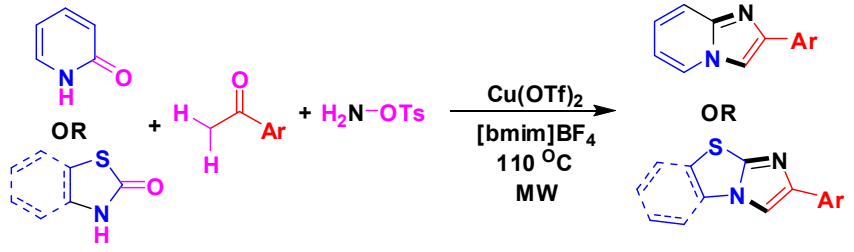
RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Copper-catalyzed multi-component reaction accessing fused imidazo-heterocycles *via* C−H functionalization

G. Santosh Kumar, S. Pushpa Ragini, A. Sanjeeva Kumar, H. M. Meshram*



Highlights

- ligand-free
- base-free
- oxidant-free
- 3 C-N bond formations in single step
- reusable catalytic system
- Multi-component reaction

Journal Name

RSCPublishing

COMMUNICATION

www.rsc.org/

Copper-catalyzed multi-component reaction accessing fused imidazo-heterocycles *via* C−H functionalization

G. Santosh Kumar, S. Pushpa Ragini, A. Sanjeeva Kumar, H. M. Meshram*

Abstract. An efficient synthesis of fused imidazo-heterocycles is described using $Cu(OTf)_2$ in $[bmim]BF_4$ by the multi-component reaction of pyridin-2(1H)-one or thiazol/benzo[d] thiazol-2(3H)-ones with O-tosylhydroxyl amine and acetophenones under microwave irradiation. The present method is very rapid and the product formation occurs *via* C-H functionalization/tandem addition-cyclization process. The ionic liquid containing copper triflate is recovered and reused four times.

Transition-metal-catalyzed direct functionalization of C−H bonds towards the C-N bond formation is of great interest and application of these strategies to build azaheterocycles has attracted intensive attention. In particular, the synthesis of fused imidazo-heterocycles (**IH**s) have received considerable attention because of their diverse biological and pharmaceutical activities[1] such as antiviral, antitumor, antimicrobial, herbicidal, antiulcer agents and immunosuppressive agents. It has wide application as selective cyclin-dependent kinase inhibitors,[2] calcium channel blockers,[3] b-amyloid formation inhibitors,[4] benzodiazepine receptor agonists[5] and liver X receptor agonists.[6] Some of the drug[7] molecule like Zolpidem (**1**), Alpidem (**2**) and Zolimidine (**3**) also containe Imidazo[1,2-a]pyridine (**IP**) moieties. In addition to this 2-arylimidazo [2,1-b] [1,3]benzothiazole derivative (YM-201627) (**4**) was found to be a potent and orally active antitumor agent and useful for treatment of solid tumors,[8] In perticular, ^{11}C-labeled imidazo[2,1-b]benzothiazole[9] (**5**) has been shown to be a superb fluoroprobe in PET analysis of Alzheimer's disease. Several synthetic protocols exist in the literature for the construction of **IP**s and its derivatives (Scheme 1). The condensa-

Medicinal chemisty and pharmacology division, CSIR-Indian Institute of Chemical Technology, Tarnaka, Hyderabad – 500 007, India. E-mail: hmmeshram@yahoo.com; Tel.: +91-40-27191640, Fax: 91-40-27160512

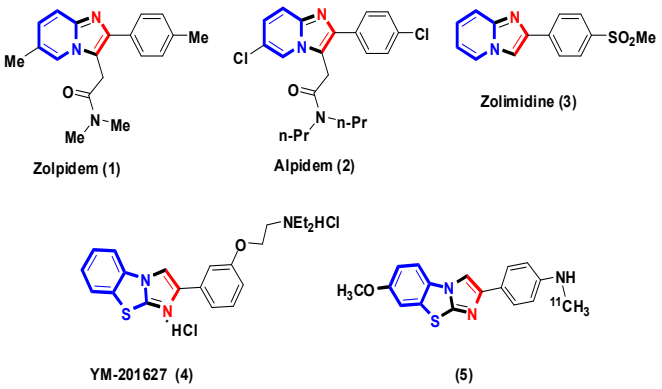
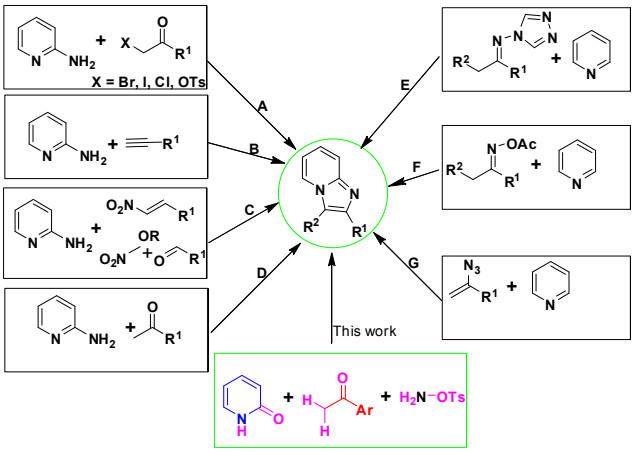


