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Journal Name

ARTICLE

N,2-dibromo-6-chloro-3,4-dihydro-2*H*-benzo[e][1,2,4] thiadiazine-7-sulfonamide 1,1-dioxide: An efficient and homogeneous catalyst for one-pot synthesis of 4*H*-pyran , pyranopyrazole and pyrazolo[1,2-b] phthalazine derivatives under aqueous media

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Ardeshir Khazaei,*[a] Mohammad Ali Zolfigol,*[a] Fatemeh Karimitabar,[a] Iraj Nikokar[b] and Ahmad Reza Moosavi-Zare[c]

N,2-dibromo-6-chloro-3,4-dihydro-2*H*-benzo[e][1,2,4] thiadiazine-7-sulfonamide 1,1-dioxide (DCDBTSD) as a highly efficient and homogeneous catalyst was successfully applied for the synthesis of 4*H*-pyran , pyranopyrazole and pyrazolo[1,2-b] phthalazine derivatives by the one-pot multi-component reaction (MCR) in water. The described method has some advantages such as mild and neutral reaction media, high yields, short reaction times, cleaner and easier reaction profiles and compliance with green chemistry protocols.

Introduction

Water as an available, inexpensive, nonflammable, nonhazardous, nontoxic, uniquely redoxstable solvent in enormous quantities, can accelerate the rate of organic reactions even for water-insoluble reactants as well as product isolation by straightforward filtration.[1] Thus, the development of synthetically useful and convergent multicomponent reactions (MCRs) using water as a green reaction medium is more demand.[1] Multi-component reactions (MCRs) play an important role in combinatorial chemistry because of the ability to preparation of target compounds with greater efficiency and atomic economy by generating structural complexity in a single step from three or more reactants.[2]

The preparation of tetrahydrobenzo[b]pyrans are important due to their significant anti-coagulant, diuretic, spasmolytic, anti-cancer, antihypertensive, calcium antagonists spasmolytic, pharmaceuticals and anti-anaphylactic properties.[3] Several methods have been introduced for the synthesis of tetrahydro-4*H*-benzopyran derivatives using different catalyst such as [cmmim]Br,[4a] hexadecyldimethylbenzyl ammonium bromide (HDMBAB),[4b] Na_2SeO_4,[4c] [Pyridine–SO_3H]Cl,[4d] magnesium oxide,[4e] (S)-proline.[4f]

Pyranopyrazoles are fused heterocyclic compounds, which are important because of their biological properties such as fungicidal,[5a] bactericidal,[5b] vasodilatory activities[5c] and they act as anticancer agents.[5d] Some catalysts have been used to promote this reaction such as imidazole,[6] [Dsim]$AlCl_4$,[7a] Silicotungstic acid,[7b] L-Proline,[7c] isonicotinic acid.[7d]

2*H*-indazolo[2,1-b]phthalazine-triones, as *N*-heterocycles compounds, show biological and pharmacological activities such as anticonvulsant, cardiotonic, and vasorelaxant.[8] Various catalysts including dodecylphosphonic acid,[9a] $Ce(SO_4)_2$,[9b] heteropolyacids,[9c] $Mg(HSO_4)_2$,[9d] silica sulfuric acid[9e] and p-TSA[9f] have been used for the synthesis of these compounds.

However, some reported methods for the synthesis of mentioned compounds suffer from one or more of disadvantages such as using toxic, corrosive, expensive and/or large amount of catalysts, long reaction time, toxic and corrosive solvents and strong acidic media. Because of the importance of these compounds, the investigation for a milder, more eco-friendly under green, neutral and aqueous conditions and faster method with higher yields is still needed.

A large group of compounds generically called *N*-halo reagents that are used as potentially reactive intermediates. These compounds are widely used in organic synthesis and in the chemistry of natural compounds. Some specific features of *N*-halo reagents such as high activity of the N-X bond and the various modes of splitting of this bond cause their wide application in organic transformations.[10-12] Having above facts and in continuation of our previous studies on the applications of *N*-halo reagents in organic synthesis,[13–21] we have recently used *N*,2-dibromo-6-chloro-3,4-dihydro-2H-benzo[e][1,2,4]thiadiazine-7-sulfonamide 1,1-dioxide (DCDBTSD) (Figure 1) as an efficient and homogeneous catalyst for the synthesis of 4H-pyran and pyrazolo[1,2-b] phthalazine and pyranopyrazole derivatives.

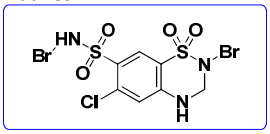
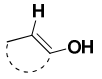


Figure 1. The structure of *N*,2-dibromo-6-chloro-3,4-dihydro-2*H*-benzo [e] [1,2,4] thiadiazine-7-sulfonamide 1,1-dioxide (DCDBTSD).

Results and discussion



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N,2-dibromo-6-chloro-3,4-dihydro-2*H*-benzo[e][1,2,4]thiadiazine-7-sulfonamide 1,1-dioxide (DCDBTSD) was prepared via a simple procedure and fully characterized by IR, UV, ^{1}H and ^{13}C NMR, XRD, TG/DTG as well as mass spectra and used as an efficient catalyst for the preparation of 4,40-(arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)s via one-pot pseudo five component condensation reaction of phenylhydrazine, acetoacetate derivatives and arylaldehydes.[13]

In order to expand the application, efficacy and the scope of DCDBTSD in the synthesis of heterocyclic compound, initially, the synthesis of 4H- pyran derivatives via the one-pot condensation reaction of reactive α-methylene group with aromatic aldehydes and malononitrile was studied.

In order to optimize the reaction conditions, the reaction of 4-hydroxycoumarine (**1**) (1 mmol), 4-nitrobenzaldehyde (**2**) (1 mmol) and malononitrile (**3**) (1.2 mmol) as model reaction was investigated in the variation of reaction parameters, such as catalyst quantity, reaction temperature and kinds of solvents. The results are summarized in Table 1.

As it is shown at Table 1, 10 mol% of DCDBTSD (0.0455 g) in water was the best reaction condition for the described reaction (Table 1, entry 3). Notably, no product was observed in the absence of catalyst (Table 1, entry 1) which further requires the use of DCDBTSD in this transformation. To optimize the reaction temperature, we also performed several experiments in water at 25, 60, and 80 °C. It was found that the excellent yield of product was achieved at 80 °C (Table 1, entry 3).

