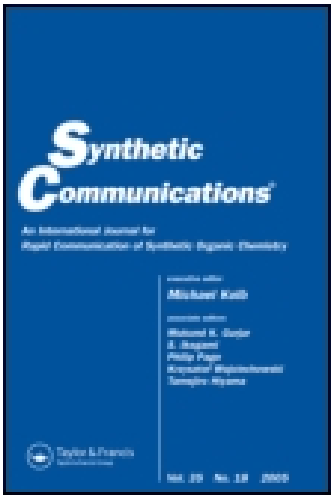

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Zirconium Tetrakis(dodecyl Sulfate) [$Zr(DS)_4$] as an Efficient Lewis Acid-Surfactant Combined Catalyst for the Synthesis of Quinoxaline Derivatives in Aqueous Media

Alireza Hasaninejad [a] , Abdolkarim Zare [b] , Mohammad Ali Zolfigol [c] & Mohsen Shekouhy [a]

[a] Department of Chemistry , Faculty of Sciences, Persian Gulf University , Bushehr, Iran

[b] Department of Chemistry , Payame Noor University (PNU) , Bushehr, Iran

[c] Faculty of Chemistry , Bu-Ali Sina University , Hamedan, Iran

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Zirconium Tetrakis(dodecyl Sulfate) [$Zr(DS)_4$] as an Efficient Lewis Acid–Surfactant Combined Catalyst for the Synthesis of Quinoxaline Derivatives in Aqueous Media

Alireza Hasaninejad,[1] Abdolkarim Zare,[2] Mohammad Ali Zolfigol,[3] and Mohsen Shekouhy[1]

[1]Department of Chemistry, Faculty of Sciences, Persian Gulf University, Bushehr, Iran
[2]Department of Chemistry, Payame Noor University (PNU), Bushehr, Iran
[3]Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

Abstract: Zirconium tetrakis(dodecyl sulfate) [$Zr(DS)_4$] efficiently catalyzes the synthesis of quinoxaline derivatives via the condensation of 1,2-diamines with 1,2-diketones in H_2O as a green media at room temperature. Using this method, the title compounds are produced in good to excellent yields and relatively short reaction times.

Keywords: 1,2-Diamine, 1,2-diketone, green chemistry, H_2O, quinoxaline, zirconium tetrakis(dodecyl sulfate)

The development of simple and efficient chemical processes or methodologies for the synthesis of biologically active compounds in water is one of the major challenges for chemists, because water is a safe, very cheap, readily available, and environmentally benign solvent.[1] Although today's environmental consciousness imposes the use of water as a

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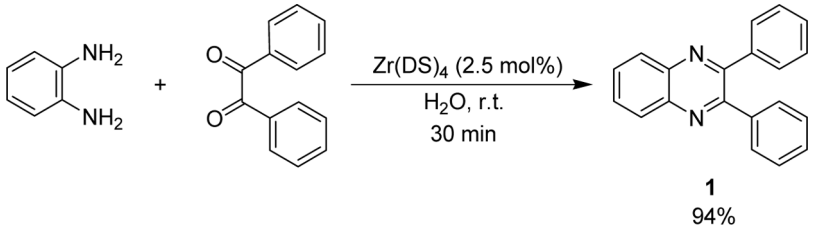
Address correspondence to Alireza Hasaninejad, Department of Chemistry, Faculty of Sciences, Persian Gulf University, Bushehr 75169, Iran. E-mail: ahassaninejad@yahoo.com or Abdolkarim Zare, Department of Chemistry, Payame Noor University (PNU), Bushehr 1698, Iran. E-mail: abdolkarimzare@yahoo.com

solvent on both industrial and academic chemists, organic solvents are still used instead of water for mainly two reasons. First, most organic substances are insoluble in water, and as a result, water does not function as a reaction medium. Second, many reactive substrates, reagents, and catalysts are decomposed or deactivated by water. Some of these problems were solved with the discovery of water-tolerant Lewis acids by Kobayashi et al.[2] After that, the successful applications of some Lewis acid–surfactant combined catalysts (LASC) such as scandium tris(dodecyl sulfate),[3] aluminum tris(dodecyl sulfate),[4] and the other Metal dodecyl sulfates[5] in organic functional group transformations in aqueous media have been reported.

