

Application of Sulfonic Acid Functionalized Nanoporous Silica (SBA-Pr-SO₃H) for One-Pot Synthesis of Quinoxaline Derivatives

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Abstract

Sulfonic acid functionalized SBA-15 (SBA-Pr-SO₃H) with pore size 6 nm was proved to be an efficient heterogeneous nanoporous solid acid catalyst in the synthesis of quinoxaline derivatives from the reaction of *o*-Phenylenediamines with 1, 2-diketone compounds in very good yields.

Keywords: One pot synthesis, Quinoxaline derivatives, SBA-Pr-SO₃H, Nanoporous solid acid catalyst

1. Introduction

Quinoxalines exhibit a wide range of biological activities. In the core part of many agrochemicals and pharmaceuticals were found quinoxaline ring (Sakata *et al.* 1988; Sato *et al.* 1996; Seitz *et al.* 2002; Gazit *et al.* 1996). Similarly, it was found that quinoxaline ring also exists in antibiotics, such as actinomycin, levomycin, and echinomycin (Brown *et al.* 2004). Its derivatives have been used as anti-viral (Lindsley *et al.* 2005) and anticancer agents (Loriga *et al.* 1997). In addition, they are used in dyes (Katoh *et al.* 2000) and organic semiconductors (Dailey *et al.* 2001). In the literature, different methods for the preparation of quinoxaline derivatives have been published (Porter *et al.* 1984). The general method for the synthesis of quinoxalines is the condensation of aryl 1, 2-diamines with 1, 2-dicarbonyl compounds in refluxing ethanol in the presence of acetic acid (Brown *et al.* 2004). The yields of products were not good. Improved methods have been reported using the different catalysts including I₂ (Bhosale *et al.* 2005, More *et al.* 2005), SA (Darabi *et al.* 2007), Montmorillonite K-10 (Huang *et al.* 2008), polyaniline-sulfate salt (Srinivas *et al.* 2007), H₆P₂W₁₈O₆₂. 24H₂O (Heravi *et al.* 2007), InCl₃ (Hazarika *et al.* 2007), MnCl₂ (Heravi *et al.* 2008), CuSO₄.5H₂O (Heravi *et al.* 2007), Zn[(L)proline] (Heravi *et al.* 2007), CAN (More *et al.* 2006), Ga(OTf)₃ (Cai *et al.* 2008), PEG-400 (Zhang *et al.* 2010), Pd(OAc)₂ (Robinson *et al.* 2005), MnO₂ (Raw *et al.* 2003), keggin heteropoly acid (Huang *et al.* 2009), and IBX (Heravi *et al.* 2006) have been explored. In continuation of our studies (Mohammadi *et al.* 2008, 2009), on the application of nanoporous heterogeneous solid catalyst to organic synthesis, in this paper we want to report an efficient method for the preparation of quinoxaline derivatives using SBA-Pr-SO₃H as a nanoporous heterogeneous acid catalyst. There are only a few reports about the application of several types of sulfonic acid functionalized ordered mesoporous silicas as nano acid catalyst in chemical transformations (Van Rhijn *et al.* 1998, Das *et al.* 2006). For example, SBA-Pr-SO₃H has been used in the synthesis of chromenes from chromanols (Kureshy *et al.* 2009), and the von Pechmann Reaction (Karimi *et al.* 2008).

The high ordered nanoporous silica, such as MCM-41 (Beck *et al.* 1992), LUS-1 (Reinert *et al.* 2003, Bonneviot *et al.* 2001) and SBA-15 (Zhao *et al.* 1998) are unique inorganic solid supports that have very high surface area with controllable pore sizes between 2 to 30 nm. They can be used as catalysts (Trong On *et al.* 2001, Mohammadi *et al.* 2007), for the preconcentration of metals (Ganjali *et al.* 2006, 2004, 2006), and as modified carbon electrodes (Badiei *et al.* 2005, Zhang *et al.* 2006, Walcarius *et al.* 1999). The SBA-15 is new nanoporous silica with hexagonal structure, large pore, high surface area, high thermal stability and also diffusion free due to thicker pore walls and larger pore

size respectively. This can be prepared by using commercially available triblock copolymer Pluronic P126 as a structure directing agent (Zhao *et al.* 1998). Integration of acidic functional groups (e.g., $-\text{SO}_3\text{H}$) into SBA-15 has been explored to produce promising solid acids. The sulfonic acid functionalized SBA-15 were usually synthesized through direct synthesis or post-grafting (Lim *et al.* 1998, Wight *et al.* 2002).

2. Experimental section

Characterization

IR spectra were recorded from KBr disk using a FT-IR Bruker Tensor 27 instrument. Melting points were measured by using the capillary tube method with an electro thermal 9200 apparatus. The ^1H NMR (250 MHz) was run on a Bruker DPX, 250 MHz. Weight change curve in nitrogen was measured on a TA instrument of TGA Q50 V6.3 with maximum heating rate of $20^\circ\text{C}/\text{min}$. Nitrogen adsorption and desorption isotherms were measured at -196°C using a Japan Belsorb II system after the samples were vacuum dried at 150°C overnight.

