Green Chemistry in Organic Synthesis: Recent Update on Green Catalytic Approaches in Synthesis of 1,2,4-Thiadiazoles

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Abstract: Green (sustainable) chemistry provides a framework for chemists, pharmacists, medicinal chemists and chemical engineers to design processes, protocols and synthetic methodologies to make their contribution to the broad spectrum of global sustainability. Green synthetic conditions, especially catalysis, are the pillar of green chemistry. Green chemistry principles help synthetic chemists overcome the problems of conventional synthesis, such as slow reaction rates, unhealthy solvents and catalysts and the long duration of reaction completion time, and envision solutions by developing environmentally benign catalysts, green solvents, use of microwave and ultrasonic radiations, solvent-free, grinding and chemo-mechanical approaches. 1,2,4-thiadiazole is a privileged structural motif that belongs to the class of nitrogen–sulfur-containing heterocycles with diverse medicinal and pharmaceutical applications. This comprehensive review systemizes types of green solvents, green catalysts, ideal green organic synthesis characteristics and the green synthetic approaches, such as microwave irradiation, ultrasound, ionic liquids, solvent-free, metal-free conditions, green solvents and heterogeneous catalysis to construct different 1,2,4-thiadiazoles scaffolds.

Keywords: green chemistry; organic synthesis; green catalysis; 1,2-4-thiadiazolederivative; green solvents; green approaches

1. Introduction

In 1991, the term "green chemistry" was first coined by Anatas, and the Environmental Protection Agency defined green chemistry or sustainable chemistry as "the designed chemical processes and products that eliminate or reduce the generation or use of hazardous substance" [1–4]. In the 1990s, green chemistry came into existence due to the prominent work of Warner, Trost, Anastas, Sheldon, Clarke and others [5–9]. Green chemistry is a new concept, introduced in the 20th century to develop new synthetic procedures, methodologies and chemical processes in the field of chemistry and chemical technology to accommodate the conventional existing procedures and strategies to make them environmentally benign and economical. This can be achieved by utilizing various approaches and strategies, such as ultrasound-assisted protocols, green solvents, solvent-free drugs synthesis, ionic liquids, microwave-assisted approaches, green reduction procedures, oxidation catalysts, solid acid–base catalysts and heterogeneous metal catalysis, etc. [10–12]. Anastas and Warner introduced the key criteria for green chemistry in a set of 12 principals that laid down the fundamentals of green chemistry [1–4,13], as illustrated in Figure 1 [14,15].

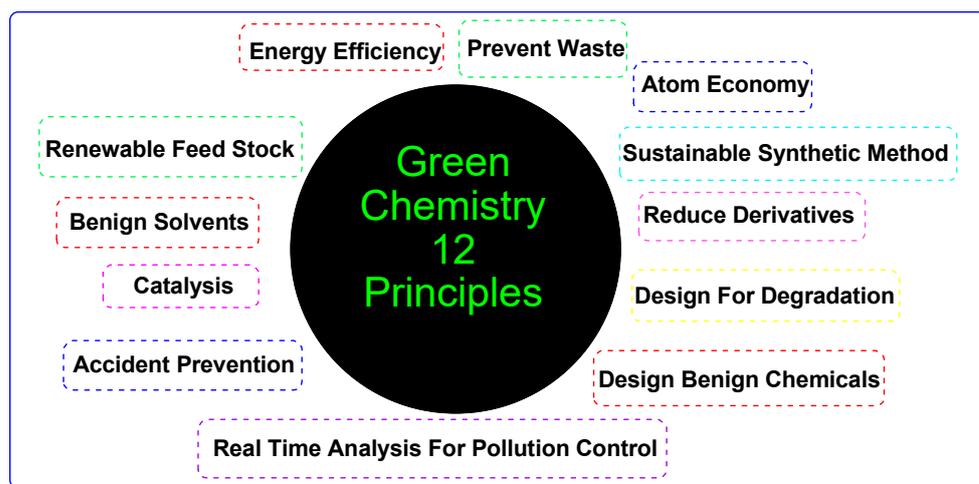



Figure 1. Twelve principles of green chemistry.

2. Green Approaches in Organic Synthesis

The concept of green chemistry introduced the environmentally benign synthetic protocols for the synthesis of heterocycles that has had a significant impact in many fields, such as the use of green solvents, solvent-free synthesis, sustainable catalytic materials, reduced energy consumption, improved atom economy, optimized reaction yields, the use of alternative energy sources, the introduction of multicomponent reactions (MCRs), ionic liquids and the design of high-efficiency and time-saving reactions that work at ambient temperatures [16–25]. Pollution and an increase in energy demands prompted the design of novel synthetic protocols to fulfill the requirements of green and sustainable chemistry to promote the synthesis of organic products in an ecofriendly environment [26,27]. The new green and sustainable synthetic approaches are listed below and have advantages over conventional synthetic approaches, as depicted in Figure 2 [28–35]:

1. Solvent-free approach;
2. Grinding approach;
3. Ball milling approach;
4. Solid–wet approach;
5. Ultrasonic-assisted approach;
6. Microwave-assisted approach;
7. MOF green synthesis approach;
8. Electrochemical green catalytic synthetic approach.

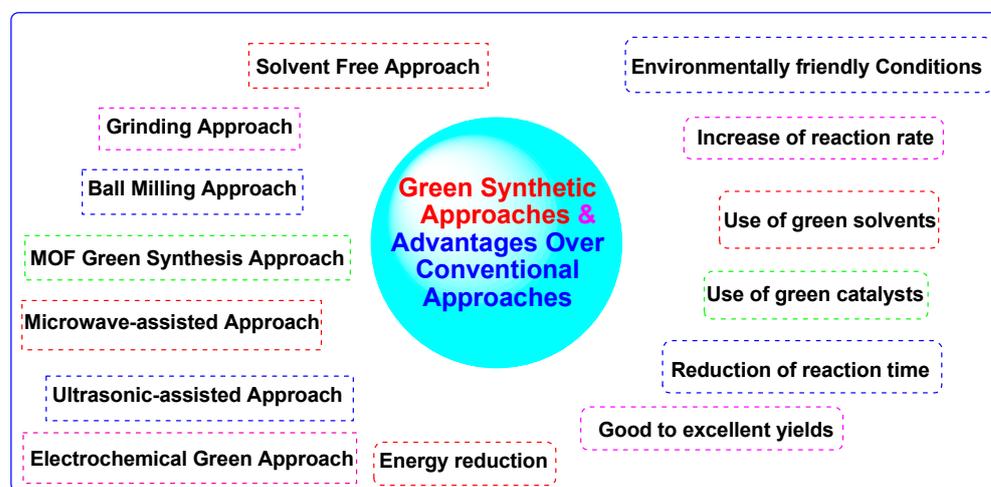



Figure 2. Green approaches and their advantages over conventional approaches.

In organic synthesis, avoiding the use of harmful and toxic solvents, as well as catalysts, was quite a difficult and highly challenging objective achieved by modern synthetic chemists. In green and sustainable organic synthesis, the ideal synthesis consists in following rational design fetchers to comprehensively implement the green chemistry principles, as displayed in Figure 3 [36–41].

