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CARBON NANOTUBES-CATALYZED SYNTHESIS OF FLUORINE-CONTAINING HETEROCYCLES.

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Fluorine-containing heterocycles play a crucial role in modern pharmaceuticals, agrochemicals, and material sciences. The quest for effective and sustainable methods to prepare fluorinated heterocycles has led to the exploration of various nanomaterials as potential catalysts. Among these, carbon nanotubes (CNTs) have emerged as promising heterogeneous catalysts for the multicomponent synthesis of heterocycles, thanks to their unique properties. These properties include tunable surface chemistry, exceptional thermal and chemical stability, and near-complete reusability. This review aims to provide an overview of the current use of CNTs as catalysts in synthesizing fluorine-containing heterocycles via multicomponent reactions. It serves as a valuable resource for practitioners interested in developing sustainable and efficient catalytic systems for synthesizing diverse fluorinated heterocyclic compounds.

Keywords: Fluorine-containing heterocycles, carbon nanotubes, tunable surface chemistry.

INTRODUCTION. One of the established trends in modern medicine design is the selective introduction of fluorine-containing substituents into drug candidates [1–6]. This strategy is typically employed to protect the most oxidatively vulnerable positions, thereby enhancing the metabolic stability of the molecule. Additionally, selective fluorination allows for precise fine-tuning of bioactivity and pharmacokinetics [7–12]. Over the past 20 years, fluorine scanning and editing have become standard steps in modern drug design. Given that heterocyclic compounds comprise over 80% of newly approved pharmaceuticals, the synthesis of fluorine-containing heterocycles is of paramount importance in modern pharmaceuticals [13–18]. Traditional synthetic approaches for preparing fluorinated heterocyclic molecules have become outdated. The high costs, labor, and material requirements fail to meet the growing demand for molecular diversity essential for designing novel chemical architectures with desired properties and bioactivity. The search for effective and sustainable processes for the preparation of heterocycles has led to exploring various nanomaterials as potential catalysts [19–25]. Carbon nanotubes (CNTs) have recently emerged as promising heterogeneous catalysts for the multicomponent synthesis of heterocycles due to their unique properties, particularly their tunable surface chemistry, exceptional thermal and chemical stability, which allow for virtually complete reusability [26–30]. This review aims to provide a snapshot of current activities using CNTs as catalysts for synthesizing fluorine-containing heterocycles via multicomponent reactions. It serves as a valuable literature resource for practitioners interested in developing sustainable and efficient catalytic systems for producing diverse fluorinated heterocyclic compounds.

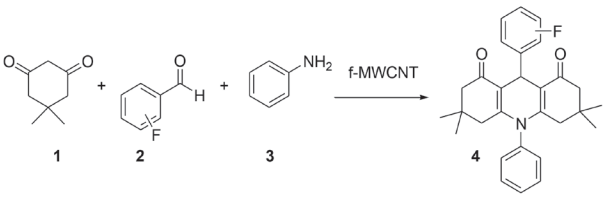
CNT-Catalyzed synthesis of fluorine-containing-heterocyclic compounds.

Nitrogen-containing heterocycles.

Nitrogen heterocyclic compounds hold a paramount place in the pharmaceutical industry due to their diverse biological activities and their role as key building blocks in many therapeutic agents [31]. These compounds, which include structures like pyridines, pyrimidines, and imidazoles, are integral to the efficacy of numerous drugs. Their presence often enhances the bioavailability, stability, and specificity of pharmaceuticals, making them essential in the development of treatments for a wide range of diseases. The versatility of nitrogen heterocyclic compounds allows for the fine-tuning of molecular interactions within biological systems, leading to improved drug-target interactions and reduced side effects [32–37]. This makes them invaluable in designing novel drugs with enhanced therapeutic profiles. As research continues to uncover new applications and mechanisms, the significance of nitrogen heterocyclic compounds in drug discovery and development only continues to grow, cementing their status as a cornerstone of medicinal chemistry [38–42].

