DOI: 10.1002/adsc.201000365

Iron-Doped Single-Walled Carbon Nanotubes as New Heterogeneous and Highly Efficient Catalyst for Acylation of Alcohols, Phenols, Carboxylic Acids and Amines under Solvent-Free Conditions

Hashem Sharghi,[a,*] Mahboubeh Jokar,[a] and Mohammad Mahdi Doroodmand[a]

[a] Department of Chemistry, Shiraz University, Shiraz 71454, Iran
Fax: (+98)-711-228-0926, phone: (+98)-711-228-4822; e-mail: shashem@chem.susc.ac.ir

Received: May 9, 2010; Revised: December 7, 2010; Published online: February 16, 2011

Abstract: Iron-doped single-walled carbon nanotubes (Fe/SWCNTs) represent an efficient and new heterogeneous reusable catalyst for the acylation of a variety of alcohols, phenols, carboxylic acids and amines with acid chlorides or acid anhydrides under solvent-free conditions. The reactions of various primary, secondary, tertiary, and benzylic alcohols, diols, phenols, as well as aromatic and aliphatic amines give acylated adducts in good to excellent yields.

Keywords: amines; carboxylic acids; heterogeneous catalyst; iron-doped single-walled carbon nanotubes; phenols; alcohols; solvent-free conditions

Introduction

The presence of the amino groups and phenolic/alcoholic hydroxy group in a wide spectrum of biologically active compounds necessitates the manipulation of the chemical reactivity of these functional groups during the synthesis of multifunctional synthetic targets possessing one or more of these groups. The protection of phenols, alcohols and amines as their acylated derivatives is a straightforward approach due to the feasibility of regeneration of the parent compound by nucleophilic deprotection. Theprotection of alcohols, phenols, acids and amines by acetyl chloride or acetic anhydride is often necessary during the course of various transformations in a synthetic sequence, especially in the construction of polyfunctional molecules such as carbohydrates, steroids, nucleosides and natural products.[1,2] Acylation reactions are frequently used in the preparation of drug candidate molecules and comprise 12% of the total chemical reactions involved in the synthesis of drugs.[3] Acylation is normally achieved by treatment with anhydrides or acid chlorides in the presence of a suitable catalyst. Various activators employed for this purpose include the nucleophilic 4-(*N*,*N*-dimethylamino)pyridine,[3] Bu_3P,[4] and other catalytic systems such as $CoCl_2$,[5a] $TaCl_5$,[5b] $ZnCl_2$,[5c] $ZrCl_4$,[5d] $InCl_3$,[5e] $Al(HSO_4)_3$,[5f] copper(II) chloride/palladium(II) chloride,[5g] I_2,[5h,i] , nitrophenylboronic acid,[5j] and polytungstic acid.[5k] Recently, the use of many triflates and perchlorates has also been reported, for example, scandium(III) triflate,[6a] bismuth(III) triflate,[6b] copper(II) triflate,[6c] indium(III) triflate,[6d] aluminum-(III) triflate,[6e] cerium(III) triflate,[6f] gadolinium(III) triflate,[6g] erbium(III) triflate,[6h] $LiClO_4$,[7a] $CuClO_4$,[7b] $Mg(ClO_4)_2$,[7c] $Fe(ClO_4)_3$,[7d] $Zn(ClO_4)_2{\cdot}6H_2O$,[2e] and perchloric acid/silica.[7e] Other catalysts such as montmorillonite,[7f] benzenesulfonamide,[8a] $La(NO_3)_3{\cdot}6H_2O$,[8b] ZnO,[8c] yttria-zirconia,[8d] trichloroisocyanuric acid,[8e] Nafion-H,[8f] and N-heterocyclic carbenes,[8g,h] have also been used for the acetylation of alcohols.

Recent efforts for the development of various catalysts such as phosphomolybdic acid,[8i] $TiCl_3(OTf)$,[8j] cobalt(II) salen complex,[8k] highlight the importance of heteroatom acylation.

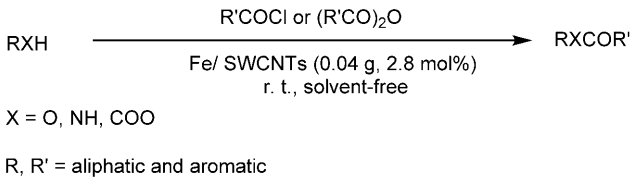
Although there are currently a number of methods available, these methods suffer from one or more disadvantages, such as long reaction times, lack of generality, the use of halogenated solvents and hazardous materials. For example, 4-(*N*,*N*-dimethylamino)pyridine is highly toxic, Bu_3P is flammable (flash point: 37 °C)[10c,d] and air-sensitive, perchlorates are explosive,[9] triflates are expensive, moisture sensitive,[7a,c] and some of them are applicable only to alcohols and phenols.[2e,7a] Many catalysts need special conditions for their preparation [$Bi(OTf)_3$, Nafion-H, yttria-zirconia, N-heterocyclic carbenes] or are a potential health hazard.[10a] $RuCl_3$ also has some disadvantages such as its high expense and the need for longer reac-

