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RECENT DEVELOPMENT ON THE RING TRANSFORMATION REACTIONS: SYNTHESIS OF FUNCTIONALIZED BENZENES, *N*-HETEROCYCLES AND FUSED RING SYSTEMS

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Abstract – Ring transformation reactions using 2*H*-pyran-2-ones as valuable synthetic precursor with several nucleophiles for designing numerous interesting scaffolds is a growing field in synthetic organic chemistry. 2*H*-Pyran-2-ones has tendency to act as very good Michael acceptor and hence functions as good electrophile. The scope of 2*H*-pyran-2-ones has been explored for the synthesis of various molecules owning significant biological importance. Additionally, their synthetic potential has been discovered for the construction of interesting photophysically active molecules. From this point of view, the development of simple and environmental benign ring transformation strategy is a dynamic research field until today. This short review describes an overview of the most recent advances in ring transformation of functionalized 2*H*-pyran-2-ones into valuable aromatic scaffolds like functionalized benzenes, *N*-heterocycles and fused ring systems.

CONTENTS

1. INTRODUCTION

2*H*-Pyran-2-ones are prevailing heterocyclic molecules representing a fundamental class of an unsaturated oxygen containing cyclic ester.[1,2] These scaffolds have gain a lot of demand due to their advantageous biological and pharmacological processes.[3] Moreover, 2*H*-pyran-2-ones found as a multifaceted synthon with wide range of potential for the synthesis of diversity oriented intermediates in synthetic as well as in medicinal chemistry. These skeletons contributed with numerous pharmacologically active compounds that owns potency as HIV protease inhibitors,[4] anti-breast cancer,[5] antifungal,[6,7] antimicrobial,[8] antitumor,[8,9] antiproliferative,[10] plant growth inhibitors[11] and chymotrypsin inhibitor.[12]

The importance of compounds cored by pyranone motif cannot be overstated in pharmaceutical chemistry. The naturally isolated products such as bufalin,[13-16] pectinatone,[17] pentylpyran-2-one,[18] nectriapyrone,[21] griseulin,[19,20] phaechromycin,[23] nigerapyrone A[25] and weilupemycin[26] are few examples of successfully implemented in biological applications. Additionally, pyranone-cored by *tert*-butyl carboxylate group are of varied interest and have been identified as an important building block towards designing natural product carbohydrates.[27] Moreover, privileged fused pyranones shows cytotoxicity,[28] anti-HIV properties and selective inhibitor of acetylcholinesterase.[29]

Moreover, the molecules with pyranone scaffolds are well systematized in displaying excellent fluorescence due to the presence of chromophore and ester group.[30] These type of molecules actively showed bright fluorescence giving white emission in organic light emitting devices,[31] an interesting dual emissive property revealing multicolour tunability[32] and azo dyes containing 2-pyranone unit was

evaluated in biological applications.[33]

The ring transformations of 2*H*-pyran-2-ones are greatly influenced by the existent of nature and position of substituents on lactone ring. The presence of electron-withdrawing group at C-3 position of lactone ring and good leaving groups at C-4 position favours carbanion induced ring-transformation reactions depending upon the type of nucleophile used. The presence of electron withdrawing group as cyano/nitrile group make the later position (C-6) more electrophilic due to electron withdrawing effect. Over the years, 2*H*-pyran-2-ones are convenient diversified scaffolds for many reactions including ring transformation, ring contraction and ring opening reactions. In addition, these compounds were categorized as versatile precursors for the synthesis of aromatic architectures through ring transformation methodology. As a result, they advanced a central position in the current research area.

In this review, we focused on last 10 years literature related to recent development on the ring transformation reactions of 2*H*-pyran-2-ones with different nucleophiles associated with the synthesis of functionalized benzenes, *N*-heterocycles and fused ring systems.

Owing to the significance of several functionalized benzenes, *N*-heterocycles and fused ring systems, numerous synthetic procedures have been published for the synthesis of similar aromatic scaffolds and most of the procedures are associated with metal-catalyzed coupling reactions. The current existing methodologies suffers from certain drawbacks such as use of expansive metal catalyst, oxidants and additives, specific reaction conditions like high temperature, high pressure, limited substrate scope. The methods also faces more limitations resembling low productivity of yields and prolong reaction time.[34-46]

Despite the availability of several exiting approaches, there is still space to develop a new approach that could overcome the problems associated with the existing approaches. Fortunately, almost all the drawbacks could be overcome by the employment of base mediated ring transformation reactions of 2*H*-pyran-2-ones offering the flexibility of introducing wide range of functional groups. The ring transformation reactions of 2*H*-pyran-2-ones are advantageous over above methods since synthesis of functionalized donor-accepter aromatic scaffolds could be obtained under mild reaction conditions as discussed below in this review. Interestingly, the easy accessibility of starting materials 2*H*-pyran-2-ones make this approach more attractive for organic synthesis.

2. SYNTHESIS OF FUNCTIONALIZED BENZENES

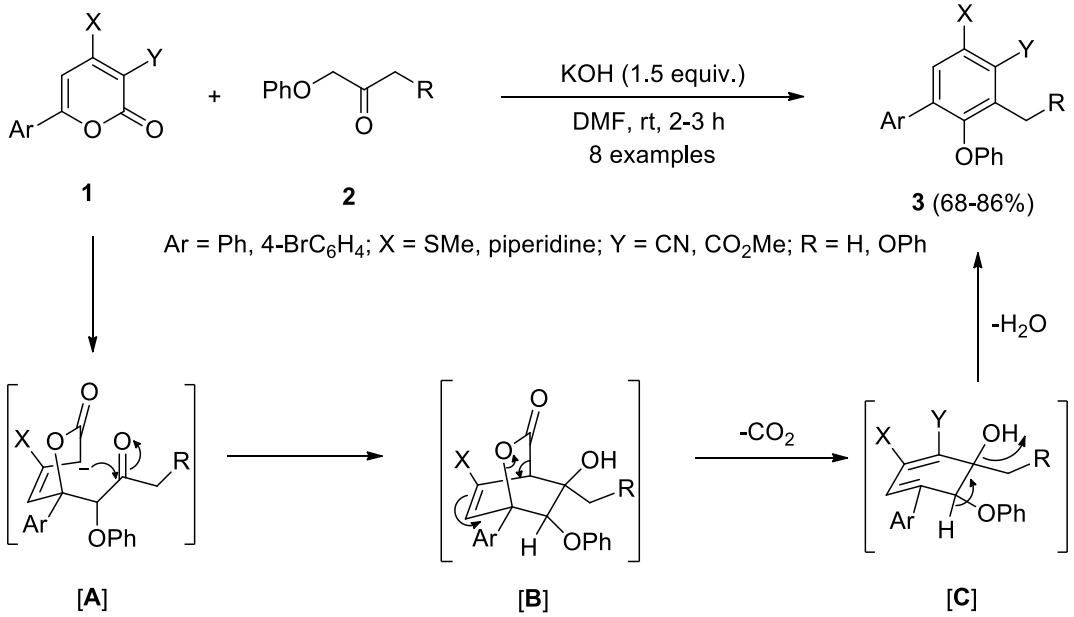
Functionalized benzenes are significantly valuable in industry and laboratory point of view and many methods are available in the literature for the synthesis of such molecules.[47-49] The building of these scaffolds using ring transformation strategy from 2*H*-pyran-2-ones involves new ring formation through C-C bond. Construction of new C-C bonds by using simple starting materials to produce molecules that are of more significant and highly desirable in light of modern concern. The fundamental process of base mediated C-C bond formation is the nucleophile attack of electron rich species to 2*H*-pyran-2-ones, which

acts as electrophiles by the employment of ring transformation strategy. There are numerous methodologies reported providing various substituted benzenes by ring transformation of functionalized 2*H*-pyran-2-ones using carbon nucleophiles.[50-59]

2-1. BIARYL-CORED FUNCTIONALIZED BENZENES

2-1-1. Synthesis of diaryl ethers

In 2009, Ram and Farhanullah[60] reported for the first time synthesis of unsymmetrical diaryl ethers **3** by base-catalyzed one-pot ring transformation of functionalized 6-aryl-2*H*-pyran-2-ones **1** with active methylene ketone **2** under mild experimental conditions (Scheme 1). The method involved C-C insertion. The detailed mechanistic pathway for the synthesis of unsymmetrical diaryl ethers **3** initiates with deprotonation of active methylene proton under basic medium generating carbanion on the carbon adjacent to carbonyl group. After that, the carbanion generated on nucleophile **2** attacks at C-6 position of pyran ring and led carbanion generation at C-3 position of pyran producing Michael adduct [**A**]. Further, there is cyclization involving the carbanion at C-3 and carbonyl functionality of the nucleophile giving bicyclic intermediate [**B**]. Finally, the desired ring transformed products were obtained *via* the simultaneous process of decarboxylation in [**B**] and dehydration in [**C**]. Furthermore, in same report synthesis of arylated benzene thioether has also been introduced and yield was reported in 52%.

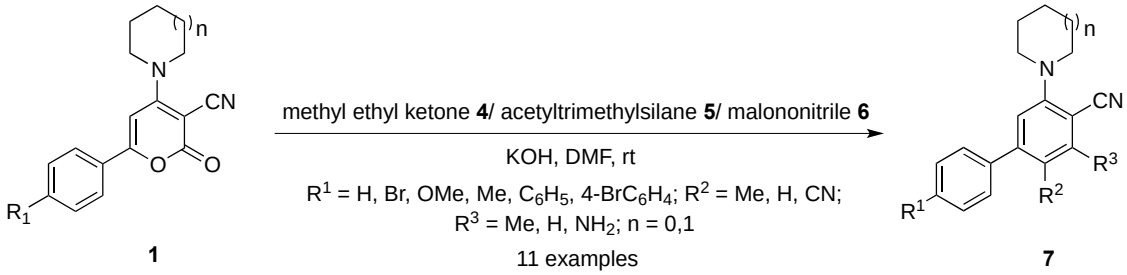


Scheme 1. Synthesis of unsymmetrical diaryl ethers **3** from functionalized 6-aryl-2*H*-pyran-2-ones **1**

2-1-2. Synthesis of biaryl-4-carbonitriles

In 2014, Goel with his co-authors[61] applied similar reaction conditions for developing the synthesis of novel biaryl-4-carbonitriles **7** in good yields. The interaction of one of the electrophilic position of parent precursors 2*H*-pyran-2-ones **1** with reactive methylene compounds **4**, **5** and **6** which acts as nucleophiles

in the presence of base in DMF at ambient temperature gave products in good yields (Scheme 2 and Table 1). The authors in this publication mainly focused on biological process of synthesized compounds. They studied antihyperglycemic activity of these derivatives and two compounds from series displayed protein tyrosine phosphatase (PTP-1B) inhibitory activity. Additionally, these compounds exhibited good glucose tolerance.



Scheme 2. Synthesis of biaryl-4-carbonitriles **7** by the transformation of 2*H*-pyran-2-ones **1**

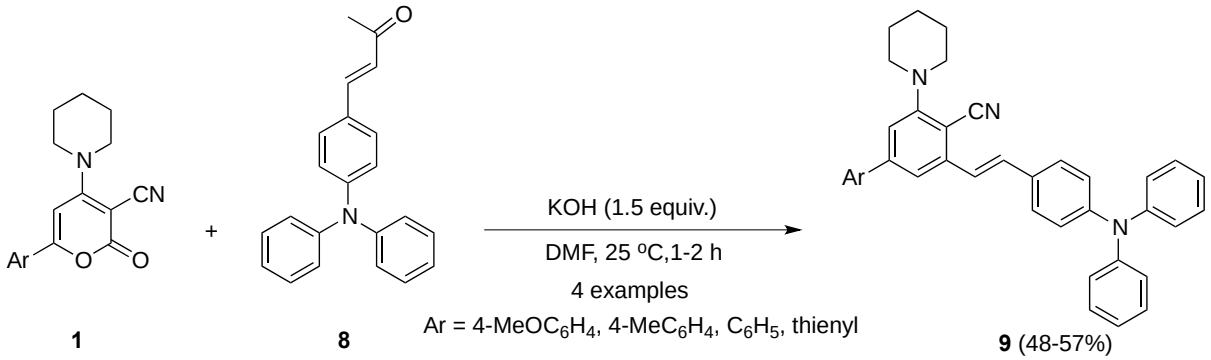
Table 1. Synthesis of biaryl-4-carbonitriles **7**

7	R^1	R^2	R^3
a	H	Me	Me
b	Br	Me	Me
c	OMe	Me	Me
d	Me	Me	Me
e	C_6H_5	Me	Me
f	4-BrC_6H_4	Me	Me
g	C_6H_5	H	H
h	C_6H_5	H	H
i	4-BrC_6H_4	H	H
j	C_6H_5	CN	NH_2
k	4-BrC_6H_4	CN	NH_2

2-1-3. Synthesis of biaryl-cored stilbenes

In 2018, Goel and group[62] investigated a facile methodology for the synthesis of diphenylamine-tethered stilbenes **9** in good yield by ring transformation of 2*H*-pyran-2-ones **1** using (*E*)-4-(4-(diphenylamino)-phenylbut-3-en-2-one **8** as a suitable nucleophile in shorter reaction time. These experiments were performed with 1.5 equiv. of KOH in DMF at room temperature for 1–2 h (Scheme 3). The prepared

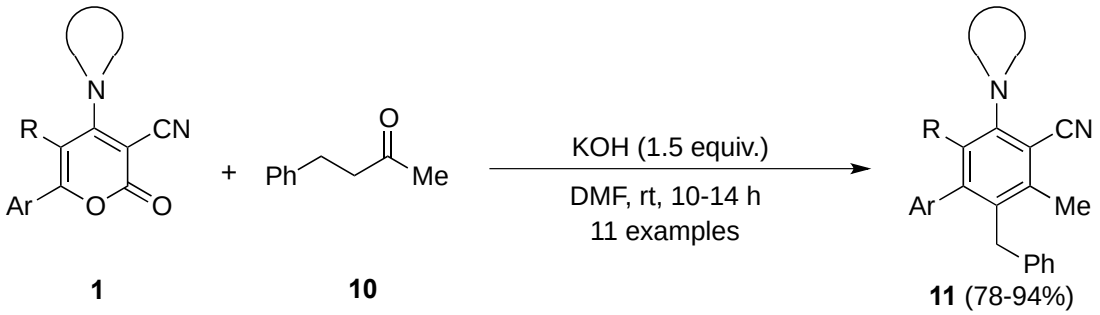
stilbenes were found to be highly fluorescent and induces white light emission in solution. The authors studied the photoisomerization between *E*/*Z* derivatives and exhibits positive solvatochromism, two photon absorption properties and good thermal stability. Additionally, compounds shows tremendous applications in biomedical imaging and fabrication of electroluminescent materials.



