Catal Lett (2008) 122:338–343
DOI 10.1007/s10562-007-9385-1

Synthesis of Condensed Benzo[*N,N*]-Heterocycles by Microwave-Assisted Solid Acid Catalysis

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Received: 9 November 2007 / Accepted: 6 December 2007 / Published online: 8 January 2008

Abstract The synthesis of several types of condensed benzo[*N,N*]-heterocycles such as benzimidazoles, benzodiazepines, quinoxalinones by a microwave-assisted solvent-free solid acid catalyzed method is described. The commercially available, inexpensive K-10 montmorillonite is an excellent catalyst for the synthesis of the target compounds. Our approach is based on the reactions of a wide variety of *o*-phenylenediamines, with ketones, aldehydes and bifunctional reagents, respectively. The cyclization reactions were initiated by microwave irradiation. The products, in most cases, were obtained in very high yields (up to 98%) and excellent selectivities in very short reaction times. The effective combination of solid acid catalysis, solvent-free conditions and microwave irradiation provides an attractive and highly ecofriendly approach for the synthesis of these important heterocycles.

Keywords Condensation · Cyclization · *o*-Phenylenediamines · Microwave · Montmorillonite K-10

1 Introduction

N-containing heterocycles play a key role in many aspects of pharmaceutical and medicinal chemistry [1]. This is especially true for condensed derivatives containing two heteroatoms such as benzimidazoles, benzodiazepines and quinoxalines and quinoxalinones. These compounds possess a wide range of biological activity [2].

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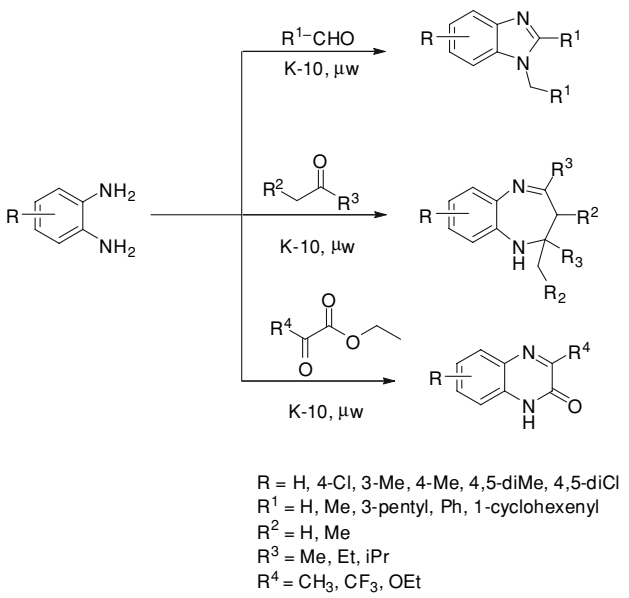
The remarkably extensive biological effects initiated considerable efforts on the synthesis of these compounds. Several reviews summarized the earlier development [3]. Here, we give a short overview of recent efforts related to the environmentally benign preparation of these compounds. Several catalytic methods were developed for the synthesis of benzodiazepines. Catalysts include zeolites [4], $InBr_3$ [5], $Sc(OTf)_3$ [6], $Yb(OTf)_3$ [7], $CeCl_3$/NaI [8], ionic liquids [9], and heteropoly acids [10]. In contrast, similar *green* catalytic methods are sporadic or nonexistent for the synthesis of benzimidazoles [11]. Only a few catalytic methods are available for the synthesis of quinoxaline derivatives [12] and the synthetic efforts are focused only on the synthesis of the quinoxaline skeleton itself [13]. Due to the biological importance of these heterocycles the development of effective, economic and sustainable synthetic methods are highly desirable.

