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PEG-OSO_3H catalyzed synthesis of spiro[acenaphthylene-thiazine]diones under sonication in aqueous medium

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Abstract: Ultrasound promoted efficient procedure has been developed for the synthesis of spiro[acenaphthylene-thiazine]-diones in water using three component reaction of acenaphthalene-1,2-dione, anilines and 3-mercaptopropionic acid in presence of polymer supported catalyst (PEG–OSO_3H) as an inexpensive catalyst. The dual role of the PEG-OSO_3H as a Bronsted acid as well as phase-transfer catalyst has successfully expedited the present multi-component reaction. Reuse of the catalyst, excellent yield and use of water as solvent make the procedure sustainable and eco-friendly.

Keywords: Ultrasound; spiro[acenaphthylene-thiazine]diones; PEG–OSO_3H; Water

1. Introduction:

The finding of new chemical approaches for preparation of organic compounds is a fundamental research in the field of synthetic organic, bioorganic and medicinal chemistry [1,2]. One approach to deal with this challenge include the growth of multicomponent reactions (MCRs), in which reactants more than two are combined mutually in a single reaction flask to produce a product that contain parts of all starting materials [3,4]. Thiazines and its derivatives have been reported for different pharmacological actions, such as anti-microbial, anti-tubercular, anti-malarial, anti-cancer, anti-inflammatory, anti-arrhythmic and anti-alzheimer activities etc [5].

Thiazine moiety is present in most valuable drugs like Cephalosporins, Xylazin and Chlormezanone etc [6]. The individuality, resourcefulness and easy accessibility build thiazines special sources of compounds [7, 8]. In view of the biological and pharmacological importance of thiazines, considerable synthetic efforts have been made to construct this class of heterocycles recently [9-11].

Molecules with spirocyclic structure containing one sp^3 carbon atom common to two rings represent an attractive class of compounds in organic chemistry [12-14]. Spiro-

acenaphthoquinones, occupy a significant place among different families of spirocyclic compounds, due to their pharmaceutical properties [15-17].

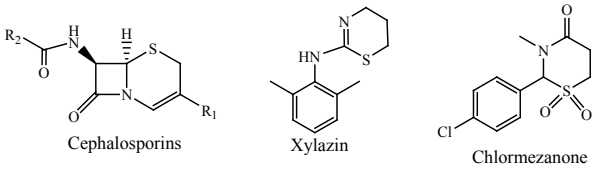
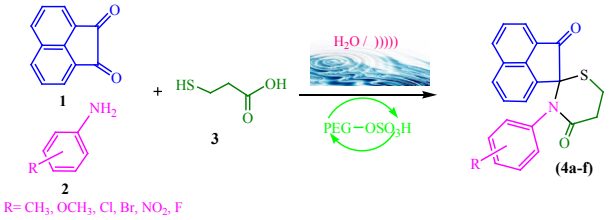


Figure-1; Some representative drugs containing 1,3-thiazine

For the put up and increasing environmental policy, organic chemists are requested to build up environmentally friendly synthetic methodologies by applying non-conventional energy sources. In previous years the improvement in synthetic protocols and to activate weakly reactive molecules, utilization of sonochemical approach is a new era change in chemical synthesis [18]. The remarkable features of the sonochemical approach are improved reaction rates, formation of products in high yields, easier handling, considered as processing aid in terms of energy protection and waste minimization compared with conventional methods [19]. In addition, reactions in aqueous medium have gained considerable momentum [20-22] because water as a solvent is generally considered as a cheap, safe and environmentally benign alternative to 'synthetic' solvents. Besides, this low solubility of organic molecule in water makes the separation of products easy by simple filtration.

Hence, inspired by these findings and due to our research based on green chemistry theme [23-25], we wish to report herein a three-component protocol for the synthesis of drug-like spiro[acenaphthylene-thiazine]diones (**4a-f**) from the reaction of acenaphthalene-1,2-dione substituted anilines and 3-mercaptopropionic acid under sonication in presence of an efficient, green, economical, recyclable polymeric catalyst PEG–OSO_3H in aqueous medium (Scheme-1). PEG–OSO_3H is a polymer supported catalyst that is functionalized by acidic groups and is a mild, non-volatile, and non-corrosive organic acid which has been used in various organic synthesis [26-28].