Quinoxaline derivatives are an important class of nitrogen-containing heterocycles and their importance has been reported in the literature.[6,7] For example, they show very interesting pharmacological properties such as antiprotozoal,[7a] antibiotic,[7b] antibacterial,[7c] antifungal,[7d] and anticancer activities.[7e,f] Several synthetic routes have been developed for the synthesis of quinoxaline derivatives[8]; however, the most common method is the condensation of 1,2-diamines with 1,2-dicarbonyl compounds in the presence of catalysts such as ceric(IV) ammonium nitrate,[9a] iodine in DMSO,[9b] sulfamic acid,[9c] $Yb(OTf)_3$,[9d] oxalic acid,[9e] *o*-iodoxybenzoic acid,[9f] $H_6P_2W_{18}O_{62}{\cdot}24H_2O$,[9g] $KHSO_4$,[9h] and polyaniline-sulfate salt.[9i] It is worth noting that the methods that have been established for the preparation of quinoxaline derivatives are associated with one or more of the following drawbacks: (i) the need for anhydrous conditions, (ii) the use of expensive catalysts, (iii) unsatisfactory yields, (iv) long reaction times, (v) harsh reaction conditions, (vi) inefficiency of the method when aliphatic or aryl 1,2-diamines with electron-withdrawing substituents are applied in the condensation reaction, and (vii) no agreement with the green chemistry protocols by the use of volatile organic solvents. Furthermore, some methods need cumbersome experimental and multistep procedures. Therefore, development of an efficient, simple, cheap, safe, and green method for the preparation of quinoxalines is desirable. As part of our program to develop more efficient and environmentally benign methods for organic syntheses using economic and ecofriendly catalysts,[9e,10] in this work, we report a facile, efficient, and practical method for the preparation of quinoxaline derivatives from 1,2-diamines and 1,2-diketones using $Zr(DS)_4$ in water at extremely mild reaction conditions (Scheme 1). It is important to note that this method has none of the previously mentioned disadvantages at all.

At first, we studied the reaction of 1,2-benzene diamine (1 mmol) with benzil (1 mmol) in H_2O (40 mL) to optimize the reaction conditions with respect to molar ratio of $Zr(DS)_4$ to the substrate and temperature (Scheme 1, Table 1). We found that 2.5 mol% of $Zr(DS)_4$ was sufficient to



Scheme 1. The condensation of 1,2-benzene diamine with benzil.

produce the desired quinoxaline in 94% yield within 30 min at room temperature (Table 1, entry 4).

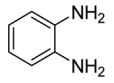
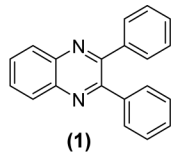
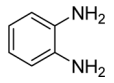
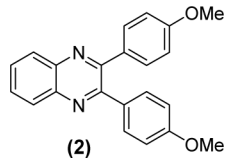
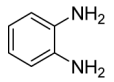
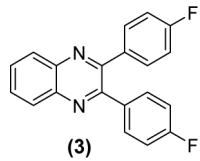
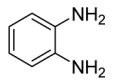
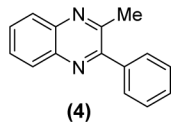
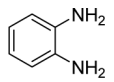
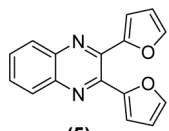
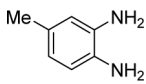
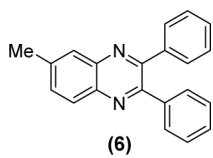
Then, the generality and the scope of the procedure was evaluated by the reaction of a number of aryl and alkyl 1,2-diamines with structurally and electronically diverse 1,2-diketones. The results are summarized in Table 2. As it can be seen from Table 2, all reactions proceeded efficiently and the desired products were produced in good to excellent yields in relatively short reaction times. We investigated the effect of electron-releasing and electron-withdrawing substituents on the aromatic ring of aryl 1,2-diamines on the reaction. As Table 2 indicates, electron-releasing groups had no significant effect on the reaction results (Table 2, entries 6–11); however, electron-withdrawing substituents decreased the yields and increased the reaction times (Table 2, entries 12 and 13). Moreover, harsher reaction conditions were needed in these cases. The results also showed that the structure and the electronic properties of the aromatic ring of 1,2-diketones had negligible effect on the yields and the reaction times. Aliphatic 1,2-diamines also afforded the corresponding quinoxalines in high yields but in harsher reaction conditions (Table 2, entries 15 and 16).