Also, the reaction could be efficiently done in all the tested solvents (Table 1, entries 3 and 7-9). The reaction using water as the solvent lead to higher yields and shorter reaction time than those using methanol, ethanol and acetonitrile as solvent. Thus, water, which additionally is an available, low-cost, safe, harmless, was chosen as the solvent for all further reactions.

Table 1. Optimization of reaction conditions for the preparation of 4*H*-pyran derivatives.[a]

Entry	Amount of catalyst/mol%	Solvent	Temp.	Time (min)	Yelid[b]
1	-	H_2O	80	240	Trace
2	5	H_2O	80	70	82
3	10	H_2O	80	30	88
4	20	H_2O	80	30	88
5	10	H_2O	60	60	79
6	10	H_2O	r.t	150	40
7	10	MeOH	80	60	70
8	10	EtOH	80	40	85
9	10	CH_3CN	80	60	78
10	10	neat	80	60	68

[a]Model reactions: 4-hydroxycoumarine **1** (1 mmol), 4-nitrobenzaldehyde **2** (1 mmol), malononitrile **3** (1 mmol) and DCDBTSD.

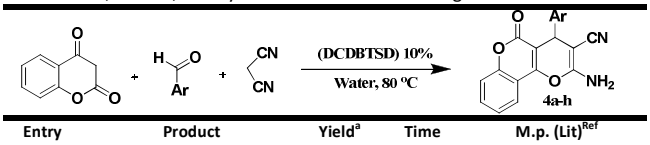
[b] Isolated yield.

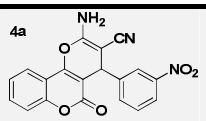
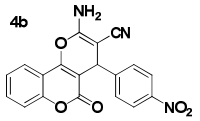
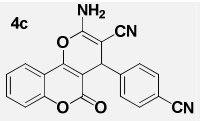
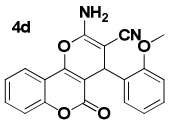
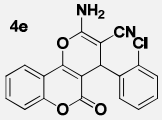
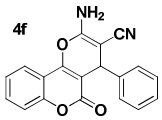
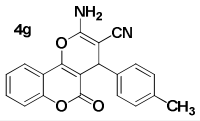
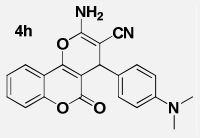
With the optimized conditions in hand, to outline this approach, the scope and generality of this protocol was next examined by employing a good range of aromatic aldehydes possessing a reactive α-methylene group and malononitrile (Scheme 1).

All the reactions proceeded efficiently under the optimized conditions (Tables 2 and 3).

Scheme 1. The synthesis of 4*H*-Pyrans.

Table 2. The preparation of 4*H*-pyran derivatives by the reaction of chroman-2,4-dione, aldehydes and malononitrile using DCDBTSD.



Entry	Product	Yield[a]	Time (min)	M.p. (Lit)[Ref]
1	4a 	95	20	263–265 (262-264)[22]
2	4b 	90	30	260–262 (258-260)[22]
3	4c 	85	25	286-288(289–290)[23]
4	4d 	82	15	250–252 (247-249)[23]
5	4e 	80	40	257–259 (256-258)[22]
6	4f 	85	60	269-271(266–268)[14]
7	4g 	85	30	253-254 (251-252)[14]
9	4h 	80	80	223-224 (223-224)[24]

[a] Isolated yield.

Table 3. The preparation of 4*H*-pyran derivatives by the reaction of naphthalen-1-ol, aldehydes and malononitrile using DCDBTSD.

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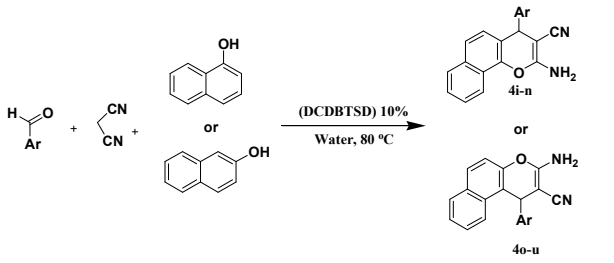
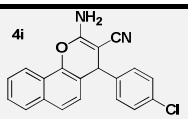
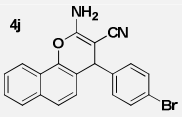
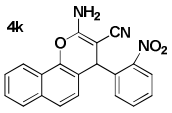
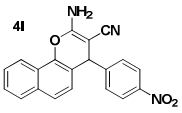
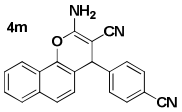
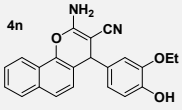
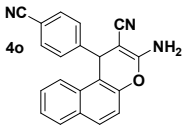
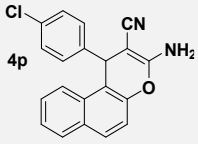
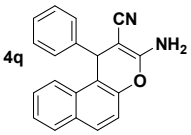
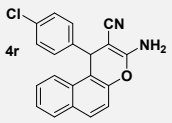
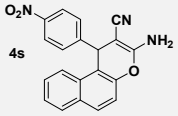
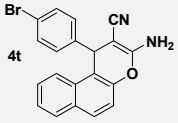
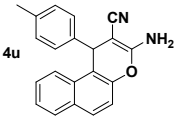


Entry	Product	Yield[a]	Time (min)	M.p. (Lit)[Ref]
1		85	20	247–248 (247-248)[24]
2		92	30	246–248 (243-244)[24]
3		86	35	207–209 (207-209)[24]
4		91	15	211–212(213-214)[24]
5		83	25	258–261 (259-260)[25]
6		87	25	225–227 (222-223)[24]
7		79	25	280–282(284-286) [25]
8		90	20	236-239 (237-238)[26]
9		85	40	290-292(291-292)[13b]
10		85	22	216–218 (214-215)[24]
11		92	30	186–188 (187-189)[27]
12		91	25	238–240 (238-240)[27]
13		84	30	271-274(273-275)[14]

[a] Isolated yield.

Aromatic aldehydes with bearing both electron-withdrawing and electron-donating groups in *ortho*, *meta* and *para* positions of the aromatic ring were converted into favorite products in good to excellent yields.

Moreover, the presented methodology was used successfully for various carbonyl compounds which have a reactive *α*-methylene group, and corresponding desired products were obtained in good to excellent yields without observing any by-products.

