

Research Article

Synthesis of 1,5-Benzodiazepine and Its Derivatives by Condensation Reaction Using H-MCM-22 as Catalyst

Sheikh Abdul Majid, Waheed Ahmad Khanday, and Radha Tomar

S.O.S in Chemistry, Jiwaji University, Gwalior 474011, India

Correspondence should be addressed to Radha Tomar, radha.tomar11@yahoo.co.in

Received 2 December 2011; Revised 24 January 2012; Accepted 7 February 2012

Academic Editor: Daehee Kang

Copyright © 2012 Sheikh Abdul Majid et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

A simple and versatile method for the synthesis of 1,5-benzodiazepines is via condensation of *o*-phenylenediamines (OPDA) and ketones in the presence of catalytic amount of H-MCM-22 using acetonitrile as solvent at room temperature. In all the cases, the reactions are highly selective and are completed within 1–3 h. The method is applicable to both cyclic and acyclic ketones without significant differences. The reaction proceeds efficiently under ambient conditions with good-to-excellent yields.

1. Introduction

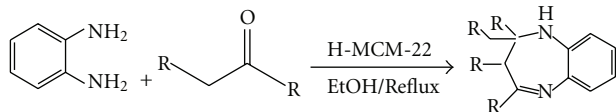
Benzodiazepines constitute an important class of biologically active compounds and their synthesis has been receiving much attention in the field of medicinal and pharmaceutical chemistry owing to their application as anticonvulsant, anti-inflammatory, analgesic, hypnotic, and sedative agents and to their hypnotic activity [1–6]. The derivatives of 1,5-benzodiazepines are also used as dyes for acrylic fibers in photography [7]. In addition, benzodiazepines are the useful precursors for the synthesis of other fused ring compounds such as triazolo-, oxadiazolo-, oxazino-, or furano-benzodiazepines [8–11]. Benzodiazepines are generally synthesized by the condensation of *o*-phenylenediamine (OPDA) with *a,b*-unsaturated carbonyl compounds, *b*-haloketones, or with ketones [12] using acidic catalysts which are critical to enhance the condensation process. Different reagents such as BF₃-etherate, polyphosphoric acid, NaBH₄, MgO/POCl₃, Yb(OTf)₃, Ga(OTf)₃, lead nitrate, L-proline, acetic acid under microwave conditions, molecular iodine, and ionic liquids have also been used for the synthesis of benzodiazepines [13–23]. Recently the synthesis of benzodiazepines has also been reported using different solid acid catalysts such as sulfated zirconia, Al₂O₃/P₂O₅, Ag₃PW₁₂O₄₀, PVP-FeCl₃, and zeolite catalysts [24–28]. Unfortunately, many of these catalysts suffer from one or more limitations, such as long reaction times, occurrence of several side

reactions, drastic reaction conditions, low yields, and tedious workup procedure. In addition, the solid oxide catalyst used previously had poor textural parameters such as low surface area and pore volume which do not support a better performance in the synthesis of benzodiazepines. These factors stimulate the search for a better catalyst, which should offer a high activity for the synthesis of 1,5-benzodiazepines under mild reaction conditions. In recent years, mesoporous materials with different structure and tunable pore diameters have been receiving much attention.

Here we demonstrate, the synthesis of 1,5-benzodiazepine using H-MCM-22 as catalyst through a condensation reaction between OPDA and ketones in acetonitrile condition. The effect of catalyst and the catalyst concentration on the above process has been investigated in detail.

2. Experimental Section

2.1. Synthesis of Catalysts Synthesis of (H-MCM-22). The hydrothermal synthesis of layered aluminosilicate MCM-22 was carried out by using hexamethylenimine as an organic template at dynamic conditions. A total of 3.110 g of anhydrous sodium aluminate (50–56% Al₂O₃, maximum 0.05% Fe₂O₃, 40–45% Na₂O, purchased from Riedel-deHaën) and 1.930 g of sodium hydroxide (97%, from Merck) was dissolved in 415 g of deionized water. The



SCHEME 1: Synthesis of 1,5-benzodiazepines using H-MCM-22 catalysts at room temperature.