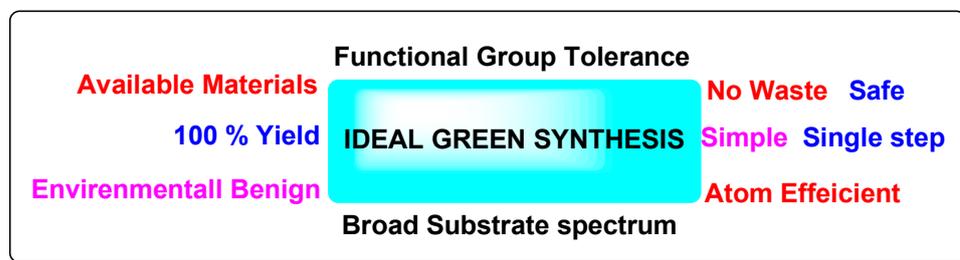



Figure 3. Characteristics of ideal green synthetic approach.

3. Green Catalysts in Organic Synthetic Approaches

The present study is a brief description of the role of catalysis in green synthetic transformations and green synthesis of drugs, chemical reagents, polymeric materials, nanomaterials and others organic materials for a sustainable future. Environmentally benign synthetic strategies are mainly possible due to the vital role of catalysts in lowering the activation energy, due to which reactions are possible at low heat energy or at room temperature and products are achieved in good-to-excellent yields by generating fever co-products, by-products and other waste substances. Catalysis is the pillar of green chemistry, and catalysts used in the green organic synthesis must be safe, easy to handle, reusable, biodegradable and cost-effective, recyclable, recovered efficiently and display a high reaction rate to afford products in maximum yields with shorter time duration and different types of green catalysts is depicted in Table 1 [42–46].

Table 1. Types of catalysts used in green organic synthesis.

Green Catalyst Type	Examples
Lewis acids catalysts in water	Scandium tris(heptadecafluorooctanesulfonate) (Sc(O$_3$ SC$_8$ F$_{17}$)$_3$) in supercritical carbon dioxide (scCO$_2$), cationic surfactant, cetyltrimethylammonium bromide (CTAB), Sc(OTf)3–SDS and rare earth metal triflates can be used in carbon–carbon bond-forming reactions in aqueous media [47,48].
Zeolites as green catalysts	H-, Cu- and Sc-zeolites as green Lewis catalysts for the carbonylation, glycosylation, aldolization, click reactions, multicomponent reactions, halogenation, cycloadditions, coupling reactions and cyclization [49].
Enzyme catalysis	Enzymatic redox catalyst, lipases, aldolases, transaminases, hydroxynitrile lyases and hydrolases [50].
Heteropoly acid-based (HPAs) catalysis	HPAs can be designed in homogeneous and heterogeneous systems such as Amberlyst-15, PCPs–SO$_3$H, BC–SO$_3$H, CMK-3-SO$_3$H, Zn–Ca–Fe, CsH$_2$PW1$_2$O$_{40}$, Ru/CMK-3, Fe$_3$O$_4$-SBA–SO$_3$H, CaFe$_2$O$_4$, H$_3$PW$_{12}$O$_{40}$, H$_5$BW$_{12}$O$_{40}$, H$_5$AlW$_{12}$O$_{40}$, H$_5$GaW$_{12}$O$_{40}$ and H$_6$CoW$_{12}$O$_{40}$ [46–62].
Natural materials and foods as catalysts	Wood ash biocatalyst [63], alginic acid [64,65], boric acid [66], tartaric acid [67,68], citric acid [69–71], pectin [72], oxalic acid [73–75], saccharin [46,76,77], wool and keratin deriving from wool fibers [78–80], feathers [81–84], silk [85,86], plant derivatives, lemon juice [87,88].

Table 1. *Cont.*

Green Catalyst Type	Examples
Nano particles (NPs)/materials as catalysts	Magnetic nano catalysts (magnetic Fe_3O_4, magnetic zinc ferrite $ZnFe_2O_4$, $CuFe_2O_4$, $CoFe_2O_4$, $NiFe_2O_4$, $NiFe_2O_4$@Cu) and oxides; ferrites with a shell; metallic with a shell [89–92], K10 clay, K10 montmorillonite and clayfen [93,94], magnesium oxide NPs, cerium oxide NPs, gold NPs, silica titanium oxide NPs, silica vanadium oxide NPs, iridium oxide NPs, molybdenum–bismuth bimetallic chalcogenide NPs, platinum–antimony tin oxide NPs, calcium oxide NPs, palladium NPs, tin oxide NPs [95–107]
Transition metals as green catalysts	$Ru(CO)_3(TPPMS)_2$ (TPPMS = $(C6H5)_2P(m$-$C6H4SO3Na))$, $RuH_2(CO)(TPPMS)_3$, $[RuH(CO)(NCMe)(TPPMS)_3][BF4]$, Rh/TPPTS complexes, Ru/(R)-BINAP,Ru/(R)-13-[(S,S)-DPEN]Cl$_2$, Ru/(S)-BINAP, Pd-DPPP, $Pd(OAc)_2$, CuI,$MnBr(CO)_5$ [108–117]
Ionic liquids as catalysts	POM-based ILs (POM-ILs) such as (4-sulfonic acid) butyltributyl amine (TBABS) such as cations and $H_5PMo_{10}V_2O_{40}$ ($Mo_{10}V_2$) such as anion (3-sulfonic acid) propylpyridine (PyPS), (4-sulfonic acid) butylpyridine (PyBS), palladium deposited oleic acid coated-Fe_3O_4 NPs (Fe_3O_4@OA–Pd) and (4-sulfonic acid) butyltrimethyl amine (TMABS) [118–121]. Acidic ionic liquids such as $[HO_3S$-$(CH_2)_3$-mim] Cl-$FeCl_3$ and Brønsted Lewis acidic ILs, (1-butyl-3-methylimidazolium hydrogen sulfate or 1-(3-sulfopropyl)-3-methylimidazolium hydrogen sulfate) ILs [122,123]. Following different ionic liquids also used as catalysts for the productions of biodiesel, which are: SBA- IL-3, PIL-3, P(VB-VS)HSO_4, MIL-101(Cr)@ MBIAILs, Fe_3O_4@HKUST-1, AILs/HPW/UiO-66-2COOH and $CoFe_2O_4$/MIL-88B(Fe)-NH2/(Py-Ps)PMo [124–131]. Ionic liquids are classified into three groups: solid catalyst with ionic liquid layers (SCILL), porous ionic liquids and supported ionic liquid phase catalyst (SILPC). Binary alkoxide ionic liquids catalyzed organic reaction and examples of such ILs are ([Pyrr1,4][NTf2]x[OiPr] 1,3-butylmethylimidazolium hydroxide([BMIM][OH]) and [C2DABCO][NTf2] [132–136].
Photocatalyst (PC)	Carbonylation approaches in organic synthesis were mediated by photocatalysts, such as $[Ir(4$-$Fppy)_2(bpy)]^+$, $Ru(bpy)_3^{2+}$, fac-$Ir(ppy)_3$, 4-CzIPN, fluorescein, $Ir[(dF(CF_3)(ppy)]_2(dtbbpy)+$, eosin and various MOFs composite-based photocatalyst were afforded for their applications in different synthetic approaches such as PCN-250-Fe_3, Uio-68-TZDC, MIL-88A(Fe), ZIF-8, Ni-MOF and $Ru(bpy)_3$@NKMOF-7. Following, different heterogeneous photocatalysis have been used in organic synthesis such as TiO_2, TiO_2 P25, dye-sensitized TiO_2, metal doped TiO_2, bismuth (III) oxide-based PCs, cadmium sulfide and cadmium-selenide-based PCs, lead halide perovskites and graphitic carbon nitrides (g-CN) PCs, [137–141].
Phase transfer catalyst (PTC)	Tetrabutylammonium bromide (TBAB), triethylbenzylammonium chloride (TEBAC) and tetrabutylammonium iodide (TBAI) are famous phase-transfer green catalysts used in organic synthetic transformations. The types of PTC are the following: onium salt phase-transfer catalysts, crown ether and polyether phase-transfer catalyst and supported phase-transfer catalysts [142–146].