We also compared the result of the present DCDBTSD with other catalysts reported in the literature such as triethylbenzylammonium Chloride (TEBA), PEI@Si–MNPs, Hexamethylenetetramine (HMT) and TiO_2 nanowires (TiO_2 NWs) for preparation of 4*H*-Pyran derivatives (Table 4). Table 4 obviously demonstrates that DCDBTSD is effective catalysts in terms of reaction time and yield of obtained product relative to other reported catalysts.

Table 4. Comparison of the results of with other catalysts reported in literature with DCDBTSD in the synthesis of 4*H*-Pyran derivatives.

Entry	Catalyst	Conditions	Time (min)	Yield[a]	Ref.
1	TEBA	H_2O, 90 °C	600	88	28
2	PEI@Si–MNPs	H_2O, Reflux	50	96	3
3	HMT	EtOH, Reflux	40	95	23
4	TiO2 NWs	EtOH/H_2O(1/1), Reflux	40	90	29
5	DCDBTSD	H_2O, 80 °C	20	95	-[b]

[a] Yields refer to isolated pure products. Based on the reaction of 4-hydroxycoumarine 1 (1 mmol), 3-nitrobenzaldehyde 2 (1 mmol), malonitrile 3 (1 mmol) in corresponding condition.
[b] The presented work.

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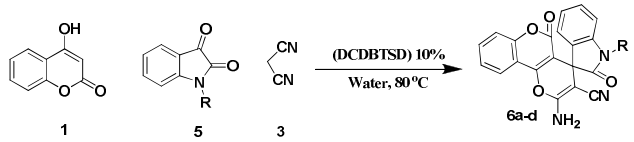
Indole holds a noticeable ability among the various heterocyclic systems because it is present as a core unit in a number of compounds having a wide spectrum of biological activates.[30]

It has been reported that the spiro-oxindole heterocyclic framework is an important structural motif in biologically relevant compounds as natural products and pharmaceuticals, e.g., surugatoxin, horsfiline, spirotryprostatin A and B, elacomine, gelsemine, alstonisine and strychnofoline.[31-37]

The development of efficient and convenient syntheses of novel bioactive organic compounds, such as spirooxindoles is an important current research area, with MCRs considered the most efficient method of preparing spirooxindoles.[38] To further expand the scope of the reaction, it was meaningful thought to replace aromatic aldehydes with *N*-alkyl isatin derivatives in order to show the versatility of this protocol (Scheme 2).

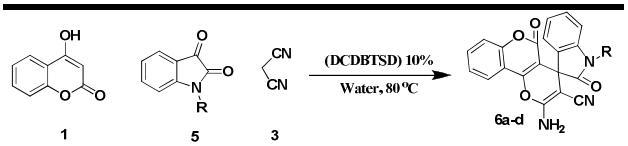
Scheme 2. Synthesis of spiro[2-amino-4*H*-pyran-oxindoles].

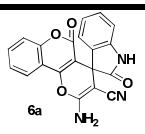
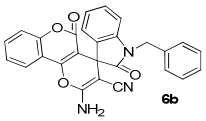
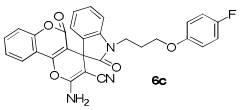
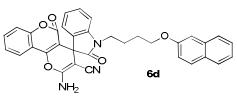


At first, N-alkyl isatin derivatives were prepared by the reaction of isatin with K_2CO_3 and alkyl halide(Scheme 3).[39]

To our surprise, *N*-alkyl isatin derivatives were easily transformed into the desired products in excellent yields (Table 5).

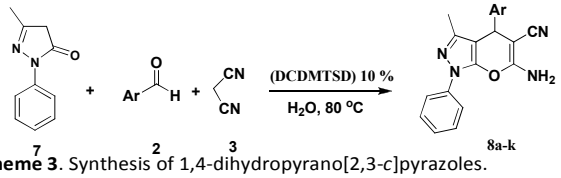
Table 5. The preparation of spiro[2-amino-4H-pyran-oxindole] derivatives.



Entry	Structure	Yield[a]	Time (min)	M.p. (Lit)[Ref]
1	 6a	95	40	296-298 (303)[40a]
2	 6b	90	45	277-279 (278-280)[40b]
3	 6c	95	30	270-272
4	 6d	95	35	268-270

[a] Isolated yield.

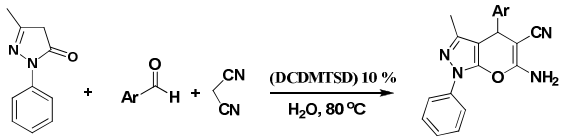
Heterocycles containing pyrazole rings are important target compounds in synthetic and medicinal chemistry because the ring is a key moiety in various biologically active compounds.[38] Pyrazole derivatives have been widely studied in the development of insecticides, acaricides, fungicides, herbicides, dyes, and reagents because of their efficiency, low toxicity, unique reaction mechanisms, safety, lack of cross-resistance, and other characteristics.[38, 41] Being inspired by the above results and also in continuation of our interests to extend the scope of the *N*-bromo sulfonamide reagent in the synthesis of heterocyclic compounds, we investigated the three-component reaction of aromatic aldehydes possessing a 3-methyl-1-phenyl-2-pyrazolin-5-one and molonitrile in the present of DCDMTSD. (Scheme 3).

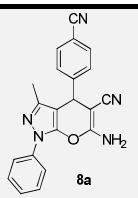
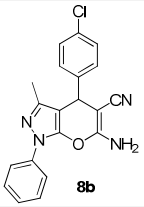
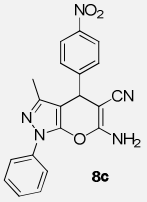


Scheme 3. Synthesis of 1,4-dihydropyrano[2,3-*c*]pyrazoles.

As can be seen from Table 6, for precursors bearing either electron-donating or electron-withdrawing, the reactions all proceeded very smoothly to provide the desired products. The property of the electronic character of substituents on the aromatic ring of the aldehyde did not exert an obvious effect on the reaction yields. All desired products were obtained in high yields and in short reaction times.

Table 6. The preparation of 1,4-dihydropyrano[2,3-*c*]pyrazole derivatives.



Entry	Product	Yield[a]	Time (min)	M.p. (Lit)[Ref]
1	 8a	80	25	198–200 (197–199)[42a]
2	 8b	92	25	230–232 (233–235)[42b]
3	 8c	95	20	194–196 (192–195)[42a]

[a] Isolated yield.

