

Sulfonated Ordered Nanoporous Carbon (CMK-5-SO₃H) as an Efficient and Highly Recyclable Catalyst for the Silylation of Alcohols and Phenols with Hexamethyldisilazane (HMDS)

Daryoush Zareyee · Mohammad S. Ghandali ·
Mohammad A. Khalilzadeh

Received: 19 January 2011 / Accepted: 8 May 2011 / Published online: 24 May 2011
© Springer Science+Business Media, LLC 2011

Abstract An environmentally friendly catalytic system for trimethylsilylation of alcohols and phenols with hexamethyldisilazane can be successfully carried out for the first time over sulfonated mesoporous carbon catalyst (CMK-5-SO₃H) in dichloromethane at ambient temperature and excellent conversions were obtained. Furthermore, the catalyst displays high activity and thermal stability (to 200 °C) and it can be reused repeatedly for at least 25 cycles without any evidence of loss of activity, confirming the stability of covalent bonding of acidic centers.

Keywords Sulfonated mesoporous carbon · CMK-5-SO₃H · Solid acid · Heterogeneous catalyst · Silylation · HMDS

1 Introduction

Among the routinely employed methodologies for the protection of hydroxyl groups in organic chemistry, silylation undoubtedly plays a major role, from both analytical and synthetic point of views [1, 2]. As it is widely known, silyl ethers are resistant to oxidation, have a good stability for most non-acidic reagents and are easily deprotected to provide the free alcohols [3]. Generally, the formation of silyl ethers carried out by treatment of parent alcohols with silyl halides or silyl triflates in the presence of stoichiometric amounts of a base [4–6], Li₂S [7], and occasionally with a nonionic super base catalyst [8–11]. However, these base-catalyzed silylation methods have serious

disadvantages, since careful extraction and filtration are required to remove ammonium salts derived from the reaction of by-produced acids and co-bases during the silylation reaction.

On the other hand, 1,1,1,3,3,3-hexamethyldisilazane (HMDS) as an inexpensive, commercially available and stable reagent, is frequently used for the trimethylsilylation of hydroxyl groups, giving ammonia as the only byproduct. Even though the handling of this reagent is easy, its main drawback is its poor silylating power which needs forceful conditions and long reaction times in many instances [12]. Therefore, a variety of catalysts have been developed for activation of this reagent, such as sulfuric acid [1, 2], (CH₃)₃SiCl [13], sulfonic acids [14], K-10 montmorillonite [15, 16], iodine [17], tungstophosphoric acid (H₃PW₁₂O₄₀) [18], LiClO₄ [19], Mg(OTf)₂ [20], CuSO₄·5H₂O [21], TBBDA, and PBBS [22], [PdCl(η³-C₃H₅)₂]-PPh₃ [23], MgBr₂·OEt₂ [24], InBr₃ [25], LaCl₃ [26], HReO₄ [27], silica supported perchloric acid [28], trichloroisocyanuric acid [29], Fe(F₃CCO₂)₃ [30], Zr(OTf)₂ [31], Bi(OTf)₃ [32], and TiCl₂(OTf)-SiO₂ [33]. Although several of these procedures are useful, some of them suffer from the use of homogenous and often corrosive catalyst, tedious workup and long reaction times. Besides, many of these reagents are expensive and non-recoverable leading to the generation of large amount of toxic waste particularly when large scale applications are considered. On these bases, developments of milder conditions were tried and investigations on green, simple and highly efficient processes over solid acid catalysts became the chemists interesting undertaking.

Solid acids are conventional materials that have wide applications in chemical production, separation, and purification and the chemical industry is currently searching for highly active and stable solid acids to improve the environmental safety of the production of chemicals [34–40].

D. Zareyee (✉) · M. S. Ghandali · M. A. Khalilzadeh
Department of Chemistry, Islamic Azad University,
Qaemshahr Branch, P.O. Box 163, Mazandaran, Iran
e-mail: zareyee@gmail.com

In other word, the green approach to chemical processes has stimulated the use of recyclable strong solid acids as replacement for unrecyclable homogenous acid catalysts. In this regard, Karimi et al. have demonstrated the application of recoverable sulfonic acid functionalized ordered mesoporous silica (MCM-41-PrSO₃H) for efficient silylation of alcohols and phenols [41].