solution was thoroughly stirred for 15 minutes, and then 25.4 g of hexamethylenimine (HMI) (99%, from Aldrich) was added dropwise with vigorous stirring. To this, 30.7 g of silica (Aerosil 200, Degussa) was added in small portions and the resulting slurry continued to be stirred vigorously. After 30 minutes of stirring, at room temperature, a gel was formed; this was then placed in an autoclave and heated at 150°C for 10 days. After immersing the autoclaves in cold water, the resulting material was washed and centrifuged until $\text{pH} \leq 9$ and subsequently dried at 70°C. A 1-gram sample of MCM-22 was calcined in the absence of air at 650°C for 7 hours, generating Na-MCM-22 zeolite. The process took place in an oven in order to remove water and organic precursor. The oven was programmed at a heating rate of 5°C/min until 650°C for 7 h. The Na-MCM-22 zeolite is converted into the H-form by the following procedure: 9.000 g of Na-MCM-22, 7.230 g of NH_4Cl , and 13.80 mL of deionized water were mixed with 0.1 M hydrochloric acid solution, in order to reach pH 4.0. The mixture was stirred at 60°C for 30 min. Then the material was filtered under suction and washed with deionized water. After the removal of chlorides, the resulting material, $\text{NH}_4\text{-MCM-22}$ zeolite, was placed in an oven at 60°C for 24 h. The ammonium form of MCM-22 was converted into H-form by calcination over 60 min at 200°C.

2.2. Characterization of the Catalysts and the Products. X-Ray Diffraction (XRD): the samples were sieved in an ABNT n° 200 (0.074 mm) sieve and then placed in an aluminum sample holder for X-ray diffraction assays, using a Shimadzu XRD 6000 equipment. The operational details of the technique were set as follows: copper $K\alpha$ radiation at 40 KV/30 mA, with a goniometer speed of 2°/min and a step of 0.02° in the 2θ range scanning from 2° to 50°. The only d-spacings of interest in the X-ray patterns were the basal spacings along the c axis.

Fourier-transform infrared (FT-IR) spectroscopy: the MCM-22 sample was submitted to physical treatment in accordance with the KBr method, which consists of mixing 0.007 g of the sample and 0.1 g of KBr, grinding and pressing the solid mixture to 5 ton for 30 s in order to form a pastille that allows the passage of light. Characterization was performed using an infrared spectrophotometer SHIMADZU FT-IR in the wavelength ranges from 2000 to 400 cm^{-1} , with increments of 650 cm^{-1} and a resolution of 4 cm^{-1} .

Characterization of the product was performed on SHIMADZU FT-IR spectrometer, and the sample was prepared with KBr and pressed into wafer/pellet. Spectra were collected in the range of 400–4000 cm^{-1} . NMR of the products was performed on BRUKER ADVANCE II 300 NMR spectrometer.

Gas chromatography for benzodiazepine was performed using Younglin gas chromatograph (YL6100 GC). A narrow-bore capillary column (25 m \times 0.22 with 0.25 μm thickness) was used and an oven temperature of 250°C was employed with injector and detector temperature of 275°C. Yield was calculated from the peak area

$$\text{Area} = \text{Height of peak} \times \text{Width at half-height}, \quad (1)$$

and % yield was calculated as

$$\% \text{ yield} = \frac{\text{Area of component}}{\text{Total area}} \times 100. \quad (2)$$

2.3. Synthesis of 1,5-Benzodiazepine. A mixture of OPDA (1 mmol, 108.1 mg), ketone (2.5 mmol, 145.2 mg), and H-MCM-22 (100 mg) was stirred in acetonitrile (4 mL) at room temperature until thin layer chromatography indicated the reaction was completed (as shown in Scheme 1). Ethyl acetate (10%) in hexane was used as the mobile phase and both the reactant and the final product were spotted on the TLC plate. The product retention factor (R_f) was observed at 0.4. The disappearance of the reactant spot on the TLC plate indicates the completion of the reaction. After completion of the reaction, ethyl acetate (20 mL) was added to the reaction mixture and the catalyst was recovered by filtration. The organic layer was concentrated and the crude product was purified by silica gel column chromatography using ethyl acetate: n-hexane (1:9) as eluent to afford the desired product.

Entry 1 (2a). Yellow solid; m.p. 137–139°C FT-IR (KBr): ν_{max} (in Cm^{-1}) 3362, 1501, 1474; ^1H NMR (300 MHz, CDCl_3): δ (ppm): 7–7.25 (m, 4H, Ar-H), 2.90–2.95 (d, 1H, CH), 3.90–4.25 (m, 2H, CH_2), 3.5 (br s, 1H, NH), 3 (s, 2H, N = C- CH_2), 2.5 (m, 3H, N = C- CH_3), 1.50–1.75 (s, 6H, 2 CH_3).