It is relevant to mention that this is the first report on the synthesis of new spiro[acenaphthylene-1,2′[1,3]-thiazine]-2,4′(1*H*)-diones derivatives (**4a-f**) installing PEG-OSO_3H catalyzed three-component protocol in water under sonication. Generally, the synthesis of thiazine involves the use of volatile carcinogenic hydrocarbons with continuous azeotropic removal of water [29,30].



Scheme 1. Synthesis of spiro[acenaphthylene-1,2′-[1,3]-thiazine]-2,4′-(1*H*)-diones

2. Results and Discussion

TABLE 1. Optimization of conditions for the multicomponent synthesis of **(4a).**

Entry	Solvent	Condition	Catatyst (20 %)	Time	Yield of 4a* (%)
1.	H_2O	US	-	60 min	<30
2.	H_2O	US	HCl	60 min	54
3.	H_2O	US	$InCl_3$	60 min	56
4.	H_2O	US	*p*-TSA	60 min	73
5.	H_2O	US	CTABr	60 min	75
6.	H_2O	US	PEG-OSO_3H	20 min	88
7.	CH_3CN	US	PEG-OSO_3H	20 min	74
8.	THF	US	PEG-OSO_3H	20 min	59
9.	EtOH	US	PEG-OSO_3H	20 min	75
10.	H_2O	Stirring	PEG-OSO_3H	20 min	No reaction
11.	H_2O	Stirring	PEG-OSO_3H	60 min	46
12.	H_2O	Reflux	PEG-OSO_3H	60 min	Mixture of products

*isolated yields

Initially, to get 3′-(2-chlorophenyl)-spiro[acenaphthylene-1,2′-[1,3]-thiazine]-2,4′-(1*H*)-dione **(4a)** we tested the reaction of acenaphthalene-1,2-dione **1** (2 mmol), *2*-chloroaniline **2** (2 mmol), and 3-mercaptopropionic acid **3** (2 mmol) as a simple model substrate in various reaction conditions. The results are shown in Table 1. It was found that when the reaction was carried out without any catalysts in aqueous medium and under sonication the yield of product was very low (Table 1,< 30%, entry 1) even after 1h irradiation. To look up for better yields, we did this reaction using different acid catalyst (Table 1, entries 2-4). Brønsted acids HCl and Lewis acid $InCl_3$ can catalyze this reaction with moderate yields. However, the use of *p*-TSA (*p*-toluenesulfonic acid), and surfactant CTABr led good to better product formation (Table 1, entries 4 & 5). Polymer supported, PEG-OSO_3H was identified as the optimal catalyst as the desired product **4a** was isolated in 88 % yield in reduced time (Table 1, entry-6). Subsequently, we further turned to testing the effect of solvents CH_3CN, tetrahydrofuran (THF) and EtOH but they showed no superiority to water (Table 1, entry 7-9) because water has higher maximum cavitation intensity (Imax) than other solvents [31].

