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Review

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Bismuth(III) catalyzed organic synthesis: a decade of progress

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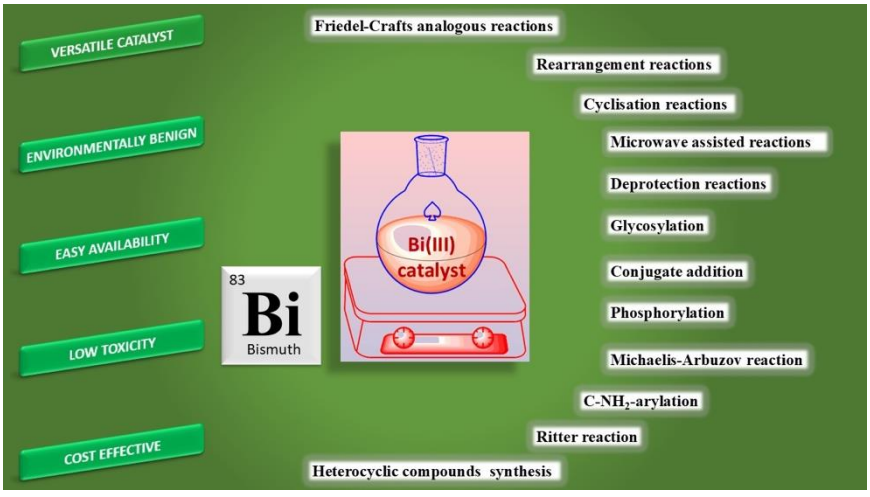
Abstract

Bismuth(III) compounds, renowned for their low toxicity, affordability, and easy handling, are pivotal in organic chemistry as Lewis acid catalysts. With the growing need for environmentally friendly reagents and a substitute for transition metal catalysts, there has been a sharp rise in interest in bismuth(III) catalysts. Over the past decade, bismuth(III) catalysts have been widely utilized for various organic transformations, facilitating the synthesis of structurally diverse molecules with a wide range of applications under mild conditions. This review summarizes the progress made over the past decade in bismuth(III)-catalyzed organic synthesis, emphasizing the fundamental bond-forming processes, the range of accessible molecular scaffolds, and the mechanistic understanding of representative reactions.



Keywords: Bismuth, bismuth(III) compounds, organic synthesis, catalysis, main group catalysis

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1. Introduction

The German word Weissmuth is where the name bismuth comes from, which means white material. Bismuth is regarded as the heaviest stable element in the periodic table and is of remarkably low toxicity and non-corrosive in nature[1–3]. With an electron configuration of $[Xe]4f^{14}5d^{10}6s^{2}6p^{3}$, the most common oxidation state exhibited by bismuth is +3, which is due to the inert pair effect. Bismuth(III) compounds also show Lewis acidity due to lanthanide contraction. These make bismuth(III) compounds excellent catalysts in synthetic organic chemistry. Bismuth(III) compounds, especially bismuth chloride ($BiCl_3$), bismuth bromide ($BiBr_3$), bismuth triflate ($Bi(OTf)_3$), and bismuth nitrate ($Bi(NO_3)_3$) have garnered greater interest as versatile catalysts

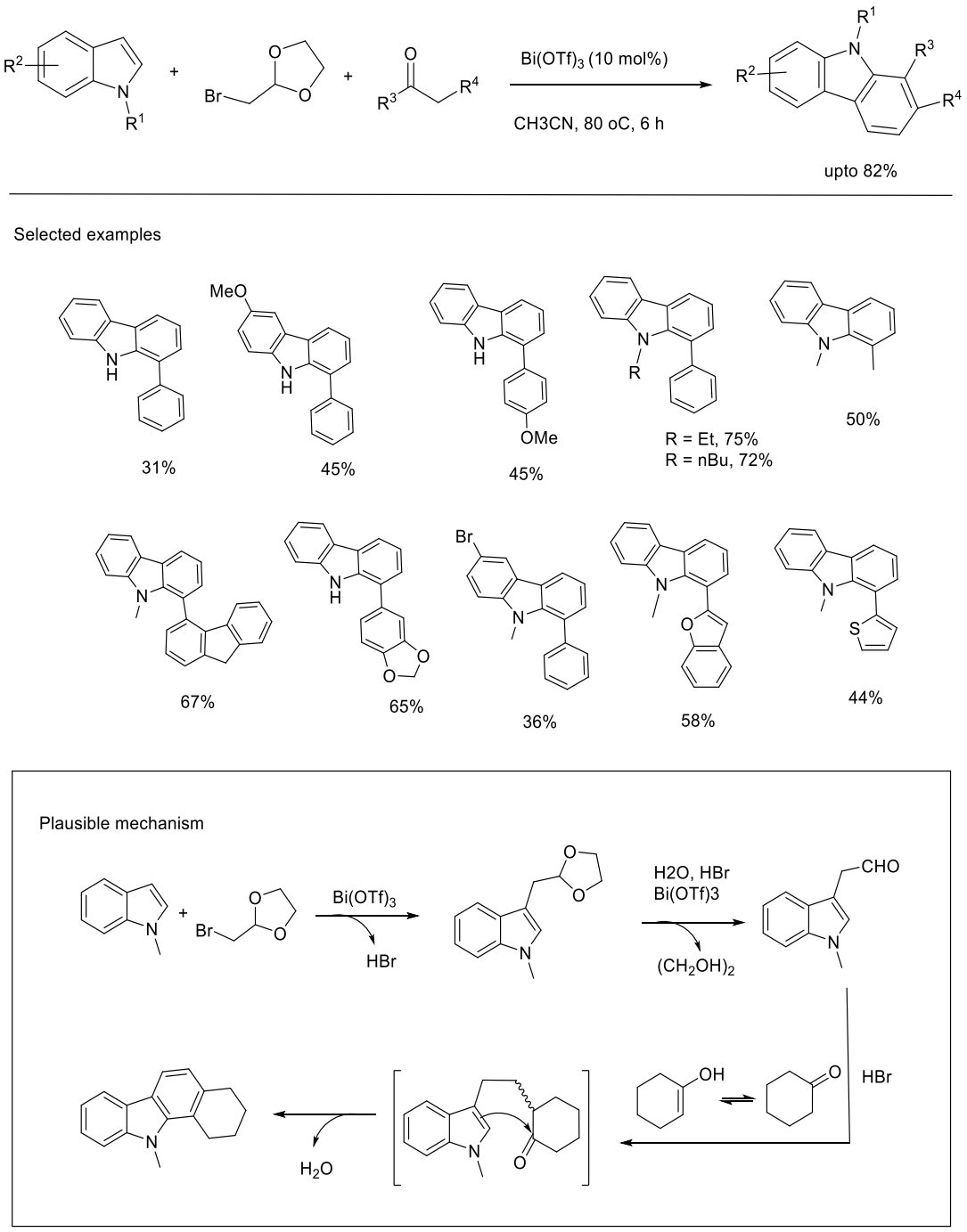
during the last three decades due to their exceptional chemical and physical qualities, which include low toxicity, air and moisture tolerance, and stability, in a variety of organic synthesis[4,5].

Furthermore, most bismuth(III) catalysts are readily available and reasonably priced. Thus, bismuth(III) catalysts provide an answer to one of the most significant, fascinating, and difficult areas of research, which is the development of non-transition-metal-catalyzed synthesis of organic compounds. Several reviews have highlighted the utility of bismuth compounds in organic synthesis; however, a comprehensive and systematically organized account of recent advances remains lacking[6,7]. In particular, the rapid expansion of bismuth(III)-catalyzed transformations over the past decade has not yet been analysed within a unified framework that classifies reactions according to fundamental bond-forming processes. In this review, we present an overview of the applications of Bismuth(III) compounds as catalysts in synthetic organic chemistry over the past decade, providing a synthesis-oriented perspective on reactivity trends, mechanistic features, and synthetic utility. We also highlight how bismuth salts can outperform conventional transition-metal catalysts, emphasizing their distinct reactivity and practical utility in organic synthesis. This review aims to illustrate the versatility and growing significance of bismuth catalysis in developing efficient, selective, and environmentally benign synthetic methodologies.

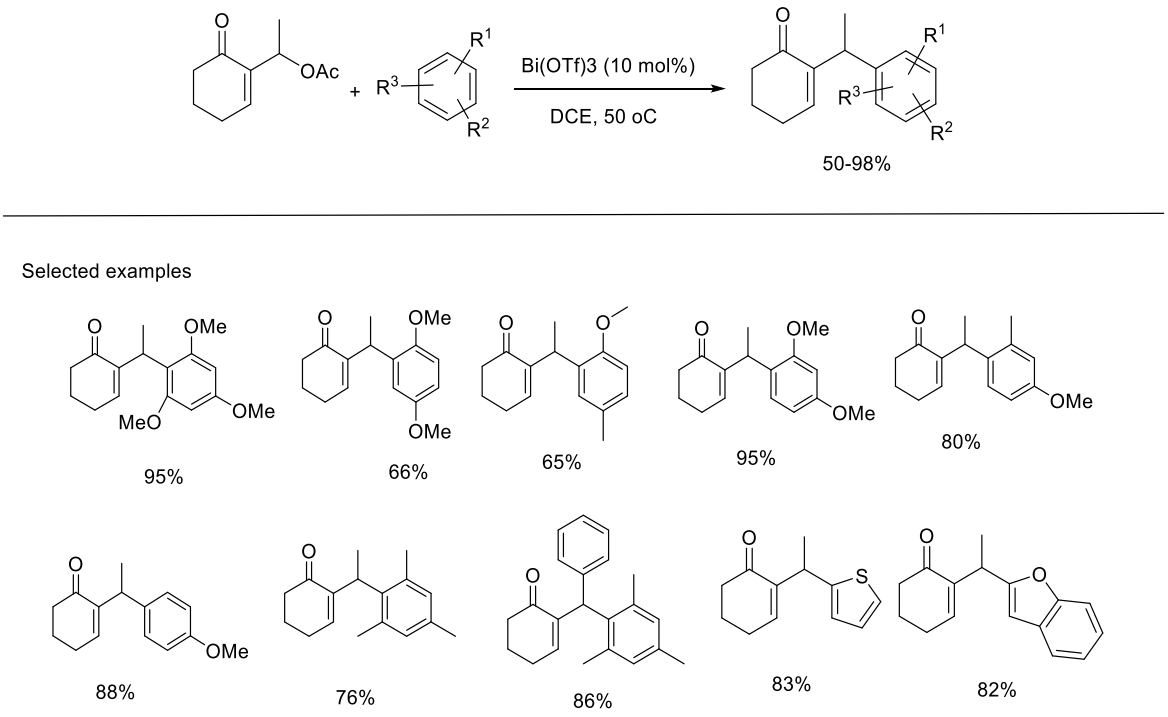
2. C-C Bond Formation

2.1. Friedel-Crafts alkylation/acylation and arylation reactions

Bismuth salts are found to be better and more efficient catalysts for some Friedel-Crafts analogous alkylation and acylation reactions. Yanlong Gu et al. synthesized carbazole derivatives by a three-component reaction involving indoles, α-bromoacetaldehyde acetals, and ketones using $Bi(OTf)_3$ as a catalyst[8]. According to the proposed mechanism, an α-tryptaldehyde type intermediate was produced by Friedel-Crafts alkylation of indole with α-bromoacetaldehyde acetal, which, in turn, underwent [4 + 2] annulation with the ketones (Scheme 1). Omrani et al. reported a Friedel-Crafts reaction for the regioselective synthesis of various functionalized conjugated enones in good to excellent yield. They used Morita-Baylis-Hillman acetates as substrates and $Bi(OTf)_3$ as a catalyst, which proved to be more effective than the aluminium chloride ($AlCl_3$) catalyst (Scheme 2)[9].

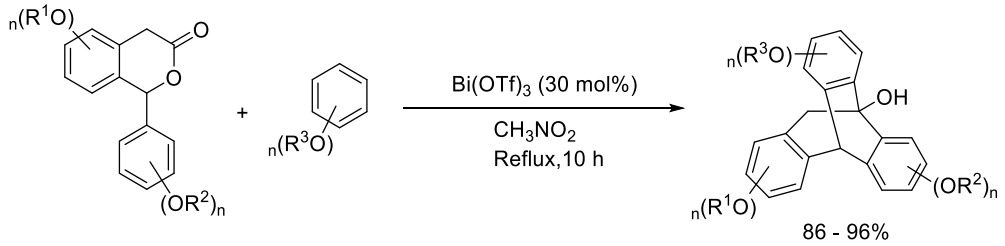


Scheme 1. $Bi(OTf)_3$ catalyzed synthesis of carbazole derivatives.

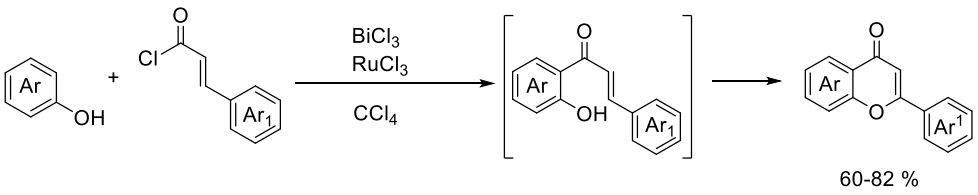


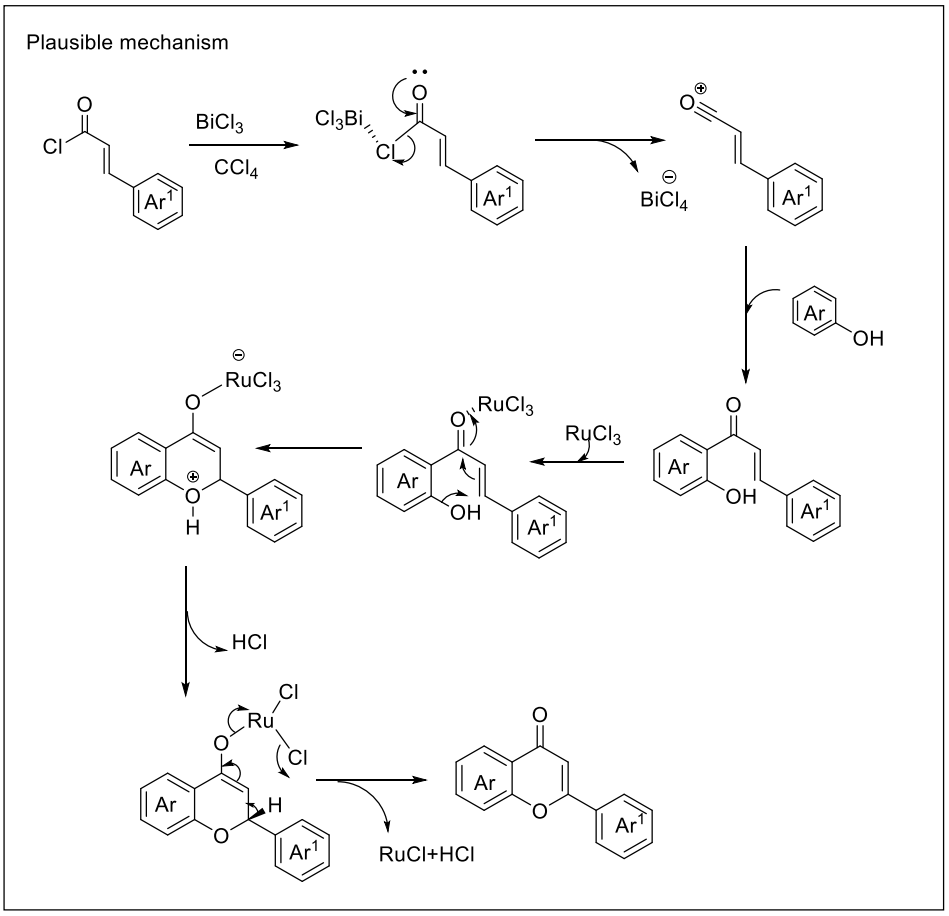
Scheme 2. $Bi(OTf)_3$ catalyzed regioselective synthesis of functionalized conjugated enones.

Chang et al. achieved the one-pot synthesis of polyoxygenated triptycenes from 1-aryl isochroman-3-ones and oxygenated arenes catalyzed by $Bi(OTf)_3$. This Friedel–Crafts type reaction demonstrates an effective ring closure through three C-C bond formation (Scheme 3)[10]. Further, they designed a route to synthesize functionalized flavones using a $BiCl_3/RuCl_3$ catalyst, which was superior to $AlCl_3$. Intermolecular ortho-acylation of substituted phenols and cinnamoyl chlorides, followed by intramolecular cyclodehydrogenation of the resultant o-hydroxychalcones in a cascade process, drives the reaction. The reaction mechanism involves coordination of $BiCl_3$ to the substrate via Bi–Cl bond formation, yielding an activated bismuth complex. Subsequent elimination of $WBiCl_4$ generates a styrylacylium-type intermediate, which undergoes a Friedel–Crafts ortho-acylation to form a new C-C bond. Introduction of $RuCl_3$ facilitates the formation of a ruthenium(III)-chelated species, which undergoes intramolecular oxa-Michael addition to generate a C-O bond. Proton transfer and the release of HCl yield an intermediate that subsequently undergoes dehydrogenation to form the flavone framework, accompanied by the elimination of RuCl and HCl. During this cyclodehydrogenation step, a redox interconversion between Ru(III) and Ru(I) is involved (Scheme 4)[11]. They also synthesized a variety of functionalized dibenzofused medium-sized oxacycles from sulfonyl o-hydroxyacetophenones and benzofused cycloesters. This Friedel-Crafts-type annulation reaction was catalyzed by $Bi(OTf)_3$, and water was the only byproduct of the reaction (Scheme 5)[12].

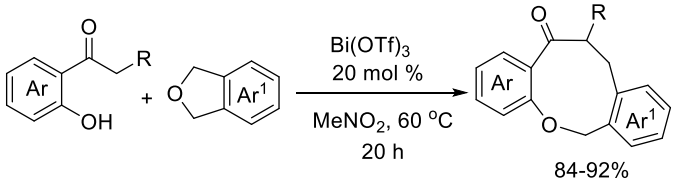


Scheme 3. $Bi(OTf)_3$ catalyzed synthesis of polyoxygenated triptycenes.





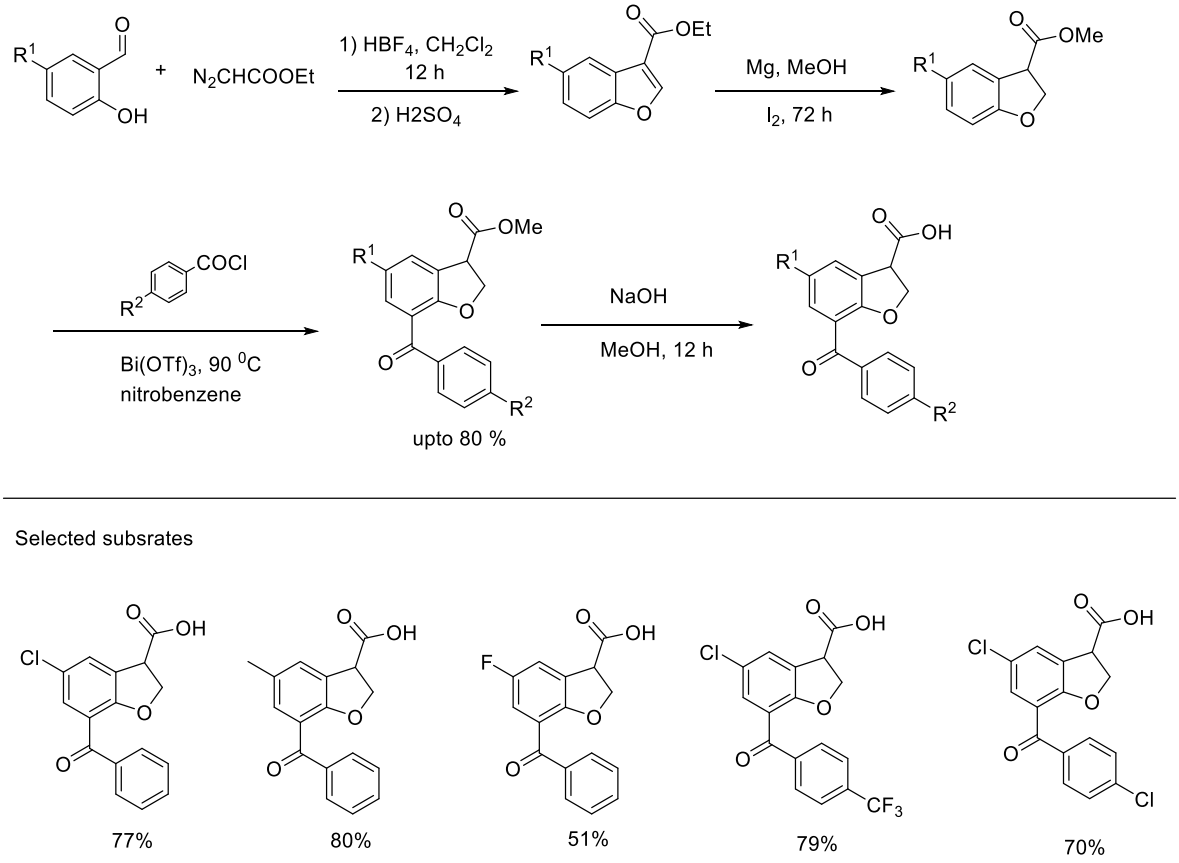
Scheme 4. $BiCl_3/RuCl_3$ catalyzed synthesis of o-hydroxychalcones.



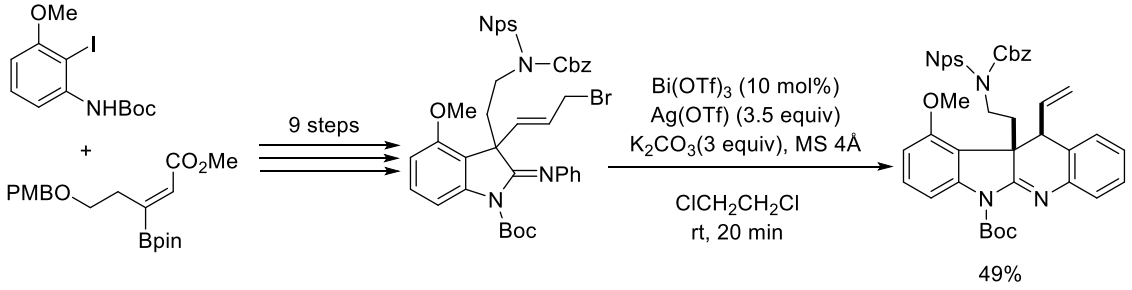
Scheme 5. $Bi(OTf)_3$ catalyzed synthesis of dibenzofused oxacycles.

While synthesizing the cyclooxygenase (COX) inhibitor BRL-3795, Shamsul et al. used $Bi(OTf)_3$ as a catalyst for the benzoylation of a benzofuran ring in the third step. It is observed that $AlCl_3$ as a catalyst could yield only a trace amount, whereas $Bi(OTf)_3$ catalyzed the reaction to give 76% yield (Scheme 6)[13]. Tsukano et al. obtained a tetracyclic compound that has the partial structure of the communesins, an indole alkaloid by Friedel-Crafts reaction of allyl bromide, using $Bi(OTf)_3$ as a catalyst in the final step (Scheme 7)[14]. Phuong et al. revealed a microwave-assisted $Bi(OTf)_3$ catalyzed synthesis of ortho-hydroxyaryl ketones by direct C-benzoylation of phenols and naphthols (Scheme 8)[15]. With bismuth catalyst arylation reaction was also

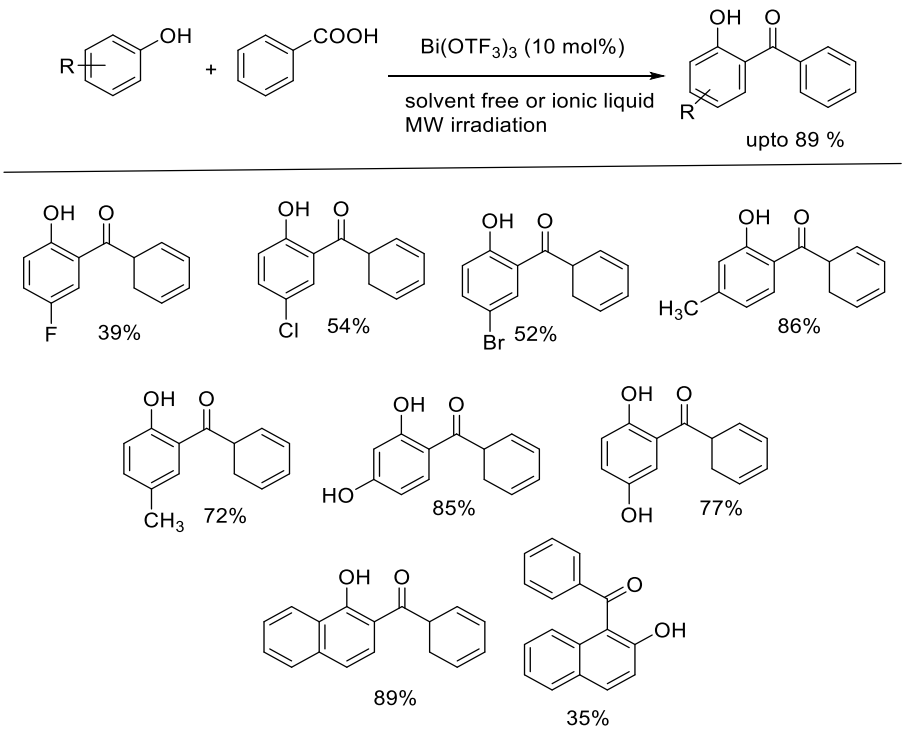
achieved. Kasama et al. achieved a $Bi(OTf)_3$-catalyzed, high chemo- and regioselective cross coupling reaction of 3-hydroxycarbazoles and arenols to yield C_1-symmetric hydroxybiaryls in a very good yield (Scheme 9)[16].



