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Synthesis of 1,2,4-Triazoles, *N*-Fused 1,2,4-Triazoles and 1,2,4-Oxadiazoles *via* Molybdenum Hexacarbonyl-Mediated Carbonylation of Aryl Iodides

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Abstract: A convenient and efficient protocol has been developed for the synthesis of 1,2,4-triazoles, *N*-fused 1,2,4-triazoles and 1,2,4-oxadiazoles using molybdenum hexacarbonyl where, for the first time, molybdenum hexacarbonyl acts as a convenient and reliable solid source of carbon monoxide. This procedure provides an easy access to a library of 1,2,4-triazole, *N*-fused 1,2,4-triazole and 1,2,4-oxadiazole derivatives in fair to good yields without the need of gaseous carbon monoxide and palladium catalysts.

Keywords: carbonylation; molybdenum hexacarbonyl; 1,2,4-oxadiazoles; 1,2,4-triazoles

Heterocyclic compounds are privileged scaffolds that have been found in a wide variety of natural products and biologically active molecules. Particularly, five-membered ring heterocyclic compounds such as 1,2,4-triazoles, *N*-fused 1,2,4-triazoles and 1,2,4-oxadiazoles have recently received significant attention in the field of chemistry, biological and material sciences. These scaffolds are known to exhibit a wide range of biological properties including antibacterial,[1] anti-inflammatory,[2] antiviral,[3] antitumour[4] and antiasthmatic activities.[5] They have also been used as bioisosters of esters, amides and as dipeptidomimetics in a number of pharmacologically important molecules.[6] Moreover, these five-membered ring scaffolds act as intermediates in the synthesis of many drugs such as maraviroc, sitagliptin, triazolam, penipanoid A and ataluren (Figure 1).[7]

Owing to their important applications, a number of methods have been developed for the synthesis of 1,2,4-triazole, *N*-fused 1,2,4-triazole and 1,2,4-oxadiazole derivatives. Among them, condensation of carboxylic acid derivatives or aldehydes with amidrazones and amidoximes followed by cyclodehydration are the most commonly explored strategies.[8] Recently, carbonylation with a subsequent intramolecular cyclization reaction has been shown to be an efficient process for the straightforward synthesis of heterocycles.[9] 1,2,4-Triazoles and 1,2,4-oxadiazoles are synthesized *via* carbamoylation of aryl iodides using a palladium catalyst and carbon monoxide (CO).[10]

However, this method has some drawbacks such as the requirement of expensive palladium reagents and the use of the toxic and cumbersome to handle CO gas. Therefore, there is a need to develop more economical, eco-friendly, palladium and CO gas free al-

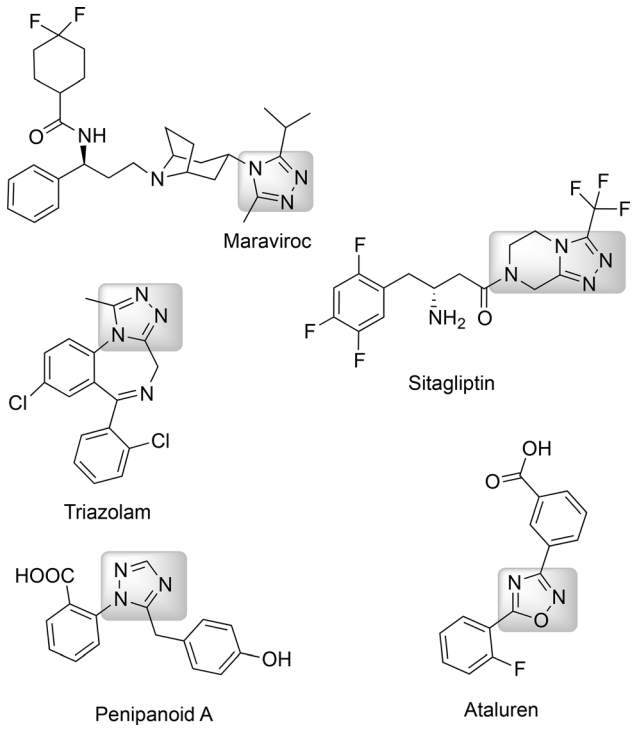
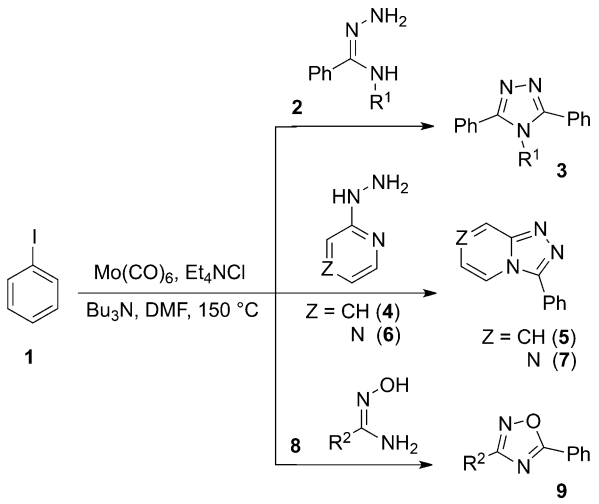