Entry 2 (2b). Yellow solid; m.p. 137–139°C; FT-IR (KBr): ν_{max} (in Cm^{-1}) 3329, 1637, 1605; ^1H NMR (300 MHz, CDCl_3): δ (ppm): 0.99 (t, 3H, $J = 6.9$ Hz), 1.25 (t, 3H, $J = 6.9$ Hz), 1.70 (q, 2H, $J = 6.9$ Hz) 2.15 (m, 2H), 2.35 (s, 3H), 2.69 (q, 2H, $J = 6.9$ Hz), 3.25 (br s, 1H, NH), 6.78–7.35 (m, 4H); ^{13}C NMR (50 MHz, CDCl_3) δ (ppm): 8.7, 10.6, 26.9, 35.5, 35.7, 42.0, 70.7, 121.7, 125.2, 126.2, 27.1, 138.0, 140.9, 175.5.

Entry 3 (2c). Yellow solid; m.p. 151–152°C; FT-IR (KBr): ν_{max} (in Cm^{-1}) 3330, 1635; ^1H NMR (300 MHz, CDCl_3): δ (ppm): 1.80(s, 3H), 2.95 (d, 1H, $J = 12.8$ Hz), 3.15 (d, 1H, $J = 12.8$ Hz) 3.45 (br s, NH), 6.55–7.0 (m, 3H), 7.15–7.35 (m, 7H), 7.55–7.65 (m, 4H); ^{13}C NMR (50 MHz, CDCl_3) δ (ppm): 167.5, 146.6, 140.1, 139.5, 138.2, 129.8, 128.6, 128.4,

128.1, 127.4, 127.1, 126.4, 125.5, 121.7, 121.5, 73.9, 43.0, 29.9.

Entry 4 (2d). Yellow solid; m.p. 164–165°C, FT-IR (KBr): ν_{\max} (in cm^{-1}): 3375; ^1H NMR (300 MHz, CDCl_3): δ (ppm): 1.48–1.84 (m, 10H), 4.15 (br s, 1H, NH), 4.69 (br s, 1H, NH), 6.37 (d, 2H), 7.71 (d,d, 2H). ^{13}C NMR (50 MHz, CDCl_3): $d = 23.50, 25.04, 39.83, 82.15, 103.35, 104.84, 119.80, 132.35, 140.62, 146.20$.

Entry 5 (2e). Yellow solid; m.p. 156–158°C, FT-IR (KBr): ν_{\max} (in cm^{-1}): 3344, 1647, 1603. ^1H NMR (300 MHz, CDCl_3): δ (ppm): 1.88–2.10 (m, 12H, 6CH_2), 2.90–2.95 (d, 1H, CH), 3.90–4.25 (m, 2H, CH_2), 3.05 (br s, 1H, NH), 6.63–6.64 (m, 1H, Ar-H), 6.73–6.77 (m, 1H, Ar-H), 7.87–7.90 (m, 1H, Ar-H).

Entry 6 (2f). Yellow solid, m.p. 94–96°C, IR(KBr): ν_{\max} 3424, 1595, 1499 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 0.93 (t, 3H, CH_3), 1.24–1.25 (m, 6H, 2CH_3), 1.60–1.65 (m, 2H, CH_2), 2.22 (m, 2H, CH_2), 2.50–2.68 (q, 2H, $J = 3.23$ Hz, CH_2), 3.00–3.20 (br s, 1H, NH), 6.62–6.71 (m, 1H, Ar-H), 6.88–6.93 (m, 1H, Ar-H), 7.04–7.14 (m, 1H, Ar-H).

Entry 7 (2g). Pale yellow solid, m.p. 138–140°C, IR(KBr): ν_{\max} 3320, 1602, 1567 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 1.72 (s, 3H, CH_3), 2.17 (s, 2H, CH_2), 2.33 (s, 6H, 2CH_3), 3.00 (br s, 1H, NH), 6.80–6.81 (m, 1H, Ar-H), 7.06–7.10 (m, 5H, Ar-H), 7.42–7.53 (m, 5H, Ar-H).