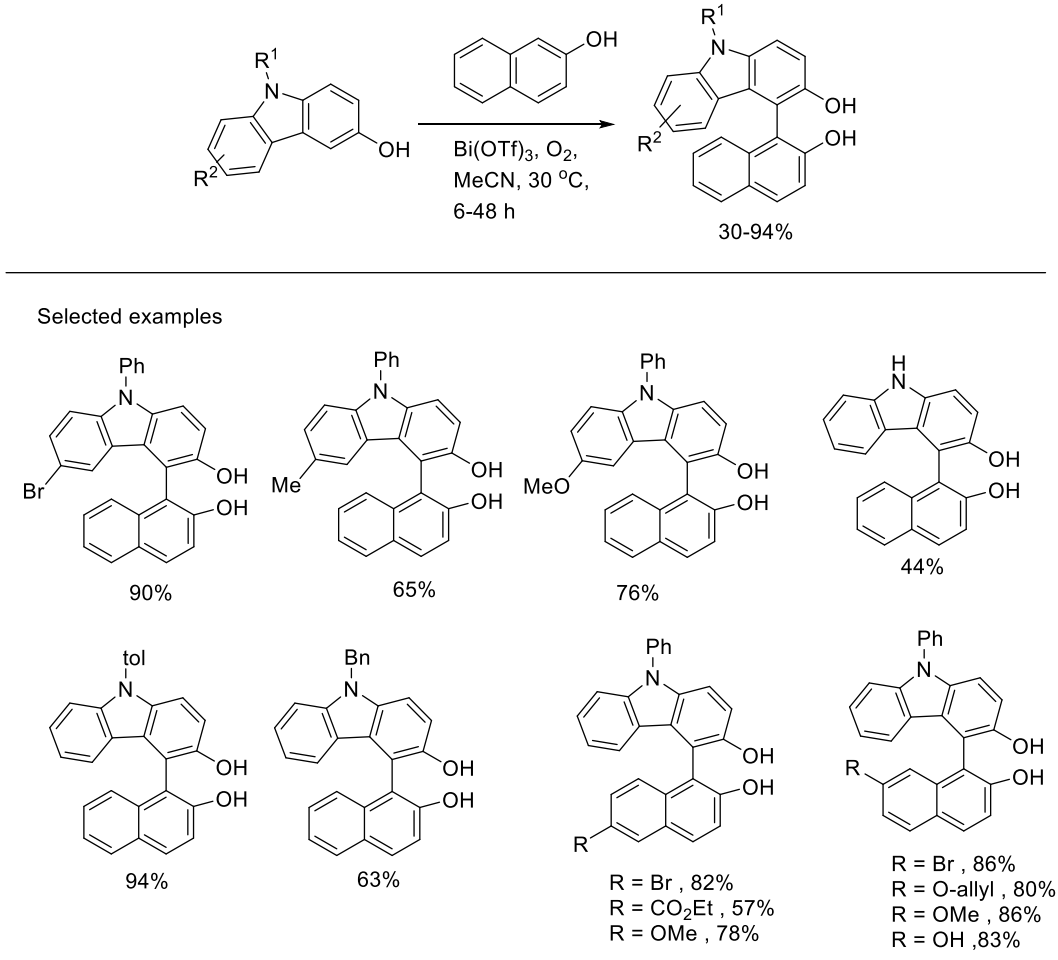
Scheme 6. $Bi(OTf)_3$ catalyzed benzoylation of benzofuran ring.



Scheme 7. $Bi(OTf)_3$ catalyzed synthesis of tetracyclic indole alkaloid.



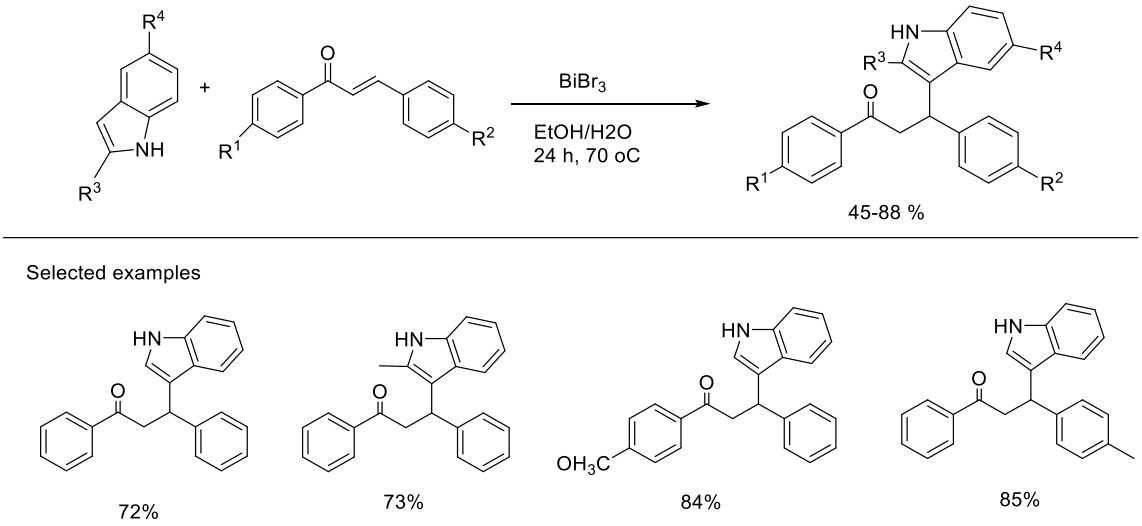
Scheme 8. $Bi(OTf)_3$-catalyzed microwave-assisted synthesis of ortho-hydroxyaryl ketones.



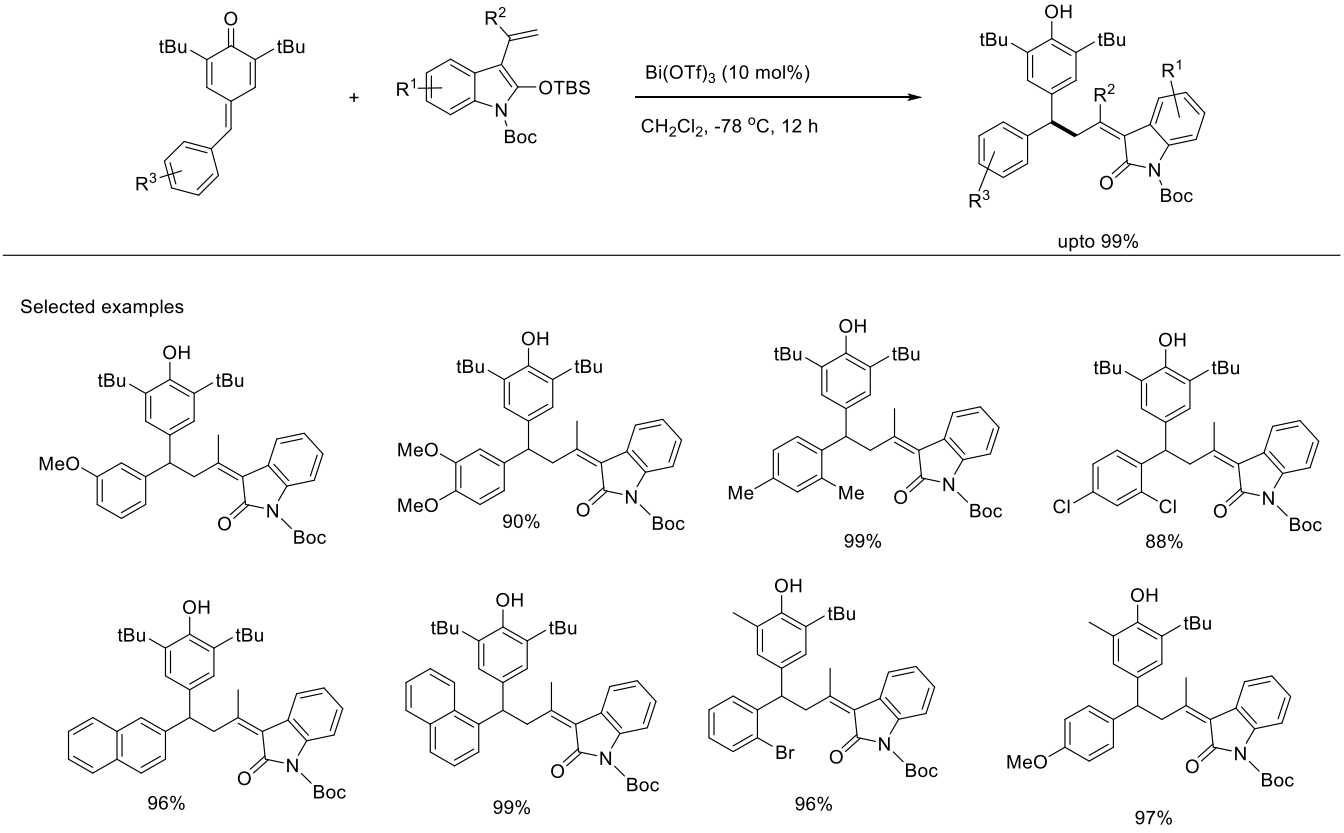
Scheme 9. $Bi(OTf)_3$-catalyzed synthesis of C_1-symmetric hydroxybiaryls.

2.2. Conjugate addition reactions

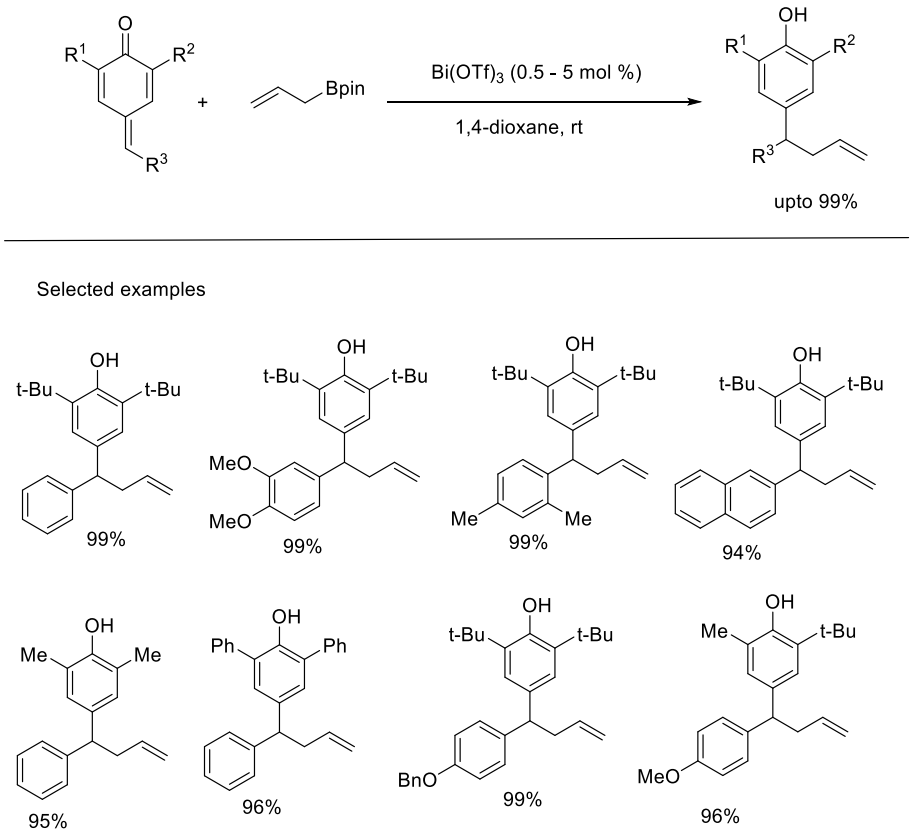
Bismuth catalysts were effective for several conjugate addition reactions. Rauwolf T et al. synthesized an array of chalcones with $BiBr_3$ as a catalyst. The reaction involved conjugate addition of indoles (Scheme 10)[17]. Xi et al. reported $Bi(OTf)_3$ catalyzed synthesis of several diphenylmethane type compounds functionalized with oxindole motifs by nucleophilic 1,6-conjugate addition reaction of paraquinone methides and 3-propenyl-2-silyloxyindoles in excellent yield (Scheme 11)[18]. Zhang et al. found that $Bi(OTf)_3$ could act as an effective catalyst for 1,6-allylation addition of paraquinone methides to allyl boronic acid pinacol ester to yield a series of allylation products with a diarylmethane motif in very good yields (Scheme 12)[19].



Scheme 10. $BiBr_3$-catalyzed synthesis of chalcones.



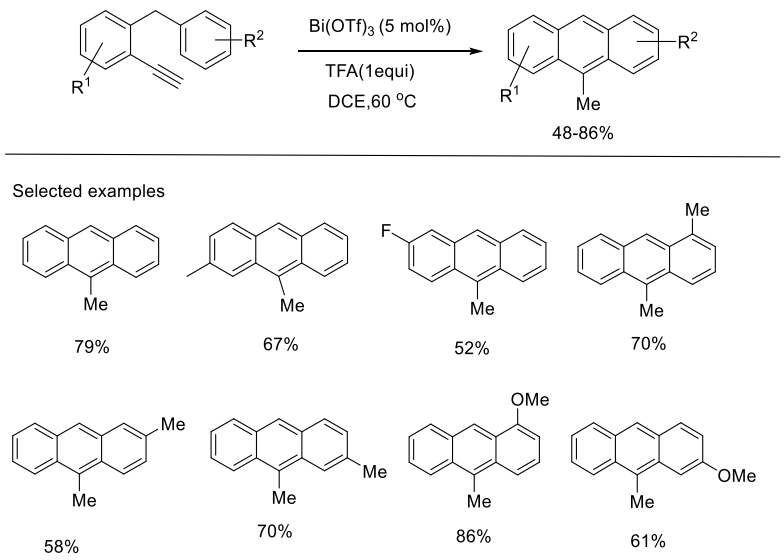
Scheme 11. $Bi(OTf)_3$-catalyzed synthesis of diphenylmethane type compounds.



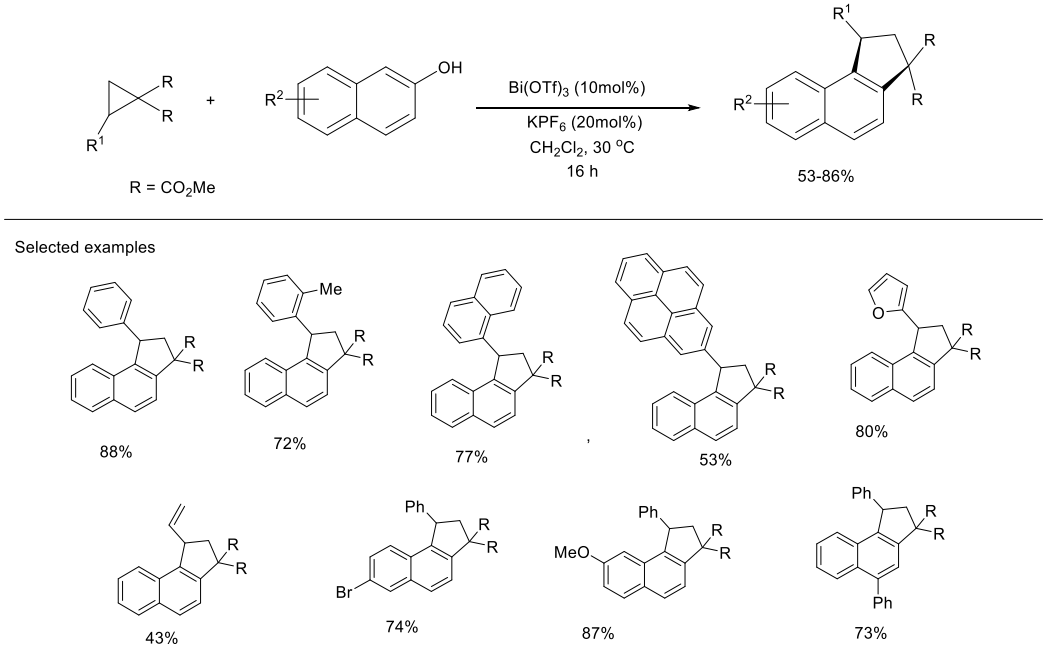
Scheme 12. $Bi(OTf)_3$-catalyzed 1,6 -allylation addition reaction.

2.3. C-C bond formation via cyclization/annulation

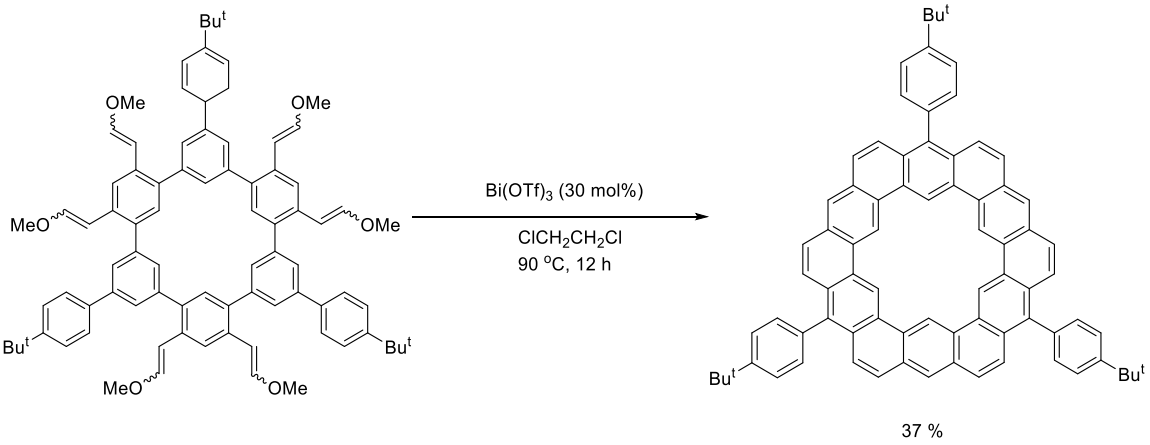
Bismuth catalysts also catalyzed several cyclization reactions. Jungmin Park et al. reported $Bi(OTf)_3$-catalyzed synthesis of anthracenes from o-alkynyldiarylmethane when trifluoroacetic acid (TFA) is present (Scheme 13)[20]. Trinadh Kaicharla et al. synthesized naphthalene fused cyclopentanes by selective dehydrative [3+2] cyclopentannulation of 2-substituted cyclopropane 1,1-dicarboxylates and 2-naphthols using $Bi(OTf)_3$ as a catalyst (Scheme 14)[21]. Wu et al. reported a facile strategy to synthesize aryl-substituted cycloarenes by cyclization of vinyl ethers using $Bi(OTf)_3$ as a catalyst (Scheme 15)[22]. R. Saget et al. synthesized a library of highly functionalized carbocycles by selective cyclization of unsaturated acetals and ketals using $Bi(OTf)_3$ catalyst at room temperature (Scheme 16)[23].



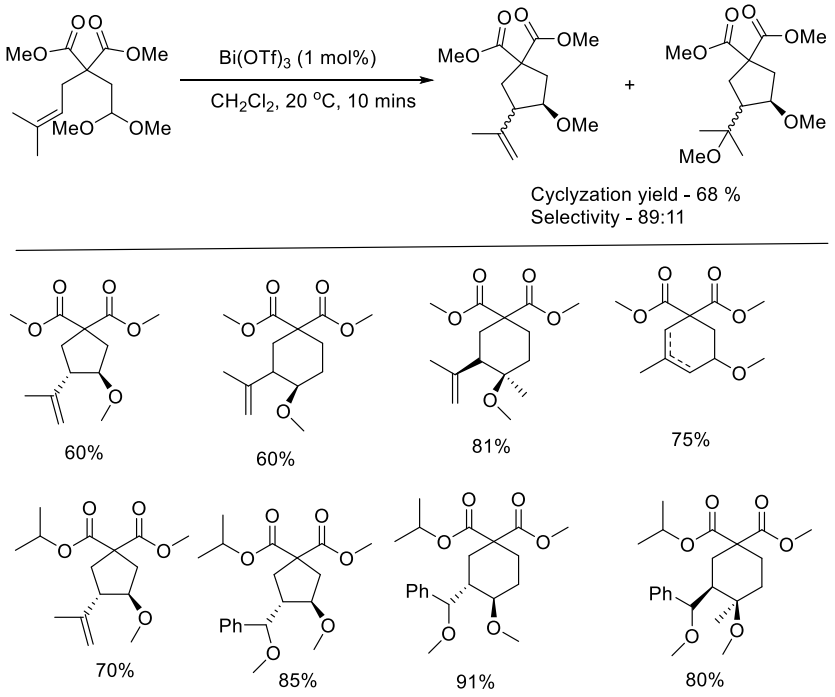
Scheme 13. $Bi(OTf)_3$-catalyzed synthesis of anthracenes from o-alkynyldiarylmethane.



Scheme 14. $Bi(OTf)_3$-catalyzed synthesis of naphthalene fused cyclopentanes.

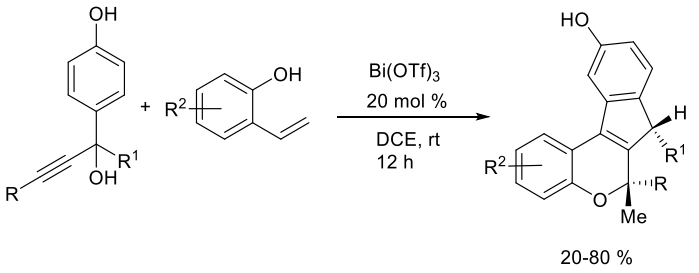


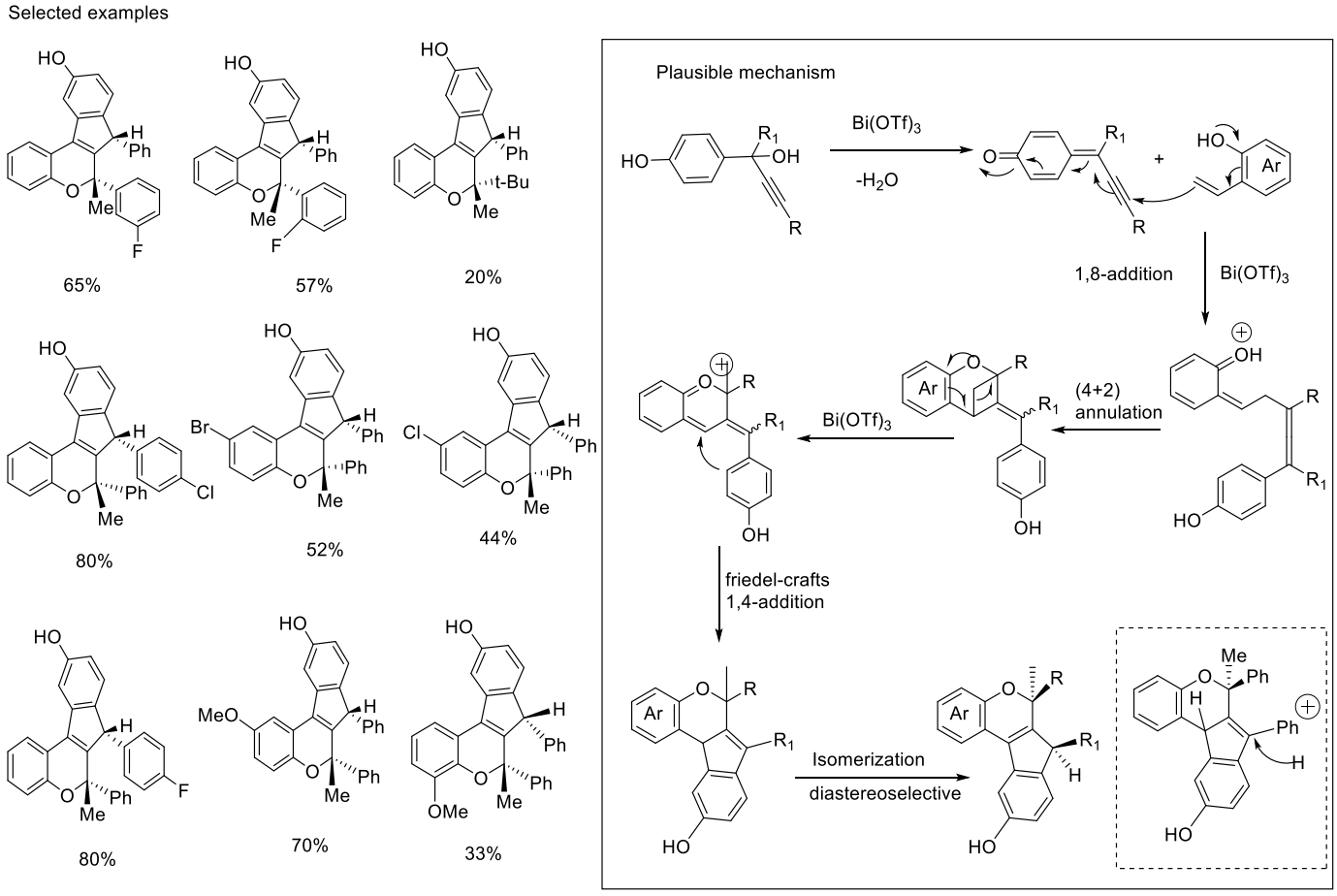
Scheme 15. $Bi(OTf)_3$-catalyzed synthesis of cycloarenes.