Expanding our recent efforts on developing contemporary efficient and ecofriendly catalytic methods, herein, we report a new effective microwave-assisted solvent-free solid acid catalyzed synthesis of condensed benzo[*N,N*]-heterocycles, including benzimidazoles, benzodiazepines and quinoxalinones. The major advantages of our approach are the use of a readily available, economic and easy to handle solid acid catalyst, the solvent-free system and the very short reaction times. In addition, the high selectivities of the reactions contribute to the prevention of waste formation.

2 Results and Discussion

The synthesis of the target compounds is based on the cyclization reaction of *o*-phenylenediamines with carbonyl compounds. The approach is summarized in Scheme 1.



Scheme 1 Synthesis of benzimidazoles, benzodiazepines and quinoxalinones with microwave-assisted K-10 montmorillonite catalyzed cyclization of *o*-phenylenediamines with aldehydes, ketones and 1,2-dicarbonyl compounds

The mechanism of the reactions is relatively well-known and can be found in details in the above references. Here, a short mechanistic scheme of the reaction of *o*-phenylenediamine with a ketone is described as illustration.

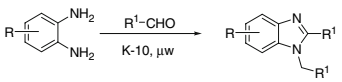
Our earlier studies [14] on solid acid-catalyzed reactions suggested the use of the well-known K-10 montmorillonite as a catalyst. Considering handling, thermal stability, surface area, activity, and cost, K-10 is far superior to other well-known solid acids such as the resinsulfonic acid Amberlyst or Dowex. It is a well-known strong solid acid for a variety of organic transformations [15] and is also used for bifunctional catalysis [16]. K-10 is prepared via high temperature mineral acid treatment of natural montmorillonite [17]. Based on solid state ^{29}Si MAS-NMR studies, its main constituent is a quartz-like material, in addition to kaolinite and montmorillonite [18]. The acid strength of K-10 highly surpasses that of the other oxide based solid acids. Its Hammett acidity constant is $H_0 = -8$, this value is as high as the acidity of concentrated nitric acid [15]. The BET surface area of K-10 montmorillonite (250 m^2g^{-1}), significantly supersedes that of sulfonic acid based resins ($\sim$10–20 m^2g^{-1}). Based on the preliminary investigations further reactions have been carried out with K-10 montmorillonite as a catalyst.

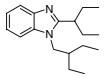
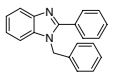
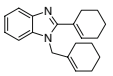
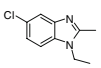
The first set of synthetic studies involved substituted *o*-phenylenediamines and aldehydes. These reactions readily produced benzimidazoles. The cyclizations were carried out in a solvent-free system. The reactants were dissolved in dichloromethane and the dry catalyst was added. After thorough mixing and 2 min stirring the solvent was removed. After solvent removal, the reactants evenly covered the surface of the catalyst. This dry mixture was subjected to microwave irradiation using a focused microwave reactor. The use of microwaves in chemical reactions became a major tool in synthetic organic and medicinal chemistry [19]. The development and use of the current reliable instruments provided a major push for these applications.

The temperature during the irradiation was kept constant using an infrared detector-controller. After the irradiation, the mixture was washed with dichloromethane to isolate the products, while the catalyst was available for recycling. The cyclization of *o*-phenylene diamine with 2 butanone was chosen to test the possibility of catalyst reuse. The reaction was attempted four consecutive times. The product yields showed no sign of catalyst deactivation after reuse, rather a slight 1–2% increase in the conversion was observed each time when the catalyst was recycled. The results of the K-10 catalyzed cyclization of *o*-phenylenediamines with aldehydes are tabulated in Table 1.