Figure 1. Selected examples of bioactive and natural compounds containing 1,2,4-triazole and 1,2,4-oxadiazole cores.

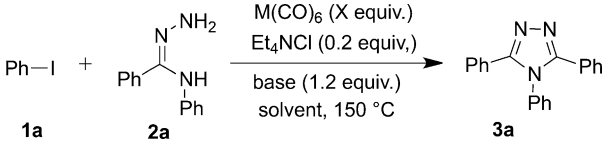


Scheme 1. Synthesis of 1,2,4-triazoles, *N*-fused 1,2,4-triazoles and 1,2,4-oxadiazoles.

ternative methods for the synthesis of 1,2,4-triazoles and 1,2,4-oxadiazoles. Recently, group VI metal carbonyl complexes such as $Cr(CO)_6$, $W(CO)_6$, $Co_2(CO)_8$, $Mo(CO)_6$ etc., have been used as solid sources of CO. Among them, $Mo(CO)_6$ has emerged as an ideal candidate and has been used in several organic transformations.[11] Inspired by these advances, recently we have described the use of $Mo(CO)_6$ as a convenient and reliable solid source of carbon monoxide for the synthesis of benzimidazoles and benzoxazoles.[12] In continuation of our work on the development of efficient synthetic methods for various biologically active heterocycles,[13] herein we report for the first time a palladium and CO gas free synthesis of 1,2,4-triazoles, *N*-fused 1,2,4-triazoles and 1,2,4-oxadiazoles from aryl halides using $Mo(CO)_6$ (Scheme 1).

The optimization studies were carried out using iodobenzene (**1a**) and *N*-phenylbenzamidrazone (**2a**) to the catalytic system of $Mo(CO)_6$, Et_4NCl and Et_3N in diglyme at 150 °C for 23 h, which gave the target product **3a** in 38% yield (Table 1, entry 1). Different solvents were examined and the results are summarized in Table 1. As shown, the solvent exerts an important effect on the yield of product **3a**. However, we found that DMF had a superior solvent effect in terms of reaction time as well as yield of the product (Table 1, entry 3). Next, various bases such as DMAP, Cs_2CO_3, K_2CO_3, Bu_3N were examined for the reaction (entries 5–8). Based on this information, it was concluded that Bu_3N was the preferred base for this transformation (Table 1, entry 8). The screening of different metal carbonyls demonstrated that $Mo(CO)_6$ was the best for this reaction, and the corresponding product was obtained in good yields (Table 1, entries 8–10). Once we had established the suitable metal carbonyl for the synthesis of 3,4,5-trisubstituted

Table 1. Optimization of the reaction conditions.[a]



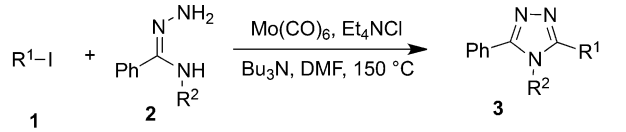
Entry	M (equiv.)	Base	Solvent	Time [h][b]	Yield [%][c]
1	Mo (0.2)	Et_3N	diglyme	23	38
2	Mo (0.2)	Et_3N	DME	19	21
3	Mo (0.2)	Et_3N	DMF	15	61
4	Mo (0.2)	Et_3N	1,4-dioxane	22	29
5	Mo (0.2)	DMAP	DMF	17	21
6	Mo (0.2)	Cs_2CO_3	DMF	23	trace
7	Mo (0.2)	K_2CO_3	DMF	23	trace
8	Mo (0.2)	Bu_3N	DMF	10	91
9	W (0.2)	Bu_3N	DMF	16	31
10	Cr (0.2)	Bu_3N	DMF	17	27
11	Mo (0.167)	Bu_3N	DMF	15	79
12	Mo (0.3)	Bu_3N	DMF	10	91
13	Mo (0.2)	Bu_3N	NMP	10	90
14[d]	Mo (0.2)	Bu_3N	DMF	10	91