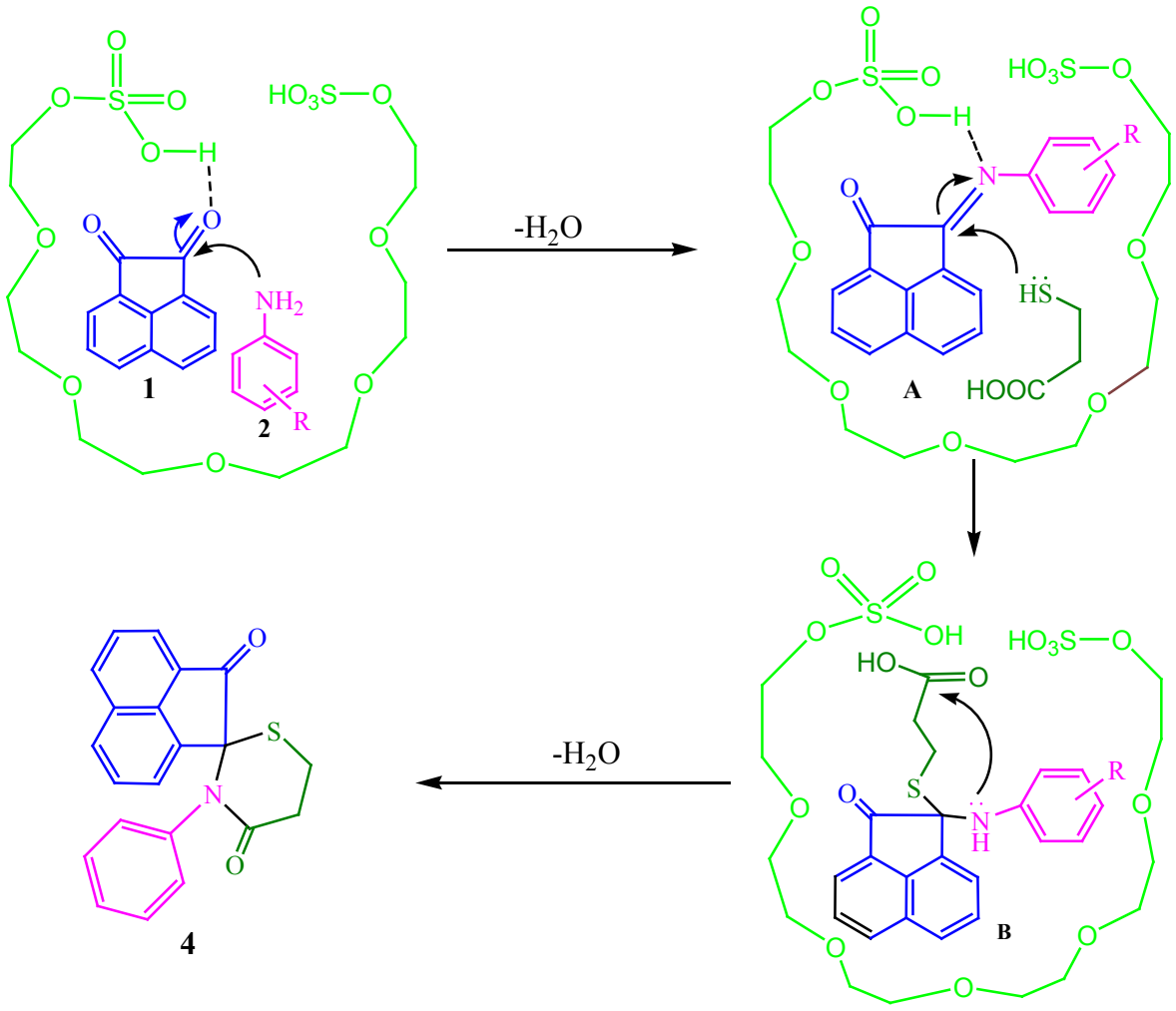
To prove the effect of sonication the present reaction was also carried out under conventional manners in both stirring and refluxing conditions in water and in presence of PEG-OSO_3H (entry 10-12) in the absence of ultrasound irradiation. As shown in Table 1, under high speed stirring on magnetic stirrer, no reaction was observed after same time but very lower yield of products was obtained after a prolonged reaction time. While, under refluxing a mixture of products were formed as detected by TLC. Thus, ultrasonic irradiation was found to have beneficial effect on the synthesis of spiro[acenaphthylene-1,2′-[1,3]-thiazine]-2,4′-(1*H*)-*dione* (**4a**). After that, the optimized reaction conditions was applied to other substituted anilines (Table-2), and results given in Table 2 showed that all the substrates reacted smoothly and efficiently to afford the spiro[acenaphthylene-1,2′-[1,3]-thiazine]-2,4′-(1*H*)-diones (**4a-f**) in good to excellent yields. All the synthesized compounds were characterized on the basis of spectral and elemental analysis.

TABLE 2 Synthesis of spiro[acenaphthylene-1,2′-[1,3]-thiazine]-2,4′-(1*H*)-diones (**4a-f**)

Entry	Products	R	Time (min)	Yield* (%)	Mp (°C)
1	**4a**	2-Cl	20	88	193-195
2	**4b**	3-Cl	20	87	191-192
3	**4c**	4-CH_3	25	85	226-228
4	**4d**	4-Br	35	88	194-197
5	**4e**	3-F	35	89	211-213
6	**4f**	4-NO_2	38	85	240-242

*Isolated yield

Sulfonic group based PEG shows double action in organic reactions: as an acid to activate the reactants and as a phase transfer catalyst to solubilise reactants in aqueous medium. The catalytic potential of PEG–OSO_3H in water may be due to the creation of hydrophobic supramolecular cavity which brings molecules close to each other as shown in scheme-2. In this particular MCR, we propose that, besides the formation of supramolecular cavity, the catalyst is also accompanied by inherent Bronsted acidity of SO_3H groups, which is capable of bonding with carbonyl oxygen of acenaphthalene-1,2-dione assisting the nucleophilic attack by the aniline and in turn facilitates the formation of imine intermediate **A** followed by reaction



Scheme-2

between the 3-mercaptopropionic acid and imine derivative yielding spiro[acenaphthylene-1,2′[1,3]-thiazine]-2,4′(1*H*)-dione **4a.** Rapid exclusion of water molecules from the hydrophobic interior of the catalyst, generated during the condensation reactions may also facilitate the condensations (Scheme-2).

