SUMMARY OF THE DISSERTATION DONE

By

RANISA SARKAR

***Roll No.* 190313700002**

To be submitted in the form of a project entitled

GREEN CHEMISTRY AND RECENT ADVANCEMENT

FROM

GOVERNMENT GENERAL DEGREE COLLEGE AT KALNA-1

MURAGACHA, MEDGACHI

PURBA BARDHAMAN – 713405

1. Introduction

Chemistry as a separate discipline took its shape in the beginning of 17^{th} century also referred to as “age of reason”. Since then the properties and use of different compounds has fascinated many Scientist. Many new molecules have been discovered, synthesized, studied and used. After gaining ample knowledge about the properties and uses of compounds whether organic and inorganic products, A need was generated to make these compounds available to all. So the commercial production of many of the compounds took place. A huge increase in the exploitation of petroleum and its related compounds also took place. Commercial production and mass utilization of dyes, drugs, educts, solvents etc. started and till now the use has been continued and will always be in use in future also.

It aims to reduce or even eliminates the production of any harmful bi-products and maximizing the desired product without compromising with the environment. The three key developments in green chemistry include use of super critical carbon di oxide as green solvent, aqueous hydrogen peroxide as an oxidizing agent and use of hydrogen in asymmetric synthesis. It also focuses on replacing traditional methods of heating with that of modern methods of heating like microwave radiations so that carbon footprint should be reduces as low as possible.

2. Definition of Green Chemistry

Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal. Green chemistry is also known as sustainable chemistry.

Green chemistry:

- Prevents pollution at the molecular level
- Is a philosophy that applies to all areas of chemistry, not a single discipline of chemistry
- Applies innovative scientific solutions to real-world environmental problems
- Results in source reduction because it prevents the generation of pollution
- Reduces the negative impacts of chemical products and processes on human health and the environment
- Lessens and sometimes eliminates hazard from existing products and processes
- Designs chemical products and processes to reduce their intrinsic hazards

3. How Green Chemistry differs from cleaning up pollution

Green chemistry reduces pollution at its source by minimizing or eliminating the hazards of chemical feed stocks, reagents, solvents, and products. This is unlike cleaning up pollution (also called remediation), which involves treating waste streams (end-of-the-pipe treatment) or cleanup of environmental spills and other releases. Remediation may include separating hazardous chemicals from other materials, then treating them so they are no longer hazardous or concentrating them for safe disposal. Most remediation activities

do not involve green chemistry. Remediation removes hazardous materials from the environment; on the other hand, green chemistry keeps the hazardous materials out of the environment in the first place.
If a technology reduces or eliminates the hazardous chemicals used to clean up environmental contaminants, this technology would qualify as a green chemistry technology. One example is replacing a hazardous sorbent [chemical] used to capture mercury from the air for safe disposal with an effective, but nonhazardous sorbent. Using the nonhazardous sorbent means that the hazardous sorbent is never manufactured and so the remediation technology meets the definition of green chemistry.

4. Green Chemistry's 12 Principles[1-9]

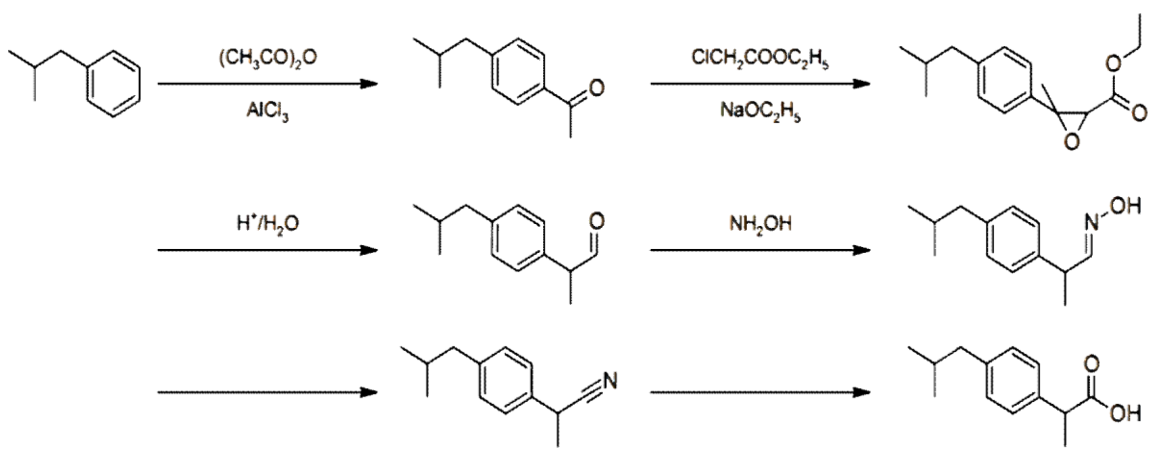
These principles demonstrate the breadth of the concept of green chemistry:

1. Prevent waste: Design chemical syntheses to prevent waste. Leave no waste to treat or clean up.
2. Maximize atom economy: Design syntheses so that the final product contains the maximum proportion of the starting materials. Waste few or no atoms.
3. Design less hazardous chemical syntheses: Design syntheses to use and generate substances with little or no toxicity to either humans or the environment.
4. Design safer chemicals and products: Design chemical products that are fully effective yet have little or no toxicity.
5. Use safer solvents and reaction conditions: Avoid using solvents, separation agents, or other auxiliary chemicals. If you must use these chemicals, use safer ones.
6. Increase energy efficiency: Run chemical reactions at room temperature and pressure whenever possible.
7. Use renewable feed stocks: Use starting materials (also known as feed stocks) that are renewable rather than depletable. The source of renewable feed stocks is often agricultural products or the wastes of other processes; the source of depletable feed stocks is often fossil fuels (petroleum, natural gas, or coal) or mining operations.
8. Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.
9. Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are effective in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and carry out a reaction only once.
10. Design chemicals and products to degrade after use: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
11. Analyze in real time to prevent pollution: Include in-process, real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.
12. Minimize the potential for accidents: Design chemicals and their physical forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

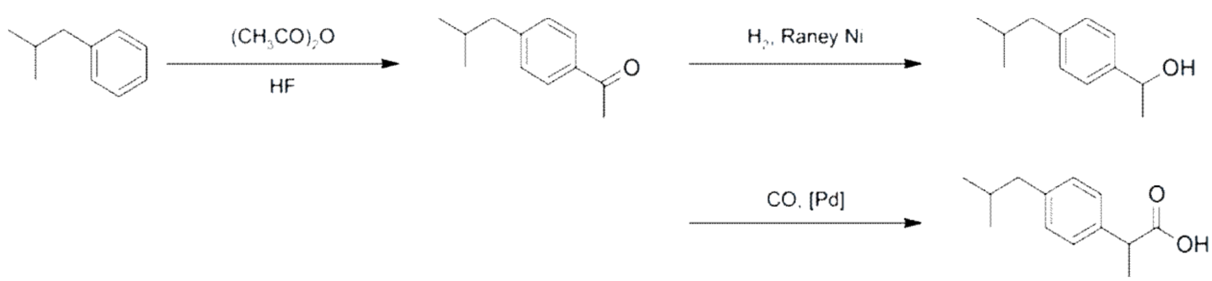
5. Literature Survey and Discussion

Green chemistry as the name indicates is a technology imbedded, environmental friendly and cost effective utilization of resources that minimize or even eliminate the production of harmful bi-products in the design and manufacturing of the product[10]. Presence of such unwanted bi products not only lowers the yield of the desired product but may also interface with the utilization of the product. Presence of these bi- product even after the purification process limits its use. Under these prospective green chemistry aims to eliminate the production of these unwanted products and hence widens the usage of products[11].

A very important example is ibuprofen which is a non steroidal anti inflammatory drug (NSAID) which is widely used for the relief of symptoms of arthritis, constipation, fever and also exerts antiplatelet effect[12] is manufactured industrially as Classic route for the production of ibuprofen is as follows[13].



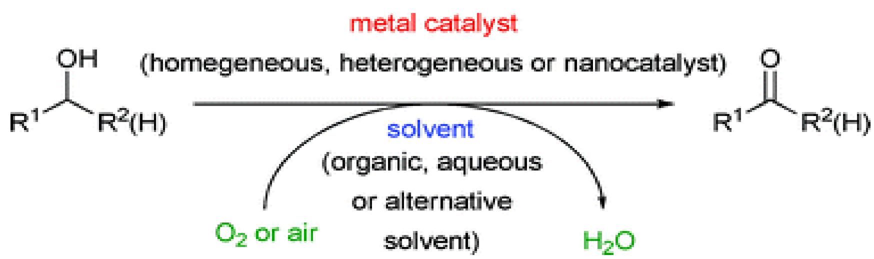
But looking at the production of unwanted bi-products which if present even in trace amounts may hinder its pharmacological activity. A new way of production of ibuprofen which is based on the principles of “Green chemistry” eliminates the production of bi-products and also an increase in the yield has been observed[14].