[a] *Reaction conditions:* **1** (1.0 equiv.), **2** (1.0 equiv.), $M(CO)_6$ (x equiv.), base (1.2 equiv.), Et_4NCl (0.2 equiv.), solvent (2 vol) and temperature 150 °C.
[b] Time at which TLC (EtOAc:hexane, 1:1) indicated complete disappearance of the starting materials.
[c] Yields reported are isolated yields.
[d] *Reaction conditions:* **1** (1.0 equiv.), 2 (1.0 equiv.), $M(CO)_6$ (0.2 equiv.), Bu_3N (1.2 equiv.), Et_4NCl (0.2 equiv.), DBU (1.0 equiv.) DMF (2 vol) at 150 °C.

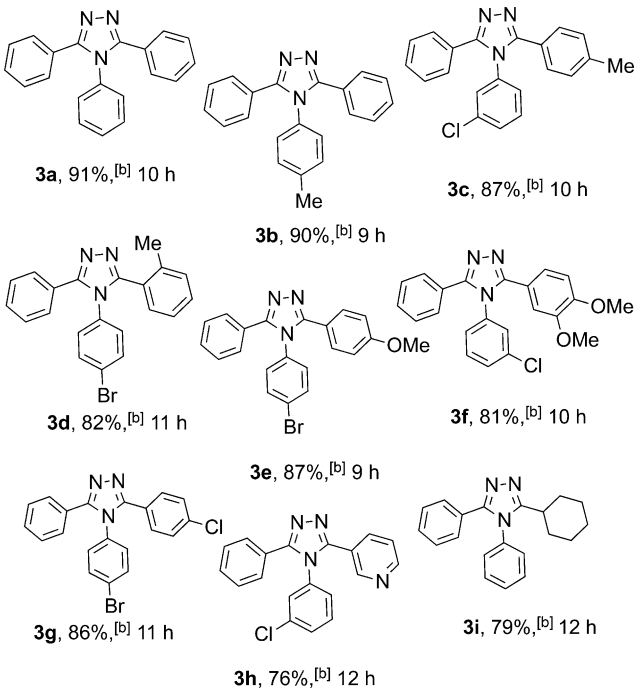
1,2,4-triazoles, we then focused on the quantity of $Mo(CO)_6$. By decreasing the quantity of $Mo(CO)_6$ from 0.2 equiv. to 0.167 equiv. (stoichiometric amount of CO) the yield of the product dropped to 79% even after prolonged reaction time (Table 1, entry 11). In contrast, no improvement of the yield was observed by increasing the quantity of $Mo(CO)_6$ (Table 1, entry 12). Next, we carried out the same reaction using NMP (a less likely CO source comparable to DMF) as a solvent under the same reaction conditions which affords the desired product **3a** in 90% yield (Table 1, entry 13). This indicates that the DMF does not lose CO in this reaction conditions (W. Yiqian et al. used DMF as a liquid source of CO).[14] And also the use of DBU[15] as additive does not affect the yield of the reaction significantly (Table 1, entry 14). Finally, based on the optimization study, the reaction conditions for the preparation of 1,2,4-triazole were set to be 0.2 equiv. of $Mo(CO)_6$, 0.2 equiv. of Et_4NCl and 1.2 equiv. of Bu_3N in DMF at 150 °C under a nitrogen atmosphere. We believe that this reaction, although not attempted in a microwave, might benefit from reaction acceleration.

With this optimized catalytic system in hand, the scope of the reaction was investigated and the results

Table 2. Synthesis of various 3,4,5-trisubstituted 1,2,4-triazoles from the corresponding aryl iodides and amidrazones[a]

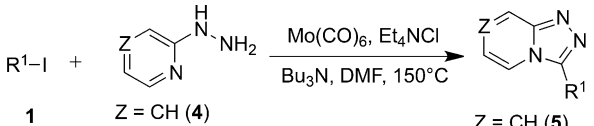


1 2 3



[a] *Reaction conditions:* **1** (1.0 equiv.), **2** (1.0 equiv.), $Mo(CO)_6$ (0.2 equiv.), Bu_3N (1.2 equiv.), Et_4NCl (0.2 equiv.) and temperature 150 °C.
[b] Yields reported are isolated yields.