It is notable that, the availability of ordered mesoporous silica also entails great opportunities for the templating synthesis of highly ordered mesoporous carbon [42–49] for reasons of both practical and fundamental interest. Carbon material is inert and has good conductivity and resistance to environmental and chemical attack. The carbon surface has been exclusively used as a support substrate, especially as electrodes with a wide potential window in electrochemistry for catalytic, analytical and biotechnological applications [46–48]. Moreover, carbonaceous solid acids can be maintained strong acidity even in water, participating in many industrially important acid-catalyzed reactions.

2 Experimental Section

2.1 General Procedure for the Trimethylsilylation of Alcohols

To a solution of alcohol (1 mmol) and hexamethyldisilazane (0.7 mmol) in dichloromethane (3 mL) the catalyst CMK-5-SO₃H (23–35 mg, 2–3 mol%) was added. The mixture was stirred at room temperature for the period of time indicated in Table 1. Reaction progress was monitored by thin layer and gas chromatography. After completion of the reaction, the product was isolated by filtration. Evaporation of the solvent under reduced pressure gave the corresponding silyl ether in good to excellent yields (Table 1).

2.2 Preparation of SBA-15

The synthesis of SBA-15 has been achieved using known procedure described by Yu et al. [50] including a mixture of P123 (0.02 mol), TEOS (1 mol), KCl (1.5 mol), HCl (6 mol), and H₂O (166 mol). Briefly, 12 g of P123 was dissolved in a mixture of 74.4 g of concentrated HCl and 375.6 g of distilled water at 38 °C, followed by the addition of 16.5 g of KCl. To the solution, 31.5 g of TEOS was added with vigorous stirring for 8 min. The mixture was kept statically at the same temperature for 24 h, and the mixture was transferred to Teflon lined autoclaves and put in an oven at 130 °C for another 24 h. The solid was recovered by filtration, washed by water. The surfactant was then extracted by refluxing with a solution of EtOH

Table 1 Synthesis of trimethylsilyl ethers using CMK-5-SO₃H (2–3 mol%) in dichloromethane at room temperature

Entry	Substrate	Cat. (mol%)	Time (min)	Yield ^a (%)
1	PhCH ₂ OH	2	30	98
2	3-ClC ₆ H ₄ CH ₂ OH	2	30	94
3	4-ClC ₆ H ₄ CH ₂ OH	2	30	99
4	3,5-(Cl) ₂ C ₆ H ₃ CH ₂ OH	2	35	98
5	4-MeC ₆ H ₄ CH ₂ OH	2	40	97
6	4-NO ₂ C ₆ H ₄ CH ₂ OH	2	120	80
7	PhCH ₂ CH ₂ OH	2	70	100
8	Pyren-1-ylmethanol	3	110	91
9	Furfuryl alcohol	2	100	90
10	1-Pentanol	2	120	92
11	1-Heptanol	2	120	95
12	2-Heptanol	2	150	100
13	2-Adamantanol	3	150	91
14	Menthol	2	110	100
15	Cyclohexanol	2	120	93
16	4- <i>tert</i> -Butyl-cyclohexanol	2	120	95
17	PhCH(OH)Ph	2	90	99
18	PhOH	2	120	93
19	4-ClC ₆ H ₄ OH	2	180	100
20	3-NO ₂ C ₆ H ₄ OH	3	180	65
21	3,5-(Me) ₂ C ₆ H ₄ OH	3	120	80
22	2-Hydroxy benzaldehyde	2	120	85
23	1-Adamantanol	3	150	90
24	(Ph) ₃ COH	(2) 3	24 (h)	(22) 50

^a Gas chromatography yields

using a Soxhlet apparatus for 36 h and the obtained SBA-15 was then dried overnight at 100 °C.

2.3 Preparation of CMK-5

Templated synthesis of CMK-5 has been achieved using known procedure described by Ryoo et al. [49, 51]. Initially, Al was incorporated into SBA-15 (molar ratio Si/Al = 20) by well dispersion of calcined SBA-15 into an aqueous solution of AlCl₃, followed by removal of H₂O by rotaevaporator and calcination in air. Impregnation of furfuryl alcohol (FA) into Al-SBA-15 was achieved by incipient wetness infiltration at room temperature. The mixture was then heated up at 80 °C oven for 16 h for Al-catalyzed polymerization of FA. The obtained composite was recovered by filtration to remove excess and unpolymerized FA, and washed by EtOH and acetone. The composite was heated to 850 °C under vacuum at a ramp of 10 °C/min, and the carbonization was carried out at the same temperature for 3 h under vacuum. Ordered

mesoporous carbon (CMK-5) was obtained by removal of silica template by HF (10% in 1: 1 EtOH–H₂O), washed with copious water and EtOH, and finally dried at 100 °C.

