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## ALUMINUM DODECATUNGSTOPHOSPHATE PROMOTED SYNTHESIS OF 1,5-BENZODIAZEPINE DERIVATIVES UNDER SOLVENT-FREE CONDITIONS

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**Abstract** – Solid heteropoly acids (AITP and AIMP) are easily used as efficient catalyst for conversion of *o*-phenylenediamines and ketones to their corresponding 2,3-dihydro-1*H*-1,5-benzodiazepines at room temperature under solvent-free conditions. The method is an easy, rapid, and high yielding reaction for the synthesis of 1,5-benzodiazepine derivatives and is applicable to both cyclic or acyclic ketones without significant difference.

## INTRODUCTION

Benzodiazepines and their derivatives are important class of bioactive molecules. Many members of this family, infact, nowadays widely used as tranquilizing, anticonvulsant, antianxiety, analgesic, sedative, antidepressive and hypnotic agents,<sup>1-3</sup> and also nevirapine analogues.<sup>4</sup> Some benzodiazepine derivatives are also used in industry, such as in photography (as dyes for acrylic fibers),<sup>5</sup> and also as antiinflammatory agent.<sup>6,7</sup> In addition, 1,5-benzodiazepines are valuable synthons used for the preparation of some fused ring benzodiazepine derivatives for the preparation of other fused ring compounds such as triaxolo-, triazolo-, oxadiazolo-, oxazino- or furano-benzodiazepines.<sup>8</sup>

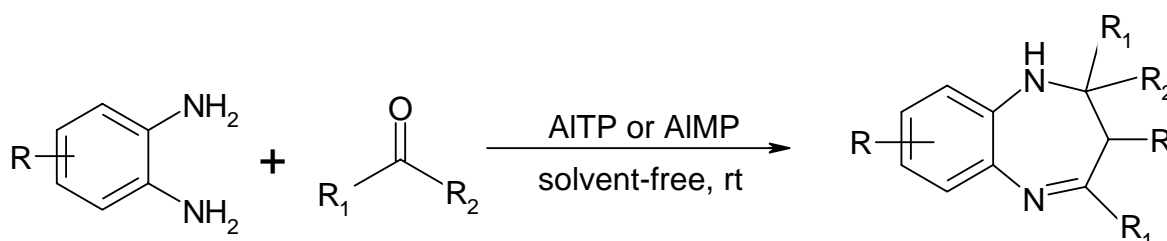
Many reagents have been reported in the literature for this condensation including Yb(OTf)<sub>3</sub>, Sc(OTf)<sub>3</sub>, MgO/POCl<sub>3</sub>, acetic acid under microwave conditions, SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>, polymer-supported FeCl<sub>3</sub>, BF<sub>3</sub>-etherate, NaBH<sub>4</sub>, SiO<sub>2</sub>, polyphosphoric acid, Al<sub>2</sub>O<sub>3</sub>/P<sub>2</sub>O<sub>5</sub>, TiCl<sub>4</sub>/Sm or zeolite.<sup>9</sup> Recently these condensations have been reported even in an ionic liquid medium.<sup>10,11</sup>

Unfortunately, many of these processes suffer from one or other limitation such as harsh reaction conditions, low product yields, tedious work-up procedures, relatively long reaction times, and

co-occurrence of several side products, and difficulty in recovery and reusability of the catalysts. Moreover, some of the reagents employed are very expensive. Therefore, the search continues for a better catalyst for the synthesis of 1,5-benzodiazepines in term of operational simplicity, reusability, economic viability, and greater selectivity.

Preparation of aluminum dodecatungstophosphate ( $\text{AlPW}_{12}\text{O}_{40}$ ) was reported in 1982 by Ono by the reaction of aluminum nitrate and dodecatungstophosphoric acid in a quantitative yield. We have also prepared aluminum dodecatungstophosphate ( $\text{AlPW}_{12}\text{O}_{40}$ , denoted as AITP hereafter) and aluminum dodecamolybdophosphate ( $\text{AlPMo}_{12}\text{O}_{40}$ , denoted as AIMP hereafter) by the addition of aluminum nitrate or by aluminum carbonate to the aqueous solution of tungstophosphoric acid and molybdophosphoric acid, respectively, which on complete evaporation of water gave the desired compound as a white (AITP) and yellow (AIMP) powders in quantitative yield. AITP prepared by both protocols gave satisfactory analytical results within the range of the experimental errors. This salt is a water stable and a nonhygroscopic compound.<sup>12-14</sup>

In continuation of our work on the catalytic properties of heteropoly acids<sup>15</sup>, herein, we have utilized AITP and AIMP as Bronsted acid and efficient catalysts for synthesis of 2,3-dihydro-1*H*-1,5-benzodiazepines by condensation of ketones with *o*-phenylenediamines (Scheme 1) under solvent-free conditions.



