



# Recent development in the synthesis of heterocycles by 2-naphthol-based multicomponent reactions

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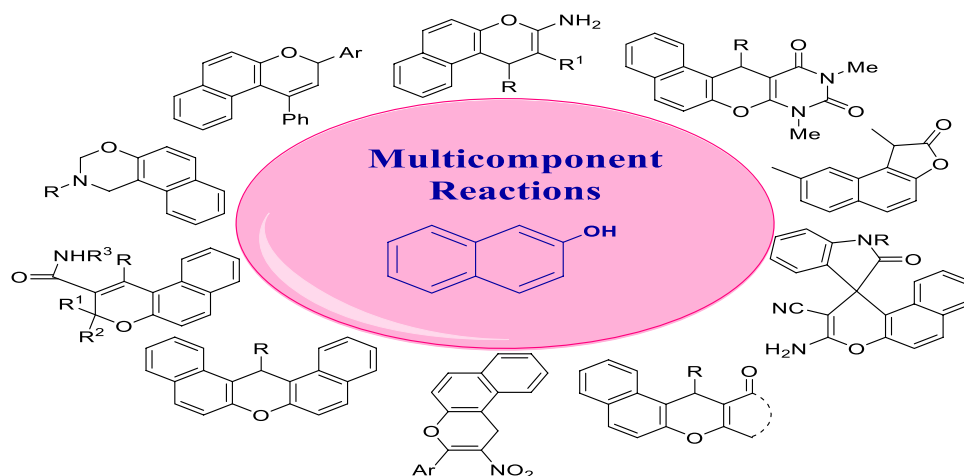
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## Abstract

2-Naphthol or  $\beta$ -naphthol is an important starting material that has drawn great attention in various organic transformations because of its attributes, such as low cost, easy to handle and eco-friendliness. The electron-rich aromatic framework of 2-naphthol with multiple reactive sites allows it to be utilized in several kinds of organic reactions eventuated to several organic molecules with potent biological properties. Multicomponent reaction approach has been tremendously utilized to explore the synthetic utility of 2-naphthol for the construction of diverse N/O-containing heterocyclic framework. In this review, we summarize recent data pertaining to multicomponent reactions, wherein heterocyclic compounds are synthesized utilizing 2-naphthol as one of the starting materials. It is anticipated that this review will stimulate the researchers to design new multicomponent strategies complying with the Green Chemistry principles for the further exploitation of 2-naphthol for the rapid synthesis of versatile biologically relevant heterocycles.

## Graphic abstract

This review provides a concise overview of the different 2-naphthol based multicomponent reactions utilized for the construction of diverse bioactive heterocyclic scaffold.



**Keywords** 2-Naphthol · Multicomponent reactions · Heterocycles · One-pot synthesis · Sustainable chemistry

## Introduction

2-Naphthol also known as  $\beta$ -naphthol, 2-hydroxynaphthalene with molecular formula  $C_{10}H_8O$  and melting point 122 °C, is a naphthalene homologue of phenol, bearing hydroxyl group at 2-position. 2-Naphthol has attracted

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considerable attention as valuable precursors for the synthesis of diverse heterocyclic compounds in organic synthesis owing to the presence of three available nucleophilic site, i.e., C-1 position, phenolic oxygen and C-3 position (to a lesser extent). This unique reactivity of 2-naphthol along with its easy accessibility and handling, moisture stability and low cost makes it a fascinating candidate for organic chemists. 2-Naphthol has been used in the design and synthesis of privileged scaffolds like xanthenes, chromenes, oxazines, furans, naphthopyrans, etc. Heterocyclic compounds hold a prominent position in medicinal chemistry owing to their wide spectrum of biological activities such as antimalarial [1], antimicrobial [2], antitumor [3], anticancer [4], antidepressant [5], antiviral [6], antidiabetic [7], anti-inflammatory [8] and anti-HIV [9]. Moreover, they also contribute in the field of material science [10], dyes and pigment science [11] as well as agrochemistry [12]. Therefore, there is considerable thrust for the development of efficient synthetic strategies for producing these compounds. MCRs open diverse avenues to create novel concatenations in one-pot fashion leading to diverse biologically potent heterocyclic scaffolds [13, 14]. Having a cascade of reactions occurring in one pot is highly beneficial in the context of modern trends for organic synthesis, where sustainability is as relevant as efficiency and selectivity. Multicomponent reactions being atom economic, efficient and extremely convergent in nature offer a number of advantages over stepwise sequential approaches [15–17]. Ring-forming multicomponent reactions involving 2-naphthol promise an enhancement of structural complexity and functional diversity. This review provides an account of synthesis of a variety of heterocyclic compounds via one-pot multicomponent reactions of 2-naphthol.

## Synthesis of heterocyclic compounds via multicomponent reactions of 2-naphthol

### Xanthene

Xanthenes and benzoxanthenes are important oxygen-containing heterocyclic scaffolds that are found in natural products as well as in pharmaceutically active agents. The xanthene nucleus also referred as 9*H*-xanthene corresponds to dibenzo[*b,e*]pyran (Fig. 1). Furthermore, based on their orientation of annulation, benzoxanthenes and their derivatives essentially exist as three plausible isomers, benzo[*a*]xanthene 2, benzo[*b*]xanthene 3 and benzo[*c*]xanthene 4 (Fig. 1). They exhibit an array of biological activities like anti-inflammatory [18], antibacterial [19], antiviral [20], antioxidant [21] and antiplasmodial [22]. Moreover, they also find applications as dyes [23], fluorescent materials for the visualization of biomolecules [24] and in laser

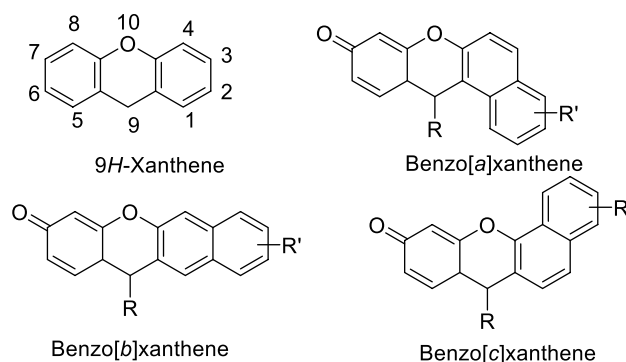
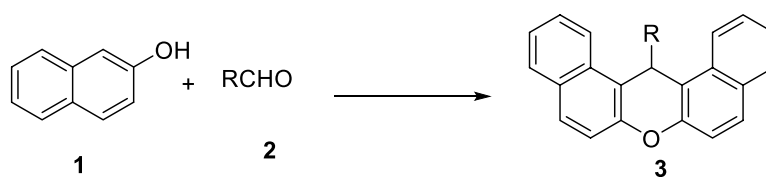


Fig. 1 Xanthenes

technology [25]. A large number of methods have been reported in the literature for the preparation and scaffold manipulation of these compounds.

The synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes 3 by condensation of 2-naphthol 1 with aldehydes 2 has been reported utilizing various Brønsted acid catalysts (Scheme 1, Table 1).

Development of efficient synthetic methodologies has become imperative in the field of organic synthesis. In this context, the principles of ‘Green Chemistry’ such as atom economy, waste reduction and efficiency are given utmost importance. Compared with homogeneous catalysts, heterogeneous catalysts have received much attention owing to their merits like high activity, ease of separation and recycling. Several methodologies involving use of heterogeneous Brønsted acid catalysts under solvent-free conditions have been reported for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes 3 like silica-supported perchloric acid (HClO<sub>4</sub>-SiO<sub>2</sub>) [26], silica sulfuric acid [27], cellulose sulfuric acid [28], aluminum hydrogen sulfate (Al(HSO<sub>4</sub>)<sub>3</sub>) [29], preyssler-type heteropolyacid, H<sub>14</sub>[NaP<sub>5</sub>W<sub>30</sub>O<sub>110</sub>] [30], poly(4-vinylpyridinium) hydrogen sulfate (P(4-VPH)HSO<sub>4</sub>) [31], silica-supported fluoroboric acid (HBF<sub>4</sub>-SiO<sub>2</sub>) [32], Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-imid-H-<sub>3</sub>PMO<sub>12</sub>O<sub>40</sub> nanoparticles [33], PEG-SO<sub>3</sub>H [34], sulfonated diatomite (diatomite-SO<sub>3</sub>H) [35], cucurbit[6]uril-OSO<sub>3</sub>H (CB[6]-OSO<sub>3</sub>H) [36], amberlyst-15 [37], phosphosulfonic acid (PSA) [38], silicotungstic acid (H<sub>4</sub>[SiW<sub>12</sub>O<sub>40</sub>]) [39], silica-supported ammonium dihydrogen phosphate (NH<sub>4</sub>·H<sub>2</sub>PO<sub>4</sub>·SiO<sub>2</sub>) [40], tungstophosphoric acid/zirconia composites (ZrTPA60B-T<sub>100</sub>) [41], magnetite-sulfuric acid (Fe<sub>3</sub>O<sub>4</sub>·SO<sub>3</sub>H) magnetic nanoparticles [42], sulfonated single walled carbon nanotube (SWCNT-SO<sub>3</sub>H) [43], sulfonic acid-functionalized mesoporous SBA-15 (SBA-15/SO<sub>3</sub>H) [44], sodium hydrogen sulfate (NaHSO<sub>4</sub>·H<sub>2</sub>O) [45], *p*-sulfonic acid calix[4]arenes [46], sulfamic acid [47], DOWEX -50 W [48], D-camphorsulfonic acid (CSA) [49], Indion-130 [50] and NaHSO<sub>4</sub>-SiO<sub>2</sub> [51]. These solvent-free protocols have emerged as a powerful



**R =** C<sub>6</sub>H<sub>5</sub>, 4-XC<sub>6</sub>H<sub>4</sub> (X= Cl, Br), 3-XC<sub>6</sub>H<sub>4</sub> (X=Cl,Br,F), 2-ClC<sub>6</sub>H<sub>4</sub>, 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 4-Me<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 2-MeOC<sub>6</sub>H<sub>4</sub>, 2-Naphthyl, 2-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 5-Br-2-HOC<sub>6</sub>H<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, Me<sub>2</sub>CH, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>, 9-Anthryl, 4-NCC<sub>6</sub>H<sub>4</sub>, 2,6-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3-MeC<sub>6</sub>H<sub>4</sub>, 3-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 3-FC<sub>6</sub>H<sub>4</sub>, 4-F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>, 2-Fluorenyl, 2-Pyridyl, 3-O<sub>2</sub>N-4-ClC<sub>6</sub>H<sub>3</sub>, 4-OHC<sub>6</sub>H<sub>4</sub>, 3-OHC<sub>6</sub>H<sub>4</sub>, 3-F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>, Me<sub>2</sub>CHCH<sub>2</sub>, 1-Naphthyl, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, 2,5-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 4-MeOCC<sub>6</sub>H<sub>4</sub>, 2-MeO-3OH-C<sub>6</sub>H<sub>4</sub>, 2,4-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3-NO<sub>2</sub>-4-HO-C<sub>6</sub>H<sub>3</sub>, 2,4,6-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>

**Scheme 1** Synthesis of 14-aryl-14H-dibenzo[*a,j*]xanthenes **3**

**Table 1** Synthesis of 14-aryl-14H-dibenzo[*a,j*]xanthenes **3** by Brønsted acid catalysts

Catalyst, reaction conditions	Examples	Yield (%)	References
HClO <sub>4</sub> -SiO <sub>2</sub> , 125 °C	14	88–98	[26]
SiO <sub>2</sub> -SO <sub>3</sub> H, 125 °C	9	81–93	[27]
Cellulose sulfuric acid, 110 °C	14	81–97	[28]
Al(HSO <sub>4</sub> ) <sub>3</sub> , 125 °C	10	85–91	[29]
H <sub>14</sub> [NaP <sub>5</sub> W <sub>30</sub> O <sub>110</sub> ], 90 °C	10	50–99	[30]
P(4-VPH)HSO <sub>4</sub> , 100 °C	13	90–96	[31]
HBF <sub>4</sub> -SiO <sub>2</sub> , 120 °C	23	87–95	[32]
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -imid-H-3-PMo <sub>12</sub> O <sub>40</sub> Nps, 110 °C	15	79–95	[33]
PEG-SO <sub>3</sub> H, 125 °C	14	82–97	[34]
Diatomite- SO <sub>3</sub> H, 90 °C	16	82–96	[35]
CB [6] - OSO <sub>3</sub> H, 110 °C	8	82–96	[36]
Amberlyst-15, 125 °C	11	80–94	[37]
PSA, 80 °C	11	74–86	[38]
H <sub>4</sub> [SiW <sub>12</sub> O <sub>40</sub> ], 110 °C	10	90–97	[39]
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> /SiO <sub>2</sub> , 125 °C	14	73–98	[40]
ZrTPA60B-T <sub>100</sub> , 130 °C	10	60–99	[41]
Fe <sub>3</sub> O <sub>4</sub> ·SO <sub>3</sub> H magnetic Nps, 100 °C	7	88–95	[42]
SWCNTs-SO <sub>3</sub> H, 70 °C	15	55–98	[43]
SBA-15/SO <sub>3</sub> H, 90–95 °C	10	79–85	[44]
NaHSO <sub>4</sub> ·H <sub>2</sub> O, 125 °C	12	87–97	[45]
NaHSO <sub>4</sub> ·H <sub>2</sub> O, MW	12	83–94	[45]
<i>p</i> -Sulfonic acid calix [4] arenes, 80 °C	10	88–98	[46]
Sulfamic acid, 125 °C	13	90–95	[47]
Sulfamic acid/MW	13	92–96	[47]
DOWEX-50 W, 70 °C	8	78–91	[48]
(±)-CSA, MW	10	54–98	[49]
Indion-130, 110 °C	13	76–92	[50]
NaHSO <sub>4</sub> ·SiO <sub>2</sub> , 125 °C	14	82–94	[51]
AFS-1, H <sub>2</sub> O, r.t.	5	75–82	[52]
PVSA, H <sub>2</sub> O, 90 °C	17	78–93	[53]
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> /SiO <sub>2</sub> , H <sub>2</sub> O, US	16	85–94	[54]
Mg(HSO <sub>4</sub> ) <sub>2</sub> , 60 °C	16	85–97	[55]
Mg(HSO <sub>4</sub> ) <sub>2</sub> , US	16	85–98	[55]
<i>p</i> TSA, 125 °C	7	81–96	[57]
<i>p</i> TSA, DCE, reflux	7	80–93	[57]
TCT, 110 °C	12	85–96	[58]

tool in the light of current paradigm shift to “Green Chemistry” due to avoidance of harmful organic solvents, decrease energy consumption, short reaction time, simple work-up, ease of isolation, environmental benign nature. Furthermore, the synergy of solvent-free reactions with non-conventional energy source like microwave irradiation used by authors [45, 47, 49] illustrates another facet of sustainable chemistry.

Furthermore, replacement of hazardous solvents with environmentally benign reaction media like water, polyethylene glycol and ionic liquids is also one of the major focus areas of green chemistry. The above condensation has also been reported utilizing acid-functionalized hybrid mesoporous organosilica, AFS-1 [52] and polyvinylsulfonic acid (PVSA) [53] in aqueous media. The high polarity, hydrogen bonding capability and hydrophobic effect of water are also known to enhance the rate of reaction. Mahdavinia and co-workers [54] have developed an ultrasound-assisted protocol for the synthesis of **3** in aqueous media using silica-supported ammonium dihydrogen phosphate ( $\text{NH}_4\cdot\text{H}_2\text{PO}_4\cdot\text{SiO}_2$ ) as catalyst. Significant reduction in reaction time and improvement in yield of the product were observed by authors under ultrasonic irradiation as compared to conventional heating method.

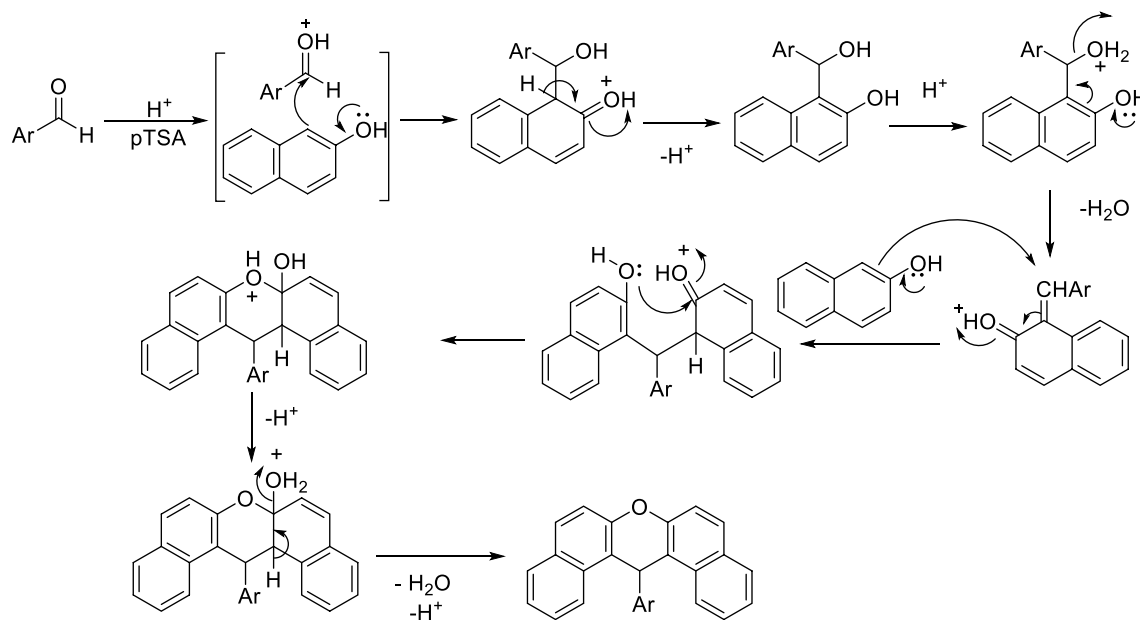
Solid Brønsted acid catalysts like magnesium hydrogen sulfate ( $\text{Mg}(\text{HSO}_4)_2$ ) [55], boric acid ( $\text{H}_3\text{BO}_3$ ) [56], *p*-toluene sulfonic acid (*p*TSA) [57], wet-2,4,6-trichloro[1,3,5]triazine (TCT) [58] were also employed for the synthesis of **3**.

The probable mechanism for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes is shown in Scheme 2.