2.4 Preparation of 4-Benzenediazoniumsulfonate

4-Benzenediazoniumsulfonate was synthesized by diazotization of *p*-sulfonic acid [52]. In a three-necked ground flask, 12.99 g (0.075 mol) of *p*-sulfonic acid was dispersed in 1 M HCl, resulting a 0.1 M suspension. To the well-stirred suspension in an ice-water bath (3–5 °C), was dropwise added a 10% excess of 1 M aqueous solution of NaNO₂ (82.5 mL). The solid *p*-sulfonic acid was slowly dissolved during of the addition of NaNO₂ and a clear solution was obtained after all of NaNO₂ solution was added. The mixture was stirred for another 45 min at the same temperature. The white precipitate formed was filtered off, washed by small amount of cold water, and dried under reduced pressure.

2.5 Preparation of Sulfonated Ordered Mesoporous Carbon (CMK-5-SO₃H)

In a typical modification, 1.2 g of CMK-5 was added in a three-necked ground flask containing 12.0 g of 4-benzenediazoniumsulfonate in 200 mL of distilled water and 200 mL of ethanol. Subsequently, the mixture was cooled down to 5 °C and 200 mL of 50 wt% H₃PO₂ aqueous solution was added. After stirring for 30 min, another 200 mL of H₃PO₂ aqueous solution was added. The mixture was stirred at 5 °C for another 30 min. The sulfonic acid functionalized carbon material (denoted as CMK-5-SO₃H) was recovered by filtration, washed thoroughly with distilled water and finally acetone, and dried in an oven at 80 °C.

3 Results and Discussion

Covalent attachment of aryl sulfonic acid on ordered mesoporous carbon with mesoporosity both inside nanopipes and between nanopipes can be produced by homogeneous reduction of 4-benzene-diazoniumsulfonate by hypophosphorous acid, which has been reported very most recently by Feng et al. [53], resulted in preparation of sulfonated ordered mesoporous carbon (CMK-5-SO₃H). This catalyst was prepared in our laboratory following described procedure (Fig. 1) and was characterized by TGA (Fig. 2), BET surface area measurement, BJH, and N₂ adsorption–desorption analysis (supporting information).

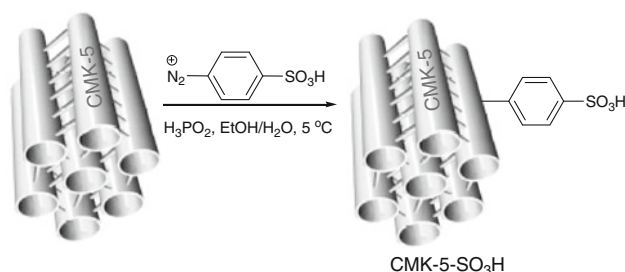


Fig. 1 Schematic representation for the preparation of sulfonated ordered mesoporous carbon (CMK-5-SO₃H)