4. Green Solvents in Organic Synthetic Approaches

The major focus of green chemistry is the elimination of solvents from chemical processes and organic synthesis or replacement of hazardous solvents with ecofriendly solvents. The attention under the remit of green chemistry is ascribed to the large volume of solvents used in the manufacture of drugs, paints, textiles, polymers, solvent extractions and purification in final formulations and other industrial products that drastically damage the environment and living organism and that must be reduced, replaced and eliminated from processes and switched to greener processes and green solvents [147–154]. The green solvents that are mostly used in organic synthesis are mentioned in Table 2.

Table 2. Green solvents in organic synthesis.

Type of Green Solvent	Examples
Aqueous and super critical carbon dioxide	H_2O, $scCO_2$, $scCO_2 + H_2O$ [121–125,155–159].
Fluorous solvents	1,1,1-trifluoroethanol,perfluoromethyl cyclohexane/toluene—[160,161].
Organic carbonates	Butylene carbonate, propylene carbonate, diethyl Carbonate and dimethyl carbonate ($CH_3OCOOCH_3$) [162–175].
Lactates and general solvents	Lactic acid, ethyl lactate, lactate dehydrogenase, transaminase and *n*-butanol [176–185].
Natural and biosolvents	Limonene and P-cymene as solvent, γ-valerolactone (GVL), sugar-derived dimethylisosorbide (DMI), glycerol and glycerol derivatives as solvents such as glycerol carbonate, glycerol-derived acetals and ketals, 2,3-propanediol, 1,3-propanediol, monoacylglycerol MAGs, diacylglycerols DAGs, triacylglycerols TAGs, glycidyl monoalkyl ethers, glycidyl dialkyl ethers, glycidyl trialkyl ethers and dihydrolevoglucosenone (cyrene), etc. [186–201]. Corn oil, glycerol, oxidoreductases, transferases, hydrolases, lyases, isomerases, ligases, dehaloperoxidase (DHP), lemon juice as solvent and eucalyptol used as solvent for the synthesis of N, O and S heterocycles, cygnet a family of green solvents and dimethyl isosorbide (DMI) solvent derived from cellulose [202–209].
Archetypal green solvents	2-methyl tetrahydrofuran (2-MeTHF) and cyclopentyl methyl ether (CPME), etc. [210–216].
Ionic liquids as solvents	1-allyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), sodium dicyanamide, sodium thiocyanate, silver nitrate, sodium nitrate, chloroauric acid, 1-ethyl-3-methyl-(EMIM), 1-butyl-3-methyl-(BMIM), 1-octyl-3 methyl (OMIM), 1-decyl-3-methyl-(DMIM), 1-dodecyl-3-methyl- docecylMIM), 1-ethyl-3-methyl imidazolium salts, etc. [217–227].
Deep eutectic solvents (DESs)	The classification and general examples of DES are as follows: Class I Cat + X-zMClx, M = Zn, Sn, Fe, Al, Ga. Class II Cat + X-zMClx• yH₂O, M = Cr, Co, Cu, Ni, Fe. Class III Cat + X-zRZ Z = CONH₂, COOH, OH. Class IV MClx + RZ = MClx-1 + ·RZ + MClx+ -1 M = Al, Zn and Z = CONH₂, OH. New type Class V RZ + RP Z = CONH₂, COOH, OH and P—C_6H_4OH, CO, NH₂. Hydrophobic deep eutectic solvents (HDESs) play a role in green chemistry. The first HDESs (cecanoic acid (DecA)) were synthesized by Osch et al. The following solvents (tetradecyl) phosphonium tetrafluoroborate (P14,666Cl), trioctylphosphine oxide (TOPO) and *N*-didodecylammonium chloride (DDDACl) have been developed as green HDESs [228–231].

5. Green Synthetic Approaches for Synthesis of 1,2,4-Thiadiazoles

Green chemistry synthetic approaches are used to synthesize heterocyclic-pharmaco phore-based bioactive therapeutic drugs, which have significant importance in medicinal and pharmaceutical chemistry. The versatile heterocyclic thiadiazole rings with different isomeric forms, such as 1,2,3-, 1,2,4-, 1,2,5- and 1,3,4-, display substantial therapeutic efficacy against a wide variety of diseases. The 1,2,4-thiadiazole scaffolds represent a five-membered nitrogen–sulfur-containing significant class of core heterocyclic structures of great interest, mainly because of the part of the structural unit of biologically active molecules: a useful intermediate in medicinal chemistry and part of the clinical drugs, which are given in Figure 4 [232–243].

1,2,4-thiadiazole is a privileged pharmacophore that exhibits a diverse and broad spectrum of biological activities, such as human leukemia cell, antibacterial, anti-inflammatory, insecticidal, herbicidal and fungicidal agents, anticonvulsant, cardiovascular, cathepsin B inhibitors, dual 5-lipoxygenase and cyclooxygenase inhibitors, antidiabetic, antiulcerative and allosteric modulators [244–252]. Synthetic chemists and pharmacists are attracted to the 1,2,4-thiadiazole moiety due to its versatile biological and pharmacological profile, and R&D scientists are interested in developing new synthetic approaches and methodologies to afford 1,2,4-thiadiazole scaffolds. This review article covers green and ecofriendly synthetic

routes to produce 1,2,4-thiadiazole hybrids and their medicinal significance from 2000 to 2022. The plethora of research about green approaches and medicinal importance cited in this review article will be helpful for researchers in future for drug discovery and the development of novel bioactive 1,2,4-thiadiazole drug candidates.

The following are different ecofriendly green synthetic strategies to produce 1,2,4-thiadiazole structural hybrids by utilizing various synthetic conditions to achieve products in high yields within a short period of time.