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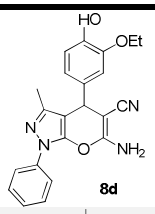
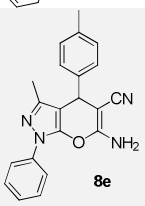
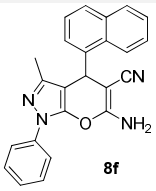
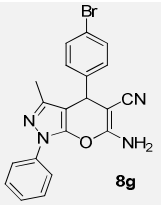
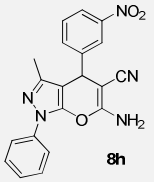
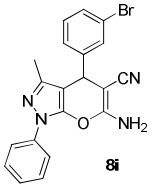
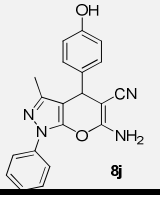
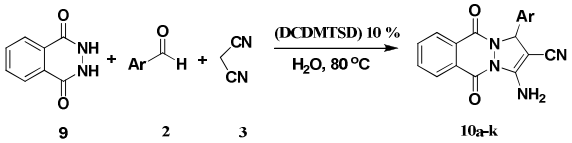
Table 6. Continued.

Entry	Product	Yield[a]	Time (min)	M.p. (Lit)[Ref]
4	 8d	83	30	173-175 (170-171)[43]
5	 8e	79	30	173-175 (172–174)[29]
6	 8f	80	35	159-162 (159-160)[43]
7	 8g	88	20	184–185 (184–185)[42b]
8	 8h	78	30	183-185 (188–191)[29]
9	 8i	80	40	166-168 (169-170)[30]
10	 8j	81	30	212–214 (210–212)[29]

[a] Isolated yield.

Heterocyclic having bridgehead hydrazine have been studied for over a century owing to their pharmacological characteristics and clinical applications.[38, 44, 45] Thus, more and more research briefs have been reported in the past five decades.[46-50] In order to expand the application of DCDBTSD in the synthesis of heterocyclic compounds, we decided to prepare 3-amino -1*H*-pyrazolo[1,2-b]phthalazine-5,10-dione by three-component reaction of aromatic aldehydes or *N*-alkyl isatin derivatives possessing a 2,3-dihydrophthalazine-1,4-dione and malonitrile (scheme 4).

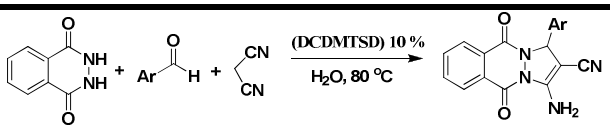


9 2 3 10a-k

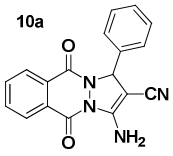
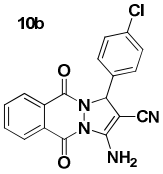
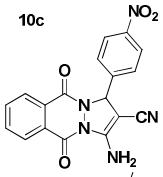
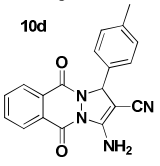
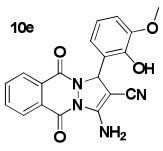
Scheme 4. Synthesis of 1*H*-pyrazolo[1,2-b]phthalazine-5,10-diones.

As is it shown in Table 7, the presented procedure provides an efficient and green approach for the synthesis of 3-amino -1*H*-pyrazolo[1,2-b]phthalazine-5,10-dione derivatives. According to the obtained results (Table 7), DCDBTSD could be applicable for the synthesis of various types of nitrogen-containing heterocyclic compounds.

Table 7. The preparation of 1*H*-pyrazolo[1,2-*b*]phthalazine-5, 10-dione derivatives.



9 2 3 10a-k

Entry	Product	Yield[a]	Time (min)	M.p. (Lit)[Ref]
1	 10a	80	30	271-273 (276–278)[38]
2	 10b	93	15	271–273 (270–272)[51]
3	 10c	95	15	229–230 (228–229)[52]
4	 10d	82	25	250-252 (253–255)[38]
5	 10e	85	35	154–156 (152–154)[52]

[a] Isolated yield.

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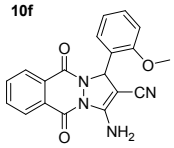
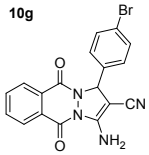
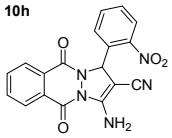
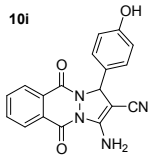
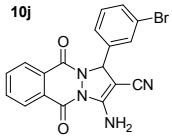
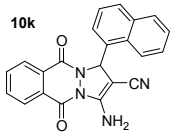
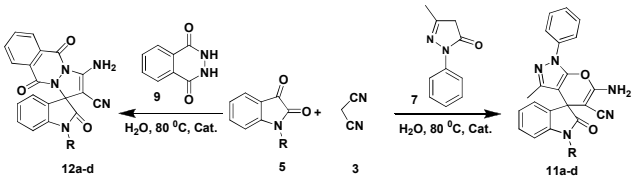
Table 7. Continued.

Entry	Product	Yield[a]	Time (min)	M.p. (Lit)[Ref]
6	10f 	80	20	250–252 (248–250)[53]
7	10g 	87	20	264–266 (263–265)[53]
8	10h 	87	20	268–268 (266–267)[53]
9	10i 	80	35	271–273 (270–272)[54]
10	10j 	81	15	274–276 (271–273)[53]
11	10k 	84	20	275–277 (276–278)[51]

[a] Isolated yield.

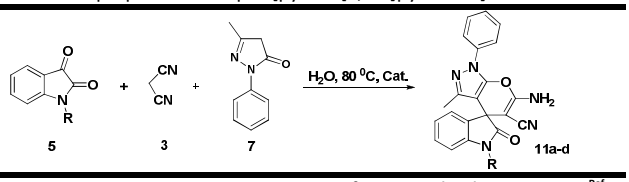
To evaluate the generality and versatility of our catalyst for the preparation of bioactive compounds, we decided synthesis of spiro[indoline-3,40-pyrano [2,3-c]pyrazole] derivatives and 3'-aminospiro[indoline-3,1'-pyrazolo [1,2-b]phthalazine]-2,5',10'-trione using DCDBTSD (scheme 7). For this purpose, we have examined the reaction of *N*-Substituted isatins, 3-methyl-1-phenyl-2-pyrazolin-5-one or 2,3-dihydrophthalazine-1,4-dione with malononitrile (scheme 5).