Figure 1. Imidazo-heeterocycle-containing drugs.

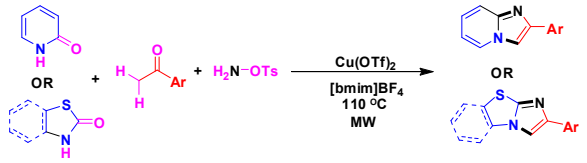


Scheme 1. Various methods for accessing imidazo[1,2-a]pyridines.

-ation between 2-aminopyridines and per-functionalized carbonyl compounds under various conditions was the most convenient method for the synthesis of **IP**s (Scheme 1. Route A).[10] Subsequently other alternative methods also reported which includes silver-catalyzed oxidative coupling/cyclization of 2- aminopyridines with terminal alkynes (Scheme 1. Route B),[11] and Fe-catalyzed method using 2-aminopyridines and nitroolefins to obtain **IP**s (Scheme 1. Route C).[12] Another method involves Cu-catalyzed oxidative coupling of 2-aminopyridines and unactivated methyl ketones in the presence of ligands or additives were reported (Scheme 1. Route D).[13] In addition to this several homogeneous Cu-catalyzed methods using pyridines with N-(alkylidene)-4H-1,2,4-triazol-4-amines (Scheme 1. Route E),[14] acetophenone oxime acetates (Scheme 1. Route F),[15] and vinyl azides (Scheme 1. Route G)[16] were accomplished to give **IP**s. Though the reported methods are satisfactory for the synthesis of these compounds, it encounter some drawbacks like high catalyst loading, harsh reaction conditions, long reaction times and low yield of the products and limited applications. Therefore, there is a scope to develop a general, efficient and high yield method by addressing the shortcomings of reported methods to afford **IH** derivatives.

In recent years technology plays major role in synthetic organic chemistry, one such technology involves microwave heating. Operational simplicity, high yields, purity of products, and enhanced reaction rates are the important features of microwave.[17] On the other hand ionic liquids are a peculiar class of reaction media with the potential to improvement in organic chemistry.[18] They are environmentally benign and are recyclable. In many reactions they are known to accelerate the rate of reaction. Among the ionic liquids, the more intensively investigated are 1,3-dialkylimidazolium salts. They are stable to air water and are compatible with various organic compounds. In the synthesis of **IP** derivatives, 2-aminopyridines are usually employed as starting materials. As 2-aminopyridines are derived from pyridin-2(1H)-ones,[19] the direct use of pyridin-2(1H)-ones to build desired IP would be of great advantage. To the best of our knowledge there is no report for the synthesis of **IH**s using pyridin-2(1H)-one/benzo[d]thiazol-2(3H)-ones.

In continuation of our research in the area of C-H activation under microwave,[20a-d] and ionic liquid assisted reactions,[20e-h] herein we wish to disclosed a novel and an efficient protocol for the synthesis of functionalized fused imidazo-heterocycles in presence of $Cu(OTf)_2$ in $[bmim]BF_4$ by the multi-component reaction of pyridin-2(1H)-one/benzo[d]thiazol-2(3H)-ones, acetophenones and O-tosylhydroxylamine under microwave conditions in good to high yields (Scheme 2). In this protocol, we synthesized different fused imidazo-heterocycles *via* C-H functionalization followed by addition and cyclization process.

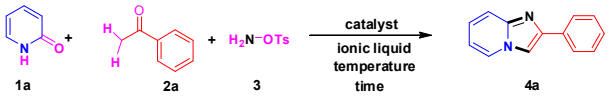


Scheme 2. Cu(II) catalyzed C-H functionalization.