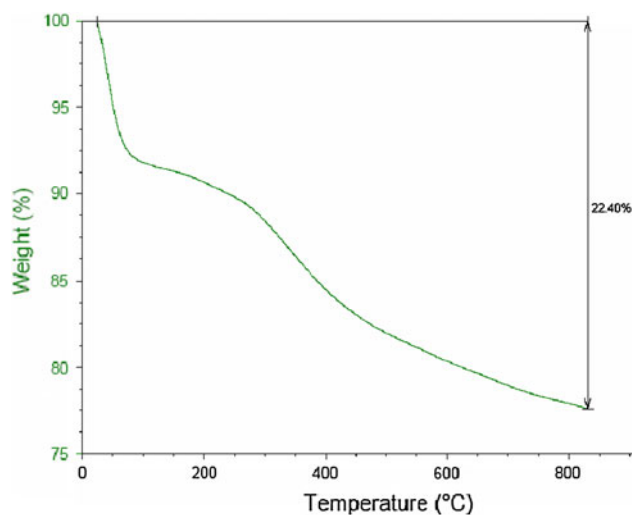


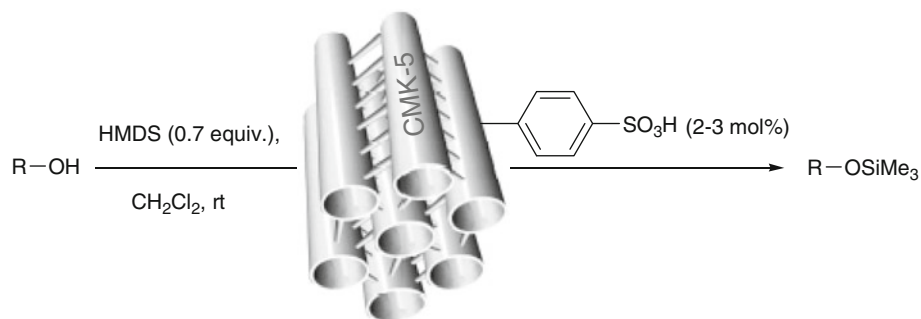
Fig. 2 TG diagram for CMK-5-SO₃H

The organic composition of the solid sulfonic acid was quantitatively determined by potentiometric titration. Typically a loading of ca. 0.87 ± 0.03 mmol/g was obtained. It is worthwhile to mention that the weight loss of CMK-5-SO₃H below 100 °C (~7 wt%) can be attributed to the physically adsorbed water. Further weight loss of CMK-5-SO₃H at higher temperature (about 200 °C) accounts for loss of the SO₃H segment. Accordingly, the total weight loss reaches 22.4%.

Due to the attributes described above for the use of sulfonated ordered nanoporous carbon in catalysis and our current interest in developing environmentally benign synthetic protocols for different organic transformations [41, 54–56], we reveal herein for the first time, highly reusable CMK-5-SO₃H catalyzed trimethylsilylation of a wide variety of alcohols and phenols at ambient temperature (Scheme 1).

At the outset, efforts were made towards the catalytic evaluation of CMK-5 towards the synthesis of silyl ethers using 1 equiv. of benzyl alcohol, 1 equiv. of HMDS and 0.02 g of CMK-5. These were stirred at room temperature in CH₂Cl₂. After 2 and 24 h, only 30 and 48% of benzyl-oxytrimethyl silane were obtained, respectively. It should

Scheme 1 Trimethylsilylation of hydroxyl groups with HMDS using CMK-5-SO₃H



be noted that, when no catalyst was used, the reaction yielded only 20% of expected product after 2 h. The same reaction was then carried out using 23 mg (2 mol%) of CMK-5-SO₃H under similar reaction conditions. Interestingly, a significant improvement was observed and the yield of silylated product was increased to 99% gas chromatography yield after stirring the mixture for only 25 min. For establishing the best reaction conditions, an optimization study was performed using the reaction of benzyl alcohol in the presence of varying amounts of HMDS and CMK-5-SO₃H. Gratifyingly, 98% of corresponding product was obtained in the presence of 0.7 mmol HMDS and 2 mol% of sulfonated catalyst CMK-5-SO₃H after only 30 min. After achieving this favorable result, in order to ascertain the scope and generality of this catalyst, we screened a range of alcohols and phenols. The experiment is shown in Scheme 1 and the results are collected in Table 1.

Compounds that were silylated in this way are benzylic, primary, hindered and unhindered secondary, and unhindered tertiary alcohols (Table 1). Generally, in the case of primary alcohols, the reactions were completed within less than 2 h in CH₂Cl₂ at room temperature accompanied by a fast evolution of NH₃ gas from the reaction mixture (Table 1, entries 1–11). This method is also efficient for the silylation of secondary alcohols (Table 1, entries 12–17). Meanwhile, primary and secondary aliphatic alcohols were readily transformed to their corresponding silyl ethers in high yields (Table 1, entries 10–16). Phenol, 4-chlorophenol, 3-nitrophenol, 3,5-dimethylphenol and 2-hydroxy benzaldehyde were also silylated in an efficient manner in excellent yields (Table 1, entries 18–22). Our successful synthesis of primary and secondary silyl ethers, led us to embark upon a study of silylation of hindered tertiary alcohols. 1-Adamantanol was converted to corresponding silylated product in good yield (Table 1, entry 23). Nevertheless, triphenylmethanol gave related silyl ether in only 22% yield under standard reaction condition after 24 h, which can be improved to 50% when 3 mol% of CMK-5-SO₃H was used after 24 h (Table 1, entry 24). It should be noted that, in the case of hindered secondary and tertiary alcohols no elimination by-products were observed at all.