Table 3. Synthesis of various [1,2,4]triazolo[4,3-*a*]pyridines and [1,2,4]triazolo[4,3-*a*]pyrazines[a]



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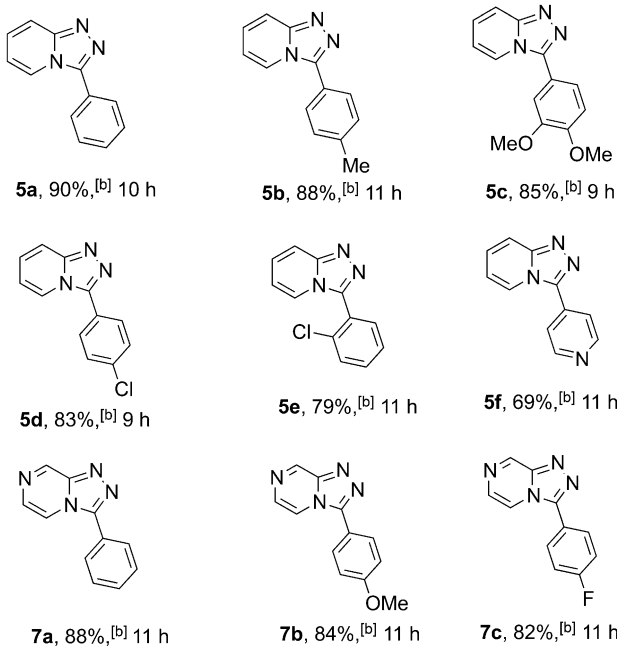


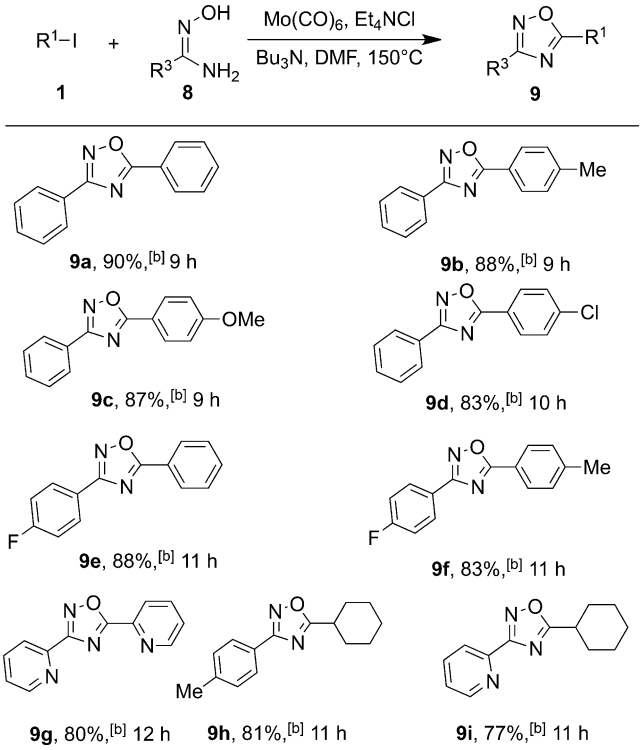
[a] *Reaction conditions:* **1** (1.0 equiv.), **4** or **6** (1.0 equiv.), $Mo(CO)_6$ (0.2 equiv.), Bu_3N (1.2 equiv.), Et_4NCl (0.2 equiv.) and temperature 150 °C.
[b] Yields reported are isolated yields.