2.1 Preparation of SBA-15

The synthesis of SBA-15 was carried out in accordance to the earlier reports (Zhao *et al.* 1998). In a typical synthesis batch, triblock copolymer surfactant as a template ($\text{P123} = \text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M_{ac}=5800$) (4.0 g) was dissolved in 30 g of water and 120 g of 2 M HCl solution. Then, TEOS (tetraethylorthosilicate) (8.50 g) was added to reaction mixture which was stirred for 8 h at 40°C . The resulting mixture was transferred into a Teflon-lined stainless steel autoclave and kept at 100°C for 20 h without stirring. The gel composition P123: HCl: H_2O : TEOS was 0.0168 : 5.854 : 162.681 : 1 in molar ratio. After cooling down to room temperature, the product was filtered, washed with distilled water and dried overnight at 60°C in air. The as-synthesized sample was calcinated at 550°C for 6 h in air atmosphere to remove the template.

2.2 Functionalization of the SBA-15 by organic groups

Functionalization of the SBA-15 catalyst was schematically shown in Fig. 1. The calcinated SBA-15 (2 g) and (3-mercaptopropyl)trimethoxysilane (10 ml) in dry toluene (20 ml) were refluxed for 24 h. The product was filtered and extracted for 6h in CH_2Cl_2 using a soxhlet apparatus, then dried under vacuum. The solid product was oxidized with H_2O_2 (excess) and one drop of H_2SO_4 in methanol (20 ml) for 24 h at rt and then the mixture was filtered and washed with H_2O , and acetone. The modified SBA-15-Pr- SO_3H was dried and used as nanoporous solid acid catalyst in the following reaction.

2.3 General procedure for the preparation of quinoxaline derivatives

The SBA-Pr- SO_3H (0.02 g) was activated in vacuum at 100°C and then after cooling to room temperature, 1,2-dicarbonyl (1 mmol), aromatic 1,2-diamine (1 mmol), dichloromethane (5 ml) was added to the catalyst. The mixture of reaction was stirred at the room temperature. The progress of reaction was monitored by TLC. The reaction mixture was filtered in order to recover the catalyst and the filtrate was evaporated on vacuum to obtain the crude product which is recrystallized from ethanol to afford pure quinoxaline **3**. The catalyst was washed subsequently with diluted acid solution, distilled water and then acetone, dried under vacuum and re-used for several times without loss of significant activity.

2.4 Spectral Data for Selected Products

3a: 2, 3-Diphenyl-quinoxaline, White solid; m.p: 128-129 $^\circ\text{C}$; **IR (KBr, cm^{-1}):** ν_{max} = 3054, 1544, 1343, 767, 730 cm^{-1} . **^1H NMR (250 MHz, CDCl_3):** δ = 7.42-7.53 (m, 6H), 7.61-7.67 (m, 4H), 7.87-7.94 (m, 2H), 8.28-8.34 (m, 2H) ppm. **MS (m/e):** 282 (M^+), 205, 179, 156, 140, 76, 50.

3b: 6-Nitro- 2, 3-diphenylquinoxaline; Light brown solid; m.p: 101-193 $^\circ\text{C}$; **IR (KBr, cm^{-1}):** ν_{max} = 3059, 2923, 1522, 1342, 697 cm^{-1} . **^1H NMR (250 MHz, CDCl_3):** δ (ppm) = 9.2 (d, 1H), 8.53 (dd, 1H), 8.39 (d, 1H), 7.6 (m, 4H), 7.42 (m, 6H). **MS (m/e):** 327 (M^+), 297, 281, 224, 207, 178, 140, 75, 51.

3c: 6-Methyl-2, 3-diphenylquinoxaline; Light yellow solid; m.p: 117-118 $^\circ\text{C}$; **IR (KBr, cm^{-1}):** ν_{max} = 3055, 2921, 1617, 1486, 1341, 752, 699 cm^{-1} . **^1H NMR (250 MHz, CDCl_3):** δ (ppm) = 8.07 (d, 1H), 7.94 (s, 1H), 7.57-7.61 (dd, 1H), 7.48-7.52 (m, 4H), 7.29-7.35 (m, 6H), 2.35 (s, 3H, CH_3). **MS (m/e):** 296 (M^+), 219, 192, 165, 89.

3d: 2, 3- Bis(4-methoxy-phenyl)-6-nitroquinoxaline; Yellow solid; m.p: 192-194 $^\circ\text{C}$; **IR (KBr, cm^{-1}):** ν_{max} = 2930, 1603, 1523, 1341, 1174, 1024, 836 cm^{-1} . **^1H NMR (250 MHz, CDCl_3):** δ (ppm) = 9.1 (d, 1H), 8.49 (dd, 1H), 8.24 (d, 1H), 7.56 (m, 4H), 6.98 (m, 4H). **MS (m/e):** 387 (M^+), 356, 342, 327, 312, 296, 282, 207, 44.