As Table 1 indicates, K-10 is an excellent catalyst for the cyclization reaction. Using a variety of substituted

Table 1 Synthesis of substituted benzimidazoles by microwave-assisted K-10 montmorillonite catalyzed cyclization of phenylenediamines and aldehydes at 80 °C[a]



Entry	diamine	aldehyde	Time [min]	Product	Conv [%] [b]
1			2		75
2			1		82[c]
3			3		98
4			5		91
5			7		70[b]
6			2		99[c] (61/39)[d]
7			1		83 (68/15)[d]
8			2		94[c]

[a] Phenylenediamine/aldehyde=1:2.1 ratio was used, [b] isolated yield, [c] Indicates new compounds, [d] ratio of the 5-/6-substituted products, the major isomer is shown

o-phenylenediamines and aldehydes good to excellent yields were obtained. Optimization of the reaction conditions revealed that the cyclization occurs readily, within minutes even at moderate temperatures. Based on the yields no clear substituent effect can be detected for either the diamine's or aldehyde's side. The reactions proceeded smoothly and were completed in 1–7 min. Despite the short reaction times, the isolated yields, in most cases, indicated practically quantitative product formation. No byproduct formation was observed; however, longer irradiation resulted in product decomposition. Several new compounds were isolated in these reactions.

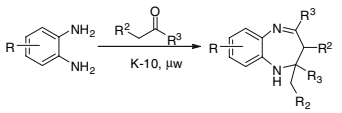
The success in the synthesis of benzimidazoles prompted us to extend these studies and carry out similar investigations with ketones in order to produce condensed seven-membered rings, namely benzodiazepines. The reactions have been conducted using the general solvent-free method discussed above. The results of these reactions are summarized in Table 2.

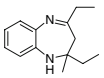
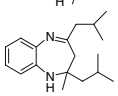
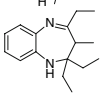
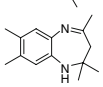
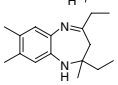
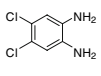
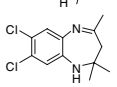
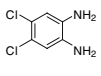
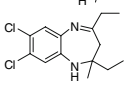
Using solid acid catalysis and microwave irradiation several substituted benzodiazepines were synthesized. The reactions took place in a very short time period (1–6 min) providing good to excellent yields and selectivities. It appears that the substituents on *o*-phenylenediamine have no significant effect on the outcome of the reaction. In contrast, the alkyl groups of the ketones apparently affect the yields. Ketones with small alkyl groups, such as acetone or methyl ethyl ketone, provided excellent, yields. In the case of 4-methyl-2-pentanone or 3-pentanone, however, the yields, although still good, were lower than those mentioned above, probably due to steric hindrance.

In order to further widen the scope of the method and to synthesize several other new compounds of pharmaceutical interest, α-ketoesters were applied as cyclization agents to obtain substituted quinoxalinones using the same general methodology. The results are summarized in Table 3.

The data indicate that the reactions readily provide the expected quinoxalinones in moderate to excellent yields during short reaction times. The substituents did not

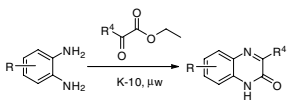
Table 2 Synthesis of substituted benzodiazepines by microwave-assisted K-10 montmorillonite catalyzed cyclization of phenylenediamines and ketones at 80 °C[a]

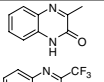
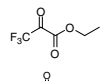
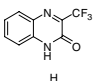
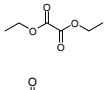
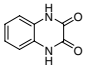
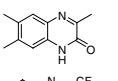
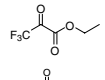


Entry	diamine	Ketone	Time [min]	Product	Yield [%][b]
1			3		93
2			3		90
3			3		80
4			2		78
5			6		95
6			3		95
7			1		94[d]
8			1		84[c][d]

[a] Phenylenediamine/ketone = 1:2.1 ratio was used, [b] Isolated yields, [c] Indicates new compounds, [d] Temperature = 70 °C

Table 3 Synthesis of substituted quinoxalinones and quinoxalindiones by microwave-assisted K-10 montmorillonite catalyzed cyclization of phenylenediamines with α-keto-esters and diethyl oxalate at 80 °C[a]