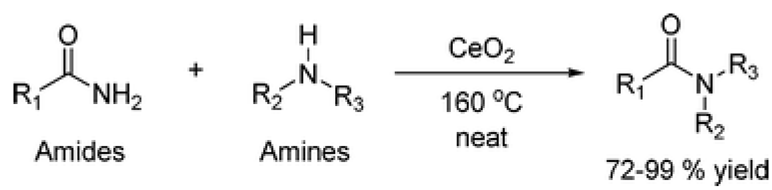
This improved synthesis won the president green chemistry challenge greener synthetic pathways award in 1997[15,16].

6. Recent advancement of Green Chemistry in Organic Synthesis

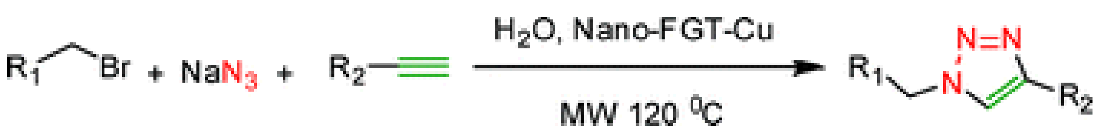
1) Oxidation of alcohol to corresponding carbonyl compounds using oxygen or even better air as stereomeric oxidants. Using this method only water is been produced as a bi-product. This reaction involves utilization of transition metals as catalyst in the form of either homogenous catalyst, Heterogenous catalyst or even better nano catalyst[17].



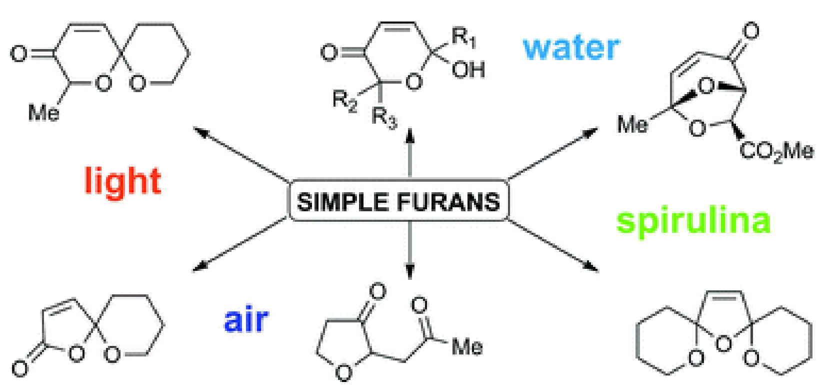
2) For transamidation of picolinamide with *n*-octylamine, cerium oxide (CeO_2) has been used which shows highest catalytic activity. This reaction has been done under solvent free conditions[17].



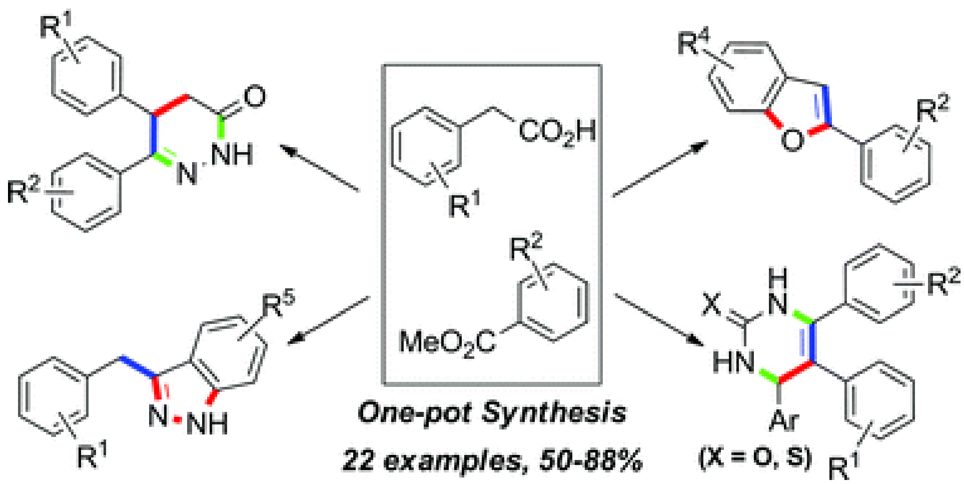
3) 1,2,3-Triazoles were synthesized in water using magnetically recoverable heterogeneous Cu catalyst *via* one-pot multi component reaction using Micro Wave irradiation. Catalyst so used can be easily recovered using an external magnet which can be efficiently recycled[17].