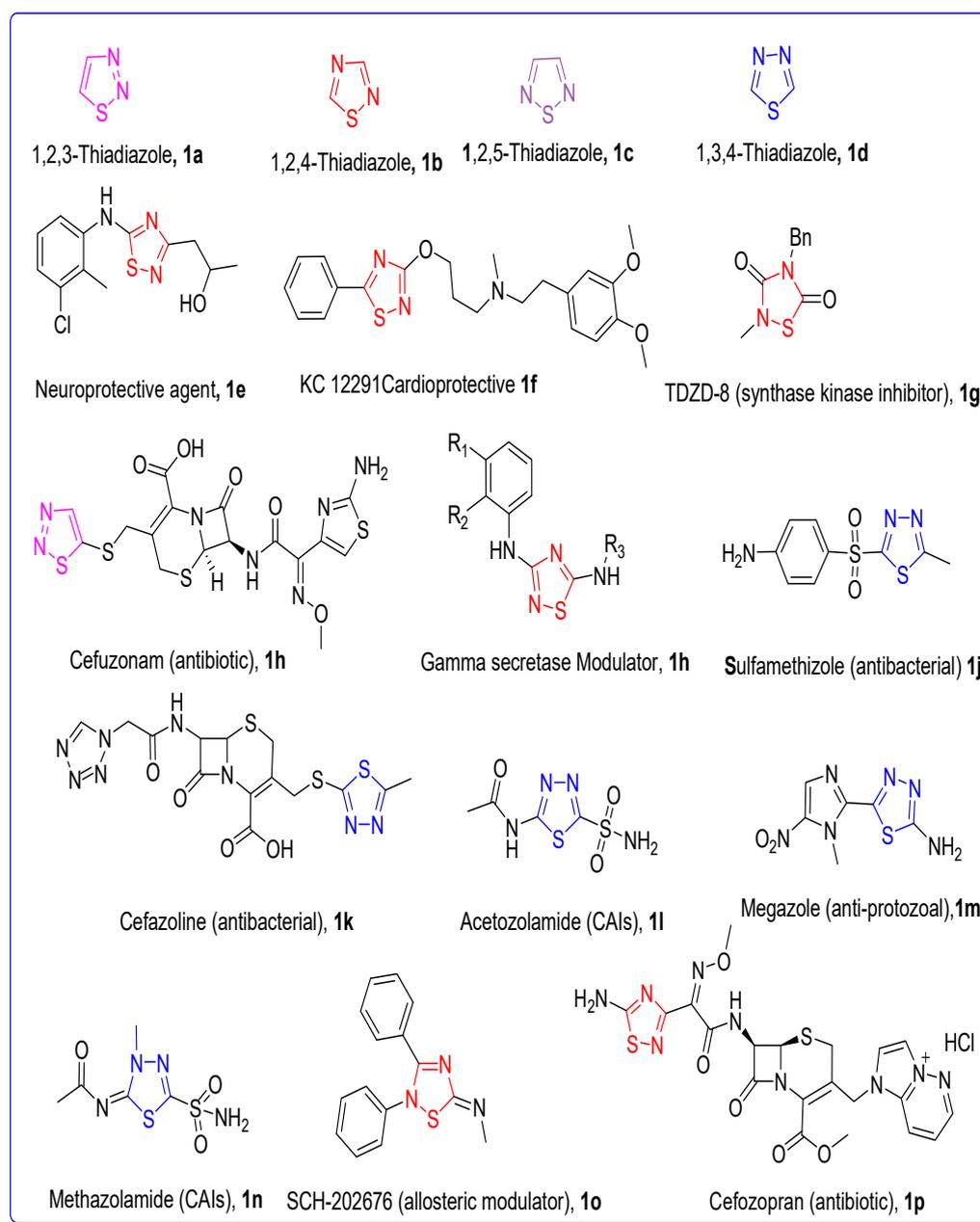
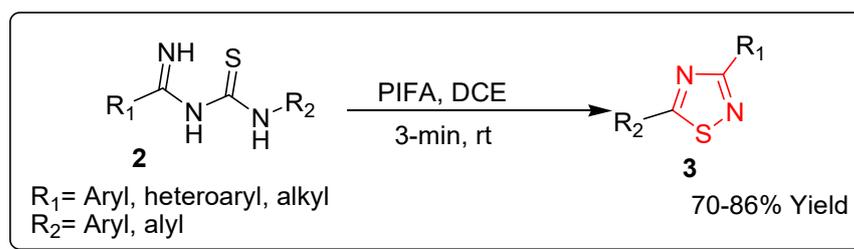



Figure 4. Bioactive thiadiazole scaffolds.

5.1. PIFA Catalyst for Formation of N–S Bond via Intramolecular Cyclization

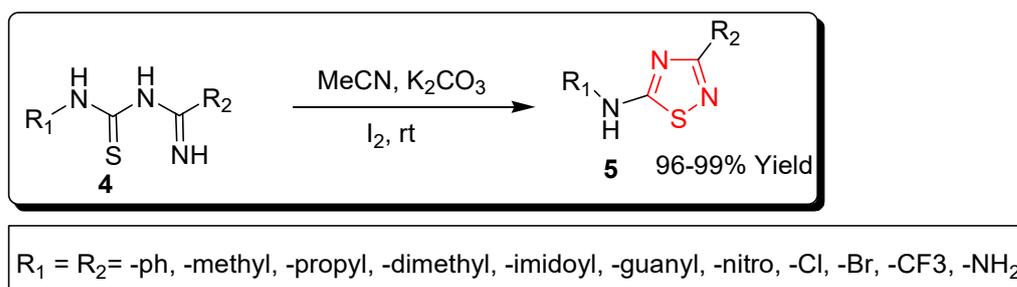
Mariappan et al. developed a synthetic green and broad substrate scope protocol for S-N bond formation via intramolecular cyclization to afford substituted 5-amino-based 1,2,4-thiadiazole derivatives in the presence of hypervalent iodine (III) as an inexpensive catalyst (Scheme 1). The merit of this synthetic approach is that it is metal-free and has a short reaction time and good-to-excellent yield of products at ambient temperature. A

mixture of *N*-(phenyl carbamothioyl) benzimidamide **2** was treated with phenyliodine (III) bis(trifluoroacetate) (PIFA) in 1,2-dichloroethane (DCE) to achieve the corresponding 1,2,4-thiadiazole derivatives **3**, as depicted in Scheme 1. The plausible mechanism suggested that the PIFA was reacted with midoyl thiourea to generate an intermediate in which the NH nucleophilic group attacks the sulfur atom to afford the corresponding product with the removal of trifluoro acetic acid and iodobenzene. The advantage of this synthetic protocol is that the product yield is good: either substrate has electron-donating or electron-withdrawing groups, or both [253].

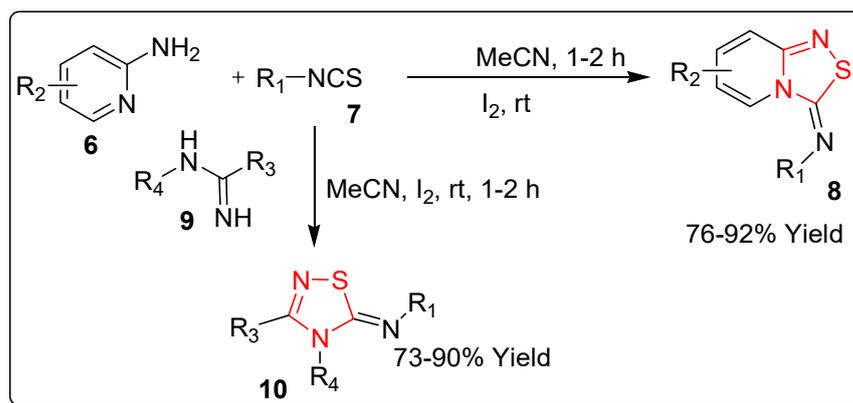
R1= Aryl, heteroaryl, alkyl
R2= Aryl, alyl

Scheme 1. Synthesis of 1,2,4-thiadiazoles **3** via intramolecular cyclization.

5.2. Molecular I_2 Catalysis and Oxidative N–S Bond Formation

Wang et al. reported an efficient synthetic approach for the construction of 5-amino- and 3,5-diamino-substituted 1,2,4-thiadiazoles via oxidative N–S Bond formation in scalable fashion by utilizing molecular iodine as the sole oxidant as displayed in Scheme 2. This transition, metal-free, short reaction time and mild reaction conditions strategy transformed imidoyl and guanyl thiourea **4** into 1,2,4-thiadiazole **5** in the presence of K_2CO_3, acetonitrile and molecular iodine as a catalyst at room temperature. The products of gram-scale synthesis were afforded in excellent yields, 96–99%, as shown in Scheme 2. The diverse electron-donating, such as methyl (Me), and electron-withdrawing, such as Cl, Br, NO_2 and CF_3, substituents on the aryl group of aromatic thioamides were well-tolerated and afforded maximum yields of the respective products. As the aromatic thioamides were weaker in nucleophilicity, which resulted in relatively lower yields with strong electron-withdrawing groups [254].