tion times and extremely dry reaction conditions.[12a] In many cases, the reported acylation methodologies are applicable to alcohols only and are not suitable for acid-sensitive substrates.[5f,6b] Some methods requires the use of an excess amounts of acylating agent.[6b,7e] Despite many acylation methods, only a few of the known methods are capable of offering truly economic and practical acylation transformations across a broad spectrum of alcohol, phenol and amine substrates. Many of these methods work well on primary or secondary alcohols only and fail to protect tertiary alcohols or less reactive phenols.[6b,8i] A few of these methods (such as metal triflates) also suffer from side reactions such as dehydration and rearrangement and might not be fully compatible for the acylation reactions with substrates bearing acid-sensitive groups.[2e,7e,10b]

Thus, there is a continuing and increasing demand for new catalysts that could help overcome the above-mentioned challenges.

Heterogeneous reagent systems have many advantages such as simple experimental procedures, mild reaction conditions and the minimization of chemical wastes as compared to their liquid phase counterparts.[11]

In continuation of our interest in the application of heterogeneous reagent systems in organic synthesis,[11] we herein report a practical, facile and selective protocol for the acylation of alcohols, phenols, acids and amines in the presence of a catalytic amount of iron-doped single-walled carbon nanotubes (Fe/SWCNTs) without use of any additives and solvent at room temperature (Scheme 1)



Scheme 1.

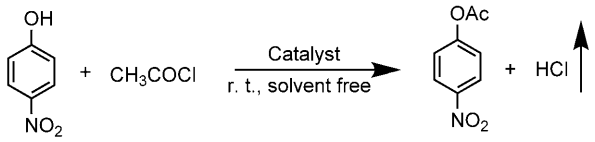
Results and Discussion

Optimization of Acylation Reaction

A simple and new acetylation methodology based on the use of iron-doped single-walled carbon nanotubes (Fe/SWCNTs**)** as the catalyst has been developed, which could represent an improvement in efficiency and convenience over previously reported procedures.[5f,6b,7e]

To find out the efficiency of Fe/SWCNTs as a general acylation catalyst for phenols bearing electron-deficient groups; 4-nitrophenol was selected as a model substrate and treated with acetyl chloride (Table 1). When the reaction was carried out in the absence of catalyst, the starting material remained unchanged (Table 1, entry 1).

Table 1. Investigation of various catalyst in the acetylation of 4-nitrophenol (1 mmol), acetyl chloride (1 mmol) at room temperature under solvent-free conditions in 30 min.



Entry	Catalyst	Yield [%][a]
1	none	0
2	$InCl_3$ (2.8 mol%)	61
3	$AlCl_3$ (2.8 mol%)	8
4	$FeCl_2$ (2.8 mol%)	5
5	$ZnCl_2$ (2.8 mol%)	0
6	$FeCl_3$ (2.8 mol%)	80
7	Fe_2O_3 (2.8 mol%)	35[b]
8	pure SWCNTs (0.04 g)	0
9	pure MWCNTs (0.04 g)	0
10	nano-Fe (2.8 mol%)	45
11	Fe-doped SWCNTs (0.04 g, 2.8 mol%)	96[c]
12	Fe-doped SWCNTs (0.02 g, 1.4 mol%)	80
13	Fe-doped SWCNTs (0.06 g, 4.2 mol%)	95

[a] Determined by ^{1}H NMR analysis.
[b] Acylation occurred not only at the OH group but also at the ortho position to the OH group on the aromatic ring to give 2-acetyl-4-nitrophenyl acetate.
[c] The reaction was completed after 15 min.

The use of indium(III) chloride, aluminum(III) chloride, iron(II) chloride, zinc(II) chloride as Lewis acid catalysts, did not provided satisfactory yields (Table 1, entries 2–5). In the presence of α-Fe_2O_3, acylation occurred not only at the OH group but also at the aromatic ring to give 2-acetyl-4-nitrophenyl acetate from 4-nitrophenol in 35% yield (Table 1, entry 7).

The reaction did not proceed when single-walled CNTs and multi-walled CNTs (MWCNTs) were employed, (Table 1, entries 8 and 9), whereas the yield of acylation product increased to 96% by the addition of Fe/SWCNTs (0.04 g, 2.8 mol%).

Notably, the catalytic activity of Fe/SWCNTs under the present conditions was shown to be superior to that of iron(III) chloride, which is known to be an efficient nanocatalyst for solvent-free acylations (Table 1, entries 11 *vs.* 7).[10e]

The optimum amount of nanocatalyst loading in the acetylation of 4-nitrophenol, was found to be 0.04 g (2.8 mol%), (Table 1, entry 11). By lowering the catalyst loading to 0.02 g (1.4 mol%), the desired product was obtained in lower yield while with an increase of the catalyst loading to 0.06 g (4.2 mol%) no

Table 2. Investigation of solvent effect for acetylation of 4-nitrophenol (1.0 mmol) based on Fe/SWCNTs (2.8 mol%, 0.04 g) and CH_3COCl (1.0 mmol) at room temperature.

