation between salicylaldehydes **1**, malononitrile **15a** and aromatic thiols **165** catalyzed by ZrP_2O_7 nanoparticles under reflux in EtOH afforded benzopyrano[2,3-*b*]pyridine derivatives **195** (Scheme 68).[266]

Scheme 68



R^1 = H, Br; R^2 = C_6H_5 (**a**), Bn (**b**), 4-MeC_6H_4 (**j**), 2-furylmethyl (**k**)

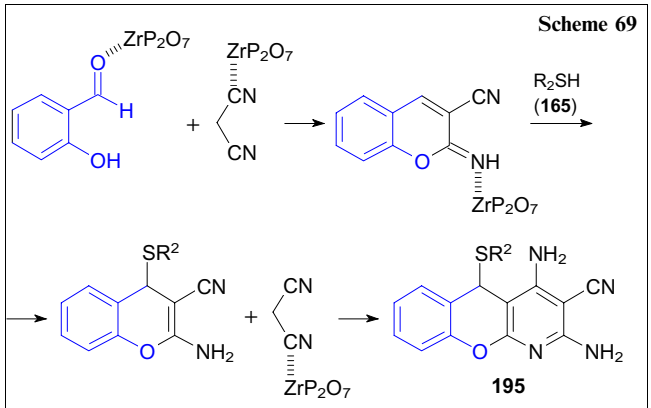
A probable mechanism for this reaction is presented in Scheme 69.

It should be noted that, to obtain similar benzopyrano[2,3-*b*]pyridines, different reaction conditions were also reported comprising the catalysis with piperidine,[267] triethylamine,[268] chitosan under solvent-free conditions [269] or SnO nanoparticles.[270] Here, the first two of the above-mentioned methods provided lower yields compared to the procedure using ZrP_2O_7 nanoparticles, and in the last one the procedure to prepare the heterogeneous catalyst is too laborious, while the method of applying the chitosan catalyst is very promising both in terms of high yields and simple experimentation.

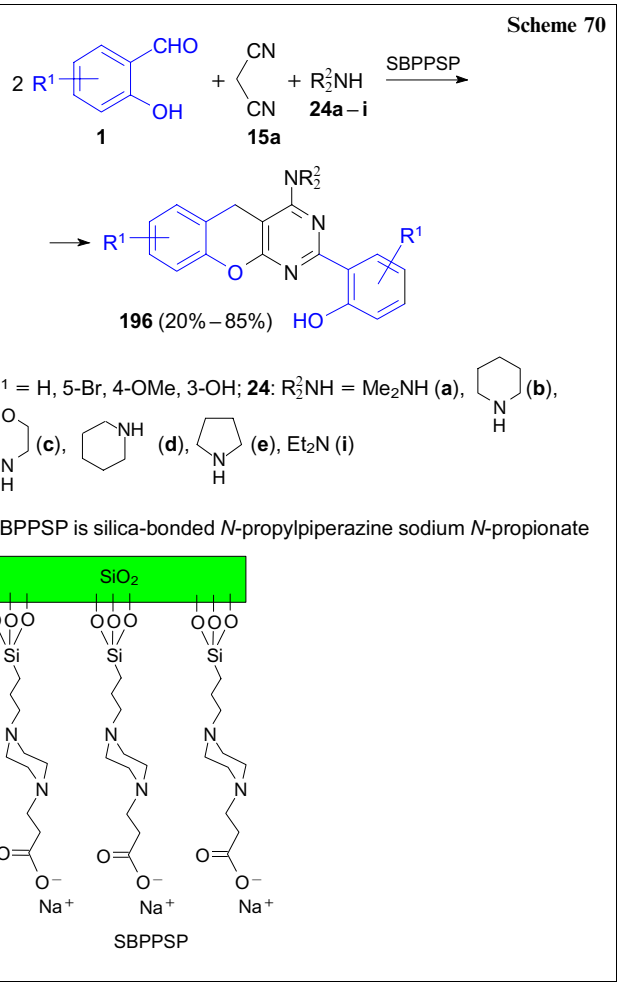
Silica-bonded *N*-propylpiperazine sodium *N*-propionate (SBPPSP) was applied as a reusable heterogeneous solid base catalyst for the synthesis of benzopyrano[2,3-*d*]pyrimidines **196**.[271] Salicylaldehydes **1**, malononitrile **15a** and secondary amines **24** were reacted at ambient temperature under solvent-free conditions (Scheme 70). Salicylaldehydes bearing both electron-donating and electron-withdrawing groups are well tolerated in this reaction. As for an amine component, the best results have been achieved by using cyclic secondary amines like piperidine (**24b**), morpholine (**24c**), and pyrrolidine (**24e**), whereas aliphatic amines such as, *e.g.*, diethylamine **24i**, did not react.