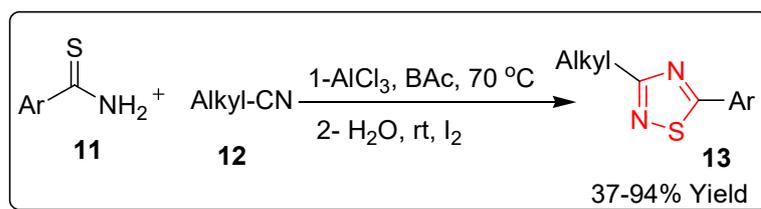
R1 = R2= -ph, -methyl, -propyl, -dimethyl, -imidoyl, -guanyl, -nitro, -Cl, -Br, -CF3, -NH2

Scheme 2. Synthesis of 1,2,4-thiadiazoles **5** via molecular I_2 as sole oxidant.

5.3. Molecular I_2 Catalysis for Regio-Specific and Expeditious Synthetic Approach

Mangarao et al. reported an expeditious approach to achieve the novel *N*-fused and 3,4-disubstuted 5-imino-1,2,4-thiadiazole hybrid structures (8,10) by treating substituted isothiocyanate **7** with 2-aminopyridine/amidine (6,9), which underwent intramolecular cyclization to form N-S bonds in the presence of an inexpensive I_2 catalyst and acetonitrile as a solvent at ambient temperature as shown in Scheme 3. The merits of this facile and highly efficient regio-specific synthetic approach are insensitivity to moisture and air, being metal-free, highly efficient in product yield, gram-scale synthesis and wide substrate spectrum [255].

R₁ = R₂ = R₃ = -methoxy, -methyl, -dimethyl, -phenyl, cyclopropyl, -propyl, cyclohexyl, -Cl, -Br

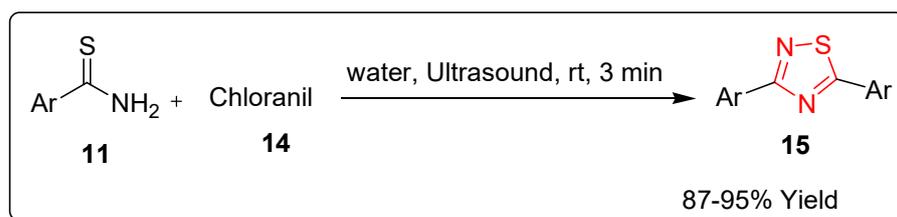
Scheme 3. Regio-specific synthesis of 3,4-disubstituted 5-imino-1,2,4-thiadiazole hybrids **8**, **10**.

5.4. Molecular I_2 Catalysis for One-Pot Green Protocol and Intramolecular Oxidative Coupling

Chai et al. afforded 3,5-disubstituted 1,2,4-thiadiazole **13** in an efficient and simple one-pot green protocol through the sequential intermolecular combination of alkyl substituted nitriles **12** with aryl substituted thiamide **11**, through intramolecular oxidative coupling of N–H and S–H bonds in an aqueous medium and iodine as the sole oxidant catalyst as depicted in Scheme 4 [256].

Alkyl-CN= CH_3CN, $CH_3CH_2CH_2CN$, $CH_3CH_2CH_2CH_2CN$, cyclopropyl-CN, butene-CN, Chloropropyl-CN, phenylacetonitrile, *o*-tolylacetonitrile, *p*-tolylacetonitrile, 3-flourophenyl acetonitrile, 4-chlorophenyl acetonitrile, naphtylacetonitile, 4-hydroxyphenylacetonitrile, 4-methoxyphenylacetonitrile, 4-nitrophenylacetonitrile
Aryl= -phenyl, 3-methylphenyl, 4-methylphenyl, 2-chlorophenyl, 4-chlorophenyl, 4-bromophenyl, 4-nitrophenyl, thiophene

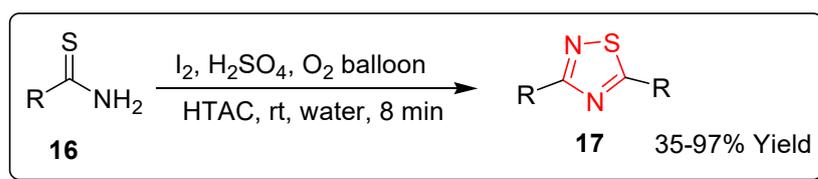
Scheme 4. One-pot green synthesis of 3,5-disubstituted 1,2,4-thiadiazoles.

5.5. Ultrasonic-Assisted Synthesis in Water

Chauhan et al. reported the conversion of thiobenzamide **11** with chloranil **14**, under ultrasound irradiation in an aqueous medium at ambient temperature, to the corresponding 1,2,4-thiadiazole **15** with a metal-free, catalyst-free, convenient and environmentally benign one-pot protocol. The sequential intermolecular combination of thiomide **11** with chloranil **14** (oxidant) through intramolecular oxidative coupling of N-H and S-H bonds afforded 3,5-disubstituted 1,2,4-thiadiazoles in good-to-excellent yields as displayed in Scheme 5 [257].

Aryl= -phenyl, 4-methylphenyl, 4-methoxylphenyl, 4-*t*-Buphenyl, 4-chlorophenyl, 4-flourophenyl, 4-nitrophenyl

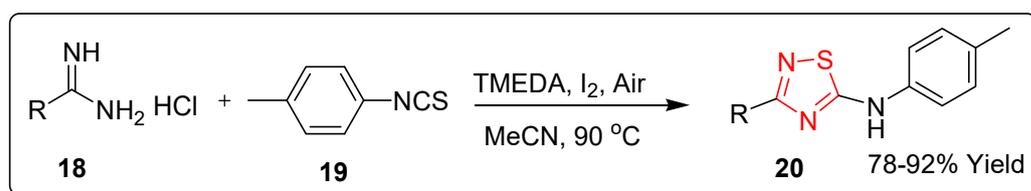
Scheme 5. Ultrasonic-assisted synthesis of 1,2,4-thiadiazoles **15**.

5.6. HTACas PTC for Green Synthesis Using Molecular Oxygen as an Oxidant

Zhao et al. developed an efficient green methodology in which molecular oxygen is used as a terminal oxidant to furnish 1,2,4-thiadizoles as depicted in Scheme 6. The oxidative dimerization of alkyl and aryl thioamides **16** was achieved in the presence of I_2 as a catalyst, hexadecyltrimethyl ammonium chloride (HTAC) as a phase transfer catalyst (PTC) and con. H_2SO_4 as a regenerative agent. The substituted thiomide underwent transformation into the substituted 1,2,4-thiadiazoles **17** in excellent yields via intramolecular oxidative coupling of N-H and N-S bonds. The lowest 35% yield indicated that the electron-withdrawing substituent on the benzene ring of benzothioamide failed to undergo the dimerization reaction compared with the electrodonating substituents [258].

R = alkyl, aryl, amino

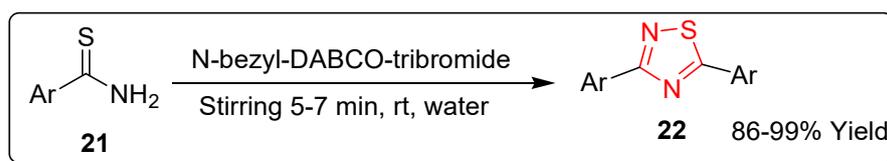
Scheme 6. Synthesis of 1,2,4-thiadiazoles **17** using molecular oxygen as oxidant.