Several Lewis acidic catalysts have been reported to catalyze the condensation of 2-naphthol and aldehydes for the

synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes **3** such as LiBr [59], ferric chloride ( $\text{FeCl}_3$ ) [60], ytterbium triflate ( $\text{Yb}(\text{OTf})_3$ ) [61], ceric ammonium nitrate (CAN) [62], iron triflate ( $\text{Fe}(\text{OTf})_3$ ) [63], bismuth chloride [64], tungsten(VI) chloride ( $\text{WCl}_6$ ) [65], tantalum chloride ( $\text{TaCl}_5$ ) [66], zirconium(IV) oxide chloride ( $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ ) [67], ceric sulfate ( $\text{Ce}(\text{SO}_4)_2$ ) [68], tetra-*n*-butylammonium bromide (TBAB) [69],  $\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$  [70], dipyridine copper chloride ( $\text{CuPy}_2\text{Cl}_2$ ) [71], dipyridine cobalt chloride ( $\text{CoPy}_2\text{Cl}_2$ ) [72], iodine [73, 74], silica-supported boron trifluoride ( $\text{BF}_3\cdot\text{SiO}_2$ ) [75] and Selectfluor<sup>TM</sup> [76]. Nanocatalysts like CuS quantum dots (CuS QDs) [77], nano-CuO [78], nano-ZnO [79],  $\text{Fe}^{2+}$  supported on hydroxyapatite-core-shell- $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles ( $\gamma\text{-Fe}_2\text{O}_3\text{-HAp-Fe}^{2+}$  Nps) [80], poly(4-vinylpyridine)-supported copper iodide nanoparticles (P4VPy-CuI Nps) [81] and ruthenium anchored on multi-walled carbon nanotubes ( $\text{Ru@SH-MWCNT}$ ) [82] have also been utilized for the above condensation (Scheme 1) (Table 2). The use of nanocatalysts offers unique properties such as high surface area, enhanced catalytic sites, chemical inertness, durability and insolubility in most solvents. Moreover, their high surface allows higher loads of the catalytic sites.

Catalyst-free condensation of 2-naphthol **1** with aldehydes **2** has been reported in various acidic ionic liquids like 1,10-disulfo-[2,20-bipyridine]-1,10-dium chloride, [BiPy] $(\text{SO}_3\text{H})_2\text{Cl}$  [83], DSIMHS [84], 1-methyl-3-propane sulfonic-imidazolium hydrosulfate ([MIMPS] $\text{HSO}_4$ ) [85], di-*n*-propylammonium hydrogen sulfate ( $[(n\text{-propyl})_2\text{NH}_2]\text{HSO}_4$ ) [86], 1,3-disulfonic acid imidazolium carboxylate ionic liquids (i.e., [DISM] $\text{CCl}_3\text{COO}$  & [DISM] $\text{CF}_3\text{COO}$ )



**Scheme 2** Mechanism for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes

**Table 2** Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes **3** by Lewis acidic catalysts

Catalyst, reaction conditions	Examples	Yield (%)	References
LiBr, 90 °C	11	77–84	[59]
LiBr, MW	11	78–86	[59]
FeCl <sub>3</sub> , 100 °C	13	81–97	[60]
Yb(OTf) <sub>3</sub> , [BPy]BF <sub>4</sub> , 110 °C	14	80–95	[61]
CAN, 120 °C	13	90–97	[62]
Fe(OTf) <sub>3</sub> , 60 °C	13	84–94	[63]
BiCl <sub>3</sub> , 110 °C	13	74–98	[64]
WCl <sub>6</sub> , 110 °C	13	78–98	[65]
TaCl <sub>5</sub> , 100 °C	15	59–96	[66]
ZrOCl <sub>2</sub> ·8H <sub>2</sub> O, 125 °C	12	90–96	[67]
Ce(SO <sub>4</sub> ) <sub>2</sub> , 100 °C	14	65–96	[68]
Ce(SO <sub>4</sub> ) <sub>2</sub> , MW	14	70–95	[68]
TBAB, 125 °C	13	65–90	[69]
TBAB, MW	13	78–95	[69]
P <sub>2</sub> O <sub>5</sub> /Al <sub>2</sub> O <sub>3</sub> , MW	20	60–95	[70]
CuPy <sub>2</sub> Cl <sub>2</sub> , 80 °C	13	92–96	[71]
CoPy <sub>2</sub> Cl <sub>2</sub> , 85 °C	16	65–97	[72]
Iodine, MW	10	75–93	[73]
Iodine, CHCl <sub>3</sub> , 60–70 °C	10	65–91	[73]
Iodine, 90 °C	13	84–95	[74]
BF <sub>3</sub> ·SiO <sub>2</sub> , 60 °C	16	82–97	[75]
BF <sub>3</sub> ·SiO <sub>2</sub> , US	16	85–98	[75]
Selectflour™, 125 °C	15	90–95	[76]
CuS QDs, 80 °C	8	87–95	[77]
CuO Nps, 100 °C	8	82–95	[78]
ZnO Nps, 80 °C	16	78–95	[79]
γ-Fe <sub>2</sub> O <sub>3</sub> -HAp-Fe <sup>2+</sup> Nps, 90 °C	20	85–95	[80]
P4VPy-CuI Nps, 80 °C	15	88–92	[81]
Ru@SH-MWCNT, EtOH, reflux	10	82–94	[82]
Ru@SH-MWCNT, EtOH, US	10	88–96	[82]

[87]) as well as basic ionic liquid like bis-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepinium-ethyl disulfate [DBU]<sub>2</sub>EDS [88]. The task-specific ionic liquids serve the dual role of catalyst as well as solvent and bears interesting properties like excellent chemical and thermal stability, non-volatility, good solvating ability, wide liquid range as well as ease of recyclability. Several catalysts were also employed in ionic liquid as reaction medium such as trifluoroacetic acid in TMGT [89], Mg(BF<sub>4</sub>)<sub>2</sub> doped in [Bmim]BF<sub>4</sub> [90] and 2-1'-methylimidazolium-3-yl-1-ethyl sulfate in [Bmim]BF<sub>4</sub> [91] (Scheme 1, Table 3). The integrity of the TMGT [89] and [Bmim]BF<sub>4</sub> [90] remains reasonably unchanged after separation from the reaction mixture and was reportedly recycled several times without any loss of activity.

The synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives **6** via one-pot condensation reaction of 2-naphthol **1** with aldehydes **2** and dimedone **4**/

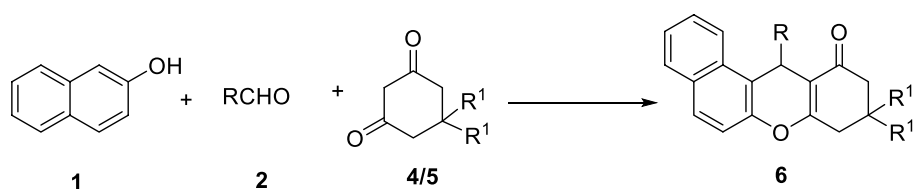
**Table 3** Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes **3** in ionic liquids

Catalyst, reaction conditions	Examples	Yield (%)	Reference
[BiPy](SO <sub>3</sub> H) <sub>2</sub> Cl <sub>2</sub> , 90 °C	9	80–98	[83]
DSIMHS, 90 °C	13	88–95	[84]
[MIMPS]HSO <sub>4</sub> , 100 °C	14	75–96	[85]
[ <i>n</i> -Pr <sub>2</sub> NH <sub>2</sub> ]HSO <sub>4</sub> , 80 °C	7	65–70	[86]
[DISM]CCl <sub>3</sub> COO, 100 °C	8	78–92	[87]
[DSIM]CF <sub>3</sub> COO, 90 °C	8	85–97	[87]
[DBU] <sub>2</sub> EDS, 120 °C	5	88–95	[88]
TFA, TMGT, 75 °C	13	86–97	[89]
[Bmim]BF <sub>4</sub> -Mg(BF <sub>4</sub> ) <sub>2</sub> , 80 °C	11	82–97	[90]
2-1'-Methylimidazolium-3-yl-1-ethyl sulfate, [Bmim]BF <sub>4</sub> , 80 °C	16	88–95	[91]

cyclohexa-1,3-dione **5** has been reported by Brønsted acids both liquids like H<sub>2</sub>SO<sub>4</sub> [92], methanesulfonic acid [93] and solid such as dodecatungstophosphoric acid [94], *p*-dodecylbenzenesulfonic acid (DBSA) [95], *p*TSA [92, 96], HY zeolite [97], 1,3,5-triazo-2,4,6-triphosphorine-2,2,4,4,6,6-hexachloride supported on boehmite nanoparticles (BNPs-TAPC) [98], nanoparticle silica-supported sulfuric acid (NPs SiO<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub>) [99], polymeric catalyst [poly(AMPS-co-AA)] [100], boronsulfonic acid (B(HSO<sub>4</sub>)<sub>3</sub>) [101], caro's acid-silica [102], *N*-sulfonic acid modified poly(styrene-maleic anhydride) (SMI-SO<sub>3</sub>H) [103], polyvinylpyrrolidone-supported triflic acid (PVPP.OTf) [104], nanocrystalline TiO<sub>2</sub>-HClO<sub>4</sub> [105] and silica-supported catalysts (HBF<sub>4</sub>/SiO<sub>2</sub>) [106] (Scheme 3, Table 4). The use of homogeneous catalysts like sulfuric acid and methanesulfonic acid has some disadvantages like corrosive nature of catalyst and more laborious work-up. The application of natural catalysts like lignosulfonic acid [107], citric acid [108], cellulose-SO<sub>3</sub>H [109], glucose sulfonic acid [110], D-xylonic acid [111], being efficient, cost-effective and biodegradable contributes to the green credentials of these protocols.

The mechanism for the formation of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives **6** in the presence of Brønsted acid (*p*TSA) is depicted in Scheme 4.

Solid catalysts showing Lewis acidic nature were reportedly used to bring the condensation of 2-naphthol **1** with cyclohexane-1,3-dione derivatives (**4/5**) and aldehydes **2** like CAN [62], ruthenium anchored on multi-walled carbon nanotubes [82], iodine [112, 113], ammonium chloride (NH<sub>4</sub>Cl) [114], cerium(III) chloride (CeCl<sub>3</sub>) [115], InCl<sub>3</sub>/P<sub>2</sub>O<sub>5</sub> [116], strontium triflate (Sr(OTf)<sub>2</sub>) [117], alum [118], ruthenium chloride hydrate [119], nano-TiCl<sub>4</sub>/SiO<sub>2</sub> [120], rice husk [121], Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O [122], Cu/SiO<sub>2</sub> [123], manganese perchlorate [124], tetrabutylammonium fluoride (TBAF) [125], cerium-impregnated-MCM-41 [126], chitosan synergistically enhanced by successive Fe<sub>3</sub>O<sub>4</sub>



**R** = C<sub>6</sub>H<sub>5</sub>, 4-XC<sub>6</sub>H<sub>4</sub> (X= Cl, Br, F), 3-XC<sub>6</sub>H<sub>4</sub> (X= Cl, Br, F), 2-XC<sub>6</sub>H<sub>4</sub> (X =Cl, Br), 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 3,5-(OMe)<sub>2</sub>-4-OHC<sub>6</sub>H<sub>2</sub>, Cyclohexyl, 4-MeOC<sub>6</sub>H<sub>4</sub>, 3-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 3-MeOC<sub>6</sub>H<sub>4</sub>, 3-MeC<sub>6</sub>H<sub>4</sub>, 4-OHC<sub>6</sub>H<sub>4</sub>, 2-HO-3-EtOC<sub>6</sub>H<sub>3</sub>, 2-MeC<sub>6</sub>H<sub>4</sub>, 2-MeOC<sub>6</sub>H<sub>4</sub>, Me<sub>2</sub>CHCH<sub>2</sub>, 3,4,5-(OMe)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 2-Thienyl, 2-OHC<sub>6</sub>H<sub>4</sub>, 3,4-(Me)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3-O<sub>2</sub>N-4-ClC<sub>6</sub>H<sub>3</sub>, 3-O<sub>2</sub>N-4-ClC<sub>6</sub>H<sub>3</sub>, 3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 2-MeOC<sub>6</sub>H<sub>4</sub>, CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, 5-Br-2-HO-C<sub>6</sub>H<sub>3</sub>, Me<sub>2</sub>CH, 4-OHC<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, C<sub>4</sub>H<sub>9</sub>, Piperonyl, 2-HO-3-MeOC<sub>6</sub>H<sub>3</sub>, CH<sub>3</sub>CH=CH, 2-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>CH=CH, CMe<sub>3</sub>, 3,4-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2-Pyridyl, 1-Naphthyl, 2-Naphthyl, 3-BrC<sub>6</sub>H<sub>4</sub>, 2-OHC<sub>6</sub>H<sub>4</sub>, 4-HO-3-MeOC<sub>6</sub>H<sub>3</sub>, 2,3-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,3-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 5-NO<sub>2</sub>-2-HO-C<sub>6</sub>H<sub>3</sub>,

**Scheme 3** Synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones **6**

**Table 4** Synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives **6** catalyzed by Brønsted acids

Catalyst, reaction conditions	Examples	Yield (%)	Reference
H <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> O, reflux	17	84–91	[92]
Methanesulfonic acid, 60 °C	21	71–94	[93]
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> , 60 °C	21	81–94	[94]
DBSA, H <sub>2</sub> O, US	15	63–93	[95]
<i>p</i> TSA, US	17	80–85	[96]
<i>p</i> TSA, 80 °C	17	82–92	[92]
HY Zeolite, 80 °C	28	70–95	[97]
BNPs-TAPC, 80 °C	12	93–99	[98]
SiO <sub>2</sub> -H <sub>2</sub> SO <sub>4</sub> Nps, DCM, r.t.	14	82–96	[99]
Poly (AMPS-Co-AA), 110 °C	18	74–88	[100]
B(HSO <sub>4</sub> ) <sub>3</sub> , 120 °C	8	78–93	[101]
CA-SiO <sub>2</sub> , 60 °C	10	75–90	[102]
SMI-SO <sub>3</sub> H, 80 °C	7	66–80	[103]
PVPP.OTf, toluene, 100 °C	14	80–95	[104]
Nano-TiO <sub>2</sub> -HClO <sub>4</sub> , 90 °C	12	87–93	[105]
HBF <sub>4</sub> -SiO <sub>2</sub> , 80 °C	21	83–94	[106]
Lignosulfonic acid, 90 °C	8	82–93	[107]
Citric acid, 120 °C	10	88–92	[108]
Cellulose-SO <sub>3</sub> H, 80 °C	10	79–95	[109]
Glucose sulfonic acid, H <sub>2</sub> O	6	78–96	[110]
D-xylonic acid, 90 °C	1	89	[111]

and silver nanoparticles [127] and trityl chloride [128] (Scheme 3, Table 5). Use of microwave or ultrasonication techniques by authors [82, 113, 124] has shown to significantly enhance the rate of the reactions, improve the yields as well as decrease the reaction time.

Tetrahydrobenzo[*a*]xanthen-11-ones **6** were also reported to be synthesized via one-pot three-component condensation of 2-naphthol **1** with cyclohexane-1,3-dione derivatives **4/5** and aldehydes **2** (Scheme 4, Table 6) using task-specific acidic ionic liquids like [BiPy](SO<sub>3</sub>H)<sub>2</sub>Cl<sub>2</sub> [83],

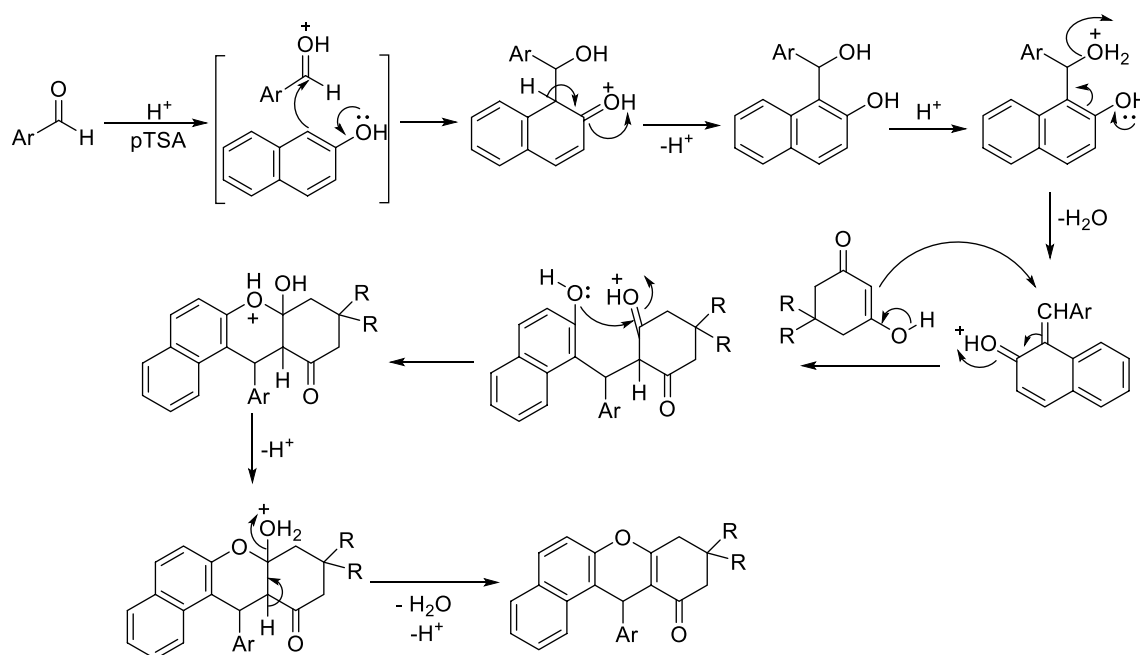
DSIMHS [84], [DBU]<sub>2</sub>EDS [88], [bmim]PF<sub>6</sub> [129], [DDPA] HSO<sub>4</sub> [130], 1-butane sulfonic acid-3-methylimidazolium tosylate ([BSMIM]Ts [131], [Dsim]Cl/[Msim]PF<sub>6</sub>/[Msim]BF<sub>4</sub>) [132] and [NMP]H<sub>2</sub>PO<sub>4</sub> [133] under solvent-free conditions.

Basic organocatalysts like imidazole and isoquinoline are also employed as catalyst for carrying out the above condensation [134] (Scheme 5, Table 7). Herein, initially imidazole or isoquinoline catalyzed Knoevenagel condensation between aldehyde and dione takes place, followed by reaction of 2-naphthol with above formed intermediate to give desired xanthene **6**. This three-component condensation reaction went well with a variety of aldehydes bearing both electron-withdrawing and electron-releasing substituents.

The condensation of dione **4**/cyclohexane-1,3-dione **5** and aromatic aldehydes **2** with 2,6-naphthalenediol **1a** for the synthesis of 3-hydroxy-12-arylbenzo[*a*]xanthen-11-ones **6a** has been described in the presence of ionic liquids, viz. [NMP]H<sub>2</sub>PO<sub>4</sub> [133] and [Bmim]BF<sub>4</sub> [135] (Scheme 6). Moreover, the synthesis of 2-hydroxy-12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives **6b** by condensation of 2,7-naphthalenediol **1b** with dione **4**/cyclohexane-1,3-dione **5** and aldehydes **2** has also been accomplished in ammonium chloride [114], [NMP]H<sub>2</sub>PO<sub>4</sub> [133], *p*TSA in ethanol under reflux as well as in [Bmim]BF<sub>4</sub> [136] (Scheme 6, Table 8).

3-Bromo-12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones **6c** were reportedly synthesized via reactions of dione **4** and aldehydes **2** with 6-bromo-2-naphthol **1d** in the presence of ammonium chloride by Foroughifar et al. [114] (Scheme 7).