Entry 8 (2h). Yellow solid; m.p. 135–136°C FT-IR (KBr): ν_{\max} (in cm^{-1}) 3352, 1501, 1474; ^1H NMR (300 MHz, CDCl_3): δ (ppm): 7–7.25 (m, 4H, Ar-H), 2.90–2.95 (d, 1H, CH), 3.90–4.25 (m, 2H, CH_2), 3.5 (br s, 1H, NH), 3 (s, 2H, $\text{N}=\text{C}-\text{CH}_2$), 2.5 (m, 3H, $\text{N}=\text{C}-\text{CH}_3$), 1.50–1.75 (s, 6H, 2CH_3).

3. Result and Discussion

The XRD patterns of samples of MCM-22 zeolite are in agreement with those already reported [30–32]. All acquired X-ray patterns identified the products as highly crystalline materials.

The FTIR spectrum of MCM-22 shows the presence of bands related to the symmetrical and asymmetrical stretching of O-H band. The band at 786 cm^{-1} refers to external symmetrical stretching, whilst the band at 1237 cm^{-1} refers to external asymmetric stretching. The bands at 1095 and 1070 cm^{-1} correspond to internal asymmetric stretching and the bands at 594 and 550 cm^{-1} are attributed to the presence of double rings in MCM-22 structure. At 1626 cm^{-1} the band is ascribed to the angular deformation of the N-H bond and water. The band at 449 cm^{-1} is related to the internal deformation of O-H bands [33]. The band centered at 1384 cm^{-1} indicates the presence of amine functional group (HMI).

Initially the focus was on the synthesis of 1,5-benzodiazepine. The reaction was carried out using H-MCM-22 through a simple condensation reaction between OPDA and

TABLE 1: Effect of weight of H-MCM-22 on the synthesis of 1,5-benzodiazepine.

Weight of catalyst mg	Reaction time Min.	Yield %
50	60	30
100	60	50
150	60	87
200	60	88

Reaction conditions: Substrate: OPDA and acetone, reaction temperature: RT, solvent: acetonitrile.

acetone using acetonitrile as solvent at room temperature and the results are given in Table 2. The catalyst was found to be highly active, affording 87% isolated yield of 1,5-benzodiazepine in 60 min. It should also be noted that when the reaction was conducted without any catalyst, the reaction does not occur. These results indicate that the acidity of the catalyst plays a critical role in this transformation and dictates the activity of the catalyst. The role of Brønsted acid site of H-MCM-22 catalyst on the formation of 1,5-benzodiazepine and the reaction mechanism are clearly depicted in Scheme 2. As H-MCM-22 showed a much higher activity than other catalysts used in this study under the optimized reaction conditions, we have used H-MCM-22 for the remaining catalytic studies.

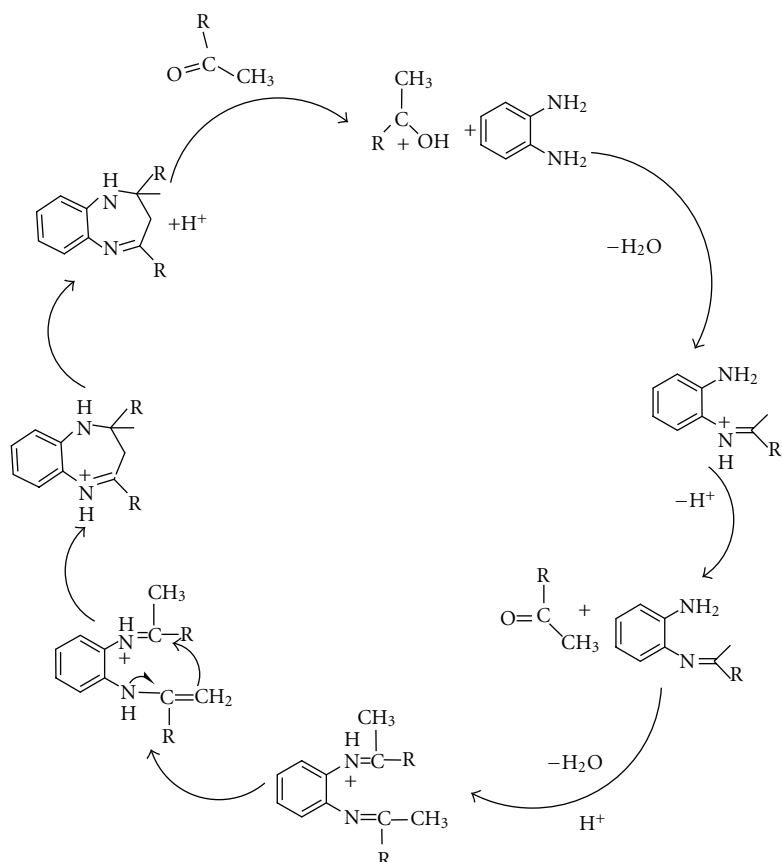
The synthesis of 1,5-benzodiazepines was also carried out over different amounts of H-MCM-22 at room temperature for 60 min and the results are given in Table 1. The weight of catalyst was increased between 50 and 200 mg. It was found that the yield increases from 30% to 87% with increase in the weight of the catalyst from 50 to 150 mg, respectively. This could be mainly due to the availability of huge number of acidic sites on the porous surface of H-MCM-22. It should be noted that the yield of the product remains constant with the further increase in the weight of the catalyst from 150 to 200 mg. Hence, we used the weight of the catalyst as 150 mg for rest of the studies.