5.7. Transition-Metal-Free Green Protocol Using Air as Oxidant

A novel and green approach was developed by Yang et al. with a broad substrate scope, mild reaction conditions, good functional group tolerance and high regioselectivity to construct the S-N bond of a 1,2,4-thiadiazole core via oxidative coupling. In this metal-free and gram-scale synthetic strategy, substituted amidines **18** and substituted isothiocyanates **19** were treated for the construction of the S-N bond via I_2 mediated oxidative coupling to produce 5-amino-1,2,4-thiadiazole derivatives **20** in the presence of TMEDA (*N*,*N*,*N*′,*N*′-tetramethyl ethylene diamine), air (oxidant) and acetonitrile as the solvent. In this synthetic pathway, 1,2,4-thiadiazoles were afforded in moderate-to-excellent yields (Scheme 7) [259].

R = -phenyl, 4-methylphenyl, 4-methoxylphenyl, 4-chlorophenyl, 4-flourophenyl, 4-pyridine, 3-methyl, 3-cyclopropyl, 3-pyrazole

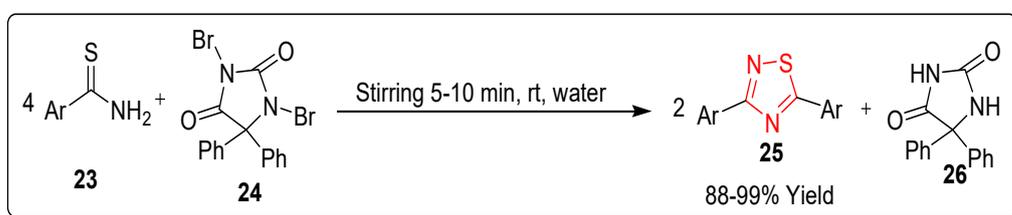
Scheme 7. Green region-selective synthesis of 5-amino-1,2,4-thiadiazoles **20**.

5.8. Solid–Solid Oxidative Coupling

Hassan Zali Boeini reported a novel, rapid, simple and efficient protocol for the conversion of the equimolar amount, pulverized thiobenzamide **21** and *N*-bezyl-DABCO-tribromide in wet solid–solid conditions to produce 1,2,4-thiadiazoles **22** in excellent yields compared with conventional methods (Scheme 8). In this green method, intramolecular oxidative coupling and efficient cyclization constructed the aryl-substituted 1,2,4-thiadiazoles. This short-term, ambient temperature and high yield are the key features of this environmentally benign approach compared with the conventional synthetic approach of 1,2,4-thiadiazoles [260].

Ar= phenyl; 4-tolyl; 4-methoxyphenyl; 4-chlorophenyl; 4-nitrophenyl;1-naphthyl; 2-naphthyl; 3-pyridyl;4-dimethylaminophenyl

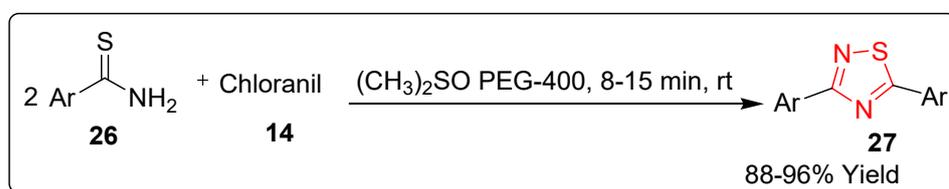
Scheme 8. Green synthesis of substituted 1,2,4-thiadiazoles **22** in solid–solid wet conditions.

5.9. Green Synthesis in Wet-Paste Conditions

Hassan Zali Boeini developed another highly efficient and rapid synthetic methodology to produce diaryl substituted 1,2,4-thiadiazoles in wet-paste conditions. The *N,N'*-dibromo phenytoin **24** was used for the rapid conversion of aryl-substituted thiobenzamides **23** to the corresponding 1,2,4-thiadiazole **25** in excellent yields (88–99%) through efficient intramolecular cyclization as depicted in Scheme 9 [261].

Ar = phenyl, 4-tolyl, 3-bromophenyl, 4-bromophenyl, 2-chlorophenyl, 4-chlorophenyl;3-chlorophenyl, 4-flourophenyl,4-methoxyphenyl

Scheme 9. Green synthesis of substituted 1,2,4-thiadiazoles **25**.

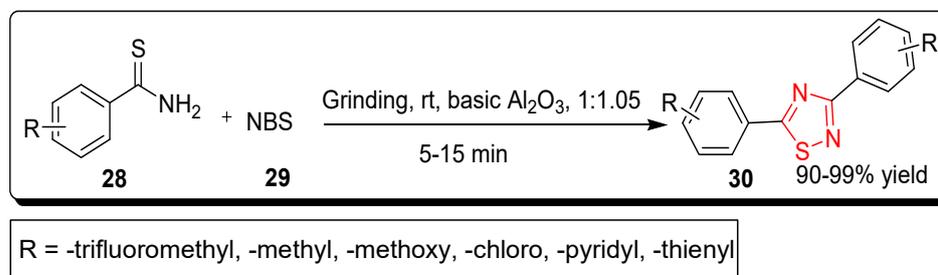
5.10. Oxidative Dimerization Using CC–DMSO in PEG-400

Khosropour and Noei developed an efficient, ecofriendly and inexpensive synthetic protocol for the construction of the1,2,4-thiadiazole privileged structural motif. The structurally diverse 3,5-diaryl-substituted 1,2,4-thiadiazole structural hybrids **27** were afforded in excellent 88–96% yields due to intramolecular oxidative dimerization and cyclization of substituted aryl thioamides **26** with chloranil **14** by utilizing a green medium of 4,6-trichloro-1,3,5-triazine-DMSO (CC-DMSO) in PEG-400 (Scheme 10). The advantages of this preparatory protocol are simplicity, very short reaction times, generality, recyclability of solvent, environmentally benign, ambient temperature and elaboration of substituted 1,2,4-thiadiazoles with high-to-excellent yields [262].

Aryl = Ph, 4-methoxyphenyl, 2-furyl, 4-chlorophenyl, 3-chlorophenyl, 20chlorophenyl, 2,4-dichlorophenyl, 4-bromophenyl, 3-bromophenyl, 4-flourophenyl

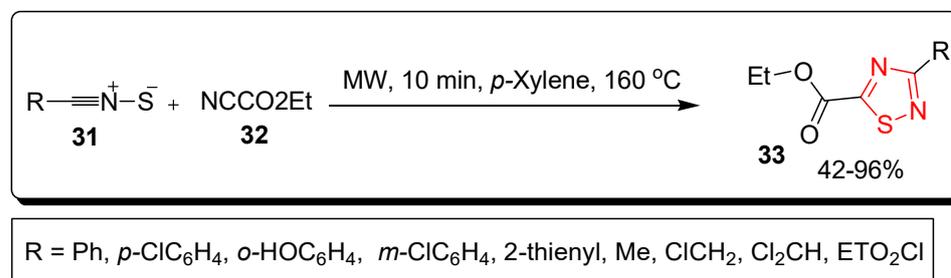
Scheme 10. Green synthesis of substituted diaryl-1,2,4-thiadiazoles **27**.

