Microwave-assisted, solvent free preparation of 1,5-benzodiazepine derivatives using nanomagnetic-supported sulfonic acid as a recyclable and heterogeneous catalyst

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A new preparation of 1,5-benzodiazepine derivatives has been achieved in good to excellent yields by the condensation of *o*-phenylenediamine with a variety of ketones employing nano-γ-Fe_2O_3–SO_3H as catalyst under microwave irradiation and solvent-free conditions. Recyclable nano-γ-Fe_2O_3–SO_3H provided high reactivity and was easily separated from the reaction mixture by using an external magnet. The advantages offered by this method are based on the principles of 'green chemistry': a facile and rapid reaction, no solvent, easy separation of products and good to excellent yields..

Keywords: nanomagnetic-supported sulfonic acid, 1,5-benzodiazepine, solvent-free condition, microwave irradiation

The benzodiazepine skeleton represents a significant class of heterocyclic compounds containing nitrogen which exhibit a number of important therapeutic and pharmacological properties. Indeed, derivatives of benzodiazepines are one of the best known classes of drugs, due to the effect upon the neurotransmitter gamma-aminobutyric acid (GABA), which results in sedative, hypnotic, anti-anxiety, anticonvulsant and muscle-relaxant action.[1] Clobazam (A) which has been marketed across the world as an anxiolytic since 1975 and as an anti-covulsant[2] since 1984 has also proved useful in the treatment of epilepsy and anxiety and has also been approved as a short term adjunctive agent in psychotic disorders such schizophrenia. Arfendazam (B) has sedative and anxiolytic effects similar to other benzodiazepine derivatives (Fig. 1).

Diazepines and their derivatives have been used as starting materials for the preparation of a number of fused ring compounds such as triazole and oxadiazole derivatives.[3] Derivatives of benzodiazepines are also used as dyes for acrylic fibres in photography, their distinct electron mobility have been exploited in layer materials for electron transformation.[4] Thus, due to the wide applications of benzodiazepine derivatives in medicine and industry, and in organic reactions, there is an imperative need to develop new methodology for the synthesis of these compounds. Various methods for the preparation of benzodiazepines are reported in the literature nine of which[5-13] are listed in Table 2. However, many of these methods have some limitations such as low to poor yields, tedious work-up procedures, hazardous and expensive reagents and solvents, and relatively long reaction times. Furthermore, the major drawback of most of the existing methods is that, the catalysts are destroyed in work-up procedures and could not be recovered nor reused. Therefore, there is an essential need for the development of clean processes and utilisation of eco-friendly and heterogeneous catalysts which can be simply recycled at the end of reactions for the synthesis of benzodiazepines. Recent developments in organic reactions lead to new eco-benign reaction procedures that save energy and uphold green reaction procedures. Microwave-assisted solvent free organic reactions show various advantages over traditional reactions in organic solvents, such reactions are reducing the load of hazardous organic solvent disposal and improve the rate and yield of organic reactions.[14]

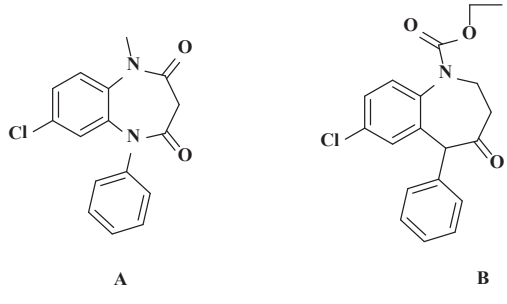

Fig. 1 Biologically and pharmaceutically active benzodiazepine derivatives.

Magnetic nanoparticles (MNP) have emerged as an alternative to porous materials and have potential applications in various fields.[15,16] These materials have attracted interest owing to their properties as magnetically recoverable, low toxicity, heterogeneous supports with a large ratio of surface area to volume. This environmentally benign and impressive process for catalyst separation has become an important tool from an economic, safety and environmental point of view.[17-20] Also, surface functionalisation of magnetic particles is an elegant way to bridge the gap between heterogeneous and homogeneous catalysis.