Scheme 3. Ring transformation of 2*H*-pyran-2-ones **1** for synthesis of diphenylamine-tethered stilbenes **9**

2-1-4. Synthesis of diarylmethanes

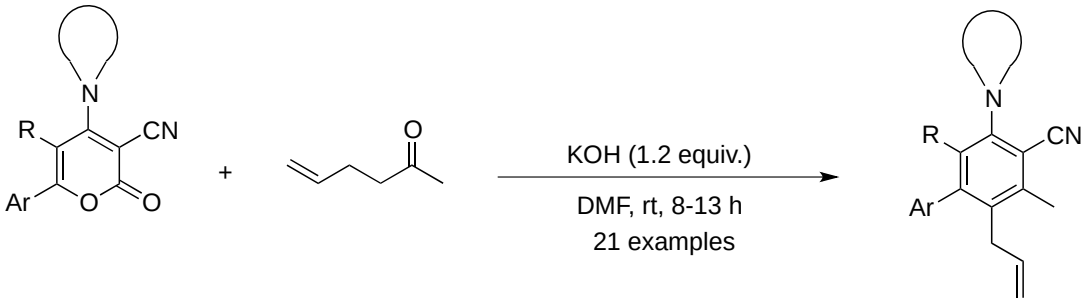
In an extensive study of ring transformation chemistry, Singh and Kole[63] in 2018 reported the efficient synthetic route for the preparation of biaryl-cored diarylmethanes **11**. This approach was free from expansive catalyst and harsh reaction conditions. This strategy showed good reactivity of polysubstituted precursor lactones **1** with 4-phenyl-2-butanone **10** at ambient temperature in duration of 10–14 h in DMF with suitable base under optimized conditions. Notably, the reactivity of starting materials **1** bearing electron withdrawing with aliphatic ketone **10** was less as compared to starting materials **1** having electron donating groups. The desired biaryl-cored diarylmethanes **11** were achieved in 78-94% yields (Scheme 4). Additionally, presence of labile –SMe group as a substituent at C-4 position of starting material led to drop the product yield.



Scheme 4. Ring transformation of 2*H*-pyran-2-ones **1** for synthesis of biaryl-cored diarylmethanes **11**

2-1-5. Synthesis of allylbenzenes

Very recently, Singh and Shetgaonkar[64] also employed similar conditions and reported simple protocol for the synthesis of fully substituted allylbenzenes **13** *via* base mediated ring transformation of 2*H*-pyran-2-ones **1**. The reactions were proceeded well in DMF at room temperature for 8–13 h utilizing 1.2 equiv. KOH. The substrate scope covered different functional groups and transformed products were achieve in 60-88% yields (Scheme 5).



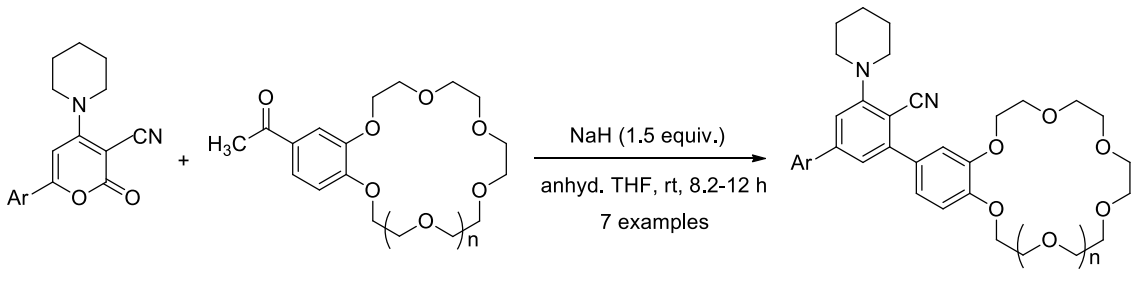
Ar = Ph, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 2,4-$Cl_2C_6H_3$, 4-MeC_6H_4, 4-$MeOC_6H_4$, 3,4-$(MeO)_2C_6H_3$, 2-thienyl, 2-fyranyl, 3-py, 1-naph, 2-naph; R = H, Me

Scheme 5. Ring transformation of 2*H*-pyran-2-ones **1** for synthesis of allylbenzenes **13**

2-2. TERARYL-CORED FUNCTIONALIZED BENZENES

2-2-1. Synthesis of benzocrown ethers

In 2016, Goel and coworkers[65] carried out the ring transformation of 2*H*-pyran-2-ones **1** with benzocrown embedded nucleophile **14** in the presence of anhyd. NaH in THF to furnish extremely fluorescent benzocrown ethers **15** in high yields (Scheme 6). Favorably, both electron donor and withdrawal partners were tolerated. Due to the existence of dimethyl amino group at C-6 of lactone (Ar = dimethylaminobiphenyl) and benzocrown ring, these skeleton underwent doubly twisted intramolecular charge transfer, which promote extension in their outstanding photophysical properties. These compounds emitted dual fluorescence in polar solvents and developed as pH sensors.

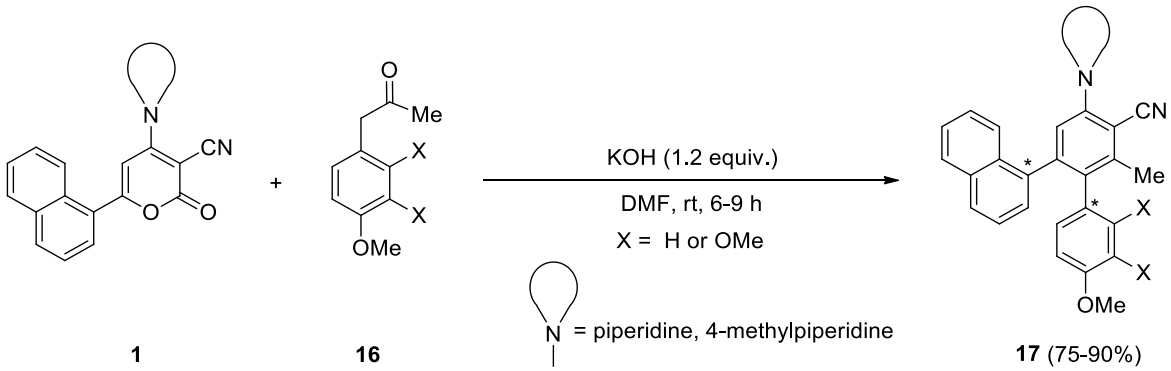


Ar = Ph, biphenyl, dimethylaminobiphenyl, pyrenyl, 4-$MeOC_6H_4$, 4-BrC_6H_4, naphthyl

Scheme 6. Synthesis of fluorescent benzocrown ethers **15** from 2*H*-pyran-2-ones **1** benzocrown embedded ketone **14**

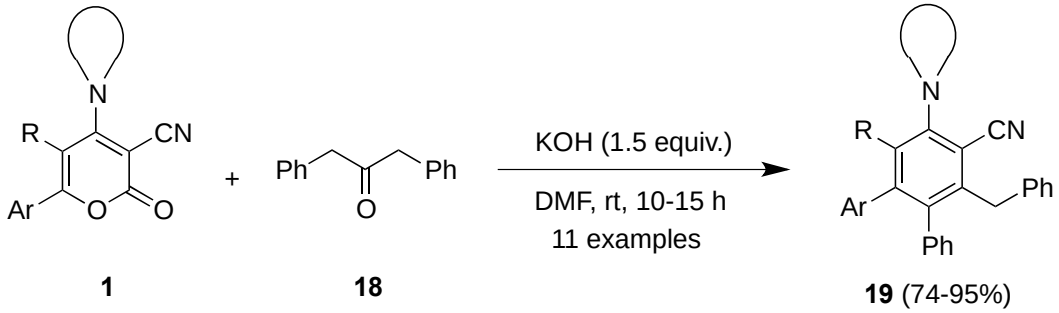
2-2-2. Synthesis of *o*-terphenyls

Moreover, the synthesis of sterically hindered *o*-terphenyls **17** was achieved *via* base-mediated ring transformation of 6-naphthyl-2*H*-pyran-2-ones **1** with substituted phenylacetones **16** in excellent yields (Scheme 7). Various naphthalene-cored biphenyls and terphenyls were synthesized under mild reaction conditions and more importantly these compounds showed process of atropisomerism with one or two stereogenic biaryl axes.[66]



Scheme 7. Ring transformation of 6-naphthyl-2*H*-pyran-2-ones **1** for synthesis of naphthyl-substituted biphenyls **17**

Following other work, Singh and Kole[63] in 2018 generalized strategy of ring transformation reactions by synthesizing teraryl-cored diarylmethanes **19** at ambient temperature. The interaction of starting lactones **1** with 1,3-diarylethanone **18** was easy under optimized reaction conditions which could furnish the expected *o*-teraryl-embedded diarylmethanes **19** in good to excellent yields (Scheme 8). The starting materials sheltered various functionalities.



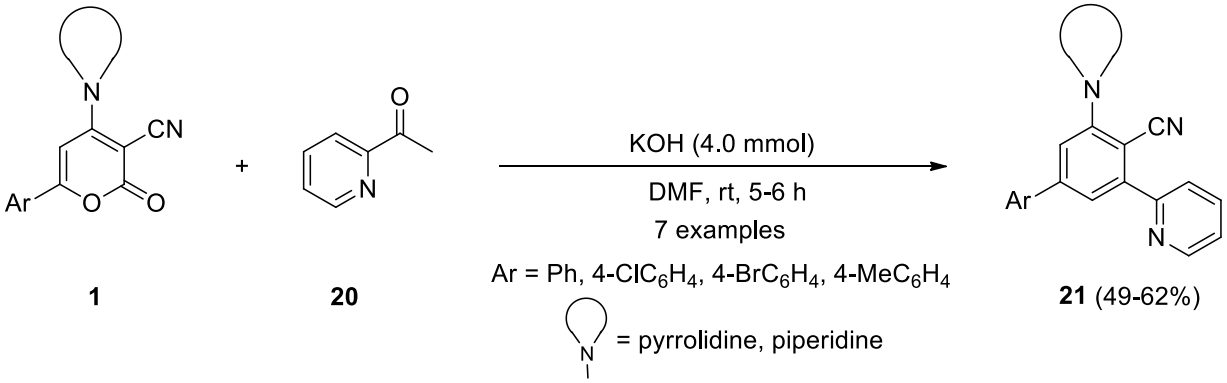
Ar = Ph, 4-BrC_6H_4, 4-ClC_6H_4, 4-MeC_6H_4, 4-MeOC_6H_4, 2-naph; R = H, Me

Scheme 8. Ring transformation of 2*H*-pyran-2-ones **1** for synthesis of teraryl-cored diarylmethanes **19**

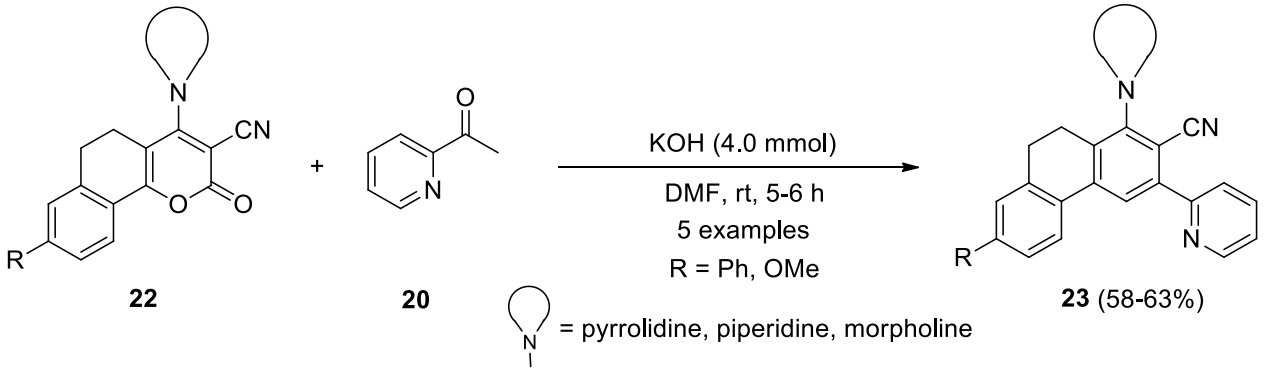
2-2-3. Synthesis of *m*-terphenyls

In 2013, Mahulikar and Patil[67] presented innovative yet environmentally benign straightforward route to produce *m*-terphenyl-cored moieties namely 3-(pyridin-2-yl)-5-*sec*-aminobiphenyl-4-carbonitriles **21**. The

ring transformation of functionalized unsaturated lactones **1** with 2-acetylpyridine **20** at room temperature in DMF utilizing KOH as base, without metal catalyst or organometallic reagents and products were attained in moderate to good yields in 5–6 h. The product formation involves insertion of two carbon atoms from carbanion used *via* C-C bond formation (Scheme 9). Similarly, authors also delineated the synthesis of 9,10-dihydro-3-(pyridin-2-yl)-1-*sec*-aminophenanthrene-2-carbonitriles **23** in same approach obtained by easy transformation of 4-*sec*-amino-2-oxo-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitrile **22** in similar conditions (Scheme 10).

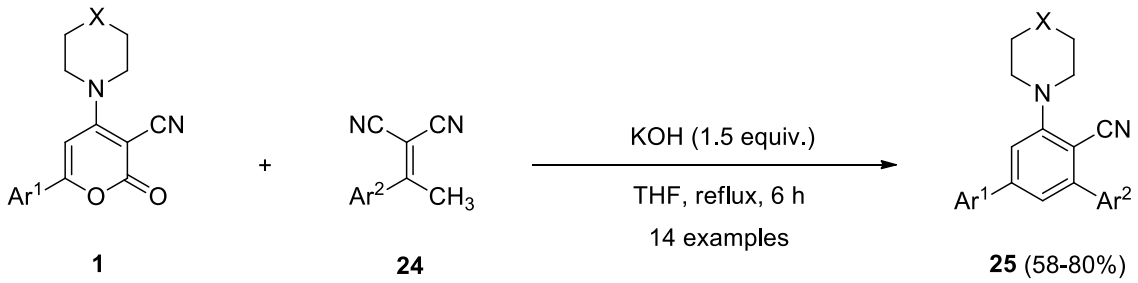


Scheme 9. Synthesis of 3-(pyridin-2-yl)-5-*sec*-aminobiphenyl-4-carbonitriles **21**



Scheme 10. Synthesis of 9,10-dihydro-3-(pyridin-2-yl)-1-*sec*-aminophenanthrene-2-carbonitriles **23**

In 2018, Pratap and coworkers[68] reported the efficient route for the synthesis of *m*-teraryls **25** in 58-80% yields by reaction of arylated 2*H*-pyran-2-ones **1** with different 2-(1-arylethylidene)malononitriles **24**. The experiments worked smoothly in THF at reflux temperature for 6 h with the presence of KOH (Scheme 11).

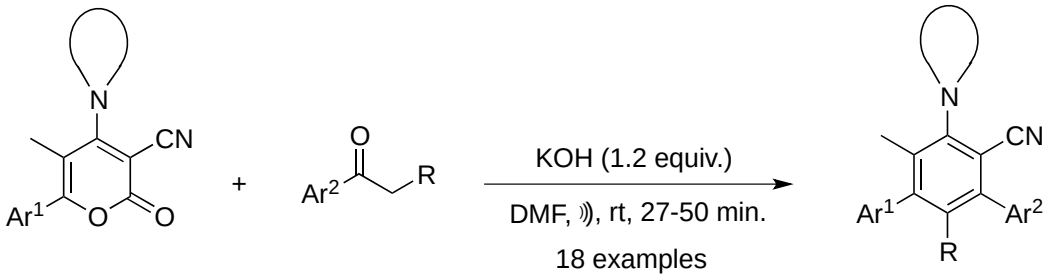


1 **24** **25** (58-80%)

Ar^1 = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 4-$MeOC_6H_4$, 4-FC_6H_4, 2,4-$Cl_2C_6H_3$, 3,4-$(MeO)_2C_6H_3$, thienyl;
Ar^2 = Ph, 4-MeC_6H_4, 4-BrC_6H_4, 4-$MeOC_6H_4$, 4-FC_6H_4, thienyl; X = O, CH_2

Scheme 11. Ring transformation of 2*H*-pyran-2-ones **1** with nucleophiles **24** in to *m*-teraryls **25**

In continuation of above work, Singh and Shetgaonkar[69] delineated the ultrasound-assisted rapid synthetic procedure to afford polyfunctionalized crowded *m*-terphenyls **27** from fully substituted lactones **1** under optimized conditions. The reactions at room temperature for shorter time provided transformed products **27** in good yields (Scheme 12).