Acridinediones are crucial subunits within heterocyclic systems, significantly influencing biology, pharmacy, and materials science [43–47]. Kaya et al. [48] demonstrated that carboxylic acid groups could be immobilized on CNTs, exploring their catalytic properties in the synthesis of acridinedione derivatives. This breakthrough opened new avenues for studying CNT catalysis, allowing comparisons

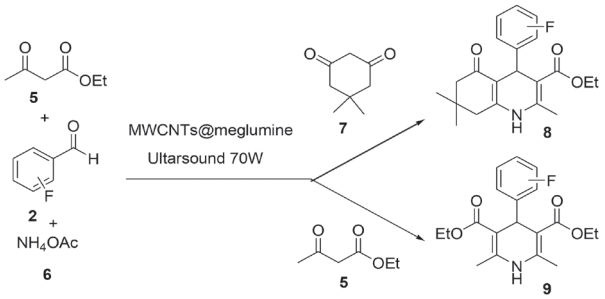
with other carbon-based materials. After their characterization, functionalized MWCNTs (f-MWCNTs) emerged as efficient catalysts for synthesizing 1,8-acridinedione derivatives. These derivatives were produced in quantitative yields in a single step using dimedone, aromatic aldehydes, and various anilines (Scheme 1).



Scheme 1. Preparation of fluorinated acridinediones.

The model reaction, catalyzed by f-MWCNTs functionalized with carboxylic acid groups in ethanol, showcased readily available, inexpensive, non-toxic, and versatile biodegradable catalysts. This highly uniform catalyst stands out for its efficiency, providing the highest yields and shortest reaction times. Its high efficiency, low environmental impact, simple work-up procedure, and easy purification are the main advantages of this method.

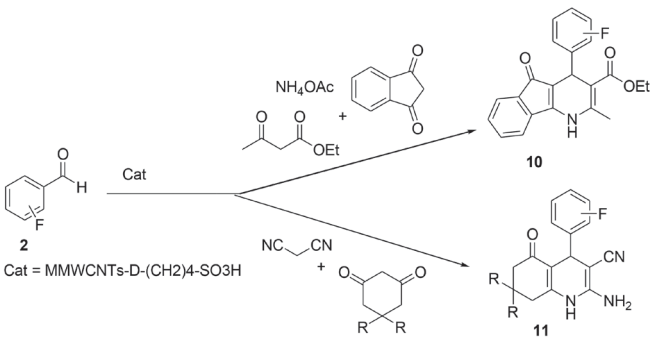
Ultrasonic irradiation offers a robust and eco-friendly method for enhancing multicomponent reactions (MCRs), providing benefits such as thermal enhancement, agitation, and activation [49]. Moradi and Zare introduced a novel method for synthesizing meglumine supported on multi-walled carbon nanotubes (MWCNTs@meglumine). This catalyst demonstrated high efficiency in synthesizing 1,4-dihydropyridine (1,4-DHP) derivatives via the Hantzsch condensation (Scheme 2) [50].



Scheme 2. Synthesis of fluorinated 1,4-dihydropyridines.

The reaction takes place at room temperature in ethanol under ultrasound irradiation (70 W), utilizing various aldehydes, ammonium acetate, and either ethyl acetoacetate or dimedone. The resulting product yields range from 82–95% (Scheme 4). The catalyst can be recovered and reused up to four times without any noticeable decrease in product yields, highlighting its high efficiency and reusability. This method offers multiple benefits, including the use of a new and highly effective heterogeneous catalyst, short reaction times, high to excellent product yields, and safe and clean conditions.

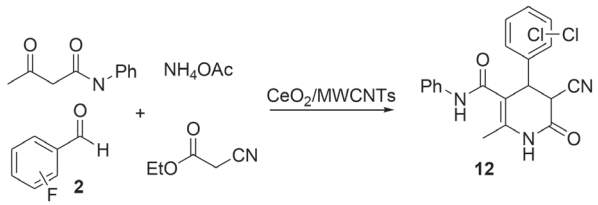
Magnetic multi-walled CNTs were functionalized with polyamidoamine (PAMAM) dendrimers and modified with butylsulfonate, resulting in MMWCNTs-D-(CH2)4-SO3H. This nanocomposite efficiently catalyzed four-component and three-component reactions to synthesize dihydro-1H-indeno[1,2-b]pyridines **10** and tetrahydrobenzo[*b*]quinolones **11**, achieving isolated yields of 85–98% and 80–98%, respectively (Scheme 3). Maleki and his colleagues [51] demonstrated the use of MMWCNTs-D-(CH2)4-SO3H in a mixture of 96% ethanol and 4% water under reflux conditions as a catalyst for the efficient production of the desired products via multicomponent cyclocondensation reactions.