Table 1. Reaction of benzene-1,2-diamine with benzil in the presence of different molar ratios of $Zr(DS)_4$ at different temperatures

Entry	Molar ratio of $Zr(DS)_4$ (mol%)	Temperature (°C)	Time (min)	Yield[a] (%)
1	1	rt	90	42
2	1.5	rt	80	71
3	2	rt	50	91
4	2.5	rt	30	94
5	3	rt	30	94
6	2.5	40	25	95
7	2.5	60	15	93

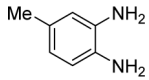
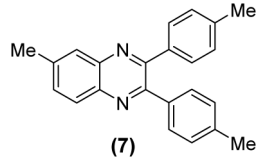
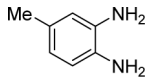
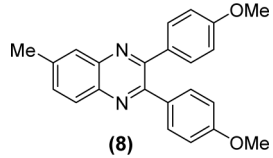
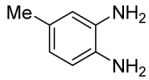
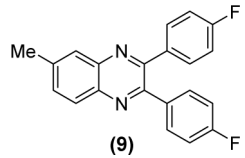
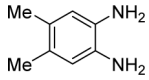
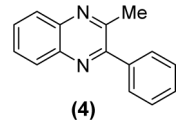
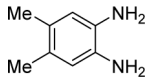
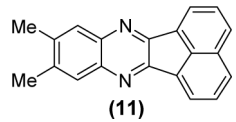
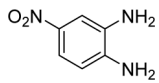
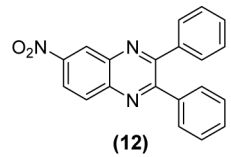
[a]Isolated yield.

Table 2. Synthesis of quinoxalines via the condensation of 1,2-diamines with 1,2-diketones using $Zr(DS)_4$ in H_2O at room temperature

Entry	1,2-Diamine	Product	Time (min)	Yield[a] (%)	Mp (°C) (lit.)
1		 (1)	30	94	129–130 (130–131)[9e]
2		 (2)	35	93	149–151 (148–150)[9e]
3		 (3)	30	95	132–134 (135–137)[9f]
4		 (4)	60	87	55–57 (56)[9a]
5		 (5)	35	89	127–129 (131)[9a]
6		 (6)	25	96	116–118 (117–118)[9f]

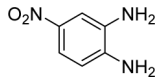
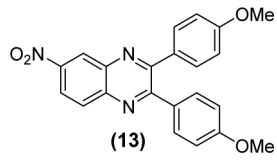
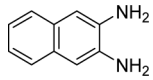
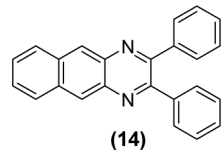
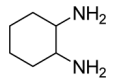
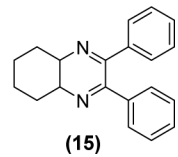
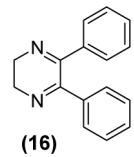
(*Continued*)

Table 2. Continued

Entry	1,2-Diamine	Product	Time (min)	Yield[a] (%)	Mp (°C) (lit.)
7		 **(7)**	35	95	139–140 (137)[9a]
8		 **(8)**	35	93	128–130 (125–127)[9f]
9		 **(9)**	25	94	163–165 (165–167)[9f]
10		 **(4)**	20	93	175–177 (172)[9c]
11		 **(11)**	15	94	302–304 (304–306)[9e]
12[b]		 **(12)**	90	86	190–192 (193–194)[9f]

(*Continued*)

Table 2. Continued

Entry	1,2-Diamine	Product	Time (min)	Yield[a] (%)	Mp (°C) (lit.)
13[b]		 **(13)**	110	83	188–190 (192–194)[9f]
14		 **(14)**	30	93	184–186 (187–188)[9a]
15[b]		 **(15)**	50	85	168–170 (167)[9c]
16[b]		 **(16)**	50	87	155–157 (158)[9c]

[a]Isolated yield.
[b]This reaction was carried out under reflux conditions.