4. Conclusion

We have successfully developed simple, convenient, environmentally benign, mild, and safe synthetic method to afford spiro[acenaphthylene-1,2′[1,3]-thiazine]-2,4′(1*H*)-diones using the polymer supported acidic catalyst PEG-OSO_3H in aqueous media under sonication. The significant advantage of this methodology is high yield, simple work-up procedure and easy handling of the catalyst. We believe that this one pot catalytic transformations would be a very attractive choice for the synthesis of spiro[acenaphthylene-1,2′[1,3]-thiazine]-2,4′(1*H*)-dione libraries in chemical as well as pharmaceutical industries.

5. Experimental Section

Melting points were determined on a Toshniwal apparatus. The purity of compounds was checked on thin layers of silica gel in various non-aqueous solvent systems, *e.g.* benzene: ethylacetate (9 : 1), benzene : dichloromethane

(8 : 2). IR spectra (KBr) were recorded on a Perkin-Elmer spectrophotometer and ^{1}H NMR and ^{13}C NMR spectra were recorded on Jeol 400 MH$_z$ using DMSO-d_6 at 400 and 100 MHz, respectively. TMS was used as internal reference. ESI Mass spectra of representative compounds were recorded on Waters UPLC-TQD Mass spectrometer. The ultrasound-assisted reactions were carried out using ultrasonic processor probe system (Processor OSONICA Q700) operating at 20 KHz, 750 W with 12.7 mm tip diameter probes and provided with an infrared sensor for temperature measurement.

Preparation of PEG–SO$_3$H [32]

At 0^{o}C, chlorosulfonic acid (10 mmol) was added to a solution of PEG-6000 (1mmol) in CH_2Cl_2 (10mL), and the resulting solution was stirred at room temperature overnight. Then, the solution was concentrated, and ether was added to it. The resulting solid mass was filtered and washed with ether to obtain PEG–OSO$_3$H as a gummy solid.

General synthesis of spiro[acenaphthylene-1,2′[1,3]-thiazolidine]-2,4′(1*H*)-dione (4a-f).

A mixture of acenaphthalene-1,2-dione **1** (2.0 mmol), aniline **2** (2.0 mmol), 3-mercaptopropionic acid (2.0 mmol) and polymer supported catalyst PEG-OSO$_3$H (10 mol %) were taken in a reaction vessel. The reaction mixture was irradiated under sonication for the appropriate time (20-38 min.) at 50 % power using 12.7 mm tip diameter probe. After completion of reaction (TLC) the water insoluble product was filtered and washed with water and crystallized from ethanol to afford the pure crystalline product. The extra water in residue was evaporated under reduced pressure and obtained gummy solid was washed with diethylether, dried and reused.

3′-(2-Chlorophenyl)-spiro[acenaphthylene-1,2′-[1,3]-thiazine]-2,4′-(1H)-dione **(4a)**

^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 2.50-2.60 (m, 1H, -CO-CH$_2$-), 3.04-3.14 (m, 2H, -CH$_2$-CH$_2$-), 4.14-4.22 (m, 1H, S-CH$_2$), 7.04-7.67 (m, 10, Ar-H); ^{13}CNMR (100 MHz, DMSO-d$_6$) δ (ppm): 24.02, 34.03, 94.20, 121.50, 123.16, 124.45, 125.13, 126.25, 127.46, 128.01, 129.89, 130.59, 131.34, 132.79, 133.08, 134.68, 135.34, 175.09, 192.65; MS (ESI, m/z, M$^+$): 379; Anal. calcd. For $C_{21}H_{14}ClNO_2S$: C, 66.40; H, 3.71; N, 3.69 %. Found: C, 66.55; H, 3.74; N, 3.72.