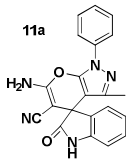
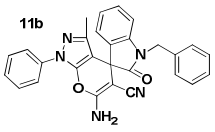
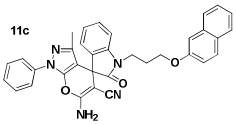
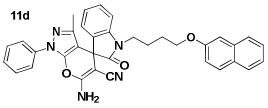


Scheme 5. Synthesis of spiro[indoline-3,4'-pyrano[2,3-c]pyrazole] (11a-d) and spiro[indoline-3,1'-pyrazolo[1,2-*b*]phthalazine]-2,5',10'-trione(12a-d) derivatives in the presence of DCDMTSD **.**

As Table 8 Table 9, indicates that the desired products were obtained in all cases with excellent yields. Our effort to use *N*-Substituted isatins as a starting material with active carbonyl functional group in the above mentioned MCR was also successful verifying to the flexibility of the existing procedure.

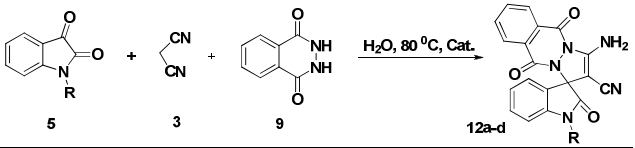
Table 8. The preparation of spiro[pyrano[2,3-c]pyrazoles] derivatives.

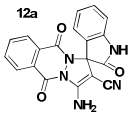
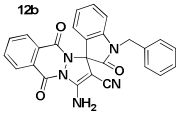


Entry	Structure	Yield[a]	Time (min)	M.p. (Lit)[Ref]
1	11a 	94	30	237-238 (236-237) [55]
2	11b 	90	35	228-230 (232–234) [56]
3	11c 	89	40	210-212
4	11d 	87	40	198-200

[a] Isolated yield.

Table 9. The preparation spiro[indoline-3,1'-pyrazolo[1,2-*b*]phthalazine] derivatives.



Entry	Structure	Yield[a]	Time (min)	M.p. (Lit)[Ref]
1	12a 	92	20	263–265 (260–261) [44]
2	12b 	90	20	260-263 (265-266) [57]

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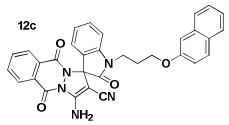
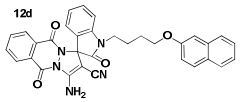
3		86	25	218--220
4		87	25	210-212

[a] Isolated yield.

Experimental

Materials

All chemicals were purchased from Merck or Fluka Chemical. The known products were identified by comparison of their physical properties such as melting points and spectral data with those reported in the literature.

General procedure for the synthesis of DCDBTSD

A solution of sodium hydroxide (6 mol.Lit^{-1}, 1mL) was added dropwise to a stirring round bottomed flask (50 mL) containing hydrochlorothizide (0.6 g, 2 mmol) in distillated water (2 mL) over a period of 10 min at room temperature. After the addition was completed, the reaction mixture was stirred for 20 min. After this time, to the stirring solution of hydrochlorothiazide, bromine (0.08 mL, 3 mmol) was slowly added over a period of 15 min at 0 °C. The insoluble brominated catalyst was removed by filtration and washed with H_2O (10 mL) to give *N*,2-dibromo-6-chloro-3,4-dihydro-2H-benzo[e][1,2,4]thiadiazine-7-sulfonamide 1,1-dioxide (DCDBTSD) in 90 % of yield (0.82 g).[13]

General procedure for the synthesis of 4a-u

Carbonyl compounds possessing a reactive α-methylene group1 (1 mmol), aromatic aldehyde 2 (1 mmol), malonitrile 3 (1.2 mmol) and DCDBTSD (0.0455 g, 10 mol%) were added to 2 mL water and the reaction mixture was stirred at 80 °C for the appropriate time as mentioned in Tables 2 and 3. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature and the solid product was obtained by simple filtration and the solid residue was finally recrystallized from EtOH.

General procedure for the synthesis of 6a-d

4-hydroxy-2*H*-chromen-2-one1 (1 mmol), isatin 5 (1 mmol), malonitrile 3 (1.2 mmol) and DCDBTSD (0.0455 g, 10 mol%) were added to 2 mL water and the reaction mixture was stirred at 80 °C for the appropriate time as mentioned in Table 5. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature and the solid product was obtained by simple filtration and the solid residue was finally recrystallized from EtOH.

General procedure for the synthesis of 8a-k

A mixture of aromatic aldehyde 2 (1 m mol), malonitrile 3 (1.2 m mol), 3-methyl-1-phenyl-2-pyrazolin-5-one 7 (1mmol) and DCDBTSD (0.0455 g, 10 mol%) were added to 2 mL water and the reaction mixture was stirred at 80 °C for the appropriate time as mentioned in Table 6. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature and the solid product was obtained by simple filtration and the solid residue was finally recrystallized from EtOH.

General procedure for the synthesis of 10a-k

A mixture of aromatic aldehyde 2 (1 m mol), malonitrile 3 (1.2 mmol), 2,3-dihydrophthalazine-1,4-dione 9 (1 mmol) and DCDBTSD (0.0455 g, 10 mol%) were added to 2 mL water and the reaction mixture was stirred at 80 °C for the appropriate time as mentioned in Table 7. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature and the solid product was obtained by simple filtration and the solid residue was finally recrystallized from EtOH.

General procedure for the synthesis of 11a-d

A mixture of isatin 5 (1 mmol), malonitrile 3 (1.2 mmol), 3-methyl-1-phenyl-2-pyrazolin-5-one 7 (1mmol) and DCDBTSD (0.0455 g, 10 mol%) were added to 2 mL water and the reaction mixture was stirred at 80 °C for the appropriate time as mentioned in Table 8. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature and the solid product was obtained by simple filtration and the solid residue was finally recrystallized from EtOH.

General procedure for the synthesis of 12a-d

A mixture of isatin 5 (1 mmol), malonitrile 3 (1.2 mmol), 2,3-dihydrophthalazine-1,4-dione 9 (1 mmol) and DCDBTSD (0.0455 g, 10 mol%) were added to 2 mL water and the reaction mixture was stirred at 80 °C for the appropriate time as mentioned in Table 9. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature and the solid product was obtained by simple filtration and the solid residue was finally recrystallized from EtOH.