Results and discussions:

We have selected pyridin-2(1H)-one **1a**, simple acetophenone **2a,** and O-tosylhydroxylamine **3** as starting materials for the optimization of reaction. Intially the reaction of pyridin-2(1H)-one **1a** (1 mmol) with simple acetophenone **2a** (1 mmol) and O-tosylhydroxylamine (2 mmol) in presence of 10 mo1% $Cu(OTf)_2$ at 70 °C under microwave irradiation for 5 min gave 2-phenylimidazo[1,2-a]pyridine **4a** in 10 % yield (Table 1, entry 1). The structure of obtained product was confirmed by means of ^1H NMR, ^{13}C NMR, IR and Mass spectrometry analysis. We presumed that the formation of fused **IH**s occurred may be *via* C-H functionalization followed by two C-N bond formations. As the ionic liquids are known to accelerated the rate of reaction, the same reaction was performed in ionic liquid (1-butyl-3-methyl imidazolium tetrafluoroborate $[bmim]BF_4$) under MW in 5 min. We were pleased to observe the remarkable improvement in the yield of desired product (45%) (Table 1, entry 2). During experiment it was noticed that increase in the MW irradiation time 10 min. gave more yield of the product (52%) (Table 1, entry 3). Later to improve the yield, the reaction was carried out at different temperatures. It was noticed that there was a gradual increase in the yield (62 %), when the temperature raised from 70 °C to 110 °C (Table 1, entry 5). Further increase in the temperature (120 °C) did not improve the yield (Table 1, entry 6). Next we examined the effect of the catalyst by performing the reaction with different ratio (15 mol% and 20 mol%) of catalyst. After screening, 20 mol% of catalyst was found suitable for maximum conversion (85%) (Table 1, entry 8). The same reaction in presence of other copper salts $CuBr_2$, CuCl and CuI gave different degree of conversion (Table 1, entries 9−11). -

Table 1. Optimization of the Reaction Conditions for the synthesis of 2-phenylimidazo[1,2-a]pyridine [a]



1a 2a 3 4a

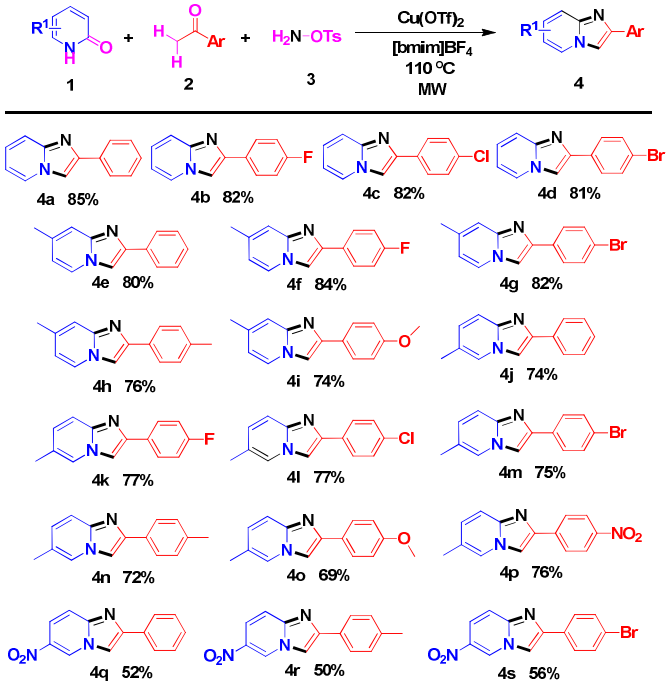
entry	catalyst (mol%)	ionic liquid	temp (°C)	time (min) microwave	yield[b]
1	$Cu(OTf)_2$ (10)	–	70	5	10
2	$Cu(OTf)_2$ (10)	$[bmim]BF_4$	70	5	45
3	$Cu(OTf)_2$ (10)	$[bmim]BF_4$	70	10	52
4	$Cu(OTf)_2$ (10)	$[bmim]BF_4$	100	10	57
5	$Cu(OTf)_2$ (10)	$[bmim]BF_4$	110	10	62
6	$Cu(OTf)_2$ (10)	$[bmim]BF_4$	120	10	60
7	$Cu(OTf)_2$ (15)	$[bmim]BF_4$	110	10	70
8	**$Cu(OTf)_2$ (20)**	**$[bmim]BF_4$**	**110**	**10**	**85**
9	$CuBr_2$ (20)	$[bmim]BF_4$	110	10	35
10	CuCl (20)	$[bmim]BF_4$	110	10	40
11	CuI (20)	$[bmim]BF_4$	110	10	50
12	$Cu(OTf)_2$ (20)	$[bmim]PF_6$	110	10	42
13	$Cu(OTf)_2$ (20)	$[Hbim]BF_4$	110	10	40
14	$Cu(OTf)_2$ (20)	$[emim]BF_4$	110	10	40