A unique approach to construct a coumarin scaffold was proposed by Nandaluru *et al.* based on the inverse electron demand Diels-Alder reaction.[272] The overall conversion of salicylaldehyde, dimethyl glutaconate **197**, carbonyl compounds **51**, **52** and pyrrolidine affording 6*H*-dibenzo[*b*,*d*]-pyran-6-one derivatives **198**, **199** comprised six reactions

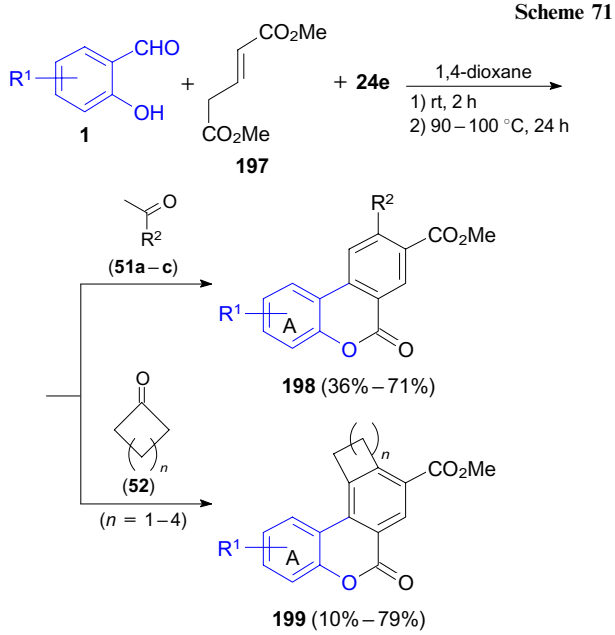
Scheme 69



Scheme 70

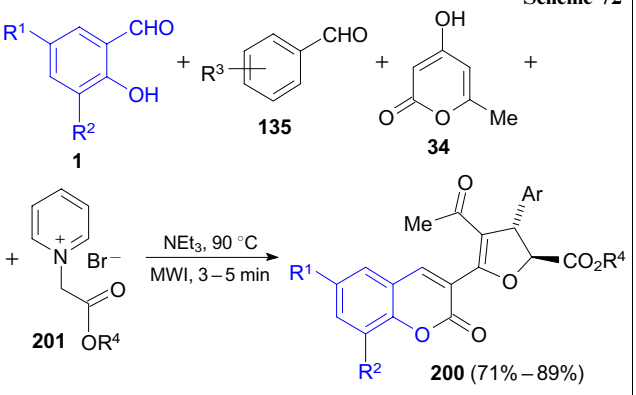


Scheme 71



R^1 = 3-OMe, 4-OMe, 5-OMe, 6-OMe, 3-Me, 4-Me, 5-Br, 5-CO_2Me, 5-NO_2; **51**: R^2 = Ph (**a**), Me (**b**), cyclo-Pr (**c**)