Conclusions

In conclusion, we demonstrated that *N*,2-dibromo-6-chloro-3,4-dihydro-2*H*-benzo[e][1,2,4]thiadiazine-7-sulfonamide 1,1-dioxide (DCDBTSD), was a remarkably effective homogeneous catalyst for the one-pot construction of the 4*H*-pyran, pyranopyrazole, pyrazolo[1,2-b] phthalazine and spiro-oxindoles derivatives in aqueous media from commercially available starting materials. The most noticeable feature within the study was that water used both as a reaction medium as well as a medium for synthesis of the catalyst. Moreover the aqueous conditions, outstanding yields, simple experimental procedure, environmentally proceeds and elimination of hazardous organic solvents are several advantages of this protocol.

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Spectral data analysis of compounds

Spiro[2-amino-4*H*-pyran-oxindole] (**6a**, Table 5). White powder; mp 292-294 °C (lit: 303 °C). IR (KBr) (υ_{max}, cm^{-1}): 3361, 3297, 3197, 2206, 1734, 11712, 1675, 1360. ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 6.869-6889 (d, 1H, *J=8* Hz, ArH), 6.938-6.976 (t, 1H, *J=7.6* Hz ArH), 7.225-7.241 (d, *J=6.4 Hz*, 2H, ArH), 7.502-7.582 (m, 2H, ArH), 7.707 (s, 2H, NH_2, D_2O exchangeable), 7.768-7.806 (t, *J=7.2* Hz, 1H, ArH), 7.954-7.973 (d, *J=7.6* Hz, 1H, ArH), 10.717 (s, 1H, NH). ^{13}C NMR (400MHz, DMSO-d_6): δ_{ppm} 48.074, 57.494, 101.89, 109.973, 112.929, 117.138, 117.441, 122.524, 123.137, 124.600, 125.482, 129.390, 133.520, 134.140, 142.657, 152.51, 155.542, 158.741, 158.906, 177.615

Spiro[2-amino-4H-pyran-oxindole] (**6b**, Table 5). White powder; mp 278-280 °C (lit: 278-280 °C). IR (KBr) (υ_{max}, cm^{-1}): 3451, 3452, 3166, 2946, 2880, 2196, 1695, 1673, 1611, 1505, 1466, 1360, 762, 746. 1H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 2.066-2.128 (m, 2H, CH_2), 3.841-3.976 (m, 2H, CH_2-N), 4.032-4.048 (d, 2H, *J=6.4* Hz, CH_2-O), 6.941-6.971 (m, 2H, ArH), 6.989-7.026 (t, *J=7.6* Hz, 1H, ArH),7.101 -7.145 (m, 3H, ArH), 7.268-7.319 (m, 2H, ArH), 7.504-7.524(d, *J=8 Hz*, 1H, ArH), 7.553-7.591 (t, *J=7.6* Hz, 1H, ArH), 7.771-7.816(m, 3H, NH_2 and ArH , D_2O exchangeable), 7.962-7.980 (d, *J=7.2* Hz, 1H, ArH). ^{13}C NMR (400MHz, DMSO-d_6): δ_{ppm} 27.27, 37.123, 47.616, 57.132, 65.708, 101.669, 108.970, 112.919, 116.127, 116.207, 116.287, 116.354, 117.184, 117.389, 123.186, 124.588, 125.539, 129.577, 132.739, 134.238, 143.346, 152.524, 155.246, 155.694, 155.753, 158.095, 158.825, 158.985, 176.109.

Spiro[2-amino-4H-pyran-oxindole] (**6c**, Table5). White powder; mp 270-272 °C. IR (KBr) (υ_{max}, cm^{-1}): 3482, 3452, 3166, 2946, 2880, 2196, 1695, 1673, 1611, 1505, 1466, 1360, 762, 746. ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 2.066-2.113 (t, 2H, *J=6.4* Hz, CH_2-O), 3.841-3.976 (m, 2H, CH_2), 4.032-4.048 (d, 2H, *J=6.4* Hz, CH_2-N), 6.926-6.960 (m, 2H, ArH), 6.989-7.026 (t, *J=7.6* Hz, 1H, ArH),7.08 -7.131 (m, 3H, ArH), 7.253-7.305 (m, 2H, ArH), 7.490-7.511(d, *J=8.4 Hz*, 1H, ArH), 7.540-7.577 (t, *J=7.6* Hz, 1H, ArH), 7.751-7.802(m, 3H, NH_2 and ArH), 7.944-7.966 (dd, *J=1.2* Hz, 1H, ArH). ^{13}C NMR (400MHz, DMSO-d_6): δ_{ppm} 27.27, 37.123, 47.616, 57.132, 65.708, 101.669, 108.970, 112.919, 116.127, 116.207, 116.287, 116.354, 117.184, 117.389, 123.186, 124.588, 125.539, 129.577, 132.739, 134.238, 143.346, 152.524, 155.246, 155.694, 155.753, 158.095, 158.825, 158.985, 176.109.

Spiro[2-amino-4H-pyran-oxindole] (**6d**, Table 5). Pale yellow powder; mp 268-270 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 1.839-1.873 (br s, 4H, CH_2), 3.794-3.824 (t, *J=6* Hz, 2H, CH_2N), 4.127-4.155 (t, *J=5.6* Hz, 2H, CH_2O), 7.002-7.039 (t, *J=7.6* Hz, 1H, ArH), 7.091-7.120 (dd, *J=2.4* Hz, 1H, ArH), 7.288-7.353 (m, 3H, ArH), 7.430-7.448 (d, *J=7.2* Hz, 2H, ArH), 7.467-7.496 (1H, ArH), 7.538-7.576 (t, *J=7.6* Hz, 1H, ArH), 7.637-7.657 (d, *J=8* Hz, 2H, ArH), 7.699 (br s, 2H, NH_2, D_2O exchangeable), 7.759-7.822 (m, 4H, ArH), 7.902-7.922(d, *J=8* Hz, 1H, ArH), 7.958-7.977 (d, *J=7.6* Hz, 1H, ArH). ^{13}C NMR (400MHz, DMSO-d_6): 23.948, 24.188, 26.387, 57.140, 67.391, 67.675, 101.726, 107.150, 117.165, 118.614, 119.225, 123.099, 123.184, 123.812, 123.909, 123.996, 126.120, 126.759, 126.830, 127.107, 127.953, 128.868, 129.571, 129.676, 132.855, 134.793, 146.983, 152.533, 155.664, 156.830, 156.994, 158,744, 176.089