are summarized in Table 2. As expected, all of the iodides formed the corresponding 3,4,5-trisubstituted 1,2,4-triazoles in good to excellent yields. Iodobenzene gave the desired product in 91% yield (Table 2, **3a**). Aryl iodides with electron-donating groups such as 4-methyl (**2c**), 2-methyl (**2d**), 4-methoxy (**2e**) and 3,4-dimethoxy (**2f**) gave the desired products in very good yields (Table 2, **3c–3f**). Aryl iodides with an electron-withdrawing group, 4-chloro (**2g**), gave the corresponding triazole **3g** in 86% yield (Table 2, **3g**). However, the use of 4-nitroiodobenzene does not provide the intended product. This may be attributed to the formation of a complex mixture of reduced products.[16] Interestingly, the steric bulk of the aryl iodides did not affect the reactivity and an 84% yield of the product was achieved with 2-methyliodobenzene (Table 2, **3d**). The heteroaryl iodide such as 3-iodopyridine (**2h**) reacted smoothly, affording the desired product **3h** in good yield (Table 2, **3h**). Alicyclic iodide, iodocyclohexane (**2i**) also underwent the reaction smoothly to give the corresponding product **3i** in 79% yield (Table 2, **3i**).

After successfully synthesizing a wide range of 1,2,4-triazoles in good yields, we turned our attention towards the synthesis of *N*-fused 1,2,4-triazoles such as [1,2,4]triazolo[4,3-*a*]pyridines and [1,2,4]triazolo[4,3-*a*]pyrazines under the optimized reaction conditions. The obtained results are presented in Table 3. It is evident from the Table 3 that this methodology can be easily applied to the synthesis of various *N*-fused 1, 2, 4-triazole derivatives. This sequential synthesis protocol also tolerates various aryl and heteroaryl iodides to provide corresponding [1,2,4]triazolo[4,3-*a*]pyridine and [1,2,4]triazolo[4,3-*a*]pyrazine derivatives in good to excellent yields (Table 3).

Encouraged by the successful synthesis of 1,2,4-triazoles and *N*-fused 1,2,4-triazoles, we sought to further extend the scope of this practical approach by replacing amidrazone with amidoxime to prepare 3,5-disubstituted-1,2,4-oxadiazoles. Fortunately, following the above protocol, we were able to prepare 3,5-disubstituted 1,2,4-oxadiazoles very efficiently. As

Table 4. Synthesis of various 3,5-disubstituted-1,2,4-oxadiazoles from the corresponding aryl iodides and amidoximes[a]

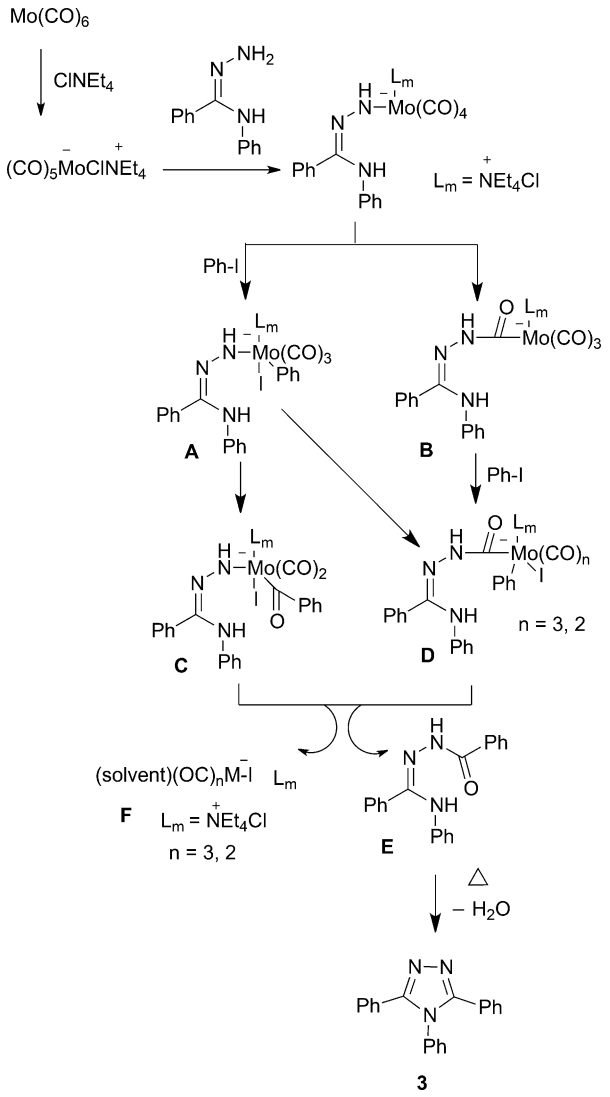


[a] *Reaction conditions:* **1** (1.0 equiv.), **8** (1.0 equiv.), $Mo(CO)_6$ (0.2 equiv.), Bu_3N (1.2 equiv.), Et_4NCl (0.2 equiv.) and temperature 150 °C.
[b] Yields reported are isolated yields.

shown in Table 4, this protocol tolerates a variety of iodides such as aromatic ones having electron-donating and electron-withdrawing substituents, heteroaryl and alicyclic iodides to provide a series of 3,5-disubstituted-1,2,4-oxadiazoles in moderate to good yields.