Scheme 72

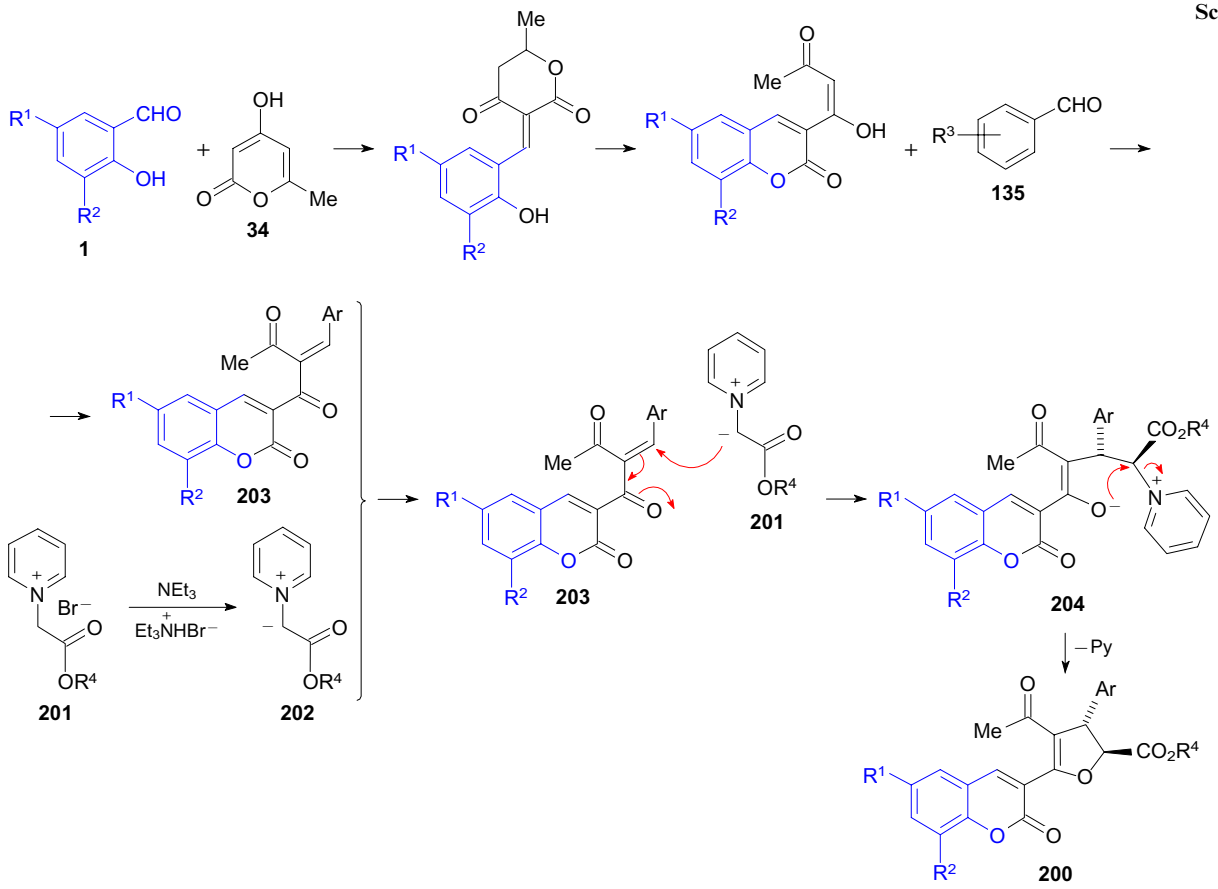


R^1 = H, Cl, Br, NO_2; R^2 = H, OMe, Cl, Br; R^3 = H, 4-NMe_2, 4-NO_2; R^4 = Et, Pr