[a] Reaction conditions pyridin-2(1H)-one **1a** (1 mmol), acetophenone **2a** (1 mmol), O-tosylhydroxylamine **3** (2 mmol), catalyst, and ionic liquid (2 mL) in microwave vial (10 mL) sealed and placed in MW reactor.
[b] Isolated yield

Later we tested the same reaction in various ionic liquids such as 1-*n*-butylimidazolium tetrafluoroborate [Hbim]BF_4, 1-butyl-3-methylimidazolium hexafluorophosphate [bmim]PF_6, and 1-ethyl-3-methylimidazolium tetrafluoroborate [emim]BF_4 and found that there is no improvement as compared to [bmim]BF_4 (Table 1, entry 12-14). From this study, the optimum conditions described for the present protocol was 20 mol% $Cu(OTf)_2$ as the catalyst in [bmim]BF_4 ionic liquid under MW irradiation at 110 ^oC temperature in 10 min. The same reaction requires 3h for completion in pre-heated (110 ^oC) conventional oil bath. This observation indicated that the effect is from not thermal but it is because of MW.

To make the present protocol general, various substituted pyridin-2(1H)-ones **1** and acetophenones **2** were examined under optimized conditions. The results are summarized in Scheme 3. A wide variety of acetophenones participated well in this conversion to afford corresponding imidazo[1,2-a]pyridines (**4**) in good to high yields. The electronic effects of substituted acetophenones studied in detail, and found that substituents on the acetophenones have influence on rate of reaction. In general, acetophenones bearing electron-

Scheme 3. Scope of pyridin-2(1H)-ones and acetophenones[a]

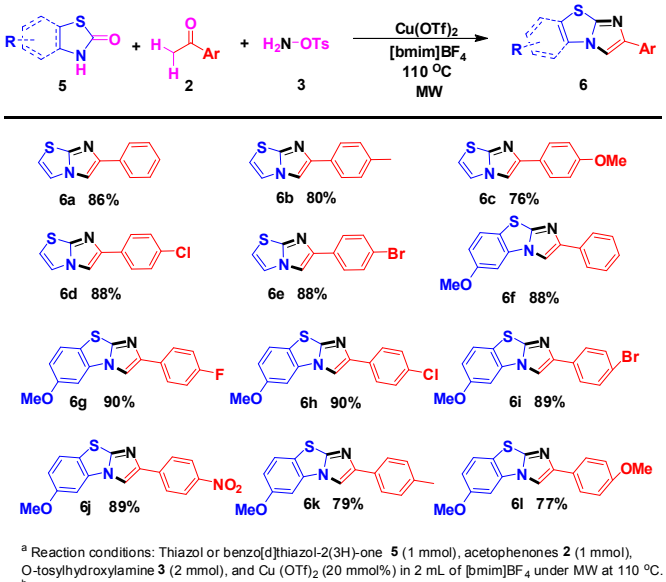


[a] Reaction conditions: Pyridin-2(1H)-ones **1** (1 mmol), acetophenones **2** (1 mmol), O-tosylhydroxyl amine **3** (2 mmol), and Cu $(OTf)_2$ (20 mmol %) in 2 mL of [bmim]BF_4 under MW at 110 ^oC.
[b] isolated yield