On the basis of the above results and previous reports,[17] a plausible mechanism was proposed and is shown in Scheme 2. Ren and Yamane suggested two possible pathways: (i) Generation of acyl metal intermediate (**C**). This would be generated by the oxidative addition of aryl halide to molybdenum complex (**A**, not isolated**)** followed by CO insertion to the phenyl-molybdenum bond. (ii) Generation of carbonyl metal intermediate (**D**). This would be generated from the aryl metal halide (**A**) or from carbonyl intermediate (**B**) by the oxidative addition of aryl halide. The formed intermediates (**C** and **D**) gave the *N*-acylamidrazone **E**, which was confirmed by ^1H, ^{13}C NMR and HR-MS [in the case of 1,2,4-oxadiazoles the intermediate *O*-acylamidoxime (**G**) also isolated and characterized]. Finally, intramolecular nucleophilic attack of amine on the carbonyl of **E** affords the corresponding 1,2,4-triazole (**3**).

In summary, we have successfully developed an efficient and CO gas free method to access 1,2,4-triazoles, *N*-fused 1,2,4-triazoles and 1,2,4-oxadiazoles *via* molybdenum-mediated carbonylation of aryl halides. In this transformation, $Mo(CO)_6$ used as a solid source of carbon monoxide. Moreover, the wide range of substrate tolerance and satisfactory product yields of our method should reasonably make it a useful supplement for the known strategies.



Scheme 2. A plausible mechanism for the preparation of 3,4,5-trisubstituted 1,2,4-triazoles.

Experimental Section

General Experimental Procedure for Synthesis of 3, 5, 7 and 9

A mixture of aryl halide **1** (0.49 mmol), amidrazone (**2, 4** or **6**) or amidoxime (**8**) (0.49 mmol), $Mo(CO)_6$ (0.098 mmol), NEt_4Cl (0.098 mmol), and NBu_3 (0.58 mmol) in DMF was heated at 150 °C under an N_2 atmosphere. After completion

of the reaction as monitored by TLC, the reaction mixture was cooled to room temperature and partitioned between water and ethyl acetate. The organic and aqueous layers were then separated and the aqueous layer was extracted with ethyl acetate twice. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to get crude. The crude was purified by silica gel column chromatography using EtOAc:hexane as eluents to afford corresponding product.

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References

[1] a) A. R. Bhat, G. V. Bhat, G. G. Shenoy, *J. Pharm. Pharmacol.* **2001**, *53*, 267; b) C. R. Katica, D. Vesna, K. Vlado, G. M. Dora, B. Aleksandra, *Molecules* **2001**, *6*, 815; c) B. S. Holla, K. N. Poorjary, B. S. Rao, M. K. Shivananda, *Eur. J. Med. Chem.* **2002**, *3*, 511; d) T. Hideo, *Jpn. Tokkyo Koho* JP. 56005480, **1981**; *Chem. Abstr.* **1981**, *95*, 80922b.

[2] a) O. Bekircan, N. Gumurkcuoglu, *Indian J. Chem.* **2005**, *44B*, 2107; b) A. A. Siddiqui, A. Arora, N. Siddiqui, A. Misra, *Indian J. Chem.* **2005**, *44B*, 838; c) J. P. Poupelin, G. Saint-Rut, O. Foussard-Blanpin, G. Narcisse, G. Uchida-Ernouf, R. Lacroix, *Eur. J. Med. Chem.* **1978**, *13*, 67; d) D. N. Nicoaides, K. C. Fylaktakidou, K. E. Litinas, D. Hadjipavlou-Litina, *Eur. J. Med. Chem.* **1998**, *33*, 715.

[3] a) E. De Clercq, *J. Clin. Virol.* **2004**, *30*, 115; b) R. W. Lambert, J. A. Martin, J. H. Merrett, K. E. B. Parkes, G. Thomas, *Pyrimidine nucleosides*, *WO Patent* 9706178, **1997**.