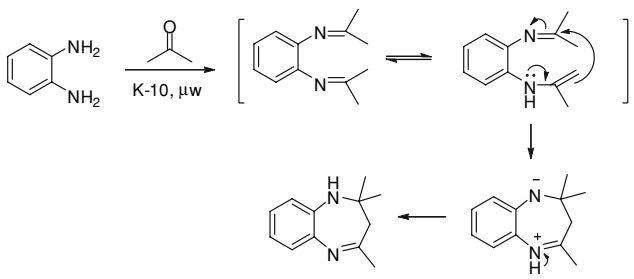
Entry	diamine	di-ketone	Time [min]	Product	Yield [%][b]
1			3		70
2			1		87
3			15		88
4			18		33[d]
5			18		82[c]
6			55		64
7			3		68[c]
8			3		53 (37/16)[e]
9			0.5		82[c] (47/35)[e]
10			6		100[c] (56/44)[f]

[a] Phenylenediamine/1,2–dicarbonyl compound=1:1.2 ratio was used, [b] Isolated yield, [c] Indicates new compounds, [d] Temperature = 130 °C, [e] Ratio of the 6-/7-substituted products, the major isomer is shown, [f] Ratio of the 5-/8-substituted products, the major isomer is shown

significantly affect the performance of the reactions. Using our new protocol, we synthesized several new quinoxalinones. It appears that further systematic variation of the starting materials could even extend the application possibilities.

It is worth mentioning that the cyclization reaction did not occur without the K-10 catalyst even under microwave irradiation. Our experiments without a catalyst did not show product formation at room temperature and conventional heating (80 °C), in 1 h reaction or using microwave irradiation for 15 min. The only exception is the reaction of phenylenediamine with ethyl pyruvate and ethyl trifluoropyruvate. In the case of ethyl pyruvate the catalytic reaction provided ~10% improvement in shorter reaction time. Using ethyl trifluoropyruvate, many secondary reactions occurred and the yield of quinoxalinone was only ~40% after 1 h, under catalyst-free conditions.

The mechanism of these reactions follows the pathway of condensations and is already described in the literature [20]. A basic pathway is illustrated above (Scheme 2). Here, we only emphasize minor differences and advantages that are due to the use of solid acid catalysis. As these reactions are carried out in a solvent-free, open reaction system, the key step is the adsorption of the carbonyl compound on the surface of the catalyst. K-10 montmorillonite is considered to be a mixed Brønsted-Lewis solid acid. The majority of the acid centers is of Lewis acid type [16]. The adsorption occurs when the electron rich carbonyl oxygen interacts with a surface Lewis acid center, and it is of rather chemical than physical nature. This Lewis acid–base interaction anchors the mostly volatile reactants (usually low molecular weight aldehydes or ketones) and initiates strong electrophilic character on the carbonyl carbon, resulting in a surface-bound intermediate of carbocationic nature. A similar anchoring effect has been observed in hydrogenation of cinnamaldehyde on Pt/K-10 catalyst [16] or in Friedel-Crafts hydroxyalkylation of indoles and pyrroles with ethyl trifluoropyruvate [21] and in electrophilic annelations [22].



Scheme 2 Mechanism of the formation of benzodiazepines via K-10 catalyzed cyclization of *o*-phenylenediamine and acetone

Formation of such intermediates is clearly supported, as all experiments were carried out under microwave irradiation in an open reaction vessel. The temperature in the microwave cavity was kept constant at the required values. Many of the low boiling point reagents (acetaldehyde, acetone, methylethylketone ethyl trifluoropyruvate etc.) would have evaporated and have been lost from the reaction mixture without strong chemical adsorption. This would have resulted in low yields. The high yields indicated that such extensive reactant loss did not occur even from the open vessel. As a minor difference from cyclocondensation the reactions in Table 3 occurred via combined condensation and nucleophilic substitution in the case of α-ketoesters. Using diethyl oxalate as a cyclization agent, double nucleophilic substitution occurred and quinoxalindiones formed (entries 3, 6).