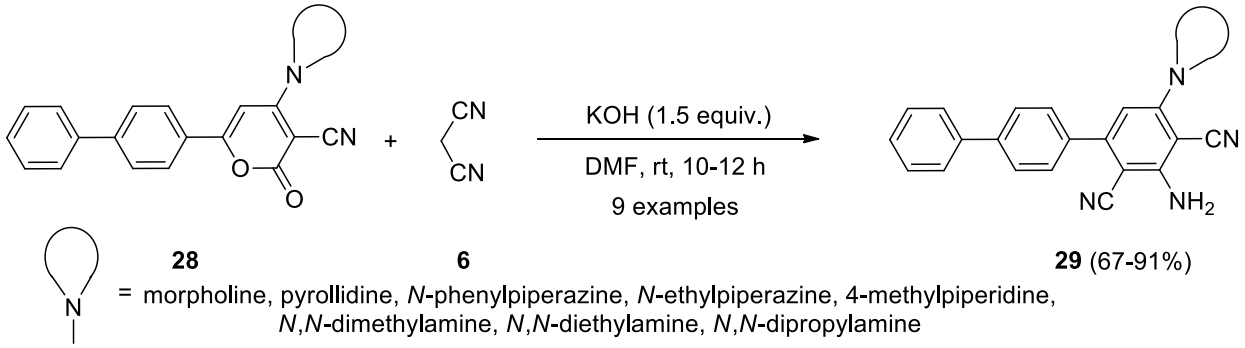
1 **26** **27** (65-89%)

Ar^1 = Ar^2 = Ph, 3-ClC_6H_4, 4-ClC_6H_4, 4-FC_6H_4, 4-$MeOC_6H_4$; R = Me, CO_2Et

Scheme 12. Ring transformation of 2*H*-pyran-2-ones **1** with nucleophiles **26** in to *m*-terphenyls **27**

2-2-4. Synthesis of *p*-terphenyls

Following their work, very recently in 2020 Singh and Chandrasekar[70] described the synthesis of thermally stable fluorescent active *p*-terphenyls **29** from 6-biphenyl-2*H*-pyran-2-ones **28** under basic conditions *via* carbanion induced ring transformation strategy using malononitrile **6** as a source of active methylene group. The electron withdrawing and donating functionalities were tolerated effectively and transformed products were obtained in good to excellent yields (Scheme 13). Furthermore, in the same report synthesis of cyclic *p*-terphenyls have been also achieved by the reaction of same starting precursors utilizing cyclic nucleophiles and products were obtained in high yields.

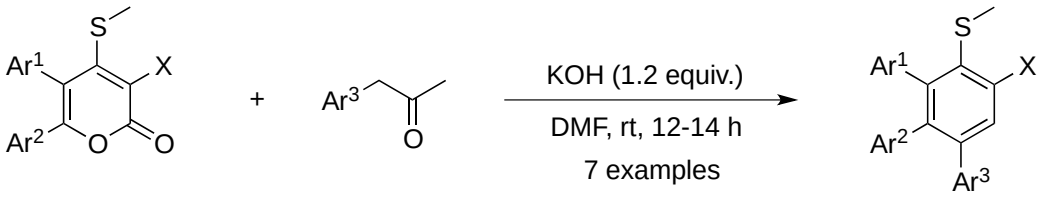


Scheme 13. Ring transformation of 6-biphenyl-2*H*-pyran-2-ones **28** with malononitrile **6** in to *p*-terphenyls **29**

2-3. QUATERARYL-CORED FUNCTIONALIZED BENZENES

2-3-1. Synthesis of chiral quateraryls

In 2007, Goel *et al.*[71] produced diversely functionalized benzenes **31** from 5,6-diaryl-2*H*-pyran-2-ones **30** through one-pot, base-mediated carbanion induced ring transformation strategy at room temperature. These transformation reactions of both parent partners **30** and **16** were readily carried out in DMF utilizing 1.5 equiv. KOH as base and resulted products **31** were accomplished in good yield (Scheme 14). This methodology is free from transition metals and allows variable flexibility.



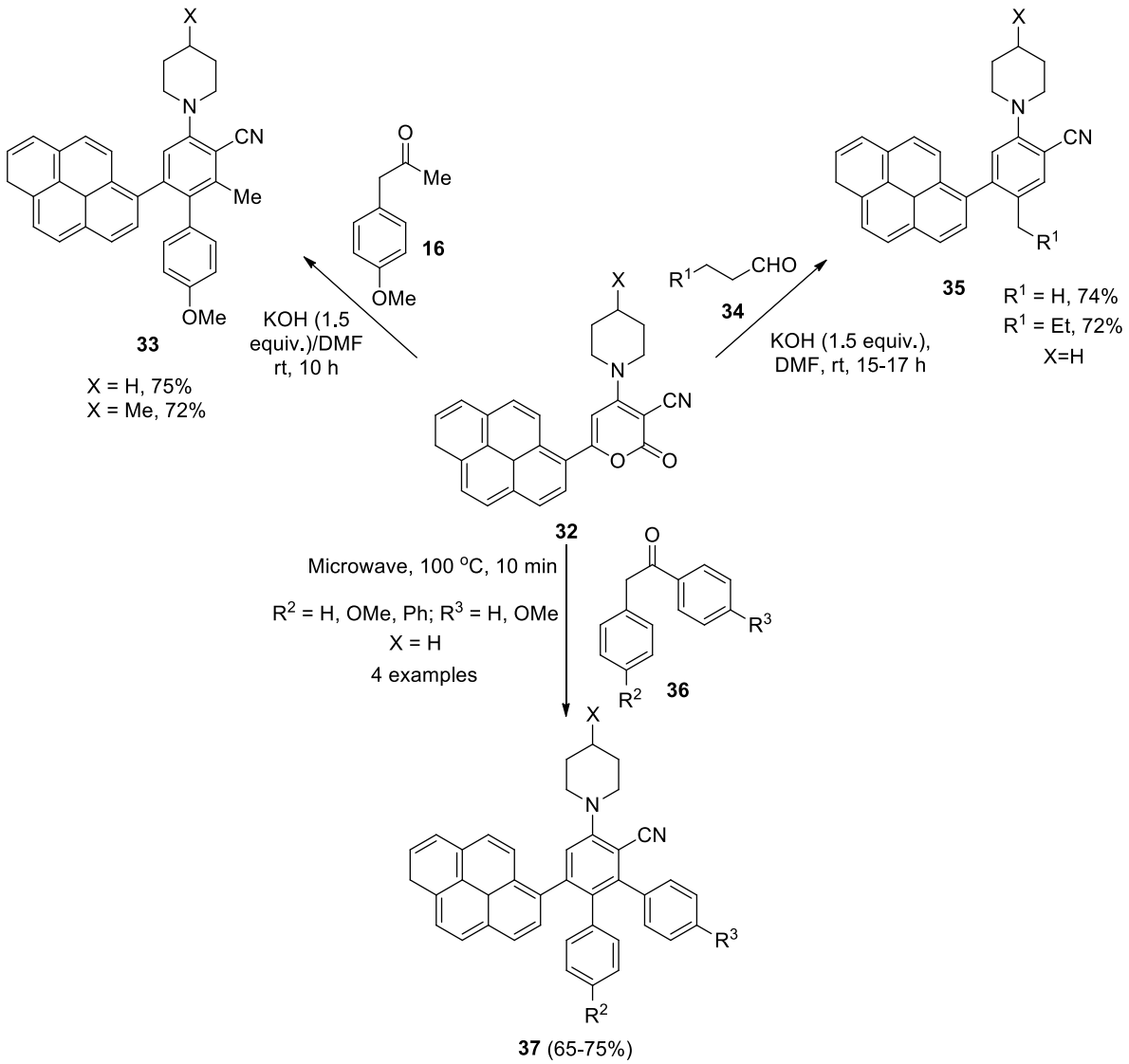
Scheme 14. Ring transformation of 5,6-diaryl-2*H*-pyran-2-ones **30** with ketone **16** in to quateraryls **31**

2-3-2. Synthesis of pyrenylarenes

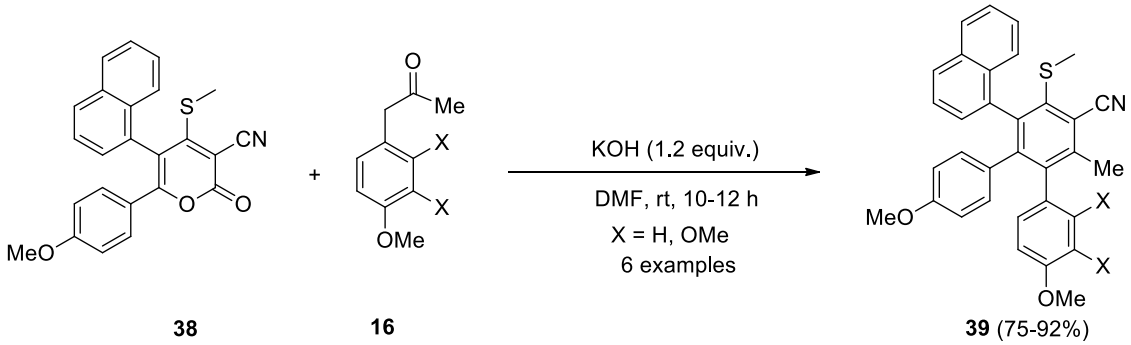
Similarly, Goel and co-authors[72] in 2011 synthesized a new sequence of functionalized non-aggregating pyrenylarene derivatives. The desired pyrenylarenes **33**, **35** and **37** were obtained in 72–75% yields by ring transformation of starting materials pyrenyl lactones **32** with different nucleophiles such as aliphatic aldehydes **34**, aryl ketone **16** and biaryl ethanone **36** containing active methylene group at room temperature for 10–17 h under alkaline medium. All reactions were carried out in dry DMF. Furthermore, authors performed these transformations at conventional heating at 100 ^{o}C and products were obtained in similar yields as that of reactions at room temperature with reduced reaction time from 17 h to 1 h. The

designed pyrenyl moieties were thermally stable and exhibits wide potential solvatochromic character due to effective charge transfer, which results because of extended conjugation within the structural architecture. Similarly, rings transformations of pyrenyl lactone **32** with 1,3-biarylethanone **36** under microwave irradiation gave pyrenyl benzenes **37** in 65-75% yield in 10 mins (Scheme 15). All the pyrenylarenes derivatives exhibits high fluorescence and upon excitation at 350 nm these compounds displayed blue emission in the range of 445-456 nm and quantum yield was reported up to 76%. The application in organic light emitting devices for these compounds was also exposed.

Likewise, sterically hindered quateraryl benzenes **39** were established by transformation of 6-(4-methoxyphenyl)-4-(methylthio)-5-(naphthalen-1-yl)-2-oxo-2*H*-pyran-3-carbonitrile **38** in 75-92% yields (Scheme 16).[66]



Scheme 15. Ring transformation of pyrenyl lactones **32** in to functionalized pyrenyl benzenes **33**, **35** and **37**



38 **16** **39** (75-92%)

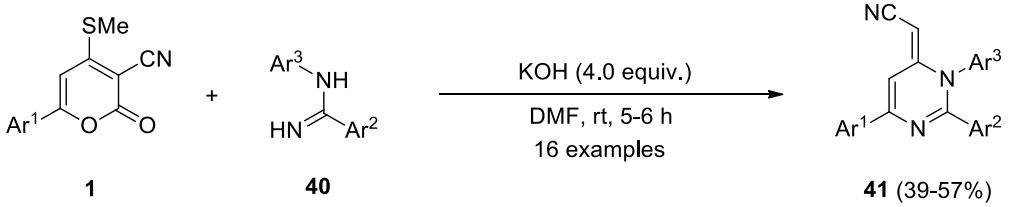
Scheme 16. Ring transformation of 2*H*-pyran-2-ones **38** for synthesis of quateraryl benzenes **39**

3. SYNTHESIS OF *N*-HETEROCYCLES

Base-induced C-N bond formation reactions have been continuously developed and significant effort has been invested in ring transformation of 2*H*-pyran-2-ones. These reactions led in the preparation of numerous important molecules. Over the years, the synthesis of 2-aminopyridines, 2-pyridinones,[73,74] imidazo[1,2-*a*]pyridines[75] and pyridin-4-ylacetonitriles[76] has been reported in good yields by ring transformation of substituted 2*H*-pyran-2-ones using respective nitrogen nucleophiles.

3-1. Synthesis of pyrimidines

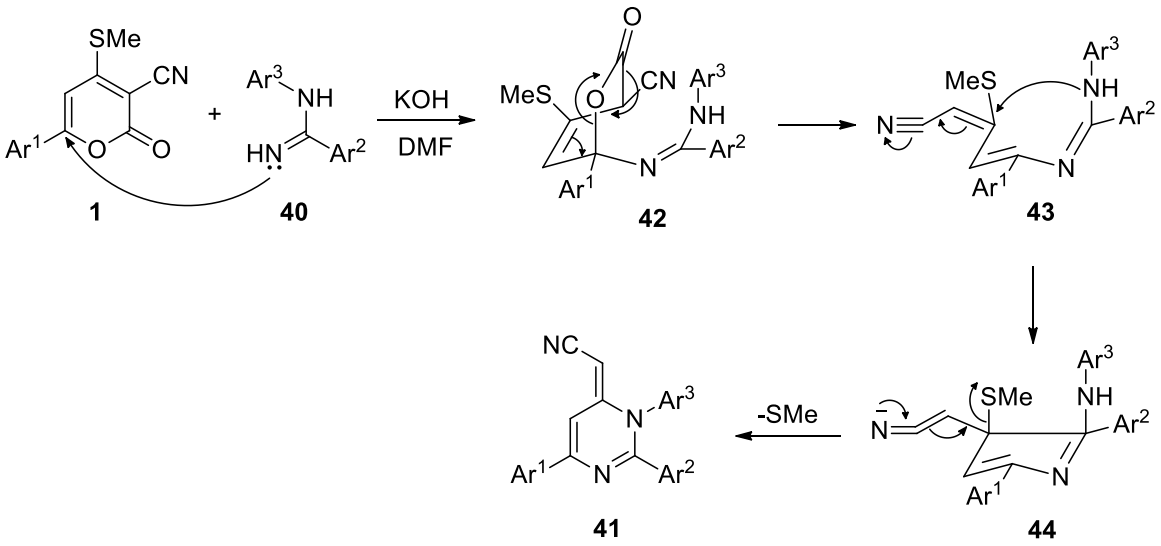
Mahulikar and Patil[77] in 2013 developed one pot highly convenient and regioselective method towards the synthesis of (2*E*)-2-(2,3,6-arylpyrimidin-4(3*H*)-ylidene)acetonitriles **41** succeeded by favorable interaction of 4-(methylthio)-2-oxo-6-aryl-2*H*-pyran-3-carbonitrile **1** and *N*-arylbenzamidine or *N*-arylpicolinamidine **40** involving KOH/DMF catalyzed ring transformation strategy at ambient temperature. These experiments offered ring transformed products in moderate yields (Scheme 17). Mechanism evolved for the above reaction could be explained in (Scheme 18) as follows, addition of the N-1 of nucleophile to the C-6 of lactone **1**, later ring cleavage due to elimination of CO_2 in intermediate **42** and recyclization involving the N-3 nitrogen of amidine and C4 of the pyran ring in intermediate **43**. Finally, deletion of the -SMe group from intermediate **44** yielded (2*E*)-2-(2,3,6-arylpyrimidin-4(3*H*)-ylidene)acetonitrile derivatives **41**.