**Scheme 1**

## RESULTS AND DISCUSSION

The reactions were carried out by taking a 1:2.5 mole ratio mixture of *o*-phenylenediamine and the ketone along with a catalytic amount of polyoxometalates (POMs), and the mixture were ground together in mortar with a pestle at room temperature for several minutes (Table 1). Cyclic ketones such as cyclohexanone also reacted effectively to produce the corresponding fused ring benzodiazepines. The results are summarized in Table 1.

Best results were obtained using 0.05 and 0.06 equivalents of AITP and AIMP, respectively, lower loading resulted in lower yields, while upper loading did not increase reaction times significantly. The synthesis of 1,5-benzodiazepine derivatives was also conducted in different solvents in the presence of catalytic amount of AITP. The results show that the efficiency and the yield of the reaction in solutions were much less than that observed under solvent-free conditions (Table 2).

**Table 1.** POM catalyzed formation of 2,3-dihydro-1*H*-1,5-benzodiazepines

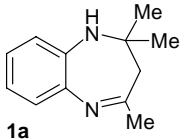
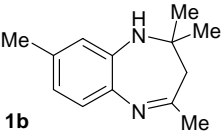
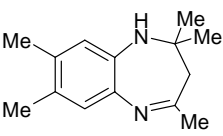
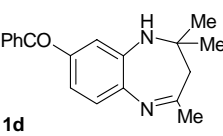
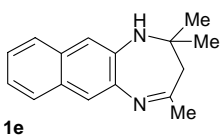
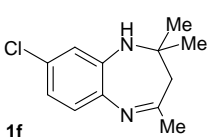
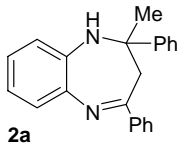
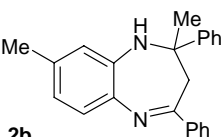
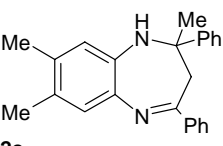
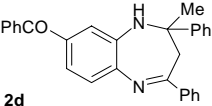
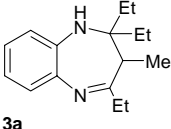
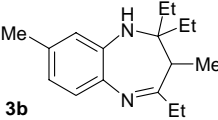
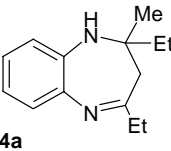
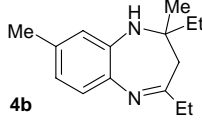
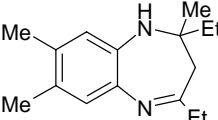
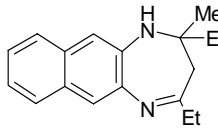
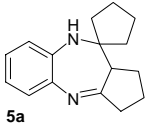
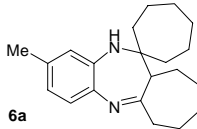
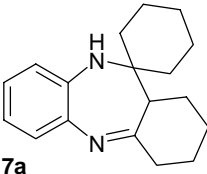
Entry	Ketone	Diamine	POM	Product	Time (min) :	mp (°C)	
						Yield (%)	Found
1	acetone	1,2-phenylenediamine	AITP		25 : 90		
			AIMP		28 : 98	141	137-139 [9a-9f]
		4-methyl-1,2-phenylenediamine	AITP		35 : 90		
			AIMP		20 : 90	138	- [9d,9f]
		4,5-dimethyl-1,2-phenylenediamine	AITP		20 : 86		
			AIMP		45 : 95	131	- [9d-9f]
	4-benzoyl-1,2-phenylenediamine	AITP		32 : 86			
		AIMP		35 : 90	136	- [9d,9f]	
	2,3-naphthalenediamine	AITP		55 : 92			
		AIMP		120 : 87	141	- [9d,9e]	
	4-chloro-1,2-phenylenediamine	AITP		65 : 92			
		AIMP		100 : 95	139	- [8]	
2	acetophenone	1,2-phenylenediamine	AITP		18 : 92		
			AIMP		55 : 90	151	151-152 [9a-9f]
		4-methyl-1,2-phenylenediamine	AITP		28 : 90		
	AIMP		64 : 90		129	- [9f]	
	4,5-dimethyl-1,2-phenylenediamine	AITP		35 : 90			
		AIMP		110 : 90	115	114-116 [9d,9e]	