3 Experimental

All *o*-phenylenediamines, ketones, aldehydes, α-ketoesters and diethyl oxalate were purchased from Aldrich and used without further purification. K-10 montmorillonite was a Fluka product. $CDCl_3$ and acetone-*d6* were used as solvents for NMR studies and tetramethylsilane and $CFCl_3$ were used as reference compound, each was purchased form Aldrich. The ^{1}H, ^{13}C and ^{19}F (whenever applicable) spectra were obtained on a 300 MHz superconducting Varian NMR spectrometer, in $CDCl_3$ solvent with tetramethylsilane as internal standards. The mass spectrometric identification of the products have been carried out by an Agilent 6850 gas chromatograph-5973N mass spectrometer system (70 eV electron impact ionization) using a 30 m long DB-5 type column (J&W Scientific). A Nicolet 380 FT-IR was used for the infrared measurements (neat samples).

3.1 General Experimental Procedure for the Microwave-Assisted K-10 Montmorillonite Catalyzed Cyclization of *o*-Phenylenediamines with Carbonyl Compounds

The selected *o*-phenylenediamine (1 mmol) and the carbonyl compound (2.1 mmol for reactions in Tables 1, 2 and 1.2 mmol for Table 3) were dissolved in 10 ml of methylene chloride. Five hundred milligram of K-10 montmorillonite was added to the mixture then stirred for 2 min. The solvent was evaporated in vacuo. The dry mixture was then transferred to a reaction tube and irradiated in a microwave oven under continuous stirring (CEM Discovery Benchmate) in an open system under atmospheric pressure at temperatures carefully selected for

each different reaction. During optimization the progress of the reaction was monitored by GC-MS. When the reaction was completed the product was dissolved in CH_2Cl_2, separated from the catalyst by filtration and the solvent was removed in vacuo. The crude product was purified by flash chromatography.

3.1.1 Spectral Data of Selected Compounds

Most products synthesized in this study are known and their spectral characterization showed satisfactory agreement with former literature data. These data are available from the authors upon request. Here, only the spectral data of new compounds are listed. In case of isomeric products the spectral data are shown for the major isomer only.

1-(2-ethylbutyl)-2-(1-ethylpropyl)-1H-1,3-benzimidazole (Table 1, Entry-2) **^{1}H NMR** (399.81 MHz, $CDCl_3$), δ (ppm) 7.72–7.78 (m, 1H, Ar), 7.26–7.32 (m, 1H, Ar), 7.16–7.22 (m, 2H, Ar), 3.98 (d, $J = 7.6$ Hz, 2H, CH_2), 2.75 (quintet, $J = 7.2$ Hz, 1H, CH), 1.78–1.97 (m, 5H, CH, CH_2), 1.20–1.40 (m, 4H, CH_2), 0.91 (t, $J = 7.2$ Hz, 6H, CH_3), 0.86 (t, $J = 7.2$ Hz, 6H, CH_3); **^{13}C NMR** (100.53 MHz, $CDCl_3$), δ (ppm) 158.7, 142.6, 135.2, 121.56, 121.52, 119.1, 109.6, 47.0, 41.6, 40.5, 27.8, 23.4, 12.1, 10.8; **MS**-$C_{18}H_{28}N_2$ (272), m/z (%): 272 (M^+, 35), 257 (15), 243 (60), 229 (20), 215 (20), 201 (100), 173 (25), 159 (70), 146 (55), 132 (80), 104 (10), 77 (20).