Entry	Solvent	Time [h]	Yield [%]
1	CH_3CN	5	15
2	$PhCH_3$	5	10
3	CH_2Cl_2	5	25
4	EtOAc	4	10
5	$CHCl_3$	4	30
6	dioxane	5	10
7	–	15 min	96[a]

[a] In the absence of solvent.

significant effect in terms of reaction rate and isolated yield of product was observed (Table 1, entries 12 and 13).

To obtain optimum reaction conditions, a range of polar and non-polar solvent were surveyed (Table 2, entries 1–6). The best rate of acetylation was observed when the reaction was carried out under neat conditions (Table 2, entry 7). Also, attempts for the acetylation of 4-nitrophenol with acetic anhydride in the presence of Fe/SWCNTs resulted in failure.

Characterization of Fe/SWCNTs

In this experiment, the Fe/SWCNTs were directly observed by means of scanning electron (SEM) and transmition electron microscopic (TEM) images as shown in Figure 1 and Figure 2. Arrays of SWCNTs doped with Fe nanoparticles are observed according to the microscopic images.

Spectroscopic techniques such as FT-IR and Raman spectrometry were also employed for further characterization of Fe/SWCNTs. To characterize the Fe/SWCNTs, the nanotube sample was mixed with about a 100-fold amount of KBr powder. The FT-IR spectrum of an Fe/SWCNT sample is shown in Figure 3. According to the FT-IR spectrum, the strong peak at around 3433 cm^{-1} is related to the O–H bond, whereas the peaks at around 1616 cm^{-1} are related to the carbonyl groups. Also, the Raman spectrum of the catalyst is shown in Figure 4. A radial breathing mode (RBM) vibration at 260 cm^{-1} show that the radius of

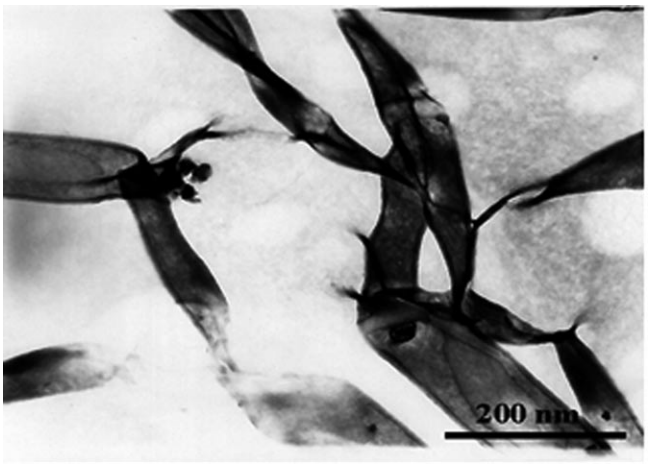


Figure 2. TEM image of Fe/SWCNTs.

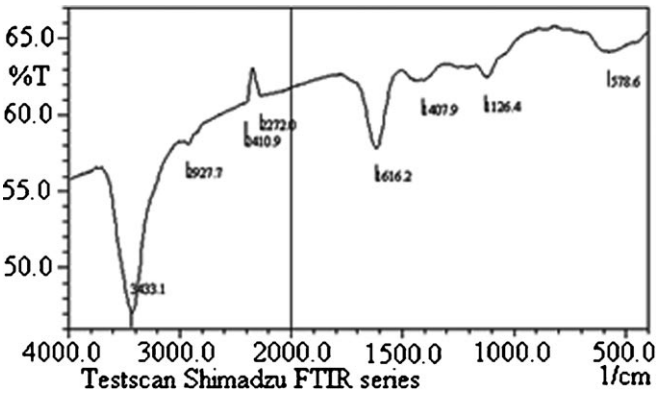


Figure 3. FT-IR spectrum of Fe/SWCNTs.

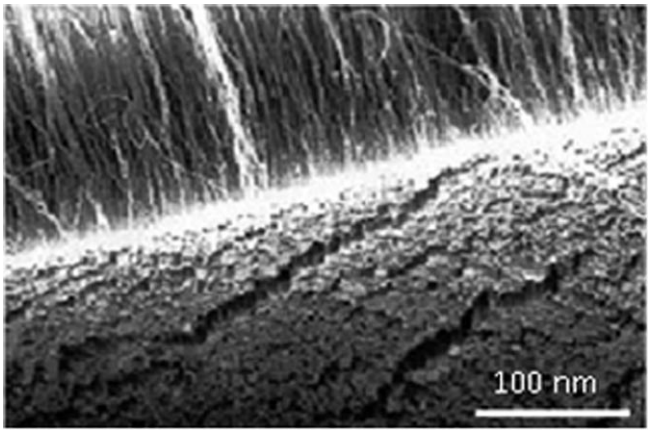


Figure 1. SEM image of Fe/SWCNTs.