In recent years, solid acid catalysts have opened new avenues and introduced an amazing and efficient system in the field of green catalysis of organic synthesis due to their environmental friendliness, ease of handling, non-toxic nature and their reusability.[21-24] Among these, sulfuric acid functionalised magnetite nanoparticles (nano-γ-Fe_2O_3–SO_3H) has been found to be a heterogeneous and effective solid acid catalyst for different organic reactions under environmentally friendly conditions with magnetic separation techniques.[25-27]

Following our interest in the catalytic application of solid acid catalysts,[25] we now report an efficient and simple method for the preparation of 1,5-benzodiazepine derivatives through the cyclocondensation of *o*-phenylenediamine or its 4-methyl derivative with a variety of ketones under solvent free conditions in the presence of a catalytic amount of nano-γ-Fe_2O_3–SO_3H.

Results and discussion

We describe a simple and efficient preparation of variously substituted 1,5-benzodiazepines (**3a–o**; R′, R″=alkyl, aryl) from *o*-phenylenediamine **1a** (1mmol) (or its 4-methyl derivative **1b**) and various α-methylene ketones (**2a–o**; R′, R″ =alkyl, aryl) (2.1mmol) using nano-γ-Fe_2O_3–SO_3H catalyst under solvent-free conditions (Scheme 1). Two techniques, conventional heating (method A) and microwave (MW) irradiation (method B) were compared. In order to find out the optimal thermal conditions, the condensation reaction between *o*-phenylenediamine **1a** (1 mmol) and acetophenone (**2a**; R′= Ph, R″=H) (2.1 mmol) to form 1,5-benzodiazepine (**3a**; R′= Ph, R″ =H) (Scheme 1) was chosen as a model reaction. A diverse

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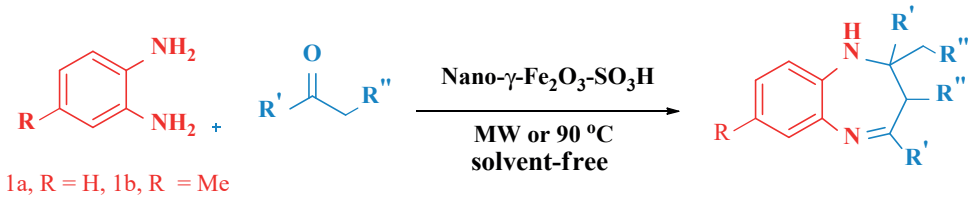


1a, R = H, 1b, R = Me

2a-n (R' , R" = alkyl, aryl)

3a-n (R',R" = alkyl, aryl)

Scheme 1

range of solvent systems, loading of catalysts and temperature were evaluated. The results are summarised in Table 1. We first used 0.0125 g of catalyst in 1,5-benzodiazepine synthesis and obtained a yield of 35% (entry 1). When the amount of nano-γ-Fe_2O_3–SO_3H catalyst was increased from 0.0125 to 0.025 and then to 0.05 g, the yield of **3a** increased to some extent (entries 1–3). Since the yield of **3a** did not show any significant improvement with a further increment of nano-γ-Fe_2O_3–SO_3H catalyst to 0.07g (entry 4), 0.05 g of catalyst was optimal.

The above experiment was also performed in various solvents including water, acetonitrile, methanol, ethanol, chloroform and dimethylsulfoxide (DMSO), but the yields were lower (entries 10–15). Therefore, solvent-free conditions appear to give the best results.

Finally, in order to study the effect of temperature on the synthesis of 1,5-benzodiazepines, we carried out the synthesis of **3a** at various temperature and results are summarised in Table 1. When the reaction was performed at room temperature, only a trace of the desired product was formed during 2h (entry 6). On the other hand, at 100 and 110 °C, (entries 8 and 9), the product yield decreased. As a results, the reaction temperature 90 °C was chosen for subsequent experiments.