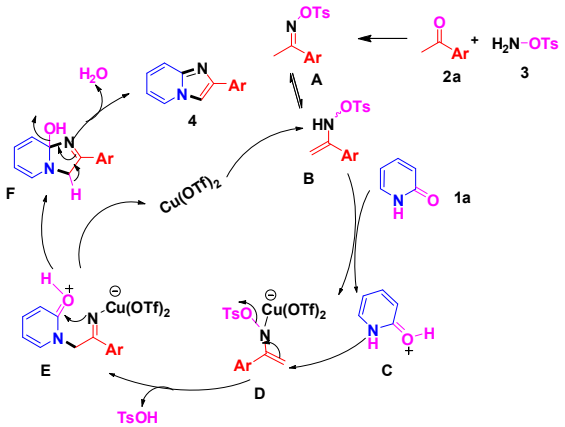
-withdrawing groups reacted faster and furnished high yields of the products (Scheme 3, **4b**, **4c**, **4d**, **4f**, **4g**, **4k**, **4l**, **4m**, **4p**, and **4s**) whereas acetophenones bearing electron-donating groups reacted slowly and gave comparatively less yields of the products (Scheme 3, **4h**, **4i**, **4n**, **4o** and **4r**). It may be presumed that electron-donating substrates were unfavorable for the nucleophilic addition step proposed in Scheme 3. It is worthy to mention that 4-methyl pyridin-2(1H)-one (**1b**) and 5-methyl pyridin-2(1H)-one (**1c**) underwent reaction with simple acetophenone (**2a**) and O-tosylhydroxylamine (**3**) in same reaction conditions to furnish corresponding products in high yields (Scheme 3, **4e** and **4j**).

Encouraged by the results obtained from the reactions of acetophenone derivatives with pyridin-2(1H)-ones, we extended our efforts to study the reaction of acetophenone derivatives with thiazol/benzo[d]thiazol-2(3H)-ones under similar reaction condition. Likewise, the electronic effects of acetophenones studied, acetophenones bearing electron-withdrawing groups reacted faster and gave the products in excellent yields (Scheme 4, **6d**, **6e**, **6g**, **6h**, **6i** and **6j**) whereas acetophenones bearing electron-donating groups reacted slowly gave comparatively less yields of the products (Scheme 4, **6b**, **6c**, **6k** and **6l**). In this method the reactions proceeded smoothly to form three C-N bonds and therefore it should provide a novel and efficient strategy for the synthesis of nitrogen containing heterocycles.

Scheme 4. Scope of thiazol/benzo[d]thiazol-2(3H)-ones and acetophenones[a]



[a] Reaction conditions: Thiazol or benzo[d]thiazol-2(3H)-one **5** (1 mmol), acetophenones **2** (1 mmol), O-tosylhydroxylamine **3** (2 mmol), and Cu $(OTf)_2$ (20 mmol%) in 2 mL of [bmim]BF_4 under MW at 110 ^oC.
[b] Isolated yield



Scheme 5. Plausible mechanistic pathway for the formation of substituted imidazo[1,2-a]pyridines.

A putative mechanism for this $Cu(OTf)_2$ catalyzed, microwave promoted synthesis of imidazo[1,2-a]pyridines **4** by the reaction of pyridin-2(1H)-one, acetopheneone, and O-tosylhydroxylamine is outlined in Scheme 5. Initially the reaction of simple acetophenone **2a** and O-tosylhydroxylamine **3** gave acetophenone oxime tosylate **A**. Then the isomerization of **A** provided enamine **B**, coordination of the copper catalyst ($Cu(OTf)_2$) to **B** furnished complex **D** *via* C-H functionalization, at the same time the *in situ* generated pyridin-2(1H)-ylidene oxonium ion **C** from pyridin-2(1H)-one **1a** attacked the inter mediate **D** to produce the species **E** with the elimination of TsOH. And intramolecular cycloaddition of **E** yields **F** with the regeneration of the catalyst $Cu(OTf)_2$. Finally, the isomerization of **E** by the elimination of water lead to the formation of the desired imidazo[1,2-a]pyridines **4**.

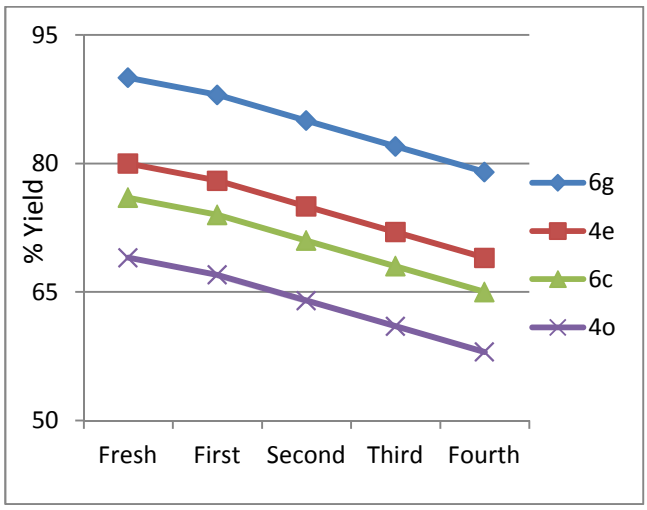


Figure 2. Reusability data for $Cu(OTf)_2/[bmim]BF_4$.