Table 1 (continued)

Entry	Ketone	Diamine	POM	Product	Yield (%)	mp (°C)						
						Found	Reported					
2	acetophenone	4-benzoyl-1,2-phenylenediamine	AITP	 <b>2d</b>	40 : 90	128	-					
			AIMP					[9f]				
3	3-pentanone	1,2-phenylenediamine	AITP	 <b>3a</b>	60 : 89	138	144-145					
			AIMP		55 : 82			[9a-9f]				
		4-methyl-1,2-phenylenediamine	AITP	 <b>3b</b>	35 : 90	143	143-145					
			AIMP		20 : 87			[9f]				
			2-butanone		1,2-phenylenediamine			AITP	 <b>4a</b>	15 : 78	139	137-138
								AIMP		55 : 93		
4	2-butanone	4-methyl-1,2-phenylenediamine	AITP	 <b>4b</b>	25 : 95	141	-					
			AIMP		95 : 90			[9f]				
		4,5-dimethyl-1,2-phenylenediamine	AITP	 <b>4c</b>	40 : 90	141	-					
			AIMP		140 : 95			[9d,9e]				
		2,3-naphthalenediamine	AITP	 <b>4d</b>	120 : 95	138	-					
			AIMP		80 : 95			[9d]				
5	cyclopentanone	1,2-phenylenediamine	AITP	 <b>5a</b>	50 : 90	139	138-139					
			AIMP		50 : 88			[9a-9f]				
6	cycloheptanone	4-methyl-1,2-phenylenediamine	AITP	 <b>6a</b>	65 : 86	131	136-137					
			AIMP		135 : 85			[9a]				

**Table 1** (continued)

Entry	Ketone	Diamine	POM	Product	Time (min) :	mp (°C)	
						Yield (%)	Found
7	cyclohexanone	1,2-phenylenediamine	AITP	 7a	20 : 87		
			AIMP		25 : 87	139	137-139 [9a,9c,9f]

<sup>a</sup>Reaction condition: diamine (1 mmol), ketone (2.5 mmol), POM (5 mol %), rt, solvent-free conditions.

<sup>b</sup>Isolated yields after column chromatography.

**Table 2.** Synthesis of some 1,5-benzodiazepine derivatives with *o*-phenylenediamine in the presence of AITP in various solvents.

Temperature (°C)	Time (h) : Yield (%)				
	CHCl <sub>3</sub>	CH <sub>3</sub> CN	CH <sub>2</sub> Cl <sub>2</sub>	CCl <sub>4</sub>	EtOH
rt	5:45	6:60	11:45	7:35	9:50
60	3:60	5:70	8:45	7:55	7:65

<sup>a</sup>Reaction conditions: *o*-phenylenediamine (1 mmol), acetone (2.5 mmol), AITP (5 mol %), solvent.

We also tested the title reaction with Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O, Al<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, AlPO<sub>4</sub> and AlCl<sub>3</sub>. Although these catalysts were active for the synthesis of 1,5-benzodiazepine derivatives, the yields were insignificant when compared to those with the AITP and AIMP (Table 3).