Ease of recycling of the catalyst is one of the advantages of our method. For the reaction of benzene-1,2-diamine with benzil, no significant loss of the product yield was observed when $Zr(DS)_4$ was reused after five times (please see Table 3).

In summary, we have introduced a highly efficient catalyst for the condensation of 1,2-diamines with 1,2-diketones in aqueous media. The promising points for the presented methodology are efficiency, generality, high yield, short reaction time, ease of handling of the catalyst, cleaner reaction profile, ease of product isolation, simplicity, potential for

Table 3. Reaction of benzene-1,2-diamine with benzil in the presence of recycled $Zr(DS)_4$

Entry	Cycle	Time (min)	Yield[a] (%)
1	—	30	94
2	1	30	95
3	2	30	93
4	3	35	92
5	4	45	94
6	5	50	89

[a]Isolated yield.

recycling of the catalyst, and finally agreement with the green chemistry protocols, which all make it a useful and attractive process for the synthesis of quinoxaline derivatives.

EXPERIMENTAL

All chemicals were purchased from Merck, Fluka, or Aldrich chemical companies. All known compounds were identified by comparison of their melting points and spectral data with those in the authentic samples. ^1H NMR (250 MHz) and ^{13}C NMR (62.5 MHz) were run on a Bruker Avance DPX-250, FT-NMR spectrometer (δ in ppm). Mass spectra were recorded on a Shimadzu GC MS-QP 1000 EX apparatus. Microanalyses were performed on a Perkin-Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

General Procedure for the Synthesis of Quinoxaline Derivatives

A mixture of 1,2-diamine (1 mmol) and 1,2-diketone (1 mmol) was added to a suspension of $Zr(DS)_4$ (0.029 g, 0.025 mmol, 2.5 mol%) in water (40 mL), and the resulting mixture was stirred at room temperature for the times reported in Table 2. Then, EtOAc (2×10 mL) was added to the reaction mixture, and the organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the crude product was purified by recrystallization from EtOH. For recovering the catalyst, aqueous phase and organic phase were centrifuged together which a tri-phase system (organic, aqueous, and solid phase) was obtained. The solid phase (catalyst) was separated and dried under reduced pressure and reused.

Selected Spectral Data of the Products

2,3-Diphenylquinoxaline **(1)**

White solid; mp 129–130 °C (lit.[9e] mp 130–131 °C); ^{1}H NMR ($CDCl_3$): $\delta = 7.29$–7.33 (m, 6H), 7.51 (m, 4H), 7.77 (m, 2H), 8.21 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 128.1$, 128.7, 129.1, 129.9, 131.0, 139.6, 141.7, 153.2; MS: $m/z = 282$ (M^+); Anal. calcd. for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 85.31; H, 4.83; N, 10.11.

9,10-Dimethylacenaphtho[1,2-*b*]quinoxaline (11)

Yellow solid; mp 302–304 °C (lit.[9e] mp 304–306 °C); ^{1}H NMR ($CDCl_3$): $\delta = 2.51$ (s, 6H), 7.78 (m, 2H), 7.89 (s, 2H), 8.03 (m, 2H), 8.34 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 20.3$, 121.5, 127.8, 128.0, 128.6, 128.9, 129.1, 139.5, 140.00, 148.5, 153.3; MS: $m/z = 282$ (M^+). Anal. calcd. for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 84.90; H, 5.24; N, 10.13.

2,3-Diphenylbenzo[*g*]quinoxaline (14)

Yellow solid; mp 184–186 °C (lit.[9a] mp 187–188 °C); ^{1}H NMR ($CDC1_3$): $\delta = 7.30$–7.34 (m, 6H), 7.48–7.53 (m, 6H), 8.03 (m, 2H), 8.59 (s, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 126.5$, 127.4, 128.0, 128.3, 129.0, 129.7, 133.8, 136.9, 139.4, 153.7; MS: $m/z = 332$ (M^+). Anal. calcd. for $C_{24}H_{16}N_2$: C, 86.72; H, 4.85; N, 8.43. Found: C, 86.93; H, 4.70; N, 8.56.