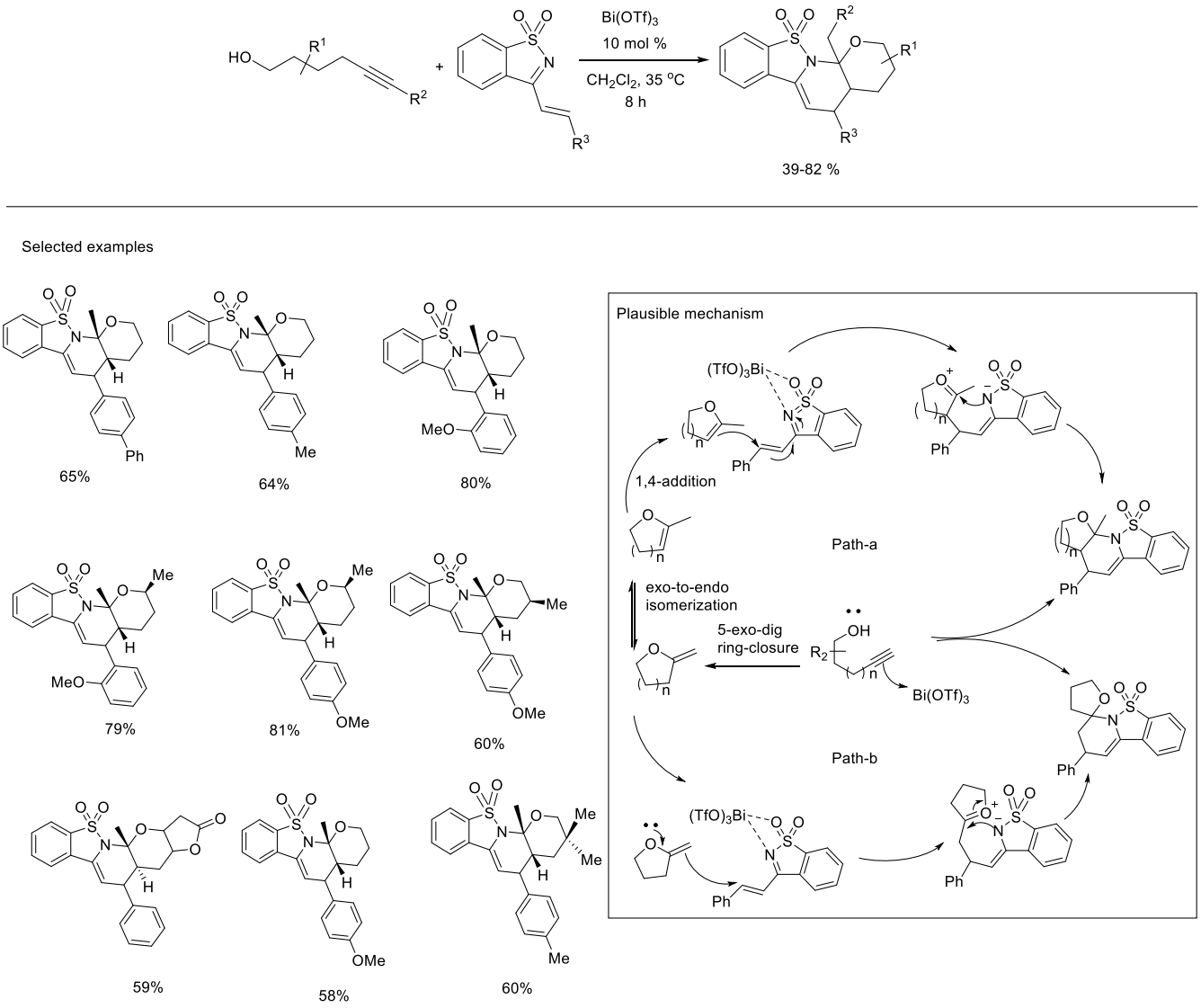
Scheme 16. $Bi(OTf)_3$-catalyzed synthesis of highly functionalized carbocycles.

Zhi-Qiang Zhu et al. unveiled the synthesis of indeno[2,1-c]chromenes from propargylic paraquinone methides (produced in situ from propargylic alcohols and 2-vinylphenol) by using $Bi(OTf)_3$ as a catalyst. The reaction involved a cascade sequence of 1,8-addition/cyclization/rearrangement of propargylic paraquinone methides. They proposed a plausible mechanism in which the reaction is initiated by $Bi(OTf)_3$-catalyzed activation of the propargylic alcohol, generating a reactive intermediate that undergoes nucleophilic addition with 2-vinylphenol. The resulting species cyclizes intramolecularly to form a strained, bridged intermediate, which subsequently opens and rearranges through bond migration. An intramolecular electrophilic aromatic substitution followed by double-bond isomerization then affords the final indeno[2,1-c]chromene product, completing the transformation (Scheme 17)[24]. Ashwini K. Nakate et al. revealed the $Bi(OTf)_3$-catalyzed synthesis of several polycyclic spiro-and-fused N, O-ketals by [4+2]-annulation of cyclic N-sulfonyl ketimines and 4-pentyn-1-ols and 5-hexyn-1-ols in an excellent yield. The reaction was diastereoselective under mild reaction conditions. They proposed a plausible mechanism in which $Bi(OTf)_3$-catalyzed intramolecular hydroalkoxylation of 5-hexyn-1-ol generates an exocyclic enol ether intermediate, which undergoes isomerization to form the corresponding endocyclic enol ether. Subsequent 1,4-addition of this species to the conjugated ketimine affords an oxocarbenium intermediate that readily undergoes intramolecular cyclization to produce the fused ketal framework (Path a). In contrast, gem-substituted 4-pentyn-1-ols follow a distinct course. Upon $Bi(OTf)_3$-catalyzed hydroalkoxylation, the resulting exocyclic enol ether directly engages in annulation with the activated conjugated ketimine without prior isomerization. The ensuing 1,4-addition generates an oxocarbenium species that undergoes intramolecular amination to furnish the spiro N, O-ketal product (Path b) (Scheme 18)[25]. Turhan et al. reported a one-pot synthesis of 3,4-dihydro-12-aryl-1H-benzo[b]xanthene-1,6,11-(2H,12H)trione and its derivatives from aromatic aldehydes, 2-hydroxy-1,4-naphthoquinone, and dimedone with $Bi(OTf)_3$ as a catalyst (Scheme 19)[26].

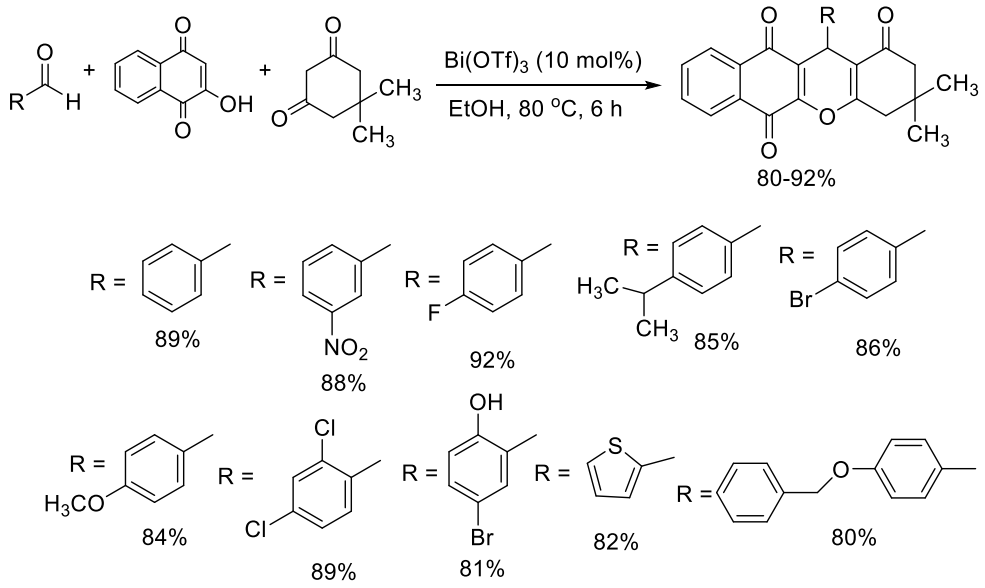




Scheme 17. $Bi(OTf)_3$-catalyzed synthesis of indeno[2,1-c]chromenes.



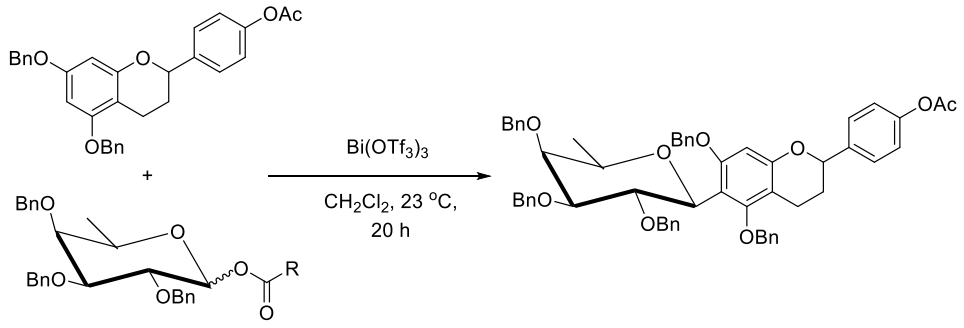
Scheme 18. $Bi(OTf)_3$-catalyzed synthesis of N,O-ketals by [4+2]-annulation.



Scheme 19. $Bi(OTf)_3$-catalyzed synthesis of 3,4-dihydro-12-aryl-1H-benzo[b]xanthene-1,6,11-(2H,12H)trione derivatives.

2.4. C-C glycosidic bond formation

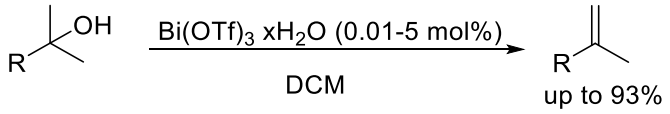
Ghosh et al. used $Bi(OTf)_3$-catalyzed C-aryl glycosylation of a flavan derivative and D-fucose derivative as the crucial step in the total synthesis of carambola flavone A (a flavonoid C-aryl glycoside with antihyperglycemic properties) (Scheme 20)[27].



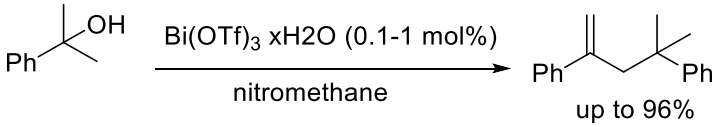
Scheme 20. $Bi(OTf)_3$-catalyzed C-aryl glycosylation of a flavan derivative and D-fucose derivative.

2.5. Dehydration followed by C-C bond formation

Kolsi et al. found out that in apolar solvents, $Bi(OTf)_3.xH_2O$ is a potent catalyst to dehydrate tertiary alcohols into alkenes (Scheme 21a). However, $Bi(OTf)_3.xH_2O$ facilitates the dimerisation of the alcohols rather than generating new C-C bonds in polar solvents (Scheme 21b)[28].



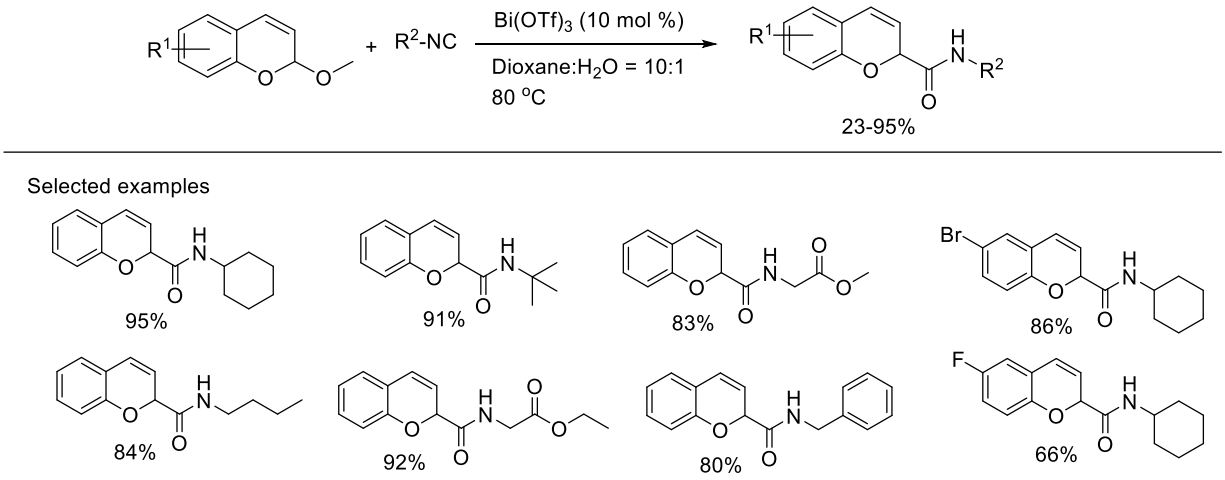
Scheme 21a. $Bi(OTf)_3.xH_2O$ catalyst to dehydrate tertiary alcohols into alkenes in apolar solvent.



Scheme 21b. $Bi(OTf)_3.xH_2O$-catalyzed dimerization of alcohols in polar solvent.

2.6. Amidation via C-C bond formation

Longyun Lyu et al. unveiled $Bi(OTf)_3$-catalyzed synthesis of 2-carboxamide 2H-chromenes from isocyanides and H-chromene acetals in a very good yield. The authors proposed a plausible mechanism in which the activation of the acetal substrate by $Bi(OTf)_3$ generates an oxocarbenium ion, which subsequently undergoes nucleophilic addition of the isocyanide to form a nitrilium intermediate. Hydrolysis of this intermediate then affords the corresponding 2-carboxamide-2H-chromene product, thereby completing the catalytic cycle. (Scheme 22)[29].

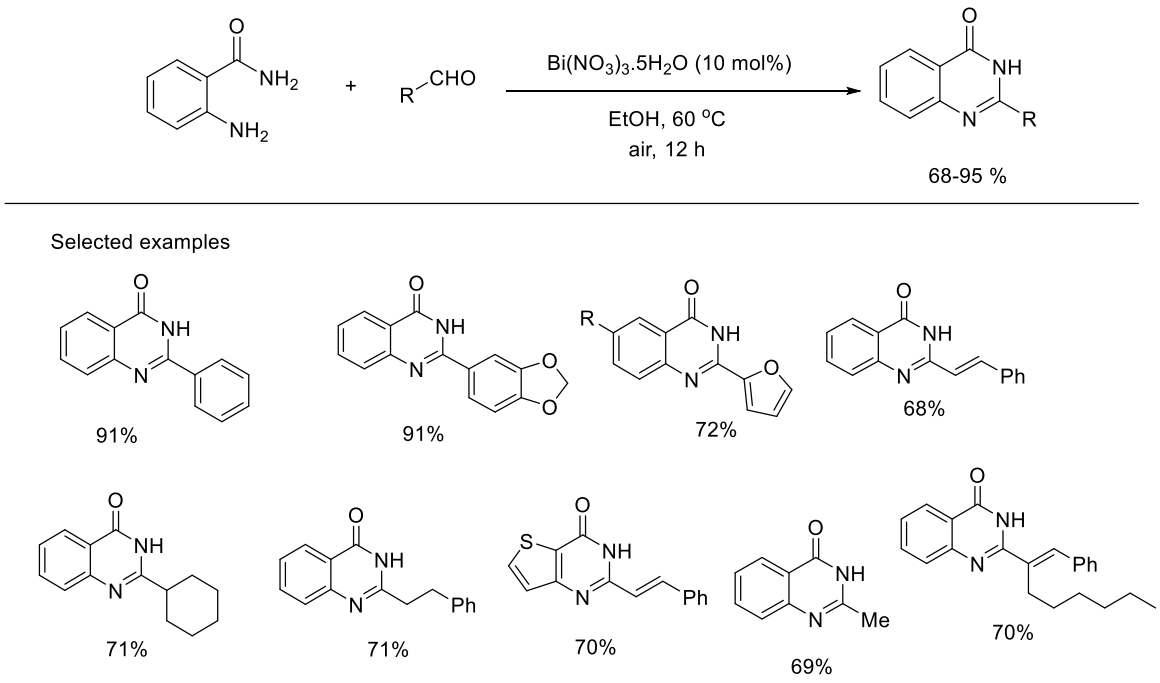


Scheme 22. $Bi(OTf)_3$-catalyzed synthesis of 2-carboxamide 2H-chromenes from H-chromene acetals.

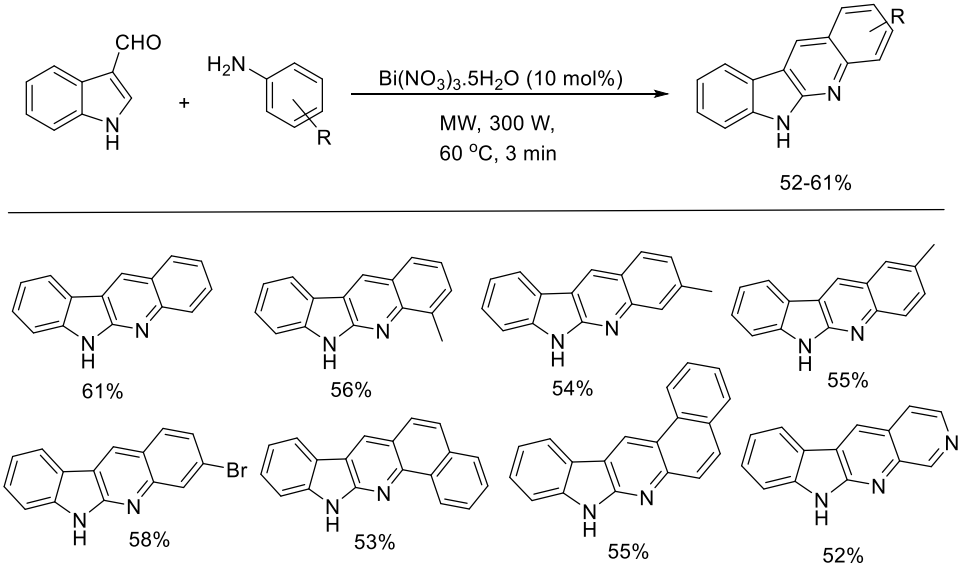
3. C-N Bond Formation

3.1. C-N bond formation via cyclisation/annulation

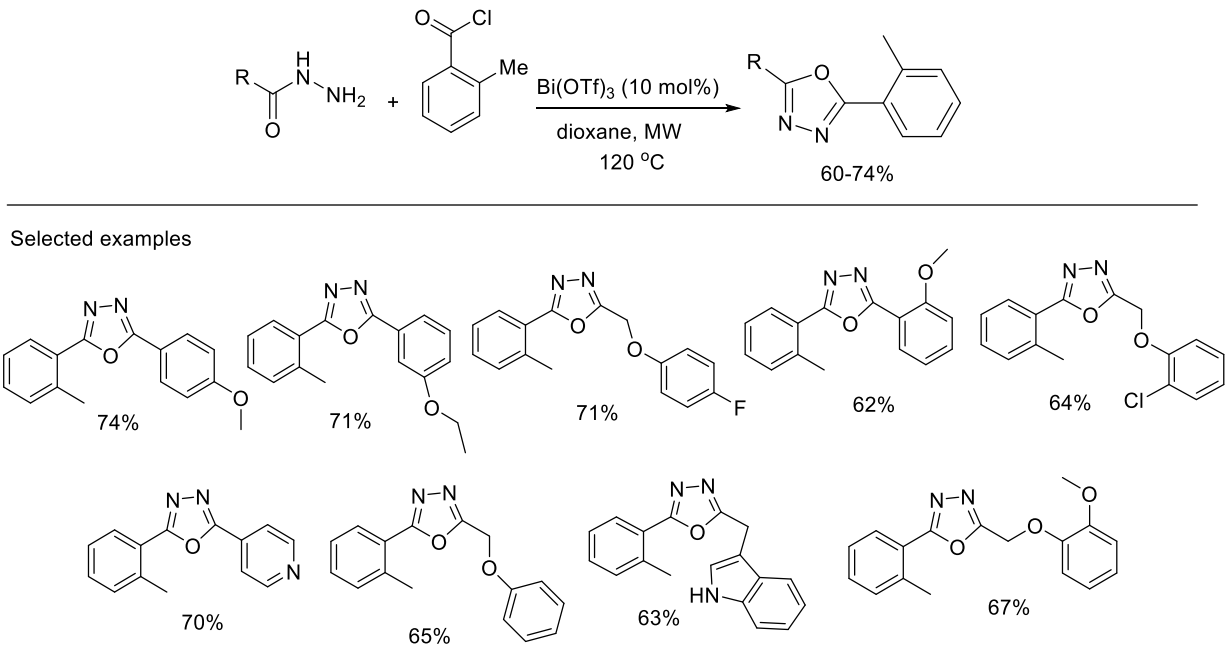
Sandeep et al. reported $Bi(NO_3)_3$ catalyzed synthesis of 2-substituted quinazolinones in aerobic conditions from aldehydes and 2-aminobenzamide in very good yield (Scheme 23)[30]. N-allylated quinazolinones, 2-aminopyridine derivatives, and annulated polyheterocyclic compounds were further produced by functionalising the quinazolinones using transition metal catalysts. Prakash achieved a $Bi(NO_3)_3$-catalyzed microwave-assisted one-pot synthesis of linear indolo[2,3-b]quinolines from indole-3-carboxyaldehyde and aniline derivatives in a very good yield (Scheme 24)[31]. Mutchu et al. reported a simplified microwave method for synthesizing 2-aryl-5-substituted-1,3,5-oxadiazoles from carboxylic acid hydrazides and aryl acid chloride using $Bi(OTf)_3$ as a catalyst. This method synthesized a library of 2-aryl,5-substituted-1,3,4-Oxadiazole derivatives in good yield (Scheme 25)[32]. Bouone et al. unveiled a $BiCl_3$-catalyzed synthesis of 4-hydroxy-2-quinolone derivatives from β-enaminones under microwave conditions (Scheme 26)[33].



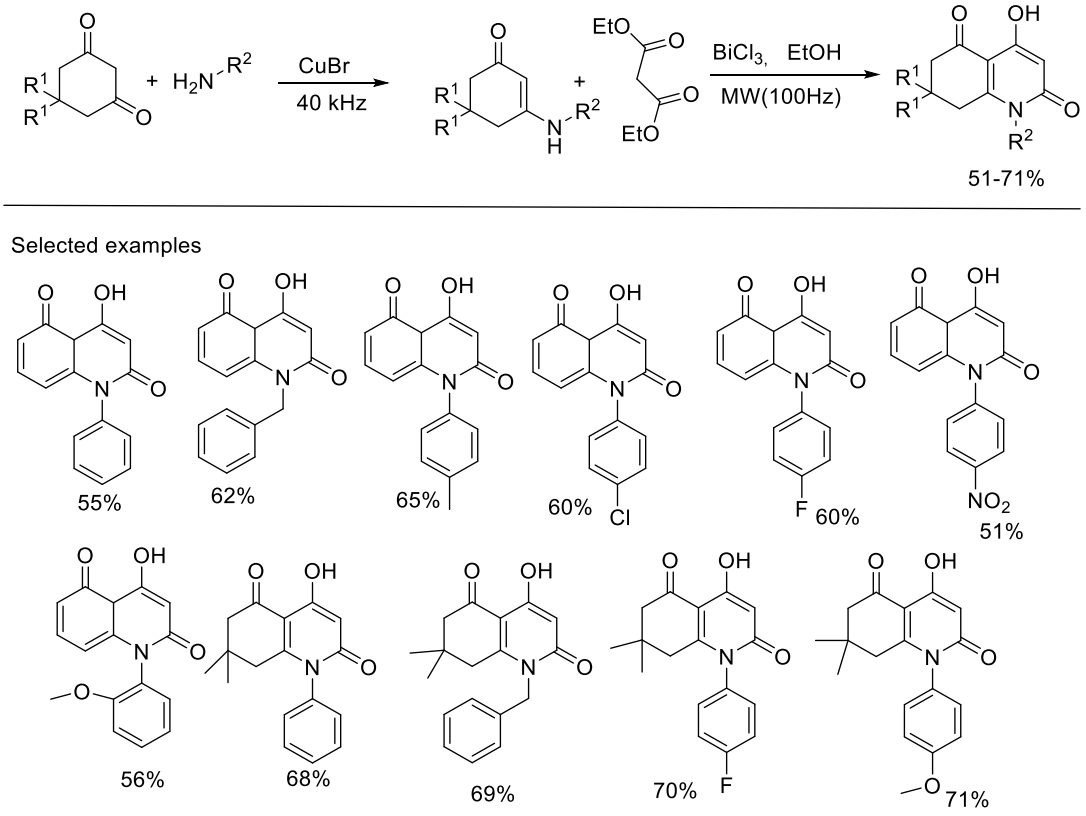
Scheme *23.* $Bi(NO_3)_3$ catalyzed synthesis of 2-substituted quinazolinones.