The excellent catalytic performance of H-MCM-22 in the synthesis of 1,5-benzodiazepine stimulated us to extend this process for the synthesis of various derivatives of benzodiazepines using various substituted OPDAs and a series of symmetrical and unsymmetrical ketones and the results are shown in Table 2. In all the cases, the reactions are highly selective and are completed within 1–3 h. The catalyst showed excellent activity in all the cases, showing 65–87% isolated yield of the corresponding derivatives of 1,5-benzodiazepine. It was found that the catalyst showed superior performance with high yields in a relatively shorter reaction time than Ersorb-4 (E4), a clinoptilolite-type zeolite catalyst reported earlier [28]. It was interesting to see that E4 needed a high temperature and a longer reaction time conditions to achieve high isolated yield of the final product whereas H-MCM-22 was active even at room temperature. These findings reveal the superior nature of the studied catalyst in this transformation.

Chlorosubstituted OPDA and substituted ketones were also used with similar success to provide the corresponding

TABLE 2: Synthesis of 1,5-benzodiazepines and its derivatives using H-MCM-22 through a condensation reaction between a series of OPDA and various ketones.

Entry	Diamine	Ketone	Product	Time (min)	Yield (%)
1				60	87
2				60	85
3				60	86
4				50	88
5				60	69
6				120	85
7				120	78
8				120	81



SCHEME 2: Reaction mechanism of the synthesis of 1,5-benzodiazepines using H-MCM-22 catalyst at room temperature [29].

benzodiazepines in high yields, which are of much interest with regard to biological activity. Chlorosubstituted benzodiazepines in good yields in the presence of this catalyst were achieved easily.

It is also important to note that the workup of the reaction mixture is very simple. The catalyst can be filtered out easily and the solvent was evaporated. Recycling experiments were conducted to find out the stability of the catalyst after the reaction. The catalyst was easily separated by centrifuge and reused after activation at 500°C for 3-4 h. The efficiency of the recovered catalyst was verified with the reaction of OPDA and Ketone (Entry 1). Using the fresh catalyst, the yield of product (2a) was 87%, while the recovered catalyst in the three subsequent recyclization gave the yields of 85%, 81%, and 75%, respectively. The small reduction in the catalytic activity after three reaction cycles may be mainly due to the loss of catalyst or catalyst structure during the recovery process. These results reveal that the catalyst can be recycled several times without much loss in its activity.

4. Conclusion

The work reported has used H-MCM-22 catalyst for the synthesis of various benzodiazepines by using substituted OPDA and a series of symmetrical and unsymmetrical ketones at room temperature. This method is quite simple and selective.

The catalyst gave high isolated yield of the derivatives of 1,5-benzodiazepine in a shorter reaction time at room temperature and can be recycled several times. We strongly hope that the highly stable H-MCM-22 catalyst could pave the way for the production of 1,5-benzodiazepine and its derivatives and create the platform for the commercialization of the process by replacing the existing homogenous catalysts which suffered from various drawbacks such as corrosion, toxicity, waste production, and high cost.

Acknowledgments

Authors are highly thankful to DRDE Gwalior for financial assistance and SAIF Chandigarh for the characterization of the synthesized materials.