Scheme 3. Synthesis of fluorinated dihydro-1*H*-Indeno[1,2-*b*]pyridines and tetrahydrobenzo-[*b*]quinolines.

These reactions were performed using readily accessible fluoro-aldehydes, 1,3-dicarbonyl compounds such as ethyl acetoacetate, 1,3-indanedione, and dimedone, along with ammonium acetate or malononitrile. Additionally, the catalyst could be conveniently recovered using magnetic techniques and reused several times without any loss in its catalytic activity.

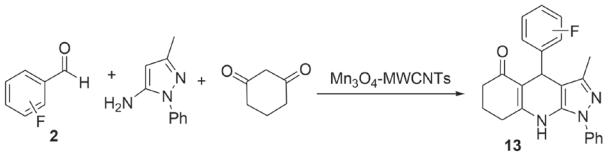
Recently, Maddila et al. [52] reported a simple and environmentally-sounding method for synthesis of composite catalysts consisting of ceria-doped multi-walled CNTs (CeO2/MWCNTs). They used this nanocomposite to synthesize pyridine-3-carboxamide derivatives **12** through a four-component reaction involving acetoacetanilide, ammonium acetate, fluorine-substituted benzaldehyde **2**, and ethyl cyanoacetate (Scheme 4).



Scheme 4. Synthesis of fluorinated pyridine-3-carboxamides.

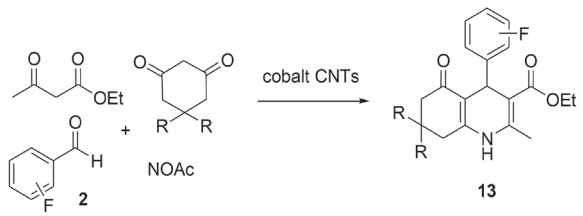
The reaction was carried out at ambient temperature in ethanol. This method has several notable advantages – it is simple to operate, has an easy work-up procedure, is cost-effective, avoids toxic solvents, reduces reaction times, ensures high yields, and eliminates the need for column chromatography. Moreover, the catalyst can be recycled and maintains its catalytic activity over several consecutive cycles.

Manganese oxide is a highly promising catalyst in organic synthesis and serves as a cathodic material in electronics. The use of manganese oxide-doped multi-walled carbon nanotubes (MWCNTs) can greatly enhance catalytic properties in multicomponent reactions (MCRs). Maddila and colleagues [53] developed MWCNTs infused with manganese oxide, creating (Mn3O4)-doped MWCNT nanocatalysts for use as heterogeneous catalysts in the preparation of quinolone moieties **13** (Scheme 5). The catalyst's effectiveness was evaluated in an efficient three-component reaction involving fluoro-aldehydes, 1,3-cyclohexanedione, and 5-amino-3-methyl-1-phenylpyrazole, in the presence of Mn-doped MWCNT nanoparticles. This heterogeneous, eco-friendly, recyclable, and efficient catalyst afforded the desired quinoline derivatives in good to excellent yields (92–98%) under environmentally conscious conditions. This protocol offers several advantages: it is simple to operate, easy to handle, affordable, and involves short reaction times with no toxic solvents. The yields are synthetically attractive, and there is no need for tedious work-ups. Additionally, the catalyst can be easily separated and reused.



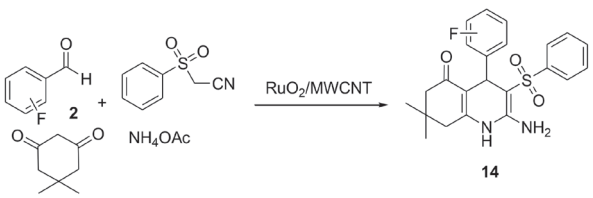
Scheme 5. Preparation of fluorine-containing quinolines.