1 **40** **41** (39-57%)

Ar^1 = Ph, 4-ClC_6H_4, 4-BrC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$NO_2C_6H_4$, 2-naphthyl; Ar^2 = Ph, 4-ClC_6H_4, 3-ClC_6H_4, 2-pyridyl; Ar^3 = 4-ClC_6H_4, 2-pyridyl

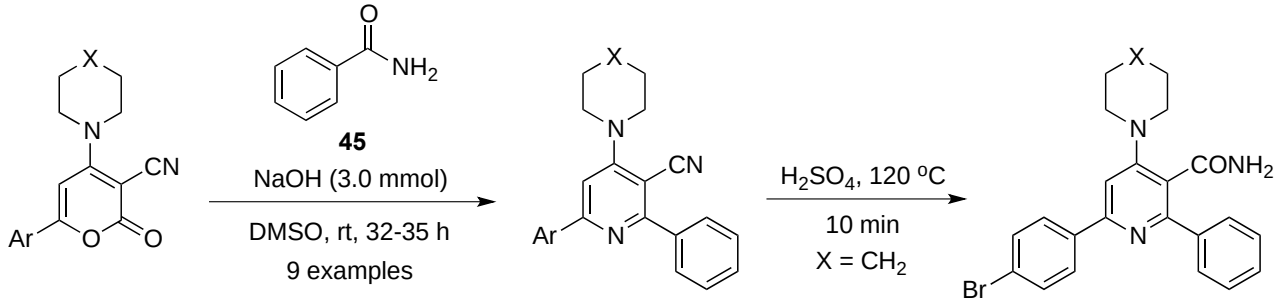
Scheme 17. The reaction of substrates **1** and **40** in to **(**arylpyrimidinylidene)acetonitriles **41**



Scheme 18. Plausible mechanism for the formation of **(**arylpyrimidinylidene)acetonitriles **41**

3-2. Synthesis of pyridines

Moreover, the synthesis of 2,6-diarylpyridines **46** in good yields by ring transformation of 2*H*-pyran-2-ones **1** under mild reaction conditions was reported in 2013 by Gupta and coworkers.[78] The reactions were carried out in DMSO in the presence of NaOH at room temperature. Further, nitrile group at 3-position of compounds was hydrolyzed by the reacting with H_2SO_4 at 120 ^oC to produced amide-cored 2,6-diarylpyridines **47** in high yields (Scheme 19). Later in same report, the synthesized products were evaluated for potent anti-tubercular agents.



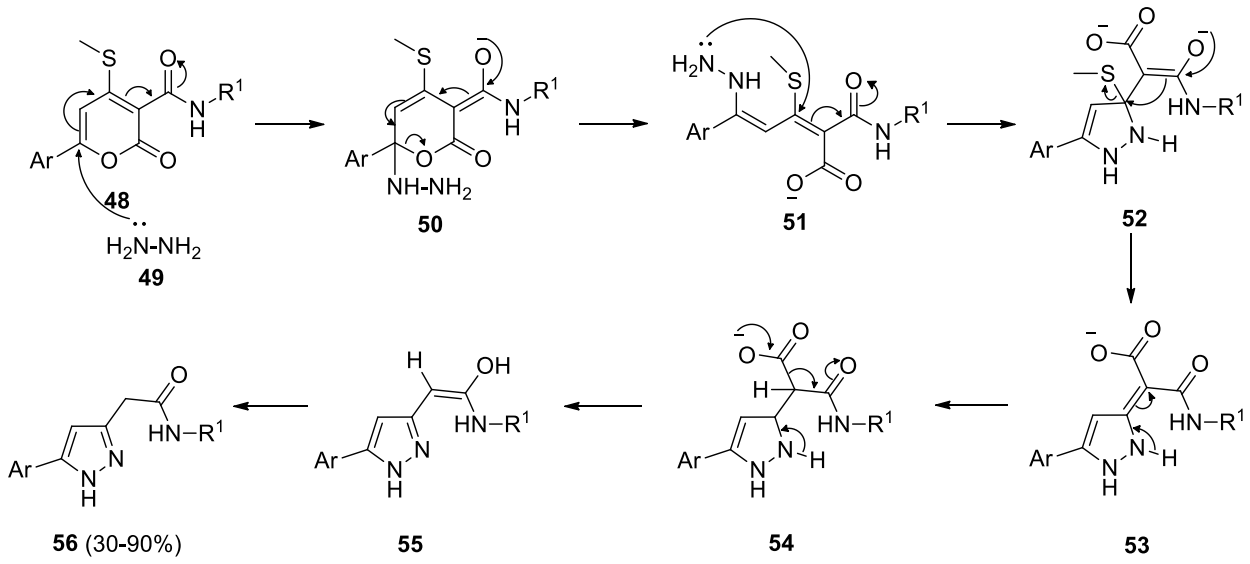
Ar = Ph, 4-BrC_6H_4, 4-ClC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$; X = CH_2, O

Scheme 19. Synthesis of 2,6-diarylpyridines **46** by ring transformation of 2*H*-pyran-2-ones **1**

3-3. Synthesis of pyrazolyl acetamides

Recently in 2019, Sharon and Rozy[79] investigated the cost-effective protocol for the synthesis pyrazolyl acetamides **56** (Scheme 20). The process involves nucleophilic attack of hydrazine **49** to C-6 position of pyran ring in substrate **48** and gives intermediate **50**. Further, intramolecular cyclization of intermediate

51 furnishes other pyrazole intermediate **52** that undergoes decarboxylation and successfully provides desired products **56**.

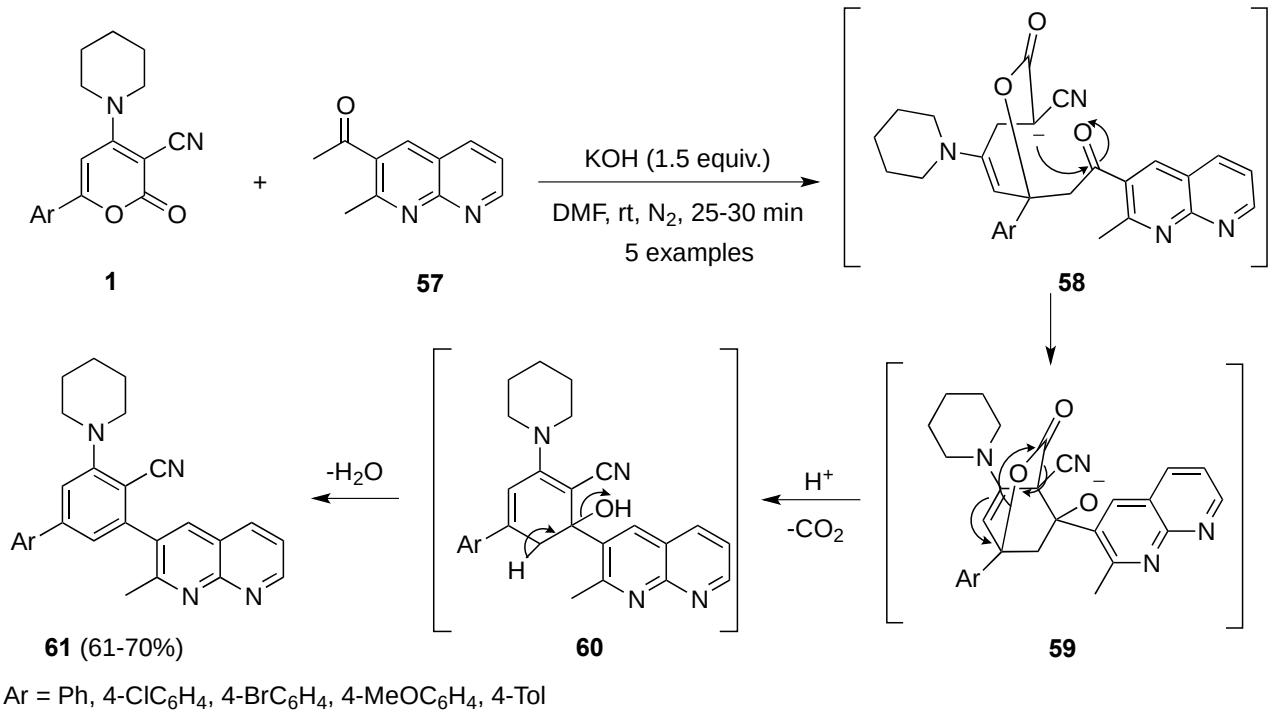


Scheme 20. Synthesis of pyrazolyl acetamides **56** from 6-aryl-2*H*-pyran-2-ones **48**

3-4. Synthesis of naphthyridines

Similarly, Goel and co-workers[80] in 2014 reported the synthesis of substituted non-aggregated functionalized naphthyridines **61** tolerating electron releasing and accepting groups *via* ring transformation of 2*H*-pyran-2-ones **1** with 1-(2-methyl-1,8-naphthyridin-3-yl)ethanone **57** under inert atmosphere at ambient temperature (Scheme 21).

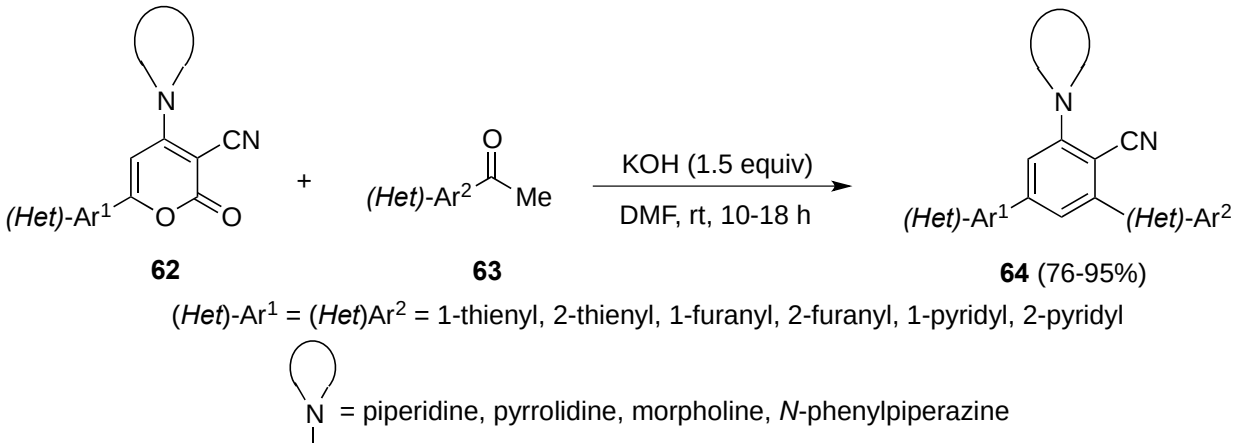
Eventually, the synthesized scaffolds showed interesting photophysical properties and metal sensing application. The proposed mechanism initiates with Michael attack of the conjugate base of nucleophile at C-6 of lactone. Intramolecular cyclization, followed by decarboxylation and dehydration gave desired compounds. The synthesized derivatives showed bright green fluorescence with positive solvatochromism effect and quantum yield of 40–49%.



Scheme 21. Synthesis of functionalized naphthyridines **61** *via* ring transformation of 2*H*-pyran-2-ones **1** with 1-(2-methyl-1,8-naphthyridin-3-yl)ethanone **57**

3-5. Synthesis of 1,3-bis(heteroaryl)benzenes

Very recently, Singh and Kanimozhi[81] synthesized 1,3-bis(heteroaryl)benzenes **64** *via* convenient carbanion-induced ring transformation reaction of 6-heteroaryl-2*H*-pyran-2-ones **62** with heteroaryl ketone **63** in DMF for 10–15 h at room temperature. The reactions underwent through Michael addition, decarboxylation and dehydration sequence to produce preferred ring transformed products in high yields (Scheme 22). Variety of *tert*-amino functionalities were significantly tolerated and reactions worked smoothly under non-hazardous conditions.



Scheme 22. Synthesis of 1,3-bis(heteroaryl)benzenes **64** *via* transformation of 6-heteroaryl lactones **62**

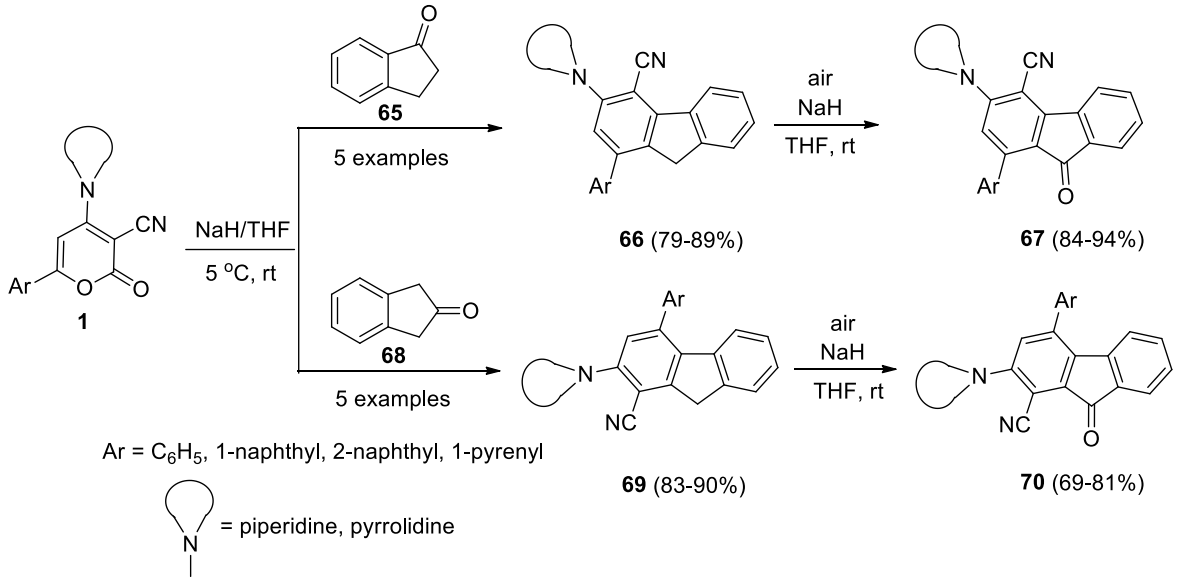
4. SYNTHESIS OF FUSED RING SYSTEMS

Fused ring systems are valuable scaffolds in chemistry and material science. Molecules embedded with fused aromatic ring systems are generally acknowledged in biological and amazing photophysical studies.[82] In addition, recent studies highlighted their applications in organic light emitting devices (OLEDs),[83] interesting bioimaging in BODIPY and optoelectronics.[84]

4-1. Synthesis of fluorenes and fluorenones

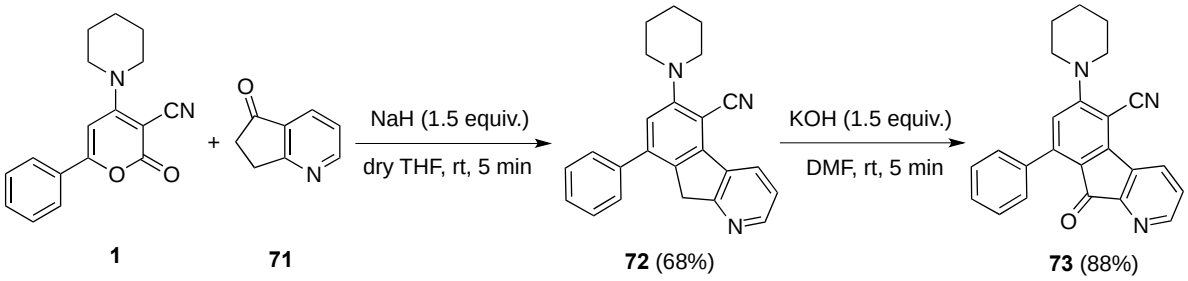
In 2009, Goel and co-authors[85] demonstrated simple and convenient route for the synthesis of fluorenes **66** and **69** which proceeds by Michael addition, decarboxylation and dehydration following ring transformation strategy using functionalized 2*H*-pyran-2-ones **1** and cyclic ketones **65** and **68** as a favorable parent precursors. NaH-Promoted ring transformation reactions in THF at low temperature delivered desired fluorenes **66** and **69** in high yields (Scheme 23). Furthermore, the synthetic utility of these reactions were extended towards preparation of fluorenones **67** and **70** in high yields. In addition, the authors demonstrated conversion of 'green light emitting derivative' into stable 'blue light emitting derivative' by changing the position of functionality within the structural architecture of studied derivative.