3e: 2, 3- Bis(4-methoxy-phenyl)-6-nitroquinoxaline; Yellow solid; m.p: 192-194 $^\circ\text{C}$; **IR (KBr, cm^{-1}):** ν_{max} = 2930, 1603, 1523, 1341, 1174, 1024, 836 cm^{-1} . **^1H NMR (250 MHz, CDCl_3):** δ (ppm) = 9.1 (d, 1H), 8.49 (dd, 1H), 8.24 (d, 1H), 7.56 (m, 4H), 6.98 (m, 4H). **MS (m/e):** 387 (M^+), 356, 342, 327, 312, 296, 282, 207, 44.

3f: 2, 3- Bis(4-fluoro-phenyl)quinoxaline; White solid; **m.p:** 135-137 °C; **IR (KBr, cm⁻¹):** $\nu_{\max}$ = 3063, 1600, 1552, 1510, 1343, 1225, 842, 764 cm⁻¹. **¹H NMR (250 MHz, CDCl₃):** δ (ppm) = 8.2 (dd, 2H), 7.82 (dd, 2H), 7.52 (dd, 4H), 7.05 (dd, 4H). **MS (m/e):** 318 (M⁺), 300, 223, 197, 177, 159, 76, 50.

3g: 2, 3- Bis(4-fluoro-phenyl)-6-nitroquinoxaline; Light yellow solid; **m.p:** 173-175 °C; **IR (KBr, cm⁻¹):** $\nu_{\max}$ = 3054, 2930, 1606, 1513, 1342, 1248, 833 cm⁻¹. **¹H NMR (250 MHz, CDCl₃):** δ (ppm) = 9.1 (d, 1H), 8.56 (dd, 1H), 8.3 (d, 1H), 7.6 (m, 4H), 7.1 (m, 4H). **MS (m/e):** 363 (M⁺), 348, 333, 317, 297, 242, 196, 75.

3h: 2, 3- Bis(4-fluoro-phenyl)-6-methoxyquinoxaline; White solid; **m.p:** 165-167 °C; **IR (KBr, cm⁻¹):** $\nu_{\max}$ = 3056, 1566, 1524, 1384, 1221, 1159, 836 cm⁻¹. **¹H NMR (250 MHz, CDCl₃):** δ (ppm) = 8.05 (d, 1H), 7.92 (s, 1H), 7.59-7.63 (dd, 1H), 7.63-7.51 (m, 4H), 7.01-7.09 (m, 4H), 2.62 (s, 3H). **MS (m/e):** 332 (M⁺), 313, 237, 211, 183, 166, 89, 75.

3i: 2, 3- Bis(4-chloro-phenyl) quinoxaline; White solid; **m.p:** 194-196 °C; **IR (KBr, cm⁻¹):** $\nu_{\max}$ = 3061, 1590, 1488, 1341, 1087, 828, 759 cm⁻¹. **¹H NMR (250 MHz, CDCl₃):** δ (ppm) = 8.14-8.18 (dd, 1H), 7.77-7.81 (dd, 1H), 7.45-7.49 (dd, 2H), 7.33-7.36 (dd, 2H); **MS (m/e):** 350 (M⁺), 331, 315, 279, 239, 213, 178, 151, 76, 50.

3j: 2, 3- Bis(4-chloro-phenyl)-6-nitroquinoxaline; Yellow solid; **m.p:** 174-176 °C; **IR (KBr, cm⁻¹):** $\nu_{\max}$ = 3088, 1527, 1341, 1090, 832 cm⁻¹. **¹H NMR (250 MHz, CDCl₃):** δ (ppm) = 9.05 (d, 1H), 8.51-8.55 (dd, 1H), 8.26-8.29 (d, 1H), 7.54-7.6 (m, 2H), 7.05-7.12 (m, 2H). **MS (m/e):** 396 (M⁺), 364, 350, 316, 240, 213, 178, 75, 50.

3k: 2, 3- Bis(4-Chloro-phenyl)-6-nitroquinoxaline; Yellow solid; **m.p:** 174-176 °C; **IR (KBr, cm⁻¹):** $\nu_{\max}$ = 3088, 1527, 1341, 1090, 832 cm⁻¹. **¹H NMR (250 MHz, CDCl₃):** δ (ppm) = 9.05 (d, 1H), 8.51-8.55 (dd, 1H), 8.26-8.29 (d, 1H), 7.54-7.6 (m, 2H), 7.05-7.12 (m, 2H). **MS (m/e):** 396 (M⁺), 364, 350, 316, 240, 213, 178, 75, 50.