1,4-Dihydropyridines (DHPs) possess notable antitumor and antibacterial properties, making them desirable calcium channel blockers for treating cardiovascular diseases [54–56]. Chen et al. have reported the successful use of a CNT-supported cobalt heterogeneous catalyst for synthesizing 1,4-DHPs **13** (Scheme 6) [57]. This synthesis was achieved by reacting various aromatic fluorine-containing aldehydes **2** and 1,3-diketones in an aqueous ethanol solution at 50°C. The resulting yields ranged from good to excellent. The CNT-catalyst could be conveniently recovered and reused. The advantages of this approach include using ethanol as an abundant and sustainable solvent, low catalyst loadings and short reaction times.



Scheme 6. Preparation of fluorinated derivatives of 1,4-DHPs.

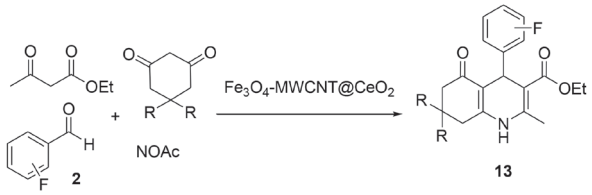
The research group led by Maddila reported the synthesis of a simple and efficient RuO2/MWCNT catalyst and investigated its catalytic activity in an environmentally sound, green synthesis of sulfonyl-quinoline derivatives (Scheme 7) [58]. This was achieved through a one-pot, four-component reaction involving fluorinated aldehydes, dimedone, phenylsulfonyl acetonitrile, and NH4OAc in ethanol, resulting in excellent yields (91–98%) of the desired products (Scheme 9). The catalyst could be easily separated from the reaction mixture and recycled up to eight times through simple filtration without a significant reduction in its catalytic efficiency. This protocol offers numerous advantages, such as being easy to handle, environmentally friendly, cost-effective, and having a short reaction time. The process is straightforward and adheres to green chemistry principles. Additionally, there is no need for purification by column chromatography, making the procedure synthetically attractive.



Scheme 7. Preparation of fluorine-containing sulfonyl-quinolines.

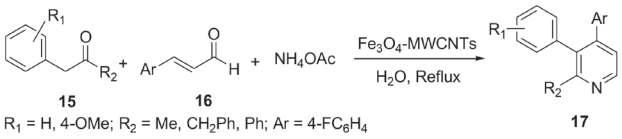
In another study [59], the catalytic activity of cerium oxide (CeO_2) supported on a nanocomposite of iron oxide and multi-walled carbon nanotubes (Fe_3O_4-MWCNT) was explored. Maddila's team described a convenient impregnation method to create the Fe_3O_4-MWCNT@CeO_2 nanocomposite. They then utilized a one-pot technique to synthesize series of tert-butyl-quinoline derivatives **13** via a four-component reaction involving fluorine substituted aromatic aldehydes **2**, dimedone, 3-butylacetoacetate, and NH_4OAc (Scheme 8). The catalytic performance was studied in aqueous ethanol. The catalyst's high specific surface area, porosity, unique exposed

surfaces, and stability contribute to its overall efficiency. The catalyst demonstrated high activity, as indicated by its notable turnover frequency. The use of ethanol as a green solvent provides an efficient and recyclable catalytic approach under operationally convenient conditions, yielding products **13** with high (90–97%) yields. This nanocomposite proved to be cost-effective and eco-friendly. Compared to current commercial methods, this new approach offers superior sustainability and efficiency.



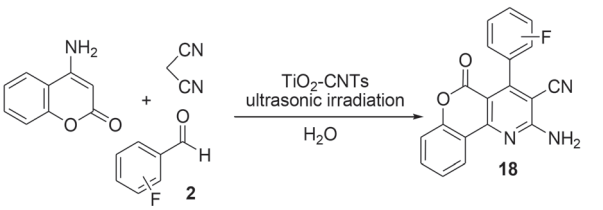
Scheme 8. Synthesis of fluorine-containing of 1,4-DHP derivatives.