Scheme 24. $Bi(NO_3)_3$-catalyzed microwave-assisted synthesis of indolo[2,3-b]quinolines.

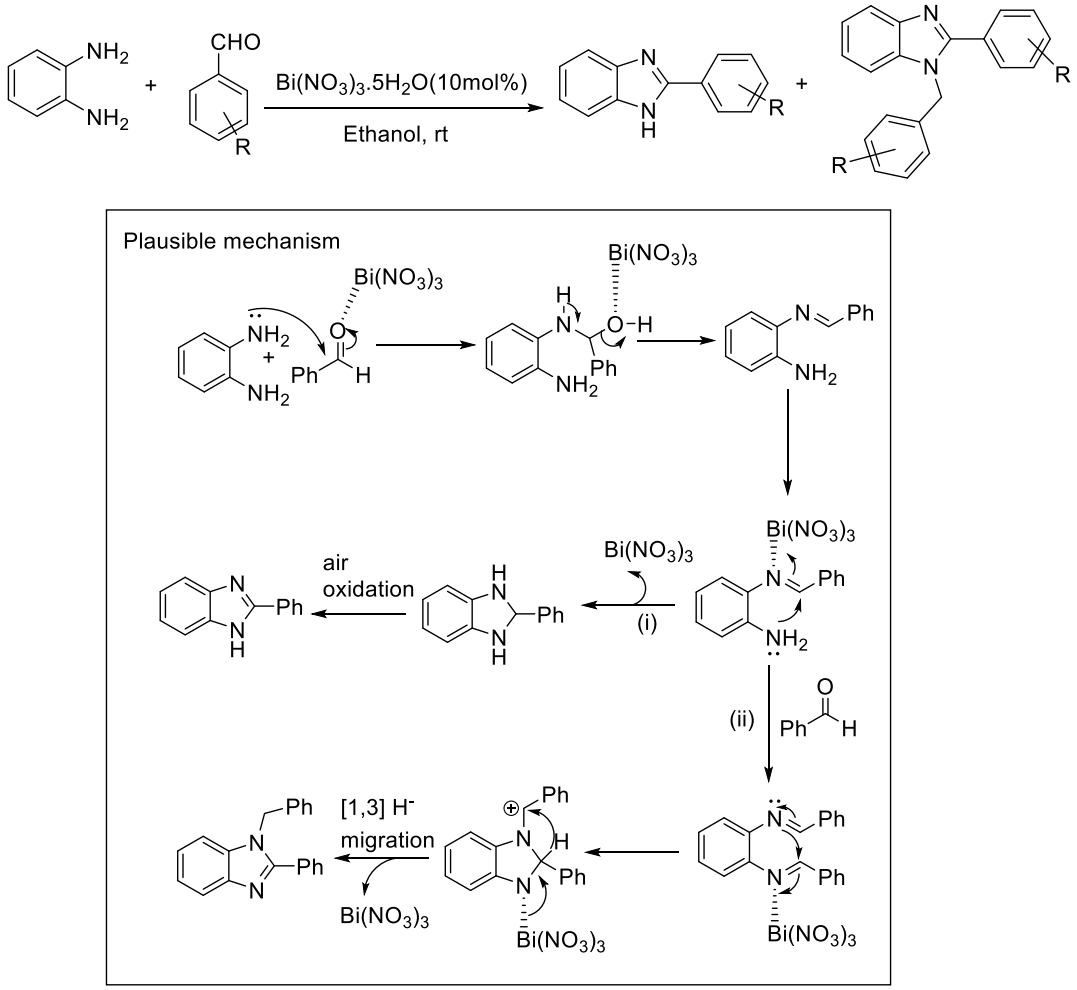


Scheme 25. $Bi(OTf)_3$-catalyzed microwave-assisted synthesis of 2-aryl,5-substituted-1,3,4-Oxadiazole derivatives.

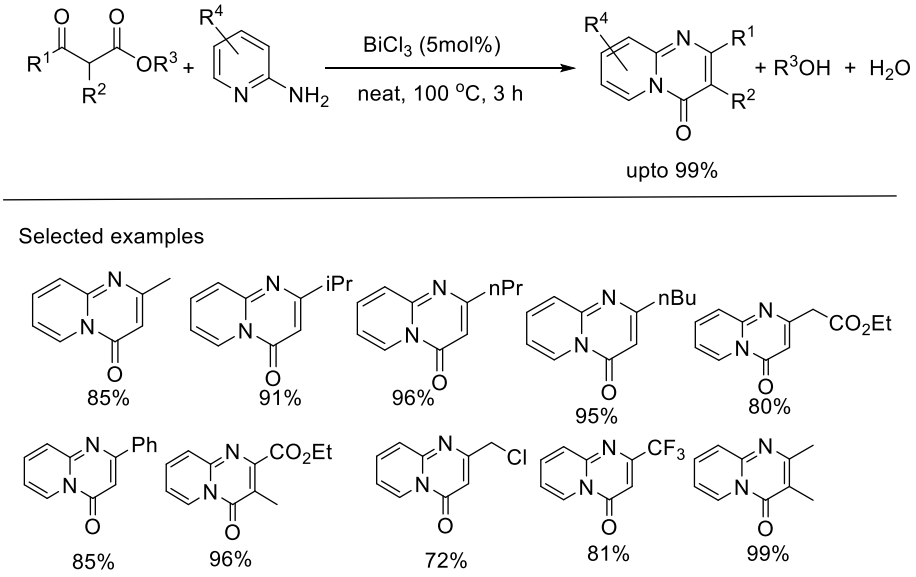


Scheme 26. $BiCl_3$-catalyzed microwave-assisted synthesis of 4-hydroxy-2-quinolones.

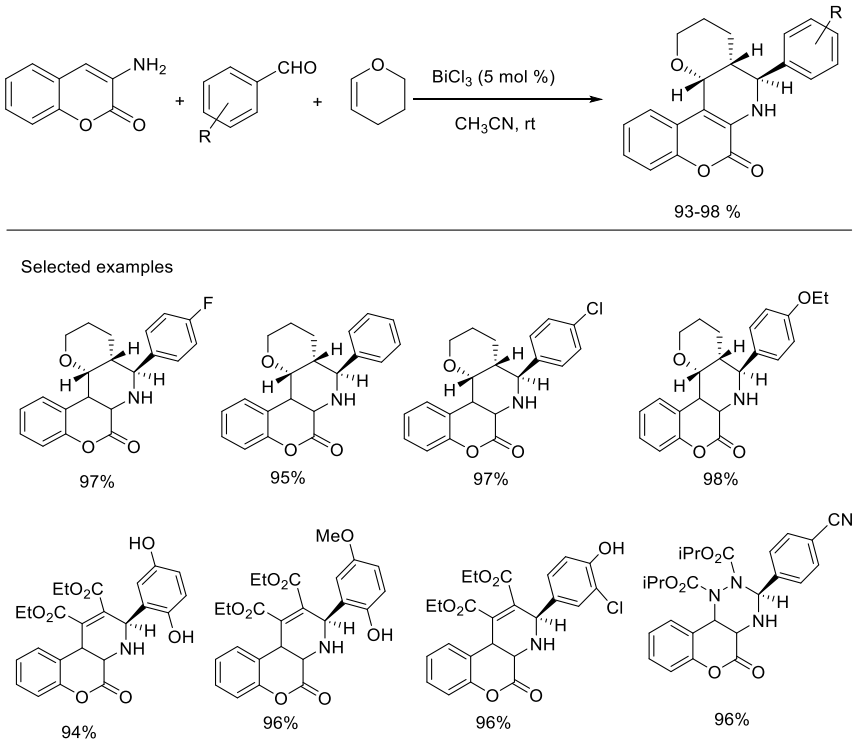
Vilas N. Mahire et al. reported a $Bi(NO_3)_3.5H_2O$-catalysed synthesis of benzimidazole derivatives from o-phenylenediamine and aromatic aldehydes. The reaction mechanism involves the coordination of bismuth nitrate to the carbonyl oxygen of the aldehyde, forming a hydrogen-bonded or Lewis acid activated complex. This activation enhances the electrophilicity of the carbonyl carbon, allowing nucleophilic attack by o-phenylenediamine, leading to the formation of a Schiff base intermediate. In the case of 2-substituted benzimidazoles, this intermediate undergoes cyclization and dehydration to form the heterocycle. For 1,2-disubstituted benzimidazoles, a second equivalent of aldehyde reacts with the intermediate, followed by intramolecular 1,3-hydride migration, which facilitates ring closure and formation of the disubstituted product. The catalyst is regenerated, and water is the only byproduct, making the process green and efficient (Scheme 27)[34]. Roslan I et al. reported a $BiCl_3$-catalyzed synthesis of several 4H-pyrido[1,2-a]pyrimidin-4-ones from 2-amino-pyridines and β-oxo esters under solvent-free conditions. This can be considered a green reaction as water and alcohol are the only co-products obtained (Scheme 28)[35]. Ch. Gurumurthy et al. reported a $BiCl_3$-catalyzed one-pot diastereoselective synthesis of tetrahydro- and dihydro-pyrido[2,3-c]coumarin from aromatic aldehydes, 3-aminocoumarin and dienophiles. This aza-Diels–Alder reaction resulted in a very high yield at room temperature, and the synthesized compounds also showed DPPH radical scavenging activity (Scheme 29)[36]. Gautam et al. synthesized a library of biologically fascinating, 1,8-dioxodecahydroacridine scaffolds from cyclohexanediones, several primary amines, and aldehydes in a single pot method using $Bi(NO_3)_3.5H_2O$ as a catalyst (Scheme 30)[37].



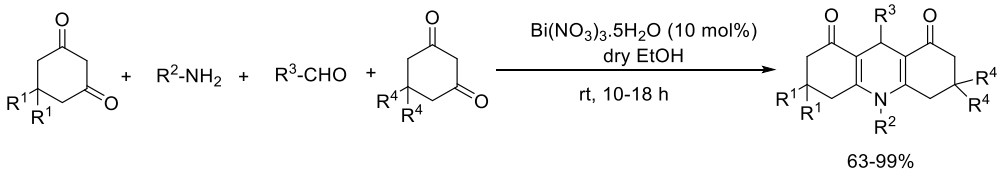
Scheme 27. $Bi(NO_3)_3.5H_2O$-catalyzed synthesis of benzimidazole derivatives.



Scheme 28. $BiCl_3$-catalyzed synthesis of 4H-pyrido[1,2-a]pyrimidin-4-ones.

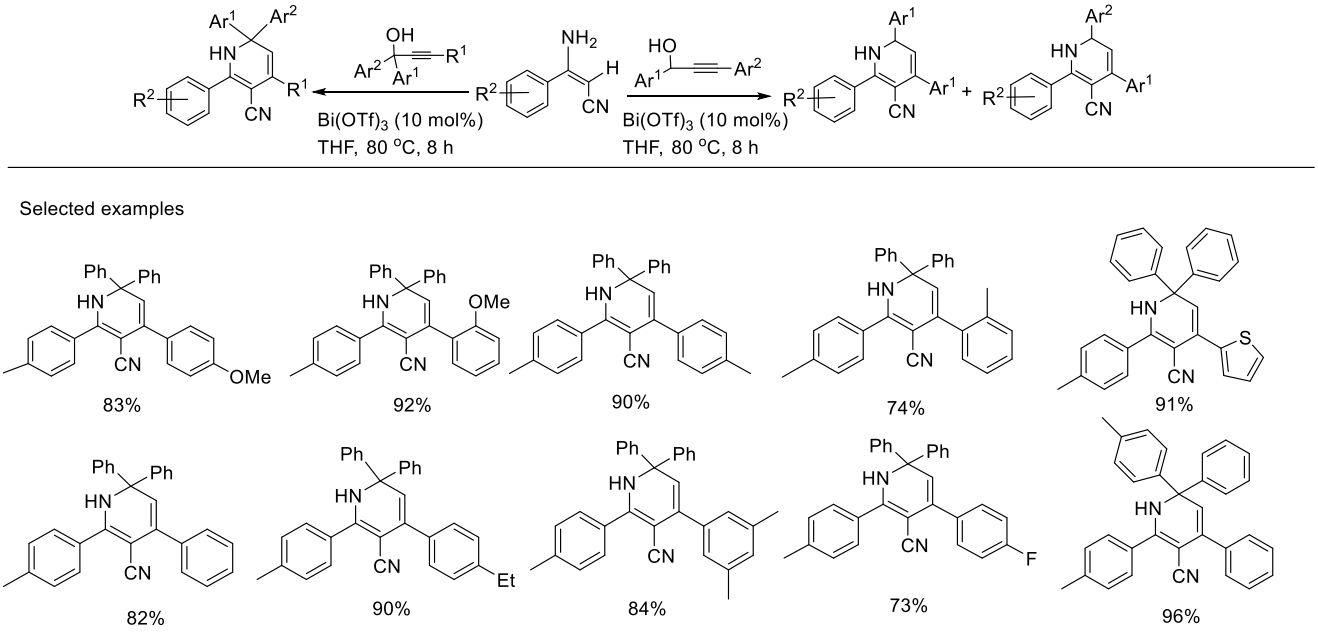


Scheme 29. $BiCl_3$-catalyzed one-pot synthesis of tetrahydro- and dihydro-pyrido[2,3-c]coumarin.

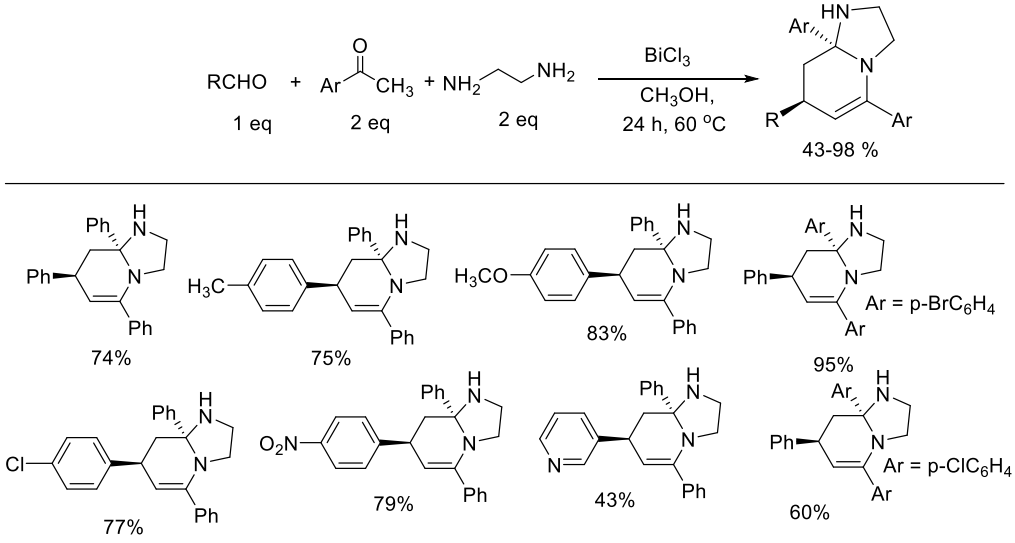


Scheme 30. $Bi(NO_3)_3.5H_2O$-catalyzed synthesis of 1,8-dioxodecahydroacridine scaffolds.

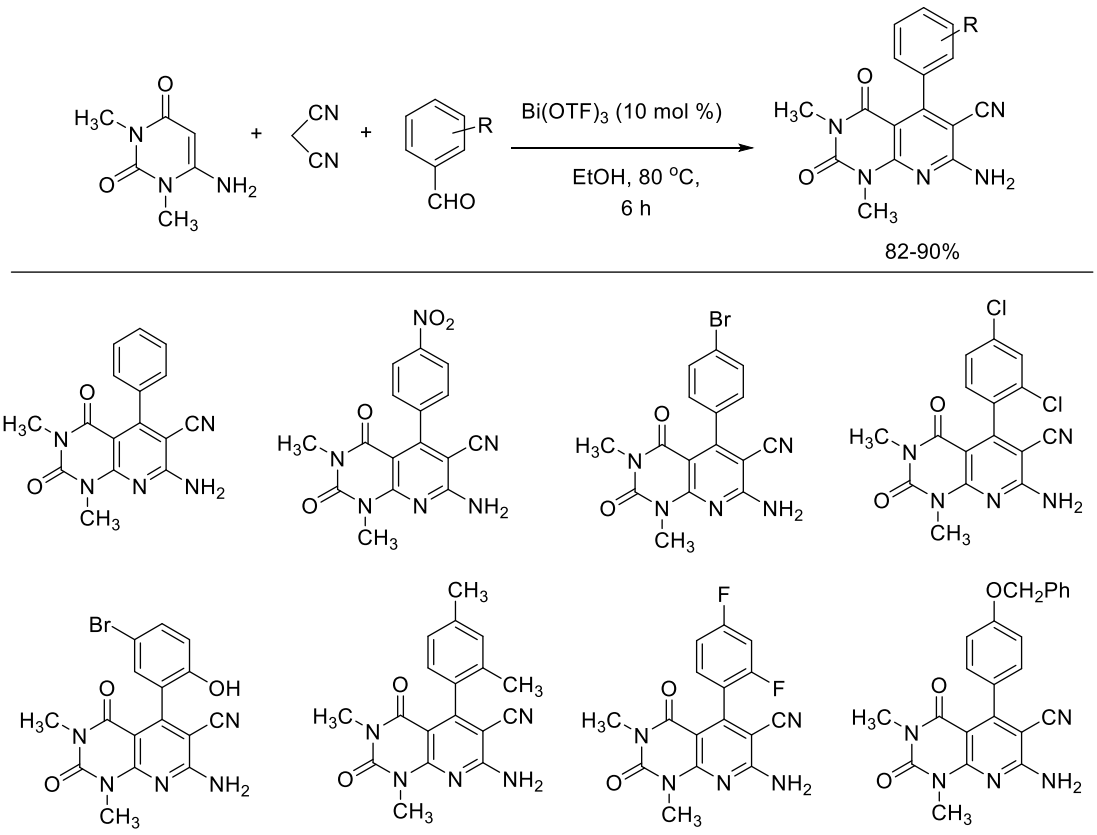
L. Du et al. discovered a highly efficient and atom-economical $Bi(OTf)_3$-catalyzed synthesis of functionalized 1,6-dihydropyrimidine-3-carbonitrile derivatives from propargylic alcohols and (E)-3-amino-3-phenylacrylonitriles. A mixture of isomers was obtained when secondary propargylic alcohols were used. The reaction proceeds via cycloaddition in mild conditions (Scheme 31)[38]. N. T. Haskin et al. achieved the multicomponent synthesis of several hexahydroimidazo[1, 2-*a*]pyridines using $BiCl_3$ as a catalyst (Scheme 32)[39]. Saglam et al. reported $Bi(OTf)_3$-catalyzed one-pot synthesis of 7-aminopyrido[2,3-d]pyrimidine-6-carbonitrile derivatives from 6-amino-1,3-dimethyluracil, with aryl aldehydes and malononitrile (Scheme 33)[40].



Scheme 31. $Bi(OTf)_3$-catalyzed synthesis of functionalized 1,6-dihydropyrimidine-3-carbonitrile derivatives.

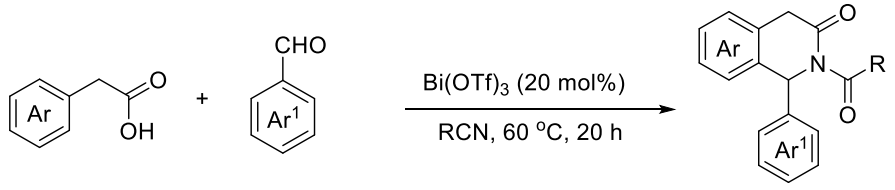


Scheme 32. $BiCl_3$-catalyzed synthesis of hexahydroimidazo[1, 2-a]pyridines.

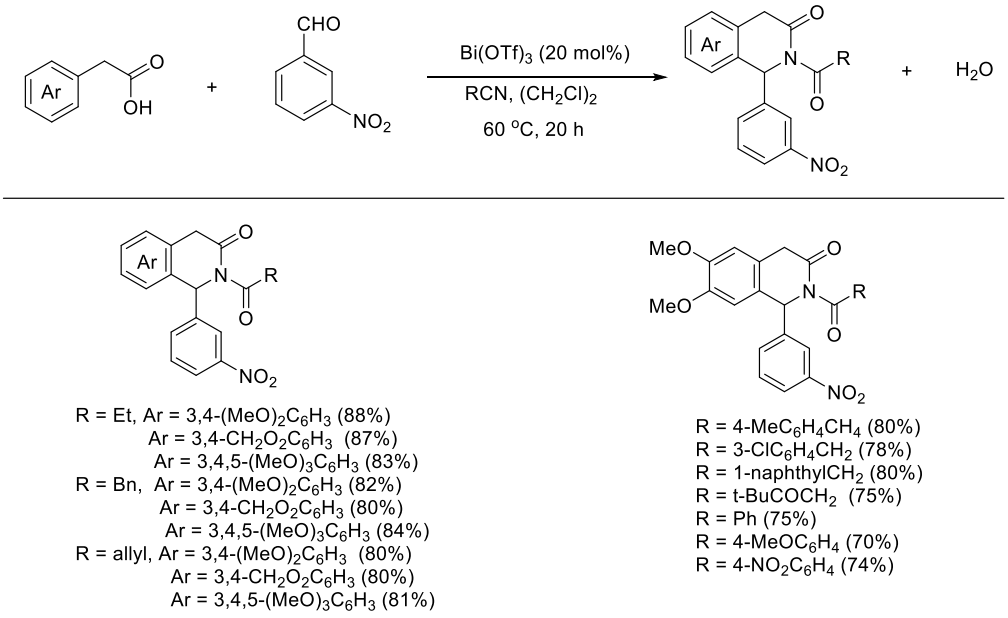


Scheme 33. $Bi(OTf)_3$-catalyzed synthesis of 7-aminopyrido[2,3-d]pyrimidine-6-carbonitrile derivatives.

Meng-Yang Chang et al. unveiled the synthesis of 1-aryl isoquinolinones or o-diaryl pyrimidines by intermolecular multicomponent reaction between oxygenated arylacetic acids and nitroarylaldehydes or trimethoxybenzene using $Bi(OTf)_3$ as a catalyst (Scheme 34a, 34b and 34c)[41].



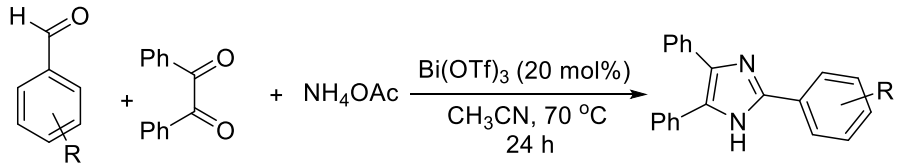
Scheme 34a. $Bi(OTf)_3$-catalyzed synthesis of 1-aryl isoquinolinones.