References

- [1] J. R. de Baun, F. M. Pallos, and D. R. Baker, "5-furoyl- 2,2,4-trimethyl-1,4-dihydro-1H-1,5-benzodiazepine as an anti-inflammatory agent," 1976, US Patent 3,978,227.
- [2] J. R. de Baun, F. M. Pallos, and D. R. Baker, "5-furoyl- 2,2,4-trimethyl-1,4-dihydro-1H-1,5-benzodiazepine as an anti-inflammatory agent," *Chemical Abstracts*, vol. 86, p. 5498d, 1977.
- [3] H. Schultz, *Benzodiazepines*, Springer, Heidelberg, Germany, 1982.

- [4] R. K. Smiley, *Comprehensive Organic Chemistry*, Pergamon, Oxford, UK, 1979.
- [5] J. K. Landquist, *Comprehensive Heterocyclic Chemistry*, vol. 1, Pergamon, Oxford, UK, 1984.
- [6] L. O. Randall and B. Kappel, "Pharmacological activity of some benzodiazepines and their metabolites," in *Benzodiazepines*, S. Garattini and E. Mussini, Eds., Raven, New York, NY, USA, 1973.
- [7] R. C. Haris and J. M. Straley, "Lifting apparatus," 1968, US Patent 1,537,757.
- [8] A. M. El-Sayed, H. Abdel-Ghany, and A. M. M. El-Saghier, "A novel synthesis of pyrano(2,3-c)-, 1,3-oxazino(2,3 b)-, 1,2,4-triazolo(3,4-b)-, oxazolo(2,3-b)-, furano(3,2-c)-, and 3-substituted- (1,5)benzodiazepin-2-ones," *Synthetic Communications*, vol. 29, no. 20, pp. 3561–3572, 1999.
- [9] J. X. Xu, H. T. Wu, and S. Jin, "Cycloaddition of benzoheteroazepine II reactions and conformations of cycloadducts on 1,5-benzothiazepines and 1,5-benzodiazepines with nitrile imine and nitrile oxides," *Chinese Journal of Chemistry*, vol. 17, no. 1, pp. 84–91, 1999.
- [10] X. Y. Zhang, J. X. Xu, and S. Jin, "Cycloaddition of benzoheteroazepine reaction of 2,3-dihydro-1h-1,5-benzodiazepines with dichlorocarbene and stereo-structures of products," *Chinese Journal of Chemistry*, vol. 17, no. 4, pp. 404–410, 1999.
- [11] K. Kim, S. K. Volkman, and J. A. Ellman, "Synthesis of 3-substituted 1,4-benzodiazepin-2-ones," *Journal of the Brazilian Chemical Society*, vol. 9, no. 4, pp. 375–379, 1998.
- [12] W. Reid and E. Torinus, "Über heterocyclische Siebenringssysteme, X. Synthesen kondensierter 5-, 7- und 8-gliedriger Heterocyclen mit 2 Stickstoffatomen," *Chemische Berichte*, vol. 92, no. 11, pp. 2902–2916, 1959.
- [13] J. A. L. Herbert and H. Suschitzky, "Syntheses of heterocyclic compounds. part xxix. substituted 2,3-dihydro-1h-1,5-benzodiazepines," *Journal of the Chemical Society*, pp. 2657–2661, 1974.
- [14] H. R. Morales, A. Bulbarela, and R. Contreras, "New synthesis of dihydro- and tetrahydro-1,5-benzodiazepines by reductive condensation of o-phenylenediamine and ketones in the presence of sodium borohydride," *Heterocycles*, vol. 24, no. 1, pp. 135–139, 1986.
- [15] D. I. Jung, T. W. Choi, Y. Y. Kim et al., "Synthesis Of 1,5-benzodiazepine derivatives," *Synthetic Communications*, vol. 29, no. 11, pp. 1941–1951, 1999.
- [16] M. S. Balakrishna and B. Kaboudin, "A simple and new method for the synthesis of 1,5-benzodiazepine derivatives on a solid surface," *Tetrahedron Letters*, vol. 42, no. 6, pp. 1127–1129, 2001.
- [17] M. Curini, F. Epifano, M. C. Marcotullio, and O. Rosati, "Ytterbium triflate promoted synthesis of 1,5-benzodiazepine derivatives," *Tetrahedron Letters*, vol. 42, no. 18, pp. 3193–3195, 2001.
- [18] X. Q. Pan, J. P. Zou, Z. H. Huang, and W. Zhang, "Ga(otf)₃-promoted condensation reactions for 1,5-benzodiazepines and 1,5-benzothiazepines," *Tetrahedron Letters*, vol. 49, no. 36, pp. 5302–5308, 2008.