Pyridines are crucial heterocyclic compounds found in various natural products and pharmaceuticals [60]. In 2019, Basavegowda et al. synthesized Fe_3O_4-multi-walled CNTs (Fe_3O_4-MWCNTs) [61]. These nanoparticles served as an efficient heterogeneous nanocatalyst for synthesizing polyfunctionalized pyridines (Scheme 9). This was achieved by condensing different ketones **15**, aromatic fluorine-containing cinnamaldehydes **16**, and ammonium acetate in water, which acted as a green solvent at ambient temperature. The method successfully produced pyridine derivatives **17** with excellent yields. The nanocatalysts could be conveniently recovered using an external magnet, eliminating the need for filtration, and reused multiple times without significant loss of activity [61].



Scheme 9. Preparation of fluorine-containing pyridines **17**.

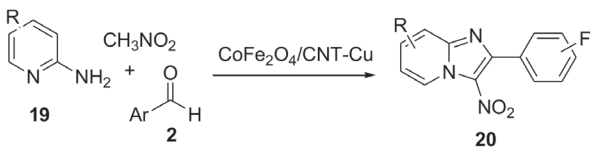
Abdolmohammadi and her colleagues developed a new and practical method for synthesizing titanium oxide immobilized on multi-walled CNTs [62]. This resulted in the creation of a nanocatalyst known as TiO_2-CNTs, which was used for the synthesis of 2-amino-5-oxo-4-aryl-5H-chromeno[4,3-b]pyridin-3-yl cyanide derivatives **18** (Scheme 10). The study showed that TiO_2-CNTs acted as a reusable and neutral heterogeneous catalyst, facilitating the formation of desired products through a three-component reaction involving 4-aminocoumarin, aromatic fluorine-substituted aldehydes **2**, and malononitrile in an aqueous medium under ultrasonic irradiation. The nanocatalyst could be recovered and reused multiple times. This protocol offers sustainable and economic benefits, including high product yields, short reaction times, a simple work-up procedure, and the use of a non-toxic and reusable catalyst.



Scheme 10. Preparation of fluorinated 5H-chromeno[4,3-b]pyridin-3-yl cyanides **18**.

Zhang and colleagues successfully synthesized a magnetic copper catalyst supported on CNTs (CoFe2O4/CNT-Cu) and investigated

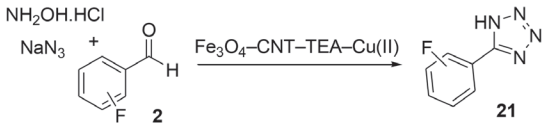
its catalytic efficiency in the one-pot synthesis of 3-nitro-2-arylimidazo[1,2-a]pyridine analogues **20** (Scheme 11) [63]. This was accomplished by condensing fluorinated 2-aminopyridines **19** with various also fluorine-containing aldehydes **2** and nitromethane. The reactions, carried out in PEG 400 under aerobic conditions, yielded high amounts of the target products. Notably, the catalyst maintained its activity over eight reuse cycles. This method offers several advantages, including short reaction times, eco-friendly conditions, simple purification, and catalyst recyclability. Interestingly, this reaction utilized fluorine substitution on two of the three components, incorporating both fluorine atoms and trifluoromethyl groups, resulting in products **20** with multiple fluorine substitutions.



Scheme 11. Synthesis of fluorine-containing 3-nitro-2-arylimidazo[1,2-a]pyridines.

Tetrazole has gained recognition as a versatile synthon and promising building block, notable for its ability to participate in multicomponent reactions (MCRs) and generate diverse heterocyclic structures [64]. Structural modificationssuch as substitution, functionalization, and cyclization–can fine-tune the bioactivity and pharmacological properties of tetrazole derivatives.

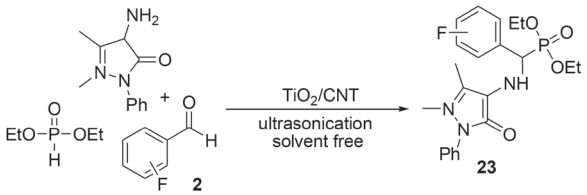
Heterogenizing carbon nanotubes (CNTs) on conductive supports presents a significant challenge but has sparked considerable interest. In response, Koukabi and colleagues developed a novel, practical, eco-friendly, and cost-effective heterogeneous catalyst for growing stable metallic copper (II) nanoparticles [65]. The process begins with synthesizing Fe3O4-CNT by depositing nanoparticles onto a magnetic CNT support. This support is then functionalized with triethanolamine (TEA), a low-cost and non-toxic ligand used to capture the copper nanoparticles. The resulting catalyst, denoted as Fe3O4-CNT-TEA-Cu(II), was synthesized using readily available materials. This Fe3O4-CNT-TEA-Cu(II) nanocatalyst was employed in the synthesis of 5-substituted fluorinated 1H-tetrazole derivatives **21** (Scheme 12) via an MCR approach, involving the reaction of aromatic aldehydes, hydroxylamine, and sodium azide at 70°C in dimethylformamide (DMF). This protocol boasts several advantages, including low catalyst loadings, broad substrate compatibility, easy magnetic separation of the catalyst from the reaction mixture, short reaction times, simple workup, affordability, and excellent yields [66].