Bis-tetrahydrobenzo[*a*]xanthen-11-ones or 5,12-diarylxantheno[2,1-*a*]xanthen-4,12-diones **7** were synthesized by reaction of 2,6-naphthalenediol **1b** with 5,5-dimethylcyclohexane-1,3-dione **4** and aromatic aldehydes **2** in [Bmim]BF<sub>4</sub> [135] (Scheme 8). It was noticed that the reactions with aldehydes bearing electron-deficient



**Scheme 4** Mechanism for the formation of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones **6**

**Table 5** Synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives **6** catalyzed by Lewis acids

Catalyst, reaction conditions	Examples	Yield (%)	Reference
CAN, 120 °C	14	85–94	[62]
Ru@SH-MWCNT, EtOH, reflux	8	82–90	[82]
Ru@SH-MWCNT, EtOH, US	8	88–96	[82]
Iodine, 60 °C	13	82–94	[112]
Iodine, AcOH, MW	9	70–89	[113]
NH <sub>4</sub> Cl, 120 °C	6	72–88	[114]
CeCl <sub>3</sub> , MeOH, 50 °C	13	76–95	[115]
InCl <sub>3</sub> , 120 °C	18	70–88	[116]
P <sub>2</sub> O <sub>5</sub> , 120 °C	18	62–80	[116]
Sn(OTf) <sub>2</sub> , DCM, 80 °C	11	70–88	[117]
Alum, 120 °C	18	85–96	[118]
RuCl <sub>3</sub> ·nH <sub>2</sub> O, EtOH, reflux	13	75–92	[119]
Nano-TiCl <sub>4</sub> /SiO <sub>2</sub> , 90 °C	12	70–96	[120]
Rice Husk, 90 °C	12	93–98	[121]
Ce(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O, 120 °C	13	85–97	[122]
Cu-SiO <sub>2</sub> , 60 °C	8	80–92	[123]
Manganese perchlorate hydrate, EtOH, US	20	75–88	[124]
TBAF, H <sub>2</sub> O, reflux	12	60–99	[125]
Ce-MCM-41, 80 °C	24	82–96	[126]
Fe <sub>3</sub> O <sub>4</sub> /CS-Ag Nps, H <sub>2</sub> O, 80 °C	21	80–95	[127]
Trityl chloride, 110 °C	15	82–94	[128]

substituent gave the corresponding bis-products when the molar concentrations of aldehyde and dimedone were doubled, whereas electron-rich aldehydes required higher concentrations (1:3:3) to afford the desired products **7**.

The synthesis of 14-aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-diones **9** by condensation of 2-hydroxy-1,4-naphthoquinone **8**, aromatic aldehydes **2** and substituted 2-naphthols **1/1a/1b** (Scheme 9, Table 9) has been reported in the presence of sulfuric acid [137], [bmim]HSO<sub>4</sub> [137], under

**Table 6** Synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives **6** in the presence of ionic liquids

Catalyst, reaction conditions	Examples	Yield (%)	References
[BiPy](SO <sub>3</sub> H) <sub>2</sub> Cl <sub>2</sub> , 90 °C	11	80–98	[83]
DSIMHS, 90 °C	13	87–93	[84]
[DBU] <sub>2</sub> EDS, 120 °C	5	90–94	[88]
[Bmim]PF <sub>6</sub> , MW	11	82–92	[129]
[DDPA]HSO <sub>4</sub> , 90 °C	16	85–93	[130]
[BSMIM]Ts, MW	18	70–89	[131]
[Dsim]Cl, 110 °C	12	86–99	[132]
[Msim]PF <sub>6</sub> , 110 °C	12	85–98	[132]
[Msim]BF <sub>4</sub> , 110 °C	12	88–99	[132]
[NMP]H <sub>2</sub> PO <sub>4</sub> , 80 °C	5	83–88	[133]

solvent-free condition by using Lewis acid like silica chloride [138], polystyrene-supported GaCl<sub>3</sub> [139], as well as Brønsted acids such as acetic acid [140], *p*TSA [141], heterogeneous nanocatalysts like Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H nanoparticles [142] and nano-Fe<sub>3</sub>O<sub>4</sub>/PEG/succinic anhydride [143].

One-pot three-component reaction of 2-naphthol **1**, 2-hydroxy-1,4-naphthoquinone **8** and isatins **10** in the presence of silicotungstic acid (H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>) [144] as well as [hmim]HSO<sub>4</sub> [145] afforded spiro[dibenzo[*a*,*i*]-xanthen-14,30-indoline]-20,8,13-triones **11** (Scheme 10). In both cases, electronic effect of the substituents on indole ring had no significant effect on the product yield as well as reaction time. Moreover, the reusability of the recycled catalyst has also been demonstrated in the above protocols.

A possible mechanism for the above three-component reaction is outlined in Scheme 11. 2-Naphthol is believed to initially react with isatin to afford condensation product, followed by addition of 2-hydroxy-1,4-naphthoquinone. Subsequently, cyclization takes place to afford the desired product.

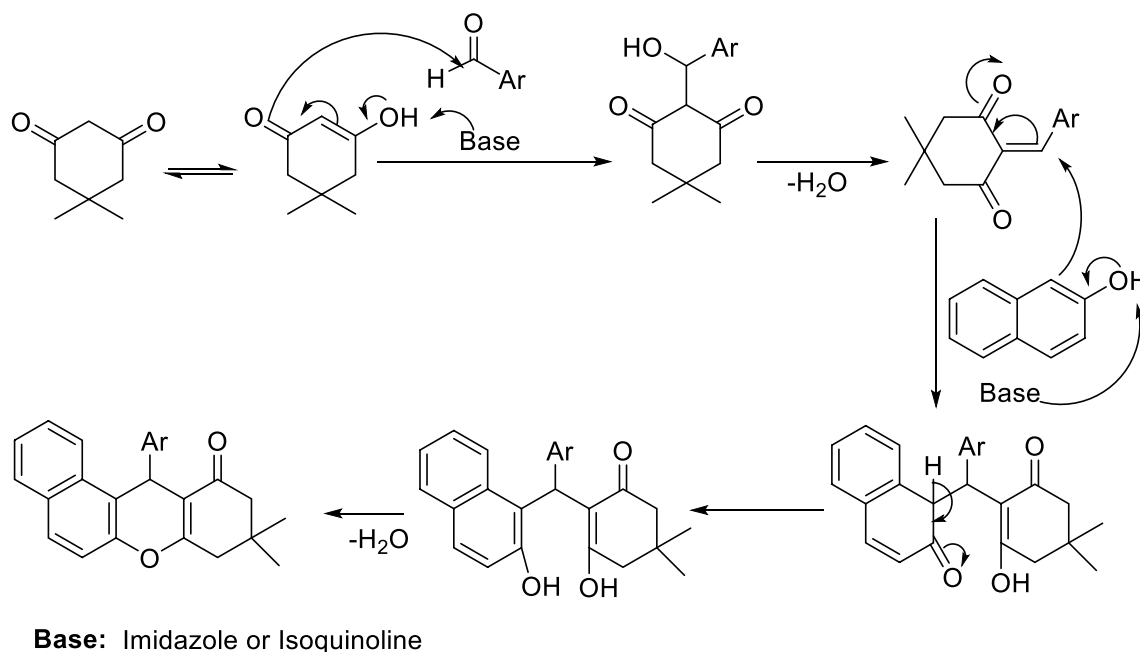
The one-pot three-component condensation of 2-naphthol **1**, isatins **10** and cyclic 1,3-dicarbonyl compounds like dime-done **4**/cyclohexa-1,3-dione **5** in the presence of mesoporous magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@MCM-41-SO<sub>3</sub>H@[HMIm]HSO<sub>4</sub>) as catalyst was successfully established for the synthesis of spiro[benzoxanthen-indoline]diones **12** [146] (Scheme 12). The above protocol offers several advantages like reusability of magnetite nanoparticle, high yield, short reaction time, solvent-free conditions and ease of isolation of product.

## Pyrans

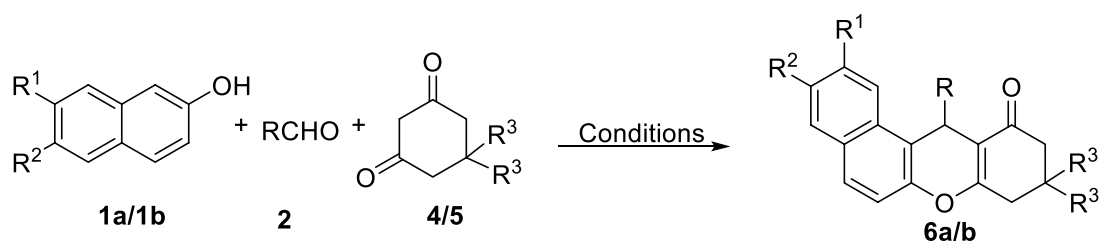
Polyfunctionalized pyrans and chromenes belong to interesting class of heterocycles due to their vast biological and pharmacological importance. Pyrans commonly classified

**Table 7** Synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives **6** in the presence of basic catalyst

Catalyst	Examples	Yield	References
Imidazole, 80 °C	16	83–97	[134]
Isoquinoline, 80 °C	16	83–98	[134]

**Scheme 5** Mechanism for the base catalyzed formation of xanthenes **6**



**R for 6a :**

4-XC<sub>6</sub>H<sub>4</sub> (X =Br, Cl, F), 4-F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>, 3-BrC<sub>6</sub>H<sub>4</sub>, 4-MeOC<sub>6</sub>H<sub>4</sub>, 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3,4-(OMe)<sub>3</sub>C<sub>6</sub>H<sub>3</sub>, 1-Naphthyl, 4-H<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>, 2-Naphthyl, 3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 4-Me<sub>2</sub>CH-C<sub>6</sub>H<sub>4</sub>

**R for 6b:**

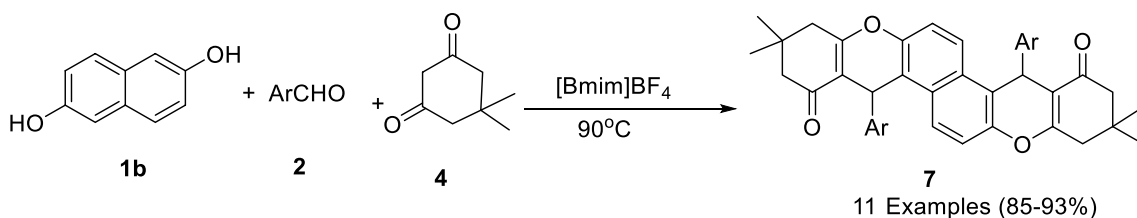
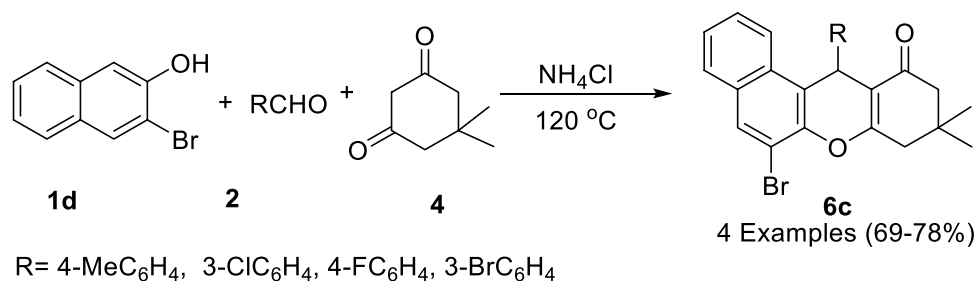
4-XC<sub>6</sub>H<sub>4</sub> (X =Br,Cl, F ), 4-OMeC<sub>6</sub>H<sub>4</sub>, 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, 2-HOC<sub>6</sub>H<sub>6</sub>, 2-ClC<sub>6</sub>H<sub>4</sub>, 3-BrC<sub>6</sub>H<sub>4</sub>, 1-Naphthyl, 2-Naphthyl, 9-Anthryl, 3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, 3-BrC<sub>6</sub>H<sub>4</sub>, 4-Me<sub>2</sub>CH-C<sub>6</sub>H<sub>4</sub>, 4-HO-3-OMe-C<sub>6</sub>H<sub>3</sub>

**Scheme 6** Synthesis of 2-/3-hydroxy-12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-ones **6a/b**

**Table 8** Synthesis of 2-/3-hydroxy-12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-ones **6a/b**

Catalyst	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Examples	Yield	References
[NMP]H <sub>2</sub> PO <sub>4</sub> , 80 °C	H	OH	CH <sub>3</sub>	3	83–87	[133]
<i>p</i> TSA, [bmim]BF <sub>4</sub> , 60 °C	H	OH	CH <sub>3</sub>	10	87–90	[135]
[NMP]H <sub>2</sub> PO <sub>4</sub> , 80 °C	OH	H	CH <sub>3</sub> , H	15	83–93	[133]
<i>p</i> TSA, EtOH, reflux	OH	H	CH <sub>3</sub> , H	23	82–96	[136]
<i>p</i> TSA, [bmim]BF <sub>4</sub> , 50 °C	OH	H	CH <sub>3</sub> , H	22	97–94	[136]
NH <sub>4</sub> Cl, 120 °C	OH	H	CH <sub>3</sub>	6	86–94	[114]

**Scheme 7** Synthesis of 3-bromo-12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-ones **6c**

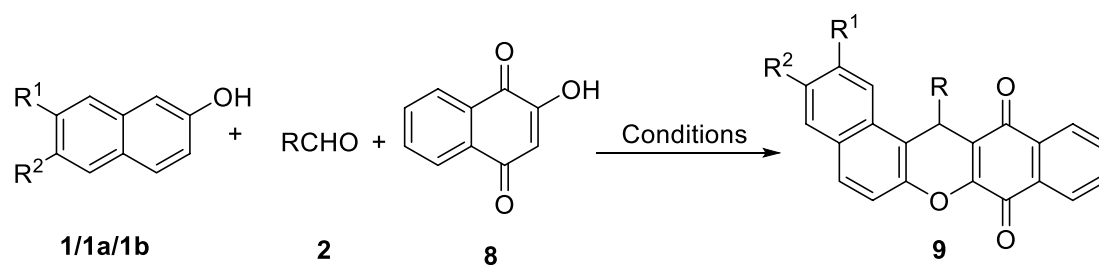


Ar = 4-ClC<sub>6</sub>H<sub>4</sub>, 4-BrC<sub>6</sub>H<sub>4</sub>, 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, 4-MeOC<sub>6</sub>H<sub>4</sub>, 2-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 2-ClC<sub>6</sub>H<sub>4</sub>, 2-Naphthyl, 3-MeC<sub>6</sub>H<sub>4</sub>, 3,4-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>

**Scheme 8** Synthesis of Bis-tetrahydrobenzo[a]xanthen-11-ones **7**

on the basis in the presence of the 2*H*- or 4*H*-pyran scaffold (Fig. 2) have been reported to possess biological properties such as antitumor [147], anti-proliferative [148], antiviral [149], antibacterial [150] and antifungal [151]. They also

find application as insect pheromones [152, 153] and photoactive materials [154, 155]. Moreover, benzopyrans or chromenes being crucial components of a variety of natural compounds like alkaloids, flavonoids and tocopherols

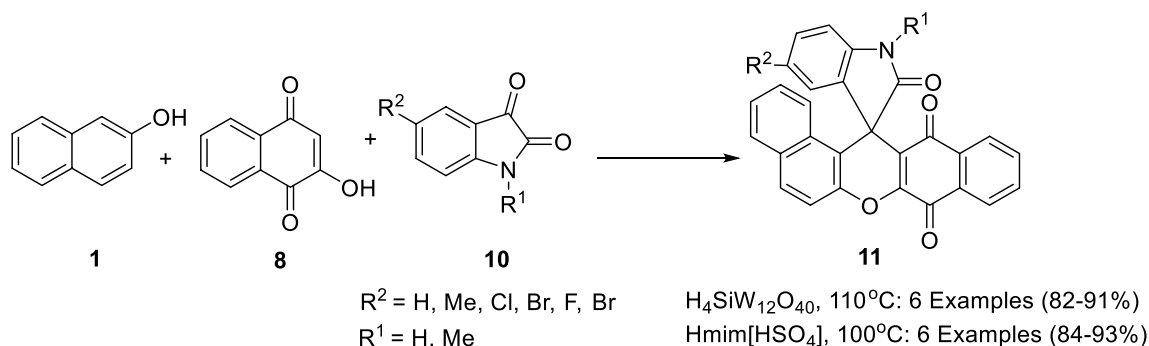


R = C<sub>6</sub>H<sub>5</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, 4-MeOC<sub>6</sub>H<sub>4</sub>, 3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2-ClC<sub>6</sub>H<sub>4</sub>, 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 2-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 4-HOC<sub>6</sub>H<sub>4</sub>, 4-BrC<sub>6</sub>H<sub>4</sub>, 3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 2-Naphthyl, 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 4-FC<sub>6</sub>H<sub>4</sub>, 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3,4,5-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 4-MeSC<sub>6</sub>H<sub>4</sub>, 2-OH-3-OMe-C<sub>6</sub>H<sub>3</sub>, 4-Me<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>

**Scheme 9** Synthesis of 14-aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-diones **9**

**Table 9** Synthesis of 14-aryl-14*H*-dibenzo[*i*]xanthene-8,13-diones **9**

Catalyst	R <sup>1</sup>	R <sup>2</sup>	Examples	Yield (%)	References
H <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> O, reflux	H, OH	H, OH	24	88–92	[137]
Bmim[HSO <sub>4</sub> ], 60 °C	H, OH	H, OH	24	87–91	[137]
Silica chloride, 110 °C	H	H	9	85–90	[138]
PS/GaCl <sub>3</sub> , EtOH, reflux	H, OH	H	13	85–93	[139]
AcOH, 60–80 °C	H	H	9	90–96	[140]
<i>p</i> TSA, 120 °C	H	H	6	60–70	[141]
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -SO <sub>3</sub> H Mnps, EtOH-H <sub>2</sub> O, reflux	H	H	13	88–97	[142]
Fe <sub>3</sub> O <sub>4</sub> /PEG/succinic anhydride Nps, EtOH, US	H	H	6	74–90	[143]