The recovery and recyclability parameter of ionic liquid containing copper catalyst was applied for four model products, such as **4e, 4o, 6c,** and **6g.** After completion of the reaction in ionic liquid $[bmim]BF_4$ containing with copper triflate the reaction mixture was extracted with ether (3x15ml), activated at 80 ^oC under reduced pressure and then subjected to the next run with the same substrates and the same reaction time. We reused $Cu(OTf)_2/[bmim]BF_4$ up to four cycles and did not notice any substantial loss in the catalytic activity of $Cu(OTf)_2/[bmim]BF_4$. These results are summarized in figure 2. We believe that the present protocol is favouring the formation of only one desired product. The ease of recovery and reuse of this reaction media may contribute to the development of green strategy for the preparation of fused **IH**s.

Conclusion:

In summary, we have developed a novel multi-component reaction for the synthesis of **IH** derivatives using $Cu(OTf)_2/[bmim]BF_4$ through C−H functionalization under microwave irradiation. The reaction is very rapid, simple and convenient. This novel method involves the formation of three new C-N bonds in a cascade pathway. The present reaction provides an excellent alternative over earlier methods in terms of high yields, operational simplicity and mild conditions. Moreover, the recovery and reusability of ionic liquid containing catalyst makes the procedure environmental friendly.

Acknowledgment

The authors G S K and A S K thank CSIR for the award of a fellowship and S P R thank to Dr. A. Kamal, Outstanding scientist and Head of the MCP Division, for his support and encouragement.

The authors also thank CSIR, New Delhi for financial support as part of XII Five Year plan programme under title ACT (CSC-0301).

References

1. (a) A. Elhakmaoui, A. Gueiffier, J. C. Milhavet, Y. Blache and J. P. Chapat, *Bioorg. Med. Chem. Lett*., 1994, **4**, 1937; (b) A. Gueiffier, M. Lhassani, A. Elhakmaoui, R. Snoech, G. Andrei, O. Chavignon, J. C. Teluade, A. Kerbal, M. Essassi, J. C. Debouzy, M. Witurowo, Y. Blache, J. Balzarini, C. E. De and J. P. Chapat, *J. Med. Chem.,* 1996, **39**, 2856; (c) J. J. Kaminsky and A. M. Doweyko, *J. Med. Chem.,* 1997, **40**, 427; (d) P. J. Beeswick, I. B. Campbell and A. Naylor, *Chem. Abstr*., 1997, **127**, 8117; (e) G. Tresaderm, J. M. Ci, G. J. Macdonald, G. A. Vega, A. I. Lucas, A. Garcia, E. Matesanz, M. L. Linares, D. Oehlrich, H. Lavreysen, I. Biesmans and A. A. Trabanco, *Bioorg. Med. Chem. Lett*., 2010, **20**, 175; (f) R. Budriesi, P. Ioan, A. Leoni, N. Pedemonte, A. Locatelli, M. Micucci, A. Chiarini and L. J. V. Galietta, *J. Med. Chem*., 2011, **54**, 3885; (g) N. U. Guzeldemirci and O. Kucukbasmaci, *Eur. J. Med. Chem*., 2010, **45**, 63; (h) T. Metaye, C. Millet, J. L. Kraimps, B. Saunier, J. Barbier and F. Begon, *Biochem. Pharmacol*., 1992, **43**, 1507.
2. C. Hamdouchi, B. Zhong, J. Mendoza, E. Collins, C. Jaramillo, J. E. De Diego, D. Robertson, C. D. Spencer, B. D. Anderson, S. A. Watkins, F. Zhanga and H. B. Brooks, *Bioorg. Med. Chem. Lett.,* 2005, **15**, 1943.
3. P. J. Sanfilippo, M. Urbanski, J. B. Press, B. Dubinsky and J. B. Jr. Moore, *J. Med. Chem*., 1991, **34**, 2060.
4. S. C. Goodacre, L. J. Street, D. J. llett, J. M. Crawforth, S. Kelly, A. P. Owens, W. P. Blackaby, R. T. Lewis, J. Stanley, A. J. Smith, P. Ferris, B. Sohal, S. M. Cook, A. Pike, N. Brown, K. A. Wafford, G. Marshall, J. L. Castro and J. R. Atack, *J. Med. Chem*., 2006, **49**, 35.
5. (a) G. Trapani, M. Franco, L. Ricciardi, A. Latrofa, G. Genchi, E. Sanna, F. Tuveri, E. Cagetti, G. Biggio and G. Liso, *J. Med. Chem*., 1997, **40**, 3109; (b) G. Trapani, M. Franco, A. Latrofa, L. Ricciardi, A. Carotti, M. Serra, E. Sanna, G. Biggio and G. Liso, *J. Med. Chem*., 1999, **42**, 3934.
6. R. R. Singhaus, R. C. Bernotas, R. Steffan, E. Matelan, E. Quinet, P. Nambi, I. Feingold, C. Huselton, A. Wilhelmsson, A. Goos-Nilsson and W. robel, *J. Bioorg. Med. Chem. Lett*., 2010, **20**, 521.
7. (a) N. Hsua, S. K. Jha, T. Coleman and M. J. Frank, *Behav. Brain Res.,* 2009, **201**, 233; (b) M. H. Wiegand, *Drugs* 2008, **68**, 2411; (c) S. M. Hanson, E. V. Morlock, K. A. Satyshur and C. J. Czajkowski, *Med. Cem*., 2008, **51**, 7243; (d) J. B. Veron, H. Allouchi, C. E. Gueiffier, R. Snoeck, G. A. E. de Clercq and A. Gueiffier, *Bioorg. Med. Chem.,* 2008, **16**, 9536; (e) T. S. Harrison and G. M. Keating, *CNS Drugs,* 2005, **19**, 65; (f) A. R. Katritzky, Y. J. Xu and H. Tu, *J. Org. Chem*., 2003, **68**, 4935; (g) G. M. Carminati, *Farmaco Ed. Prat*., 1978, **33**, 68.