Scheme 12. Synthesis of fluorinated 5-substituted 1H-tetrazoles.

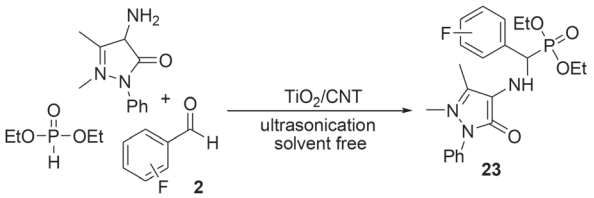
Safari and Gandomi – Ravandi successfully synthesized Pt-CNTs, which demonstrated excellent catalytic efficiency [67]. These nanoparticles were first utilized in a multicomponent reaction (MCR) synthesis, where they facilitated the formation of 2,3-dihydroquinazolin-4(1H)-one derivatives **22** through a three-component coupling reaction of isatoic anhyd-

ride, fluorine-containing aldehydes **2**, and amines (Scheme 13). The reaction was conducted with ultrasonication in ethanol. This novel catalyst offers a promising alternative for synthesizing pharmacologically significant quinazolinones. The method boasts several advantages, including environmental friendliness, catalyst reusability up to five times, high yields, short reaction times, simple work-up procedures, and the use of readily available starting materials. Consequently, this approach represents a synthetically attractive method for preparing dihydroquinazolinones **22**.



Scheme 13. Synthesis of dihydroquinazolinones.

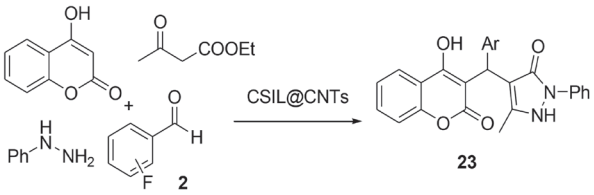
α-Aminophosphonates, the phosphorus analogues of amino acids [68–71], demonstrate bioisosterism and are medicinally important scaffolds possessing a diverse range of biological activities [72–76]. Therefore, their synthesis [77, 78], particularly fluorinated derivatives, has received significant attention [79–83]. Ramana's group reported the use of a TiO2/CNT nanocomposite as a heterogeneous catalyst for MCR synthesis of substituted α-aminophosphonates **23** by reacting a mixture of 4-aminoantipyrine, aromatic aldehydes **2**, diethyl phosphite, and TiO_2/CNT nanocomposite under ultrasonication and solvent-free conditions (Scheme 14) [84]. This methodology offers some advantages, such as a short reaction time, solvent-free conditions, convenient work-up, synthetically yields and reuse of the catalyst.



Scheme 14. Synthesis of antipyrine based fluorine-containing α-aminophosphonates.

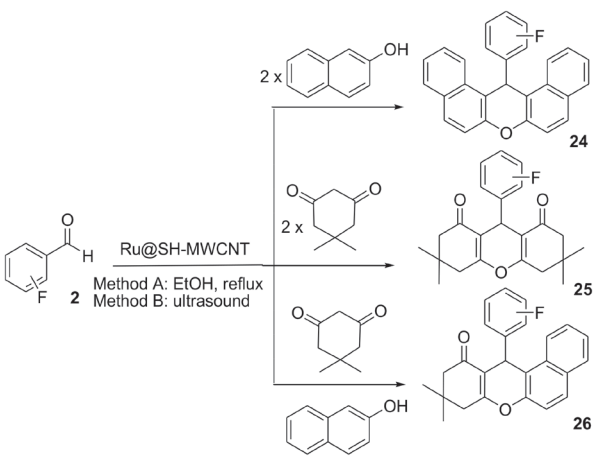
Other types of heterocyclic systems.