**Scheme 10** Synthesis of spiro[dibenzo[*a,i*]-xanthene-14,30-indoline]-20,8,13-triones **11**

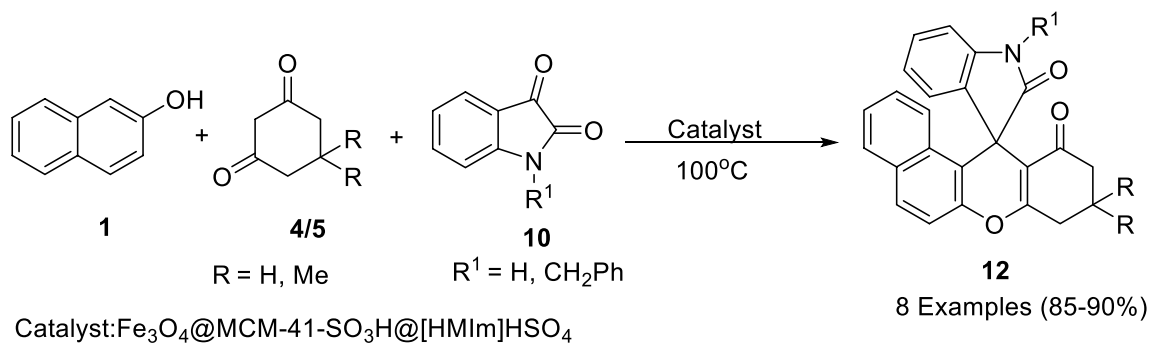
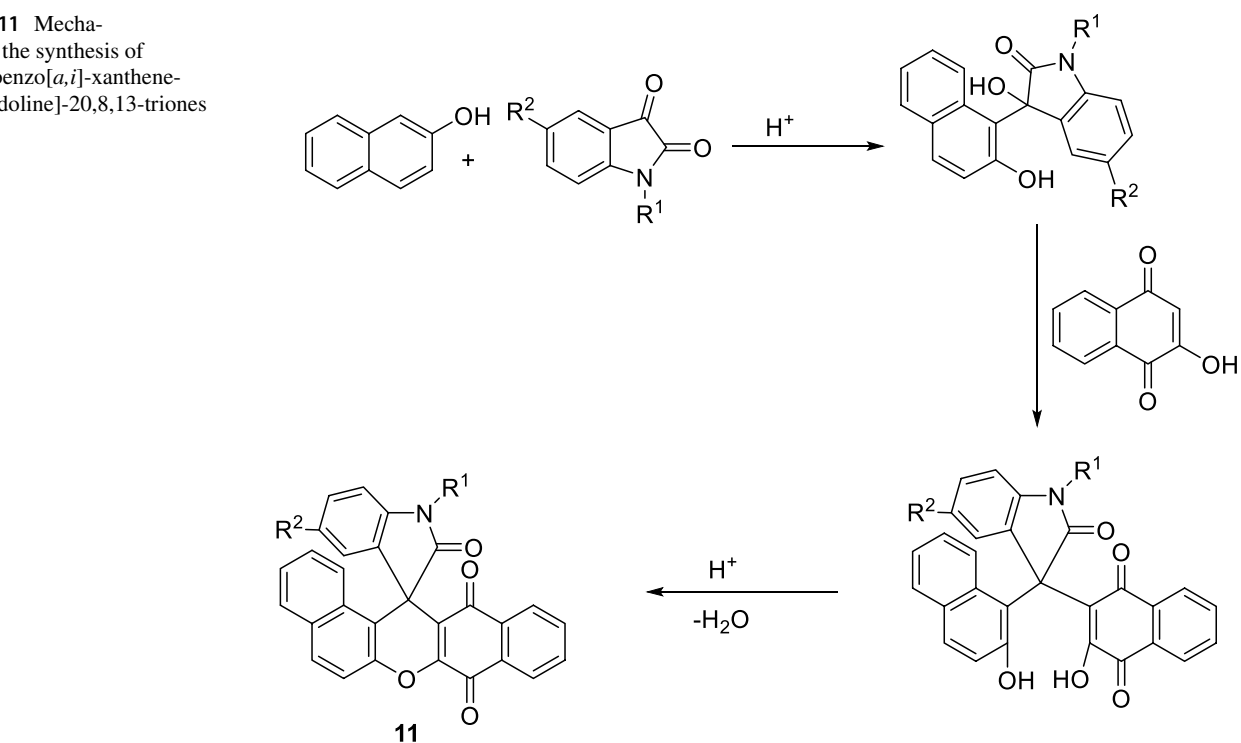
hold a position of prominence attributed to their biological activities which include antibacterial [156], antimicrobial [157], antioxidant [158], anti-hyperglycemic and anti-dyslipidemic [159]. Benzopyrans, a bicyclic organic compound that results from the fusion of a benzene ring to a pyran ring, include commonly structural skeletons such as 4*H*-chromene (4*H*-1benzopyran) and 2*H*-chromene (2*H*-1-benzopyran). Based on fusion of benzene or naphthalene ring with 2*H*-chromene, they are called as benzo[*c*]chromene, benzo[*f*]chromene, benzo[*g*]chromene and benzo[*h*]chromene (Fig. 2).

The synthesis of 3-amino-1*H*-benzo[*f*]chromenes **16**, via MCRs of 2-naphthol **1**, aldehydes **2** and malononitrile **13**/ethyl cyanoacetate **14**/cyanoacetamide **15** has been described under various conditions (Scheme 13).

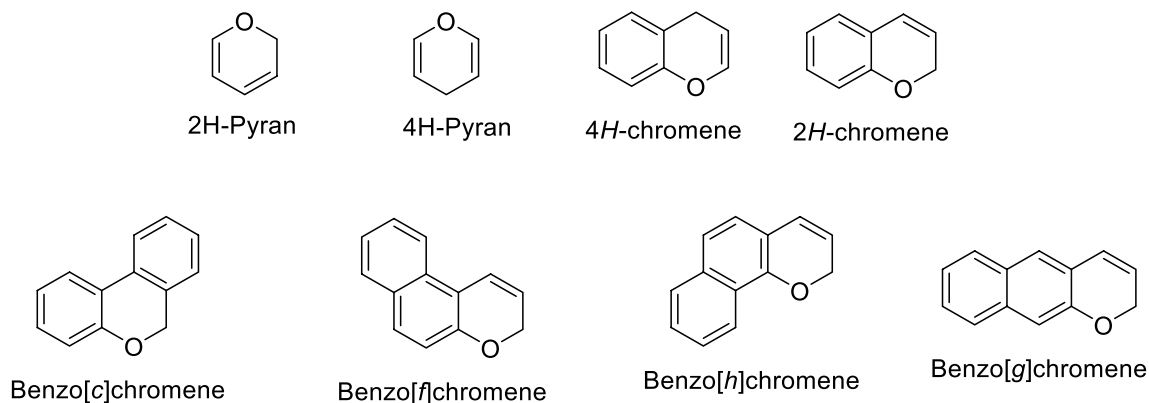
Acid catalysts like CAN [62], TBAC [160], ferric hydrogen sulfate [161], disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>) [162], molecular sieves 5A<sup>o</sup> [163], SBA-15@methenamine-HPA [164], nano-sawdust-BF<sub>3</sub> [165] and titanium tetrachloride (TiCl<sub>4</sub>) [166] were used for the synthesis of **16**.

Various basic catalysts [167–182] were employed for the condensation of 2-naphthol with aldehydes and active methylene compounds. (Scheme 13, Table 10). The

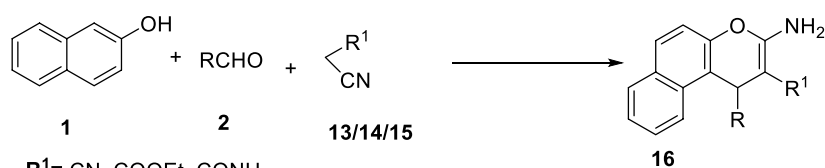
**Scheme 11** Mechanism for the synthesis of spiro[dibenzo[*a,i*]-xanthene-14,30-indoline]-20,8,13-triones **11**



**Scheme 12** Synthesis of spiro[benzoxanthene-indoline]diones **12**



**Fig. 2** Pyrans



$\text{R}^1 = \text{CN}, \text{COOEt}, \text{CONH}_2$

$\text{R} = 4\text{-O}_2\text{NC}_6\text{H}_4, 4\text{-XC}_6\text{H}_4$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), 2-Furyl,  $\text{C}_6\text{H}_5$ , 2- $\text{XC}_6\text{H}_4$  ( $\text{X} = \text{Cl}, \text{Br}$ ), 4- $\text{MeOC}_6\text{H}_4$ , 4- $\text{MeC}_6\text{H}_4$ ,  $\text{CH}_3(\text{CH}_2)_3$ , 3- $\text{ClC}_6\text{H}_4$ , 3,4-(OMe) $_2\text{C}_6\text{H}_3$ , 4- $\text{Me}_2\text{NC}_6\text{H}_4$ , 3- $\text{O}_2\text{NC}_6\text{H}_4$ , 2- $\text{MeC}_6\text{H}_4$ , 3- $\text{MeC}_6\text{H}_4$ , 4- $\text{NCC}_6\text{H}_4$ , 2,4- $\text{Cl}_2\text{C}_6\text{H}_3$ , 2,4,6- $\text{F}_3\text{C}_6\text{H}_2$ , 2- $\text{F}_3\text{CC}_6\text{H}_4$ , 3- $\text{MeOC}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5\text{CH}=\text{CH}$ , 4- $\text{HO-3-MeOC}_6\text{H}_3$ , 4- $\text{Cl-3-O}_2\text{NC}_6\text{H}_4$ , 4- $\text{HOC}_6\text{H}_4$ , 2-Pyridyl, 2,3- $\text{Cl}_2\text{C}_6\text{H}_3$ , 4- $\text{F}_3\text{CC}_6\text{H}_4$ , 2-Thienyl, 4- $\text{MeCONHC}_6\text{H}_4$ ,

**Scheme 13** Synthesis of 3-amino-1H-benzo[f]chromenes **16**

clean, transition-metal-free and environmentally friendly approaches for the synthesis of **16** have been realized using organocatalysts like diazabicyclo[2.2.2]octane (DABCO) [167], morpholine [168], piperazine [169], potassium phthalimide (POPI) [170], tetraethylammonium 2-(carbamoyl)benzoate (TEACB) [171] and triazine-based porous organic polymer TPOP-2 [172]. These procedures offer

many advantages including short reaction times, low cost and straightforward work-up.

Nanocatalysts like tetragonal  $\text{ZrO}_2$  nanoparticles (t- $\text{ZrO}_2$  NPs) [173], nano-mixed  $\text{CuO-ZnO}$  [174], nano-silica-bonded aminoethylpiperazine (SB-APP) [175], 1,5,7-triazabicyclo-[4,4,0]-dec-1-ene (TBD) a cyclic guanidine base anchored by mesoporous silica nanoparticles (MSN) [176] and nano-polypropylenimine dendrimer (DAB-PPI-G1)

**Table 10** Multicomponent synthesis of 3-amino-1H-benzo[f]chromenes **16**

Reaction conditions	$\text{R}^1$	Examples	Yield (%)	References
CAN, 120 °C	CN, COOEt	11	68–91	[62]
TBAC, 100 °C	CN	13	88–95	[160]
$\text{Fe}(\text{HSO}_4)_3$ , $\text{CH}_3\text{CN}$ reflux	CN	4	80–88	[161]
$\text{Na}_2\text{HPO}_4$ , 120 °C	CN	9	83–95	[162]
MS 5A <sup>0</sup> , MW	CN, COOEt, $\text{CONH}_2$	14	60–95	[163]
SBA-15@methenamine-HPA, $\text{H}_2\text{O}$ , 100 °C	CN	5	91–97	[164]
nano-sawdust- $\text{BF}_3$ , EtOH, reflux	CN	11	83–93	[165]
$\text{TiCl}_4$ , r.t.	CN, COOEt	11	75–95	[166]
DABCO, EtOH, r.t.	CN	18	71–99	[167]
Morpholine, $\text{H}_2\text{O}$ , r.t.	CN	5	88–93	[168]
Piperazine, MW	CN	5	82–95	[169]
POPI, Ballmilling	CN	11	96–99	[170]
TEACB, Ballmilling	CN	8	95–98	[171]
TPOP-2, $\text{H}_2\text{O}$ , 80 °C	CN	5	82–88	[172]
t- $\text{ZrO}_2$ Nps, water, 80 °C	CN	3	89–94	[173]
Nano-CuO-ZnO, $\text{H}_2\text{O}$ , reflux	CN	12	12–93	[174]
SB-APP, 80 °C	CN	13	80–95	[175]
TBD-MSN, $\text{H}_2\text{O}$ , r.t.	CN	1	85	[176]
DAB-PPI-G1, 110 °C	CN, COOEt	6	88–92	[177]
Amano <sup>®</sup> lipase AS, $\text{CH}_3\text{CN}$ , 40 °C	CN	8	34–84	[178]
Bael fruit extract (BFE), EtOH r.t.	CN	6	89–94	[179]
$\text{Na}_2\text{CO}_3$ , 150 °C	CN	8	90–100	[180]
$\text{Na}_2\text{CO}_3$ , ball milling	CN	2	>99	[181]
$\text{MgO}$ , DMF, reflux	CN	3	83–91	[182]
$\text{KF-Al}_2\text{O}_3$ , EtOH, 80 °C	CN, COOEt	9	66–83	[183]
PVPy, 80 °C	CN	15	86–93	[184]
3-HPAF, 70 °C	CN	11	83–93	[185]
$\text{Et}_2\text{NH}(\text{CH}_2)_2\text{CO}_2\text{H}[\text{AcO}]$ , 60 °C	CN	7	81–90	[186]

[177], were utilized for the above condensation. Biocatalysts like “Amano” lipase AS [178] and bael fruit extract (BFE) [179] were also used as catalyst for the synthesis of **16** by Jiang et al. and Shinde and co-workers, respectively. The exploitation of low cost, biodegradable and highly efficient catalyst, i.e., BFE, obtained from the rind of *Aegle marmelos* (bael) fruit offers benefits like elimination of toxic catalysts/reagents, reuse of catalyst and excellent yield of product in a very short reaction time.

Catalytic activity of other basic catalysts such as sodium carbonate [180, 181], high surface MgO [182], KF-Al<sub>2</sub>O<sub>3</sub> [183] and poly(4-vinyl pyridine) [184] was also demonstrated by various researchers. Recyclable basic ionic liquids such as 3-hydroxypropanaminium acetate [185] and [Et<sub>2</sub>NH(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>H]AcO [186] were also employed as catalyst for above condensation.

The possible reaction pathway for this three-component reaction catalyzed by base proceeds via the Knoevenagel condensation of aldehyde and active methylene compound to afford Knoevenagel adduct. Thereafter, nucleophilic

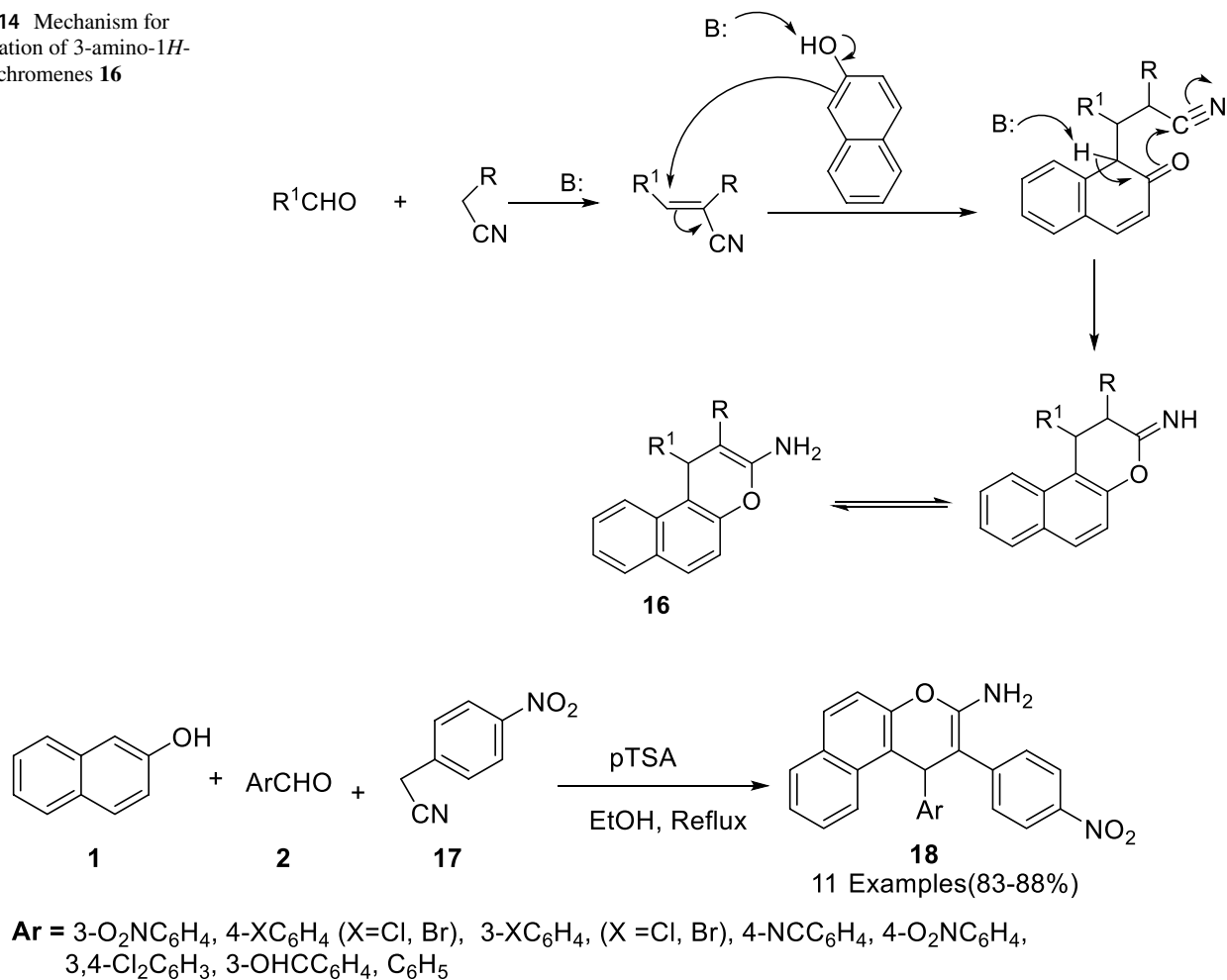
addition of the OH group of 2-naphthol to the CN moiety of adduct occurs through Michael addition. This is followed by intramolecular cyclization to form 3-amino-1*H*-benzo[*f*]chromenes **16** (Scheme 14).

The synthesis of 1,2-bis(4-nitrophenyl)-1-benzo[*f*]chromen-3-amine derivative **18** has been described by one-pot three-component reaction of 2-naphthol **1**, aromatic aldehydes **2**, 4-nitrophenyl acetonitrile **17** by using *p*TSA as the catalyst in ethanol reflux (Scheme 15) [187].

The synthesis of benzo[*f*]chromenes **19–20** via condensation of aromatic aldehydes **2** and malononitrile **13** with 2,3-dihydroxynaphthalene **1c** or 2,7-dihydroxynaphthalene **1b** using guanidine hydrochloride as the catalyst under solvent-free conditions [188] (Scheme 16) and CuO–ZnO nanocatalyst in water under reflux conditions [177] (Scheme 17), respectively, has been reported. CuO–ZnO nanocatalyst used by Albadi and co-workers was reportedly recycled up 6 times without any significant loss of its catalytic activity.