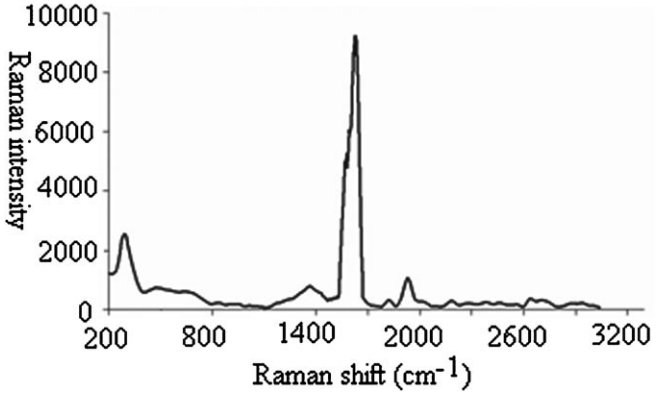


Figure 4. Raman spectrum of Fe/SWCNTs.

the Fe/SWCNTs is about 3 nm. Also, the peak at 1350 cm^{-1} (D-band) reveals the doping of the SWCNTs with iron nanoparticles[12a–d] The Raman spectrum exhibits a tangential mode (1450–1650 cm^{-1}) and a disorder mode (1250–1350 cm^{-1}), the ratio of which indicates the defect extent of SWCNTs.[12e]

Fe/SWCNTs-Catalyzed Acylation of Phenols and Alcohols

Encouraged by our preliminary results, we subjected a series of alcohols and phenols to acylation under the optimized conditions with the Fe/SWCNTs catalyst as summarized in Table 3. The described methodology illustrates a very simple acylation procedure, with wide applicability, extending the scope to benzylic, primary, secondary, tertiary, alcohols. Sterically hindered and electron-deficient phenols are efficiently acylated under similar conditions. Excellent results were obtained in each case affording the corresponding acetylated derivatives of the alcohols and phenols in 80–98% yields after 8–120 min at room temperature under solvent-free conditions. Acetyl chloride was preferred over the corresponding acetic anhydride. The reaction with the acid anhydride was too

Table 3. Fe/SWCNTs (0.04 g, 2.8 mol%) catalyzed acylation of alcohols and phenols (1.0 mmol) using acid chlorides (1.0 mmol).

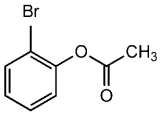
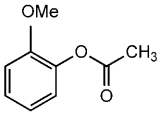
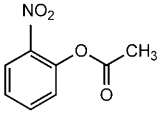
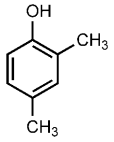
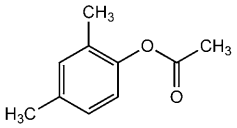
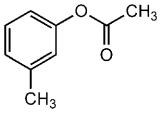
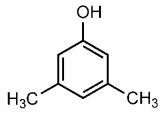
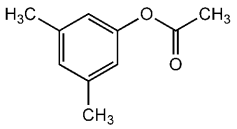
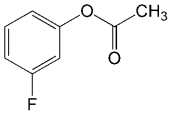
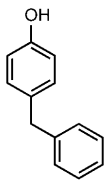
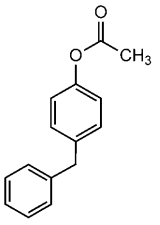
Entry	Substrate	Acylation reagent[a]	Product		Time [min]	Yield [%][b]
1	2-BrC_6H_4OH	CH_3COCl		**1**	20	94
2	2-$OMeC_6H_4OH$	CH_3COCl		**2**	15	98
3	2-$NO_2C_6H_4OH$	CH_3COCl		**3**	30	88
4		CH_3COCl		**4**	12	95
5	3-MeC_6H_4OH	CH_3COCl		**5**	15	92
6		CH_3COCl		**6**	12	90
7	3-FC_6H_4OH	CH_3COCl		**7**	15	89
8		CH_3COCl		**8**	10	98

Table 3. (Continued)