3′-(3-Chlorophenyl)-spiro[acenaphthylene-1,2′-[1,3]-thiazine]-2,4′-(1H)-dione **(4b)**

^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 2.52-2.63 (m, 1H, -CO-CH$_2$-), 3.06-3.16 (m, 2H, -CH$_2$-CH$_2$-), 4.16-4.24 (m, 1H, S-CH$_2$), 7.02-7.64 (m, 10, Ar-H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ (ppm): 24.10, 34.23, 95.10, 120.51, 122.45, 123.46, 124.56, 125.33, 126.45, 128.11, 129.79, 131.50, 132.60, 133.46, 133.89, 134.68, 173.09, 191.45; MS (ESI, m/z, M$^+$): 379; Anal. calcd. For $C_{21}H_{14}ClNO_2S$: C, 66.40; H, 3.71; N, 3.69 %. Found: 66.53; H, 3.75; N, 3.73.

3′-(4-Methylphenyl)-spiro[acenaphthylene-1,2′-[1,3]-thiazine]-2,4′-(1H)-dione **(4c)**

^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 2.11(s, 3H, CH$_3$), 2.58-2.67 (m, 1H, -CO-CH$_2$-), 3.06-3.19 (m, 2H, -CH$_2$-CH$_2$-), 3.88-3.97 (m, 1H, S-CH$_2$), 7.12-7.84 (m, 10, Ar-H); ^{13}CNMR(100 MHz, DMSO-d$_6$) δ (ppm): 17.09, 23.72, 33.23, 93.60, 121.56, 123.06, 123.86, 124.66, 125.73, 126.75, 128.09, 129.59, 131.59, 132.69, 133.28, 134.56, 173.54, 191.25; MS (ESI, m/z, M$^+$) 359.10; Anal. calcd. for $C_{22}H_{17}NO_2S$: C, 73.51; H, 4.77; N, 3.90 %. Found: C, 73.65; H, 4.80; N, 3.93 %.

3′-(4-Bromophenyl)-spiro[acenaphthylene-1,2′-[1,3]-thiazine]-2,4′-(1H)-dione **(4d)**

^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 2.53–2.66 (m, 1H, -CO-CH$_2$-), 3.05–3.17 (m, 2H, -CH$_2$-CH$_2$-), 4.18–4.27 (m, 1H, S-CH$_2$-),

7.09–7.68 (m, 10, Ar-H); ^{13}CNMR(100 MHz, DMSO-d_6) δ(ppm): 23.43, 34.63, 94.66, 121.80, 122.86, 123.76, 124.86, 125.83, 126.65, 127.08, 129.19, 130.49, 131.79, 132.08, 133.68, 173.67, 190.75; MS (ESI, m/z, M^+): 379; Anal. calcd. For $C_{21}H_{14}BrNO_2S$: C, 59.44; H, 3.33; N, 3.30 %. Found: C, 59.58; H, 3.35; N, 3.32 %.

3′-(3-Fluorophenyl)-spiro[acenaphthylene-1,2′-[1,3]-thiazine]-2,4′-(1H)-dione **(4e)**

^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 2.52-2.65 (m, 1H, -CO-CH_2-), 3.11-3.21(m, 2H, -CH_2-CH_2-), 4.15–4.26 (m, 1H, S-CH_2-), 7.22–7.69 (m, 10, Ar-H); ^{13}CNMR (100 MHz, DMSO-d_6) δ(ppm): 24.62, 34.43, 93.50, 120.59, 122.86, 123.68, 124.89, 125.13, 125.95, 126.75, 127.56, 128.01, 129.79, 130.59, 131.67, 132.79, 133.08, 175.09, 192.85; MS (ESI, m/z, M^+): 365; Anal. calcd. For $C_{21}H_{14}FNO_2S$: C, 69.41; H, 3.88; N, 3.85 %. Found: C, 69.65; H, 3.91; N, 3.88 %.

3′-(4-Nitrophenyl)-spiro[acenaphthylene-1,2′-[1,3]-thiazine]-2,4′-(1H)-dione **(4f)**

^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 2.62–2.71 (m, 1H, -CO-CH_2-), 3.09–3.19 (m, 2H, -CH_2-CH_2-), 4.16–4.26 (m, 1H, S-CH_2-), 7.02–7.64 (m, 10, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 25.04, 34.63, 95.60, 121.50, 122.45, 123.16, 124.46, 125.13, 126.25, 128.01, 129.89, 130.59, 132.79, 133.08, 135.68, 134.56, 136.39, 174.09, 191.65; MS (ESI, m/z, M^+): 390; Anal. calcd. For $C_{21}H_{14}N_2O_4S$: C, 64.60; H, 3.61; N, 7.18 %. Found: C, 64.51; H, 3.58; N, 7.21%.