Fused 1*H*-benzo[*f*]chromen-indoles **22** were synthesized regioselectively by triethylamine-catalyzed condensation of

**Scheme 14** Mechanism for the formation of 3-amino-1*H*-benzo[*f*]chromenes **16**

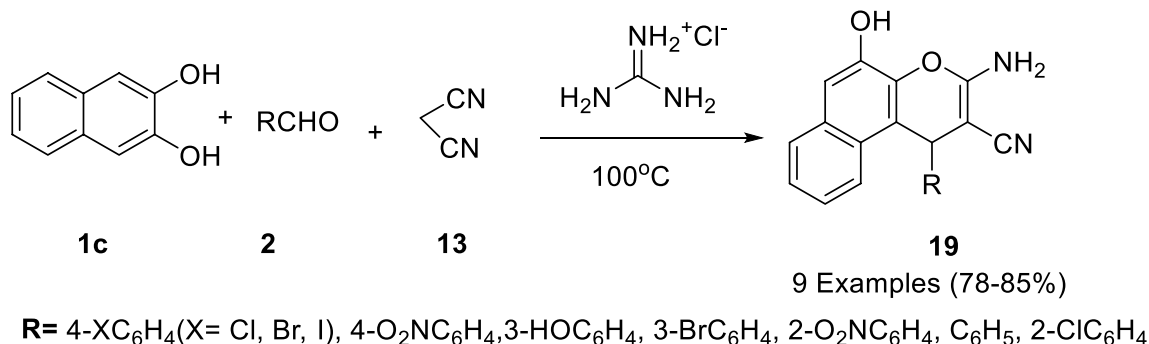


**Scheme 15** Synthesis of 1,2-bis(4-nitrophenyl)-1-benzo[*f*]chromen-3-amine **18**

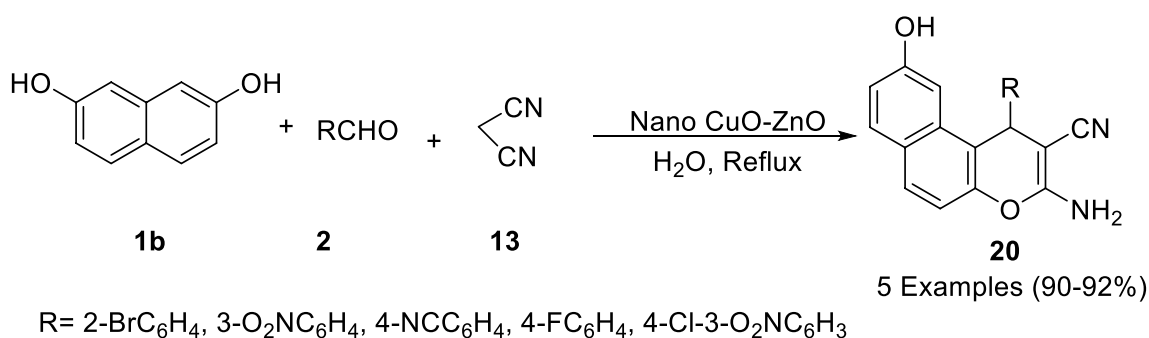
2-naphthol **1** with aromatic aldehydes **2** and 3-cyanoacetyl-indoles **21** in methanol under both ultrasonic irradiations and conventional conditions (Scheme 18) [189]. The reaction promoted by ultrasound offered better yields and much lower reaction times than the conventional heating. Notably, aldehydes with electron-donating substituents on phenyl ring furnished lower yields of furans than those with electron-withdrawing substituents.

Condensation of 2-naphthol **1** and aldehydes **2** was carried out with a variety of substrates under different

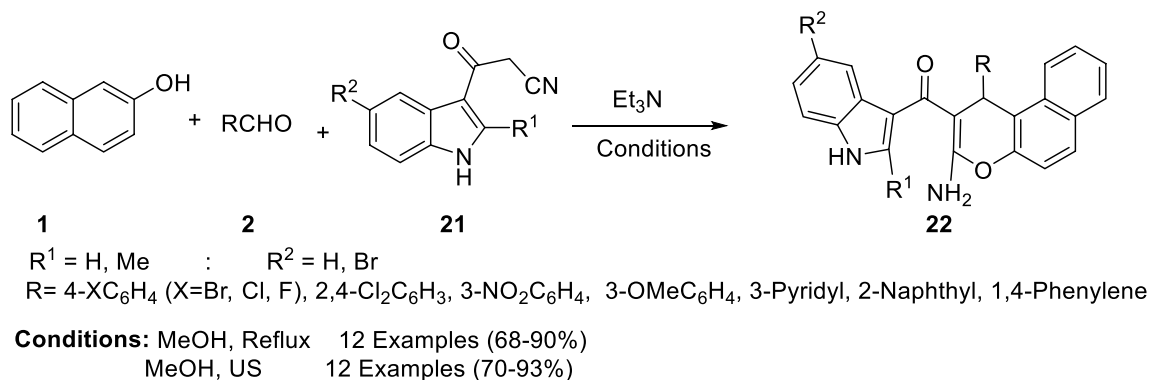
conditions to afford chromenes. One-pot three-component condensation reactions of 2-naphthol **1** and aldehydes **2** with cyclopentane-1,3-dione **23** with strontium triflate afforded 8,9-dihydrobenzo-*[f]*cyclopenta[*b*]chromen-10(11*H*)-ones **26** [117], with Meldrum's acid **24** in the presence of cerium(III) chloride [115] as well as TBAF yielded benzo[*f*]chromen-3-ones **27** [125], with indane-1,3-dione **25** gave benzo[*f*]indeno[1,2-*b*]chromen-12(13*H*)-one **28** in the presence of cerium-impregnated-MCM-41 [126], respectively (Scheme 19).



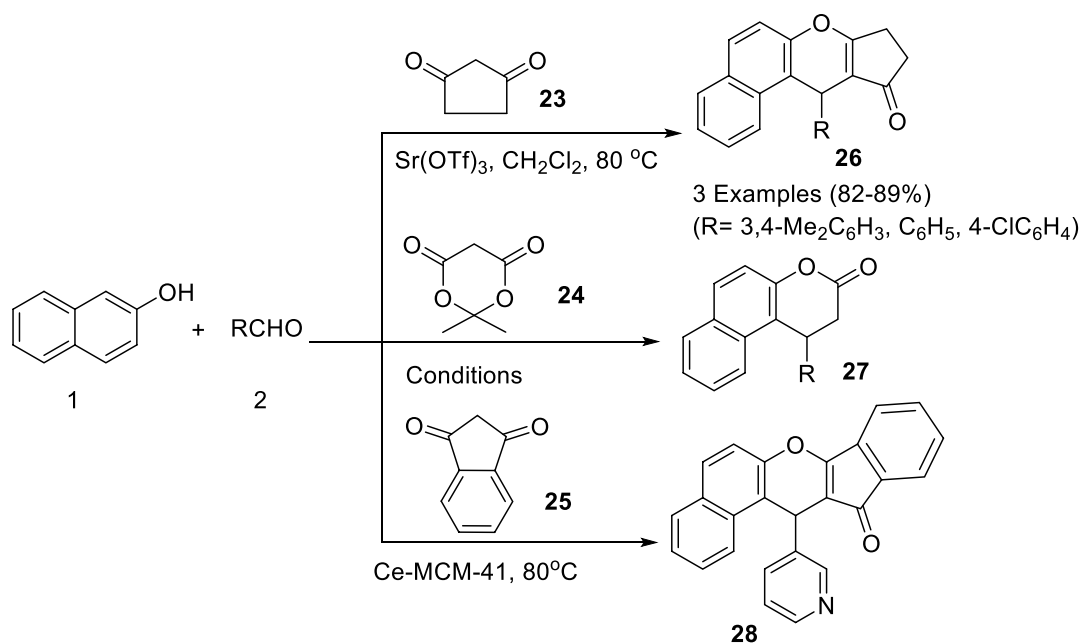
**Scheme 16** Synthesis of benzo[*f*]chromenes **19**



**Scheme 17** Synthesis of benzo[*f*]chromenes **20**



**Scheme 18** Synthesis of Fused 1*H*-benzo[*f*]chromen-indoles **22**

**Conditions:**

CeCl<sub>3</sub>, MeOH, 50 °C: 5 Examples (70–94%): R= 2-Thienyl, 4-MeOC<sub>6</sub>H<sub>4</sub>, 4-FC<sub>6</sub>H<sub>4</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>  
 TBAF, H<sub>2</sub>O, Reflux: 5 Examples (72–99%): R= 4-MeOC<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, 4-XC<sub>6</sub>H<sub>4</sub> (X= F, Cl), 2-Naphthyl

**Scheme 19** Synthesis of 8,9-dihydrobenzo[*f*]cyclopenta[*b*]chromen-10(11*H*)-ones **26**, benzo[*f*]chromen-3-ones **27**, benzo[*f*]indeno[1,2-*b*]chromen-12(13*H*)-one **28**

The synthesis of naphtho[10,20:5,6]pyrano-[3,2-*c*]chromen-6-ones **30** was accomplished by three-component condensation reaction of 2-naphthol **1**, aromatic aldehydes **2** and 4-hydroxycoumarin **29** catalyzed by reusable catalysts like 1-methyl-3-(2-(sulfoxy)ethyl)-1*H*-imidazol-3-ium chloride [190], melamine trisulfonic acid (MTSA) [191], potassium 2-oxoimidazolidine-1,3-diide (POImD) [192], respectively (Scheme 20). The electronic and steric effects of substituents in aromatic aldehydes had no significant effect on the yields of the product in all three above-mentioned protocols [190–192].

Triethylamine-catalyzed one-pot three-component condensation reaction between naphthols like 2-naphthol **1**/6-bromonaphthol **1e**, formaldehyde **31** and trans- $\beta$ -nitrostyrene **32** for the formation of benzo[*f*]chromene derivatives **33** was carried out by Bhattacharjee and co-workers [193] (Scheme 21). Reactions attempted using aliphatic nitroalkene in place of trans- $\beta$ -nitrostyrene in the above condensation were unfruitful.

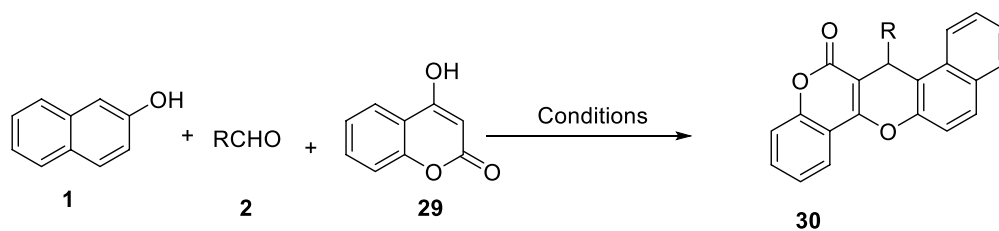
Boron trifluoride etherate has been successfully employed as catalyst for the synthesis of chromenes **36a–c** via condensation of aldehydes **2** and acetylacetone **34**/ethylacetoacetate **35** with 2-naphthol **1** as well as its derivatives like 2,3-dihydroxynaphthalene **1c** and 2,7-dihydroxynaphthalene **1b** and by Mashraqui and co-workers [194] (Scheme 22).

One-pot multicomponent condensation of 2-naphthol **1** with aromatic aldehydes **2** and  $\beta$ -oxobenzenepropane (dithioates) **37** has been described using catalytic amount of BF<sub>3</sub>·OEt<sub>2</sub> for the regioselective synthesis of several 1*H*-naphtho[2,1-*b*]pyrans **38** under solvent-free conditions (Scheme 23) [195]. The reactions attempted using phenol or 1-naphthol instead of 2-naphthol were not successful due to their lower reactivity.

Benzo[5,6]chromeno[2,3-*d*]pyrimidine-9,11(10*H*)-dione derivatives **40a–c** were reportedly synthesized by one-pot multicomponent condensation reaction of 2-naphthols **1/1a/1b** with aromatic aldehyde **2** and 1,3-dimethyl barbituric acid **39** in the presence of indium trichloride [116], phosphorus pentoxide [116], iodine [196], iodine in acetic acid [113], ZrOCl<sub>2</sub>/nano-TiO<sub>2</sub> [197] and alum (KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O) [198] (Scheme 24) (Table 11).

Moreover, Nandi and co-workers have reported the synthesis of benzo[5,6]chromeno[2,3-*d*]pyrimidine-9,11(10*H*)-diones **40** by reacting 2-naphthol **1** with 6-amino-1,3-dimethyl uracil **41** and aromatic aldehydes **2** using indium trichloride under solvent-free conditions [199] (Scheme 25). The reaction attempted using aliphatic aldehydes did not give desired product.

Cimarelli and co-workers [200] have reported the stereoselective synthesis of 2,3-dihydro-1*H*-benzo[*f*]



**Conditions:** [BPy]BF<sub>4</sub>, 80°C; 19 Examples (84-92%)

**R** = 4-MeOC<sub>6</sub>H<sub>4</sub>, 2-MeOC<sub>6</sub>H<sub>4</sub>, 3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 4-CNC<sub>6</sub>H<sub>4</sub>, 4-OHCC<sub>6</sub>H<sub>4</sub>, 3-BrC<sub>6</sub>H<sub>4</sub>, 2-ClC<sub>6</sub>H<sub>4</sub>, 4-OH-3-O<sub>2</sub>NC<sub>6</sub>H<sub>3</sub>, 2,3-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,3-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3,4,5-(OMe)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 4-XC<sub>6</sub>H<sub>4</sub> (X=I, Br, Cl)

**Conditions:** MTSA, 120°C; 8 Examples (81-91%)

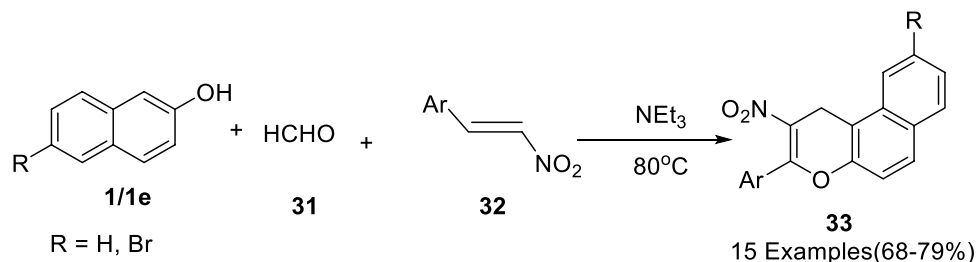
**R** = C<sub>6</sub>H<sub>5</sub>, 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, 4-FC<sub>6</sub>H<sub>4</sub>, 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>

**Conditions:** POImD, r.t.; 16 Examples (82-97%)

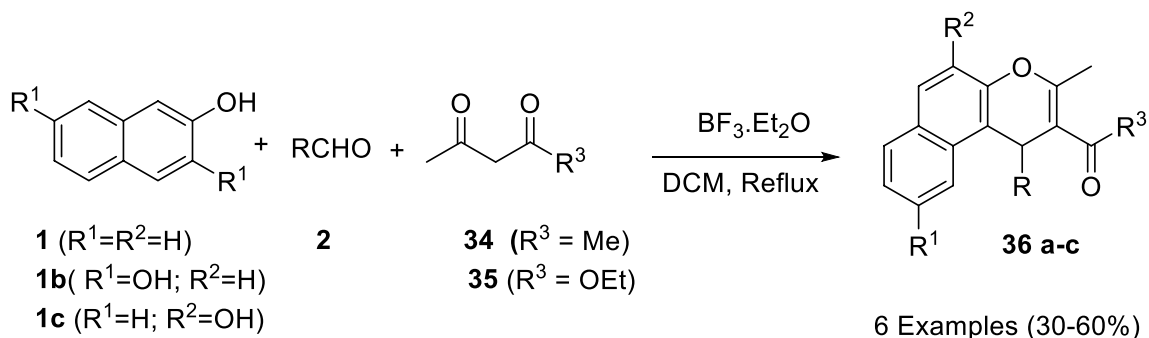
**R** = C<sub>6</sub>H<sub>5</sub>, 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,3-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 4-XC<sub>6</sub>H<sub>4</sub> (X=Cl, Br, I), 3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 4-HOC<sub>6</sub>H<sub>4</sub>, 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 2-ClC<sub>6</sub>H<sub>4</sub>, 3,4,5-(OMe)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 2-MeOC<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 4-MeOC<sub>6</sub>H<sub>4</sub>

**Scheme 20** Synthesis of naphtho[10,20:5,6]pyrano-[3,2-c]chromen-6-ones **30**

**Scheme 21** Synthesis of benzo[*f*]chromenes **33**



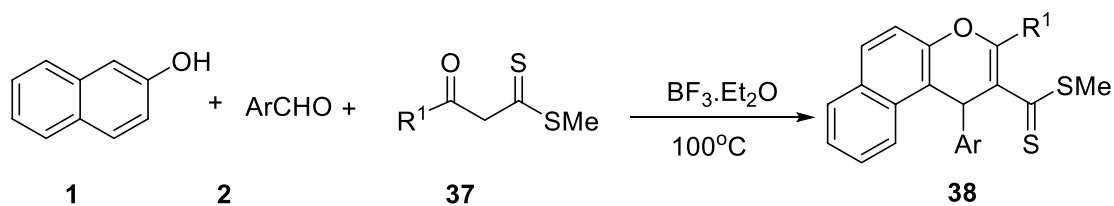
**Ar** = C<sub>6</sub>H<sub>5</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 4-BrC<sub>6</sub>H<sub>4</sub>, 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, 3,4,5-(OMe)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 2-ClC<sub>6</sub>H<sub>4</sub>, 3-FC<sub>6</sub>H<sub>4</sub>, 2-Thienyl, 4-MeOC<sub>6</sub>H<sub>4</sub>



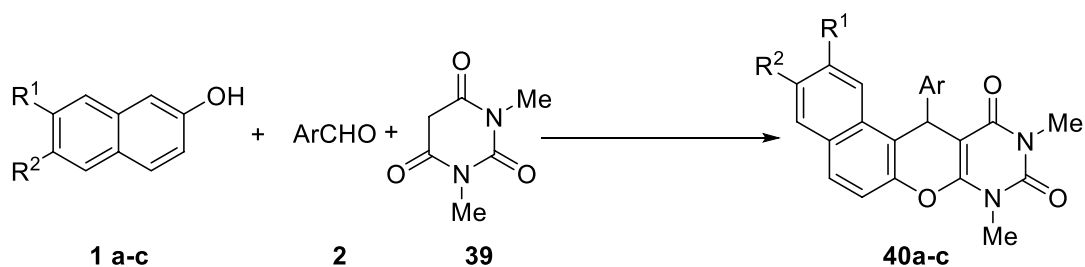
**R** = 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, 4-MeOC<sub>6</sub>H<sub>4</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, CH(CH<sub>3</sub>)<sub>2</sub>