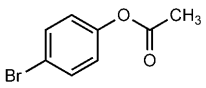
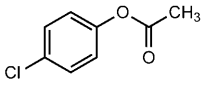
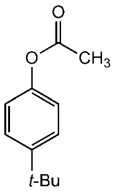
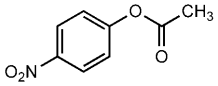
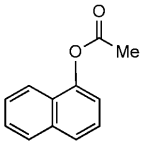
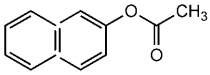
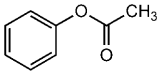
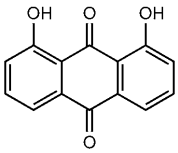
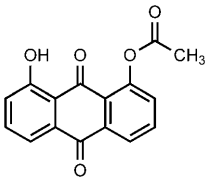
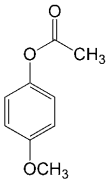
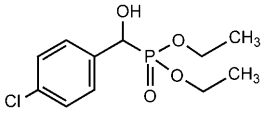
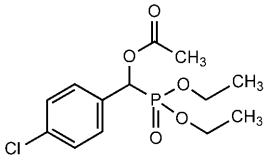
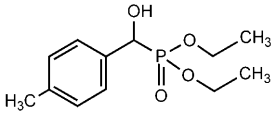
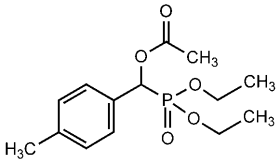
Entry	Substrate	Acylation reagent[a]	Product		Time [min]	Yield [%][b]
9	4-BrC_6H_4OH	CH_3COCl		**9**	20	94
10	4-ClC_6H_4OH	CH_3COCl		**10**	20	98
11	4-*t*-BuC_6H_4OH	CH_3COCl		**11**	18	94
12	4-$NO_2C_6H_4OH$	CH_3COCl		**12**	15	96
13	1-naphthol	CH_3COCl		**13**	8	95
14	2-naphthol	CH_3COCl		**14**	10	93
15	C_6H_5OH	CH_3COCl		**15**	18	98
16		CH_3COCl		**16**	30	81[c]
17	4-$MeOC_6H_4OH$	CH_3COCl		**17**	15	96
18		CH_3COCl		**18**	48	90[d]
19		CH_3COCl		**19**	40	89[d]

Table 3. (Continued)

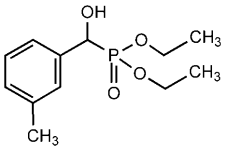
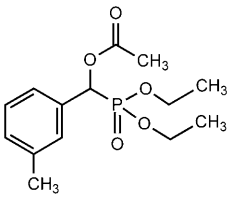
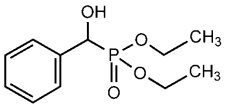
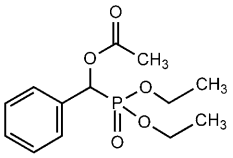
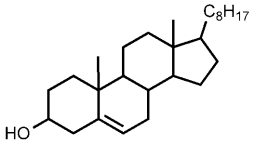
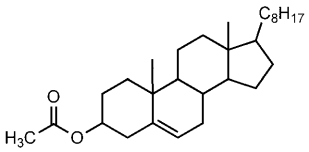
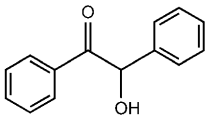
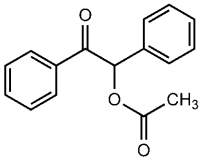
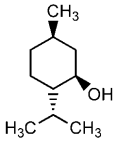
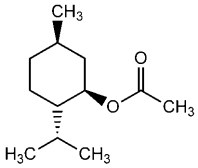
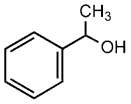
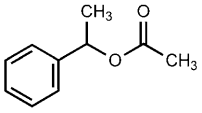
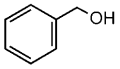
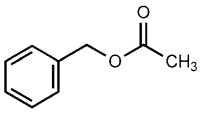
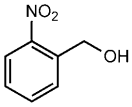
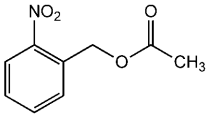
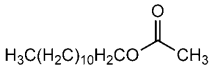
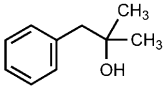
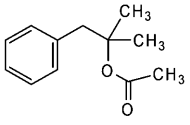
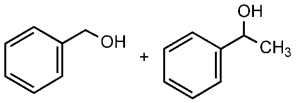
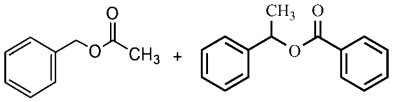
Entry	Substrate	Acylation reagent[a]	Product		Time [min]	Yield [%][b]
20		CH_3COCl		**20**	40	88[d]
21		CH_3COCl		**21**	35	87[d]
22		CH_3COCl		**22**	70	84[e]
23		CH_3COCl		**23**	120	88
24		CH_3COCl		**24**	20	83
25		CH_3COCl		**25**	15	89
26		CH_3COCl		**26**	10	97[f]
27		CH_3COCl		**27**	30	89
28	$CH_3(CH_2)_{10}CH_2OH$	CH_3COCl		**28**	15	91
29		CH_3COCl		**29**	60	80
30		CH_3COCl			15	73 + 21

Table 3. (Continued)