8. A. Nobuaki, I. Yukitaka, Y. Mayumi, K. Sadao, T. Katsunori, S. Kiyohiro, M. Akira, K. Masafumi and S. Masayuki, *Cancer Lett*., 2006, **38**, 119.
9. B. H. Yousefi, A. Manook, A. Drzezga, B. V. Reutern, M. Schwaiger, H. J. Wester and G. Henriksen, *J. Med. Chem*., 2011, **54**, 949.
10. (a) E. S. Hand and W. W. Paudler, *J. Org. Chem*., 1978, **43**, 2900; (b) N. Denora, V. Laquintana, M. G. Pisu, R. Dore, L. Murru, A. Latrofa, G. Trapani and E. Sanna, *J. Med. Chem*., 2008, **51**, 6876; (c) D. Zhu, J. Chen, D. Wu, M. Liu, J. Ding and H. Wu, *J. Chem. Res.,* 2009, **2**, 84; (d) D. J. Zhu, J. X. Chen, M. C. Liu, J. C. Ding and H. Y. Wu, *J. Braz. Chem. Soc*., 2009, **20**, 482; (e) S. E. Kazzouli, S. Berteina-Raboin, A. Mouaddib and G. Guillaumet, *Tetrahedron Lett.,* 2003, **44**, 6265; (f) M. Ueno, T. Nabana, H. Togo, *J. Org. Chem*., 2003, **68**, 6424; (g) A. J. Stasyuk, M. Banasiewicz, M. K. Cyra´nski and D. T. Gryko, *J. Org. Chem*., 2012, **77**, 5552; (h) T. J. Donohoe, M. A. Kabeshov, A. H. Rathi and I. E. D. Smith, *Org. Biomol. Chem*., 2012, **10**, 1093; (i) Z. G. Le, Z. B. Xie and J. P. Xu, *Molecules,* 2012, **17**, 13368; (j) J. S. Yadav, B. V. Subba Reddy, Y. Gopal Rao, M. Srinivas, A. V. Narsaiah,. *Tetrahedron Lett*., 2007, **43**, 7717; (k) Y. Y. Xue, Z. C. Chen and Q. G. Zheng, *Synthesis,* 2002, **11**, 1505; (l) S. Kumar and D. P. Sahu, *ARKIVOC,* 2008, ***xv***, 88; (m) A. R. Katritzky, D. O. Tymoshenko, D. Monteux, V. Vvedensky, G. Nikonov, C. B. Cooper and M. J. Deshpande, *J. Org. Chem*. 2000, **65**, 8059; (n) R. J. Sundberg, D. J. Dahlhausen, G. Manikumar, B. Mavunkel, A. Biswas, V. Srinivasan, K. King and P. Waid, *J. Heterocycl. Chem*., 1988, **25**, 129.
11. C. He, J. Hao, H. Xu, Y. Mo, H. Liu, J. Han and A. Lei, *Chem. Commun*., 2012, **48**, 11073.
12. S. Santra, A. K. Bagdi, A. Majee and A. Hajra, *Adv. Synth. Catal*., 2013, **355**, 1065; (b) S. Santra, S. Mitra, A. K. Bagdi, A. Majee and A. Hajra, *Tetrahedron Lett.,* 2014, **55**, 5151; (c) H. Yan, Y. Wang, C. Pan, H. Zhang and S. Yang, *Eur. J. Org. Chem.,* 2014, 2754.