**Scheme 22** Synthesis of chromenes **36a-c**

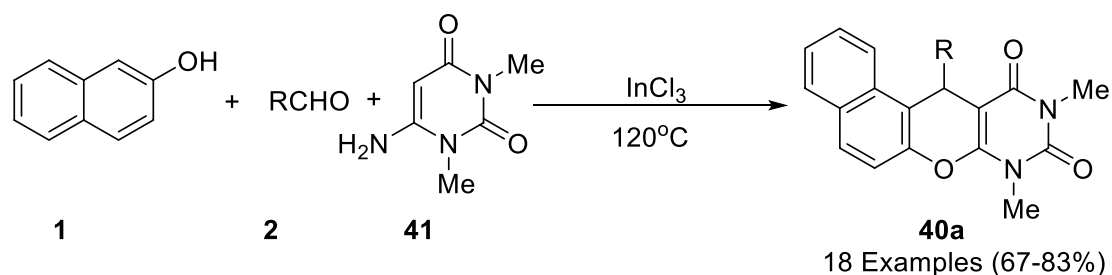




10 Examples (70-80%)

Ar = C<sub>6</sub>H<sub>5</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>**Scheme 23** Synthesis of 1*H*-naphtho[2,1-*b*]pyrans **38****40a**: R<sup>1</sup> = R<sup>2</sup> = H;Ar = C<sub>6</sub>H<sub>5</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 2-ClC<sub>6</sub>H<sub>4</sub>, 2-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 3,4-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2-FC<sub>6</sub>H<sub>4</sub>, 4-BrC<sub>6</sub>H<sub>4</sub>, 4-NCC<sub>6</sub>H<sub>4</sub>, 2-Naphthyl, 2-BrC<sub>6</sub>H<sub>4</sub>, 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3-ClC<sub>6</sub>H<sub>4</sub>, 4-FC<sub>6</sub>H<sub>4</sub>**40b**: R<sup>1</sup> = OH, R<sup>2</sup> = H;Ar = C<sub>6</sub>H<sub>5</sub>, 4-OMeC<sub>6</sub>H<sub>4</sub>, 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 2-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 2-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 3,4,5-(OMe)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 4-FC<sub>6</sub>H<sub>4</sub>, 2-OMeC<sub>6</sub>H<sub>4</sub>, 4-NCC<sub>6</sub>H<sub>4</sub>, 4-F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>, 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>**40c**: R<sup>1</sup> = H, R<sup>2</sup> = OH;Ar = 4-ClC<sub>6</sub>H<sub>4</sub>, 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>**Scheme 24** Synthesis of Benzo[5,6]chromeno[2,3-*d*]pyrimidine-9,11(10*H*)-diones **40a-c****Table 11** Synthesis of Benzo[5,6]chromeno[2,3-*d*]pyrimidine-9,11(10*H*)-dione derivatives **40a-c**

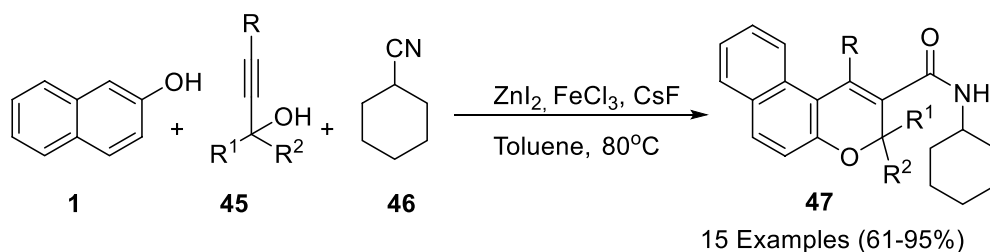
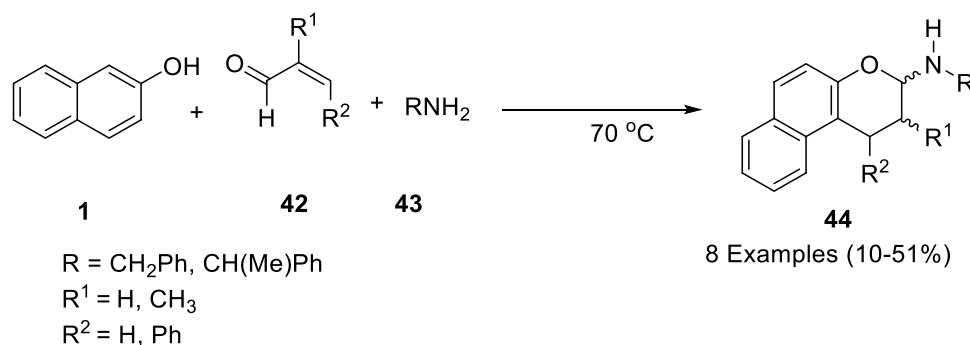
Reaction conditions	R <sup>1</sup>	R <sup>2</sup>	Examples	Yield (%)	References
InCl <sub>3</sub> , 120 °C	H	H	9	63–72	[116]
P <sub>2</sub> O <sub>5</sub> , 120 °C	H	H	9	58–67	[116]
I <sub>2</sub> , 120 °C	H	H	12	59–84	[196]
I <sub>2</sub> , AcOH, 120 °C	H	H	6	66–74	[113]
ZrOCl <sub>2</sub> /nano-TiO <sub>2</sub> , 100 °C	H	H	9	80–85	[197]
Alum, PEG-400, 60 °C	H, OH	H, OH	21	76–92	[198]



**R** = 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 4-FC<sub>6</sub>H<sub>4</sub>, 4-HOC<sub>6</sub>H<sub>4</sub>, 3-HOC<sub>6</sub>H<sub>4</sub>, 2-HOC<sub>6</sub>H<sub>4</sub>, 2-HO-3-MeOC<sub>6</sub>H<sub>3</sub>, 2-ClC<sub>6</sub>H<sub>4</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, 4-MeOC<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 4-BrC<sub>6</sub>H<sub>4</sub>, 2-HO-3-EtOC<sub>6</sub>H<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 5-O<sub>2</sub>N-2-HOC<sub>6</sub>H<sub>3</sub>, 5-Br-2-HOC<sub>6</sub>H<sub>3</sub>, 2-MeOC<sub>6</sub>H<sub>4</sub>,

**Scheme 25** Synthesis of benzo[5,6]chromeno[2,3-*d*]pyrimidine-9,11(10*H*)-diones **40a**

**Scheme 26** Synthesis of 2,3-dihydro-1*H*-benzo[*f*]chromen-3-amines **44**



**R** = C<sub>6</sub>H<sub>5</sub>, 4-XC<sub>6</sub>H<sub>4</sub> (X = Cl, F), 4-MeC<sub>6</sub>H<sub>4</sub>, 4-CMe<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, 4-Cyclopropyl-C<sub>6</sub>H<sub>4</sub>, 2-Thienyl, 4-NCC<sub>6</sub>H<sub>4</sub>  
**R**<sup>1</sup> = Me  
**R**<sup>2</sup> = Me, C<sub>6</sub>H<sub>5</sub>, *n*-C<sub>6</sub>H<sub>13</sub>

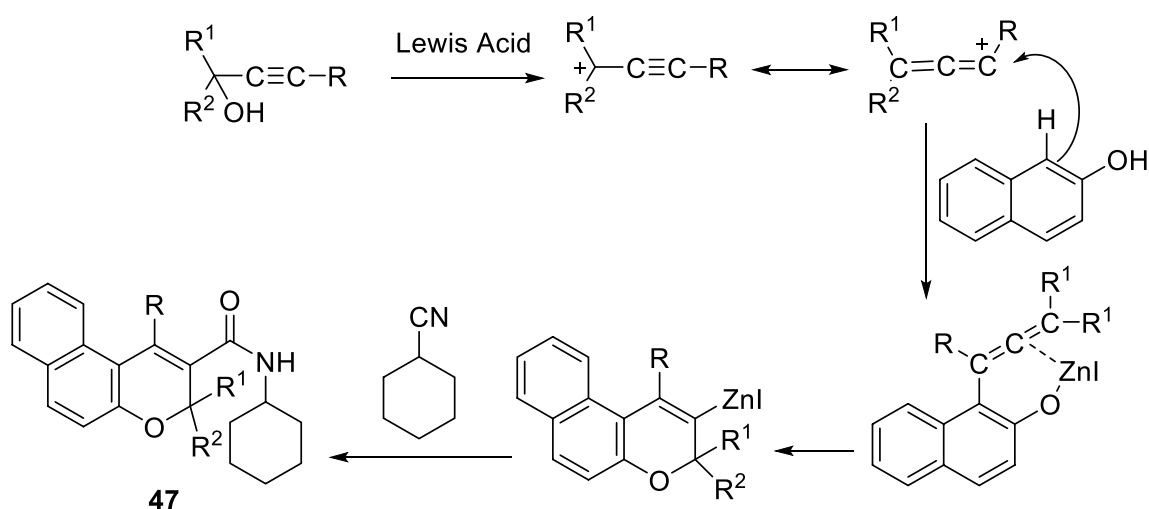
**Scheme 27** Synthesis of 3*H*-Benzo[*f*]chromene-2-carboxamides **47**

chromen-3-amine derivatives **44** under catalyst and solvent-free conditions (Scheme 26) via three-component one-pot reaction between 2-naphthol **1**,  $\alpha$ ,  $\beta$ -unsaturated aldehydes **42** and chiral phenylethylamine **43**.

3*H*-Benzo[*f*]chromene-2-carboxamides **47** were synthesized from three-component cyclocondensation reaction of 2-naphthol **1**, propargyl alcohols **45** and cyclohexylisocyanide **46** in the presence of ZnI<sub>2</sub> and FeCl<sub>3</sub> (Scheme 27) [201]. The mechanism for the formation of **47** is depicted in Scheme 28. Reactions attempted using

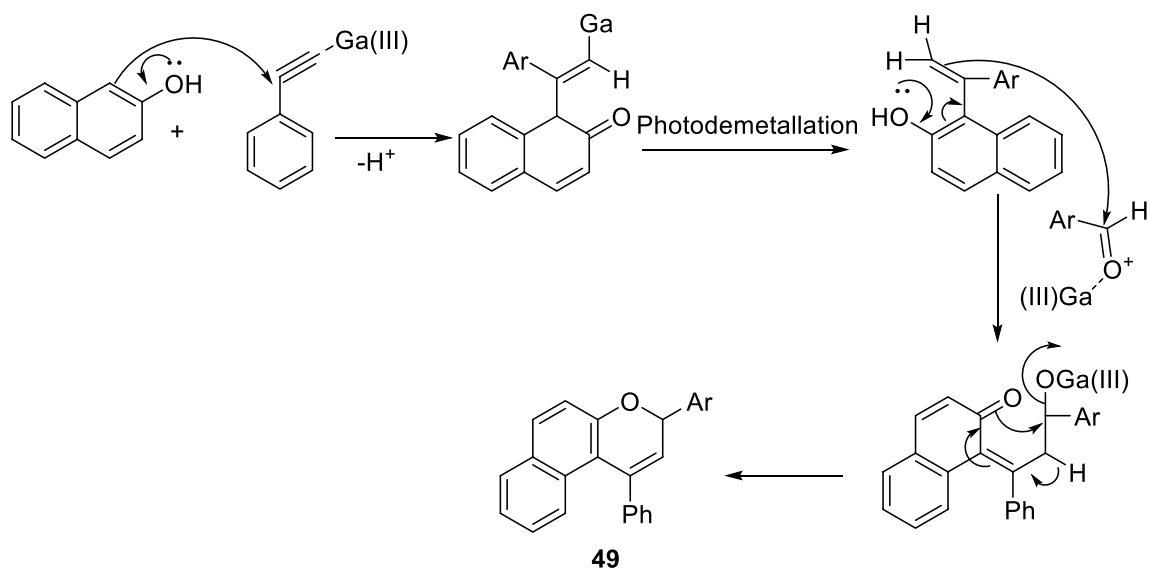
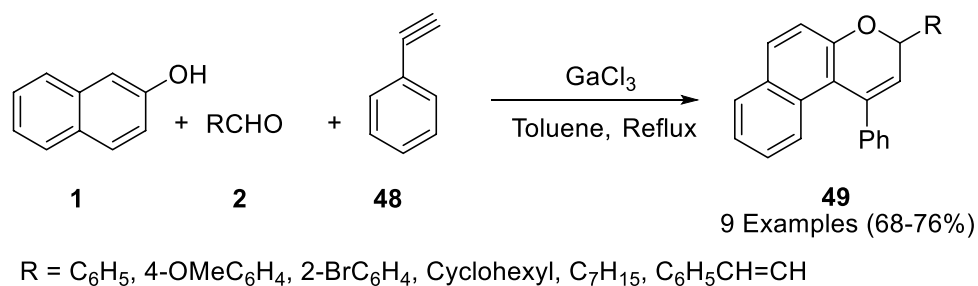
either 2-methyl-3-butyn-2-ol or other isocyanides such as *t*-butylisocyanide and isopropylisocyanide gave a mixture of unidentified product.

Yadav et al. [202] have described the synthesis of 1,3-dialkyl-3*H*-benzo[*f*]chromenes **49** by reaction of 2-naphthol **1**, aldehydes **2** and phenyl acetylene **48** using catalytic amount of gallium chloride in toluene as solvent under reflux conditions (Scheme 29). The reaction is believed to proceed via arylation of alkyne to afford vinylnaphthalene-2-ol which subsequently undergoes cyclization with aldehyde to give the desired chromenes **49** (Scheme 30).



**Scheme 28** Mechanism for the synthesis of 3H-Benzo[f]chromene-2-carboxamides **47**

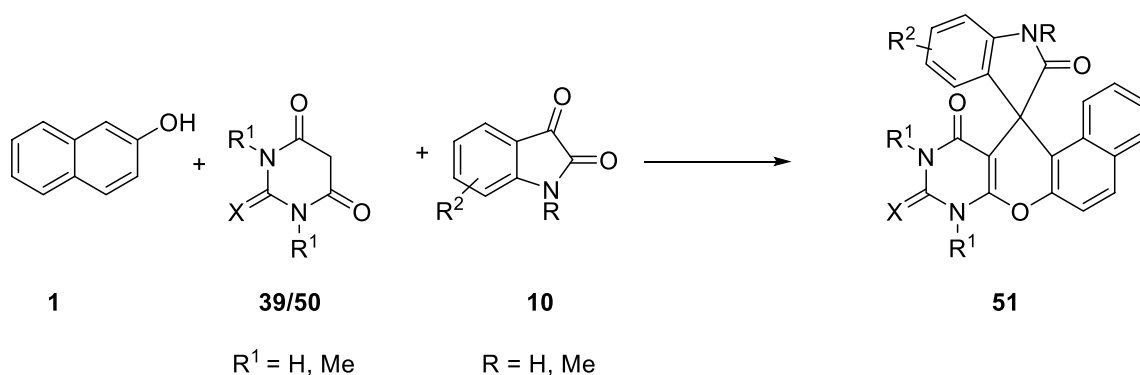
**Scheme 29** Synthesis of 1,3-diaryl-3H-benzo[f]chromenes **49**



**Scheme 30** Mechanism for the synthesis of 1,3-diaryl-3H-benzo[f]chromenes **49**

Spiroanthopyrano[2,3-*d*]pyrimidine-5,3'-indolines **51** were reportedly synthesized by one-pot condensation of 2-naphthol **1**, barbituric acids **39**/thiobarbituric acid **50** with

isatins **10** and under solvent-free and catalyst-free conditions [203] and also in the presence of [Hmim]HSO<sub>4</sub> under solvent-free conditions [145], sodium dodecyl sulfate (SDS) in



**Scheme 31** Synthesis of spironaphthopyrano[2,3-*d*]pyrimidine-5,3'-indolines **51**

**Table 12** Synthesis of spironaphthopyrano[2,3-*d*]pyrimidine-5,3'-indolines **51**

Catalyst, reaction conditions	X	Examples	Yield	References
130 °C	O	H	70–87	[203]
[Hmim]HSO <sub>4</sub> , 100 °C	O	H, 5-Br	82–90	[145]
SDS, H <sub>2</sub> O, 50 °C	O	H, 5-R (Cl/Br/F, Me, OMe, Et), 7-F, 6-Cl, 7-Me	82–92	[204]
SDS, H <sub>2</sub> O, 50 °C	S	H, 5-R (Cl/Br/F, Me, Et), 6-Br, 7-F, 6-Cl, 7-Me	80–92	[204]
SBA-Pr-SO <sub>3</sub> H, 140 °C	O	H, 5-Br/NO <sub>2</sub> /Cl	63–88	[205]

water [204] and sulfonic acid-functionalized SBA-15 (SBA-Pr-SO<sub>3</sub>H) [205] (Scheme 31, Table 12).

The mechanistic pathway for the formation of spironaphthopyrano[2,3-*d*]pyrimidine-5,3'-indolines **51** catalyzed by SBA-Pr-SO<sub>3</sub>H is depicted in Scheme 32. Initially, acid-catalyzed condensation of 2-naphthol with isatin takes place to furnish intermediate **A**. Then, a subsequent addition of barbituric acid to the intermediate **A**, followed by a cyclization and dehydration provides the desired product **51** (Scheme 32).

Asadi and co-workers [203] have efficiently synthesized a series of spironaphthopyrano[1,2-*b*]indeno-7,3-indolines **52** by multicomponent reactions of 2-naphthol **1**, indane-1,3-dione **25** and isatins **10** under solvent-free conditions without any catalyst (Scheme 33). Electron-withdrawing substituents on isatin were found to reduce the reaction time.

The synthesis of spiro-oxindoles with fused chromenes **53** (Scheme 34), through the three-component reaction of isatin derivatives **10**, malononitrile **13** or cyanoacetic ester **14** and 2-naphthol **1** compounds using *L*-proline [206], indium trichloride [207] and cellulose-SO<sub>3</sub>H [138] (Table 13).

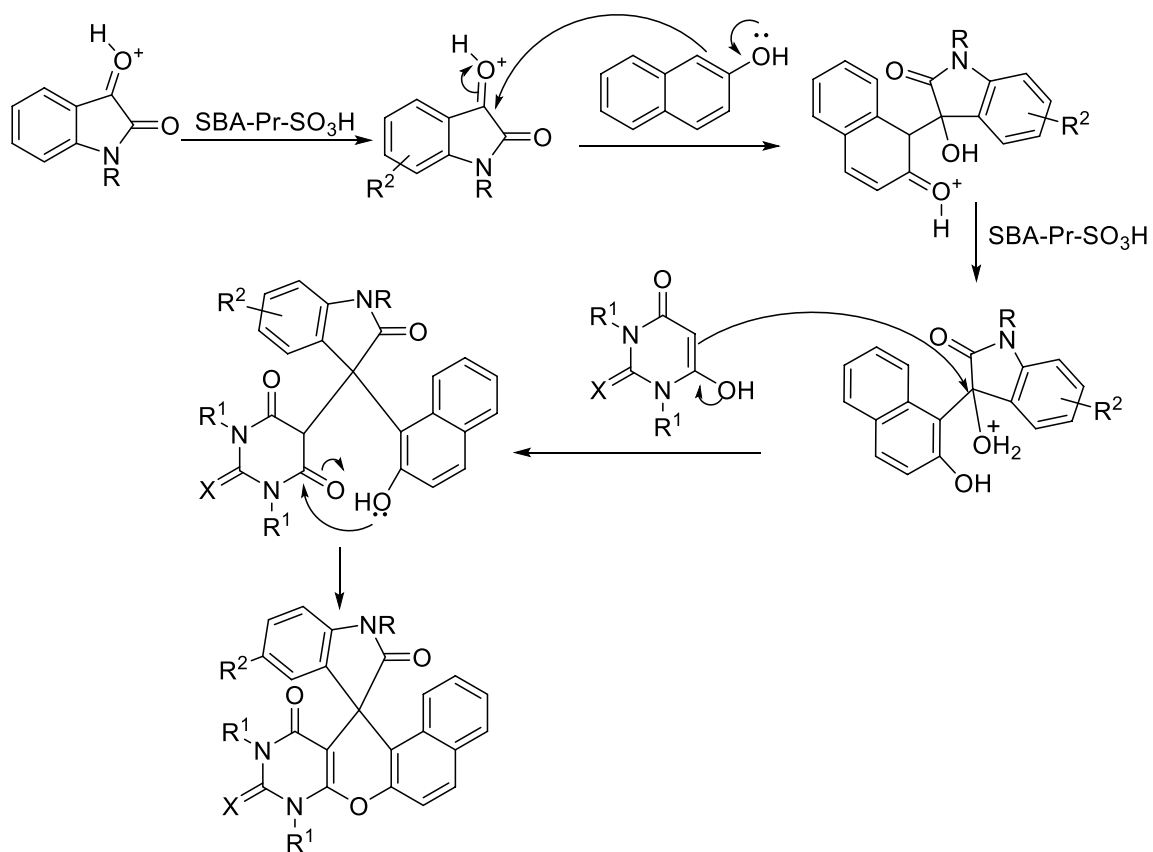
2-Aminospiro[benzo[*g*]chromene-4,11'-indeno[1,2-*b*]quinoxaline]-3-carbonitriles **56** were reportedly synthesized by condensation of malononitrile **13** or ethyl 2-cyanoacetate **14**, ninhydrin **54**, 1,2-phenylenediamine **55**, 2-naphthol **1** under refluxing or ultrasound irradiation at room temperature in good yields (Scheme 35) [208] using green and recyclable trifluoroethanol as catalyst. The reaction time under ultrasonic irradiation was significantly reduced as compared to conventional heating.