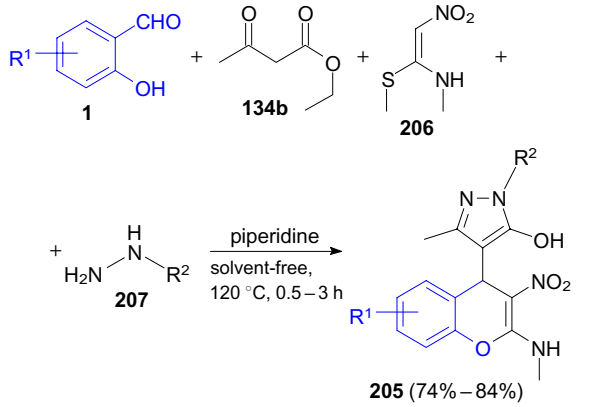
including Knoevenagel condensation, transesterification, enamine formation, an inverse electron demand Diels-Alder reaction, 1,2-elimination and transfer hydrogenation (Scheme 71). Both dienophiles and dienes for the main inverse electron demand Diels-Alder step were produced *in situ* by a secondary amine-catalyzed strategy. The highest yields were achieved for 5-methoxy- and 5-methyl-substituted salicylaldehyde, other substitution patterns gave similar results, whereas 6-methoxy-substituted salicylaldehyde did not enter the reaction at all. Generally, this MCR procedure allows the synthesis of a series of previously reported A-ring functionalized 6*H*-dibenzo[*b*,*d*]pyran-6-ones in superior yields (by up to 44%) compared to those obtained *via* a stepwise protocol.[273, 274]

An effective diastereoselective approach to C3-dihydrofuran-functionalized coumarins **200** *via* the four-component reaction between salicylaldehydes **1**, substituted benzaldehydes **135**, 6-methyl-4-hydroxy-2-pyranone **34** and pyridinium bromide **201** was developed by Sun *et al.*[275] The Et_3N-catalyzed reaction proceeded smoothly under solvent-free conditions under MWI to provide coumarins **200** in 71% – 89% yields (Scheme 72). Electronic effects both in

Scheme 73



Scheme 74



R^1 = H, 5-Br, 5-Cl, 3,5-Br, 5-NO_2, 4-OMe, 3-OEt; R^2 = H, C_6H_5

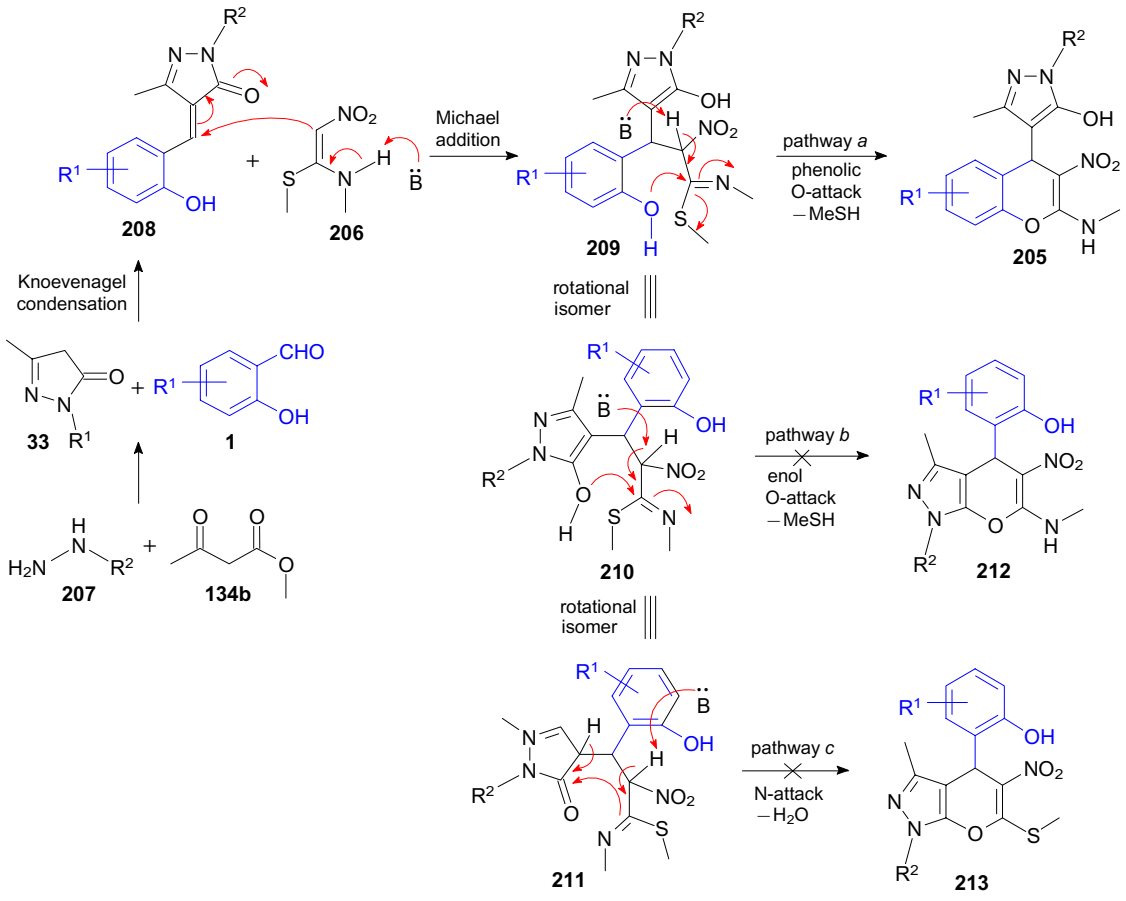
salicylaldehydes and in the benzaldehyde components influence the product yields. Thus, the presence of electron-donating substituents in the positions 2 and 5 of salicylaldehydes **1** as well as in the *para*-position of benzaldehydes **135** renders these compounds more reactive and provides higher yields of coumarins **200** compared to those substituted with electron-withdrawing substituents.