3l: 2, 3- Bis(4-Chloro-phenyl)-6-methylquinoxaline; White solid; **m.p:** 176-178 °C; **IR (KBr, cm⁻¹):** $\nu_{\max}$ = 2923, 1484, 1340, 1088, 831 cm⁻¹. **¹H NMR (250 MHz, CDCl₃):** δ (ppm) = 8.05 (d, 1H), 7.92 (s, 1H), 7.59-7.63 (dd, 1H), 7.63-7.51 (m, 4H), 7.3-7.35 (m, 4H), 2.62 (s, 3H); **MS (m/e):** 364 (M⁺), 349, 329, 293, 227, 192, 165, 146, 89, 76.

3. Results and Discussion

At the beginning of this work, the condensation reaction of *o*-Phenylenediamines with benzil in the presence of nanoporous acid catalyst of SBA-Pr-SO₃H was employed as the model reaction to screen the suitable reaction conditions (scheme 1). A plausible mechanism was shown in scheme 2. Among different conditions, we found using CH₂Cl₂ as solvent in room temperature give the best result on the yields and time of the reaction (Table 1) and then these conditions were chosen as the optimized condition. Thus, under the optimized reaction conditions, this reaction was effected using various 1,2-diamines and 1,2-dicarbonyl compounds, and the results were summarized in Table 2. It can be seen when the electron-donating substituents present in diamine part, increased yields of products were observed, whereas the effect was reverse with the electron withdrawing substituent. On the other hand, substituents on aromatic 1, 2-diketone had no significant effect on the product yields.

The efficiency of various catalysts in synthesis of quinoxalines derivatives has been compared in Table 3. The best yield and short reaction time is attributed to the high efficiency of the nano-catalyst of SBA-Pr-SO₃H.

Preparation and characterization of catalyst

Pure Nanoporous compound SBA-15 was synthesized with triblock poly(ethylene oxide)-b-poly(propyleneoxide)-bpoly(ethyleneoxide) copolymer (Pluronic, EO₂₀PO₇₀EO₂₀, P123) as the template (Zhao *et al.* 1998). A schematic illustration for the preparation of SBA-Pr-SO₃H was shown in Fig. 1. First, the calcined SBA-15 silica was functionalized with (3-mercaptopropyl)trimethoxysilane (MPTS) and then, the thiol groups were oxidized to sulfonic acid by hydrogen peroxide.

The TGA analysis of SBA-Pr-SO₃H confirmed the amount of organic groups on SBA-15. The weight reduction in the temperature range between 200-600 °C (about 15%) indicated that the amount of organic group was 1.2 mmol/g.

The nitrogen adsorption-desorption isotherm SBA-Pr-SO₃H (Fig. 2) shows type-IV adsorption behavior with the hysteresis loops appearing at relatively high pressure, suggesting that the prepared samples have regular mesoporous framework structures. The surface area, average pore diameter calculated by the BET method and pore volume of SBA-Pr-SO₃H are 440 m²g⁻¹, 6.0 nm and 0.660 cm³ g⁻¹, respectively, which are smaller than those of SBA-15 due to the immobilization of sulfonosilane groups into the pores. Table 4 shows the obtained results from the nitrogen adsorption studies at -196 °C.

4. Conclusion

In summary, we have described the use of nano acid Catalyst of SBA-Pr-SO₃H in the synthesis of quinoxaline derivatives under mild conditions. SBA-Pr-SO₃H was proved to be an efficient heterogeneous nanoporous solid acid

catalyst with pore size of 6 nm. Furthermore, excellent yields, mild reaction conditions, short reaction times and easy work-up procedures make it, a facile and superior method for the synthesis of quinoxalines as compared in Table 3.