The synthesis of 10-methyl-8*H*-spiro[benzo[5,6]chromeno[2,3-*c*]pyrazole-11,3'-indol]-2'(1'*H*)-ones **58** by four-component reactions of phenylhydrazine/hydrazine hydrate **57**, isatins **10**, ethylacetoacetate **35** and 2-naphthol **1** using nano-Co<sub>3</sub>S<sub>4</sub> under microwave irradiation (Scheme 36) [209]. The method offers several advantages including utilization of microwave irradiation as clean procedure, high atom economy, high yields, shorter reaction times, low catalyst loading and reusability of the catalyst.

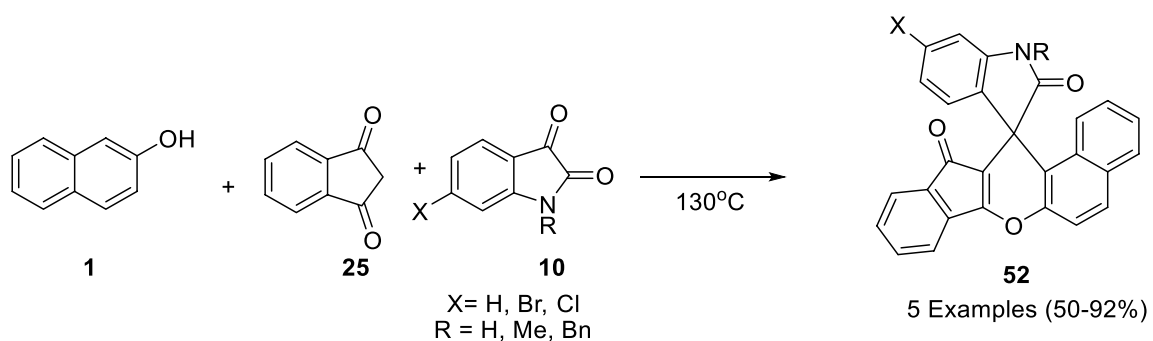
### 1,3-Oxazines

Oxazines are six-membered heterocyclic compounds which contain one nitrogen and one oxygen atom. Depending on the relative position of the heteroatoms, i.e., oxygen and nitrogen atom, they are known to exist in 3 isomeric forms, viz. 1,2-oxazine, 1,3-oxazine and 1,4-oxazine. 1,3-Oxazines are privileged heterocyclic scaffolds with interesting biological activities such as antimicrobial [210], non-nucleoside reverse transcriptase inhibitor [211], nonsteroidal progesterone receptor agonists [212], and antitumor [213].

Azizian and co-workers [214] investigated the microwave-assisted one-pot condensation reaction of *N,N,N',N'*-tetramethylguanidine (TMG) **59**, aryl-/heteroaryl-aldehydes **2** and 2-naphthol **1** using acetic acid as catalyst for the synthesis of 1-aryl-*N,N*-dimethyl-1*H*-naphtho[1,2-*e*] [1, 3]-oxazine-3-amine derivatives **60** (Scheme 37). Scheme 38 represents the mechanism for the formation of **60**. The first step involves the formation of intermediate by reaction of the

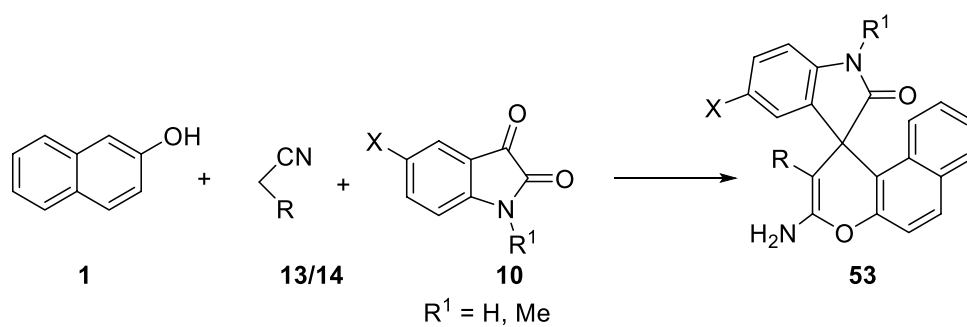


**Scheme 32** Mechanism for formation of spironaphthopyrano[2,3-*d*]pyrimidine-5,3'-indolines **51**



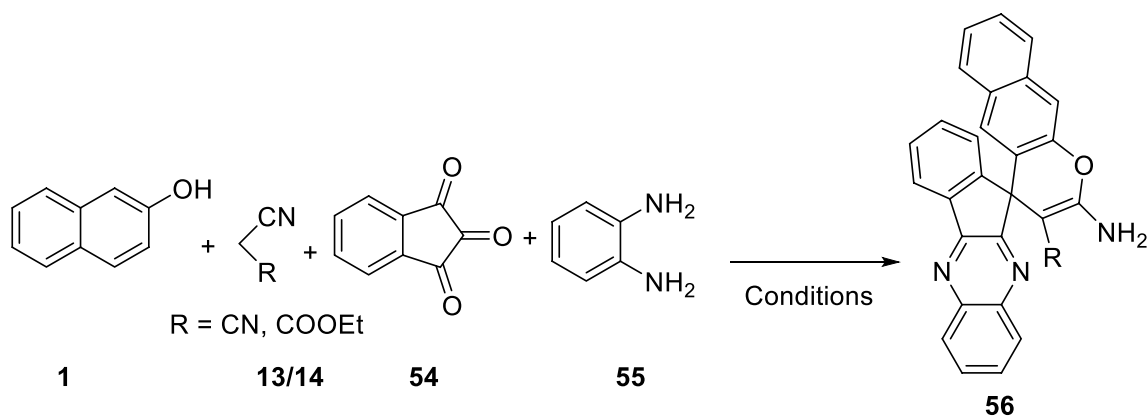
**Scheme 33** Synthesis of spironaphthopyrano[1,2-*b*]indeno-7,3-indolines **52**

**Scheme 34** Synthesis of spirooxindoles with fused chromenes **53**



**Table 13** Synthesis of spiro-oxindoles with fused chromenes **53**

Catalyst, reaction conditions	R	R <sup>2</sup>	Examples	Yield	References
L-Proline, CH <sub>3</sub> CN, reflux	CN, COOEt	H, 5-Cl/Br	6	75–90	[206]
InCl <sub>3</sub> /SiO <sub>2</sub> /MW	CN, COOEt	H	3	84–89	[207]
InCl <sub>3</sub> /CH <sub>3</sub> CN, reflux	CN, COOEt	H	3	65–75	[207]
Cellulose-SO <sub>3</sub> H, 55 °C	CN	H	1	85	[98]

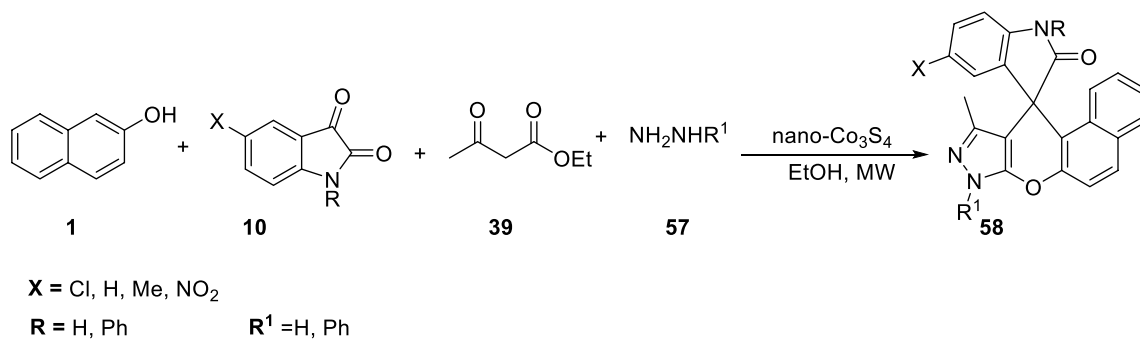
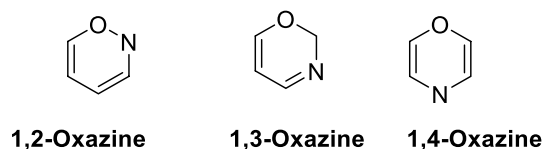
**Conditions:**

trifluoroethanol, US

2 Examples (85-87%)

trifluoroethanol, Reflux

2 Examples (88-90%)

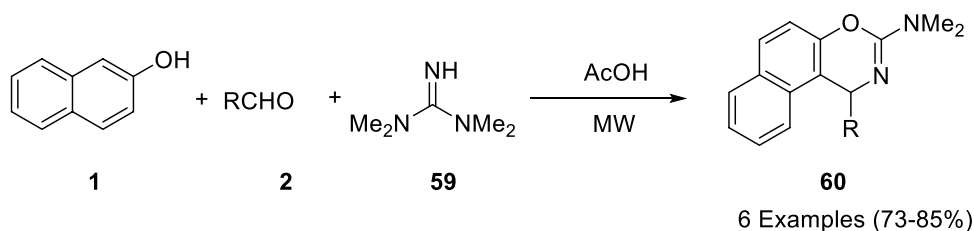
**Scheme 35** Synthesis of 2-aminospiro[benzo[*g*]chromene-4,11'-indeno[1,2-*b*]quinoxaline]-3-carbonitriles **56****Scheme 36** Synthesis of 10-methyl-8*H*-spiro[benzo[5,6]chromeno[2,3-*c*]pyrazole-11,3'-indol]-2'(1'*H*)-ones **58****Fig. 3** Oxazines

aldehyde with TMG. Subsequently, addition of 2-naphthol to the intermediate occurs, followed by cyclization to afford the corresponding products **60**.

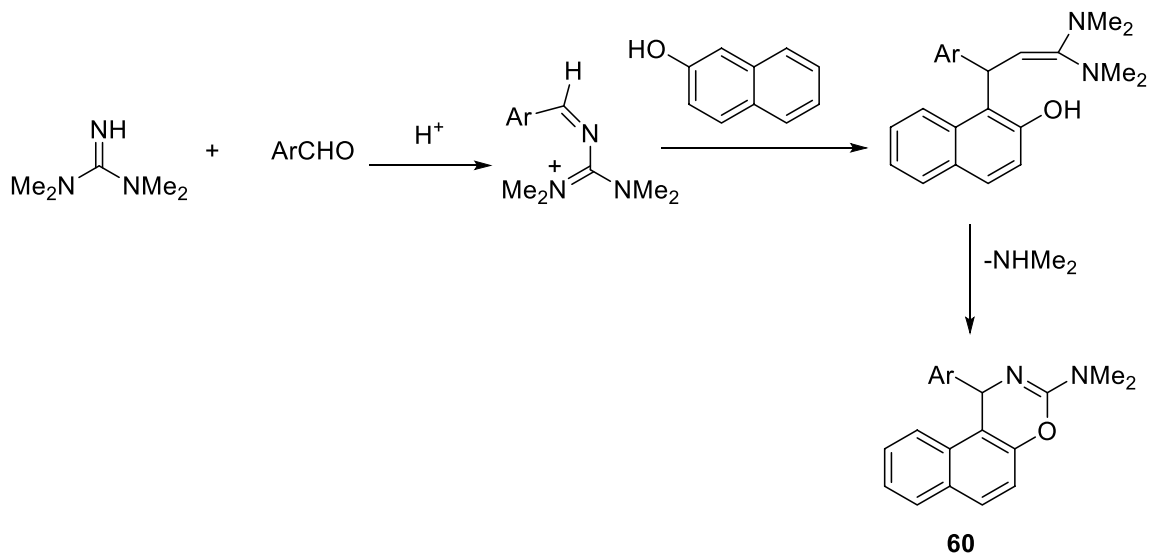
Several 1,2-dihydro-1-arylnaphtho[1,2-*e*] [1, 3] oxazine-3-ones **62** were synthesized by three-component condensation of 2-naphthol **1**, aldehydes **2** and urea **61** in the presence of nano-silica-supported ferric chloride [215], potassium carbonate and copper nanoparticles [216], ZnO nanoparticles [217], AgI nanoparticles [218], sulfuric acid-functionalized silica-coated magnetic nanoparticles (MgFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H) [219], magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles [220] as nanocatalysts (Table 14) (Scheme 39).

Several other catalysts such as *p*TSA [221], iodine [222], montmorillonite K10 clay [223], zinc triflate [224],

**Scheme 37** Synthesis of 1-aryl-*N,N*-dimethyl-1*H*-naphtho[1,2-*e*] [1, 3] -oxazine-3-amine derivatives **60**



R = C<sub>6</sub>H<sub>5</sub>, 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 2-Thienyl, 2-Furanyl, 2-BrC<sub>6</sub>H<sub>4</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, 3-MeC<sub>6</sub>H<sub>4</sub>



**Scheme 38** Mechanism for formation of 1-aryl-*N,N*-dimethyl-1*H*-naphtho[1,2-*e*] [1, 3] -oxazine-3-amine **60**

phosphomolybdic acid [225], Amberlite IRA-400 Cl resin [226], graphene oxide [227], TMSCl/NaI [228], *N*-propane sulfonic acid pyridinium hydrogen sulfate ([PSPy]HSO<sub>4</sub>) [229], RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> [230], cellulose sulfuric acid/SDS [231] and thiamine hydrochloride (VB<sub>1</sub>) [232] were also found to effect the above synthesis. The condensation of 2-naphthol **1** and aldehydes **2** with thiourea **63** instead of urea **61** leads to the formation of 1,2-dihydro-3*H*-naphtho[1,2-*e*] [1, 3] oxazine-3-thione **64** [219, 220, 230, 231] (Scheme 40, Table 15).

An efficient stereoselective synthesis of diverse trans-naphtho[1,2-*e*] [1, 3] oxazines **66** via one-pot condensation reaction of 2-naphthol **1**, 3-amino-5-methylisoxazole **65** and arylaldehydes **2** catalyzed by bismuth(III) trifluoromethane sulfonate has been described by Shafiee et al. [233] (Scheme 41). Aldehydes with both electron-donating and electron-withdrawing substituents afforded the desired product in high stereoselectivity.

Catalyst-free synthesis of 1,3-disubstituted-2,3-dihydro-1*H*-naphth[1,2-*e*] [1, 3] oxazines **68** was achieved by Turgut and co-workers [234] via condensation of 2-naphthol **1** with two equivalents of aryl-/heteroaryl-aldehydes **2** in the presence of ammonia **67** at room temperature (Scheme 42).

The synthesis of 2,3-dihydro-1,2,3-trisubstituted-1*H*-naphth[1,2-*e*] [1, 3] oxazines **70** has been described by condensation reaction of 2-naphthol **1** with aldehydes **2** and primary amines **69** using Brønsted acids like *p*TSA [235], sulfamic acid [235], 1,3-disulfoimidazolium trifluoroacetate ([DSIM]CF<sub>3</sub>COO) [235], as well as triphenyl sulfophosphonium chlorometallates [236] with both Brønsted acid and Lewis acid property (Scheme 43, Table 16).

Various catalysts like sodium hydrogen sulfate [237], [Bmim]HSO<sub>4</sub> [237], TBAB [237], iron(III) trifluoroacetate ([Fe(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>] [238], Fe<sub>3</sub>O<sub>4</sub>@nano-cellulose/TiCl [239], silica-supported boron trifluoride, BF<sub>3</sub>-SiO<sub>2</sub> [240], thiamine hydrochloride (VB1) [241], glycerol [242], Fe<sub>3</sub>O<sub>4</sub>@

**Table 14** Synthesis of 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-ones **62**

Catalyst, reaction conditions	Examples	Yield	References
FeCl <sub>3</sub> /SiO <sub>2</sub> Nps, 150 °C	9	78–92	[215]
K <sub>2</sub> CO <sub>3</sub> , Cu Nps, PEG-400, r.t.	10	74–93	[216]
ZnO nps, 150 °C	10	76–94	[217]
AgI Nps, 140 °C	9	79–92	[218]
MgFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -SO <sub>3</sub> H, MW	13	81–97	[219]
Fe <sub>3</sub> O <sub>4</sub> nps, toluene, reflux	4	88–94	[220]
pTSA, 160 °C	7	58–64	[221]
pTSA, MW	7	69–82	[221]
Iodine, 140–150 °C	22	50–93	[222]
Montmorillonite K10 clay, 160 °C	14	10–90	[223]
Zn(OTf) <sub>2</sub> , AcCN, reflux	9	70–84	[224]
H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> DMF, 100°C	10	84–92	[225]
Amberlite IRA-400 Cl resin, 20 °C	12	78–88	[226]
Graphene oxide, 120 °C	8	84–89	[227]
TMSCl/NaI in AcCN/DMF (4:1), 140 °C	13	62–89	[228]
[PSPy]HSO <sub>4</sub> , 120 °C	10	90–95	[229]
RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub> , toluene, reflux	7	74–90	[230]
Cellulose sulfuric acid, SDS, H <sub>2</sub> O, 80 °C	9	80–90	[231]
VB <sub>1</sub> , 150 °C	4	85–92	[232]

MAP Nps [243], alum [244] were explored for the one-pot multicomponent condensation reaction of 2-naphthol **1**,

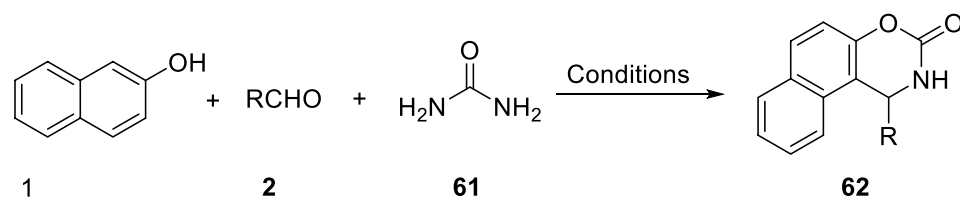
formaldehyde **31** and primary amines **69** for the synthesis of 2,3-dihydro-1*H*-naphtho-[1,2-*e*] [1, 3] oxazine derivatives **71** (Scheme 44, Table 17).