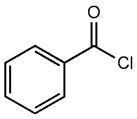
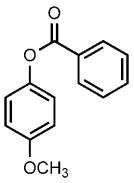
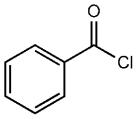
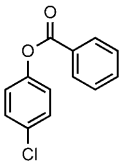
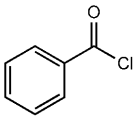
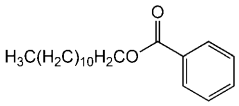
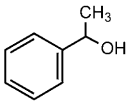
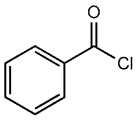
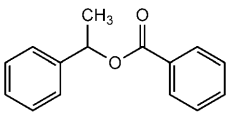
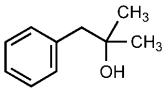
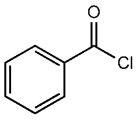
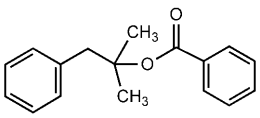
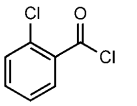
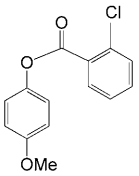
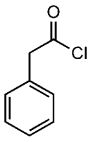
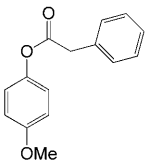
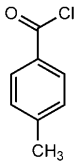
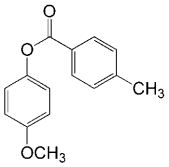
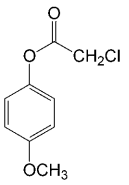
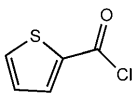
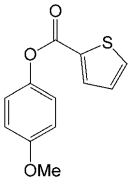
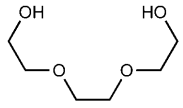
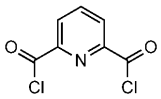
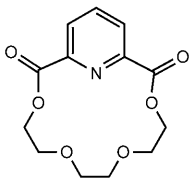
Entry	Substrate	Acylation reagent[a]	Product		Time [min]	Yield [%][b]
31	4-$MeOC_6H_4OH$			**30**	25	90
32	4-ClC_6H_4OH			**31**	28	92
33	$CH_3(CH_2)_{10}CH_2OH$			**32**	25	86
34					120	trace
35					120	trace
36	4-$MeOC_6H_4OH$			**33**	30	90
37	4-$MeOC_6H_4OH$			**34**	20	89
38	4-$MeOC_6H_4OH$			**35**	12	94
39	4-$MeOC_6H_4OH$	$ClCH_2COCl$		**36**	25	81
40	4-$MeOC_6H_4OH$			**37**	28	87

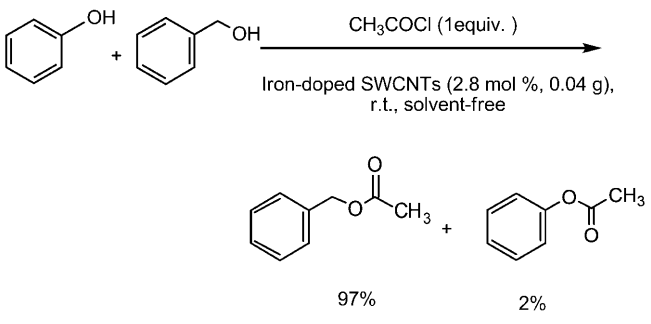
Table 3. (Continued)

Entry	Substrate	Acylation reagent[a]	Product		Time [min]	Yield [%][b]
41				**38**	120	80

[a] Acylation reagent (1 equiv.) for each OH function was used.
[b] Isolated yields.
[c] The corresponding monoacetate was prepared and the reaction was carried out at 70 °C.
[d] The reaction was carried out at 90 °C.
[e] The reaction was carried out with 1.2 equiv. acetyl chloride.
[f] The reaction was carried out on a 100-mmol scale.

slow to have practical application. The reactions were clean and fast and the products were isolated mostly in excellent yields after simple work-up using a short pad of silica gel if necessary. No competitive Fries rearrangement was observed for phenolic substrates.[13a,d] Phenolic compounds containing both electron-deficient and electron-donating groups (Table 3, entries 1–17) were acylated equally efficiently under these reaction conditions. We have observed that both 1-hydroxynaphthalene and 2-hydroxynaphthalene were also acylated in excellent yields (Table 3, entries 13 and 14). 4-Nitrophenol (entry 12) and 2-naphthol (entry 14) were converted into the corresponding acetate derivatives much more quickly than the procedure reported previously (15 min *vs.* 5 h and 10 min *vs.* 3 h, respectively).[13b,c] Acylation of 1,8-dihydroxyanthraquinone at room temperature was, however, sluggish; it could be completely acylated in an oil bath at 70 °C (Table 3, entry 16). Both primary and secondary alcohols react very well (Table 3, entries 22–28) and hindered tertiary alcohol (Table 3, entry 29) is also acylated smoothly without any side product detected. No selectivity between primary and secondary hydroxy groups was observed (Table 3, entry 30). Our results show that acetylation of α-hydroxyphosphonates with acetyl chloride under the reaction conditions required a higher temperature to obtain a high yield and also during the reaction no C–P bond cleavage was observed (Table 3, entries 18–21).[8j] The reaction of benzoin and 2,2′-[ethane-1,2-diylbis(oxy)]diethanol was slow under similar conditions (Table 3, entries 23 and 41). Successful acylations using both cholesterol and optically active substrates were performed by using 1.2 equivalents of acetyl chloride, 0.04 g of Fe/SWCNTs (2.8 mol%) at room temperature under solvent-free conditions with excellent yield (Table 3, entry 22). To access the feasibility of applying this method in a preparative scale, we carried out the acylation of benzyl alcohol with acetyl chlorides on a 100-mmol scale in the presence of the heterogeneous catalyst. As expected, the reaction proceeded similar to the case in a lower scale (Table 3, entry 26). Selective acetylation of one hydroxy group in the presence of the other one is a frequent synthetic problem. The chemoselectivity of the system was studied by competitive acetylation of an equimolar mixture of benzyl alcohol and phenol. Indeed, a mixture of benzyl alcohol and phenol furnished only the expected benzyl acetate on reaction with 1.0 equivalent of acetyl chloride (Scheme 2, Table 3, entry 30)