**Table 3.** Reaction of *o*-phenylenediamine with acetone in the presence of different catalysts After 20 h.

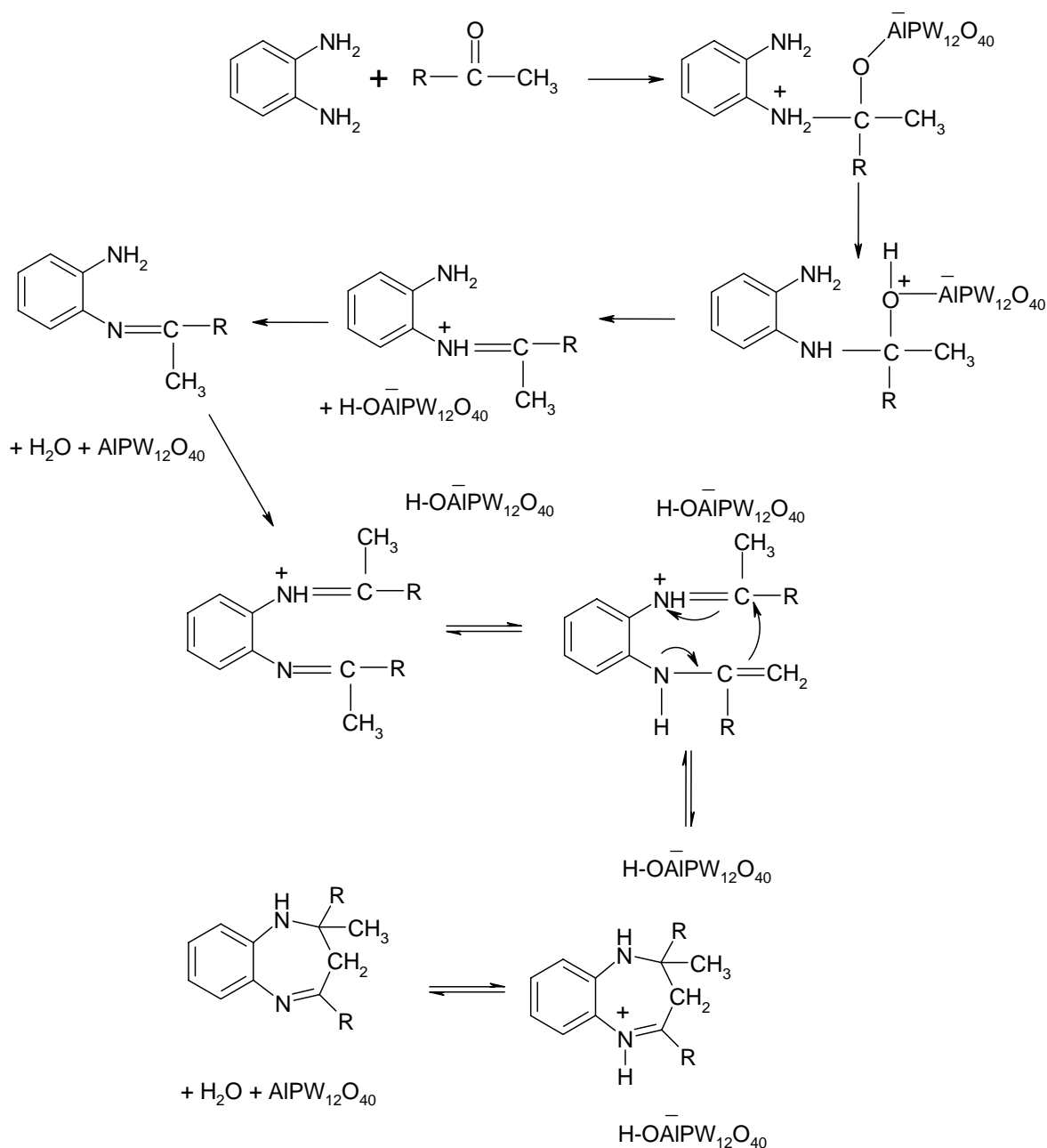
Entry	Ketone	Yield (%)				
		Al <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O	Al <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Al(PO <sub>4</sub> )	AlCl <sub>3</sub>
1	acetone	55	35	15	43	15
2	acetophenone	28	23	21	56	21
3	2-butanone	19	17	11	31	41

<sup>a</sup>Reaction condition: *o*-phenylenediamine (1 mmol), acetone (2.5 mmol), catalyst (5 mol %), rt, solvent-free conditions.