1,3-Oxazine-4-thione derivatives **74** were synthesized via one-pot two-step domino protocol from ammonium thiocyanate **72** and acid chlorides **73** and 2-naphthol **1** in the presence of an effective recyclable bifunctional organocatalyst, i.e., *L*-proline as in water [245] (Scheme 45). It was further noticed that benzoyl chlorides with electron-withdrawing substituents increased the rate of reaction and gave higher yields than those with electron-releasing groups.

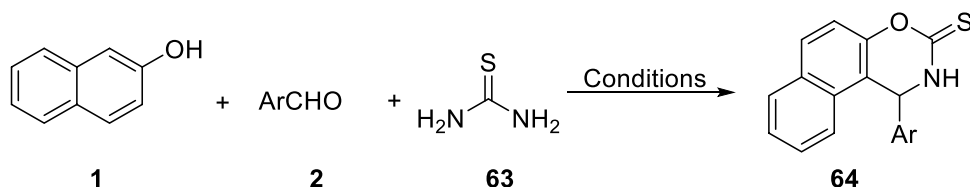
## Furan

Furans, an aromatic five-membered aromatic ring with oxygen as heteroatom (Fig. 3), constitute core entities in many natural products are very imperative among heterocyclic structures owing to their remarkable biological properties like anticancer, antidepressant, anti-anxiolytic, anti-inflammatory, muscle relaxant, antihypertensive, antidiuretic, anti-ulcer, antihistaminic, antiarrhythmic and analgesic. [246].

An efficient one-pot synthesis of benzamidobenzo[*b*]furans **77** has been developed via reaction of arylglyoxals **75**, benzamide **76** and 2-naphthol **1** using yttrium nitrate hexahydrate or tungstate sulfuric acid (TSA) as a catalyst under solvent-free conditions [247, 248] (Scheme 46). TSA employed as catalyst by Vahabinia and co-workers can be recycled over three times without significant loss of activity.



**R** = 4-*X*C<sub>6</sub>H<sub>4</sub> (*X* = Cl, Br, F), 2-ClC<sub>6</sub>H<sub>4</sub>, 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 4-MeOC<sub>6</sub>H<sub>4</sub>, 3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,3-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3-MeO-4-HOC<sub>6</sub>H<sub>3</sub>, 4-HOC<sub>6</sub>H<sub>4</sub>, 2-Furyl, 4-MeCC<sub>6</sub>H<sub>4</sub>, 3-*X*C<sub>6</sub>H<sub>4</sub> (*X*=Cl, Br, F), 4-EtOC<sub>6</sub>H<sub>4</sub>, 2-Thienyl, 3-MeC<sub>6</sub>H<sub>4</sub>, 3-EtO-4-HO-C<sub>6</sub>H<sub>3</sub>, 4-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 4-NCC<sub>6</sub>H<sub>4</sub>, 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3,4,5-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 3-MeOC<sub>6</sub>H<sub>4</sub>, 3-F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>, 2,5-(OH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2-OH-5-OMeC<sub>6</sub>H<sub>3</sub>, 4-Me<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>,

**Scheme 39** Synthesis of 1,2-dihydro-1-arylnaphtho[1,2-*e*] [1, 3] oxazine-3-ones **62****Scheme 40** Synthesis of 1,2-dihydro-3*H*-naphtho[1,2-*e*] [1, 3] oxazine-3-thiones **64**

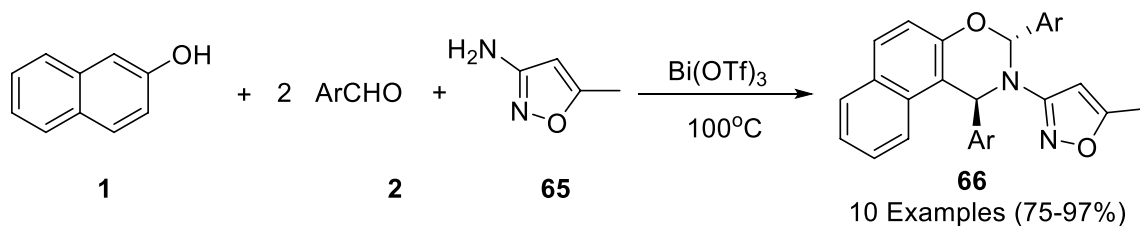


**Table 15** Synthesis of 1,2-dihydro-3*H*-naphtho[1,2-*e*][1,3]oxazine-3-thiones **64**

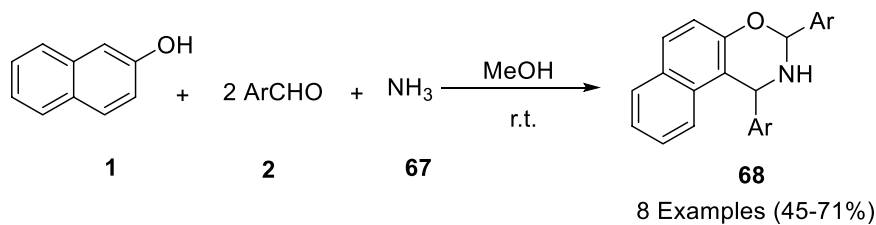
Catalyst, reaction conditions	Examples	Yield	References
(MgFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -SO <sub>3</sub> H), MW	3	88–92	[219]
Fe <sub>3</sub> O <sub>4</sub> nps, toluene, reflux	2	80–85	[220]
RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub> , toluene, reflux	4	70–82	[230]
Cellulose sulfuric acid, SDS, H <sub>2</sub> O, 80 °C	3	80–84	[231]

**Table 16** Synthesis of 2,3-dihydro-1,2,3-trisubstituted-1*H*-naphth[1,2-*e*][1,3]oxazines **70**

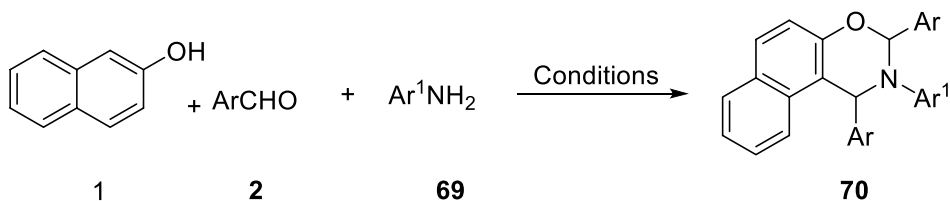
Catalyst, reaction conditions	Examples	Yield	References
<i>p</i> TSA, 80 °C	12	88–95	[235]
<i>p</i> TSA, aq. EtOH, r.t.	12	82–87	[235]
Sulfamic acid, 80 °C	12	90–97	[235]
Sulfamic acid, aq. EtOH, r.t.	12	84–92	[235]
[DSIM]CF <sub>3</sub> COO, 80 °C	12	93–98	[235]
[DSIM]CF <sub>3</sub> COO, aq. EtOH, r.t.	12	88–94	[235]
[TPSP]FeCl <sub>4</sub> , aq. EtOH, r.t.	10	89–94	[236]
[TPSP]FeCl <sub>4</sub> , 80 °C	10	94–98	[236]
[TPSP] <sub>2</sub> Zn <sub>2</sub> Cl <sub>6</sub> , aq. EtOH, r.t.	10	88–92	[236]
[TPSP] <sub>2</sub> Zn <sub>2</sub> Cl <sub>6</sub> , 80 °C	10	92–97	[236]



Ar = 4-NCC<sub>6</sub>H<sub>4</sub>, 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 3-BrC<sub>6</sub>H<sub>4</sub>, 2-BrC<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 4-FC<sub>6</sub>H<sub>4</sub>, 3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, 2-ClC<sub>6</sub>H<sub>4</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>

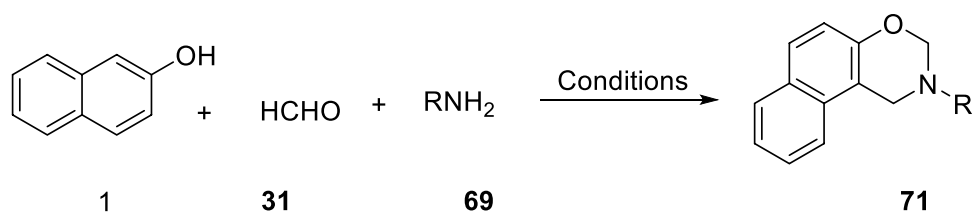
**Scheme 41** Synthesis of trans-naphtho[1,2-*e*][1,3]oxazines **66****Scheme 42** Synthesis of 1,3-disubstituted-2,3-dihydro-1*H*-naphth[1,2-*e*][1,3]oxazines **68**

Ar = 3,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3-HOC<sub>6</sub>H<sub>4</sub>, 3,4,5-(OMe)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 2-Thienyl, 2-Pyridyl, 3,4-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2-OH-3-BrC<sub>6</sub>H<sub>3</sub>, 3-PhOC<sub>6</sub>H<sub>4</sub>

**Scheme 43** Synthesis of 2,3-dihydro-1,2,3-trisubstituted-1*H*-naphth[1,2-*e*][1,3]oxazines **70**

Ar = C<sub>6</sub>H<sub>5</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 2-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>

Ar<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, 4-MeOC<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 4-Me<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, n-Butyl



R = H, 2-MeC<sub>6</sub>H<sub>4</sub>, 3-MeC<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 2-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 3-MeOC<sub>6</sub>H<sub>4</sub>, 4-MeOC<sub>6</sub>H<sub>4</sub>, 4-EtOC<sub>6</sub>H<sub>4</sub>, 2-EtOC<sub>6</sub>H<sub>4</sub>, 4-FC<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 4-BrC<sub>6</sub>H<sub>4</sub>, 2,4,6-Br<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 4-EtC<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, n-Butyl, n-Hexyl, Cyclohexyl, 2-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2-HOC<sub>6</sub>H<sub>4</sub>, 4-Cl-2-HOC<sub>6</sub>H<sub>3</sub>, 2,6-(Me<sub>2</sub>CH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>,

**Scheme 44** Synthesis of 2,3-dihydro-1*H*-naphtho-[1,2-*e*] [1,3] oxazines **71**

**Table 17** Synthesis of 2,3-dihydro-1*H*-naphtho-[1,2-*e*] [1,3] oxazine derivatives **71**

Catalyst, reaction conditions	Examples	Yield	References
Bmim[HSO <sub>4</sub> ], 60 °C	14	87–93	[237]
TBAB, H <sub>2</sub> O, r.t.	14	85–93	[237]
NaHSO <sub>4</sub> , r.t.	14	85–96	[237]
Fe(CF <sub>3</sub> CO <sub>2</sub> ) <sub>3</sub> , SDS, H <sub>2</sub> O, r.t.	7	82–89	[238]
Fe <sub>3</sub> O <sub>4</sub> @nano-cellulose/TiCl, r.t.	14	80–98	[239]
BF <sub>3</sub> –SiO <sub>2</sub> , r.t., US	18	80–94	[240]
BF <sub>3</sub> –SiO <sub>2</sub> , 80 °C	18	56–85	[240]
VB1, H <sub>2</sub> O, r.t.	6	87–92	[241]
Glycerol 90 °C	2	68–76	[242]
Fe <sub>3</sub> O <sub>4</sub> @MAP Nps, Ultrasonication	6	88–93	[243]
Alum, H <sub>2</sub> O, r.t.	14	72–90	[244]

Several naphthofuran-2(3*H*)-one analogues **80** were efficiently synthesized by three-component condensation reaction using 2-naphthols **1/1d**, acetaldehyde **78** and carbon monoxide **79** in the presence of a palladium catalyst (Scheme 47) [249].

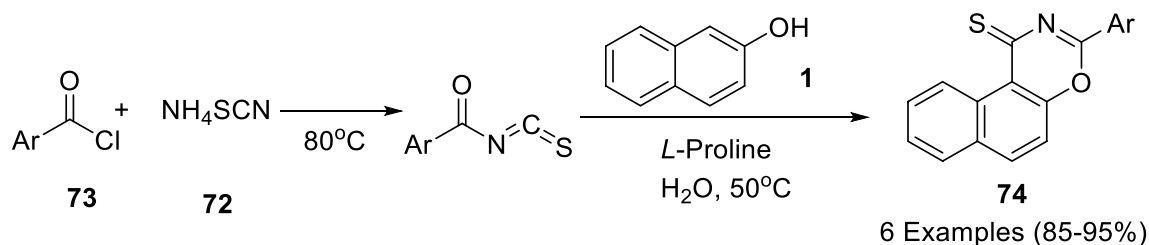
## Miscellaneous

The reaction of dimethyl acetylenedicarboxylate (DMAD) **41** with 2-naphthols **1** in the presence of trimethyl or triphenylphosphite **81** leads to stable dimethyl oxa-2λ<sup>5</sup>-phosphaphenanthrene derivatives **82** [250] (Scheme 48).

One-pot, solvent-free microwave-assisted synthesis of 1,3,2-aryldioxaborines **84** in the presence of acidic alumina by reaction of 2-naphthol **1**, phenylboronic acid **83** and aldehydes **2** (Scheme 49) has been reported by Reza Naimi-Jamal and co-workers [251]. The above method is tolerant to different aromatic and aliphatic aldehydes as well as naphthols.

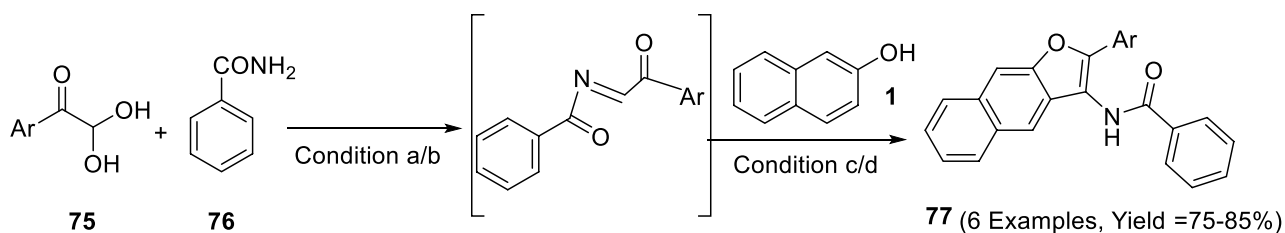
## Conclusion

A plethora of heterocyclic compounds like xanthenes, furans, pyrans and oxazines have been reportedly synthesized from 2-naphthol analogues. This review exemplifies the multicomponent reactions of 2-naphthol as building block for the synthesis of a variety of heterocyclic compounds. The potential of 2-naphthol in multicomponent reactions is still being discovered; thus, this review might

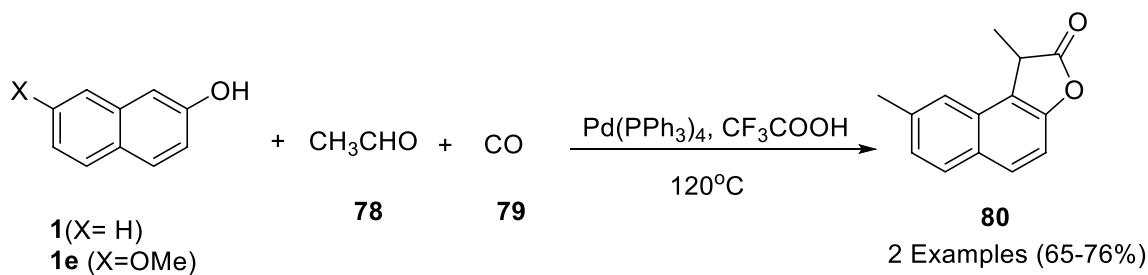
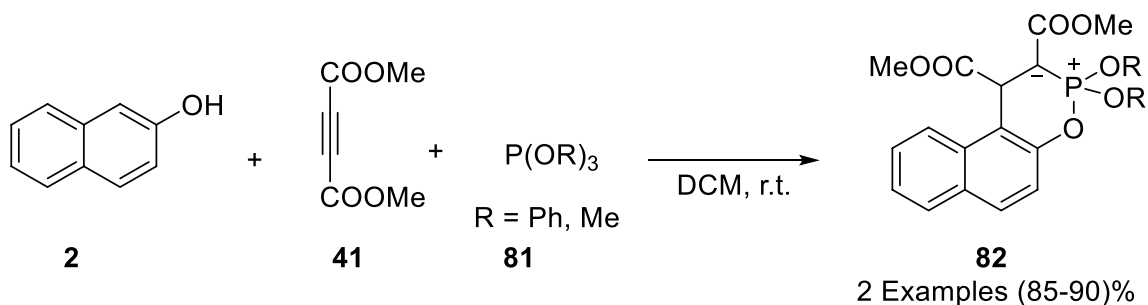
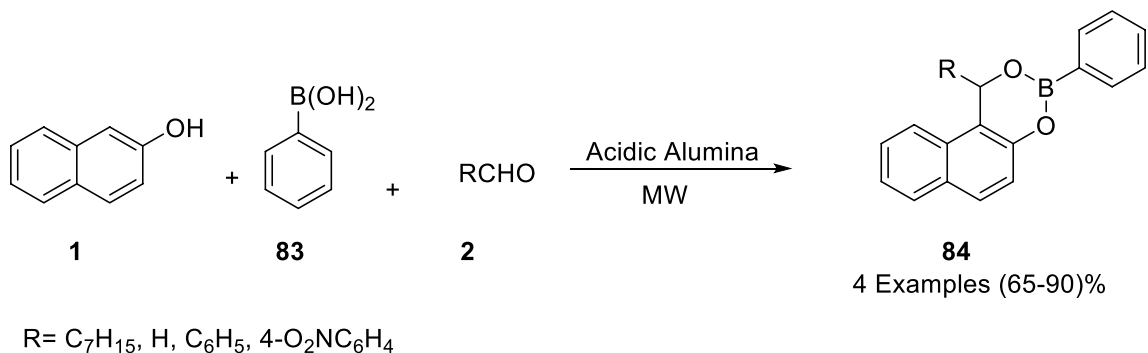


Ar = 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 2-MeC<sub>6</sub>H<sub>4</sub>, 3-MeC<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, 4-BrC<sub>6</sub>H<sub>5</sub>, 3,5-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>

**Scheme 45** Synthesis of 1,3-oxazine-4-thione derivatives **74**



**Condition a:**  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $70^\circ\text{C}$ ; **Condition b:** TSA  $120^\circ\text{C}$   
**Condition c:**  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $100^\circ\text{C}$ ; **Condition d:** TSA  $120^\circ\text{C}$   
 Ar =  $\text{C}_6\text{H}_5$ , 4- $\text{BrC}_6\text{H}_4$ , 4- $\text{ClC}_6\text{H}_4$ , 4- $\text{MeOC}_6\text{H}_4$ , 3- $\text{MeOC}_6\text{H}_4$

Scheme 46 Synthesis of benzamidobenzo[*b*]furans **77**Scheme 47 Synthesis of naphthofuran-2(3*H*)-one analogues **80**Scheme 48 Synthesis of dimethyl oxa-2 $\lambda^5$ -phosphaphenanthrenes **82**Scheme 49 Synthesis of 1,3,2-aryldioxaborines **84**

trigger new ideas to use 2-naphthol as a building block for future research in heterocyclic chemistry.

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