5.11. Basic Alumina Catalyst for Synthesis of Substituted 1,2,4-Thiadiazoles via Grinding Approach

Xu et al. developed a solvent-free, environmentally benign synthetic approach to synthesize 3,5-disubstituted-1,2,4-thiadiazole structural hybrids **30** in excellent yields (90–99%) through the reaction of substituted thiomide **28** with NBS **29** in the presence

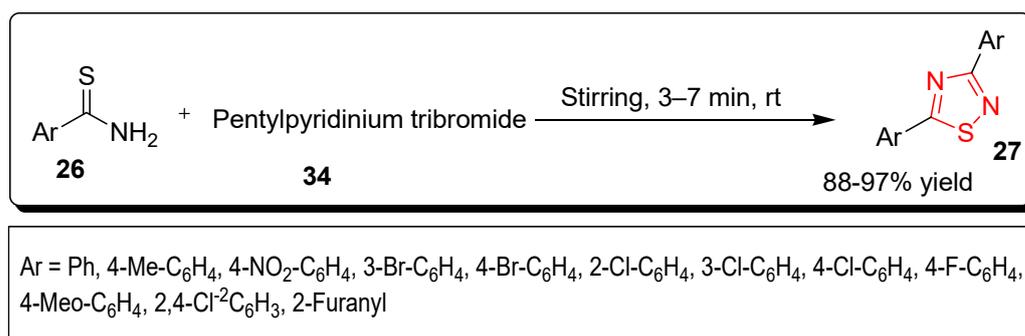
of basic alumina and grinding this reaction mixture for 5–15 min at room temperature as shown in Scheme 11. This synthetic protocol displayed advantages over existing strategies to access substituted 1,2,4-thiadiazoles in terms of efficiency, higher yields, short duration of reaction time and neat conditions. This facile and highly efficient methodology showed compatibility with variety of functional groups such as the trifluoromethyl, methyl, methoxy, chloro, pyridyl and thienyl groups [263].

Scheme 11. Green synthesis of substituted diaryl-1,2,4-thiadiazoles **30** via grinding.

5.12. Synthesis of 1,2,4-Thiadiazole-5-Carboxylates by Microwave-Assisted Approach

Fordyce et al. generated the substituted ethyl 1,2,4-thiadiazole-5-carboxylate scaffolds **33** by the cycloaddition of 0.56 molar oxathiazolone **31** with 0.5 molar ethyl cyanoformate (ECF) **32** in the presence of *p*-xylene solvent under microwave-assisted heating at 160 °C for 10 min as represented in Scheme 12. The solvent and excessive ethyl cyanoformate were removed under reduced pressure, and residue was subjected to purification and spectroscopic characterizations. The merits of microwave-assisted green synthetic methodology were the shorter reaction time and easy work-up to produce ethyl-1,2,4-thiadiazole-5-carboxylate products in moderate-to-good yields [264].

Scheme 12. Microwave-assisted synthesis of substituted-1,2,4-thiadiazoles **33**.

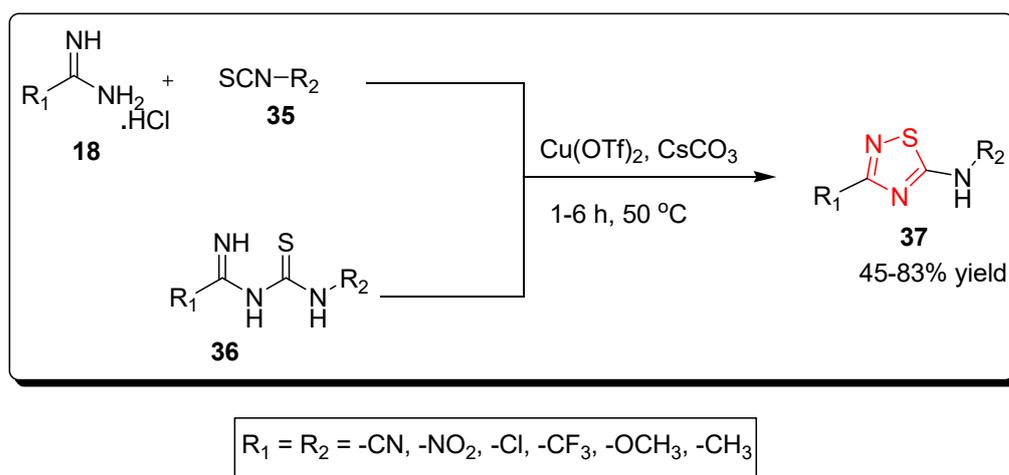
5.13. Green Synthesis of 1,2,4-Thiadiazole via Ionic Liquids

Zali-Boeini et al. reported the synthesis of a new facile and efficient environmentally friendly methodology to afford 3,5-disubstituted-1,2,4-thiadiazole by using pentyl pyridinium tribromide ionic liquids as the solvents, as well as reagent to carry out the oxidative dimerization of aryl thiomide. An equimolar mixture of arythiomide and pentylpyridinium tribromide ionic liquids was mixed together and stirred for 3–7 min at ambient temperature to obtain substituted 1,2,4-thiadiazole structural motifs in excellent yields. The recyclable pentylpyridinium tribromide compound, named room-temperature ionic liquids (RTILs), can be used 4–5 times to carry out oxidative dimerization. This synthetic approach is smooth, rapid, clean and environmentally benign and achieved products in 88–97% yield (Scheme 13) [265].

Ar = Ph, 4-Me-C$_6$H$_4$, 4-NO$_2$-C$_6$H$_4$, 3-Br-C$_6$H$_4$, 4-Br-C$_6$H$_4$, 2-Cl-C$_6$H$_4$, 3-Cl-C$_6$H$_4$, 4-Cl-C$_6$H$_4$, 4-F-C$_6$H$_4$, 4-Meo-C$_6$H$_4$, 2,4-Cl-^{2}C$_6$H$_3$, 2-Furanyl

Scheme 13. Synthesis of 1,2,4-thiadiazoles **27** via RTIL.

5.14. Copper Salts as Catalyst for Green One-Pot Synthetic Protocol for N–S Bond Formation

Kim et al. described a one-pot environmentally benign synthetic approach to obtain 3-substituted-1,2,4-thiadizole under different solvents (THF, DMF and CH$_3$CN), catalysts (CuI, CuCN, CuBr$_2$, Cu(OAc)$_2$·H$_2$O, Cu(OTf)$_2$, CuSO$_4$) and Cs$_2$CO$_3$ as basic agents for the facilitation of the reaction. The substituted amidines **18** reacted with substituted isothiocyanates **35** or substituted thioureas **36** and directly underwent N–S Bond formation via intramolecular cyclization in the presence of Cu(OTf)$_2$ catalyst, basic agent CsCO$_3$ and solvents (THF and acetonitrile) to achieve substitute-1,2,4-thiadiazole structural hybrids **37** in moderate-to-good yields as shown in Scheme 14 [266].