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References

- Badiei, A., Norouzi, P., Tousi, F. (2005). Study of Electrochemical Behavior and Adsorption Mechanism of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ on Mesoporous Modified Carbon Paste Electrode. *Eur. J. Sci. Res.*, 12, 39-45.
- Beck, S., Vartuli, J. C., Roth, W. J., Kresge, C. T., Leonowicz, M. E., Schmitt, K. D., Chu, C. T-W., Olson, D. H., Sheppard, E. W., McCullen, S. B., Higgins, J. B., Schlenker, J. L. (1992). A new family of mesoporous molecular sieves prepared with liquid crystal templates. *J. Am. Chem. Soc.*, 114, 10834-10843.
- Bhosale, R. S., Sarda, S. R., Ardhapure, S. S., Jadhav, W. N., Bhusare, S. R., Pawar, R. P. (2005). An efficient protocol for the synthesis of quinoxaline derivatives at room temperature using molecular iodine as the catalyst. *Tetrahedron Lett.*, 46, 7183-7186.
- Bonneviot, L., Morin, M., Badiei, A. (2001). Mesoporous Metal or Non-Metal Oxides and Method for Making Same. Patent WO 01/55031 A1.
- Brown In, J. D., Taylor, C. E., Wipf, P., Eds. (2004). *The Chemistry of Heterocyclic Compounds Quinoxalines: Supplements II*, John Wiley and Sons: New Jersey.
- Brown, D. J. (2004). *Quinoxalines: Supplement II. In The Chemistry of Heterocyclic Compounds*; Taylor, E. C., Wipf, P., Eds.; John Wiley & Sons: New Jersey.
- Cai, J.-J., Zou, J.-P., Pan, X.-Q., Zhang, W. (2008). Gallium (III) triflate-catalyzed synthesis of quinoxaline derivatives. *Tetrahedron Lett.*, 49, 7386-7390.
- Dailey, S., Feast, W. J., Peace, R. J., Sage, I. C., Till, S., Wood, E. L. (2001). Synthesis and device characterisation of side-chain polymer electron transport materials for organic semiconductor applications. *J. Mater. Chem.*, 11, 2238-2243.
- Darabi, H. R., Mohandessi, S., Aghapoor, K., Mohsenzadeh, F. (2007). A recyclable and highly effective sulfamic acid/MeOH catalytic system for the synthesis of quinoxalines at room temperature, *Catal. Commun.*, 8, 389-392.
- Das, B., Venkateswarlu, K., Holla, H., Krishnaiah, M. (2006). Sulfonic acid functionalized silica: A remarkably efficient heterogeneous reusable catalyst for α -monobromination of carbonyl compounds using *N*-bromosuccinimide, *J. Mol. Catal. A: Chem.*, 253, 107-111.
- Gangali, M. R., Hajiagha Babaei, L., Badiei, A., Mohammadi Ziarani, G., Tarlani, A. (2004). Novel Method for the Fast Preconcentration and Monitoring of a ppt Level of Lead and Copper with a Modified Hexagonal Mesoporous Silica Compound and Inductively Coupled Plasma Atomic Emission Spectrometry, *Anal. Sci.*, 20, 725-729.
- Ganjali, M. R., Daftari, A., Hajiagha Babaei, L., Badiei, A., Saberyan, K., Mohammadi Ziarani, G., Moghimi, A. (2006). Pico level monitoring of silver with modified hexagonal mesoporous compound (MCM-41) and inductively coupled plasma atomic emission spectrometry, *Water, Air, Soil Pollut.*, 173, 71-80.
- Ganjali, M. R., Hajiagha Babaei, L., Badiei, A., Saberian, K., Behbahani, S., Mohammadi Ziarani, G., Salavati-Niasari, M. (2006). A novel method for fast enrichment and monitoring of hexavalent and trivalent chromium at the PPT level with modified silica MCM-41 and its determination by inductively coupled plasma optical emission spectrometry, *Quim. Nova*, 29, 440-443.
- Gazit, A., App, H., McMahon, G., Chen, J., Levitzki, A., Bohmer, F. D. (1996). Tyrphostins. 5. Potent inhibitors of platelet-derived growth factor receptor tyrosine kinase: Structure-activity relationships in quinoxalines, quinolines, and indole tyrphostins. *J. Med. Chem.*, 39, 2170-2177.
- Hazarika, P., Gogoi, P., Konwar, D. (2007). Efficient and green method for the synthesis of 1,5-benzodiazepine and quinoxaline derivatives in water. *Synth. Commun.*, 37, 3447-3454.
- Heravi, M. M., Bakhtiari, Kh., Bamoharram, F. F., Tehrani, M. H. (2007). Wells-Dawson type heteropolyacid catalyzed synthesis of quinoxaline derivatives at room temperature *Monatsh. Chem.*, 138, 465-467.
- Heravi, M. M., Bakhtiari, Kh., Oskooie, H. A., Taheri, Sh. (2008). MnCl_2 -promoted synthesis of quinoxaline derivatives at room temperature, *Heteroat. Chem.*, 19, 218-220.