Hote et al. developed chitosan-supported ionic liquid CNTs (CSIL@CNTs) as a novel, highly reusable, and metal-free catalyst. This catalyst was employed in a one-pot, four-component reaction involving phenyl hydrazine, ethyl acetoacetate, 4-hydroxy coumarin, and fluoro-substituted aldehydes**2** in aqueous ethanol. The reaction produced highly functionalized and biologically relevant benzyl pyrazolyl coumarin derivatives in high to excellent yields (Scheme 15) [85].This approach offers several significant advantages. Firstly, CSIL@CNTs can be recycled without losing catalytic activity. Secondly, high conversion levels can be achieved under reflux conditions without the need for an inert atmosphere. Additionally, the reaction rates are high, eliminating the need for chromatographic purification. Finally, the work-up procedure is straightforward, and the catalyst is easy to prepare. Furthermore, the method exhibits notable chemoselectivity.



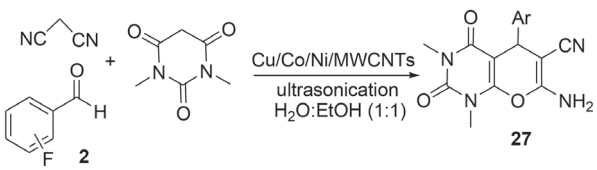
Scheme 15. Synthesis of fluorinated benzyl pyrazolyl coumarin derivatives.

Tabatabaeian reported a novel and highly efficient ruthenium-based catalyst, Ru@SH-MWCNT, prepared by immobilizing Ru(CO)4 on functionalized MWCNTs [86]. This heterogeneous catalyst was successfully employed in the MCR of fluorinated benzaldehydes **2**, β-naphthol, and dimedone to synthesize derivatives such as 14-aryl-14-H-dibenzo[a,j]xanthenes **24**, 1,8-dioxo-octahydroxanthenes **25**, and tetrahydrobenzo[a]xanthene-11-ones **26** (Scheme 16). The reactions were carried out in ethanol under reflux conditions with ultrasonic treatment, resulting in yields ranging from good to excellent. The catalyst could be recovered and reused at least four times without any noticeable loss of activity.



Scheme 16. Synthesis of fluorinated xanthene derivatives.

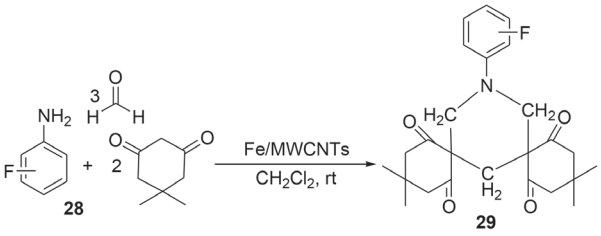
Group led by Naeimi described a convenient synthetic approach to the synthesis of pyrano[2,3-d]pyrimidine derivatives **27** (Scheme 17) [87] using MCRs under ultrasonic and nanocatalytic conditions. The Knoevenagel reaction products **27** were synthesized by reacting a series of fluorine-containing aldehydes **2** with 3-diethyl barbituric acid and malononitrile using Cu/Co/Ni/MWCNTs as the catalyst in anaqueous ethanol under ultrasonic treatment (55 W) at ambient temperature. The products **27** were obtained in excellent yields (>95%). The use of ultrasonication allowed toreduce the reaction time. The catalyst was found to be both recoverable and highly stable when subjected to ultrasonic treatment. The utilization of trimetallic MWCNTs proved to be extremely effective in the synthesis of pyrano[2,3-d]pyrimidine derivatives 69. This is due to the nature of the active site, cost-effective catalyst loading, simple work-up, ability to be reused, and environmentally friendly reaction conditions.



Scheme 17. Synthesis of fluorine-containing pyrano[2,3-d]pyrimidine derivatives.