Spiro[pyrano[2,3-c]pyrazole] (**11a**, Table 8). White powder; mp 237-238 °C (lit: 236-237 °C). IR (KBr) (υ_{max}, cm^{-1}): 3410, 3287, 3124, 2202, 1692, 1655, 1526, 1132. ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 1.560(s, 3H, CH_3),6.955-6.974 (d, *J=7.6* Hz, 1H, ArH), 7.03-7.067 (t, *J=7.6* Hz, 1H, ArH), 7.190-7.208 (d, *J*=7.2 Hz, 1H, ArH), 7.286-7.324 (t, *J=7.6* Hz ,2H, ArH), 7.353-7.390 (t, *J=7.2* Hz ,1H, ArH), 7.516-7.556 (t, *J=8.4* Hz 2H, ArH), 7.612 (s, 2H, NH_2, D_2O exchangeable), 7.796-7.815 (d, *J* = 7.6 Hz 2H, ArH) 10.774 (s,1H, NH). ^{13}C NMR (400MHz, DMSO-d_6): δ_{ppm} 12.17, 48.24, 56.62, 96.82, 110.32, 118.40, 118.43, 120.60, 123.12, 125.38, 127.05, 129.76, 129.94, 132.60, 137.71, 142.07, 144.42, 145.40, 161.46, 161.50, 177.98.

Spiro[pyrano[2,3-c]pyrazole] (**11b**, Table 8). Pale yellow powder; mp 228-230 °C (lit: 232–234°C). IR (KBr) (υ_{max}, cm^{-1}): 3390, 3314, 3191, 2904, 2200, 2208, 1701, 1662, 1396, 746. ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}:1.368 (s, 3H, CH_3), 4.943-5.096 (AB-q, 2H, CH_2), 7.094-7.130 (t, *J=7.6* Hz, 2H, ArH), 7.276-7.399 (m, 6H, ArH), 7.444-7.462 (d, *J=7.2* Hz, 2H, ArH), 7.523-7.563 (t, *J=7.6* Hz, 2H, ArH), 7.697 (s, 2H, NH_2, D_2O exchangeable), 7.801-7.821 (d, *J=8* Hz, 2H, ArH). ^{13}C NMR (400MHz, DMSO-d_6): δ_{ppm} 12.19, 43.79, 47.98, 56.33, 96.58, 110.00, 118,42, 120.67, 123.93, 125.33, 127.13, 128.08, 129.06, 129.83, 129.95, 131.82, 136.51, 137.67, 142.60, 144.33, 145.46, 161.59, 161.63, 161.67, 176.61.

Spiro[pyrano[2,3-c]pyrazole] (**11c**, Table 8). Yellow powder; mp 210-212 °C. IR (KBr) (υ_{max}, cm^{-1}): 3401, 3380, 3021, 2890, 2870, 2238, 1702, 1691, 1610, 1515, 1450, 1341, 1203,755. ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 1.516(s, 3H, CH_3), 2.152-2.303 (m, 2H,CH_2), 3.933-4.06 (m, 2H, CH_2N), 4.189-4.213(t, *J=7.6* Hz, 2H, CH_2O), 7.079-7.135 (t, *J=7.6* Hz, 1H, ArH), 7.168-7.304 (m, 4H, ArH), 7.344-7.393 (m, 3H, ArH), 7.444-7.480 (t, *J=7.2* Hz, 1H, ArH), 7.518-7.558 (t, *J=7.6* Hz, 1H, ArH), 7.697 (s, 2H, NH_2, D_2O exchangeable), 7.797-7.859(m, 5H, ArH). ^{13}C NMR (400MHz, DMSO-d_6): δ_{ppm} 12.30, 26.94, 37.37, 37.63, 47.87, 56.47, 96.49,107.23, 101.45, 118.65, 119.23, 120.65, 123.80, 124.06, 126.84, 127.11, 127.16, 127.99, 128.99, 129.76, 129.94, 132.02, 134.71, 137.68, 142,68, 144.34, 145.48, 156.78, 161.46, 161.46, 161.50, 176.33.

Spiro[pyrano[2,3-c]pyrazole] (**11d**, Table 8). Yellow powder; mp 198-200 °C. IR (KBr) (υ_{max}, cm^{-1}): 3370, 3329, 3181, 2944, 2875, 2207, 1699, 1662, 1601, 1552, 1467, 1395, 1359, 1219,751, 652. 1H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 1.504(s, 3H, CH_3), 1901(br s, **4**H,CH_2), 3.881-3.911(t, *J=6* Hz 2H, CH_2N), 4.151-4.179(t, *J=6.4* Hz 2H, CH_2O), 7.112-7.189(m, 2H, ArH), 7.251-7.287(t, *J=7.2* Hz, 2H, ArH), 7.329-7.406(m, 4H, ArH), 7.439-7.476(t, J=7.6 Hz, 1H, ArH), 7.520-7.60(t, d, *J=7.2* Hz, 2H, ArH), 7.647(s, 2H, NH_2), 7.798-7.837(m, 5H, ArH); ^{13}C NMR (400MHz, DMSO-d_6): δ_{ppm} 12.28, 18.99, 19.04, 24.40, 26.55, 47.87, 56.39, 96.56, 107.16, 109.55, 118.23,

119.20, 120.64, 123.72, 123.97, 125.31, 126.82, 127.13, 127.96, 128.91, 129.73, 129.94, 131.96, 134.79, 137.68, 142.86, 144.31, 145.49, 156.98, 161.49. 161.54, 176.34.

Spiro[indoline-3,1'-pyrazolo[1,2-*b*]phthalazine] (**12b**, Table 9). Yellow powder; mp 260-263 °C (lit: 265-266 °C). IR (KBr) (υ_{max}, cm^{-1}): 3310, 3270, 3020, 2895, 2229, 1720, 1666, 1662, 1593, 1494, 1349, 1083, 791, 759. ^{1}H NMR (400 MHz, DMSO-d_6) δH: 4.957(s, 2H, CH_2), 7.062-7.082(d, *J=8* Hz, 1H, ArH), 7.191-7.231(t, *J=8* Hz, 1H, ArH), 7.306-7.348(m, 1H, ArH), 7.367-7.441 (m, 4H, ArH), 7.582-7.620 (t, *J=7.6* Hz, 1H, ArH), 7.892-7.925 (m, 3H, ArH), 7.962-7.981 (d, *J=7.6* Hz, 1H, ArH), 8.091(br s, 3H, NH_2 and ArH). ^{13}C NMR (400MHz, DMSO-d_6): δ_{ppm} 43.47, 82.12, 111.43, 111.99, 113.44, 118.72, 124.06, 125.61, 126.16, 127.88, 128.20, 129.19, 133.08, 135.70, 137.98, 146.57, 150.05, 163.12.