A plausible mechanism for the synthesis of the corresponding product **200** is illustrated in Scheme 73. The first reaction step comprises the Knoevenagel condensation. At the same time, pyridinium ylide **202** generated by the reaction of pyridinium bromide **201** with Et_3N undergoes the Michael addition with intermediate **203** to give enolate **204**. The latter eliminates pyridine and cyclizes simultaneously to afford dihydrofuran-functionalized coumarins **200**. In total, one carbon–oxygen and two carbon–carbon bonds in dihydrofuran ring are generated in this MW-assisted four-component domino reaction.

An elegant synthetic approach to a combinatorial library of biologically significant pyranopyrazoles and chromenopyrazoles **205** was developed based on application of nitroketene *N*,*S*-acetal **206**, a unique versatile synthon bearing three functionalities on an ethene motif, in reaction between ethyl acetoacetate **134b**, hydrazine hydrates **207** and salicylaldehyde **1** (Scheme 74).[276] This domino reaction sequence provides the formation of C–C, C–O, C–N, C=C, C=N bonds and one stereocentre in a single operation through condensation/Knoevenagel/Michael/annulation reactions. The particular advantage of this procedure is that the target heterocycles are isolated by simple filtration.

A probable mechanism for the formation of chromenopyrazoles **205** is shown in Scheme 75. The initial step is condensation of ethyl acetoacetate **134b** with hydrazine hydrate affording pyrazolone **33**, which undergoes the Knoevenagel condensation with salicylaldehyde **1** to give Michael acceptor **208**. Adduct **208** immediately reacts with nitroketene *N*,*S*-acetal **206** *via* Michael-type addition reaction forming open-chain intermediate **209**. The latter undergoes intramolecular phenolic O-cyclization through pathway *a* to afford compound **205** with elimination of MeSH. Intermediate **209** can exist in two rotameric forms **210** and **211**, that could possibly undergo enolic N- or O-cyclizations *via* pathways *b* or *c* to produce compounds **212** and **213**, respectively. It should be noted that no traces of **212** or **213** were detected, and only compound **205** was

Scheme 75



formed exclusively suggesting phenolic O-cyclization *via* pathway *a* to be more facile.

3. Conclusion

Salicylaldehydes, being commercially available and easily accessible starting materials, are efficiently utilized in a plethora of MCRs, mostly in (*pseudo*)three- as well as in four-component reactions. In this review, we focused our attention on the MCRs with the participation of at least one molecule of salicylaldehyde wherein both hydroxyl and aldehyde groups are involved in the reaction. We tried to cover applications of salicylaldehydes as privileged synthons for the synthesis of a wide range of various heterocylic systems such as chromenes, coumarins and xanthenes.

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