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REFERENCES

1. (a) Grieco, P. A. *Organic Synthesis in Water*; Blackie Academic and Professional: London, 1998; (b) Anastas, P. T.; Williamson, T. C. (Eds). *Green Chemistry* (ACS Symposium Series 626), American Chemical Society: Washington, DC, 1996; (c) Li, C.-J.; Chan, T.-H. *Organic Reactions in Aqueous Media*; Wiley: New York, 1997; (d) Anastas, P.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press, Oxford, 1998; (e) Li, C.-J. Organic reactions in aqueous media with a focus on carbon–carbon bond formations: A decade update. *Chem. Rev.* **2005**, *105*, 3095–3165.

2. (a) Kobayashi, S.; Manabe, K.; Nagayama, S. *Modern Carbonyl Chemistry*; J. Otera (Ed.); Wiley-VCH: Weinheim, 2000; (b) Manabe, K.; Mori, Y.; Wakabayashi, T.; Nagayama, S.; Kobayashi, S. Organic synthesis inside particles in water: Lewis acid–surfactant combined catalysts for organic reactions in water using colloidal dispersions as reaction media. *J. Am. Chem. Soc.* **2000**, *122*, 7202–7207; (c) Kobayashi, S.; Nagayama, S.; Busujima, T. Lewis acid catalysts stable in water: Correlation between catalytic activity in water and hydrolysis constants and exchange rate constants for substitution of inner-sphere water ligands. *J. Am. Chem. Soc*. **1998**, *120*, 8287–8288.
3. (a) Mnabe, K.; Aoyama, N.; Kobayashi, S. Friedel-Crafts-type Conjugate addition of indoles using a Lewis acid–surfactant combined catalyst in water. *Adv. Synth. Catal*. **2001**, *343*, 174–176; (b) Mori, Y.; Kakumoto, K.; Manabe, K.; Kobayashi, S. Michael reactions in water using Lewis acid–surfactant combined catalysts. *Tetrahedron Lett.* **2000**, *41*, 3107–3111.
4. (a) Firouzabadi, H.; Iranpoor, N.; Nowrouzi, F. The facile and efficient Michael addition of indoles and pyrrole to α,ß-unsaturated electron-deficient compounds catalyzed by aluminium dodecyl sulfate trihydrate $[Al(DS)_3] \cdot 3H_2O$ in water. *Chem.Commun*. **2005**, 789–791; (b)Firouzabadi, H.; Iranpoor, N.; Khoshnood, A. Aluminum tris(dodecyl sulfate) trihydrate $Al(DS)_3 \cdot 3H_2O$ as an efficient Lewis acid–surfactant combined catalyst for organic reactions in water: Efficient conversion of epoxides to thiiranes and to amino alcohols at room temperature. *J.Mol.Cat.A:Chem*. **2007**, *274*, 109–115.
5. Zolfigol, M. A.; Salehi, P.; Ghaderi, A.; Shiri, M.; Tanbakouchian, Z. An eco-friendly procedure for the synthesis of polysubstituted quinolines under aqueous media. *J. Mol. Cat. A: Chem*. **2006**, *259*, 253–258.
6. (a) Brock, E. D.; Lewis, D. M.; Yousaf, T. I.; Harper, H. H. Reactive dyes and their use. WO 9951688, 1999; (b) Thomas, K. R.; Marappan,V.; Jiann, T. L.; Chang-Hao, C.; Yu-ai, T. Chromophore-labeled quinoxaline derivatives as efficient electroluminescent materials. *Chem. Mater.* **2005**, *17*, 1860–1866; (c) Dailey, S.; Feast, J. W.; Peace, R. J.; Saga, R. C.; Till, S.; Wood, E. L. Synthesis and device characterisation of side-chain polymer electron transport materials for organic semiconductor applications. *J. Mater. Chem*. **2001**, *11*, 2238–2243; (d) Jonathan, L. S.; Hiromitsu, M.; Toshisha, M.; Vincent, M. L.; Hiroyuki, F. Quinoxaline-oligopyrroles: Improved pyrrole-based anion receptors. *Chem. Commun.* **2002**, 862–863.
7. Hui, X.; Desrivot, J.; Bories, C.; Loiseau, P. M.; Franck, X.; Hocquemiller, R.; Figadere, B. Synthesis and antiprotozoal activity of some new synthetic substituted quinoxalines. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 815–820; (b) Dell, A.; William, D. H.; Morris, H. R.; Smith, G. A.; Feeney, J. Roberts, G. C. K. Structure revision of the antibiotic echinomycin. *J. Am. Chem. Soc.* **1975**, *97*, 2497–2502; (c) Jaso, A.; Zarranz, B.; Aldana, I.; Monge, A. Synthesis of new quinoxaline-2-carboxylate1, 4-dioxide derivatives as anti-*Mycobacterium tuberculosis* agents. *J. Med. Chem.* **2005**, *48*, 2019–2025; (d) Aguirre, G.; Cerecetto, H.; DiMaio, R.; Gonzales, M.; Alfaro, M. E. M. A.; Jaso, A.; Zarranz, B.; Ortega, M. A.; Aldana, I.; Monge-Vega,