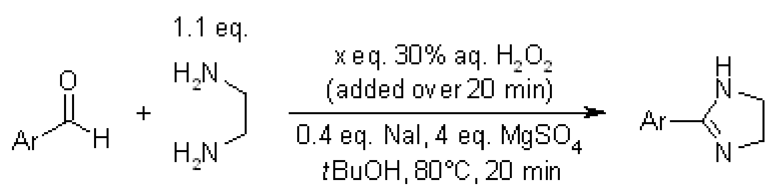
4) A greener way of utilizing air, sun light, water and spirulina to transform readily available furan derivatives into a wide range of synthetically useful polyoxygenated compounds which are commonly found in natural products is now possible with green chemistry[17].



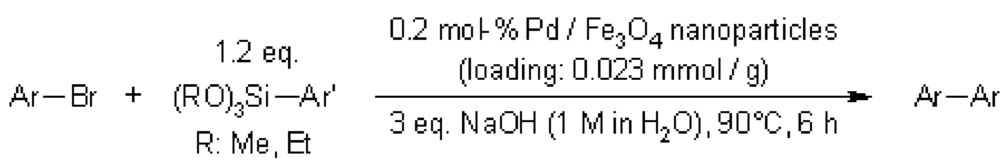
5) For synthesizing useful heterocycles in medicinal chemistry such as pyridazinones, dihydropyrimidinones, and dihydropyrimidinthiones, a "green", mild and highly efficient one-pot triple cascade has been developed involving Claisen– decarboxylation, electrophilic reaction, and subsequent heterocyclization. In addition, indazoles and benzofurans could also besynthesized *via* a double cascade. To develop the cascade process, a direct Claisen–decarboxylation reaction was firstly optimized. This reaction was then coupled with electrophilic reactions including alkylation, Michael addition or aldol reaction to enable the preparation of various aryl ketones in a one-pot fashion[17].



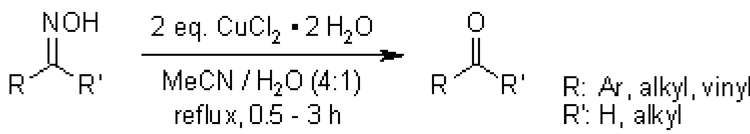
6) A new environmentally friendly, efficient and easy process for the synthesis of 2-imidazolines has been developed which aims to give a better results which can be performed by reacting aldehydes with ethylenediamine using hydrogen peroxide as an oxidant in the presence of sodium iodide and anhydrous magnesium sulfate as catalyst. Using this synthesis no production of bi-products were observed[18].



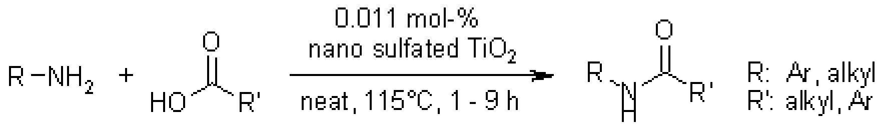
7) A new method of Hiyama Cross-Coupling was recently modified using Magnetically Recoverable Pd/Fe_3O_4-Catalyst. Cross coupling of Aryl Bromides with Aryl Siloxanes was done to yield desired product which requires comparatively less time and energy[19].



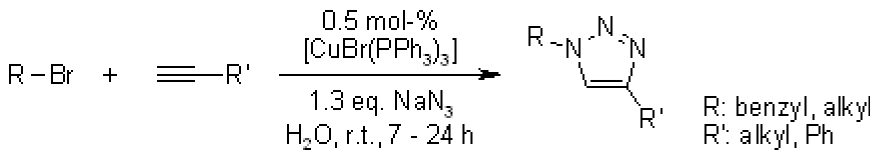
8) A new method of preparing Carbonyl compounds in very good yields has been developed. This can be done by treating oximes with 2 molar equivalent of $CuCl_2 \cdot 2H_2O$ in the presence of acetonitrile and water in ratio 4:1 and reflexing the resulting solution for about three hours. An added advantage of recovering cupric salts can also be done in this method[20].