We also carried out synthesis of **3a** using various other iron oxide catalysts to compare the catalytic activity of prepared nano-γ-Fe_2O_3–SO_3H as catalyst under solvent-free conditions. The results are shown in Table 2. $FeCl_2.4H_2O$, $FeCl_3.6H_2O$ and bulk-Fe_2O_3 as homogeneous catalysts showed very poor yields compared with nano-γ-Fe_2O_3–SO_3H and all other heterogeneous catalyst (nano-γ-Fe_2O_3) used in this study under solvent free reaction condition (entries 11–14). However, we used 0.05g of bulk-Fe_2O_3–SO_3H to investigate effect of –SO_3H group in synthesis of benzodiazepine, this reaction showed good performance of respective diazepine during 2h (entry 15). Also, in order to compare the catalytic activity of nano-γ-Fe_2O_3–SO_3H, the yields of 1,5-benzodiazepine using other catalysts recently reported are included in Table 2, entries 1–9).

From the above observations, it is clear that nano-γ-Fe_2O_3–SO_3H plays a specific role compared to other catalysts, due to its nano-active surface and acidic sites

Thus, employing 0.05 g of nano-γ-Fe_2O_3–SO_3H as catalyst under solvent free condition at 90 °C for the synthesis of 1,5-benzodiazepine derivatives was considered as optimal. Having optimised the reaction conditions, we applied them to the synthesis of other 1,5-benzodiazepines. The reaction of *o*-phenylenediamine and various substituted ketones, which afforded the corresponding products **3a–o** under two different sets of conditions and the yields are listed in Table 3. All the products **3a–o** are known compounds and the literature melting points of each are listed in Table 3.

As shown in Table 3 (entries 1–8), in the reaction of *o*-phenylenediamines with acetophenones **2a–h** the desired products **3a–h** were obtained in good to excellent yields. Note that, when using cyclic ketones such as cyclopentanone and

Table 1 Effects of amount of catalyst, duration of reaction and solvent on the yield of 1,5-benzodiazepine (**3a**; R′=Ph, R″=H) prepared from *o*-phenylenediamine **1a** and acetophenone (**2a**; R′=Ph, R′=H) (Scheme 1)[a]

Entry	Nano-γ-Fe_2O_3–SO_3H/g	Conditions	Time/h:min	Yield/%[b]
1	0.0125	Solvent free/90°C	2	35
2	0.025	Solvent free/90°C	2	63
3	0.05	Solvent free/90°C	2	90
4	0.07	Solvent free/90°C	2	85
5	0.05	Solvent free[c]/90°C	00:06	92
6	0.05	Solvent free/25°C	2	Trace
7	0.05	Solvent free/80°C	2	70
8	0.05	Solvent free/100°C	2	85
9	0.05	Solvent free/110°C	2	80
10	0.05	Reflux /H_2O	2	20
11	0.05	Reflux /EtOH	2	30
12	0.05	Reflux /MeOH	2	40
13	0.05	Reflux /CH_3CN	2	35
14	0.05	Reflux /$CHCl_3$	2	40
15	0.05	Reflux /DMSO	2	65

[a]Reaction conditions: a mixture of *o*-phenylenediamine **1a** (1equiv.) and acetophenone (**2a**; R′=Ph, R″=H) (2.1 equiv.) was reacted with nano-γ-Fe_2O_3–SO_3H.

[b]Isolated yield.

[c]Microwave condition.

Table 2 Comparison of nano-γ-Fe_2O_3–SO_3H with other recently reported acid catalysts in the preparation of 1,5-benzodiazepine (**3a**; R′=Ph, R″=H) from *o*-phenylenediamine **1a** (1equiv.) and acetophenone (**2a**; R′=Ph, R″=H) (2.1 equiv.) (Scheme 1)[a]