Conflict of interest:

The authors confirm that this article content has no conflict of interest.

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References

1. Newman, D. J.; Cragg G. M. Natural products as sources of new drugs over the last 25 years *J. Nat. Prod*. (**2007**) 70, 461-477.
2. Li, J. W. H.; Vederas J. C. Drug discovery and natural products: end of an era or an endless frontier? *Science* (**2009**) 325, 161-165.
3. Domling A; Ugi I. Multicomponent reactions with isocyanides. *Angew. Chem., Int. Ed.,* (**2000**) 39, 3168-3210.
4. Zhu, J.; Bienayme H. Eds. Multicomponent reactions: wiley-: weinheim, germany, **2005.**
5. Badshah, S. L; Naeem, A. A review on bioactive thiazine and benzothiazine derivatives: green synthesis methods and their medicinal importance and their references, *Molecules* (**2016**) 21, 1054-1074.
6. Sallal, Z. A. Synthesis and characterization of new oxazine, thiazine and pyarazole derived from chalcone. *Baghdad Science Journal* (**2014**), 11, 2.
7. Al-Khamees, H. A.; Bayomi, S. M.; Kandil, H. A.; El-Tahir, K. E. H. Synthesis and pharmacological screening of a new series of 3-(4-antipyryl)-2-arylthiazolidin-4-ones. *Eur. J. Med. Chem*. (**1990**) 25, 103-106.
8. Bano, M.; Barot, K. P.; Jain, S. V.; Ghate, M. D. Identification of 3-hydroxy-4(3,4-dihydro-3-oxo-2H-1,4-benzoxazin-4-yl)-2,2-dimethyldihydro-2H-benzopyran derivatives as potassium channel activators and anti-inflammatory agents. *Med. Chem. Res*. (**2015**) 24, 3008-3020.
9. Mitra, S.; Mukherjeeb, S.; Hajra, A. Peroxide-free Synthesis of Benzo[b][1,4]thiazine 1,1-dioxide and Its Antimicrobial Study. ***RSC Adv.***, (**2016**), **6**, 201-207.
10. Sathishkumar, M.; Sathiyanarayanan, K. I. Domino condensation–heterocyclisation reactions: iodine catalyzed four component synthesis of 1,3-thiazine. *RSC Adv*., (**2014**), 4, 8808-8811.
11. Kröger, D.; Brockmeyer, F.; Kahrs, C. Three-component reaction for a rapid access to underexplored 1,3-thiazine-2-thiones. ***Org. Biomol. Chem.***, (**2015**), **13**, 7223-7229.
12. Teng, H. L.; Huang, H.; Wang, C. J. Catalytic asymmetric construction of spiro(γ-butyrolactam-γ-butyrolactone) moieties through sequential reactions of cyclic imino esters with morita–baylis–hillman bromides. *Chem. Eur. J.* (**2012**) 18, 12614-12618.
13. Subba Reddy B. V.; Karthik, G.; Rajasekaran, T.; Antony, A.; Sridhar, B. $Rh_2(OAc)_4$ catalyzed substrate selective [4+2]/[2+2] cycloaddition of acylketenes: a highly chemo- and regioselective synthesis of spiro(oxindolyl)oxazinones

and β-lactams. *Tetrahedron Lett*. (**2012**) 53, 2396-2401.