- Heravi, M. M., Taheri, Sh., Bakhtiari, Kh., Oskooie, H. A. (2007). On Water: A practical and efficient synthesis of quinoxaline derivatives catalyzed by $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, *Catal. Commun.*, 8, 211-214.
- Heravi, M. M., Tehrani, M. H., Bakhtiari, Kh., Oskooie, H. A. (2007). $\text{Zn}[(\text{L})\text{proline}]$: A powerful catalyst for the very fast synthesis of quinoxaline derivatives at room temperature, *Catal. Commun.*, 8, 1341-1344.
- Heravi, M., Bakhtiari, Kh., Tehrani, M. H., Javadi, N. M., Oskooie, H. (2006). Facile synthesis of quinoxaline derivatives using o-iodoxybenzoic acid (IBX) at room temperature, *ARKIVOC*, xvi 16-22.
- Huang, T.-K., Shi, L., Wang, R., Guo, X.-Z., Lu, X.-X. (2009). Keggin type heteropolyacids-catalyzed synthesis of quinoxaline derivatives in water, *Chin. Chem. Lett.*, 20, 161-164.
- Huang, T. K., Wang, R., Shi, L., Lu, X. X. (2008). Montmorillonite K-10: An efficient and reusable catalyst for the synthesis of quinoxaline derivatives in water, *Catal. Commun.*, 9, 1143-1147.
- Karimi, B., Zareyee, D. (2008). Design of a Highly Efficient and Water-Tolerant Sulfonic Acid Nanoreactor Based on Tunable Ordered Porous Silica for the von Pechmann Reaction, *Org. Lett.*, 10, 3989-3992.
- Katoh, A., Yoshida, T., Ohkanda, J. (2000). Synthesis of quinoxaline derivatives bearing the styryl and phenylethynyl groups and application to a fluorescence derivatization reagent. *Heterocycles*, 52, 911-920.
- Kureshy, R. I., Ahmad, I., Pathak, K., Khan, N. H., Abdi, S. H. R., Jasra, R. V. (2009). Sulfonic acid functionalized mesoporous SBA-15 as an efficient and recyclable catalyst for the synthesis of chromenes from chromanols, *Catal. Commun.*, 10, 572-575.
- Lim, M. H., Blanford, C. F., Stein, A. (1998). Synthesis of Ordered Microporous Silicates with Organosulfur Surface Groups and Their Applications as Solid Acid Catalysts, *Chem. Mater.* 10, 467-470.
- Lindsley, C. W., Zhao, Z., Leister, W. H., Robinson, R. G., Barnett, S. F., Defeo-Jones, D., Jones, R. E., Hartman, G. D., Huff, J. R., Huber, H. E., Duggan, M. E. (2005). Allosteric Akt (PKB) inhibitors: Discovery and SAR of isozyme selective inhibitors. *Bioorg. Med. Chem. Lett.*, 15, 761-764.
- Loriga, M., Piras, S., Sanna, P., Paglietti, G. (1997). Quinoxaline chemistry. Part 7. 2-[aminobenzoates]- and 2-[aminobenzoylglutamate] quinoxalines as classical antifolate agents. Synthesis and evaluation of in vitro anticancer, anti-HIV and antifungal activity. *Farmaco*, 52, 157-166.
- Mohammadi Ziarani G., Badiei A., Miralami A. (2007). The study of solvent effect on the diastereoselectivity of Diels-Alder reaction in the presence of nanoporous silica-supported cerium sulfonate catalyst, *Eur. J. Sci. Res.*, 18, 282-286.
- Mohammadi Ziarani, G., Badiei, A., Abbasi, A., Farahani, Z. (2009). Cross-aldol Condensation of Cycloalkanones and Aromatic Aldehydes in the Presence of Nanoporous Silica-based Sulfonic Acid ($\text{SiO}_2\text{-Pr-SO}_3\text{H}$) under Solvent Free Conditions. *Chin. J. Chem.*, 27, 1537-1542.
- Mohammadi Ziarani, G., Badiei, A., Khaniania, Y., Haddadpour, M. (2010). One Pot Synthesis of Polyhydroquinolines Catalyzed by Sulfonic Acid Functionalized SBA-15 as a New Nanoporous Acid Catalyst under Solvent Free Conditions, *Iran. J. Chem. & Chem. Eng.*, 29, 1-10.
- Mohammadi Ziarani, G., Badiei, A., Miralami, A. (2008). A study of the Diastereoselectivity of Diels-Alder reactions on the Ce- SiO_2 as support. *Bull. Korean Chem. Soc.*, 29, 47-50.
- More, S. V., Sastry, M. N. V., Wang, C. C., Yao, C. F. (2005). Molecular iodine: A powerful catalyst for the easy and efficient synthesis of quinoxalines, *Tetrahedron Lett.*, 46, 6345-6348.
- More, S. V., Sastry, M. N. V., Yao, C. F. (2006). Cerium (IV) ammonium nitrate (CAN) as a catalyst in tap water: A simple, proficient and green approach for the synthesis of quinoxalines, *Green Chem.*, 8, 91-95.
- Porter, A. E. A. (1984). In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C.W., Eds.; Pergamon: Oxford, pp 157-197.
- Raw, S. A., Wilfred, C. D., Taylor, R. J. K. (2003). Preparation of quinoxalines, dihydropyrazines, pyrazines and piperazines using tandem oxidation processes, *Chem. Commun.*, 2286.
- Reinert, P., Garcia, B., Morin, C., Badiei, A., Perriat, P., Tillement, O., Bonnevot, L. (2003). Cationic templating with organic counterion for superstable mesoporous silica, Nanotechnology in mesostructure Materials, *Stud. Surf. Sci. Catal.*, 146, 133-136.
- Robinson, R. S., Taylor, R. J. K. (2005). Quinoxaline synthesis from α -hydroxy ketones via a tandem oxidation process using catalysed aerobic oxidation, *Synlett*, 1003-1005.