Spiro[indoline-3,1'-pyrazolo[1,2-*b*]phthalazine] (**12c**, Table 9). Yellow powder; mp 218-220 °C. IR (KBr) (υ_{max}, cm^{-1}): 3434, 3434, 3029, 2926, 2870, 2228, 1727, 1661, 1628, 1613, 1597, 1470, 1371, 1259, 1180, 837, 762, 748. ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 2.136- 2.184 (m, 2H, CH_2), 3.917-3.951 (t, *J=6.8* Hz, 2H, CH_2N), 4.164-4.193(t, *J=5.6* Hz, 2H, CH_2O), 7.094- 7.122(dd, *J=2.4* Hz, 1H, ArH), 7.170-7.208(t, *J=7.6* Hz, 1H, ArH), 7.241-7.261 (m, 2H, ArH), 7.332-7.372 (m, 1H, ArH), 7.439-7.480 (m, 1H, ArH), 7.439-7.480(m, 1H, ArH), 7.588-7.629 (m, 1H, ArH), 7.762-7.787 (d, *J=8* Hz 1H, ArH), 7.809-7.884 (m, 2H, ArH), 7.892-7.956(m, 5H, ArH), 8.090 (br s, 2H, NH_2); ^{13}C NMR (400MHz, DMSO-d_6): δ_{ppm} 26.93, 37.37, 37.63, 65.51, 81.50, 107.23, 111.08, 111.91, 113.43, 118.65, 119.06, 123.80, 124.06, 125.58, 126.10, 126.87, 127.11, 127.99, 128.96, 129.74, 133.10, 134.66, 138.11, 147.10, 150.30, 156.64, 163.00.

Spiro[indoline-3,1'-pyrazolo[1,2-*b*]phthalazine] (**12d**, Table 9). Yellow powder; mp 210-212 °C. IR (KBr) (υ_{max}, cm^{-1}): 3430, 3401, 3180, 2931, 2870, 2221, 1720, 1668, 1610, 1603, 1590, 1470, 1370, 1240, 1110, 768, 750, 718. ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}:1.846 (br s, 4H, $2CH_2$), 3.784-3.816 (t, *J=7.6* Hz, 2H, CH_2N), 4.115-4.147 (t, *J=6.8* Hz, 2H, CH_2O), 7.098-7.126 (dd, *J=2.4* Hz, 1H, ArH), 7.188-7.226 (t, *J=7.6* Hz, 1H, ArH),7.249-7.268 (d, *J=8* Hz, 1H, ArH), 7.289-7.298 (d, *J=2* Hz, 1H, ArH), 7.327-7.363(t, *J=7.2* Hz, 1H, ArH), 7.439-7.475(t, *J=7.2* Hz, 1H, ArH), 7.645-7.683 (t, *J=7.6* Hz, 1H, ArH), 7.782-7.831 (m, 3H, ArH), 7.889-7.921 (m , 3H, ArH), 8.089 (br s, 2H, NH_2); ^{13}C NMR (400MHz, DMSO-d_6): δ_{ppm} 23.97, 26.40, 37.35, 37.60, 67.39, 81.61, 107.15, 111.13, 111.94, 113.37, 118.59, 119.11, 123.82, 124.01, 125.58, 126.12, 126.84, 127.12, 127.97, 128.88, 129.73, 133.08, 134.73, 138.11, 146.96, 150.10, 156.80, 162.93.

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Graphical Abstract

N,2-dibromo-6-chloro-3,4-dihydro-2H-benzo[e][1,2,4] thiadiazine-7-sulfonamide 1,1-dioxide: An efficient and homogeneous catalyst for one-pot synthesis of 4H-pyran , pyranopyrazole and pyrazolo[1,2-b] phthalazine derivatives under aqueous media

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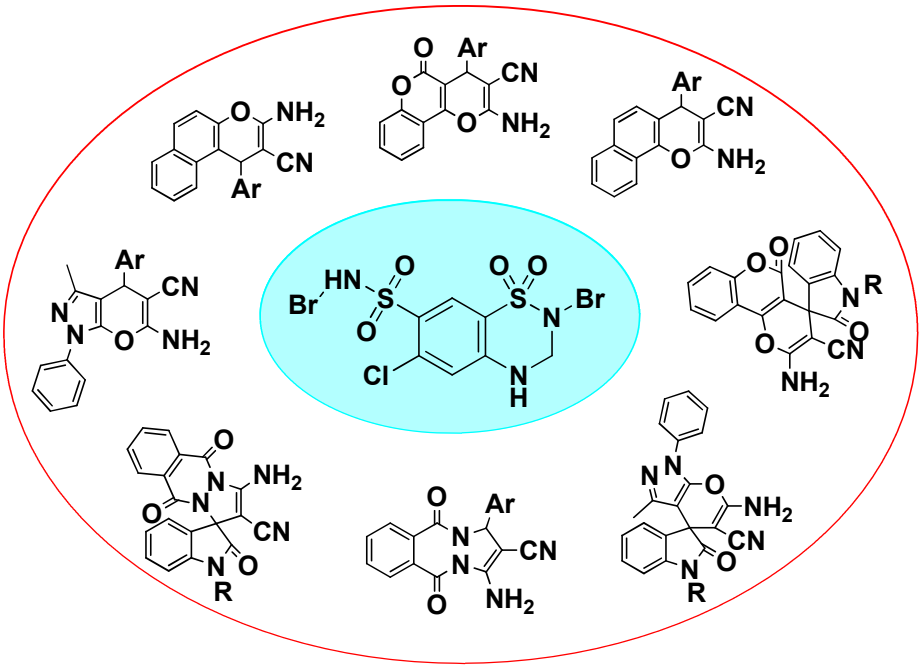

DCDBTSD was successfully applied for the synthesis of 4H-pyran , pyranopyrazole and pyrazolo[1,2-b] phthalazine derivatives by the one-pot multi-component reaction in water.