2-cyclohex-1-en-1-yl-1-(cyclohex-1-en-1-yl-methyl)-1H-1,3-benzimidazole (Table 1, Entry-5) **^{1}H NMR** (399.81 MHz, $CDCl_3$), δ (ppm) 7.61–7.68 (m, 1H, Ar), 7.18–7.34 (m, 3H, Ar), 6.15 (septet, $J = 1.6$ Hz, 1H, CH), 5.33 (septet, $J = 1.6$ Hz, 1H, CH), 4.61 (d, $J = 1.6$ Hz, 2H, CH_2), 2.48–2.56 (m, 2H, CH_2), 2.20–2.28 (m, 2H, CH_2), 1.50–1.85 (m, 12H, CH_2); **^{13}C NMR** (100.53 MHz, $CDCl_3$), δ (ppm) 155.3, 136.3, 135.5, 134.4, 133.1, 132.3, 128.9, 123.9, 122.5, 119.1, 110.4, 50.4, 28.1, 26.1, 25.6, 24.7, 22.4, 22.3, 22.1, 21.6; **MS**-$C_{20}H_{24}N_2$ (292), m/z (%): 292 (M^+, 100), 277 (25), 263 (55), 249 (55), 237 (30), 223 (20), 197 (50), 183 (40), 169 (40), 119 (10), 75 (25).

5-chloro-1-ethyl-2-methyl-1H-benzimidazole (Table 1, Entry-6) **^{1}H NMR** (399.81 MHz, $CDCl_3$), δ (ppm) 7.64 (d, $J = 1.2$ Hz, 1H, Ar), 7.24 (d, $J = 5.6$ Hz, 1H, Ar), 7.19 (d, $J = 5.6$ Hz, 1H, Ar), 4.12 (q, $J = 7.2$ Hz, 2H, CH_2), 2.59 (s, 3H, CH_3), 1.39 (t, $J = 7.2$ Hz, 3H, CH_3); **^{13}C NMR** (100.53 MHz, $CDCl_3$), δ (ppm) 149.9, 141.5, 127.8, 122.7, 118.9, 109.9, 109.4, 38.9, 15.0, 13.8; **MS**-$C_{10}H_{11}ClN_2$ (194.5), m/z (%): 194 (M^+, 85), 179 (100), 165 (10), 144 (10), 126 (10), 89 (25), 75 (20).

1-ethyl-2,4-dimethyl-1H-benzimidazole (Table 1, Entry-8) **^{1}H NMR** (399.81 MHz, $CDCl_3$), δ (ppm) 7.12–7.16 (m, 2H, Ar), 7.02–7.05 (m, 1H, Ar), 4.14 (q, $J = 7.6$ Hz, 2H, CH_2), 2.65 (s, 6H, CH_3), 1.39 (t, $J = 7.6$ Hz, 3H, CH_3); **^{13}C NMR** (100.53 MHz, $CDCl_3$), δ (ppm) 146.0, 134.1, 128.9, 122.9, 122.5, 106.8, 90.3, 38.9, 17.0, 15.0, 13.6; **MS**-$C_{11}H_{14}N_2$ (174), m/z (%): 174 (M^+, 100), 159 (65), 145 (55), 130 (10), 117 (5), 104 (10), 88 (10), 70 (30).

7,8-dichloro-2,4-diethyl-2-methyl-2,3-dihydro-1H-1,5-benzodiazepine (Table 2, Entry-8) **^{1}H NMR** (300.12 MHz, $CDCl_3$), δ (ppm) 8.09 (s, 1H, Ar), 8.08 (s, 1H, Ar), 4.10 (bs, 1H, NH), 2.72 (q, $J = 7.8$ Hz, 2H, CH_2), 2.10–2.32 (m, 2H, CH_2), 1.57–1.67 (m, 2H, CH_2), 1.42 (s, 3H, CH_3), 1.28 (t, $J = 7.8$ Hz, 3H, CH_3), 0.85 (t, $J = 7.8$ Hz, 3H, CH_3); **^{13}C NMR** (100.53 MHz, $CDCl_3$), δ (ppm) 174.6, 154.9, 139.9, 129.2, 124.8, 124.4, 119.0, 71.0, 37.4, 36.4, 30.6, 23.5, 10.3, 8.8; **MS**-$C_{14}H_{18}Cl_2N_2$ (285), m/z (%): 285 (M^+, 16), 256 (115), 255 (100), 215 (27), 201 (17); IR (neat): 3330 (NH stretch), 2920 (alkyl CH stretch), 1630 (C=N stretch), 1570 (Aromatic C=C).