Entry	Catalyst/g	Conditions	Time/h	Yield/%[b]	Ref.
1	$Hg(OTf)_2$ (0.5 mol%)	EtOH/RT	6.5	90	5
2	Silver substituted silicotungstic acid (10 mol %)	CH_3CN/Reflux	12	89	6
3	$PhB(OH)_2$ (20 mol %)	CH_3CN/Reflux	12	93	7
4	*p*-nitrobenzoic acid (0.5 equiv)	CH_3CN/RT	7	90	8
5	Zinc montmorillonite (0.05g)	Solvent free/RT	12	81	9
6	$NaClO_4$ (2 mol%)	Water/RT	3	85	10
7	2,4.6-trichloro-1,3,5-triazine (4 mol%)	MeOH/RT	12	99	11
8	H-MCM-22 Zeolite (0.1 g)	CH_3CN/RT	1	86	12
9	$NbCl_5$ (10 mol %)	*n*-Hexane/50°C	6	91	13
10	None	Solvent free/90°C	5	Trace	This work
11	$FeCl_2.4H_2O$ (0.05g)	Solvent free/90°C	2	Trace	This work
12	$FeCl_3.6H_2O$ (0.05g)	Solvent free/90°C	2	Trace	This work
13	Bulk-Fe_2O_3 (0.05g)	Solvent free/90°C	2	Trace	This work
15	Nano-γ-Fe_2O_3 (0.05g)	Solvent free/90°C	2	40	This work
14	Bulk-Fe_2O_3–SO_3H (0.05g)	Solvent free/90°C	2	60	This work
16	Nano-γ-Fe_2O_3–SO_3H (0.05 g)	Solvent free/90°C	2	90	This work

[a]Reaction condition: a mixture of *o*-phenylenediamine **1a** (1equiv.) and acetophenone (**2a**; R′=Ph, R″=H) (2.1 equiv.) was reacted under various sets of conditions with various acid catalysts.

[b]Isolated yield.

Table 3 Preparation of 1,5-benzodiazepines (**3a–o**; R′, R″=alkyl, aryl) from *o*-phenylene-diamines (**1a**, R=H or **1b**, R=Me) and various ketones (**2a–o**; R′, R″=alkyl, aryl) catalysed by nano-γ-Fe_2O_3–SO_3H

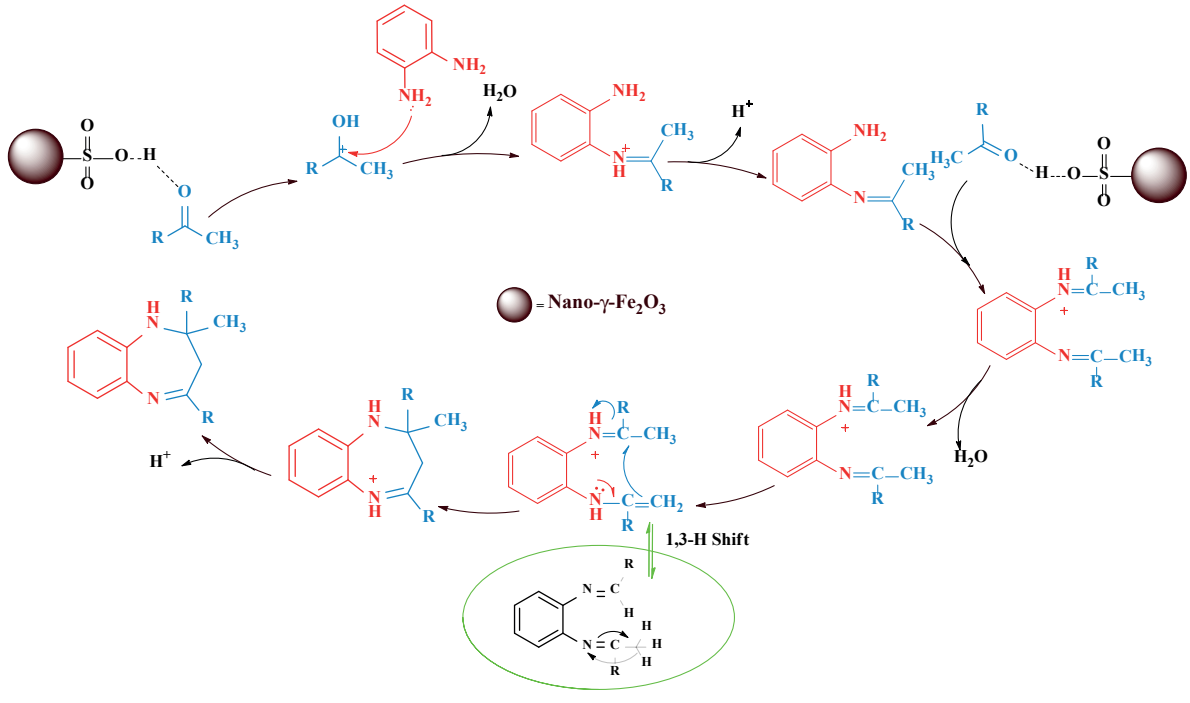
Product	R	R′	R”	Method A		Method B		M.p./°C[Ref.]
				Time/min	Yield/%[b]	Time/min	Yield/%[b]	
3a	H	C_6H_5	H	120	90	6	93	150–151(lit. 150–152)[12]
3b	H	*p*-ClC_6H_4	H	180	85	6	95	142–144 (lit. 143–145)[9]
3c	H	*p*-BrC_6H_4	H	110	88	6	90	146–148 (lit. 145–146)[7]
3d	H	*p*-$O_2NC_6H_4$	H	120	87	7	93	154–156 (lit. 157)[7]
3e	H	*p*-HOC_6H_4	H	75	90	6	90	218–220 (lit. 219–220)[7]
3f	H	*p*-$CH_3OC_6H_4$	H	85	90	7	91	116–117 (lit. 114–116)[7]
3g	H	*p*-$CH_3C_6H_4$	H	90	89	8	90	98–100 (lit. 98–99)[7]
3h	H	*m*-$O_2NC_6H_4$	H	90	90	10	90	86–88 (lit. 86–88)[5]
3i	H	$-(CH_2)_4-$		90	88	10	95	136–138 (lit. 137–139)[7]
3j	H	$-(CH_2)_3-$		80	85	9	90	138–140 (lit. 137–138)[7]
3k	H	CH_3	CH_3	105	89	8	87	136–138 (lit. 137–139)[12]
3l	H	CH_3	H	60	90	6	95	137–139 (lit. 137–139)[12]
3m	Me	C_6H_5	H	90	89	7	90	90–92 (lit. 92)[9]
3n	Me	CH_3	H	75	85	9	85	125–127 (lit. 127–129)[9]