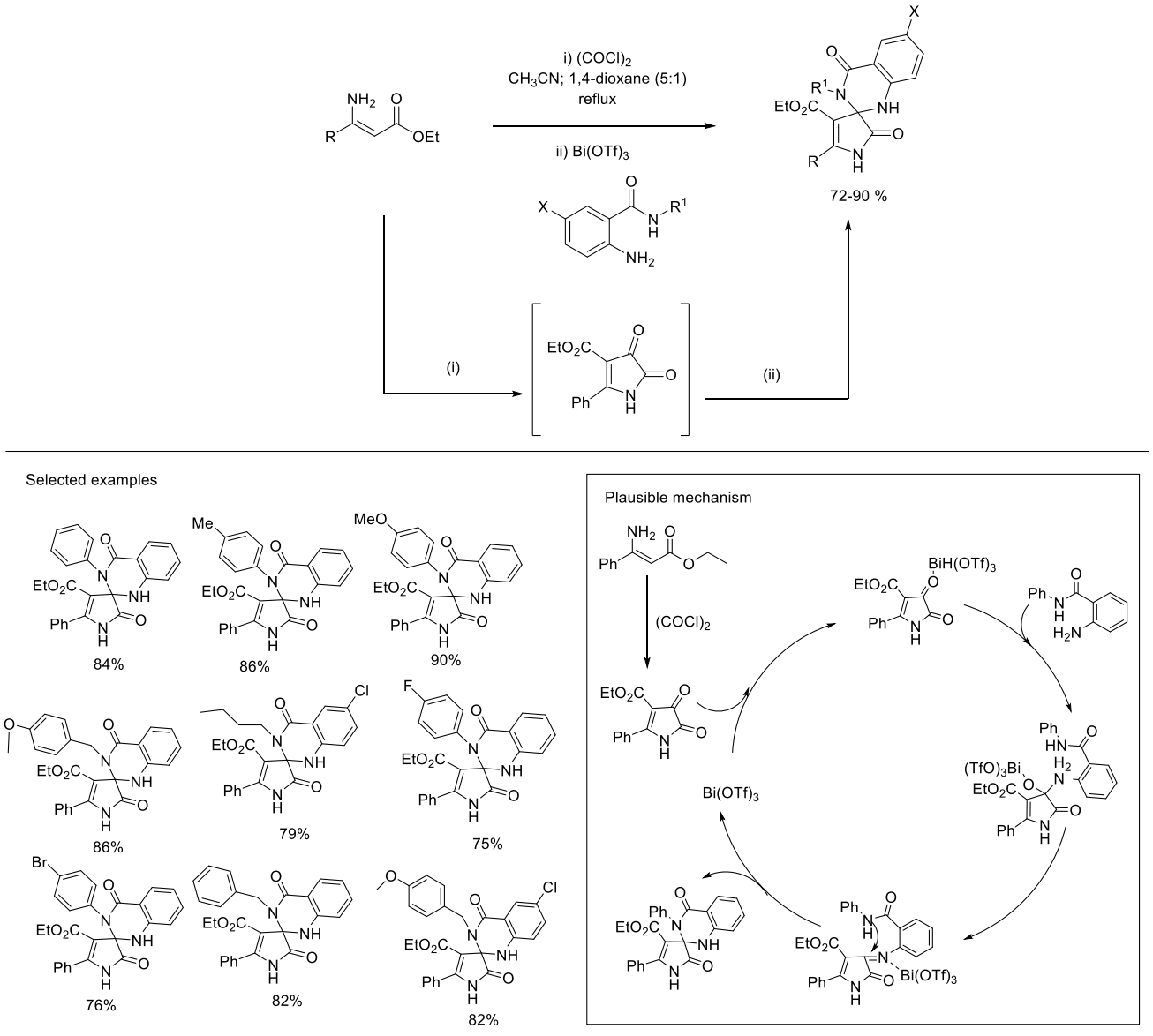
Scheme 34b. $Bi(OTf)_3$-catalyzed synthesis of 1-aryl isoquinolinones and o-diaryl pyrimidines.

Scheme 34c. $Bi(OTf)_3$-catalyzed synthesis of o-diaryl pyrimidines.

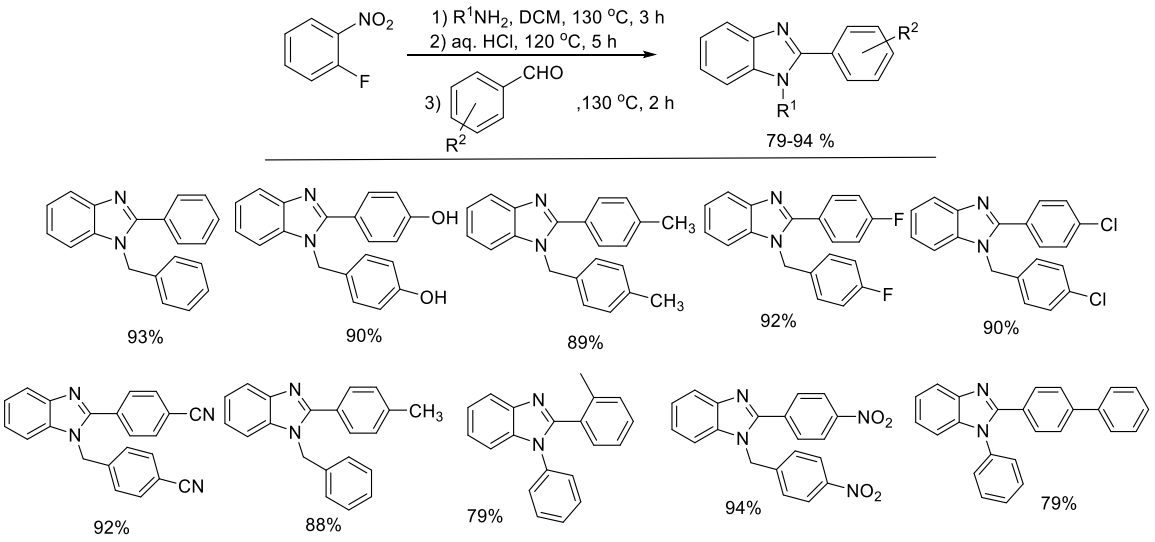
S. C. Thorp et al. unveiled the multicomponent synthesis of a library of 2,4,5-trisubstituted imidazoles by using Bismuth triflate as a catalyst (Scheme 35)[42]. Anil Kumar Soda et al. reported a cascade synthesis of novel spiro [pyrrole-3,2′-quinazoline] carboxylate derivatives from ethyl (Z)-3-amino-3-phenylacrylates and 2-amino-N-alkyl/arylbenzamides by using $Bi(OTf)_3$ as the catalyst. They proposed a plausible mechanism in which the reaction is initiated by the cyclization of ethyl (Z)-3-amino-3-phenylacrylate with oxalyl chloride to generate a reactive intermediate. Subsequent spiro annulation of this intermediate with 2-amino-N-phenylbenzamide in the presence of a Lewis acid catalyst furnishes the desired product. The transformation likely proceeds through transient intermediates, which facilitate the formation of the spiro framework under the reaction conditions (Scheme 36)[43]. Venkateswarlu et al. reported a $Bi(OTf)_3$-catalyzed synthesis of several 2-disubstituted benzimidazoles from *o*-fluorobenzonitrile, aniline and aldehyde derivatives in a very good yield. The authors proposed that the reaction goes through N-arylation. The synthesized compounds also exhibited anticancer activity (Scheme 37)[44].



Scheme 35. $Bi(OTf)_3$-catalyzed synthesis of 2,4,5-trisubstituted imidazoles.



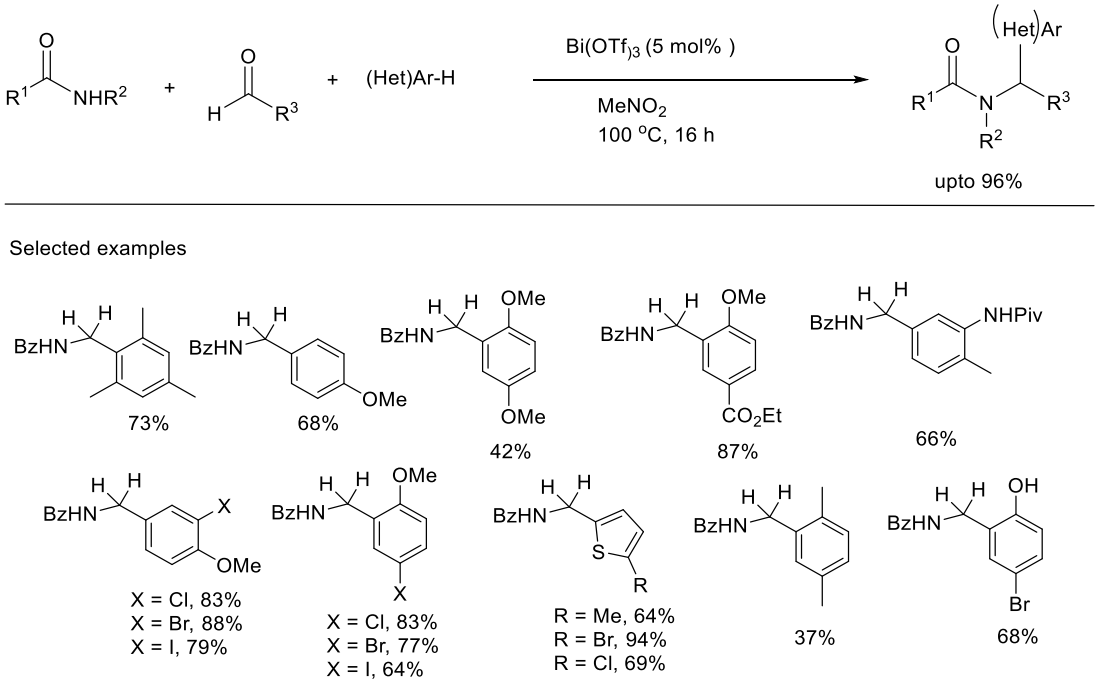
Scheme 36. $Bi(OTf)_3$-catalyzed synthesis of novel spiro [pyrrole-3,2'-quinazoline] carboxylates.



Scheme 37. Bi(OTf)$_3$-catalyzed synthesis of 2-disubstituted benzimidazoles.

3.2. Amidoalkylation reaction

Angelika E. Schneider and her co-worker achieved the synthesis of α-substituted amides from amides, aldehydes, and (hetero)arenes by using Bi(OTf)$_3$ as a catalyst. The reaction has a huge scope as formaldehyde, alkyl, and aryl aldehydes can be used in the reaction, and water is the only byproduct that is formed (Scheme 38)[45].

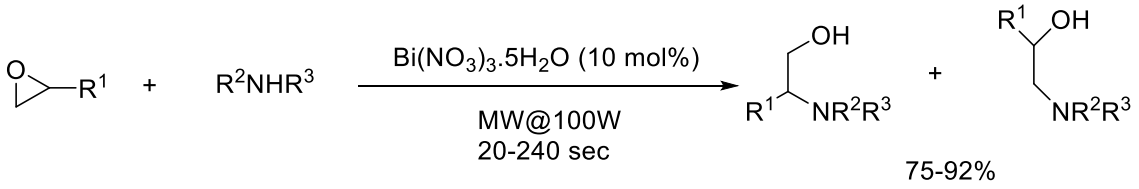


Scheme 38. Bi(OTf)$_3$-catalyzed synthesis of α-substituted amides

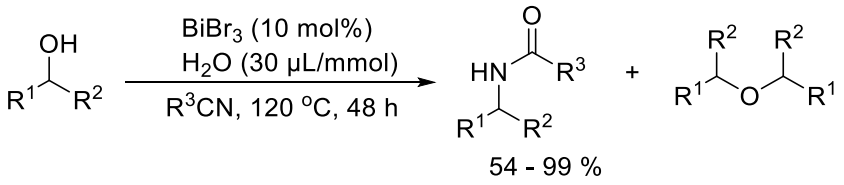
3.3. Aminolysis/amide formation reaction

Several researchers achieved Shobha Aminolysis and amide formation reactions by using Bismuth catalysts. Bansal et al. reported a Bi(NO$_3$)$_3$-catalyzed solvent-free microwave synthesis of several β-amino alcohols by

the ring opening of epichlorohydrin and styrene oxide with amines (Scheme 39)[46]. Ueno et al. developed an environmentally friendly Ritter reaction of 2° alcohols with nitriles catalyzed by $BiBr_3$ (Scheme 40)[47]. The product yield increased when a small amount of water was added, indicating that Bismuth salts are not deactivated by water.



Scheme 39. $Bi(NO_3)_3$-catalyzed microwave-assisted synthesis of β-amino alcohols.

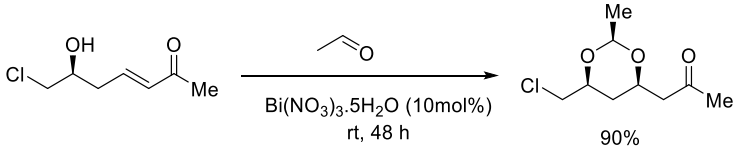


Scheme 40. $BiBr_3$-catalyzed Ritter reaction of 2° alcohols.

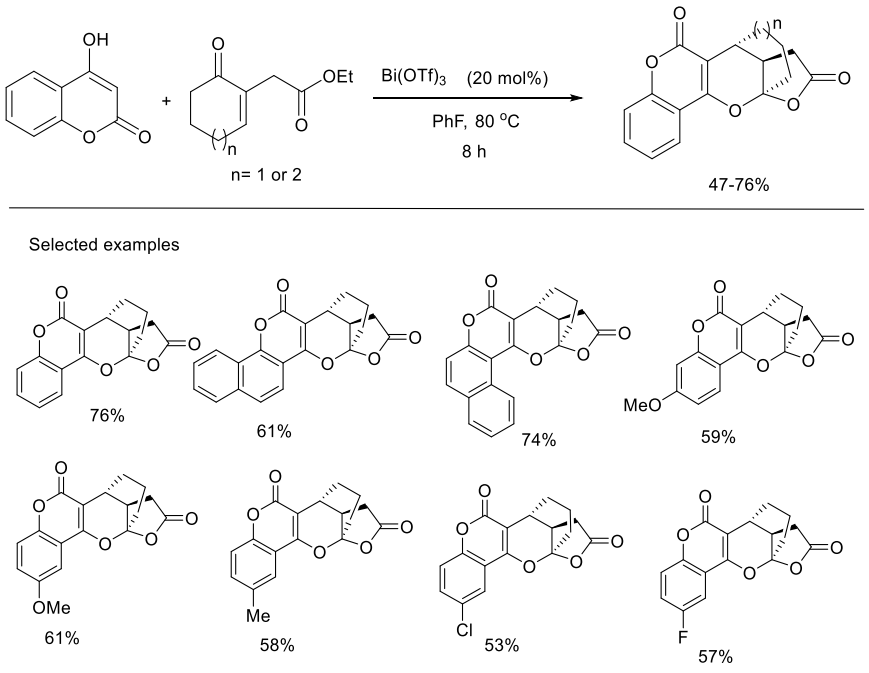
4. C-O Bond Formation

4.1. Acetal/ketal formation

Fangjun Xiong et al. employed $Bi(NO_3)_3.5H_2O$ to catalyze a two-component hemiacetal/oxa-Michael addition reaction of (S)-α,β-unsaturated ketone with acetaldehyde, to synthesize a 1,3-syn-diol acetal motif, which was further used to synthesize an asymmetric pitavastatin calcium **(**Scheme 41)[48]. Akshay B. Rathod synthesized 3D polycyclic bridged chromano-furopyranones and pyrano-furopyranones by annulation of hydroxy-pyranones and unsaturated γ-ketoesters, using $Bi(OTf)_3$ as a catalyst (Scheme 42)[49].



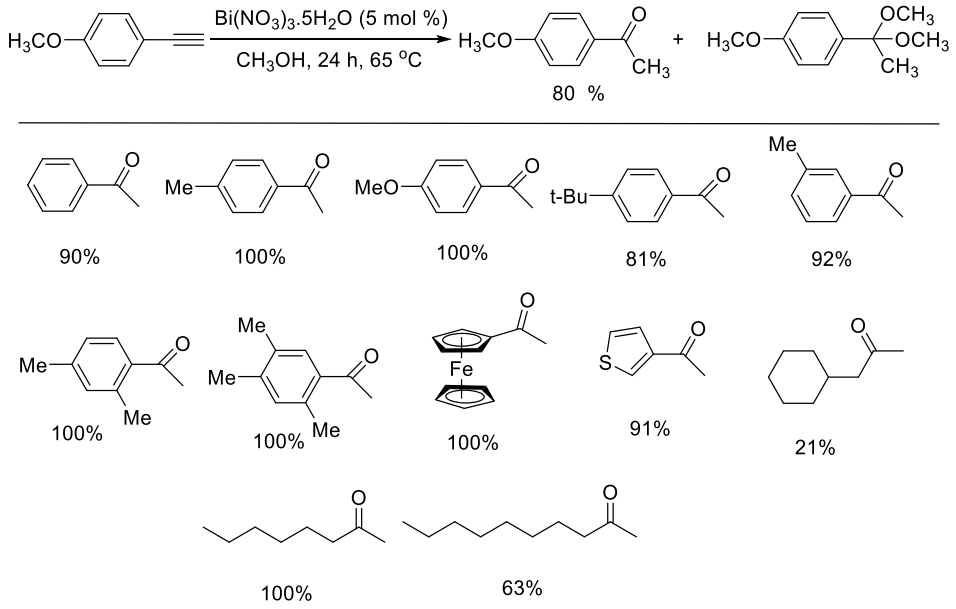
Scheme *41.* $Bi(NO_3)_3.5H_2O$ to catalyzed synthesisis of 1,3-syn-diol acetal motif.



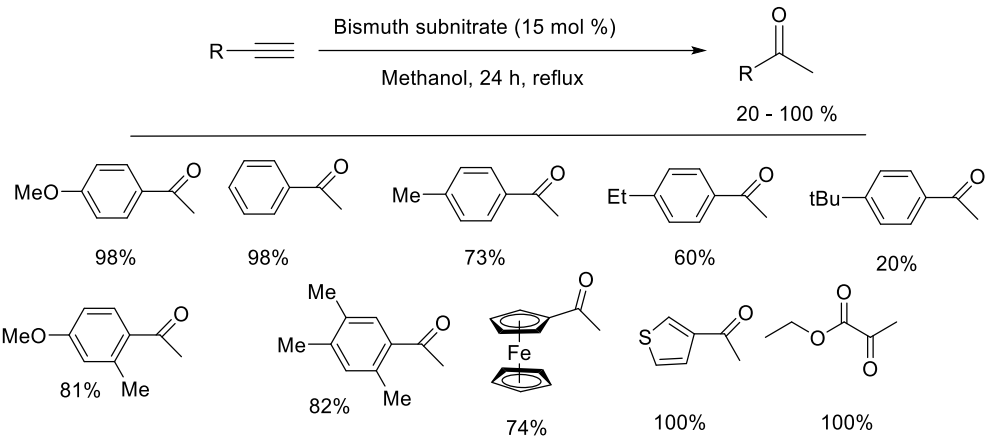
Scheme 42. $Bi(OTf)_3$-catalyzed synthesis of furopyranones.

4.2. C-O bond formation via hydration

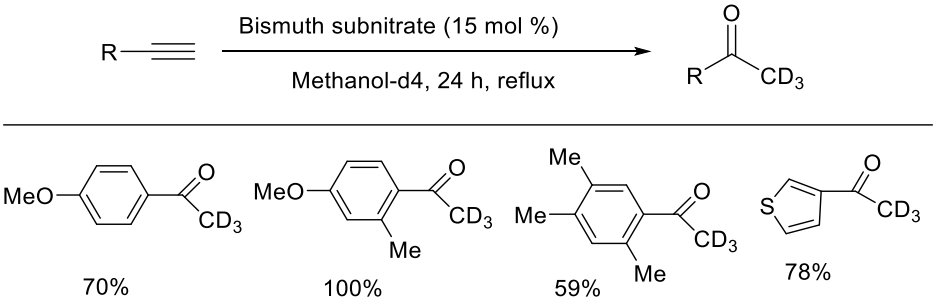
S.B Otvos et al. reported an environmentally friendly $Bi(NO_3)_3{\cdot}5H_2O$-catalyzed synthesis of methyl ketones by Markovnikov-type hydration of terminal acetylenes (Scheme 43)[50]. Z. Szecsenyi et al. achieved bismuth subnitrate ($BiONO_3$) catalyzed synthesis of methyl ketones from terminal acetylenes (Scheme 44a). When the reaction medium was changed to methanol-d_4 trideuteromethyl ketones were obtained (Scheme 44b)[51].



Scheme 43. $Bi(NO_3)_3{\cdot}5H_2O$-catalyzed synthesis of methyl ketones.



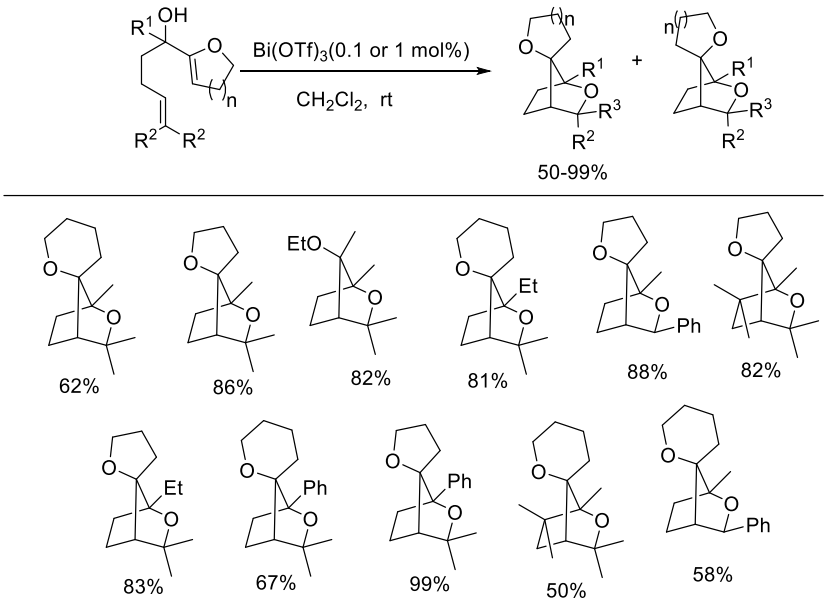
Scheme 44a. ($BiONO_3$)-catalyzed synthesis of methyl ketones.



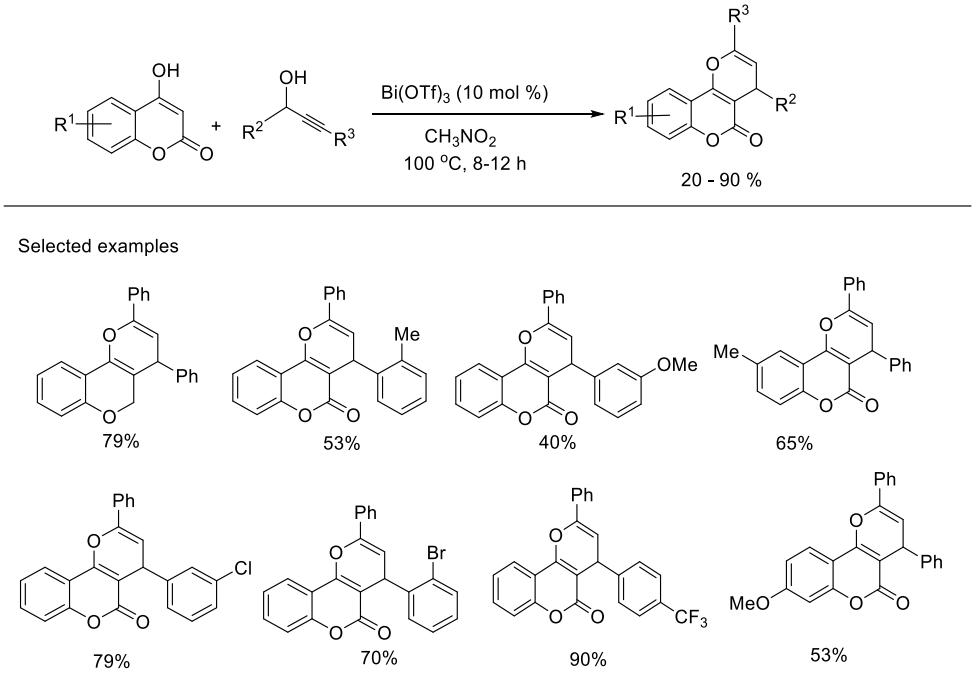
Scheme 44b. ($BiONO_3$)-catalyzed synthesis of trideuteromethyl ketones.