A reasonable pathway for the reaction of diamine with ketone in the presence of AIPW<sub>12</sub>O<sub>40</sub> is presented by Scheme 2. In order to show the merit of the present work in comparison with recently reported protocols, we compared the results of the 1,5-benzodiazepine derivative synthesis from various ketones

and diamines in the presence of  $\text{Yb}(\text{OTf})_3$ ,  $\text{MgO}/\text{POCl}_3$ ,  $\text{SO}_4^{2-}/\text{ZrO}_2$ ,  $\text{Sc}(\text{OTf})_3$ , and AITP with respect to the amounts of the catalysts used, reaction times and yields of the products (Table 4). Comparison of Keggin type POM with these catalysts for this reaction show that activity of AITP and AIMP seems to be higher than or equal with other known catalysts (Table 4).

In this study, we have introduced aluminium dodecatungstophosphate (AITP) and aluminum dodecamolybdophosphate (AIMP) as new highly effective non-hygroscopic, non-corrosive, heterogeneous and environmentally benign catalysts for the efficient synthesis of a variety of 1,5-benzodiazepine derivatives in high yields.



**Scheme 2**

**Table 4.** Comparison of AlTP with several catalysts for synthesis of 1,5-benzodiazepine derivatives with *o*-phenylenediamine.

Entry	Ketone	Time (h) : Yield (%)					
		AlTP	Yb(OTf) <sub>3</sub>	MgO/POCl <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>	Sc(OTf) <sub>3</sub>	Zeolite
1	acetone	0.4 : 90	4 : 96	0.8 : 90	2-3 : 94	3 : 96	4 : 98
2	acetophenone	0.3 : 92	4 : 99	0.8 : 87	2-3 : 96	3 : 93	4 : 95
3	2-butanone	0.2 : 78	4 : 93	0.8 : 80	2-3 : 91	3 : 90	4 : 87
4	3-pentanone	1 : 89	4 : 95	-	2-3 : 84	3 : 89	-
6	cyclohexanone	0.3 : 87	4 : 89	0.8 : 80	2-3 : 80	-	-
7	cyclopentanone	0.8 : 90	4 : 99	0.8 : 65	2-3 : -	3 : 87	-

## EXPERIMENTAL

Tungstophosphoric acid and molybdophosphoric acid (HTP and HMP), which are cheap, reusable, heterogeneous and easily available catalysts, were purchased from Merck and were purified by extraction with Et<sub>2</sub>O from aqueous solution of the acid. After evacuation at 150-300 °C for 1-2 h under reduced pressure, pure HTP and HMP were obtained.<sup>16</sup>

AlTP can be prepared from cheap and commercially available chemicals in a quantitative yield in aqueous media. In contrast to many other Lewis acids, storage of this compound does not need special precautions, e.g. it can be stored on a bench top for months without losing its catalytic activity. In addition, as a non-hygroscopic, non-corrosive and a water stable compound, the handling of AlTP is easy which makes this catalyst suitable for the large-scale operations.

All solvents were reagent grade. All reaction mixtures were stirred magnetically and were monitored by GC or TLC. IR spectra were recorded on a Perkin-Elmer FT/IR-Impact 400D spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Bruker A W 200 MHz spectrometer in CDCl<sub>3</sub>-d<sub>6</sub> using TMS as an internal standard.

**Typical procedure:** A mixture of diamine (1 mmol), ketone (2.5 mmol) and POM (0.05 mmol) were ground together in mortar with a pestle at rt for several minutes (Table 1). In cases when the mixture stuck to the walls of the mortar, it was taken off the walls with a spatula and grinding was redone. The reaction was monitored by TLC, NMR and mass were used for analysis of the products. After completion of the reaction, 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was added to the reaction mixture and the catalyst was recovered by filtration. The organic layer was concentrated and the products was purified by silica gel column

(100-200 mesh) and eluted with EtOAc:n-hexane (2:8) to afford pure compound in 80-98% yield. The wet catalyst was recycled and no appreciable change in activity was noticed after few cycles. The spectral data of the some of the compounds are given below. The catalyst was removed and the residue was purified by SiO<sub>2</sub> gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/MeOH 95:5 as eluent.

#### Selected spectroscopic data:

**2,2,4-Trimethyl-2,3-dihydro-1H-1,5-benzodiazepine (1a):** yellow solid; mp 137–139 °C; IR; <sup>1</sup>H NMR;<sup>9a,c</sup> <sup>13</sup>C NMR;<sup>9a,h</sup> GC/MS: M<sup>+</sup>=188.