A. Quinoxaline N,N′-dioxide derivatives and related compounds as growth in hibitors of *Trypanosoma cruzi*: Structure–activity relationships. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 3835–3839; (e) Gali-Muhtasib, H. U.; Diab-Assaf, M.; Haddadin, M. J. Quinoxaline 1,4-dioxides induce G_2/M cell cycle arrest and apoptosis in human colon cancer cells. *Cancer Chemoth. Pharm*. **2005**, *55*, 369–378; (f) Toshima, K.; Ozawa, T.; Kimura, T.; Matsumara, S. The significant effect of the carbohydrate structures on the DNA photocleavage of the quinoxaline-carbohydrate hybrids. *Bioorg. Med. Chem. Lett*. **2004**, *14*, 2777–2779.

8. (a) Venkatesh, C.; Singh, B.; Mahata, P. K.; Ila, H.; Junjappa, H. Heteroannulation of nitroketene N,S-arylaminoacetals with $POCl_3$: A novel highly regioselective synthesis of unsymmetrical 2,3-substituted quinoxalines. *Org. Lett*. **2005**, *7*, 2169–2172; (b) Xekoukoulotakis, N. P.; Hadjiantonious-Maroulis, C. P.; Maroulis, A. J. Synthesis of quinoxalines by cyclization of α-arylimino oximes of a-dicarbonyl compounds. *Tetrahedron Lett.* **2000**, *41*, 10299–10302; (c) Antoniotti, S.; Duñach, E. Direct and catalytic synthesis of quinoxaline derivatives from epoxides and ene-1,2-diamines. *Tetrahedron-Lett*. **2002**, *43*, 3971–3973; (d) Robinson, R. S.; Taylor, R. J. K. Quinoxaline synthesis from α-hydroxy ketones via a tandem oxidation process using catalysed aerobic oxidation. *Synlett* **2005**, 1003–1005; (e) Gopaland, D. V.; Subrahmanyam, M. Single-stepsynthesis of 2-methylquinoxaline from 1,2-phenylenediamine and 1,2-propanediol over modified HY zeolites. *Catal. Commun*. **2001**, 219–223; (f) Staszewska, A.; Stefanowicz, P.; Szewczuk, Z. Direct solid-phase synthesis of quinoxaline-containing peptides. *Tetrahedron Lett.* **2005**, *46*, 5525–5528; (g) Das, B.; Venkateswarlu, K.; Suneel, K.; Majhi, A. An efficient and convenient protocol for the synthesis of quinoxalines and dihydropyrazines via cyclization–oxidation processes using $HClO_4 \cdot SiO_2$ as a heterogeneous recyclable catalyst. *TetrahedronLett*. **2007**, *48*, 5371–5374.
9. (a) More, S. V.; Sastry, M. N. V.; Yao, C.-F. Cerium (IV) ammonium nitrate (CAN) as a catalyst in tap water: A simple, proficient and green approach for the synthesis of quinoxalines. *Green Chem*. **2006**, *8*, 91–95; (b) Bhosale, R. S.; Sarda, S. R.; Ardhapure, S. S.; Jadhav, W. N.; Bhusare, S. R.; Pawar, R. P. An efficient protocol for the synthesis of quinoxaline derivatives at room temperature using molecular iodine as the catalyst. *Tetra hedron Lett*. **2005**, *46*, 7183–7186; (c) Darabi, H. R.; Mohandessi, S.; Aghapoor, K.; Mohsenzadeh, F. A recyclable and highly effective sulfamic acid/MeOH catalytic system for the synthesis of quinoxalines at room temperature. *Catal Commun*. **2007**, 389–392; (d) Wang, L.; Liu, J.; Tian, H.; Qian, C. Ytterbium triflate catalyzed heterocyclization of 1,2-phenylenediamines and alkyl oxalates under solvent-free conditions via Phillips reaction: A facile synthesis of quinoxaline-2,3-diones derivatives. *Synth. Commun*. **2004**, *34*, 1349–1357; (e) Hasaninejad, A.; Zare, A.; Mohammadizadeh, M. R.; Shekouhy, M. Oxalic acid as an efficient, cheap, and reusable catalyst for the preparation of quinoxalines via condensation of 1,2-diamines with α-diketones at room temperature. *Arkivoc* **2008**, *8*, 28–35; (f) Heravi, M. M.; Bakhtiari, K.; Tehrani, M. H.; Javadi, N. M.; Oskooie, H. A. Facile