4.3. C-O bond formation via cyclization/annulation

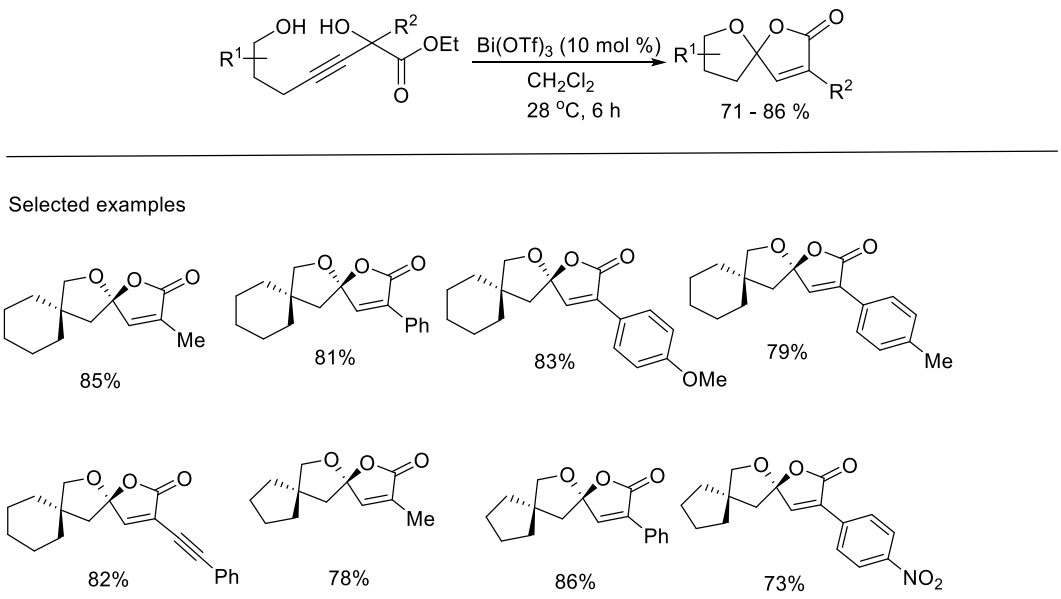
Pierrick Ondet et al. achieved the $Bi(OTf)_3$-catalyzed synthesis of bridged polycyclic ethers with an additional oxaspirocycle by double cyclization of certain α-hydroxy enol ethers synthesized from ketone precursors (Scheme 45).[52] Kim J et al. unveiled the regioselective synthesis of pyranocoumarins from 4-hydroxycoumarins and propargyl alcohols using a $Bi(OTf)_3$ as a catalyst. The reaction proceeds via propargylation and intramolecular cyclization reactions (Scheme 46).[53] Kontham et al. synthesized [5,5]-oxaspirolactones (Scheme 47a) and [6,5]-oxaspirolactones (Scheme 47b) from propargylic diol esters and propargylic diol esters, respectively, by employing π-electrophilic activation of alkynols, using $Bi(OTf)_3$ as a catalyst.[54]



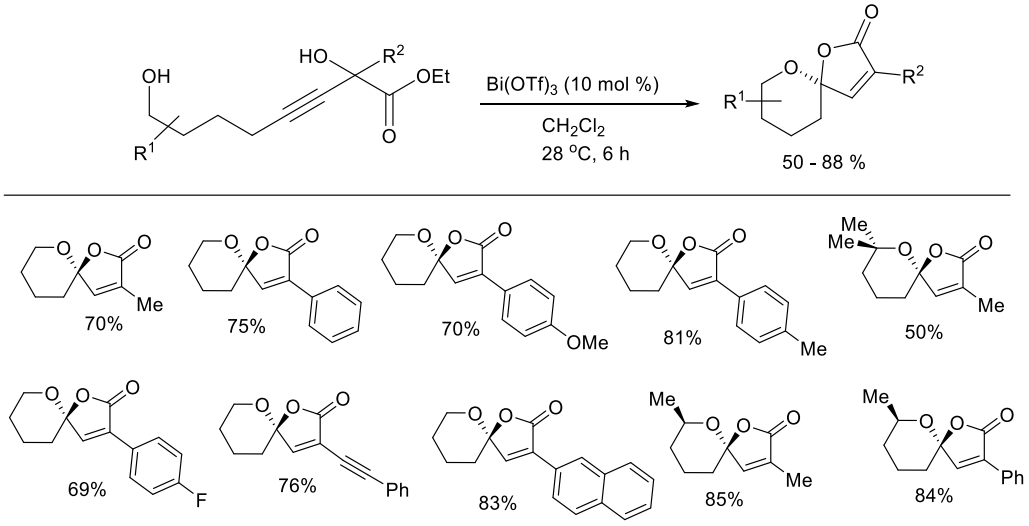
Scheme *45.* $Bi(OTf)_3$-catalyzed synthesis of bridged polycyclic ethers.



Scheme *46.* $Bi(OTf)_3$-catalyzed regioslelective synthesis of pyranocoumarins.

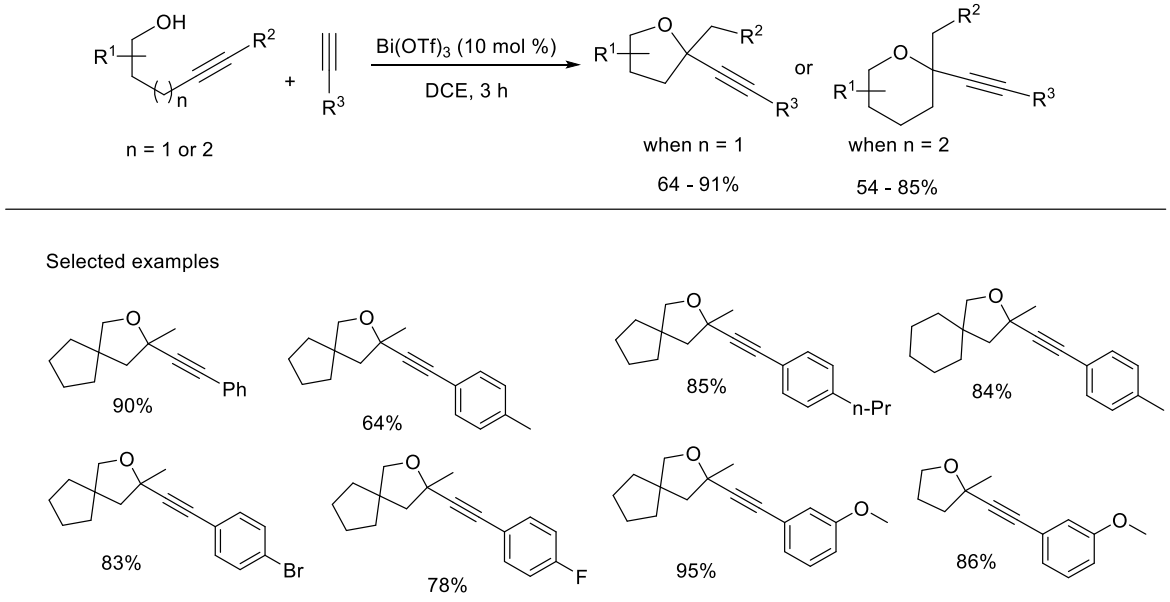


Scheme 47a. Bi(OTf)3-catalyzed regioslelective synthesis of [5,5]-oxaspirolactones.

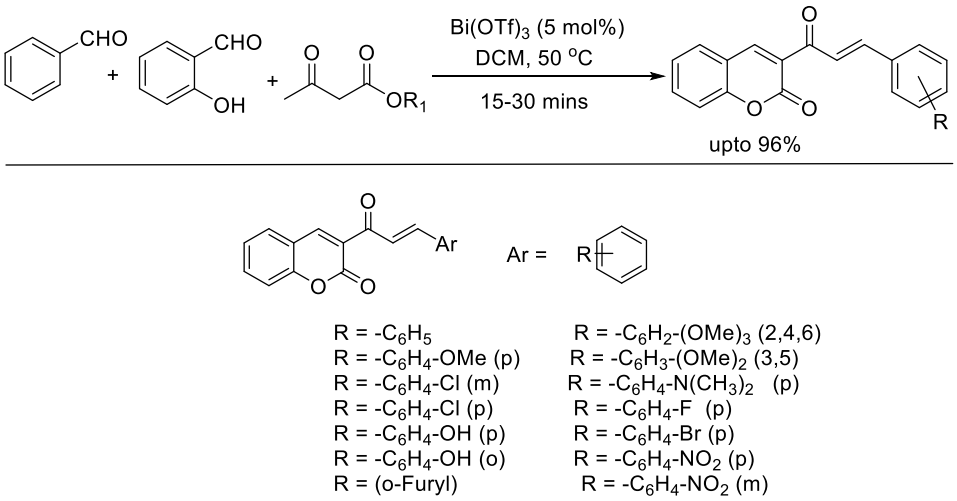


Scheme 47b. Bi(OTf)$_3$-catalyzed regioslelective synthesis of [6,5]-oxaspirolactones.

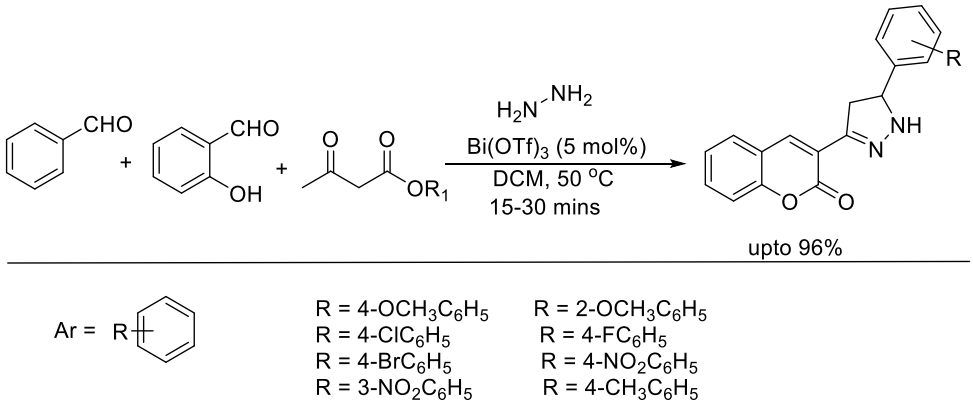
Pratapure et al. reported a Bi(OTf)$_3$ catalyzed cascade synthesis of various 2 alkynyl tetrahydrofurans from alkynols and terminal alkynes. The reaction goes through intramolecular hydroalkoxylation of alkynols followed by hydroalkynylation of the formed cyclic enol ethers (Scheme 48).[55] Mahmoud. Abd El Aleem and his co-worker unveiled Bi(OTf)$_3$-catalyzed synthesis of several coumarin-chalcone hybrid compounds and coumarins linked to pyrazoline from salicylaldehyde, an α-ketoester and an aromatic aldehyde (hydrazine hydrate was added for pyrazolyl coumarins synthesis) in a single step (Scheme 49a, 49b).[56]



Scheme 48. $Bi(OTf)_3$-catalyzed synthesis of 2-alkynyl tetrahydrofurans.

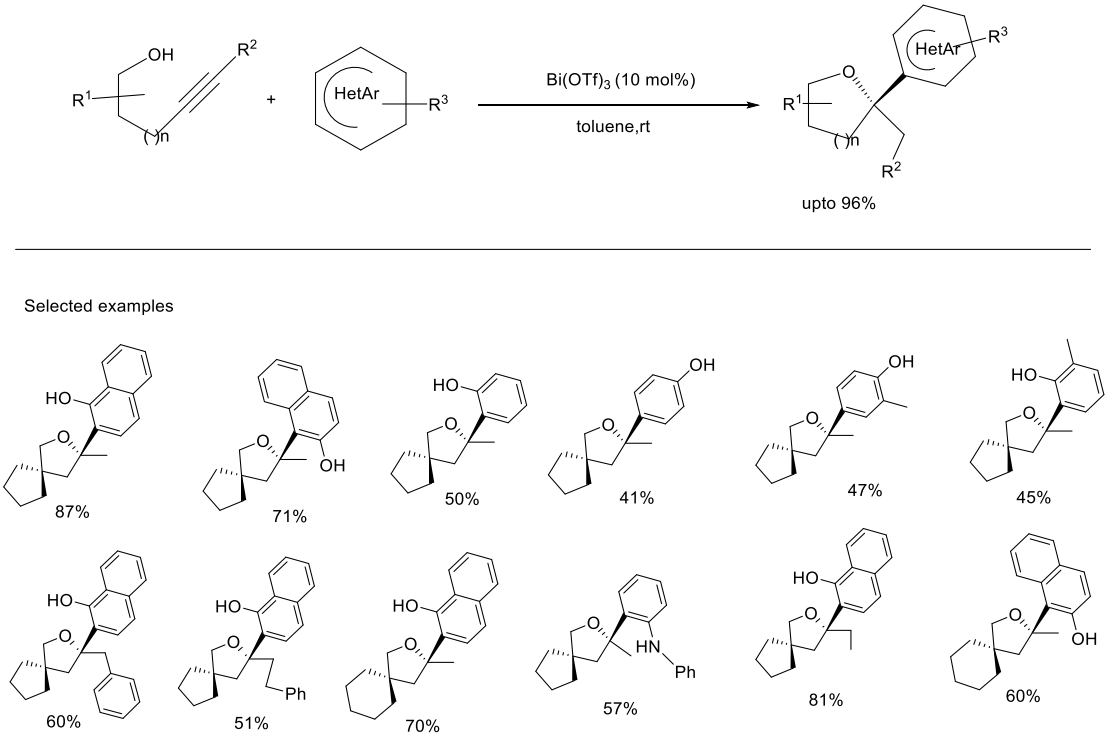


Scheme 49a. $Bi(OTf)_3$-catalyzed synthesis of coumarin-chalcone hybrid.

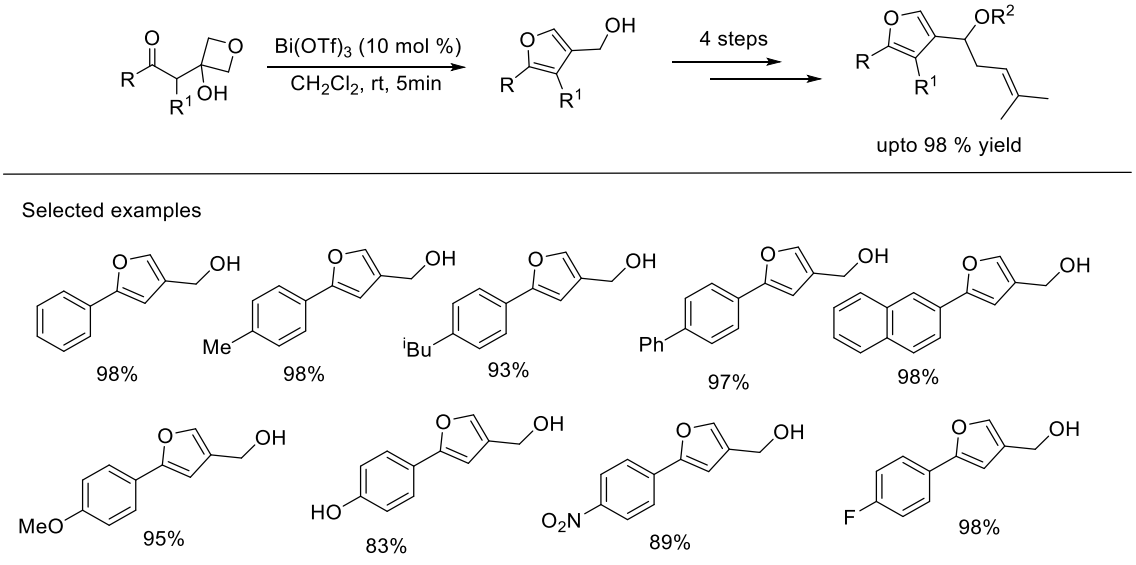


Scheme 49b. $Bi(OTf)_3$-catalyzed synthesis of coumarins linked to pyrazoline.

Ashwini K. Nakate et al. achieved a $Bi(OTf)_3$ catalyzed cascade synthesis of 2-(Hetero)aryl tetrahydrofurans and tetrahydropyrans via hydroalkoxylation of alkynols and intermolecular (hetero)arylation (Scheme 50).[57] Kataria et. al. achieved a $Bi(OTf)_3$-catalyzed synthesis of hydroxy methyl-derived polysubstituted furans in an excellent yield in 5 minutes. The reaction proceeds via cycloisomerisation of α-hydroxy oxetanyl ketones. This method was used in the total synthesis of shikonofurans J, D, E and C natural products (Scheme 51).[58]



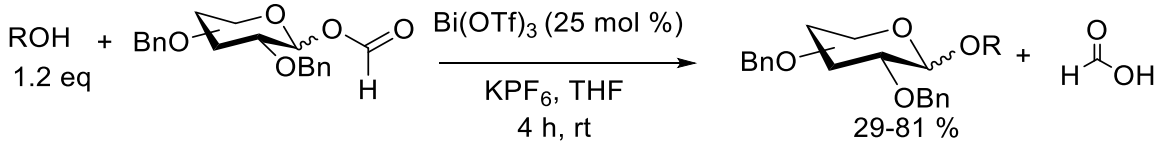
Scheme 50. $Bi(OTf)_3$ catalyzed synthesis of 2-(Hetero)aryl tetrahydrofurans and tetrahydropyrans.



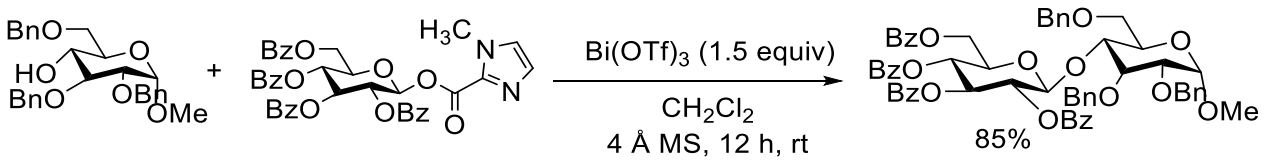
Scheme 51. $Bi(OTf)_3$-catalyzed synthesis of hydroxy methyl-derived polysubstituted furans.

4.4. C-O glycosidic bond formation reactions

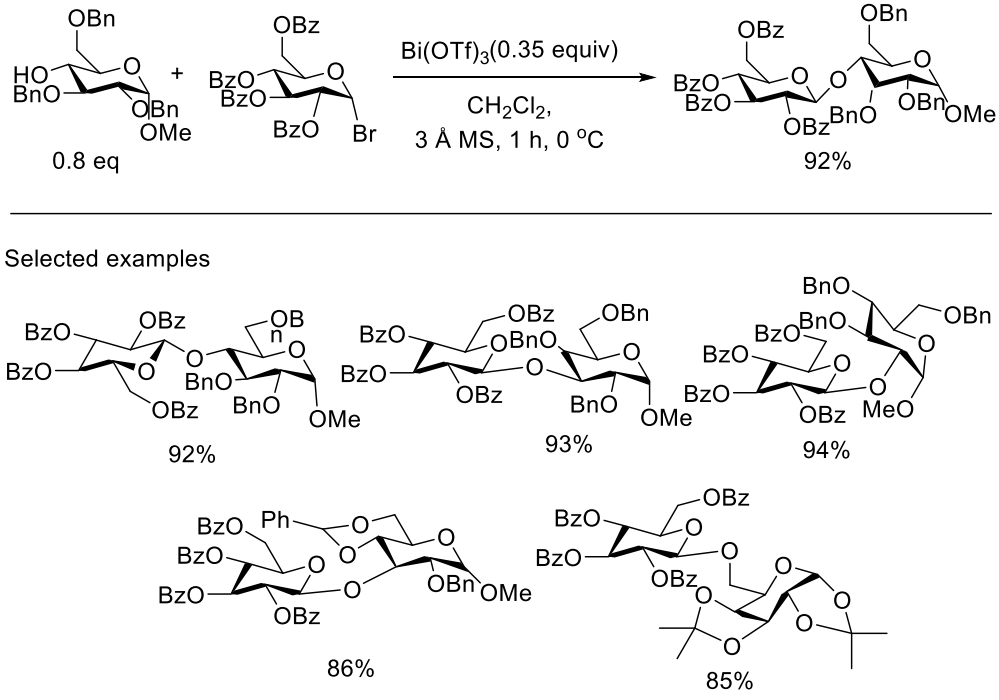
L. Yang et al. performed a $Bi(OTf)_3$-promoted glycosylation of alcohols using glycosyl formate to synthesize benzyl glycosyl formates (Scheme 52)[59] whereas J. Chen et al. achieved a $Bi(OTf)_3$-promoted glycosylation using glycosyl-1-methylimidazole-2-carboxylates (Scheme 53).[60] Demchenko et al. found that $Bi(OTf)_3$ acts as an effective catalyst for activating glycosyl bromides and glycosyl chlorides. With various glycosyl acceptors, $Bi(OTf)_3$ promotes glycosidation of differently protected glucosyl, galactosyl and mannosyl halides to give the corresponding disaccharides (Scheme 54).[61]



Scheme 52. $Bi(OTf)_3$-promoted glycosylation to synthesize benzyl glycosyl formats.



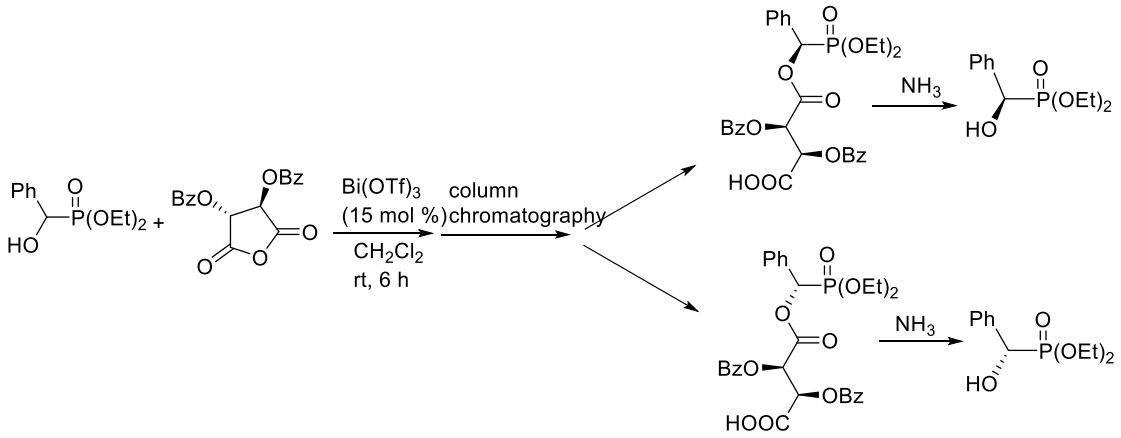
Scheme 53. $Bi(OTf)_3$-catalyzed glycosylation of glycosyl-1-methylimidazole-2-carboxylates.



Scheme 54. $Bi(OTf)_3$ as catalyst for activating glycosyl bromides and glycosyl chlorides.

4.5. Esterification

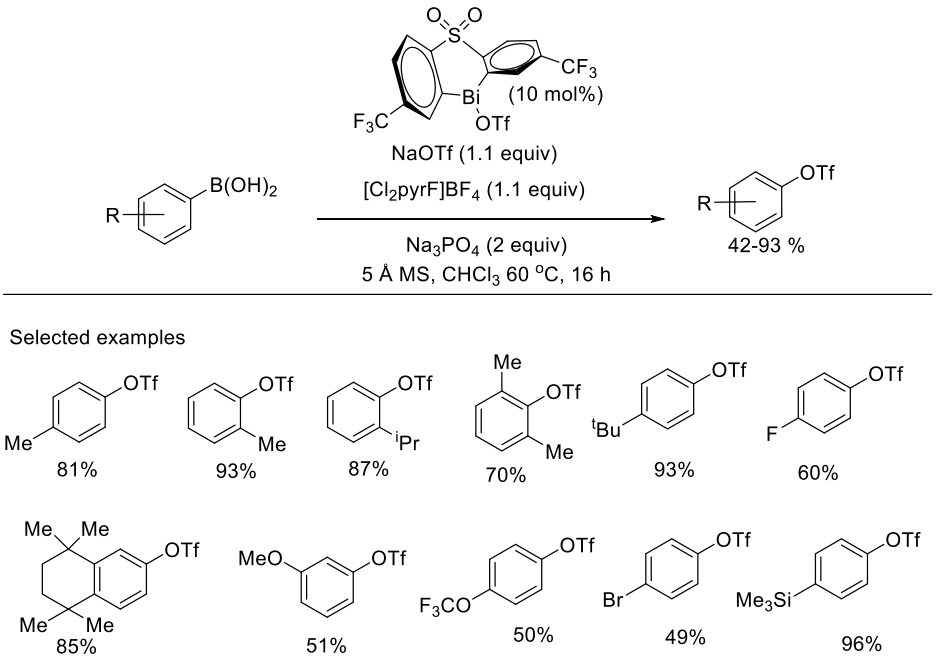
B. Kaboudin et al. synthesized efficiently optically active α-hydroxyphosphonates through resolution of the racemates using $Bi(OTf)_3$ as a catalyst. Treating racemic diethyl 1-hydroxy-1-phenylmethylphosphonate with (+)-dibenzoyl-L-tartaric anhydride in the presence of $Bi(OTf)_3$ yielded two diastereomers, which were separated by column chromatography. The isolated diastereomers were hydrolysed to yield chiral phosphonates (Scheme 55).[62]



Scheme 55. $Bi(OTf)_3$-catalyzed synthesis of optically active α-hydroxyphosphonates through resolution of the racemates.

4.6. Oxidative coupling

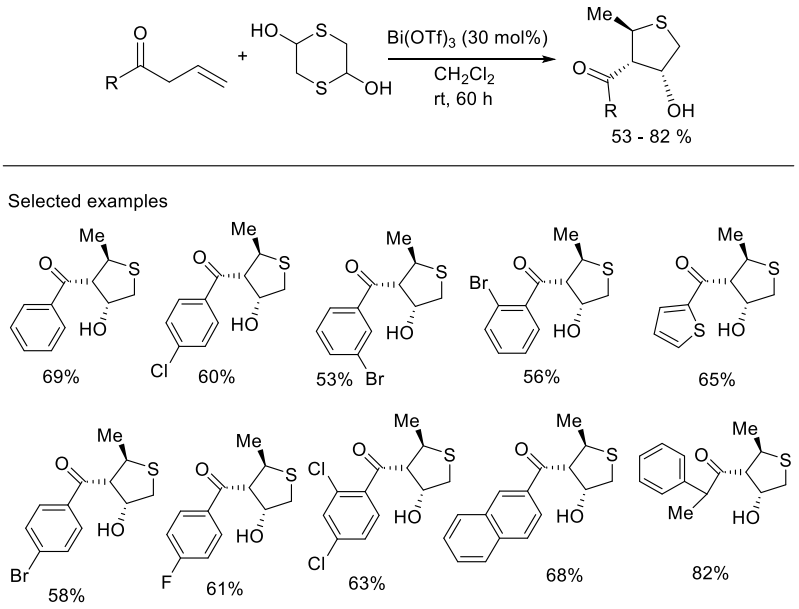
O. Planas et al. reported the synthesis of aryl triflates formed from cross-coupling reaction of arylboronic acids with perfluoroalkyl sulfonate salts catalyzed by bismuth where a Bi(III)/Bi(V) redox cycle is involved (Scheme 56)[63]. The sulfone ligand aids the formation of C(sp^2)-O bonds by using Sodium triflate and Potassium triflate as coupling partners.