[a] Reaction conditions: a mixture of *o*-phenylenediamine **1a** (1equiv.) (or its 4-methyl derivative **1b**), acetophenone (**2a–o**; R′, R″=alkyl, aryl) (2.1 equiv.) and nano-γ-Fe_2O_3–SO_3H (0.05 g) was heated (Method A) or subjected to microwave irradiation (360 W) (Method B) under solvent-free conditions at 90 °C.
[b] Isolated yield.

cyclohexanone, the corresponding 1,5-benzodiazepine products **3i,j** were achieved in excellent yields (entries 9 and 10). 2-Butanone as an unsymmetrical ketones was also able to give a single product **3k** due to the ring closure occurring selectively only from one side of the carbon skeleton. We also studied a different *o*-phenylenediamine, 4-methyl-benzene-1,2-diamine **1b** with an aromatic and aliphatic ketone and excellent yields of the respective products **3m** and **3n** under the optimised reaction conditions were obtained. Additionally, to develop the generality of the reaction and to embrace green chemistry, the cyclocondensation reactions were carried out under the optimised conditions but under microwave irradiation. Using microwave irradiation gave high yields in very short reaction times (6–12 min) and the products were obtained in good to excellent yields. Thus, this methodology becomes an efficient strategy for the quick synthesis of 1,5-benzodiazepine derivatives.

This is a substantial finding: due to the magnetic property of nano-γ-Fe_2O_3–SO_3H, recovery of the catalyst is very simple and efficient from the reaction mixture during workup procedure. Hence, the catalyst was separated easily from the reaction mixture by using an external magnet. The isolated catalyst was washed with acetone, dried in air and re-used for five runs without any significant loss of activity. In each run, the desired pure product (**3a**) was obtained after separation and products were purified by recrystallisation to afford the pure product in good to excellent yield without the need for flash or column chromatography for purification of products. The isolated yields of the product for five successive runs were: 90, 90, 89, 88 and 87% which demonstrates the excellent recyclability of this catalyst.

Based on reports in the literature[12] a plausible mechanism for the formation of 1,5-benzodiazepine is proposed in Scheme 2. The amino groups of *o*-phenylenediamine attack the protonated



Scheme 2

carbonyl groups of the molecules of ketone in the presence of nano-γ-Fe_2O_3–SO_3H giving the intermediate diimine. Then, a tautomeric 1,3-hydrogen shift of the methyl group occurs to form an intermediate bicylcic enamine **B**, which cyclises to afford the seven membered ring of 1,5-benzodiazepine **3**.