13. (a) A. K. Bagdi, M. Rahman, S. Santra, A. Majee and A. Hajra, *Adv. Synth. Catal*., 2013, **355**, 1741; (b) D. C. Mohan, R. R. Donthiri, S. N. Rao and S. Adimurthy, *Adv. Synth. Catal*., 2013, **355**, 2217; (c) Z. J. Cai, S. Y. Wang and S. J. Ji, *Adv. Synth. Catal*., 2013, **355**, 2686; (d) K. Pericherla, P. Kaswan, P. Khedar, B. Khungar, K. Parang and A. Kumar, *RSC Adv*., 2013, **3**, 18923; (e) X. Meng, Y. Wang, C. Yu and P. Zhao, *RSC Adv*., 2014, **4**, 27301.
14. J. Yu, Y. Jin, H. Zhang, X. Yang and H. Fu, *Chem. A Eur. J*., 2013, **10**, 1002.
15. H. Huang, X. Ji, X. Tang, M. Zhang, X. Li, H. Jiang, *Org. Lett*., 2013, **15**, 6254.
16. D. R. Reddy, P. Venkatanarayana, R. N. Naresh Kumar, D. Bairagi and S. Adimurthy, *J. Org. Chem*., 2014, **79**, 11277.
17. (a) D. Richard, K. S. L. Carpenter and J. K. Mark, *J. Org. Chem*., 2007, **72**, 284; (b) S. Caddick, *Tetrahedron,* 1995, **51**, 10403; (c) G. Mayetich, K. Wheless, In Microwave-Enhanced Chemistry; H. M. Kinsington, S. J. Haswell, Eds.; *American Chemical Society*: *Washington, DC*, 1997, 455.
18. (a) S. Orikoshi, T. Hamamura, M. Kajitani, M. Yoshizawa-Fujita and N. Serpone, *Organic Process Research & Development,* 2008, **12**, 1089; (b) Y. He, X. Shen, *Journal of Photochemistry and Photobiology A*: *Chemistry*, 2008, **197**: 253; (c) S. Chowdhury, R. S. Mohan, and J. L. Scott, *Tetrahedron,* 2007, **63**, 2363; (d) J. S. Yadav, B. V. S. Reddy and K. Premalatha, *Adv. Synth. Catal*., 2003, **345**, 948; (e) D. B. Zhao, Wu, M. Y. Kou and E. Z. Min, *Catal. Today*, 2002, **74**, 157; (f) R. J. Sheldon, *Chem. Soc., Chem. Commun*., 2001, 2399; (g) T. Welton, *Chem. Rev*., 1999, **99**, 2071.
19. V. Helmut and K. Konrad, *Chem. Ber*., 1984, **117**, 1523.
20. (a) N. N. Rao and H. M. Meshram, *Tetrahedron Lett*., 2012, **53**, 3963; (b) N. N. Rao and H. M. Meshram, *Tetrahedron Lett*., 2013, **54**, 1315; (c) N. N. Rao and H. M. Meshram, *Tetrahedron Lett*., 2013, **54**, 5087; (d) M. R. Reddy, N. N. Rao, K. Ramakrishna and H. M. Meshram, *Tetrahedron Lett*. 2014, **55**, 1898; (e) H. M. Meshram, P. Ramesh, G. S. Kumar and B. C. K. Reddy, *Tetrahedron Lett*., 2010, **51**, 4313; (f) H. M. Meshram, B. M. Babu, G. S. Kumar, P. B. Thakur and V. M. Bangade, *Tetrahedron Lett*., 2013, **54**, 2296; (g) G. S. Kumar, S. P. Ragini and H. M. Meshram, *Tetrahedron Lett*., 2013, **54**, 5974; (h) B. M. Babu, G. S. Kumar, P. B. Thakur and V. M. Bangade, *Tetrahedron Lett*., 2014, **55**, 3473.