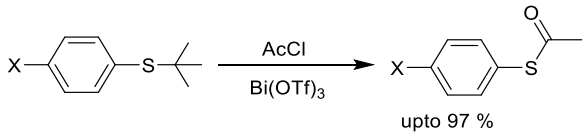
Scheme 56. Synthesis of aryl triflates using Bismuth.

4. C-S and C-P Bond Formation

Borthakur and his co-worker discovered a one-pot strategy to synthesize several substituted tetrahydro-thiophenes from β,γ-unsaturated ketones and 1,4-dithiane-2,5-diol using $Bi(OTf)_3$ as a catalyst. The reaction proceeded via tandem isomerisation, and Michael's reaction was followed by an aldol reaction, which is highly diastereoselective (Scheme 57).[64] Martyn Jevric et al. synthesized several thioacetates from thioethers by using AcCl and $Bi(OTf)_3$ as a combination for a catalyst. A variety of thioacetates containing dithiafulvene, dicyanoethylene, di-hydroazulene, fulleropyrrolidine, and triazole units was synthesized using this method (Scheme 58).[65]



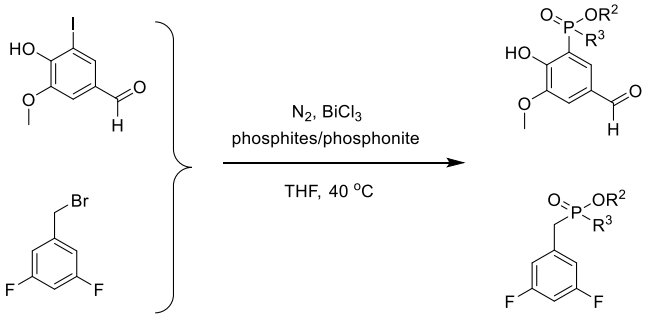
Scheme 57. $Bi(OTf)_3$-catalyzed synthesis of tetrahydro-thiophenes.



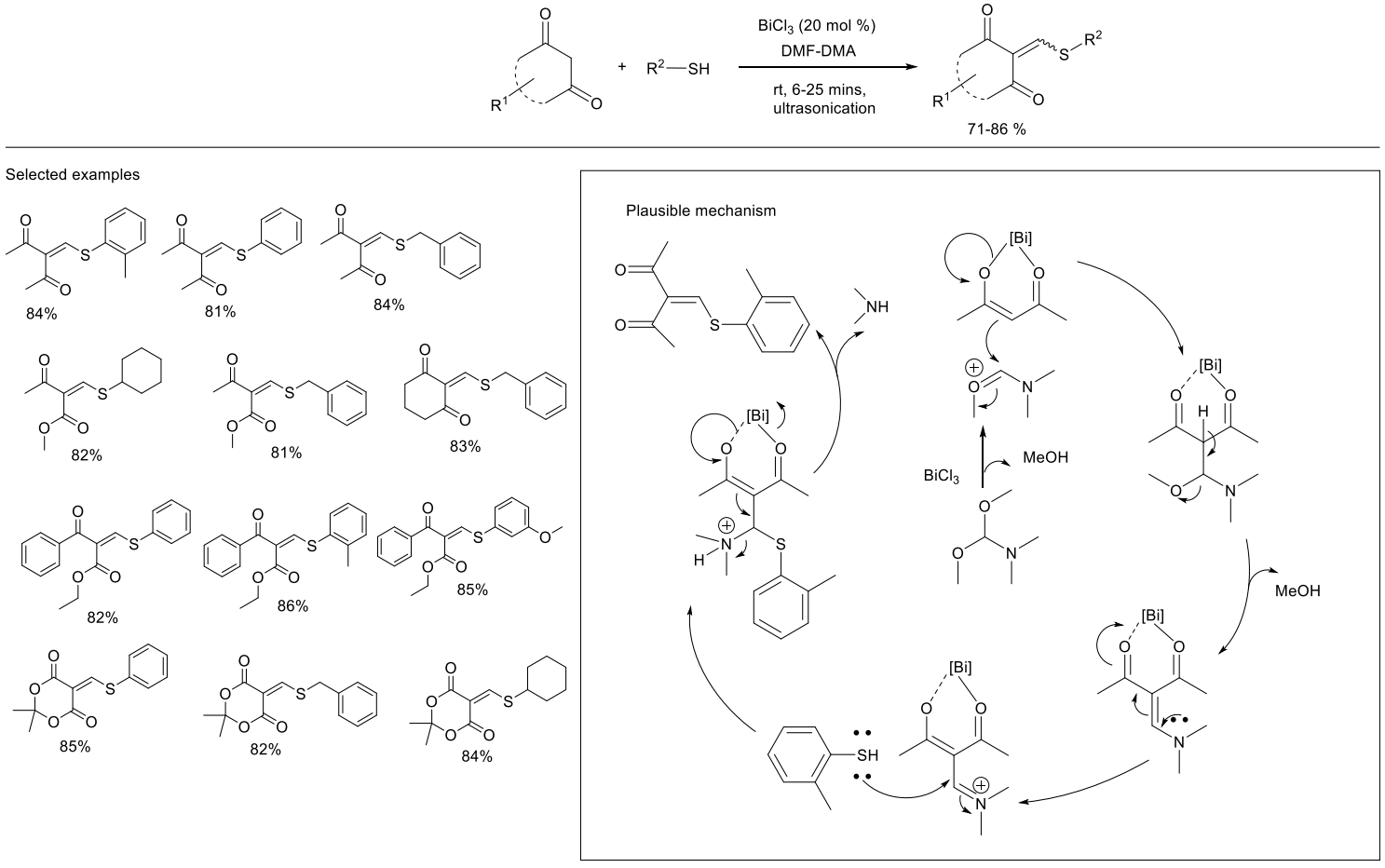
Scheme 58. $Bi(OTf)_3$/AcCl catalyzed synthesis of thioacetates from thioethers.

Ch. Subramunyam et al. found a $BiCl_3$-catalyzed Michaelis-Arbuzov reaction for the synthesis of substituted arylphosphonate/phosphinates from 5-Iodovanillin/3,5-difluorobenzylbromide, phosphites and dimethyl phenylphosphonite under nitrogen atmosphere. The synthesized compounds also showed good antibacterial and antifungal activity when subjected to in-vitro antibacterial and antifungal studies (Scheme 59)[66]. Panchal et al. reported a $BiCl_3$–catalyzed one-pot, three-component synthesis of thioenol ethers under ultrasonication. In this approach, β-ketoesters, 1,3-diones, or 2-oxindoles are coupled with N,N-dimethylformamide dimethyl acetal (DMF-DMA) and thiols in the presence of $BiCl_3$ under ultrasonication. The authors proposed a plausible mechanism. The 1,3-dicarbonyl compound, existing in keto–enol equilibrium, acts as a nucleophile and reacts with Lewis acid–activated DMF-DMA to afford an initial adduct. Subsequent activation by $BiCl_3$ generates an enamine species that equilibrates with the corresponding iminium ion.

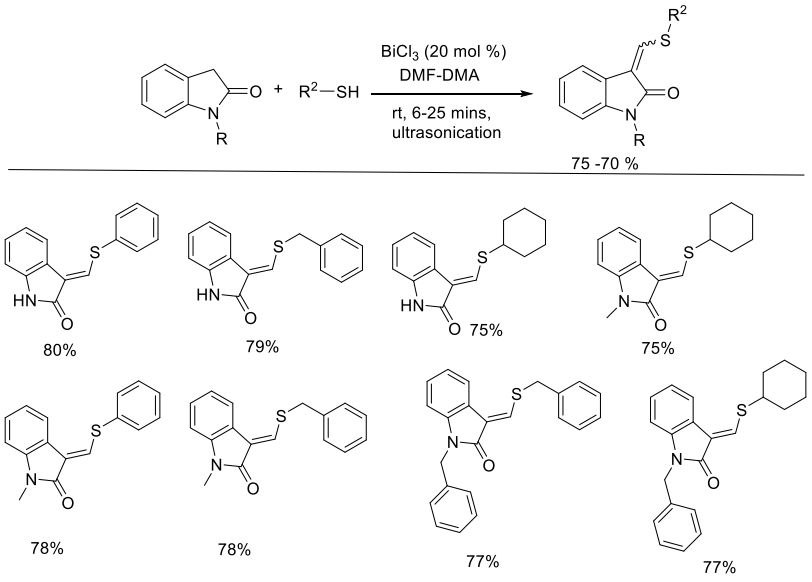
Nucleophilic addition of the thiol to this electrophilic intermediate produces a thioenolate-type intermediate, which undergoes thermodynamically favored elimination of N,N-dimethylamine to yield the final thioenol ether product (Scheme 60a and 60b).[67]



Scheme 59. $BiCl_3$-catalyzed Michaelis-Arbuzov reaction for the synthesis of substituted arylphosphonate/phosphinates.



Scheme 60a. $BiCl_3$–catalyzed synthesis of thioenol ethers β-ketoesters and 1,3-diones.

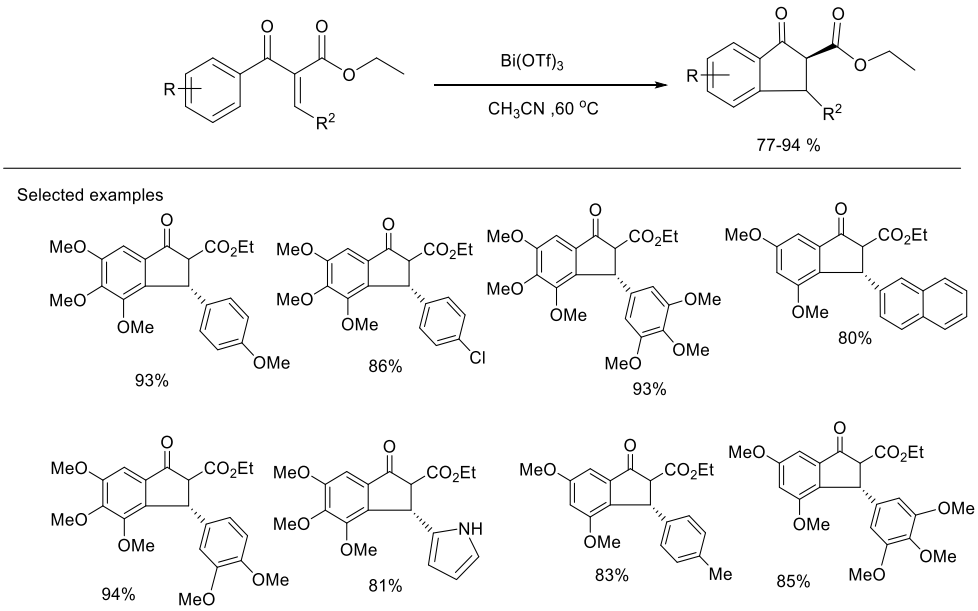


Scheme 60b. $BiCl_3$–catalyzed synthesis of thioenol ethers from 2-oxindoles.

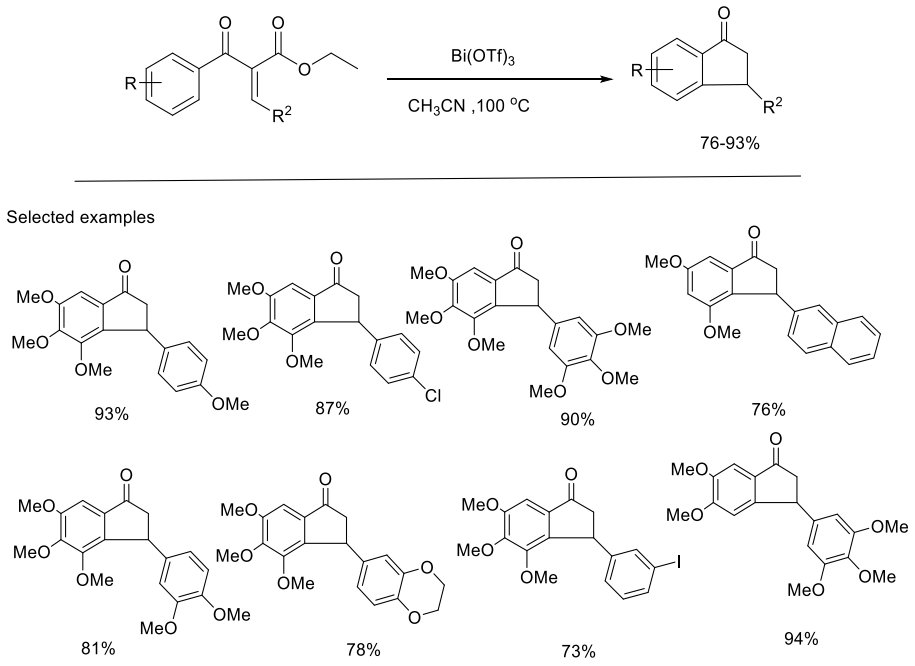
5. Rearrangement Reactions

6.1. Nazarov rearrangements

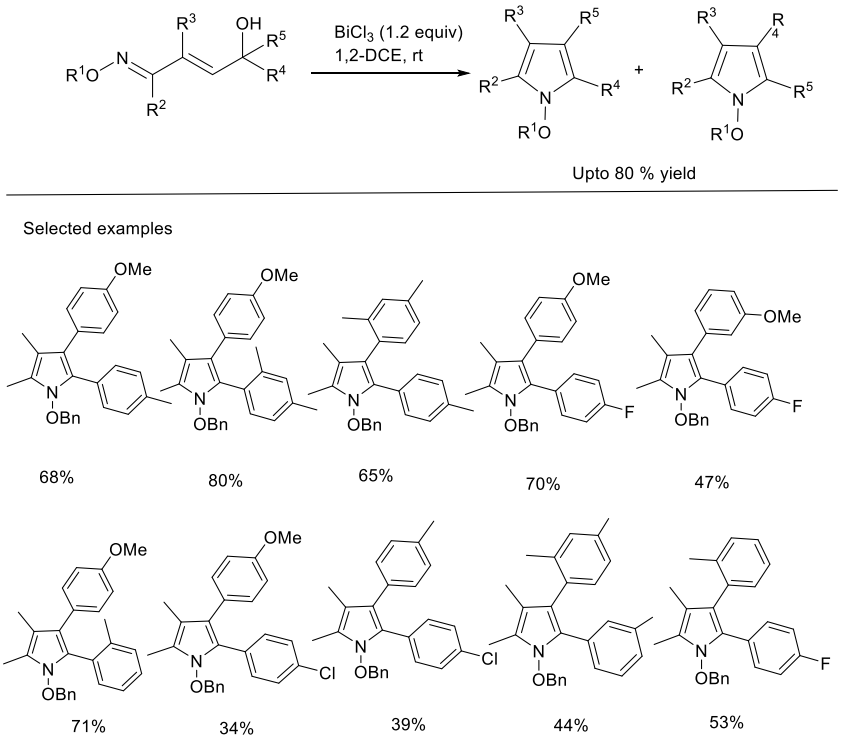
Bismuth (III) catalysts have garnered special attention for their role as catalysts in rearrangement reactions. M. T Rodrigues et al. achieved the $Bi(OTf)_3$-catalyzed Nazarov reaction for the synthesis of 3-aryl-2-carboethoxy-1-indanones (Scheme 61a) and 3-aryl-1-indanones (Scheme 61b) from aryl vinyl ketones[68]. Some derivatives showed biological activity against the human cancer line cells. Gaonkar and co-workers developed a $BiCl_3$-catalyzed aza-Nazarov cyclization coupled with a 1,2-Wagner–Meerwein rearrangement for the divergent synthesis of highly substituted pyrroles (Scheme 62a). Iso-Nazarov cyclization was also successfully employed, enabling the divergent synthesis of indenes under Bi(III) catalysis (Scheme 62b). The Bi(III) catalyst serves as an effective Lewis acid catalyst, enabling controlled electrocyclization and rearrangement under conditions[69].



Scheme 61a. $Bi(OTf)_3$-catalyzed synthesis of 3-aryl-2-carboethoxy-1-indanones.



Scheme 61b. $Bi(OTf)_3$-catalyzed synthesis of 3-aryl-1-indanones.

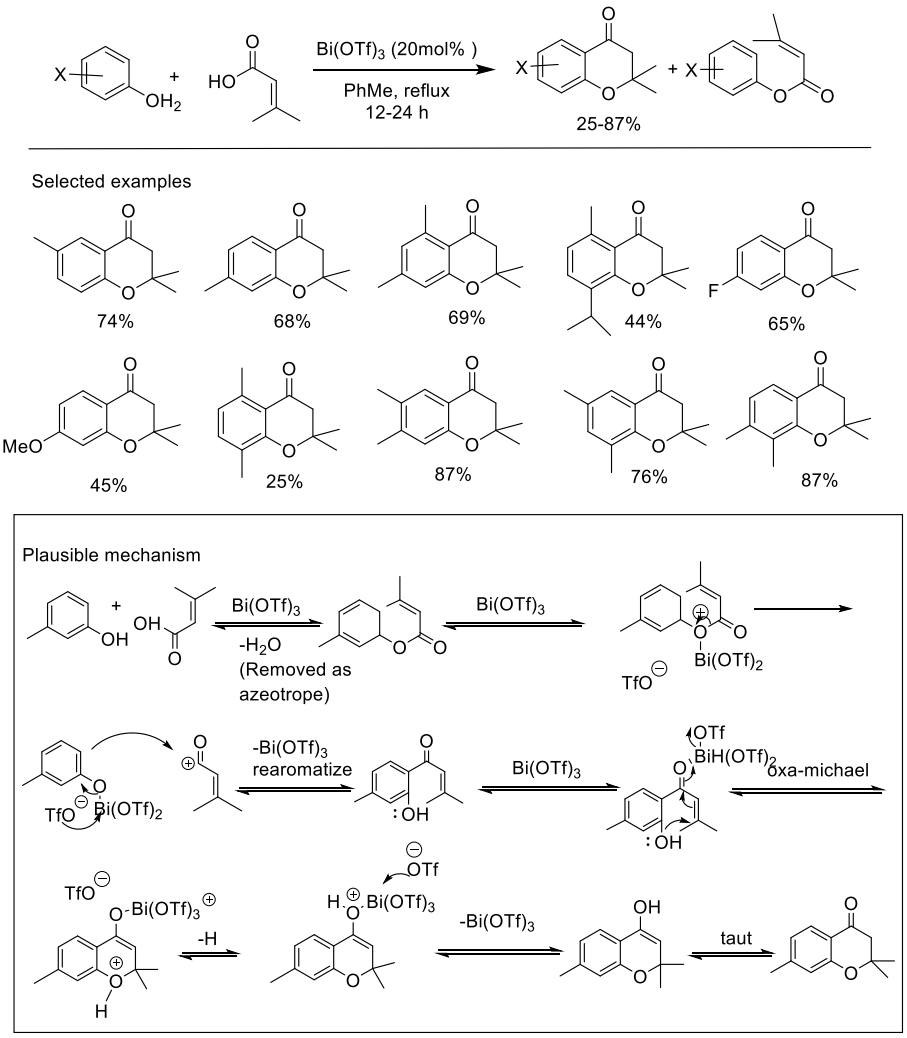


Scheme 62a. $BiCl_3$-catalyzed synthesis of substituted pyrroles.

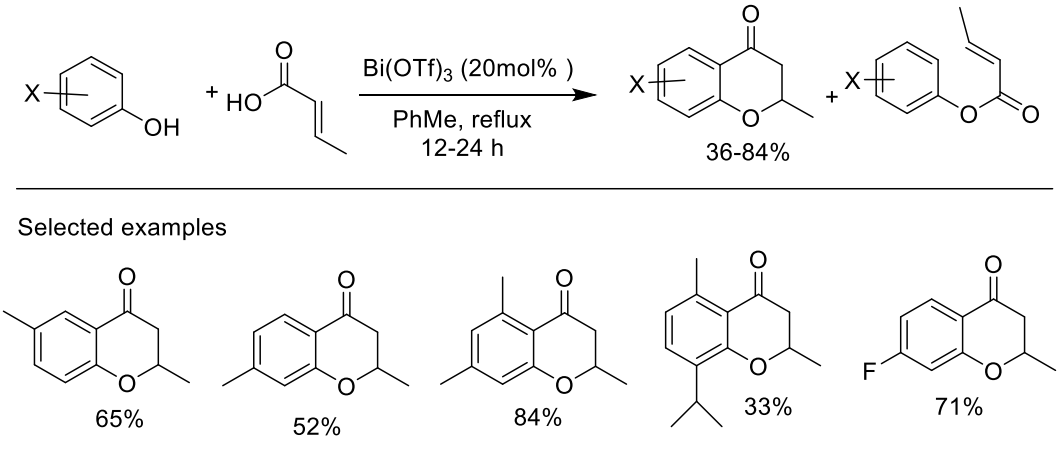
Scheme 62b. $BiCl_3$-catalyzed synthesis of indenes.

6.2. Fries-type rearrangement & oxa-Michael tandem reactions

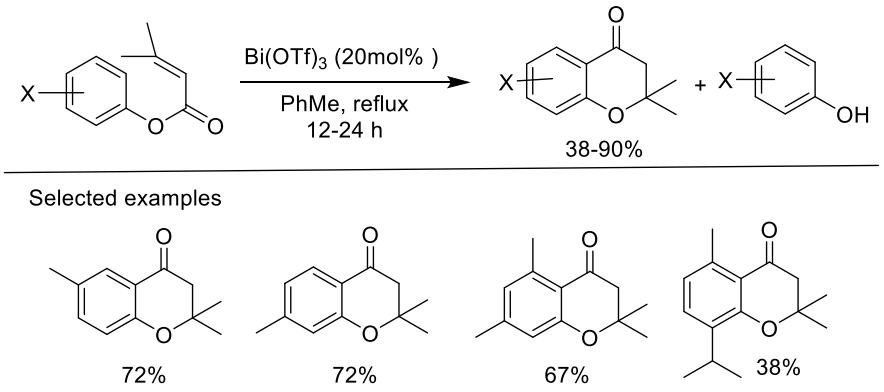
Kevin Meraz et al. reported a $Bi(OTf)_3$-catalyzed tandem reaction of electron-rich phenols and 3,3-dimethylacrylic acid (Scheme 63a) or trans-crotonic acid (Scheme 63b), which yielded 4-chromanones. The corresponding aryl esters also yielded 4-chromanones (Scheme 63c). The authors proposed a plausible reaction mechanism. They found that the first intermediate formed in the reaction was the aryl ester, using thin-layer chromatography, where water was the byproduct. Although the generated water could potentially deactivate the catalyst, its removal through azeotropic distillation with boiling toluene minimizes such degradation. The aryl ester subsequently undergoes a Fries-type rearrangement to yield a hydroxyaryl ketone intermediate. Under $Bi(OTf)_3$ catalysis, this intermediate is rapidly transformed into the cyclized product through a sequence of intramolecular reactions. The process likely involves a ring-closure step via an oxa-Michael addition, followed by proton transfer, catalyst release, and tautomerization to furnish the final product. In contrast, under aluminum chloride conditions, strong coordination of the phenolic and carbonyl groups suppresses nucleophilicity and hampers the ring-closing step, accounting for the lower efficiency of that catalyst system (Scheme 63a). The reaction mechanism involved esterification, a Fries rearrangement, and an oxa-Michael ring closure.[70]



Scheme 63a. $Bi(OTf)_3$-catalyzed synthesis of 4-chromanones from 3,3-dimethylacrylic acid.



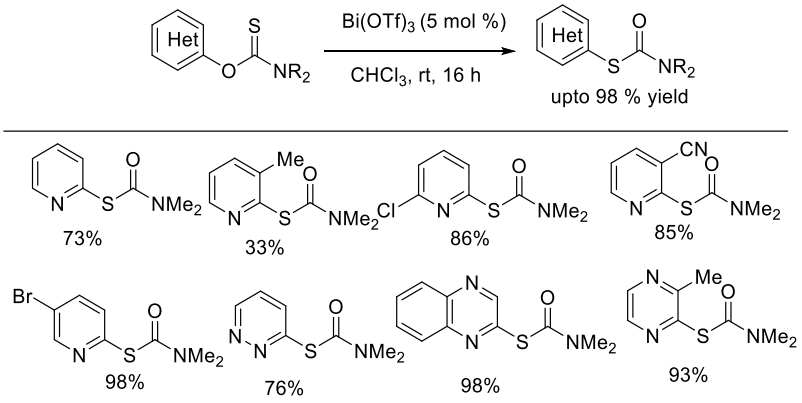
Scheme 63b. $Bi(OTf)_3$-catalyzed synthesis of 4-chromanones from trans-crotonic acid.