Experimental

All chemicals were obtained from Merck and used without any further purification. Melting points were recorded on an electro thermal 9100 apparatus and are uncorrected. A microwave LG oven MG 555f model was used. UV-Vis spectra were obtained on a Shimadzu UV-1650PC spectrophotometer. The IR spectra were recorded on a PerkinElmer model 783 spectrophotometer (Waltham, MA, USA). NMR spectra were obtained on a Bruker Avance 300 spectrometer (^{1}H NMR at 400 Hz, ^{13}C NMR at 100 Hz) in $CDCl_3$ using TMS as an internal standard. Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz.

Nano-γ-Fe_2O_3–SO_3H was prepared according to the literature[25] and characterised by XRD, TG, SEM, TEM, XPS and FTIR. Its acidity function, H0=1.65 was determined spectroscopically, as described in one of our recent articles.[27]

Synthesis 1,5-benzodiazepine under conventional thermal method (method A)

A mixture of *o*-phenylenediamine (1 mmol), ketone (2.1 mmol) and nano-γ-Fe_2O_3–SO_3H (0.05g) was mixed and heated at 90°C. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and the catalyst removed by external magnet. The products were purified by recrystallisation to afford the pure product in good to excellent yield. All products were characterised by melting point, IR, ^{1}H NMR and ^{13}C NMR spectroscopy (Table 3, entry 1).

Synthesis 1,5-benzodiazepine under microwave irradiation method (method B)

The reaction substances of method A were heated in a microwave oven at 360 W for 6 minutes. The reaction mixture was then worked-up a similar way to method A.

2-Methyl-2,4-diphenyl-2,3-dihydro-1H-1,5-benzodiazepine (**3a**): Yellow solid; m.p. 150–151 °C (EtOH); IR (KBr) ν_{max}/cm^{-1}: 3332 (NH), 2961 (C–H aromatic) 2855 and 1925 (C–H aliphatic), 1634 (C=N), 1594 and 1455 (C=C); ^{1}H NMR: δ 1.271 (s, 3H, CH_3), 2.47 (d, 2H, CH_2 a,b), 4.64 (br s, 1H, NH), 6.89–7.12 (q, 3H, C_6H_4), 7.14–7.39 (m, 11H, C_6H_5); ^{13}C NMR: δ 29.9 (CH_3), 43.3 (C-3), 73.7 (C-2), 119.7 (C-9), 119.9 (C-7), 125.9 (C-6), 125.9 (C-8), 126.7 (C-4"), 127.5 (C-2", 6"), 127.7 (C-3", 5"), 128.1 (C-3', 5'), 128.3 (C-2', 6'), 129.5 (C-4'), 138.1 (C-1'), 139.5 (C-5a), 140.1 (C-1"), 147.6 (C-9a), 167.8 (C-4).

2-Methyl-2,4-bis(4-bromophenyl)-2,3-dihydro-1H-1,5-benzodiazepine (**3c**): Yellow solid; m.p. 146–148 °C (EtOH); ^{1}H NMR: δ 1.52 (s, 3H, CH_3), 2.60 (d, 1H, CHa), 2.83 (d, 1H, CHb), 3.29 (br s, 1H, NH), 6.80–6.83 (t, 1H, C_6H_4), 7.01–7.11 (m, 2H, C_6H_4), 7.25–7.30 (m, 2H, C_6H_4), 7.33–7.46 (d, 7H, C_6H_4). ^{13}C NMR: δ 29.9 (CH_3), 43.3 (C-3), 72.1 (C-2), 121.2 (C-9), 121.3 (C-7), 122.2 (C-6), 124.7 (C-8), 126.8 (C-4"), 127.6 (C-4'), 128.7 (C-2", 6"), 128.8 (C-3", 5"), 131.4 (C-2', 6'), 131.5 (C-3', 5'), 137.7 (C-1'), 138.3 (C-5a), 140.2 (C-1"), 147.1 (C-9a), 166.2 (C-4).