Reported catalytic benzoylation reactions of functional groups such as OH are more limited in number than their corresponding acetates in the literature. The catalytic activity of Fe/SWCNTs for the benzoylation of alcohols and phenols with benzoyl chloride and their derivatives was also studied. Different benzoylation reactions of alcohols and phenols were cleanly completed after a short period and the yields were excellent (Table 3, entries 31 and 32 and 36-40). A primary alcohol could be benzoylated very well, (Table 3, entry 33) whereas the secondary and tertiary



Scheme 2.

Table 4. Fe/SWCNTs (2.8 mol%, 0.04 g) catalyzed acylation of amines (1.0 mmol) using acid anhydrides (1.0 mmol) at room temperature.

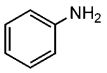
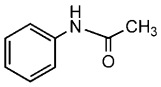
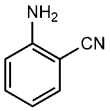
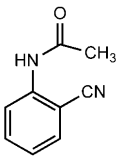
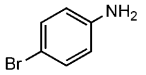
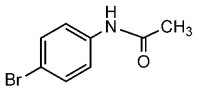
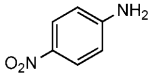
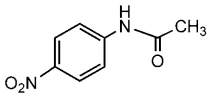
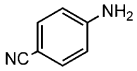
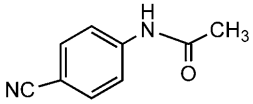
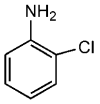
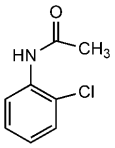
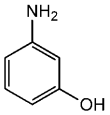
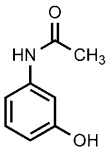
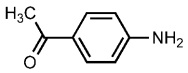
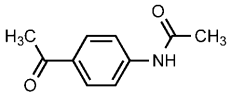
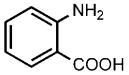
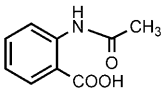
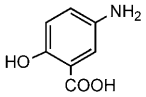
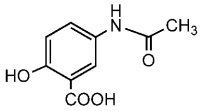
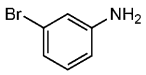
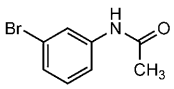
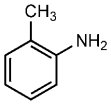
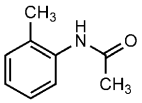
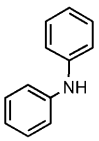
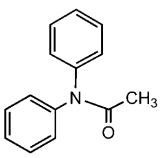
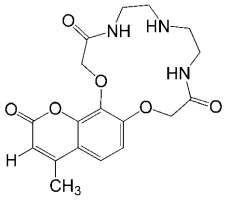
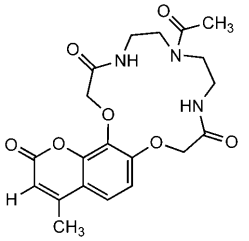
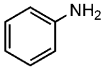
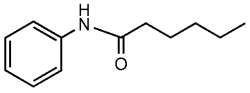
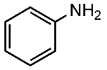
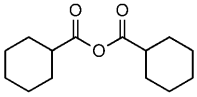
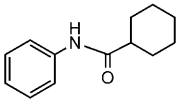
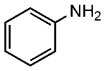
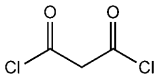
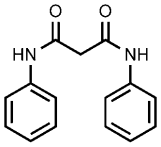
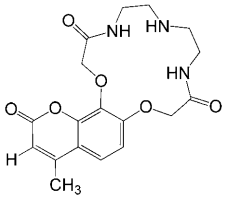
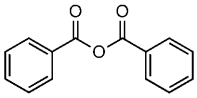
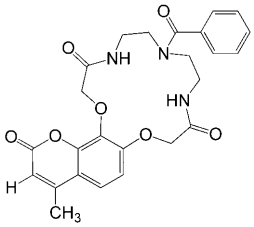
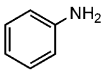
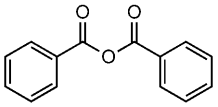
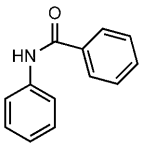
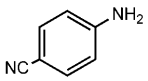
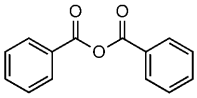
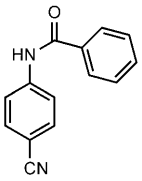
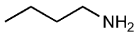
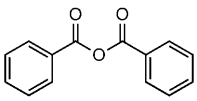
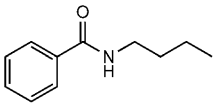
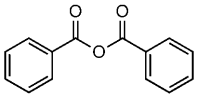
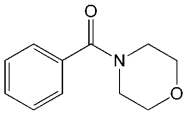
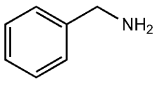
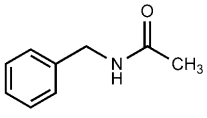
Entry	Substrate	Acylation reagent[b]	Products		Time [min]	Yield [%][b]
1		$(CH_3CO)_2O$		**39**	20	98
2		$(CH_3CO)_2O$		**40**	15	91
3		$(CH_3CO)_2O$		**41**	15	89
4		$(CH_3CO)_2O$		**42**	20	89
5		$(CH_3CO)_2O$		**43**	18	85
6		$(CH_3CO)_2O$		**44**	10	91
7		$(CH_3CO)_2O$		**45**	10	90
8		$(CH_3CO)_2O$		**46**	20	81
9		$(CH_3CO)_2O$		**47**	25	84
10		$(CH_3CO)_2O$		**48**	20	83
11		$(CH_3CO)_2O$		**49**	18	94
12		$(CH_3CO)_2O$		**50**	10	91
13		$(CH_3CO)_2O$		**51**	30	90