Sakata, G., Makino, K., Kurasawa, Y. (1988). Recent Progress in the Quinoline Chemistry. Synthesis and Biological Activity. *Heterocycles*, 27, 2481-2515.

Sato, N. (1996). In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F., Eds.; Elsevier Science Ltd: Oxford, Chapter 6.03, p 6.

Seitz, L. E., Suling, W. J., Reynolds, R. C. (2002). Synthesis and antimycobacterial activity of pyrazine and quinoxaline derivatives. *J. Med. Chem.*, 45, 5604-5606.

Srinivas, C., Kumar, C. N. S. S. P., Jayathirtha Rao, V., Palaniappan, S. (2007). Efficient, convenient and reusable polyaniline-sulfate salt catalyst for the synthesis of quinoxaline derivatives, *J. Mol. Catal. A: Chem.*, 265, 227-230.

Trong On, D., Desplantier-Giscard, D., Danumah, C., Kaliaguine S. (2001). Perspectives in catalytic applications of mesostructured materials, *Appl. Catal. A: Gen.*, 222, 299-357.

Van Rhijn, W. M., De Vos, D., Sels, B. F., Bossaert, W. D., Jacobs, P. A. (1998). Sulfonic acid functionalised ordered mesoporous materials as catalysts for condensation and esterification reactions, *Chem. Commun.*, 317-318.

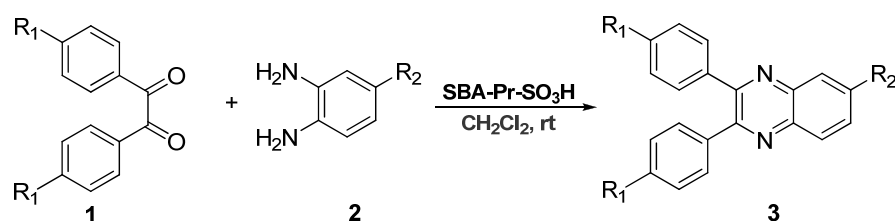
Walcarius, A., Despas, C., Bessiere, J. (1999). Selective monitoring of Cu(II) species using a silica modified carbon paste electrode, *Anal. Chim. Acta*, 385, 79-89.

Wight, A. P., Davis, M. E. (2002). Design and preparation of organic-inorganic hybrid catalysts, *Chem. Rev.* 102, 3589-3614.

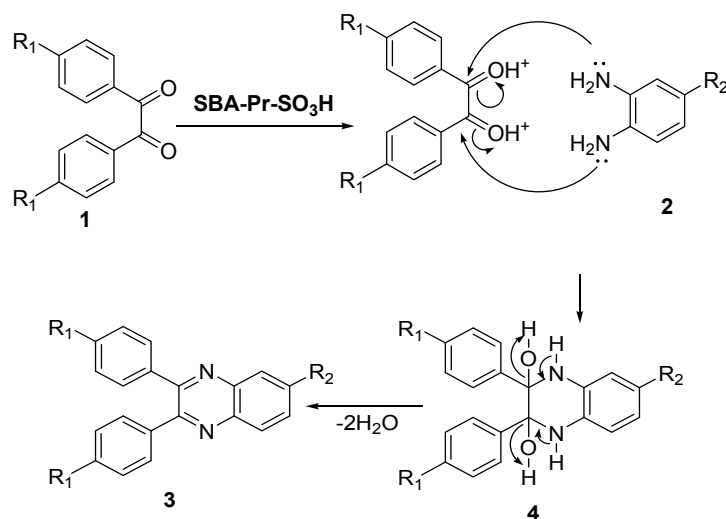
Zhang, H.-X., Cao, A.-M., Hu, J.-S., Wan, L.-J., Lee, S.-T. (2006). Electrochemical sensor for detecting ultratrace nitroaromatic compounds using mesoporous SiO₂-modified electrode, *Anal. Chem.*, 78, 1967-1971.

Zhang, X. Z., Wang, J. X., Sun, Y. J., Zhan, H. W. (2010). Synthesis of quinoxaline derivatives catalyzed by PEG-400, *Chin. Chem. Lett.* 21, 395-398.

Zhao, D., Huo, Q., Feng, J., Chmelka, B. F., Stucky, G. D. (1998). Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures, *J. Am. Chem. Soc.* 120, 6024-6036.