14. Han, Y.; Wu, Q.; Sun, J.; Yan C. G. Synthesis of the functionalized spiro [indino-3,5'-pyrroline]- 2,2'-diones via three component reaction of arylamines, acetylenedicarboxylates, and isatins. *Tetrahedron* (**2012**) 68, 8539-8544.
15. Wei, A. C.; Ali, M. A.; Yoon, Y. K.; Ismail, R.; Choon, T. S.; Kumar, R. S. A facile three-component [3+2]-cycloaddition for the regioselective synthesis of highly functionalised dispiropyrrolidines acting as antimycobacterial agents. *Bioorg. Med. Chem. Letts*. (**2013**) 23, 1383-1386.
16. Kumar, R. R.; Perumal, S.; Manju, S. C.; Bhatt, P.; Yogeeswari P.; Sriram, D. An atom economic synthesis and antitubercular evaluation of novel spiro-cyclohexanones. *Bioorg. Med. Chem. Lett.* (**2009**) 19, 3461-3465.
17. Zheng, J.; Li, Y. Basic ionic liquid-catalyzed one-pot synthesis of the spiroacenaphthylene derivatives in water medium. *Mendeleev Commun.* (**2012**), 22, 148-149.
18. Lorimer, J. P.; Mason, T. J. Sonochemistry. Part 1-The physical aspects. *Chem. Soc. Rev.* (**1987**) 16, 239-274.
19. Mehrabi, H. Ultrasound-assisted synthesis of aromatic 1,2-diketones from oximinoketones under neutral conditions in aqueous media. *Ultrason. Sonochem*. (**2012**) 19, 125-129.
20. Lindström, U. M. Stereoselective organic reactions in water, *Chem. Rev*. (**2002**) 102, 2751-2772.
21. Butler R. N.; Coyne A. G. Water: Nature's reaction enforcer comparative effects for organic synthesis "in-water" and "on-water" *Chem. Rev*. (**2010**) 110, 6302-6337.
22. Breslow, R. Hydrophobic effects on simple organic reactions in water. *Acc. Chem. Res*., (**1991**) 24, 9-164.
23. Singh, R.; Ganaie, S. A. An eco-compatible synthesis of novel spiro acenaphthylene-1, 2′[1, 3]-thiazolidine]-2, 4′(1H)-diones using thiamine hydrochloride as efficient catalyst in aqueous medium, *Res Chem Intermed*. (**2017**) 43, 45-55.
24. Dandia, A.; Singh, R.; Joshi, J.; Maheshwari, S; Soni, P. Ultrasound promoted catalyst-free and selective synthesis of spiro [indole-3, 4′-pyrazolo [3, 4-e][1, 4] thiazepines] in aqueous media and evaluation of their anti-hyperglycemic activity. *RSC Adv.* (**2013**) 133, 18992-19001.
25. Dandia, A.; Singh, R.; Bhaskaran. S.; Samant, S. D, Versatile three component procedure for combinatorial synthesis of biologically relevant scaffold spiro[indole-thiazolidinones] under aqueous conditions. *Green Chem* (**2011**) 13, 1852-1859.
26. Wang, R.; Qian, W.; Bao, W. Imidazobenzothiazine and primidobenzothiazine derivatives synthesis via an aliphatic S_N2 substitution/Cu(I) catalyzed ullmann coupling cascade process Tetrahedron *Lett*. (**2010**) 53, 442-445.
27. Gong, K.; Fang, D.; Wang, H-L.; Zhou X-Li; Liu Z-L., The one-pot synthesis of 14-alkyl- or aryl-14*H*-dibenzo[*a,j*] xanthenes catalyzed by task-specific ionic liquid. *Dyes Pigm* (**2009**) 80, 30-33.
28. Paul, S.; Das, A. R. Dual role of the polymer supported catalyst PEG-OSO_3H in aqueous reaction medium: synthesis of highly substituted structurally diversified coumarin and uracil fused spirooxindoles. *Tetrahedron Lett.* (**2013**) 54, 1149-1154.
29. Rajopadhye, M.; Popp, F. D. Synthesis of spiro[3*H*-indole-3,2′-tetrahydro-1,3-thiazine]-2,4′(1*H*)-diones. *J. Heterocycl. Chem*. (**1985**) 22, 93-96.
30. **Joshi, K. C.; Dandia, A.; Ahmed. N.; Studies in spiroheterocycles: Part IX: A new elegant synthesis and reactions of some novel fluorine-containing spiro[3*h*-indole-3,2'-tetrahydro-1,3-thiazine]-2,4'(1*H*)-diones.** *Heterocycles* **(1986) 24, 2479-2485.**
31. Mason, T. J.; Lorimer, J. P. Sonochemistry: theory, application and uses of ultrasound in chemistry, John Wiley and Sons, New York, 1988
32. Wang, X.; Quan, Z.; Wang, F.; Wang, M.; Zhang, Z.; Li, Z.; PEG-OSO_3H as catalyst for 3,4-dihydropyrimidones via biginelli reaction under microwave and solvent-free conditions *Synth Commun* (**2006**) 36: 451-456.