In addition, Goel and group[86] in 2016 employed ring transformation strategy for designing amazing new fluoregenic azafluorene **72** and azafluorenone **73**. The transformation reaction of 2*H*-pyran-2-one **1** with 6,7-dihydro-5*H*-cyclopenta[*b*]pyridin-5-one **71** in the presence of NaH in dry THF at room temperature for only 5 minutes provided azafluorene **72** in 68% yield, followed by interaction with KOH in DMF gave azafluorenone **73** in 88% yield (Scheme 24).



Scheme 23. Synthesis of fluorenes **66** & **69** and fluorenones **67** & **70** from lactones **1**

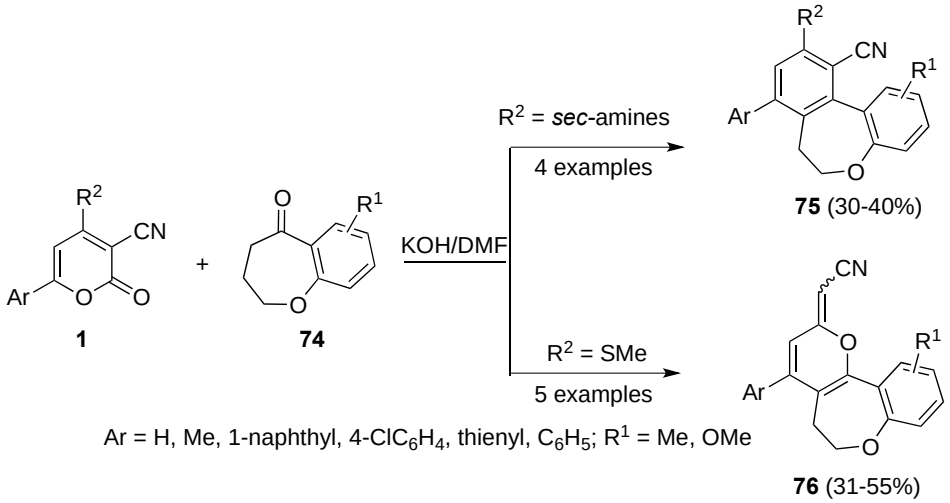
Eventually, azafluorenone **73** displayed interesting solvatochromic shifts varying polarity index of different polar-nonpolar solvents that infers intramolecular charge transfer within the molecule, whereas azafluorene fail to show same properties. Additionally, azafluorenone **73** was found as excellent biocompatible fluorescent probe selective in staining or live cell imaging of intracellular lipid droplets in HeLa and 3T3-L1 pre-adipocyte cells.



Scheme 24. Synthesis of new fluoregenic azafluorene **72** and azafluorenone **73**

4-2. Synthesis of oxaheterocycles

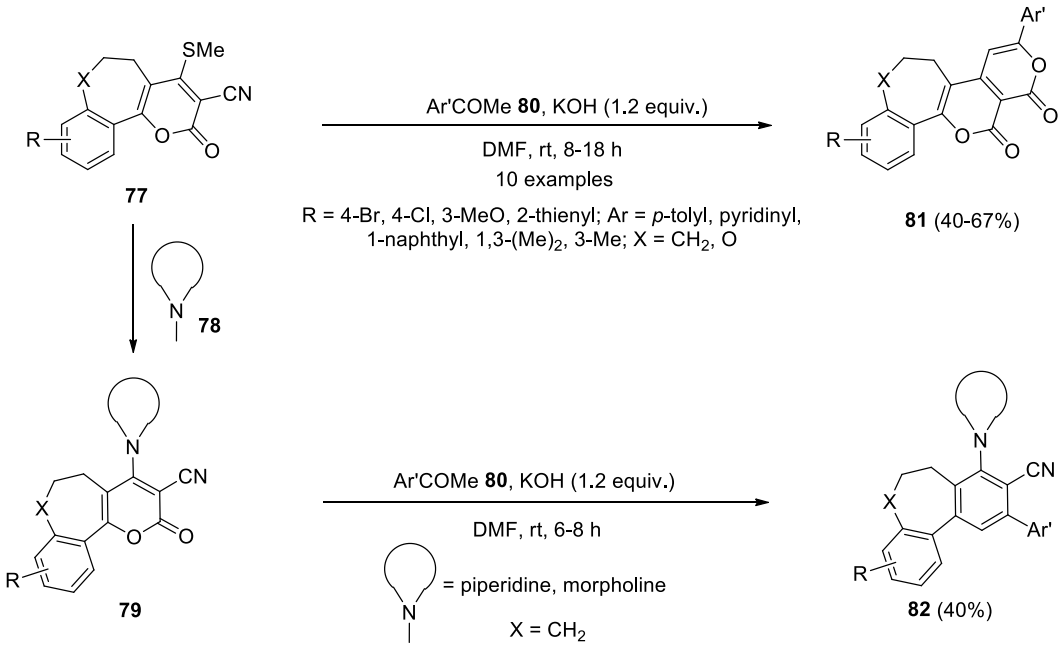
A concise synthesis of heterocyclic benzo[*b*]pyrano[2,3-*d*]oxepine **76** and dibenzo[*b*,*d*]oxepine **75** by base mediated ring transformation of 2*H*-pyran-2-ones **1** through condensation, cyclization and effective C-C insertion was demonstrated by Tandon and coworkers.[87] As a result, reactions provided two products. The starting materials were synthesized by the reaction of synthon with cyclic ketone under alkaline medium. The heterocyclic compounds named as 3,4-dihydro-2*H*-benzo[*b*]oxepin-5(2*H*)-ones **74** were used as nucleophile and products **75** and **76** were reported in moderate yields (Scheme 25). The formation of both reaction products involved few key steps like generation of Michael adduct that led ring to open, recyclization involving C-3 of pyran ring and carbonyl function of bicyclic ketone and Michael adduct enolization followed by elimination of methyl mercaptan respectively.



Scheme 25. Transformation of pyranone **1** with heterocyclic nucleophiles **74** in to benzo[*b*]pyrano[2,3-*d*]oxepine **76** and dibenzo[*b*,*d*]oxepine **75**

In continuation of above work, Ram and group[88] in 2012 disclosed the efficient and convenient synthesis of oxaheterocycles **81** in moderate to good yields from rigid 4-(methylthio)-2-oxo-5,6-dihydro-2*H*-benzo[*b*]pyrano[2,3-*d*]oxepine-3-carbonitrile **77**. The reaction of aryl methyl ketones **80** with substrates **77** in alkaline medium at ambient temperature for 8–18 h gave trioxabenzo[3,4]cyclohepta[1,2-*a*]naphthalene-6,7-diones **81**. The establishment of these products comprises the generation of carbanion *insitu*, which attacks at C-4 of substrate, followed by ring closure and hydrolyses.

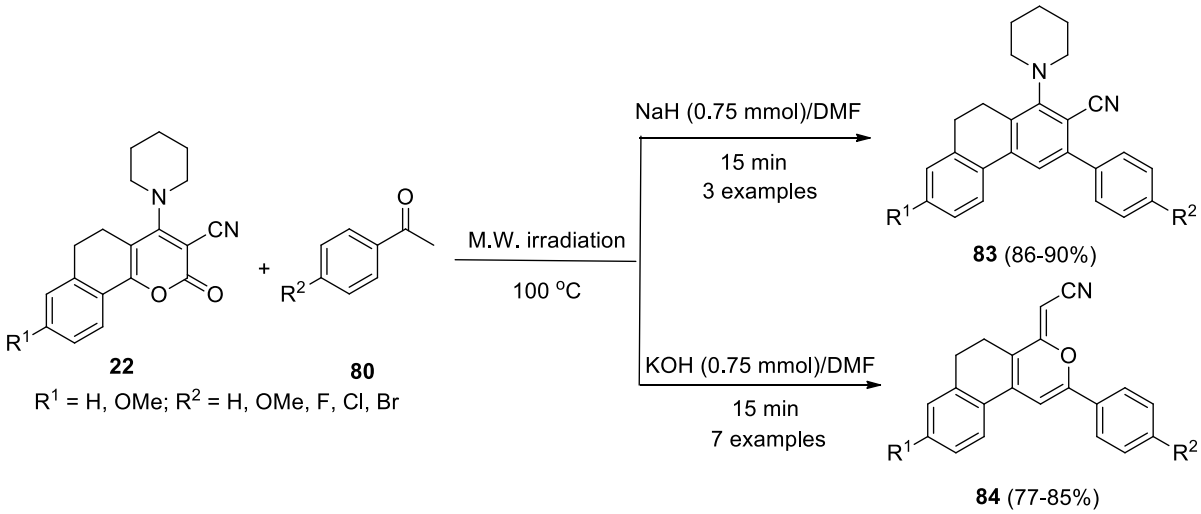
Furthermore, reaction of substrates **77** with secondary amines **78** afforded 4-(*tert*-amino)-2-oxo-5,6-dihydro-2*H*-benzo[*b*]pyrano[2,3-*d*]oxepine-3-carbonitrile **79** which provided 2-aryl-4-*sec*-amino-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene-3-carbonitrile **82** in 40% (Scheme 26). The formation of this product involves Michael addition, followed by intramolecular cyclization, dehydration and decarboxylation.



Scheme 26. Synthesis of oxaheterocycles **81** and **82** from 2*H*-benzo[*b*]pyrano[2,3-*d*]oxepine-3-carbonitrile **77** and **79** respectively

Furthermore, Pratap and group[89] conveyed non-catalytic base promoted microwave assisted synthesis of partially reduced isochromenes **84** and phenanthrenes **83** in excellent yields. The starting precursors 4-(piperidin-1-yl)-5,6-dihydro-2*H*-benzo[*h*]-chromen-2-ones **22** were synthesized according to reported procedures. It is interesting to note that the reaction of precursors **22** with aryl ketones **80** under microwave irradiation at 100 ^{o}C in the presence of 1.5 equiv. of NaH in DMF provided 3-phenyl-1-(piperidin-1-yl)-9,10-dihydrophenanthrene-2-carbonitriles **83** in 86-90% yields. Whereas,

same reaction with existence of 1.5 equiv. KOH gave (Z)-2-(2-aryl-5,6-dihydro-4*H*-benzo[*f*]isochromen-4-ylidene)acetonitriles **84** in 77-85% yields (Scheme 27).

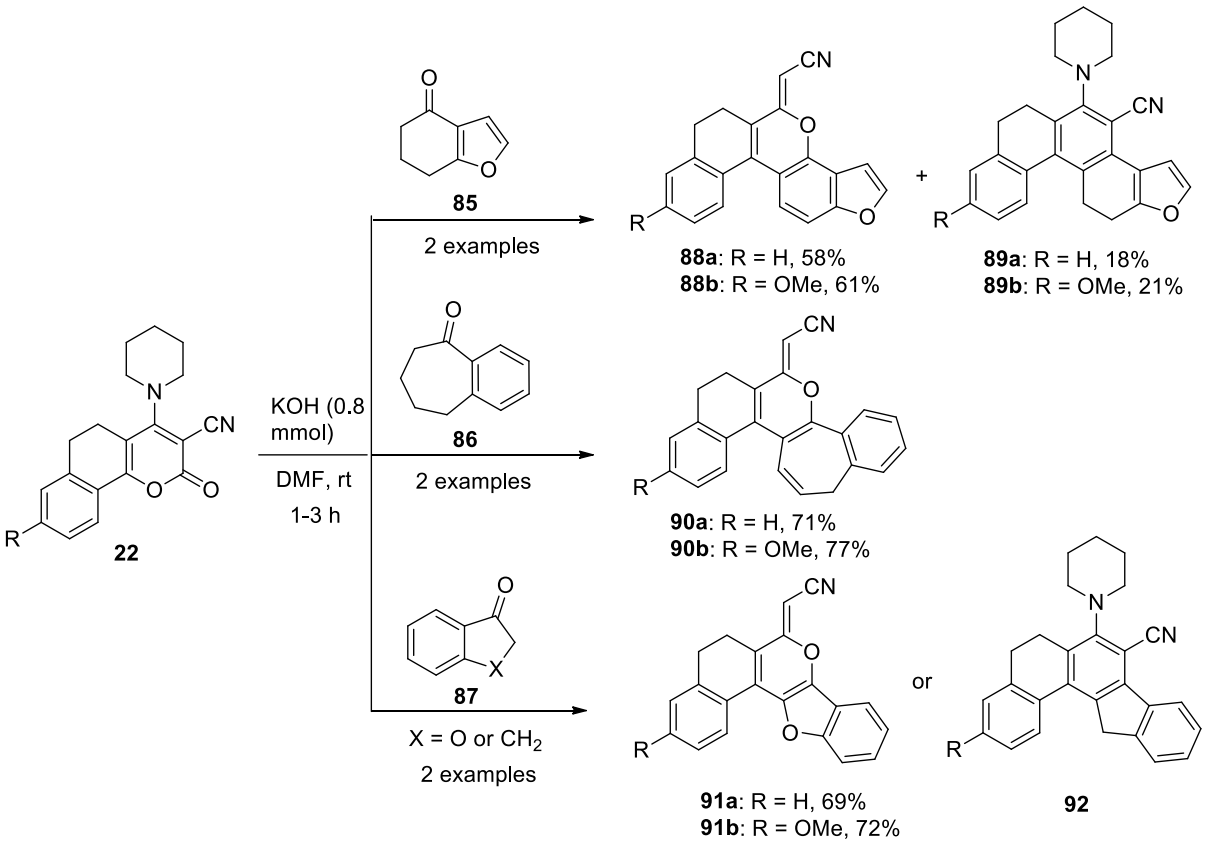


Scheme 27. Microwave-assisted synthesis of isochromenes **84** and phenanthrenes **83** by the transformation of precursors **22**

In 2012, Pratap and coworkers[90] reported the KOH promoted concise synthesis of oxygen annulated polycyclic aromatic structures using bicyclic ketone as nucleophile. The process involves ring transformation of 2-oxo-4-(piperidin-1-yl)-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles with different nucleophiles and products were obtained in excellent yields.