2-Methyl-2,4-bis(4-methoxyphenyl)-2,3-dihydro-1H-1,5-benzodiazepine (**3f**): Yellowish solid; m.p. 119–120 °C (EtOH); IR (KBr) ν_{max}/cm^{-1}: 3295 (NH), 3019 (C–H aromatic), 2964 and 2911 (C–H aliphatic), 1633 (C=N), 1594 and 1476 (C=C); ^{1}H NMR: δ 1.71 (s, 3H, CH_3), 2.90 (d, 1H, CHa), 3.03 (d, 1H, CHb), 3.06 (br s, 1H, NH), 3.52 (d, 3H, OCH_3), 3.79 (t, 3H, OCH_3), 6.74–6.94 (m, 5H, C_6H_4), 7.02–7.05 (t, 2H, C_6H_4), 7.24–7.30 (q, 1H, C_6H_4), 7.51–7.60 (q, 4H, C_6H_4); ^{13}C NMR: δ 29.9 (CH_3), 43.05 (C-3), 55.5 (OCH_3), 55.5 (OCH_3), 73.5 (C-2), 113.6 (C-9), 113.7 (C-3", 5"), 121.7 (C-3', 5'), 121.9 (C-7), 126.0 (C-6), 126.7 (C-1'), 128.3 (C-2', 6'), 129.0 (C-8), 132.3 (C-2', 6'), 138.3 (C-1"), 140.3 (C-5a), 140.8 (C-9a), 158.8 (C-4"), 161.2 (C-4'), 167.3 (C-4).

2-Methyl-2,4-bis(4-methylphenyl)-2,3-dihydro-1H-1,5-benzodiazepine (**3g**): Pale yellow crystalline solid; m.p. 98–100 °C (EtOH); ^{1}H NMR: δ 1.66 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.91 (d, 1H, CHa), 3.08 (d, 1H, CHb), 3.44 (br s, 1H, NH), 6.83 (t, 1H, C_6H_4), 7.08–7.12 (m, 3H, C_6H_4), 7.28–7.32 (q, 3H, C_6H_4), 7.49 (d, 2H, C_6H_4), 7.57 (d, 2H, C_6H_4).

2-Methyl-2,4-bis(3-nitrophenyl)-2,3-dihydro-1H-1,5-benzodiazepine (**3h**): Light brown crystals; m.p. 86–88 °C (EtOH); ^{1}H NMR: δ 1.90 (s, 3H, CH_3), 3.00 (d, 1H, CHa), 3.25 (d, 1H, CHb), 3.55 (br s, 1H, NH), 6.81–7.08 (m, 1H, C_6H_4), 7.10–7.13 (m, 2H, C_6H_4), 7.18–7.36 (m, 3H, C_6H_4), 7.83–7.99 (m, 3H, C_6H_4), 8.02–8.07 (t, 2H, C_6H_4), 8.30 (s, 1H, C_6H_4).

2,2,4-Trimethyl-2,3-dihydro-1H-1,5-benzodiazepine (**3l**): Yellow solid; m.p. 137-139 °C (EtOH); IR (KBr) $\nu_{max/}$cm^{-1}: 3297 (NH), 2962 (C–H aromatic), 2955 and 2925 (C–H aliphatic), 1634 (C=N), 1594 and 1475 (C=C); ^{1}H NMR: δ 1.27 (s, 6H, CH_3), 2.16 (s, 2H, CH_2), 2.31 (s, 3H, CH_3), 4.47 (br s, 1H, NH), 7.22–7.28 (m, 2H, C_6H_4), 7.38–7.40 (q, 2H, C_6H_4).

Conclusions

In conclusion, we have successfully achieved a simple and efficient method for the synthesis of 1,5-benzodiazepine derivatives from various aromatic, aliphatic and cyclic ketones, in good to excellent yields using nano-γ-Fe_2O_3–SO_3H as a heterogeneous and recoverable catalyst under solvent-free conditions. This catalyst could be easily separated and reused up to five times with no significant loss of activity and selectivity. This new method has several advantages: it is rapid, gave good yields under mild reaction conditions and the products were easily purified without the need for column nor flash chromatography.

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