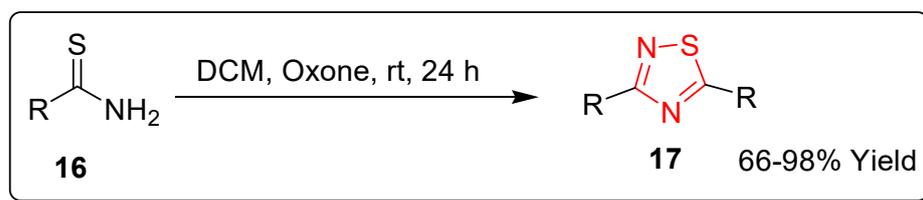
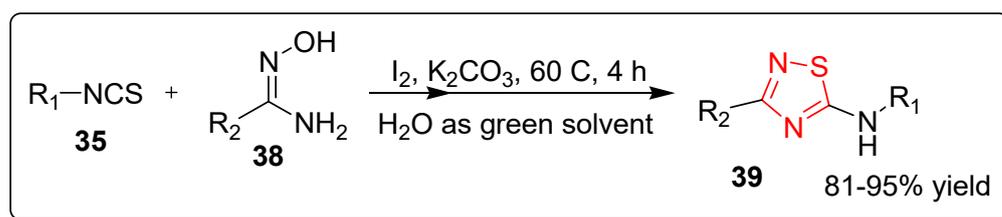
R$_1$ = R$_2$ = -CN, -NO$_2$, -Cl, -CF$_3$, -OCH$_3$, -CH$_3$

Scheme 14. Green synthesis of 5-amino-1,2,4-thiadiazoles via copper catalysis.

5.15. Oxidative Dimerization of Thioamides by Using Oxone as Safe Oxidant

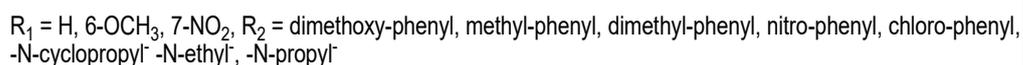
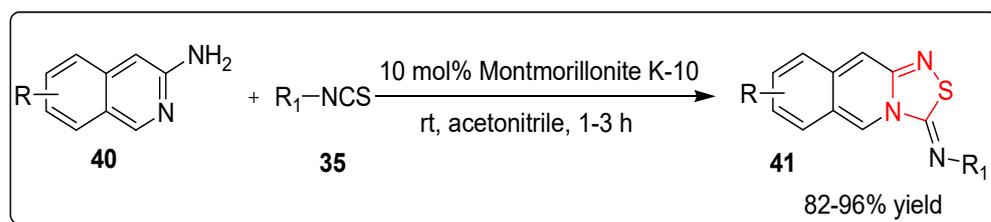
Yoshimura et al. selected the ecofriendly, inexpensive, safe and readily available oxone as an oxidative dimerization agent. They developed an efficient, novel synthetic protocol to furnish 1,2,4-thiadiazole **17** structural motifs in good-to-excellent yields through the treatment of substituted thioamide **16** with oxone as oxidant in the presence of DCM at ambient temperature, as displayed in Scheme 15. In the present synthetic protocol, both the EW and ED substituents furnished 1,2,4-thiadiazoles in good yields, which is the main advantage of this green strategy [267].

5.16. Molecular I$_2$ as Catalyst for Synthesis of 1,2,4-Thiadiazoles via Oxidative N–S Bond Formation

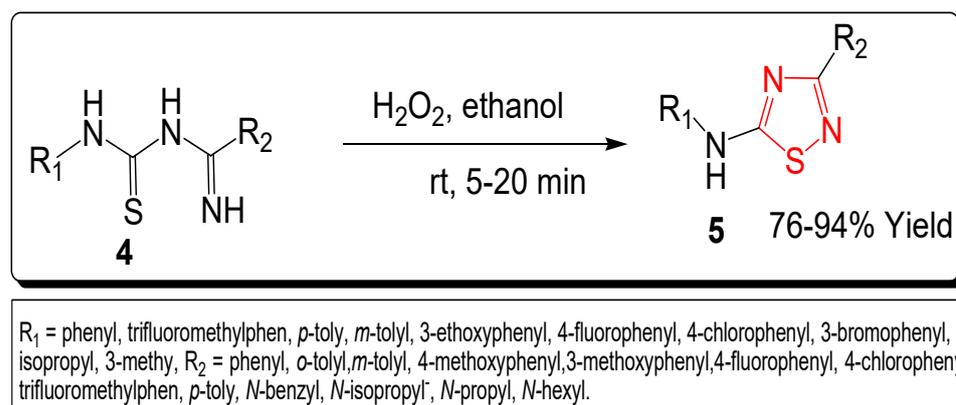
Jatangi et al. reported a facile, efficient, environmentally benign and convenient synthetic approach for the synthesis of 3-substituted 5-amino-1,2,4-thiadiazole scaffolds in a scalable fashion. In this metal-free and high-substrate-tolerance methodology, the reaction of substituted isothiocynates **29** and substituted amidoximes **38** was carried out at 60 °C in the presence of I$_2$, with potassium carbonate and water as green solvents, to

afford substituted 1,2,4-thiadiazole derivatives **39** in good-to-high yields, as depicted in Scheme 16 [268].

Scheme 15. Green synthesis of 1,2,4-thiadiazoles **17** via oxone as safe oxidant.

Scheme 16. Green strategy for synthesis of 5-amino-1,2,4-thiadiazoles **39**.

5.17. Synthesis of N-Fused Imino-1,2,4-Thiadiazolo Isoquinoline via Montmorillonite K10-Catalyst

Chacko and Shivashankar for the first time reported the green, recoverable, inexpensive, nontoxic and efficient oxidizing montmorillonite K10-catalyst for the rapid construction of N–S Bond formation to afford 1,2,4-thiadiazolo isoquinoline structural hybrids in good yields. In this simple synthetic protocol, 3-aminoisoquinolines **40** were coupled with substituted isothiocyanates **35** to construct the N–S Bond of 1,2,4-thiadiazole core to achieve N-fused imino-1,2,4-thiadiazolo isoquinoline scaffolds in excellent yields as displayed in Scheme 17 [269].

Scheme 17. Green synthesis of *N*-fused imino-1,2,4-thiadiazolo isoquinolines **41**.

5.18. H_2O_2-Catalyzed Synthesis of 1,2,4-Thiadiazoles

Cao et al. reported the hydrogen-peroxide-mediated synthetic transformations of substituted thiourea **4** into 1,2,4-thiadiazoles **5** through the construction of the N–S Bond under metal-free synthetic conditions with ethanol as the sole solvent at ambient temperature as shown in Scheme 18. The advantages of this synthetic strategy are large-scale preparation, operationally simple, ethanol as the green solvent and clean by-products. 1,2,4-thiadiazole structural hybrids were obtained in good-to-excellent yields [270].

Scheme 18. Green synthesis of 1,2,4-thiadoazole derivatives 5.

6. Conclusions

Advances in green synthetic organic chemistry may result in a more ecofriendly future with the help of green technologies, processes and synthetic reaction conditions, such as green solvents, green catalysts, solvent-free and less energy-consuming strategies and microwave- and ultrasonic-assisted approaches that transform reactants into products with sustainability. The chemical industrial sector and academic research mostly rely on hazardous catalysis and solvents. Therefore, alternative green solvents and green catalysis are the future of our ecosystem in reducing or even eliminating these hazardous materials' effects on the environment and can lead to the optimized yield of products in a shorter period of time, in accordance with all 12 principles of green chemistry. In this plethora of research, various green catalytic approaches have been applied to furnish different 1,2,4-thiadiazole structural hybrids in good-to-excellent yields by utilizing various green solvents, solvent-free procedures, ionic liquid approaches, grinding and chemo-mechanical protocols, microwave- and ultrasonic-assisted time reduction techniques. We think that the next decade will be a major mark of applying green and sustainable catalysis methodologies to promote organic transformations in academia and industry alike.

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