**2-Methyl-2,4-diphenyl-2,3-dihydro-1H-1,5-benzodiazepine (2a):** yellow solid; mp 151–152 °C; IR 3330 (s br), 1635 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR;<sup>9a,i</sup> <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 167.5, 146.6, 140.1, 139.5, 138.2, 129.8, 128.6, 128.4, 128.1, 127.1, 127.1, 126.4, 125.5, 121.7, 121.5, 73.9, 43.0, 29.9; GC/MS: M<sup>+</sup>=312.

**2,2,4-Triethyl-3-methyl-2,3-dihydro-1H-1,5-benzodiazepine (3a):** yellow solid; mp 144–145 °C; IR 3330 (s br), 1638 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 0.76–1.48 (m, 13H), 1.61 (s, 3H), 2.87 (q, 1H, J=7.0 Hz), 3.75 (s br, 1H), 6.65–7.40 (m, 4H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 173.8, 142.4, 139.0, 132.7, 126.7, 118.0, 117.5, 68.7, 46.2, 35.6, 28.4, 28.0, 12.2, 11.5, 7.8, 7.3; GC/MS: M<sup>+</sup>=244.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

1. (a) H. Schutz, *Benzodiazepines*, Springer, Heidelberg, 1982. (b) J. K. Landquist, in *Comprehensive Heterocyclic Chemistry*, ed. by A. R. Katritzky and C. W. Rees, Vol. 1, Pergamon, Oxford, 1984, p. 166.
2. L. O. Randall and B. Kappel, in: *Benzodiazepines*, ed. by S. Garattini, E. Mussini, and L. O. Randall, Raven Press, New York, 1973. p. 27.
3. J. R. De Baun, F. M. Pallos, and D. R. Baker, US Patent 3,978,227, 1976 (*Chem. Abstr.*, 86 1977, 5498d3).
4. M. D. Braccio, G. Grossi, G. Roma, L. Vargiu, M. Mura, and M. E. Marongiu, *Eur. J. Med. Chem.*, 2001, **36**, 935.
5. R. C. Haris and J. M. Straley, US. Patent 1,537,757, 1968 (*Chem. Abstr.*, 1970, 73 100054w).
6. P. Fruscella, M. Sottocorno, M. D. Braccio, L. Diomede, N. Piccardi, A. Cagnotto, G. Grossi, M. Romano, T. Mennini, and G. Roma, *Pharmacological Res.*, 2001, **43**, 445.