The significant transformation of substrate **22** with 4,5,6,7-tetrahydrobenzofuran-4-one **85** under basic medium provide two products, (6,7-dihydro-1,4-dioxabenzo[*g*]cyclopenta[*a*]phenanthren-5-ylidene)-acetonitrile **88** as major product in moderate yield and 6,7,12,13-tetrahydro-5-(piperidin-1-yl)-1-oxacyclopenta[*a*]benzo[*c*]phenanthrene-4-carbonitrile **89** as minor product in useful yields (Scheme 28).

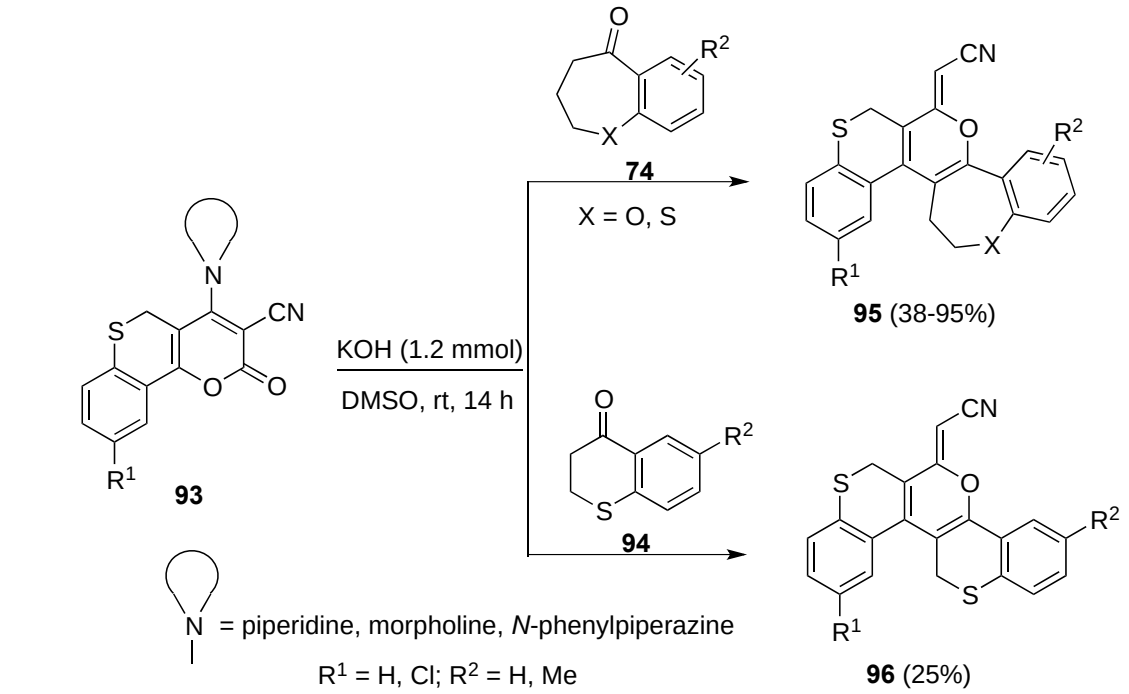
The synthetic pathway revealed that Michael addition of nucleophile to lactone ring of other substrate was first and common step for the formation of both products. However, for the synthesis of major product, the reaction underwent smoothly by intramolecular enolate addition to enamine followed by decarboxylation and loss of piperidine. This sequence of steps was possible as piperidine was found as good leaving group. Therefore, oxaheteroaromatic products were achieved in major yield. Whereas, synthesis of minor product includes intramolecular enamine addition to carbonyl experiencing dehydration. Also, similar interactions of same substrates **22** with benzosuberone **86** and 2,3-dihydrobenzofuran-3-one **87** successfully provided (5,6-dihydro-14*H*-8-oxabenzosuberano[1,2-*c*]phenanthren-7-ylidene)acetonitriles **90** and (5,6-dihydro-8,13-dioxaindeno[1,2-*c*]phenanthren-7-ylidene)acetonitriles **91** in high yields under same reaction conditions.



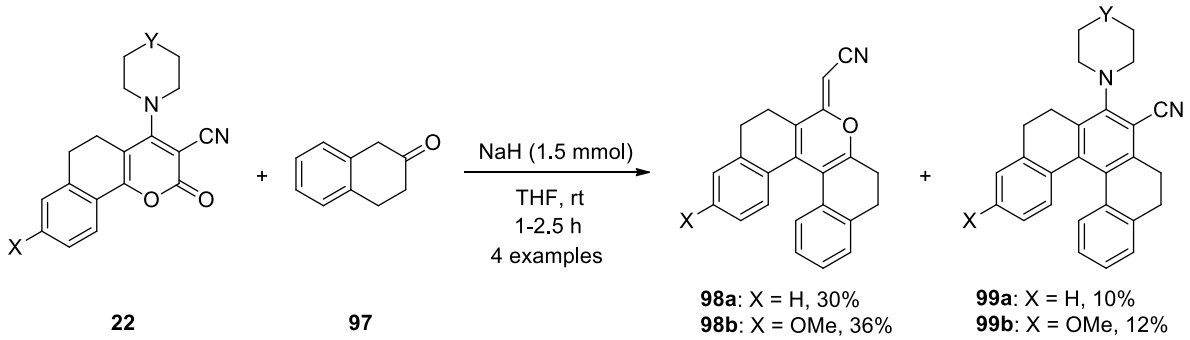
Scheme 28. Synthesis of oxygen annulated polycyclic aromatic structures **88-91** using bicyclic ketone **85-87** as nucleophile from 2-oxo-4-(piperidin-1-yl)-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles **22**

Moreover, in the same year Ram and co-authors[91] in 2012 developed convenient protocol for the 'S' shaped oxygen and sulfur containing heterocycles **95** and **96** *via* NaOH induced transformation of 2*H*-pyran-2-ones **1** in DMSO at room temperature for 14 h. The reaction between 4-*sec*-amino-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitriles **93** and cyclic nucleophiles **74** provided (*Z*)-2-(1,2-dihydro-10*H*-thiochromeno[3,4-*c*]pyrano[3,2-t*d*]benzo[*b*]oxepin-2*H*-ylidene)acetonitriles **95** in 38-95% yields. Likewise reaction of same substrate with thiochroman-4-ones **94** gave 2-(7,8-dihydrobenzo[*f*]thiochromeno[4,3-*c*]isochromen-6(13*H*)-ylidene)acetonitriles **96** in only 25% yield (Scheme 29).

Likewise, Goel and his co-workers[92] constructed functionalized 7-oxa[5]helicenes **98** and [5]helicenes **99** in useful yields *via* NaH-mediated ring transformation of 5,6-dihydro-4-amin-1-yl-2-oxo-2*H*-benzo[*h*]chromene-3-carbonitriles **22** by their interaction with 2-tetralones **97** in THF (Scheme 30).



Scheme 29. Synthesis of oxygen and sulfur containing polycyclic aromatic compounds **95** and **96** from 2*H*-pyran-2-ones **93**

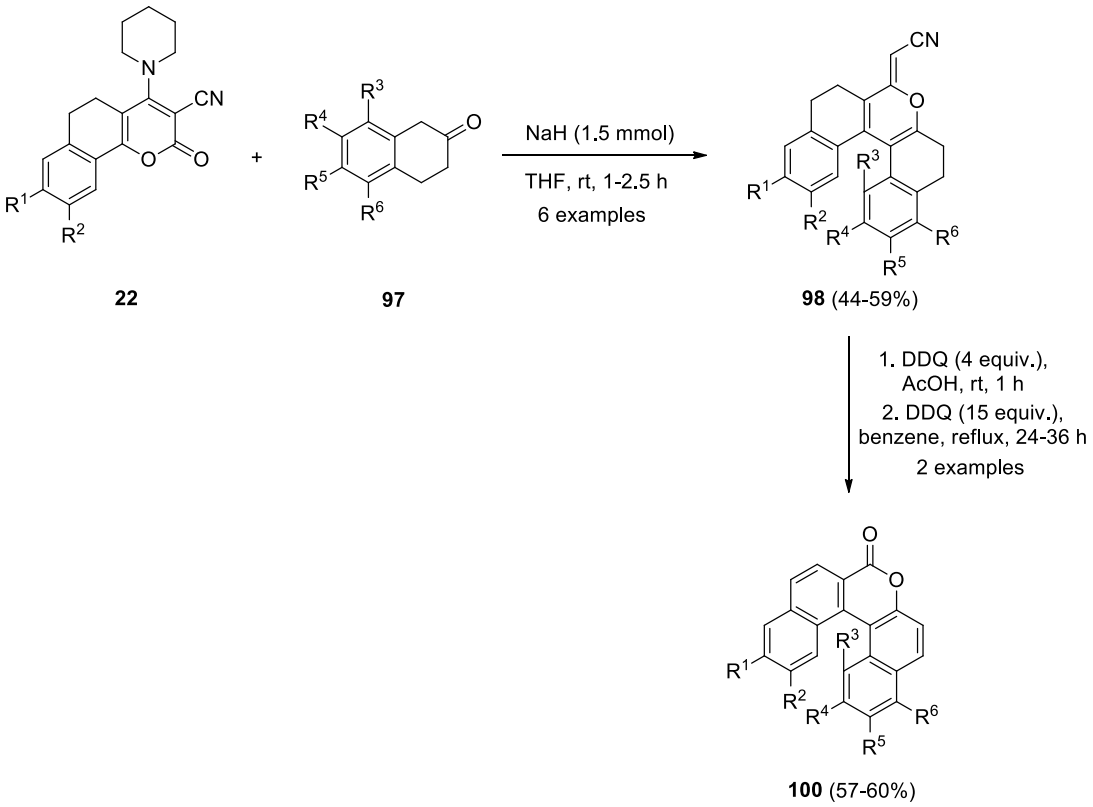


Scheme 30. NaH-Catalyzed synthesis of 7-oxa[5]helicenes **98** and [5]helicenes **99** from 5,6-dihydro-4-amin-1-yl-2-oxo-2*H*-benzo[*h*]chromene-3-carbonitriles **22**

The simple, cost-effective and non-catalytic approach to design partly reduce thia- and oxa-thia[5]helicenes was disclosed in 2012 by Pratap and his co-workers.[93] The starting materials were easily transformed in to desired heterocycles in alkaline medium and delivered products in high yields. Additionally, the designed compounds were evaluated for carcinogenic properties.

Furthermore, Goel and co-workers[94] in 2013 used same procedure to build a diverse novel oxygen bearing heterocycles in moderate yields. Base promoted reaction of both the parent partners **22** and **97** at room temperature in THF efficiently furnished (*Z*)-2-(5,6-dihydro-1*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4(2*H*)-ylidene)acetonitriles **97**. The substrate scope enclosed successfully by positioning numerous substituents on both the parent partners. Through

aromatization of product with DDQ provided 4*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-ones **100** in good yields (Scheme 31). The synthetic way proceeds *via* cyclic nucleophile-induced ring transformation of poly-substituted lactones initiated by Michael addition reaction.



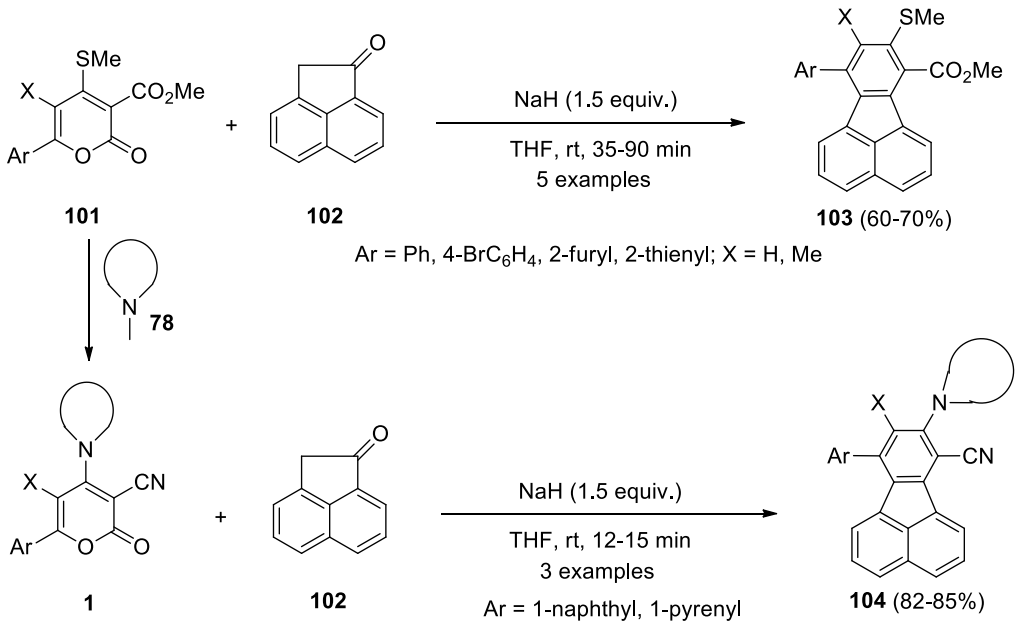
22 **97** **98** (44-59%) **100** (57-60%)

Scheme 31. The synthesis of (*Z*)-2-(5,6-dihydro-1*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4(2*H*)-ylidene)acetonitriles **98** and 4*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-ones **100**

4-3. Synthesis of fluoranthenes

In 2010, Goel and group[95] prepared thermally stable fluoranthenes **103** and **104** with donor-acceptor functionalities from 4-methylthio-2*H*-pyran-2-ones **101** without organometallic reagents under simple and efficient reaction conditions in 35–90 minutes. These compounds emitted yellow light in organic light emitting devices (OLEDs). Later, other substrates 4-*tert*-amino-2*H*-pyran-2-ones **1** were easily converted in to fluoranthenes **103** and **104** in high yields and 2*H*-acenaphthylen-1-one was used as carbanion source (Scheme 32).

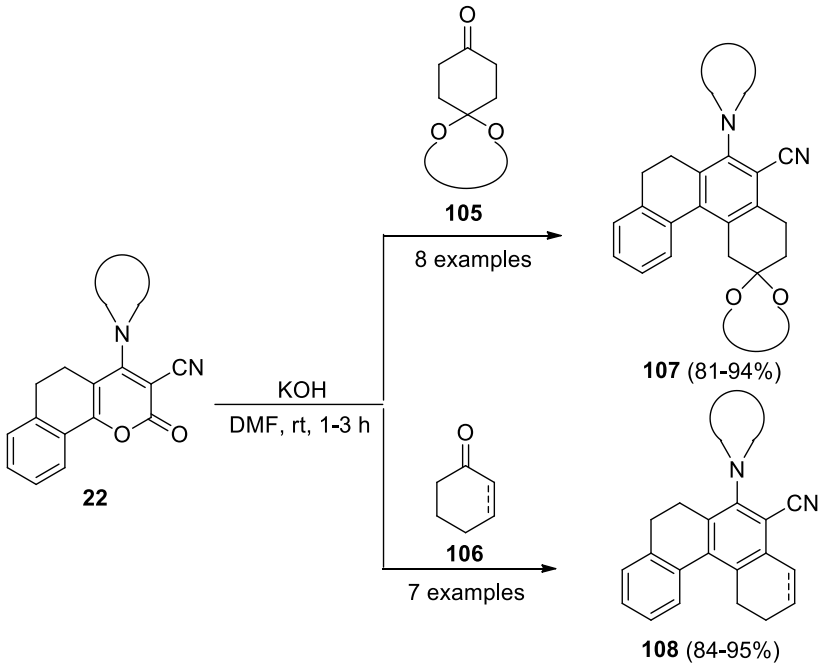
In addition to earlier report, later in 2014 Goel *et al.*[96] presented new donor-accepter fluoranthenes named FLUN-550, which was developed as selective and non-toxic fluorescent probe for staining intracellular lipid droplets. It turned to display an interesting vitro live cell imaging properties even in low concentration and demonstrated amazing photoluminescence (PL) property. Hence, this molecular probe is able to use for multicolour imaging applications.