To demonstrate whether the protection of alcohols catalyzed by CMK-5-SO₃H is actually proceeding in a heterogeneous pathway, the silylation of benzyl alcohol was carried out in dichloromethane in which the catalyst was filtered off at approximately 50% conversion and the resulting clear solution stirred for additional time in the absence of the solid. No significant increase in the yield occurs after removal of the catalyst, thus indicating the solution does not contain any catalytically active species that could have leached from the solid to solution and confirm the covalent stability of acidic centers attached to mesoporous carbon.

Compared with traditional liquid acid catalysts, the catalyst CMK-5-SO₃H has the attractive property in that it can be easily recycled. Consequently, after the completion of the first run silylation of benzyl alcohol under the conditions described in Table 1, which afford the corresponding benzyloxytrimethyl silane in 98% yield, a new silylation reaction was then accomplished by removal of solution using syringe and then addition of fresh reactants to the reaction mixture. Gratifyingly, CMK-5-SO₃H successfully reused in more than twenty-five successive runs and exhibited consistent activity to afford an average yield of 97.5% with virtually no significant loss of performance, which clearly demonstrates the practical recyclability of this catalyst. This reusability demonstrates the high stability and turnover of CMK-5-SO₃H under the conditions employed. Noticeably, the recyclability test was stopped after twenty-five runs, although it can be done continuously.

4 Conclusions

In summary, sulfonated ordered nanoporous carbon (CMK-5-SO₃H), is an efficient, thermally stable (to 200 °C), and recoverable catalyst for the silylation of alcohols in dichloromethane at ambient temperature. In view of excellent catalytic capacity, outstanding stability, the exceedingly simple workup and uncomplicated recovery, CMK-5-SO₃H was proved the best catalyst for this reaction. Most importantly, this procedure is significant from the viewpoint of avoiding pollution. As a consequence, this

system represents a substantial improvement over previous methods, wherein product separation would produce a large amount of wastes. Additionally, by this method, primary, bulky secondary, tertiary and phenolic hydroxyl functional groups were protected in good to excellent yields. To the best of our knowledge, there has not been reported silylation of alcohols using sulfonated carbon in which the catalyst can be recovered and reused over several reaction cycles without considerable loss of reactivity. Further studies will be focusing on exploring of this solid sulfonic acid for other types of functional group transformations in our laboratories.

5 Supplementary Data

Experimental procedure and characterization data (TGA, BET, BJH, and N₂ adsorption–desorption isotherm) for CMK-5 and CMK-5-SO₃H, and general procedure for the trimethylsilylation of alcohols is available.

Acknowledgments The authors acknowledge the Islamic Azad University of Qaemshahr Research Councils for support of this study.