- [19] R. Kumar, P. Chaudhary, S. Nimesh, A. K. Verma, and R. Chandra, "An efficient synthesis of 1,5-benzodiazepine derivatives catalyzed by silver nitrate," *Green Chemistry*, vol. 8, no. 6, pp. 519–521, 2006.
- [20] V. Sivamurugan, K. Deepa, M. Palanichamy, and V. Murugesan, "[(1)proline]₂zn catalysed synthesis of 1,5-benzodiazepine derivatives under solvent-free condition," *Synthetic Communications*, vol. 34, no. 21, pp. 3833–3846, 2004.
- [21] P. Minothora, S. S. Julia, and A. T. Constantinos, "An efficient method for the synthesis of 1,5-benzodiazepine derivatives under microwave irradiation without solvent," *Tetrahedron Letters*, vol. 43, no. 9, pp. 1755–1758, 2002.
- [22] W. Y. Chen and J. Lu, "Molecular iodine catalyzed one-pot synthesis of 1,5-benzodiazepine derivatives under solvent-free conditions," *Synlett*, vol. 2005, no. 8, pp. 1337–1339, 2005.
- [23] D. V. Jarikote, S. A. Siddiqui, R. Rajagopal, D. Thomas, R. J. Lahoti, and K. V. Srinivasan, "Room temperature ionic liquid promoted synthesis of 1,5-benzodiazepine derivatives under ambient conditions," *Tetrahedron Letters*, vol. 44, no. 9, pp. 1835–1838, 2003.
- [24] B. M. Reddy, P. M. Sreekamth, and V. R. Reddy, "Modified zirconia solid acid catalysts for organic synthesis and transformations," *Journal of Molecular Catalysis A*, vol. 225, pp. 71–78, 2005.
- [25] B. Kaboudin and K. Navae, "Alumina/phosphorus pentoxide (app) as an efficient reagent for the synthesis of 1,5-benzodiazepines under microwave irradiation," *Heterocycles*, vol. 55, no. 8, pp. 1443–1446, 2001.
- [26] J. S. Yadav, B. V. S. Reddy, S. Praveenkumar, K. Nagaiah, N. Lingaiah, and P. S. Saiprasad, "Ag₃pw₁₂o₄₀: a novel and recyclable heteropoly acid for the synthesis of 1,5-benzodiazepines under solvent-free conditions," *Synthesis*, no. 6, pp. 901–904, 2004.
- [27] M. A. Chari and K. Syamasundar, "Polymer (PVP) supported ferric chloride: an efficient and recyclable heterogeneous catalyst for high yield synthesis of 1,5-benzodiazepine derivatives under solvent free conditions and microwave irradiation," *Catalysis Communications*, vol. 6, no. 1, pp. 67–70, 2005.
- [28] A. Hegedüs, Z. Hell, and A. Potor, "A simple environmentally-friendly method for the selective synthesis of 1,5-benzodiazepine derivatives using zeolite catalyst," *Catalysis Letters*, vol. 105, no. 3-4, pp. 229–232, 2005.
- [29] D. Shobha, M. A. Chari, S. T. Selvan et al., "Room temperature synthesis of 1,5-benzodiazepine and its derivatives using cage type mesoporous aluminosilicate catalysts," *Microporous and Mesoporous Materials*, vol. 129, no. 1-2, pp. 112–117, 2010.
- [30] Y. J. He, G. S. Nivarthi, F. Eder, K. Seshan, and J. A. Lercher, "Synthesis, characterization and catalytic activity of the pillared molecular sieve MCM-36," *Microporous and Mesoporous Materials*, vol. 25, no. 1–3, pp. 207–224, 1998.
- [31] S. L. Lawton, A. S. Fung, G. J. Kennedy et al., "Zeolite MCM-49: a three-dimensional MCM-22 analogue synthesized by in situ crystallization," *The Journal of Physical Chemistry*, vol. 100, no. 9, pp. 3788–3798, 1996.
- [32] S. B. C. Pergher, A. Corma, and V. Fornés, "Preparation and characterization of MCM-22 zeolite and its layered precursor," *Química Nova*, vol. 26, no. 6, pp. 795–802, 2003.
- [33] A. Corma, C. Corell, and J. Pérez-Pariente, "Synthesis and characterization of the MCM-22 zeolite," *Original Research Article Zeolites*, vol. 15, no. 1, pp. 2–8, 1995.