Scheme 32. Synthesis of stable donor-acceptor fluoranthenes **103** and **104**

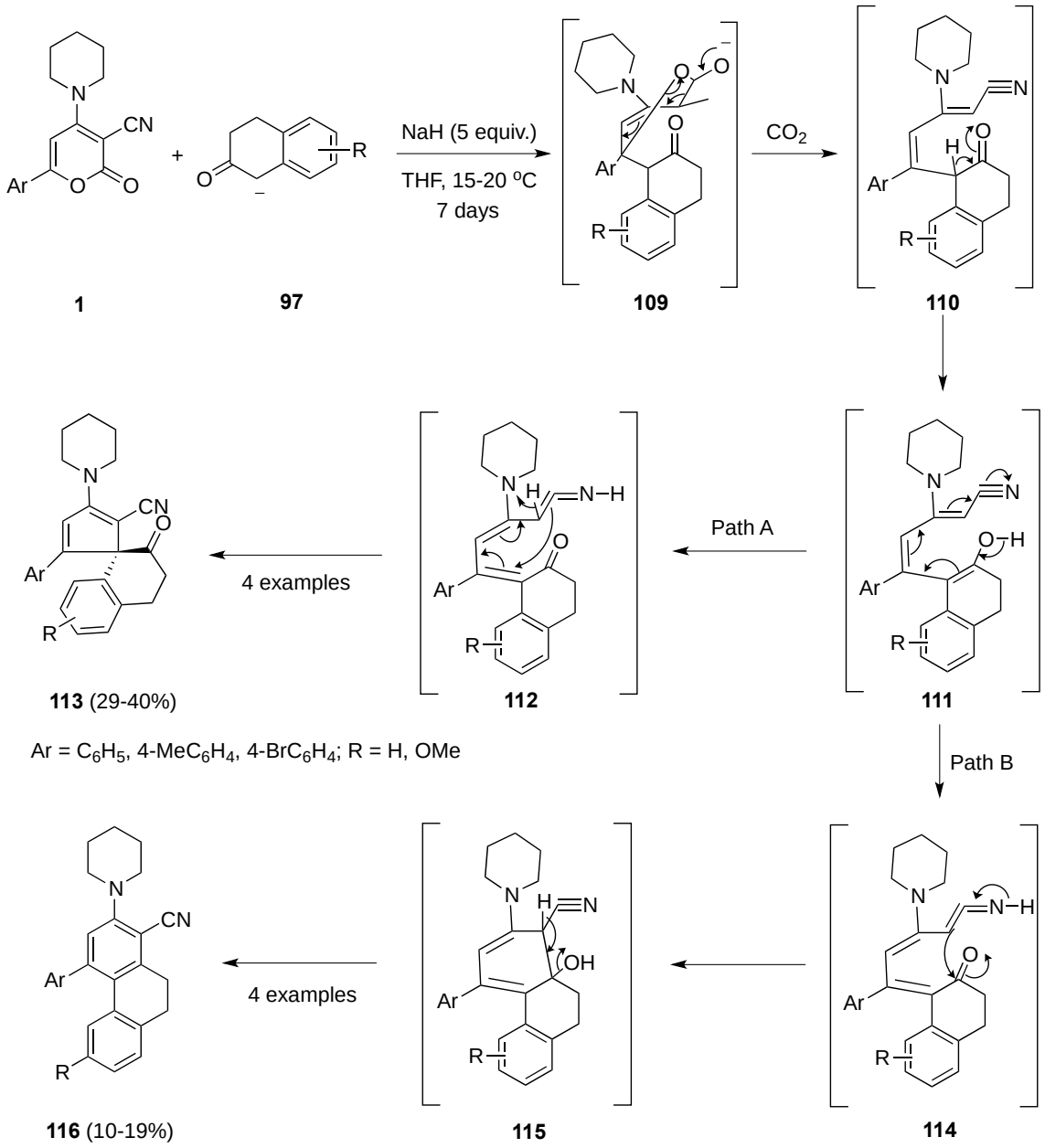
4-4. Synthesis of spirocyclic and phenanthrene-cored compounds

Later in 2010, Pratap and co-workers[97] described synthetic route for the preparation of partially reduced fused polycyclic scaffolds. The reaction of substrate **22** with different cyclic ketones **106** and 1,4-hexanedione monocycloalkene ketals **105** in alkaline conditions at ambient temperature afforded benzo[*c*]phenanthrenes **108** and its ketals **107** in excellent yields (Scheme 33).



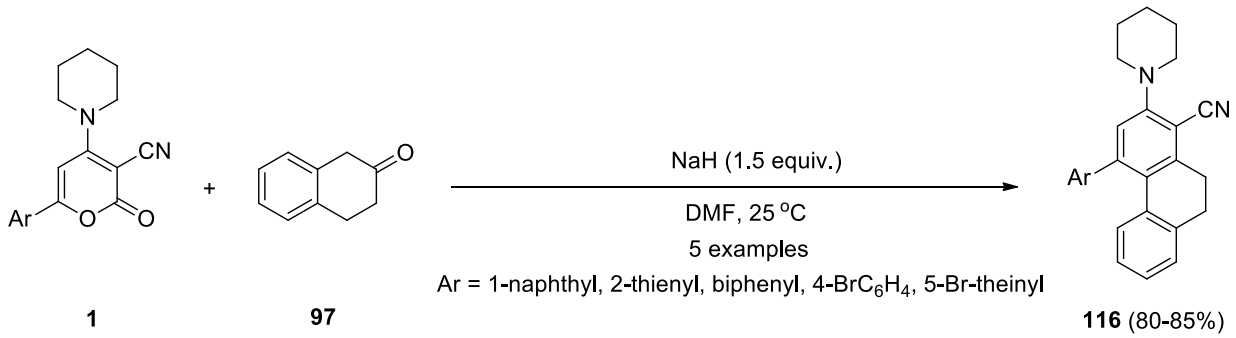
Scheme 33. Synthesis of partially reduced benzo[*c*]phenanthrenes **108** and its ketals **107**

In 2012, Ram and co-authors[98] developed a unique and prolong carbanion induced ring switching ring transformation of substituted parent precursors with cyclic nucleophile under basic conditions. The significant interactions of both electrophilic **1** and nucleophilic **97** parent partners were performed successfully with 2-tetralone **97** using 5.0 equiv. of NaH in THF at 15–20 °C for 7 days. The products **113** and **116** were achieved in useful to moderate yields. The mechanism begins with Michael addition of 2-tetralone to C-6 position of 2*H*-pyran-2-ones with the formation of intermediate **109**. Further through loss of carbon dioxide gave intermediate **110**, which on enolization provided intermediate **111**. After that intermediate **111** undergoes cyclization through generation of five membered ring producing corresponding spiranes **113**. Similarly, cyclization of **111** involving carbonyl functionality of ketone, followed by dehydration gave phenanthrenes **116** as product (Scheme 34).



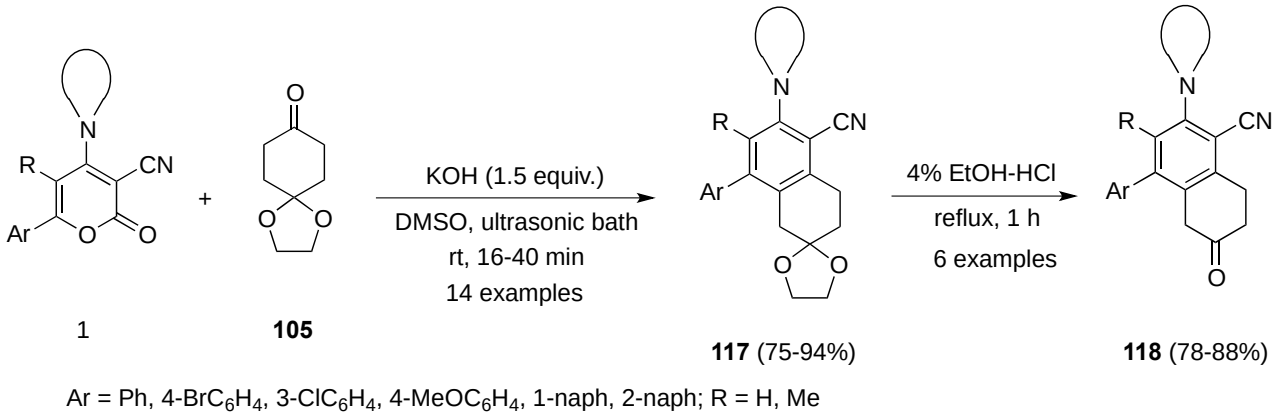
Scheme 34. Synthesis of functionalized spiranes **113** and phenanthrenes **116**

In 2014, Goel and co-authors[99] designed C_2-bridged dihydrophenanthrene (DHP) teraryls **116** *via* ring transformation of 2*H*-pyran-2-ones **1** with 2-tetralone **97** under mild reaction conditions using NaH as base and DMF as solvent at 25 °C for less than 10 minutes (Scheme 35). The desired products **116** were achieved in 80-85% yields. Derivatives showed blue emission from 462–493 nm in solution and 458–482 nm for solid.



Scheme 35. Synthesis of C_2-bridged dihydrophenanthrene (DHP) **116** from starting lactones **1**

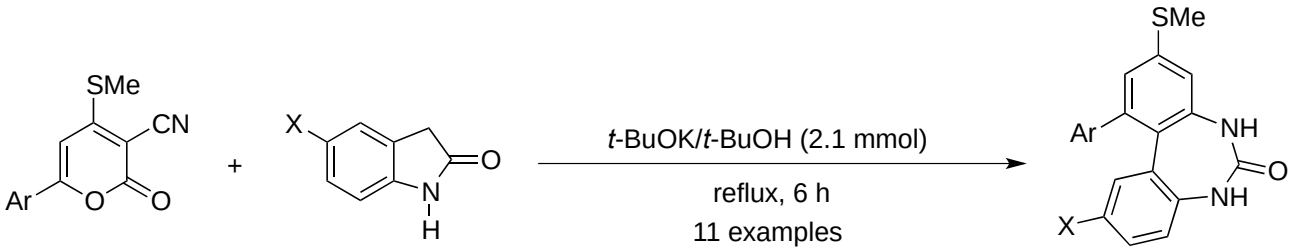
Recently, Singh and Shetgaonkar[100] successfully achieved functionalized spirocyclic ketals and 2-tetralones **118** in shorter reaction time under ultrasonic irradiation. The starting materials could be easily reacted with 1,4-cyclohexanedione monoethylene ketal **105** in DMSO at room temperature and effectively transformed in to desired ketals **117** yielding up to 75–94%. In order attain functionalized 2-tetralones **118**, further acetal group was cleaved/hydrolyzed by treatment of ketals with 4% ethanolic HCl at refluxed temperature for 1 h. The resulted expected products **118** were obtained in 78–88% yield. This procedure gave high yields of products in metal free environment with the tolerance of variety of functional groups (Scheme 36).



Scheme 36. Synthesis of functionalized ketals **117** and 2-tetralones **118** from 2*H*-pyran-2-ones **1**

4-5. Synthesis of diazepinones

Furthermore, Ram and coworkers[101] investigated the facile synthetic procedure for the preparation of functionalized 5,7-dihydro-6*H*-dibenzo[*d*,*f*][1,3]diazepin-6-ones **120** using cyclic carbanion source. The expected products **120** were achieved in moderate yield *via* substantial transformation of 2*H*-pyran-2-one-3-carbonitriles **1** and indolin-2-ones **119** were used as nucleophiles. These experiments were accomplished in THF with existence of potassium *tert*-butoxide or *in tert*-butanol at refluxed temperature for 6 h (Scheme 37).



1 **119** **120** (38-58%)

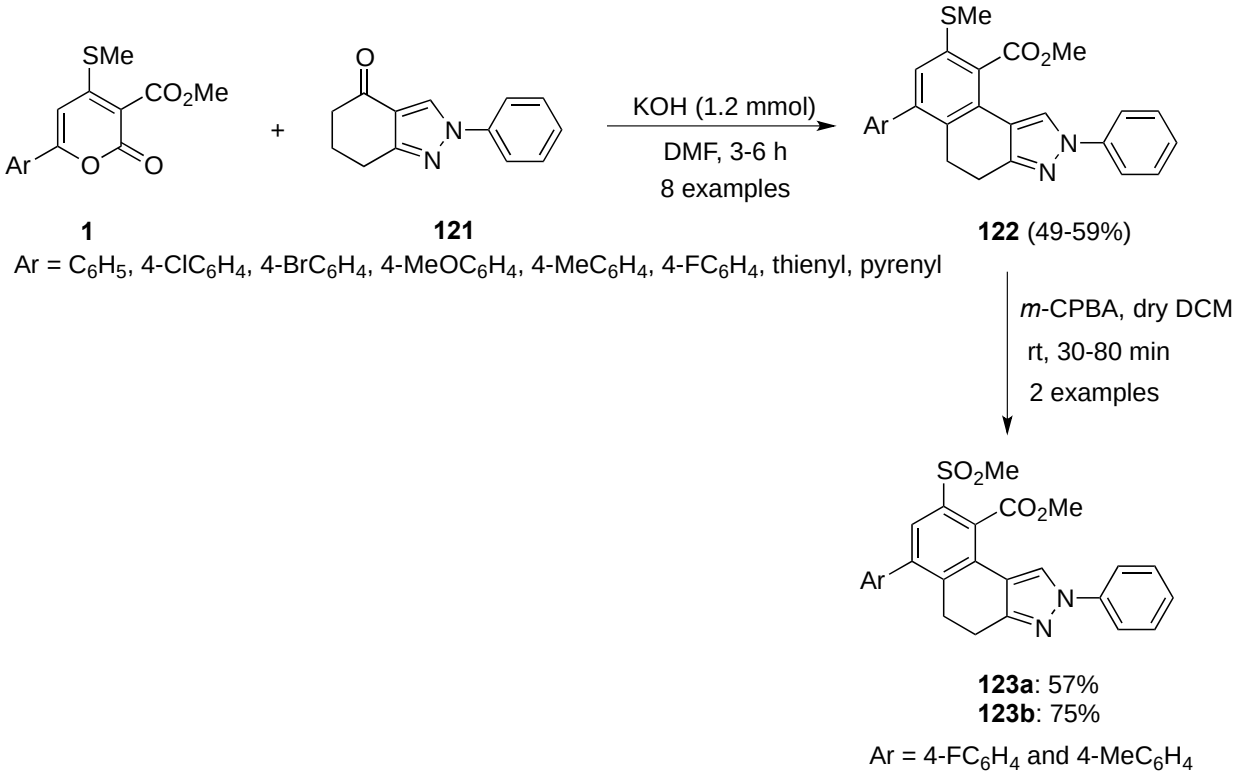
Ar = C_6H_5, 4-BrC_6H_4, 4-ClC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-pyridyl, 2-furyl, 2-thiophenyl, 4-acetamidophenyl, 2-naphthyl