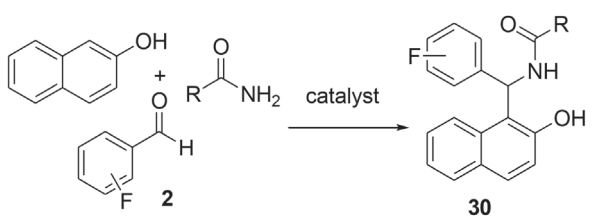
Spiro compounds are widely used in medicinal chemistry due to their presence in a numerous natural productsas well as in synthetic molecules of biological relevance [88]. Sharghi et al. described synthesis of bis-spiro piperidines **29** (Scheme 18) in high yields via coupling of dimedone, formaldehyde with fluorinated anilines **28** in the presence of Fe/MWCNTs in dichloromethane at ambient temperature (Scheme 33) [89]. This nanocatalyst demonstrated high efficiency and reusability, making it advantageous for one-pot synthesis. The protocol benefitted from operationally convenient reaction conditions, short reaction times, simple purification, and high yields. Furthermore, the catalyst can be recycled up to ten times without any loss of catalytic properties. It should be emphasized that this example

stands out from the previously discussed data, as in this case, the fluorine is located not on the carbonyl compound (benzaldehydes) but on the amino group-bearing reagent.



Scheme 18. Synthesis of fluorinated bis-spiro-substituted piperidines.

Fluorine-containing amines are an important class of biologically active compounds and have been a focus of the synthetic community for quite some time [90–94]. Rakhtshah et al. described synthesis of a heterogeneous nanocatalyst formed by immobilizing a Co(II) Schiff base complex on MWCNTs. The catalyst proved to be a convenient, eco-friendly, and recyclable aggregation. It was applied for the one-pot three-component synthesis of 1-amidoalkyl-2-naphthols 30 (Scheme 36) [95] by the cyclocondensation of 2-naphthol with acetamide and fluorinated aldehydes **2** under solvent-free conditions. The reported procedure offered numerous advantages including stability, recyclabilityas well as operationally convenient experimental conditions and simple work-up procedures.



Scheme 19. Synthesis of fluorine-containing amidoalkylnaphthol derivatives.

CONCLUSIONS. Based on the data discussed in this article, it is evident that the synthesis of fluorine-containing heterocycles via CNT catalysis is largely underdeveloped. While there are numerous examples of various CNT catalysts and heterocyclic systems, fluorine-containing reagents are limited to fluorine-substituted benzaldehyde. Additionally, the incorporation of fluorine atoms in these systems is mostly restricted to a single fluorine in the para position on the aromatic ring.

Despite this, the data suggests that fluorine atoms do not interfere with CNT catalysis. The size, electronegativity, and lipophilicity of fluorine appear to have minimal, if any, impact on the outcome of CNT-catalyzed heterocyclization. Given the significant importance of fluorinated heterocyclic compounds in the pharmaceutical, agrochemical, and materials industries, and the advantages of CNT-catalyzed reactions, it is anticipated that there will be a substantial increase in research in this area.

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КАТАЛІЗОВАНИЙ ВУГЛЕЦЕВИМИ НАНОТРУБКАМИ СИНТЕЗ ФТОРВМІСНИХ ГЕТЕРОЦИКЛІВ

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Фторовмісні гетероцикли відіграють вирішальну роль у сучасній фармацевтиці, агрохімії та матеріалознавстві. Пошуки ефективних і стійких методів отримання фторованих гетероциклів стали причиною дослідження різних наноматеріалів як потенційних каталізаторів. Серед них вуглецеві нанотрубки (ВНТ) стали перспективними гетерогенними каталізаторами для багатокомпонентного синтезу гетероциклів завдяки своїм унікальним властивостям. Ці властивості включають у себе регульований хімічний склад поверхні, виняткову термічну та хімічну стабільність і можливість майже повного повторного використання. Це дослідження має на меті надати огляд поточного використання ВНТ як каталізаторів у синтезі фторвмісних гетероциклів за допомогою багатокомпонентних реакцій. Він є цінним ресурсом для практиків, зацікавлених у розробленні стійких та ефективних каталітичних систем для синтезу різноманітних фторованих гетероциклічних сполук.

Ключові слова: фторвмісні гетероцикли, вуглецеві нанотрубки, регульована хімія поверхні.

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