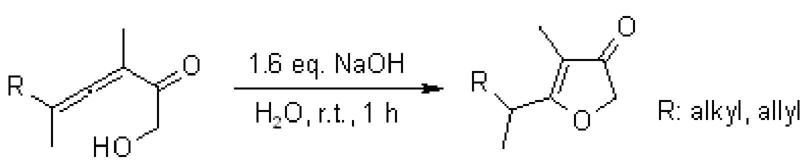
9) Nanosized sulfated titanium dioxide which was prepared by a sol-gel hydrothermal process showed high catalytic activity in adirect amidation of fatty acids as well as benzoic acids with various amines under solvent-free conditions[21].



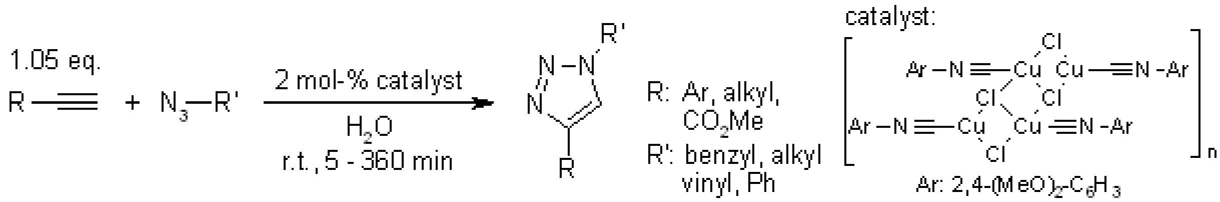
10) A new catalytic method for preparing pure triazoles has been developed which is based on commercially available $[CuBr(PPh_3)_3]$. This method do not require any special conditions, and can work ven in the absence of additive. This method does not require any purification step also[22].



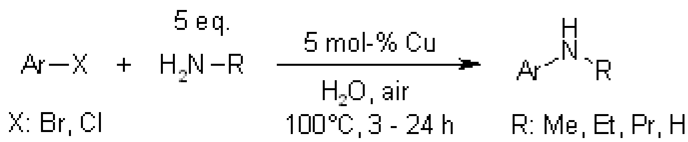
11) A simple, cost efficient and effective method of synthesis of 3(2*H*)-furanones by cycloisomerization of allenic hydroxyketones has been carried out in water. This method eliminates the use of any expensive metal catalyst[23].



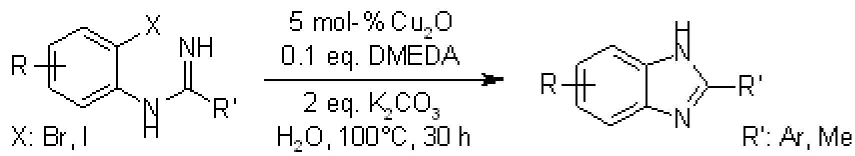
12) Copper(I) isonitrile complex has been found to be an efficient heterogeneous catalyst for azide-alkyne 1,3-dipolar cycloadditions and three-component reactions of halides, sodium azide and alkynes to form 1,4-disubstituted 1,2,3-triazoles in high yields under mild conditions in water[24].



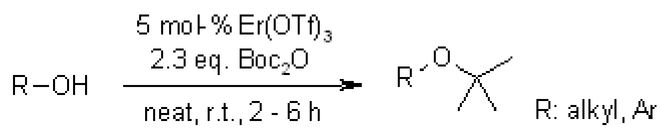
13) A new, easily fiscible and practical method for Ullmann amination of aryl halides with aqueous methylamine and other aliphatic primary amines under organic solvent- and ligand-free condition at 100°C using powdered copper as catalyst in air gives a very good yield of *N*-arylamines as main products. The presence of a small amount of air is essential. This method is not suitable with Secondary amines and aniline as they do not react under these conditions[25].



14) A straightforward, efficient, and sustainable method for intramolecular *N*-arylation yeilds a variety of substituted benzimidazoles in high yields using Cu_2O as the catalyst, DMEDA as the ligand, and K_2CO_3 as the base. Remarkably, the reaction was exclusively carried out in water, rendering the methodology highly valuable from both environmental and economical points of view[26].