[4] a) R. Sarges, H. R. Howord, R. G. Browne, L. A. Label, P. A. Seymourand, B. K. Koe, *J. Med. Chem.* **1990**, *33*, 2240; b) B. S. Holla, K. N. Poojary, K. S. Bhat, N. S. Kumari, *Indian J. Chem.* **2005**, *44B*, 2114; c) A. Chimirri, S. Grasso, A. M. Montforte, A. Rao, M. Zappala, *Farmaco* **1996**, *42*, 4331.

[5] a) Y. Naito, F. Akahoshi, S. Takeda, T. Okada, M. Kajii, H. Nishimura, M. Sugiura, C. Fukaya, Y. Kagitani, *J. Med. Chem.* **1996**, *39*, 3019; b) L. De Luca, G. Giacomelli, M. Taddei, *J. Org. Chem.* **2001**, *66*, 2534.

[6] a) Y. Hitotsuyanagi, S. Motegi, H. Fukaya, K. Takeya, *J. Org. Chem.* **2002**, *67*, 3266; b) G. D. Diana, D. L. Volkots, T. J. Nitz, T. R. Bailey, M. A. Long, N. Vescio, S. Aldous, D. C. Pevear, F. J. Dutko, *J. Med. Chem.* **1994**, *37*, 2421; c) S. Borg, R. C. Vollinga, M. Labarre, K. Payza, L. Terenius, K. Luthman, *J. Med. Chem.* **1999**, *42*, 4331.

[7] For selected examples, see: a) M. Naveen, H. Upendar Reddy, J. Iqbal, M. Pal, *Tetrahedron* **2010**, *66*, 4919; b) Y. Bo, C. Lin, F. Ruiying, G. Zhiping, *Eur. J. Pharmacol.* **1999**, *380*, 145; c) C. S. Li, C.-Y. An, X.-M. Li, S.-S. Gao, C.-M. Cui, H.-F. Sun, B.-G. Wang, *J. Nat. Prod.* **2011**, *74*, 1331; d) X. Zhou, T. Xu, K. Wen, X.-W. Yang, S. H. Xu, Y. Liu, *Biosci. Biotechnol. Biochem.* **2010**, *74*, 1089; e) C. Chen, C. H. Senanayake, T. J. Bill, R. D. Larsen, T. R. Verhoeven, P. J. Reider, *J. Org. Chem.* **1994**, *59*, 3738.

[8] a) N. A. Meanwell, J. L. Romine, M. J. Rosenfeld, S. W. Martin, A. K. Trehan, J. J. K. Wright, M. F. Malley, J. Z. Gougoutas, C. L. Brassard, J. O. Buchanan, M. E. Federic, J. S. Fleming, M. Gamberdella, K. S. Hartl, G. B. Zavoico, S. M. Seiler, *J. Med. Chem.* **1993**, *36*, 3884; b) A. Reichelt, J. R. Falsey, R. M. Rzasa, O. R. Thiel, M. M. Achmatowicz, R. D. Larsen, D. Zhang, *Org. Lett.* **2010**, *12*, 792; c) G. Hajos, A. Messmer, *J. Heterocycl. Chem.* **1978**, *15*, 463; d) G. Jones, *Advances in Heterocyclic Chemistry*, (Ed.: A. R. Katritzky), Elsevier Science, San Diego, **2002**; Vol. 83, pp 1–70; e) S. Chiou, H. J. Shine, *J. Heterocycl. Chem.* **1989**, *26*, 125; f) A. R. Gangloff, J. Litvak, E. J. Shelton, D. Sperandio, V. R. Wang, K. D. Rice, *Tetrahedron Lett.* **2001**, *42*, 1441; g) Y. Wang, R. L. Miller, D. R. Sauer, S. W. Djuric, *Org. Lett.* **2005**, *7*, 925; h) L. Duchet, J. C. Legeay, D. Carrié, L. Paquin, J. J. V. Eynde, J. P. Bazureau, *Tetrahedron* **2010**, *66*, 986.

[9] a) X-F. Wu, L. He, H. Neumann, M. Beller, *Chem. Eur. J.* **2013**, *19*, 12635; b) S. Gao, M. Chen, M-N. Zhao, W. Du, Z-H. Ren, Y-Y. Wang, Z-H. Guan, *J. Org. Chem.* **2014**, *79*, 4196; c) X. Wu, P. Nilsson, M. Larhed, *J. Org. Chem.* **2005**, *70*, 346.