synthesis of quinoxaline derivatives using *o*-iodoxybenzoic acid (IBX) at room temperature. *Arkivoc* **2006**, *16*, 16–22; (g) Heravi, M. M.; Bakhtiari, K.; Bamoharram, F. F.; Tehrani, M. H. Wells– Dawson type heteropolyacid catalyzed synthesis of quinoxaline derivatives at room temperature. *Monatsh. Chem*. **2007**, *138*, 465–467; (h) Oskooie, H. A.; Heravi, M. M.; Bakhtiari, K.; Taheri, S. An efficient and facile synthesis of quinoxaline derivatives catalyzed by $KHSO_4$ at room temperature. *Monatsh. Chem*. **2007**, *138*, 875–877; (i) Srinivas, C.; Kumar, C. N. S. S. P.; Rao, V. J.; Palaniappan, S. Efficient, convenient and reusable polyaniline–sulfate salt catalyst for the synthesis of quinoxaline derivatives. *J. Mol. Cat. A: Chem*. **2006**, *265*, 228–231.

10. Hasaninejad, A.; Parhami, A.; Zare, A.; Khalafi-Nezhad, A.; Nasrolahi Shirazi, A.; Moosavi Zare, A. R. Magnesium sulfate as an efficient and very cheap reagent for the preparation of bis(indolyl)methanes. *Polish J. Chem.*. **2008**, *82*, 565–569; (b) Zare, A.; Hasaninejad, A.; Khalafi-Nezhad, A.; Parhami, A.; Moosavi Zare, A. R. A Solvent less protocol for the Michael addition of aromatic amidest to α,β-unsaturated esters promoted by microwave irradiation. *J. Iran. Chem. Soc*. **2008**, *5*, 100–105; (c) Khalafi-Nezhad, A.; Parhami, A.; Zare, A.; Moosavi Zare, A. R.; Hasaninejad, A.; Panahi, F. Trityl chloride as a novel and efficient organic catalyst for room temperature preparation of bis(indolyl)methanes under solvent-free conditions in neutral Media. *Synthesis* **2008**, 617–621; (d) Hasaninejad, A.; Zare, A.; Sharghi, H.; Shekouhy, M. P_2O_5/SiO_2: An efficient, green and heterogeneous catalytic system for the solvent-free synthesis of *N*-sulfonyl imines. *Arkivoc* **2008**, *11*, 64–74; (e) Zare, A.; Hasaninejad, A.; Beyzavi, M. H.; Parhami, A.; Moosavi Zare, A. R.; Khalafi-Nezhad, A.; Sharghi, H. Zinc oxide–tetrabutylammonium bromide tandem as a highly efficient, green, and reusable catalyst for Michael addition of pyrimidine and purine nucleobases to α,β-unsaturated esters under solvent-free conditions. *Can. J. Chem*. **2008**, *86*, 317–324.