6,7-dimethyl-3-(trifluoromethyl)quinoxalin-2(1H)-one (Table 3, Entry-5) **^{1}H NMR** (300.12 MHz, Acetone-D6), δ (ppm) 7.66 (s, 1H, Ar), 7.26 (s, 1H, Ar), 2.41 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 1.29 (bs, 1H, NH), **^{13}C NMR** (75.46 MHz, Acetone-*d6*), δ (ppm) 160.5, 151.6, 144.3, 133.7, 132.1, 129.9, 129.1, 122.4 (q, $J = 277$ Hz, CF_3), 115.7, 20.4, 19.2; **^{19}F NMR** (282.40 MHz, $CFCl_3$), δ (ppm) -69.63; **MS**-$C_{11}H_9N_2OF_3$ (242), m/z (%): 242 (M^+, 100), 227 (10), 213 (33), 199 (55), 179 (20), 116 (8).

6,7-dichloro-3-(trifluoromethyl)quinoxalin-2(1H)-one (Table 3, Entry-7) **^{1}H NMR** (300.12 MHz, Acetone-*d6*), δ (ppm) 8.11 (s, 1H, Ar), 7.66 (s, 1H, Ar), 2.98 (bs, 1H, NH); **^{13}C NMR** (75.46 MHz, Acetone-*d6*), δ (ppm) 161.6, 151.8, 137.3, 134.3, 131.9, 130.5, 127.7, 122.5 (q, $J = 275$ Hz, CF_3), 117.8; **^{19}F NMR** (282.40 MHz, $CFCl_3$), δ (ppm) -70.05; **MS**-$C_9H_3N_2Cl_2F_3O$ (282), m/z (%): 282 (M^+, 100), 254 (20), 234 (90), 158 (15), 97 (10), 69 (15).

5-methyl-3-(trifluoromethyl)quinoxalin-2(1H)-one (Table 3, Entry-10) **^{1}H NMR** (300.12 MHz, $CDCl_3$), δ (ppm) 6.84–6.95 (m, 2H, Ar), 6.58–6.62 (m, 1H, Ar), 4.10 (bs, 1H, NH), 2.55 (s, 3H, CH_3); **^{13}C NMR** (75.46 MHz, $CDCl_3$), δ (ppm) 171.6, 150.1, 134.1, 132.6, 131.7, 131.0, 128.2, 126.7, 116.6, 30.5; **^{19}F NMR** (282.40 MHz, $CFCl_3$), δ (ppm) -70.21; **MS**-$C_{10}H_7N_2OF_3$ (228), m/z (%): 228 (M^+, 100), 208 (52), 199 (57), 179 (26), 159 (14), 131 (10).

4 Conclusions

A new solid acid catalyzed, effective, economic and clean synthetic method has been developed for the synthesis of condensed benzo[*N,N*]-heterocycles such as benzimidazoles, benzodiazepines and quinoxalinones. Our method incorporates the advantages of solid acid catalysis and the use of microwave irradiation. While the reactions provide the products in good to excellent yields and selectivities, they occur under mild conditions, in short reaction times and in a solvent-free reaction system. In addition, the new

method made possible the selective synthesis of a wide range of new compounds. This simple and effective process provides a novel way for the environmentally benign synthesis of the target compounds that might extend the possibilities in their chemical and biomedical applications.

Acknowledgement Financial support provided by the University of Massachusetts Boston, and National Institute of Health (R-15 AG025777-02) is gratefully acknowledged.

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