7. G. Grossi, M. D. Braccio, G. Roma, V. Ballabeni, M. Tognolini, F. Calcina, and E. Barocelli, *Eur. J. Med. Chem.*, 2002, **37**, 933.
8. (a) M. Essaber, A. Baouid, A. Hasnaoui, A. Benharref, and J. P. Lavergne, *Synth. Commun.*, 1998, **28**, 4097. (b) A. M. El-Sayed, H. Abdel-Ghany, and A. M. M. El-Saghier, *Synth. Commun.*, 1999, **29**, 3561. (c) K. V. V. Reddy, P. S. Rao, and D. Ashok, *Synth. Commun.*, 2000, **30**, 1825.
9. (a) Yb(OTf)<sub>3</sub>: M. Curini, F. Epifano, M. C. Marcotullio, and O. Rosati, *Tetrahedron Lett.*, 2001, **42**, 3193. (b) Sc(OTf)<sub>3</sub>: S. K. De and R. A. Gibbs, *Tetrahedron Lett.*, 2005, **46**, 1811. (c) MgO/POCl<sub>3</sub>: M. S. Balakrishna and B. Kaboudin, *Tetrahedron Lett.*, 2001, **42**, 1127. (d) CH<sub>3</sub>COOH under microwave: P. Minothora, S. S. Julia, and A. T. Constantinos, *Tetrahedron Lett.*, 2002, **43**, 1755. (e) SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>: B. M. Reddy and P. M. Sreekanth, *Tetrahedron Lett.*, 2003, **44**, 4447. (f) polymer-supported FeCl<sub>3</sub>: M. Adharvana Chari and K. Syamasundar, *Catal. Commun.*, 2005, **6**, 67. (g) BF<sub>3</sub>-etherate: J. A. L. Hebert and H. Suschitzky, *J. Chem. Soc., Perkin Trans 1*, 1974, 265. (h) NaBH<sub>4</sub>: H. R. Morales, A. Bulbarela, and R. Contreas, *Heterocycles*, 1986, **24**, 135. (i) SiO<sub>2</sub>: D. I. Jung, T. W. Choi, Y. Y. Kim, I. S. Kim, Y. M. Park, Y. G. Lee, and D. H. Jung, *Synth. Commun.*, 1999, **29**, 1941. (j) Polyphosphoric acid : D. I. Jung, T. W. Choi, Y. Y. Kim, I. S. Kim, Y. M. Park, Y. G. Lee, and D. H. Jung, *Synth. Commun.*, 1999, **29**, 1941. (k) Al<sub>2</sub>O<sub>3</sub> under microwave: B. Kaboudin and K. Navaee, *Heterocycles*, 2001, **55**, 1443. (l) W. Zhong, Y. Zhang, and X. Chen, *Tetrahedron Lett.*, 2001, **42**, 73. (m) Zeolite: A. Hegedus, Z. Hell, and A. Potor, *Catal. Lett.*, 2005, **105**, 229.
10. J. S. Yadav, B. V. S. Reddy, B. Eshwaraiyah, and K. Anuradha, *Green Chem.*, 2002, **6**, 592.
11. D. V. Jarikote, S. Siddiqui, R. Rajagopal, T. Daniel, R. J. Lahoti, and K. V. Srinivasan, *Tetrahedron Lett.*, 2003, **44**, 1835.
12. (a) T. Baba, J. Sakai, and Y. Ono, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2657. (b) T. Baba, H. Watanabe, and Y. Ono, *J. Phys. Chem.*, 1983, **87**, 2406.
13. (a) H. Firouzabadi, N. Iranpoor, and K. Amani, *Green Chem.*, 2000, **3**, 131. (b) H. Firouzabadi, N. Iranpoor, and K. Amani, *Synthesis*, 2002, 59. (c) H. Firouzabadi, N. Iranpoor, K. Amani, and F. Nowrouzi, *J. Chem. Soc., Perkin Trans 1*, 2002, 2601. (d) H. Firouzabadi, N. Iranpoor, and K. Amani, *Synthesis*, 2003, 408. (e) H. Firouzabadi, N. Iranpoor, and A. A. Jafari, *J. Mol. Catal.*, 2005, **247**, 14. (f) H. Firouzabadi, N. Iranpoor, and A. A. Jafari, *J. Mol. Catal.*, 2006, **244**, 168.
14. (a) H. Firouzabadi, N. Iranpoor, F. Nowrouzi, and K. Amani, *Chem. Commun.*, 2003, 764. (b) H. Firouzabadi, N. Iranpoor, and A. A. Jafari, *J. Mol. Catal.*, 2005, **227**, 97. (c) H. Firouzabadi, N. Iranpoor, and A. A. Jafari, *Tetrahedron Lett.*, 2005, **46**, 2683. (d) H. Firouzabadi, N. Iranpoor, F. Nowrouzi, and K. Amani, *Tetrahedron Lett.*, 2003, **44**, 5343. (e) H. Firouzabadi, N. Iranpoor, F. Nowrouzi, and K. Amani, *Tetrahedron Lett.*, 2003, **44**, 951. (f) H. Firouzabadi, N. Iranpoor, and A. A.

- Jafari, *Lett. Org. Chem.*, 2006, **3**, 25. (g) H. Firouzabadi, N. Iranpoor, and F. Nowrouzi, *Tetrahedron*, 2004, **60**, 10843. (h) H. Firouzabadi and A. A. Jafari, *J. Iranian Chem. Soc.*, 2005, **2**, 85.
15. (a) R. Fazaeli, S. Tangestaninejad, H. Aliyan, and M. Moghadam, *Appl. Catal. A*, 2006, **309**, 44. (b) R. Fazaeli, S. Tangestaninejad, and H. Aliyan, *Can. J. Chem.*, 2006, **84**, 812. (c) R. Fazaeli, S. Tangestaninejad, and H. Aliyan, *Catal. Commun.*, 2007, **8**, 205. (d) R. Fazaeli, S. Tangestaninejad, and H. Aliyan, *Appl. Catal. A*, 2007, **318**, 218.