15) An eco-compatible method for the formation of *tert*-butyl ethers of alcohols and phenols is performed in solvent-free conditions at room temperature using catalytic amount of $Er(OTf)_3$. The catalyst is easily recovered and reused several times without loss of activity. In addition, the *tert*-butyl group is removed very quickly from alcohols and phenols in methanol in the presence of $Er(OTf)_3$ using MW irradiation[27].



16) Used and exhausted vegetable oil has been used currently by researchers as a fuel for vehicles by making very less modifications in the cars of present use and a shocking result was found that by using vegetable oil CO_2 emission has been reduced to almost 67% without compromising with the efficiency of the vehicle.

7. Conclusion

It is clear that Green chemistry not only helps us in designing of new ways to synthesize the desired product economically, user friendly and it also helps to save the environment. A good flow of knowledge between the Industries and research institutions/ universities undergoing such types of research topics will not only enable us to expand our knowledge but it would also help to protect the environment. Government should also make some strict rules in governing the industries to use eco-friendly ways of production.

References

1) “The 12 principles of green chemistry” United states environmrental protection agency. Retrieved 2006-07-31.
2) http://en.wikipedia.org/wiki/Green_chemistry
3) http://www.greeningschools.org/docs/twelveprinciplesofgreenchemistry.pdf
4) http://www.towson.edu/saacs/green.htm
5) http://web.njit.edu/~mitra/green_chemistry/Green_Chemistry.htm
6) http://www2.gvsu.edu/gilliamj/
7) http://profmaster.blogspot.com/2007/06/green-chemistry-12-rules.html
8) http://greenchemistry.yale.edu/javascript/tinymce/plugins/filemanager/files/principles-of-green-chemistry.pdf
9) http://academic.scranton.edu/faculty/cannm1/intro.html
10) “Green chemistry”. United states environmental protection agency 2006-06-28. Retrieved 2011-03-23.
11) http://www.organic-chemistry.org/topics/green-chemistry.shtm
12) Van Esch, A; Van Steensel-Moll, HA; Steyerberg, EW; Offringa, M; Habbema, JD; Derksen-Lubsen, G (1995)..Archives of pediatrics & adolescent medicine 149 (6): 632–7. PMID 7767414
13) http://en.wikipedia.org/wiki/File:Boots_synthesis_of_ibuprofen.png
14) http://en.wikipedia.org/wiki/File:BHC_synthesis_of_ibuprofen.png
15) “Ibuprofen-a case study in green chemistry (pdf). Royal society of chemistry.
16) Kjonaas, R. A.; Williams, P. E.; Counce, D. A.; Crawley, L. R. (2011). Journal of Chemical Education 88 (6): 825–828. Doi:10.1021/ed100892p.
17) http://pubs.rsc.org/en/journals/journalissues/gc
18) G.-y. Bai, K. Xu, G.-f. Chen, Y.-h. Yang, T.-y. Li, Synthesis, 2011, 1599-1603.; M. C. Wilkinson, Org. Lett., 2011, 13, 2232-2235.
19) B. Sreedhar, A. S. Kumar, D. Yada, Synlett, 2011, 1081-1084.
20) N. Quan, X.-X. Shi, L.-D. Nie, J. Dong, R.-H. Zhu, Synlett, 2011, 1028-1032.
21) M. Hosseini-Sarvari, E. Sodagar, M. M. Doroodmand, J. Org. Chem., 2011, 76, 2853-2859.
22) S. Lal, S. Diez-González, J. Org. Chem., 2011, 76, 2367-2373.
23) M. Poonoth, N. Krause, J. Org. Chem., 2011, 76, 1934-1936. M. Liu, O. Reiser, Org. Lett., 2011, 13, 1102-1105.
24) M. Liu, O. Reiser, Org. Lett., 2011, 13, 1102-1105.
25) K. C. Chunavala, G. Joshi, E. Suresh, S. Adimurthy, Synthesis, 2011, 635-641.
26) J. Peng, M. Ye, C. Zong, F. Hu, L. Feng, X. Wang, Y. Wang, C. Chen, J. Org. Chem., 2011, 76, 716-719.
27) A. Procopio, P. Costanzo, M. Curini, M. Nardi, M. Oliverio, R.Paonessa, Synthesis, 2011, 73-78.