References

- Greene TW, Wuts PGM (1991) Protective groups in organic synthesis, 2nd edn. Wiley, New York
- Kocienski PJ, Enders R, Noyori R, Trost BM (eds) (1994) In protective groups. Thieme, Stuttgart
- Langer SH, Connell S, Wender I (1958) *J Org Chem* 23:50
- Corey EJ, Venkateswarlu A (1972) *J Am Chem Soc* 94:6190
- Chaudhary SK, Hernandez O (1979) *Tetrahedron Lett* 20:99
- Lombardo L (1984) *Tetrahedron Lett* 25:227
- Olah GA, Gupta BGB, Narang SC, Malhotra R (1979) *J Org Chem* 44:4272
- D'Sa BA, McLeod D, Verkade JG (1997) *J Org Chem* 62:5057
- D'Sa BA, Verkade JG (1996) *J Am Chem Soc* 118:12832
- Martinez GR, Grieco PA, Williams E, Kanai K, Srinivasan CV (1982) *J Am Chem Soc* 104:1436
- Aizpurua JM, Palomo C (1985) *Tetrahedron Lett* 26:475
- Bruynes CA, Jurriens TK (1982) *J Org Chem* 47:3966
- Gautret P, El-Ghamarti S, Legrand A, Coutrier D, Rigo B (1996) *Synth Commun* 26:707
- Goldschmidt AGT (1979) German Patent 2 758884. *Chem Abstr* 90:6530c
- Zhang ZH, Li TS, Yang F, Fu CG (1998) *Synth Commun* 28:3105
- Mojtahedi MM, Saidi MR, Bolourchian M, Heravi MM (2002) *Phosphorus Sulfur Silicon Relat Elem* 177:289
- Karimi B, Golshani B (2000) *J Org Chem* 65:7228
- Firouzabadi H, Iranpoor N, Amani K, Nowrouzi F (2002) *J Chem Soc Perkin Trans* 1:2601
- Saidi MR, Azizi N (2004) *Organometallics* 23:1457
- Firouzabadi H, Iranpoor N, Sobhani S, Ghassamipour S (2004) *J Organomet Chem* 689:3197
- Akhlaghinia B, Tavakoli S (2005) *Synthesis* 11:1775
- Ghorbani-Vaghei R, Zolfigol MA, Chegeny M, Veisi H (2006) *Tetrahedron Lett* 47:4505
- Shurakawa E, Hironaka K, Otsuka H, Hayashi T (2006) *Chem Commun* 37:3927
- Mojtahedi MM, Abbasi H, Abaee MS (2006) *J Mol Catal A* 250:6
- Yadav JS, Reddy BVS, Basak AK, Baishya G, Vankat Narsaiah A (2006) *Synthesis* 22:3881
- Narsaiah A (2007) *J Organomet Chem* 692:3614
- Reis PM, Royo B (2007) *Catal Commun* 8:1057
- Shaterian HR, Shahrekipoor F, Ghashang M (2007) *J Mol Catal A* 272:142
- Khazaei A, Zolfigol MA, Rostami A, Ghorbani-Choghamarani A (2007) *Catal Commun* 8:543
- Firouzabadi H, Iranpoor N, Jafari AA, Jafari MR (2008) *J Organomet Chem* 693:2711
- Moghadam M, Tangestaninejad S, Mirkhani V, Mohammadpour-Baltork I, Chahardahcheric S, Tavakoli Z (2008) *J Organomet Chem* 693:2041
- Kadam ST, Kim SS (2009) *J Organomet Chem* 694:2562
- Firouzabadi H, Iranpoor N, Farahi S (2009) *J Organomet Chem* 694:3923
- Olah GA, Pradeep SI, Prakash GKS (1986) *Synthesis* 7:513
- Corma A (1995) *Chem Rev* 95:559
- Herron N, Farneth WE (1996) *Adv Mater* 8:959
- Harton B (1999) *Nature* 400:797
- Anastas PT, Kirchhoff MM (2002) *Acc Chem Res* 35:686
- Clark JH, Macquarrie DJ (1998) *Chem Commun* 8:853
- Okuhara T (2002) *Chem Rev* 102:3641
- Zareyee D, Karimi B (2007) *Tetrahedron Lett* 48:1277
- Tamai H, Kakii H, Hirota Y, Kumamoto T, Yasuda H (1996) *Chem Mater* 8:454
- Kawashima D, Aihara T, Kobayashi Y, Kyotani T, Tomita A (2000) *Chem Mater* 12:3397
- Lee J, Sohn K, Hyeon T (2001) *J Am Chem Soc* 123:5146
- Li Z, Jaroniec M (2001) *J Am Chem Soc* 123:9208
- Besenhard JO, Friz HP (1983) *Angew Chem Int Ed Engl* 22:950
- Rice RJ, Pontikos NM, McCreery RL (1990) *J Am Chem Soc* 112:4617
- Tanaka H, Aramata A (1997) *J Electroanal Chem* 437:29
- Joo SH, Choi SJ, Oh I, Kwak J, Liu Z, Terasaki O, Ryoo R (2001) *Nature* 412:169
- Yu C, Fan J, Tian B, Zhao D, Stucky GD (2002) *Adv Mater* 14:1742
- Kurk M, Jaroniec M, Kim T-W, Ryoo R (2003) *Chem Mater* 15:2815
- Bouchet MJ, Rendon A, Wermuth CG, Goeldner M, Hirth C (1987) *J Med Chem* 30:2222
- Wang X, Liu R, Waje MM, Chen Z, Yan Y, Bozhilov KN, Feng P (2007) *Chem Mater* 19:2395
- Karimi B, Zareyee D (2005) *Tetrahedron Lett* 46:4661
- Karimi B, Zareyee D (2008) *Org Lett* 10:3989
- Karimi B, Zareyee D (2009) *J Mater Chem* 19:8665