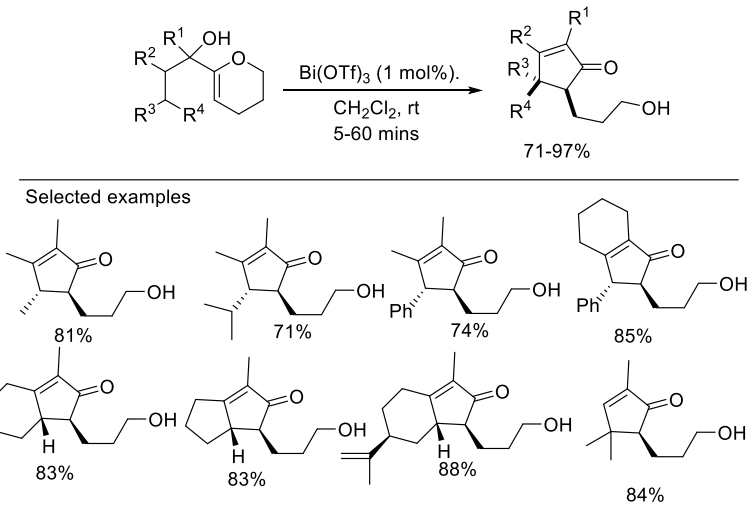
Scheme 63c. $Bi(OTf)_3$-catalyzed synthesis of 4-chromanones from aryl esters.

6.3. Other rearrangements

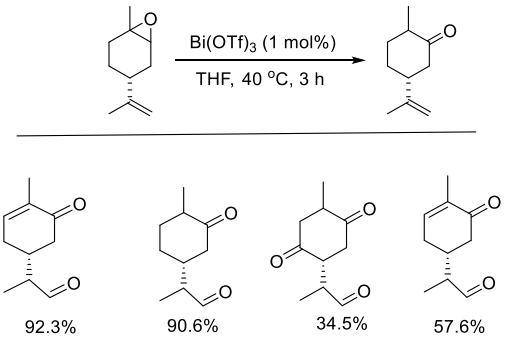
Okuda et al. reported a $Bi(OTf)_3$ catalyzed Newman-Kwart rearrangement (NKR) of aza-arenes under ambient temperature conditions (Scheme 64)[71]. They were also able to achieve NKR of thiophenes. Luisa Lempenauer et al. revealed a $Bi(OTf)_3$-catalyzed diastereoselective synthesis of polysubstituted cyclopentenones by ring rearrangement of various tertiary allylic alcohols (Scheme 65)[72]. P. S. Löser et al. reported a $Bi(OTf)_3$ catalyzed synthesis of dihydrocarvone by Meinwald rearrangement of (+)-limonene oxide (Scheme 66)[73]. Several mono and biscarbonyl compounds were synthesized by rearrangement of mono and bisepoxides respectively. The authors used deconvolution approach for screening ten catalysts ($BF_3.Et_2O$, $Bi(OTf)_3$, $AlCl_3$, $ZnBr_2$, $MgCl_2.6H_2O$, CuCl, $CuCl_2$, $NiCl_2(PPh_3)_2$, $Pd(OAc)_2/PPh_3$, Al_2O_3) and $Bi(OTf)_3$ was found to be the best catalyst as Bismuth salts are efficient in oxidation and acylation of alcohols. Ming Jin et al. discovered a novel cascade $Bi(OTf)_3$-catalyzed synthesis of β-aminophosphonates from α-phosphoryl formaldehydes and homoallylic amine[74]. The cascade reaction follows the sequence of Enamine−Imine Tautomerism and Aza-Cope rearrangement. The diastereomers formed were easily separated by column chromatography (Scheme 67).



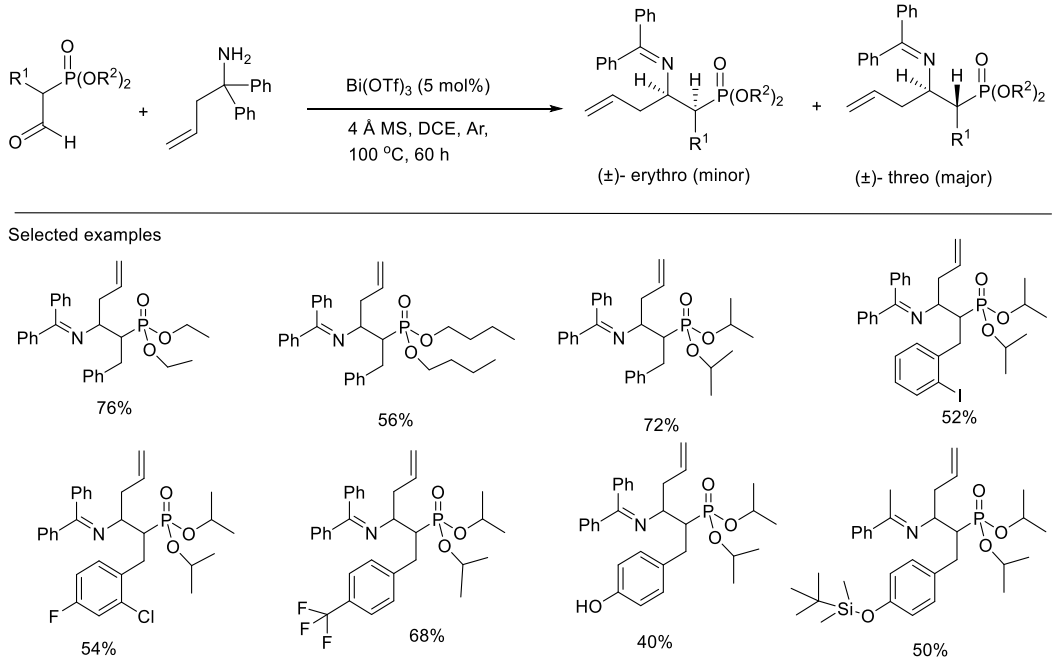
Scheme 64. $Bi(OTf)_3$-catalyzed Newman-Kwart rearrangement (NKR) of aza-arenes.



Scheme 65. $Bi(OTf)_3$-catalyzed diastereoselective synthesis of polysubstituted cyclopentenones.



Scheme 66. $Bi(OTf)_3$ catalyzed synthesis of dihydrocarvone.

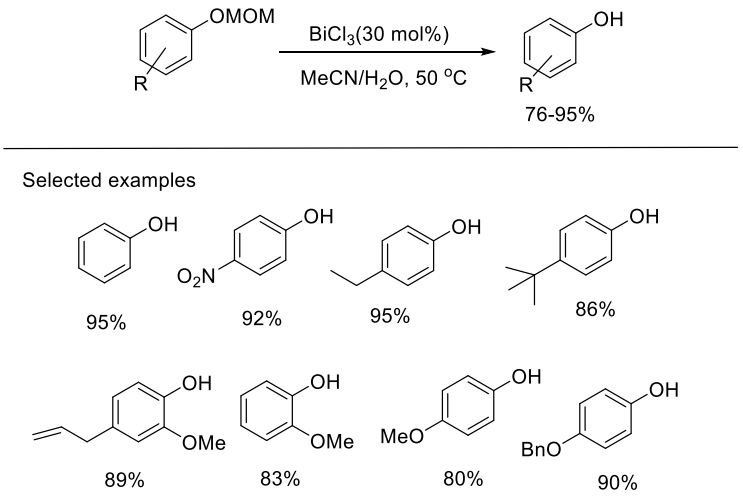


Scheme 67. $Bi(OTf)_3$-catalyzed synthesis of β-aminophosphonates.

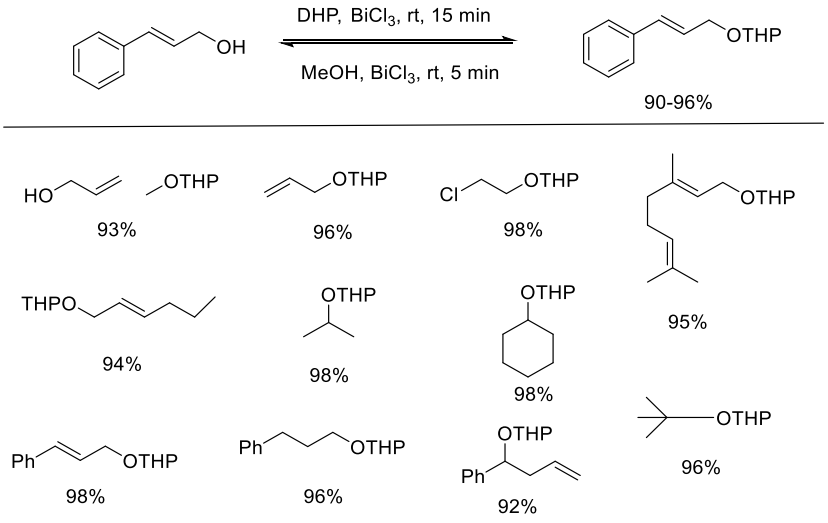
7. Other Transformations

7.1. Protection and deprotection

Oghale Obaro-Best et al. reported a $BiCl_3$-catalyzed deprotection of phenolic methoxymethyl ethers (Scheme 68)[75]. Durga et al. achieved a $BiCl_3$-catalyzed tetrahydropyranylation of 1°, 2 °,3°, allylic, benzylic alcohols, and symmetric diols without using any solvent in a very good yield[76]. Adding methanol resulted in depyranylation of alcohols (Scheme 69).



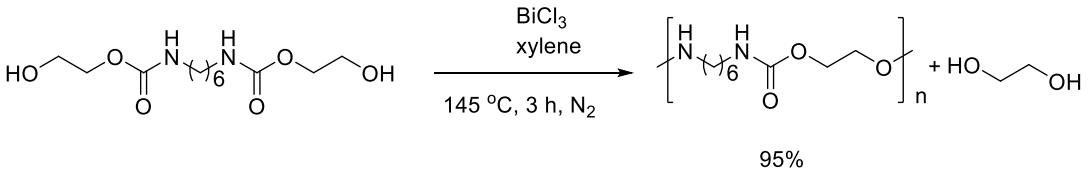
Scheme 68. $BiCl_3$-catalyzed deprotection of phenolic methoxymethyl ethers.



Scheme 69. $BiCl_3$-catalyzed tetrahydropyranylation of 1°,2 °,3°, allylic, benzylic alcohols, and symmetric diols.

7.2. Polycondensation

Bismuth catalysts were effective for polycondensation reactions also. Bungo Ochiai et al. unveiled a $BiCl_3$ catalyzed for self-polycondensation of a bishydroxyurethane monomer for the synthesis of non-isocyanate polyurethane (Scheme 70).[77]

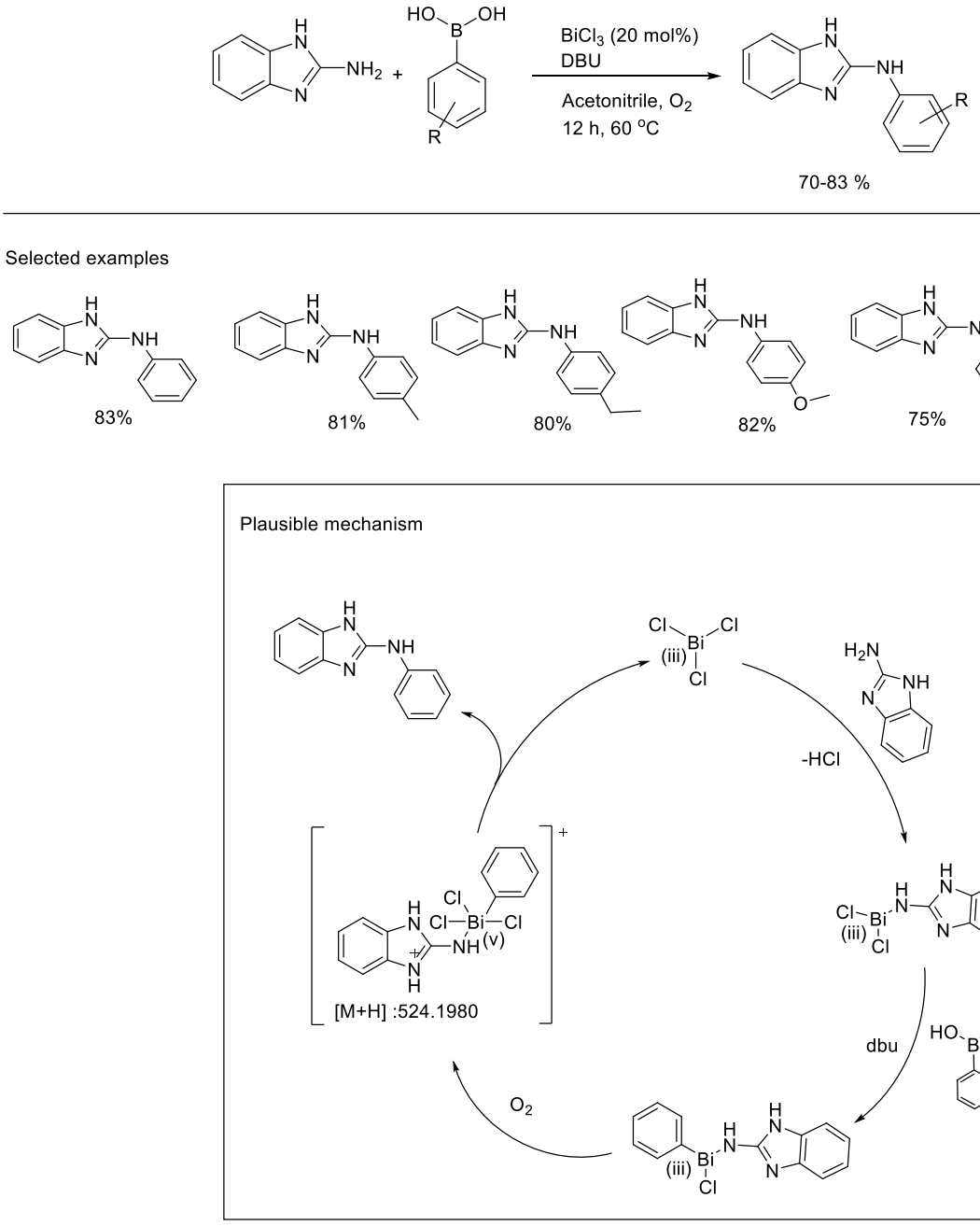


Scheme 70. $BiCl_3$-catalyzed synthesis of non-isocyanate polyurethane.

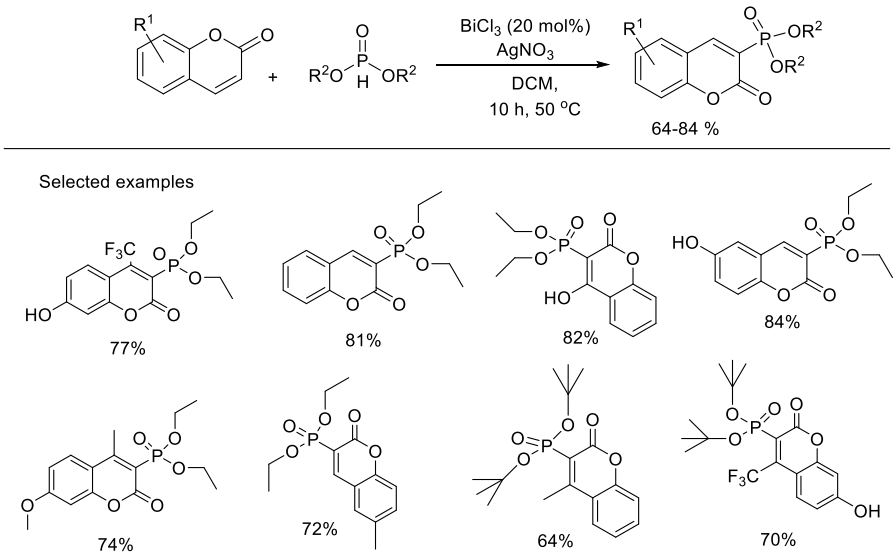
8. Contributions From Our Research Group

Our group reported the $BiCl_3$-catalyzed synthesis of N- arylbenzimidazole with various arylboronic acids via C-NH_2-arylation of 2-aminobenzimidazoles. A plausible mechanism involves initial coordination of $BiCl_3$ with 2-aminobenzimidazole, accompanied by elimination of HCl. Subsequent transmetallation with phenylboronic acid in the presence of DBU forms a Bi(III) intermediate. The lone pair on the imidazole nitrogen participates in aromatic delocalization, reducing its basicity and preventing coordination with bismuth; consequently, the coupling occurs selectively at the exocyclic amino group. Molecular oxygen serves as the terminal oxidant, generating a high-valent Bi(V) species, which then undergoes reductive elimination to afford the desired imidazole derivative while regenerating the Bi(III) catalyst, thus completing the catalytic cycle (Scheme 71a). This reaction shows the superiority of bismuth over other metals because of its ability to form Bi(V) complexes in catalytic cycles of redox reactions more efficiently. Phosphorylation of various substituted coumarins catalyzed by $BiCl_3$ was also achieved (Scheme 71b).[78]

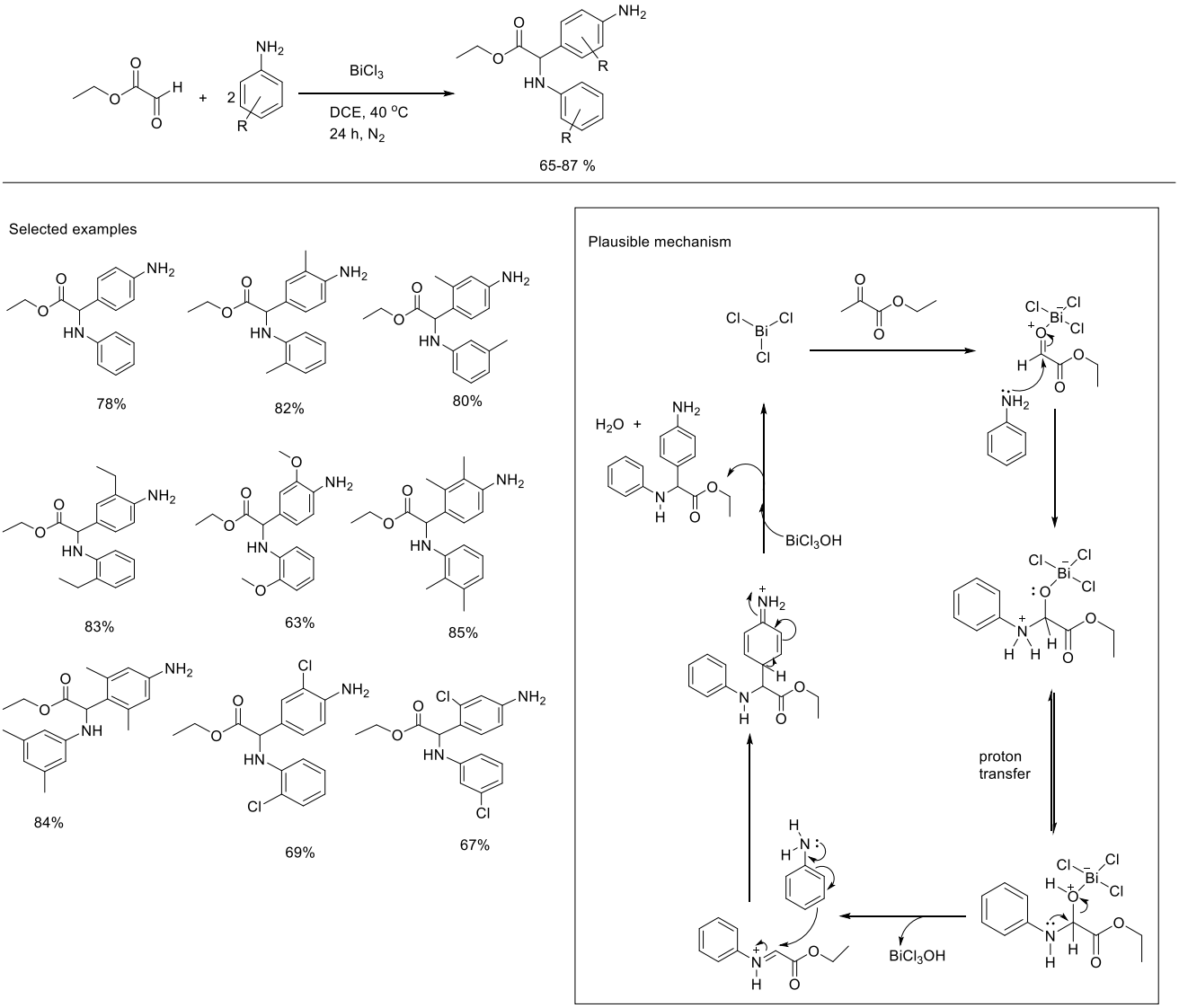
The novel biologically active molecules formed were obtained in a high yield under mild reaction conditions. Further, a novel $BiCl_3$-catalyzed synthesis of glycine derivatives such as ethyl 2-(4-aminophenyl)-2-(phenylamino) acetate in good yield from ethyl glyoxylate and aniline derivatives was achieved. The proposed reaction suggests the coordination of the carbonyl oxygen of ethyl glyoxylate to $BiCl_3$, resulting in the formation of an activated adduct. Subsequent polarization of the carbonyl group facilitates nucleophilic attack by aniline at the carbon center. A proton transfer from nitrogen to oxygen then generates a hydroxylated intermediate, followed by the elimination of $BiCl_3OH$ to produce an imine-like species. The nucleophilic addition of a second aniline molecule and subsequent deprotonation, mediated by $BiCl_3OH$, affords the final product, with the catalyst regenerated and water as the only byproduct. The C–C bond formation occurs preferentially at the para position of aniline, explaining the reduced reactivity observed with para-substituted anilines due to steric hindrance. The reaction is very green, as the only byproduct obtained is water (Scheme 72).[79] We also accomplished the $BiCl_3$-catalyzed cyclization of phenylacetylene and ethyl 2-(arylimino)acetates to synthesize quinoline-2-carboxylate derivatives under mild reaction conditions (Scheme 73).[80] This reaction is commercially and environmentally attractive as the previously reported works involved costly catalysts or harsh conditions.



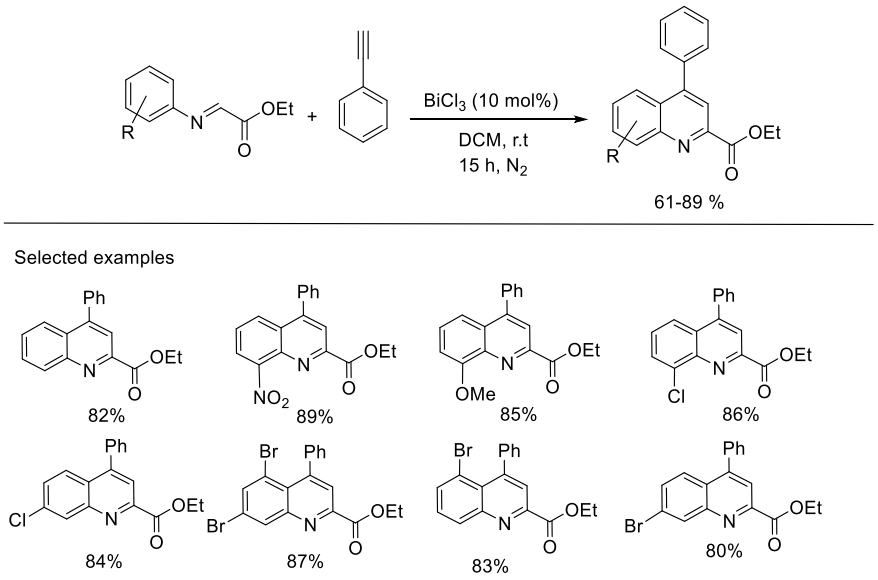
Scheme 71a. $BiCl_3$-catalyzed synthesis of N- arylbenzimidazole with various arylboronic acids.



Scheme 71b. $BiCl_3$-catalyzed phosphorylation of substituted coumarins.



Scheme 72. $BiCl_3$-catalyzed synthesis of glycines.



Scheme 73. $BiCl_3$-catalyzed synthesis of quinoline-2-carboxylate derivatives.

When analysing the catalyst screening performed by the researchers in their works discussed in this review, we can see that the bismuth catalysts always performed better, giving higher yield in a shorter time with more selectivity, compared to various transition metal catalysts ($CuCl_2$, $CuBr_2$, $Cu(OTf)_2$, $Cu(OAc)_2$, $Fe(OTf)_3$, $Sc(OTf)_3$, $Zn(OTf)_3$, $ZnCl_2$, $FeCl_2$, AgOTf, AuCl etc.) and main group metal catalysts ($Al(OTf)_3$, $AlCl_3$, $In(OTf)_3$, $InCl_3$, $Hg(OTf)_2$ etc). This shows the excellent efficacy and versatility of the Bismuth catalyst.

Conclusions

In conclusion, Bismuth(III) compounds have emerged as wonderful catalysts in synthetic organic chemistry. They have proven to be highly effective, offering a unique blend of advantages such as low toxicity, easy availability, cost-effectiveness and versatility. They do not impose health hazards like many other metal catalysts. Furthermore, this review demonstrates that the mild reaction conditions, high yield, high selectivity, and reaction-specific performance, aided by Bismuth(III) catalysts, make it an excellent substitute for all transition metal catalysts, including copper catalysts. The diversity of molecules obtained through bismuth catalysis demonstrates its efficiency and broad synthetic potential. However, the full scope of Bismuth(III) compounds is yet to be explored. Future scientists should concentrate on extending the range of reactions catalyzed by bismuth(III) compounds and investigate designing new ligands to increase their efficiency and applications in synthesis and industry. This review hopes to inspire further investigation into this promising area of organic chemistry.

Acknowledgements

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