Scheme 37. Synthesis of 5,7-dihydro-6*H*-dibenzo[*d*,*f*][1,3]diazepin-6-ones **120** from 2*H*-pyran-2-one-3-carbonitriles **1**

Additionally, same group in 2013 carried out synthesis of 3-alkenyl-2-oxindoles by new efficient and direct alkenylation of 6-aryl-4-methylthio-2*H*-pyran-2-one-3-carbonitriles via base catalyzed ring transformation strategy.[102]

4-6. Synthesis of 2*H*-benzo[*e*]indazole-9-carboxylate

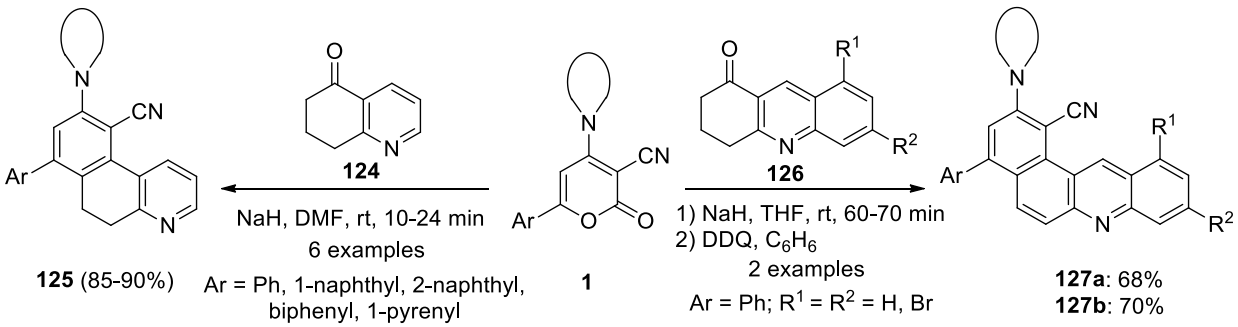
Meanwhile, Goel and co-workers[103] designed easy new distinct synthetic pathway for the construction of substituted 2*H*-benzo[*e*]indazole-9-carboxylate **122** from lactones **1** using ring transformation strategy. The base mediated transformation of lactones **1** with 2-phenyl-6,7-dihydro-2*H*-indazol-4(5*H*)-one **121** provided desired compounds **122** in moderate yields. The quality of prepared compounds was improved by their evaluation for biological activity. The products **122** exhibited very good tolerance for glucose uptake and hence proved as important units to cure diabetes with better lipid profile. The protocol was further extended to afford the significant oxidation of -SMe to -SO_2Me by *m*-CPBA in dry DCM at room temperature for 30–80 minutes to newly formed 2*H*-benzo[*e*]indazole-9-carboxylates **123a** and **123b** in moderate yields (Scheme 38).



Scheme 38. Base-mediated transformation of lactone **1** into 2*H*-benzo[*e*]indazole-9-carboxylate **122**

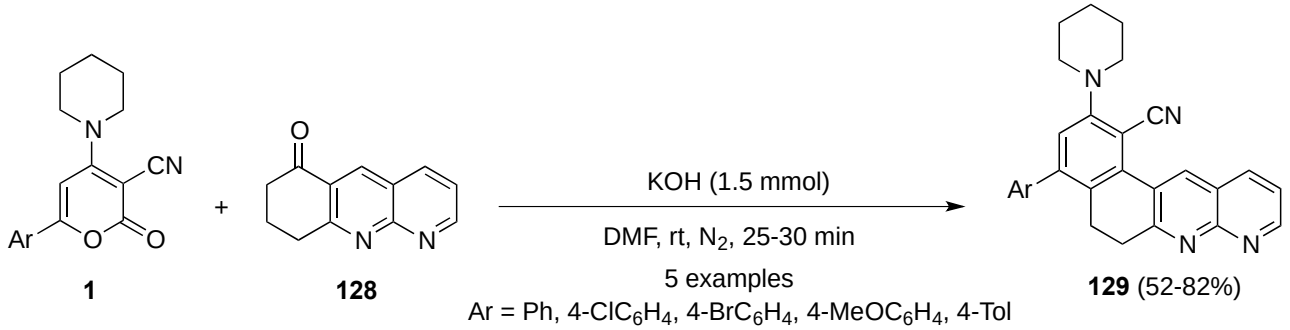
4-7. Synthesis of benzo[*f*]quinolones and benzo[α]acridines

In same way, further Goel and co-workers[104] in 2012 conveyed the synthesis of non-aggregating bipolar *N*-heterocyclic scaffolds like benzo[*f*]quinolones **125** and benzo[*α*]acridines **127**. The ring transformation of 2*H*-pyran-2-ones **1** with *N*-heterocyclic ketones **124** and **126** under mild reaction conditions provided the desired products **125** and **127** in high yields. The synthesized products possessed good potential in organic electronics and organic light emitting devices (OLEDs) (Scheme 39).



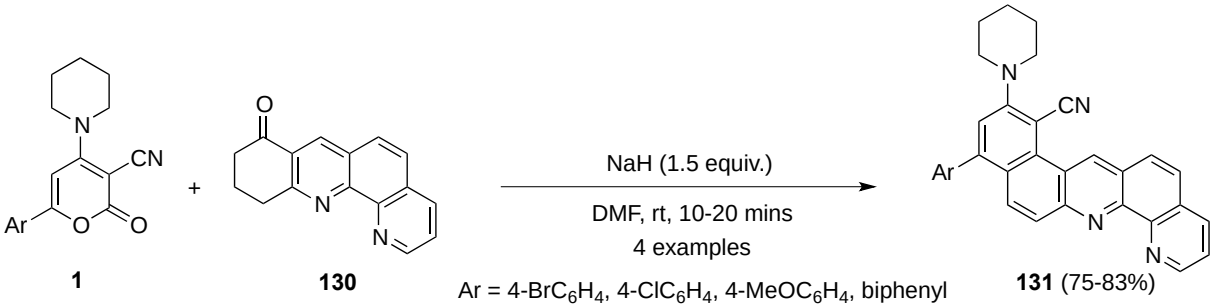
Scheme 39. Synthesis benzo[*f*]quinolones **125** and benzo[α]acridines **127** from lactones **1**

The ultimate synthesis of 5,6-dihydronaphtho[2,1-*b*]-1,8-naphthyridines **129** was also described using 8,9-dihydrobenzo[*b*]-1,8-naphthyridin-6(7*H*)-one **128** as carbanion source in same reaction conditions (Scheme 40).[82]



Scheme 40. Synthesis of functionalized naphthyridines **129** from lactones **1**

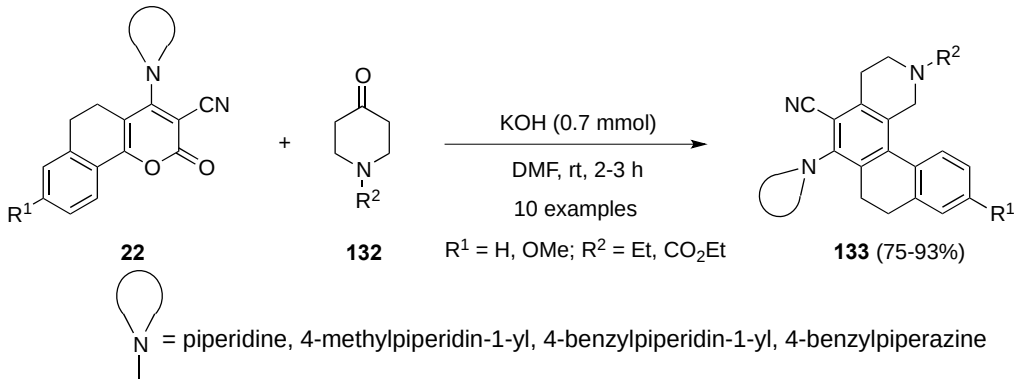
In 2015, Goel and group[105] also described synthesis of iron(III)-selective highly conjugated fluorescent compounds named as naphtho[2,1-*b*][1,10]phenanthrolines (NAPs) **131** in 75-83% in 10–20 minutes involving base promoted ring transformation of substituted 2*H*-pyran-2-ones **1** using fused cyclic nucleophilic ketone **130** under efficient reaction conditions (Scheme 41). One of the derivative (Ar = 4-BrC_6H_4) in the series was identified as direct visualizer of labile Fe^{+3} pools in a multicellular organism.



Scheme 41. Synthesis of naphtho[2,1-*b*][1,10]phenanthrolines (NAPs) **131** from lactones **1**

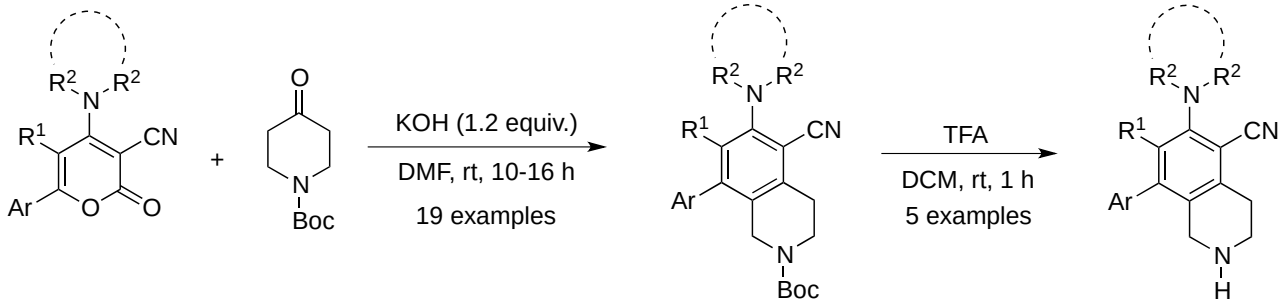
4-8. Synthesis of tetrahydroisoquinolines

In similar way, Pratap and group[106] explored the synthesis of a new class of moderately reduced polycyclic aromatic skeletons naphtho[2,1-*h*]isoquinolines **133** by reaction of starting lactones **22** with heterocyclic nucleophiles *N*-substituted-4-piperidone **132**. The reaction products **133** were obtained in good to excellent yields (Scheme 42).



Scheme 42. Synthesis reduced polycyclic aromatic skeletons naphtho[2,1-*h*]isoquinolines **133**

In continuation of above work, Singh and Kole[107] reported versatile and convenient protocol for the synthesis of multifunctionalized tetrahydroisoquinolines **135** and **136** under mild reaction conditions. In this approach, highly flexible tetrahydroisoquinolines **135** were accomplished by nucleophile-mediated ring transformation reaction of polysubstituted 2-pyrones **1** using *tert*-butyl-4-oxopiperidine-1-carboxylate **134** as nucleophile in polar aprotic solvent with KOH at ambient temperature for 10–16 h (Scheme 43). These reactions worked smoothly producing *N*-Boc-protected products **135** in good to excellent yields. The substrate scope successfully covered both electron donating and electron withdrawing groups. In addition, the reaction was proceeding well with substrates embedded with naphthyl and thienyl ring at C-6 position. Furthermore, acid mediated deprotection of Boc group provided tetrahydroisoquinolines **136** in 86–94% yields. This methodology is far superior in terms of simplicity in workup and use of readily available reagents in place of expansive catalysts.



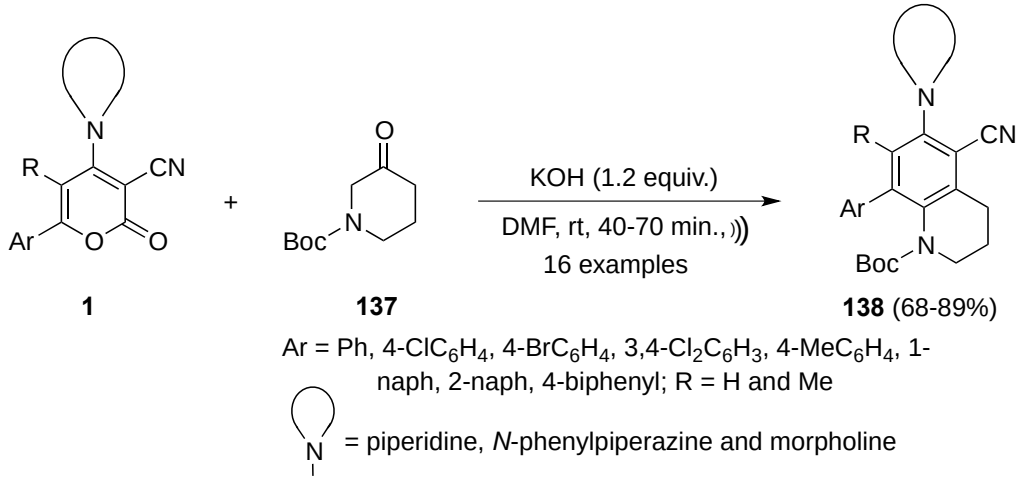
1 **134** **135** (66-95%) **136** (86-94%)

Ar = Ph, 4-ClC_6H_4, 4-BrC_6H_4, 2,4-$Cl_2C_6H_3$, 3,4-$(MeO)_2C_6H_3$, 4-$MeOC_6H_4$, 4-MeC_6H_4, 1-naph, 2-naph, 2-thienyl; R^1 = H, Me

$R^2_N R^2$ = piperidine, *N*-methylpiperazine, *N*-phenylpiperazine, pyrrolidine, morpholine, diethylamine

Scheme 43. Synthesis of tetrahydroisoquinolines **135** and **136** via transformation of 2*H*-pyran-2-ones **1**

Very recently, Singh *et al.*[108] achieved the rapid synthesis of substituted blue fluorescing tetrahydroisoquinolines **138** from similar parent substrates **1** following the above method. The parent lactones **1** were reacted with *tert*-butyl-3-oxopiperidine-1-carboxylate **137** under ultrasonic bath at room temperature for the duration of 40–70 minutes (Scheme 44). Many functionalities were tolerated with the structural pattern. This molecules displayed good emission and positive solvatochromism based on polarity of solvents.



Scheme 44. Synthesis of tetrahydroisoquinolines **138** from parent lactones **1**

CONCLUSION

Ring transformation methodologies are generally used method for the construction of numerous multi-functionalized compounds formed by the construction of new ring involving a typical mechanism. The type of compounds listed in this review found to display their effective participation in several pharmacological processes as well as important scaffolds used in material science, beneficial at industrial level as precursors. The ring transformations of substituted mimicking 2*H*-pyran-2-ones are used for designing various interesting scaffolds of extraordinary biological significance. The scope of this review mainly involves focus on the compounds, which could assemble the important entity of many drug molecules of biological essential. So far, several scaffolds that have been reported *via* ring transformation reactions are highly fluorescent in nature due to possible conjugation and presence of different functionalities in the structural design as well as used as an important entities as phosphors and in organic light emitting devices (OLEDs) due their outstanding photophysical and electrochemical properties.

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