Scheme 1. Synthesis of quinoxaline derivatives using SBA-Pr-SO₃H as efficient nano acid catalyst



Scheme 2. The proposed mechanism

Table 1. The Optimization of reaction conditions in the synthesis 2, 3- Diphenyl-quinoxaline 3

no	Solvent	T°C	time	Yield %
1	—	25	24 h	60
2	—	80	5 h	60
3	CH ₂ Cl ₂	25	10 min	95

Table 2. The SBA-Pr-SO₃H catalyzed the synthesis of quinoxaline derivatives

Entry	R ₁	R ₂	Product	Time (min)	Yield (%)	mp °C	mp Lit.
1	H	H	3a	10	95	128-129	129-128 ¹
2	H	NO ₂	3b	20	90	191-193	194-193 ¹
3	H	CH ₃	3c	5	98	117-118	118-117 ¹
4	OCH ₃	H	3d	15	95	150-152	152-151 ¹
5	OCH ₃	NO ₂	3e	25	90	192-195	194-192 ¹
6	OCH ₃	CH ₃	3f	15	95	124-126	125-127 ¹
7	F	H	3g	5	97	135-137	135-137 ¹
8	F	NO ₂	3h	10	90	173-175	174-176 ¹
9	F	CH ₃	3i	5	95	165-167	165-167 ¹
10	Cl	H	3j	10	95	194-196	195-196 ²
11	Cl	NO ₂	3k	15	90	174-176	176 ²
12	Cl	CH ₃	3l	5	95	176-178	180 ²

¹ (Heravi *et al* ARKIVOC, 2006), ² (Heravi, *et al* Catal. Commun., 2007)

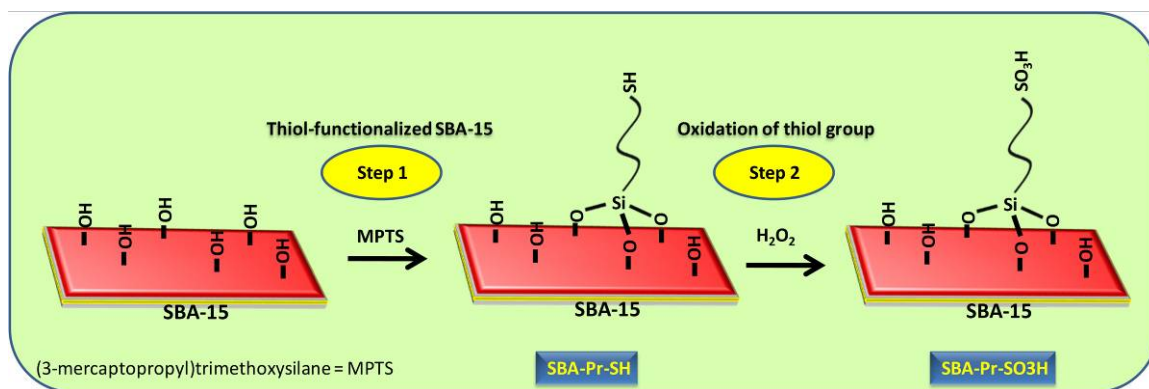
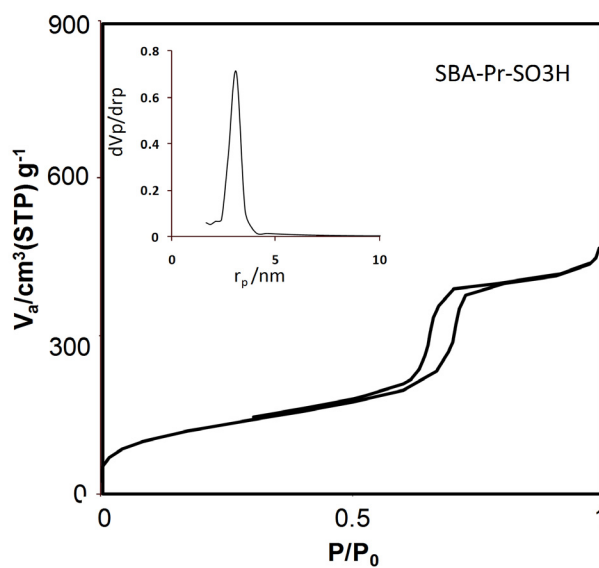
Table 3. Comparison of efficiency of various catalysts in synthesis of quinoxaline derivatives 3c

Entry	Catalyst	Condition	Time	Yield (%)	Ref.
1	polyaniline-sulfate salt	CH ₂ Cl ₂	15 min	92	1
2	Montmorillonite K-10	H ₂ O	2.5 h	100	2
3	molecular iodine	DMSO	50 min	90	3
4	Keggin type heteropolyacids	H ₂ O	1 h	92	4
5	PEG-400	free	10-60 min	93	5
6	SBA-Pr-SO ₃ H	CH ₂ Cl ₂	5 min	98	This work

¹(Srinivas *et al.* 2007), ²(Huang *et al.* 2008), ³(Bhosale *et al.* 2005), ⁴(Huang *et al.* 2009), ⁵(Cai *et al.* 2008)

Table 4. Porosimetry values for SBA-15 and functionalized SBA-15

	Surface area (cm ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore radius (nm)
SBA-15	649	0.806	3.1
SBA-Pr-SO ₃ H	440	0.660	3.0

Figure 1. Schematic illustration for the preparation of SBA-Pr-SO₃HFigure 2. N₂ adsorption-desorption isotherms and pore size distribution (inset) SBA-Pr-SO₃H