[10] a) S. T. Staben, N. Blaquiere, *Angew. Chem.* **2010**, *122*, 335; *Angew. Chem. Int. Ed.* **2010**, *49*, 325; b) T. L. Andersen, W. Caneschi, A. Ayoub, A. T. Lindhardt, M. R. C. Couri, T. Skrydstrup, *Adv. Synth. Catal.* **2014**, *356*, 3074.

[11] a) N. F. K. Kaiser, A. Hallberg, M. Larhed, *J. Comb. Chem.* **2002**, *4*, 109; b) K. Yamazaki, Y. Kondo, *J. Comb. Chem.* **2004**, *6*, 121; c) J. Georgsson, A. Hallberg, M. Larhed, *J. Comb. Chem.* **2003**, *5*, 350; d) M. A. Herrero, J. Wannberg, M. Larhed, *Synlett* **2004**, 2335; e) X. Wu, R. Ronn, T. Gossas, M. Larhed, *J. Org. Chem.* **2005**, *70*, 3094; f) G. Lesma, A. Sacchetti, A. Silvani, *Synthesis* **2006**, 594; g) X. Wu, A. K. Mahalingam, Y. Wan, M. Alterman, *Tetrahedron Lett.* **2004**, *45*, 4635; h) I. Suresh, M. K. Girish, *Synth. Commun.* **2004**, *34*, 721; i) J. Spencer, N. Anjum, H. Patel, R. P. Rathnam, J. Verma, *Synlett* **2007**, 2557; j) X. Wu, P. Nilsson, M. Larhed, *J. Org. Chem.* **2005**, *70*, 346; k) J. R. Chen, J. Liao, W. J. Xiao, *Can. J. Chem.* **2010**, *88*, 331; l) H. Cao, W. J. Xiao, *Can. J. Chem.* **2005**, *83*, 826; m) L. He, M. Sharif, H. Neumann, M. Beller, X. F. Wu, *Green Chem.* **2014**, *16*, 3763; n) W. Ren, M. Yamane, *J. Org. Chem.* **2010**, *75*, 3017; o) K. Penta Rao, A. K. Basak, A. Raju, V. S Patil, K. L. Reddy, *Tetrahedron Lett.* **2013**, *54*, 5510.

[12] K. Eshetu, T. Ramu, N. Mangarao, I. Bhargavi, V. Siddaiah, *Eur. J. Org. Chem.* **2015**, 5929.

[13] a) N. Mangarao, G. Mahaboob Basha, T. Ramu, R. Srinuvasarao, S. Prasanthi, V. Siddaiah, *Tetrahedron Lett.* **2014**, *55*, 177; b) N. Mangarao, T. Ramu, R. Srinuvasarao, S. Prasanthi, V. Siddaiah, *Synthesis* **2015**, *47*, 517; c) T. Ramu, N. Mangarao, R. Srinuvasarao, K. Siva Pra-

sada Kumar, V. Siddaiah, *Tetrahedron Lett.* **2015**, *56*, 690.
[14] W. Yiqian, A. Mathias, L. Mats, H. Anders, *J. Org. Chem.* **2002**, *67*, 6232.
[15] J. Spencer, R. P. Rathnam, H. Patel, N. Anjum, *Tetrahedron* **2008**, *64*, 10195.
[16] a) H. Alper, J. F. Petrignani, F. W. B. Einstein, A. C. Willis, *J. Am. Chem. Soc.* **1983**, *105*, 1701; b) S. T. Massey, B. Mansour, L. McElwee-White, *J. Organomet. Chem.* **1995**, *485*, 123; c) P. Nordeman, L. R. Odell, M. Larched, *J. Org. Chem.* **2012**, *77*, 11393.
[17] a) W. Ren, M. Yamane, *J. Org. Chem.* **2010**, *75*, 8410; b) B. Roberts, D. Liptrot, L. Alcaraz, T. Luker, M. J. Stocks, *Org. Lett.* **2010**, *12*, 4280; c) W. Ren, M. Yamane, *J. Org. Chem.* **2010**, *75*, 3017; d) J. Takaya, K. Sangu, N. Iwasawa, *Angew. Chem.* **2009**, *121*, 7224; *Angew. Chem. Int. Ed.* **2009**, *48*, 7090.