Table 4. (Continued)

Entry	Substrate	Acylation reagent[b]	Products		Time [min]	Yield [%][b]
14		$(CH_3CO)_2O$		**52**	40	89
15		$(CH_3(CH_2)_3CH_2CO)_2O$		**53**	20	79
16				**54**	30	81
17				**55**	15	91[c]
18				**56**	40	87[d]
19				**57**	20	88
20				**58**	20	88
21				**59**	15	90
22				**60**	18	90
23		$(CH_3CO)_2O$		**61**	20	94

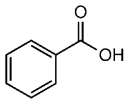
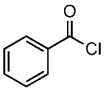
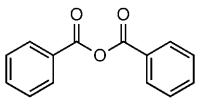
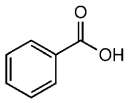
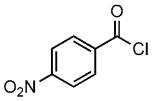
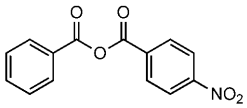
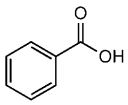
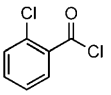
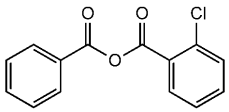
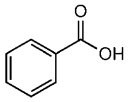
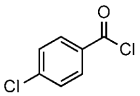
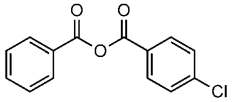
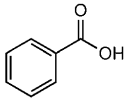
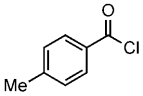
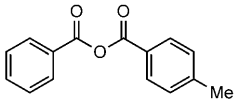
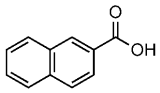
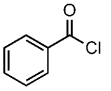
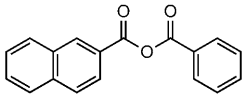
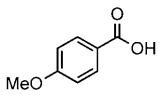
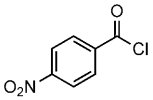
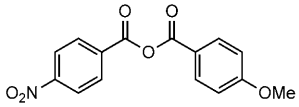
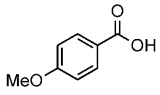
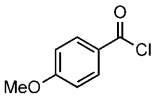
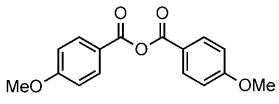
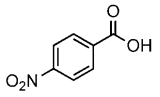
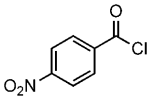
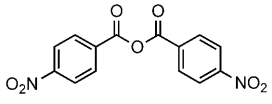
[a] Acylation reagent (1.0 equiv.) for each NH or NH_2 function was used.
[b] Isolated yields.
[c] Acylation reagent is malonyl dichloride.
[d] The reaction was carried out at 90 °C.

alcohols failed (Table 3, entries 34 and 35). Acid-sensitive alcohols are also reacted in high yield without the formation of any side product (Table 3, entries 17–21).

Fe/SWCNTs-Catalyzed Acylation of Amines

The catalytic activity of Fe/SWCNTs was also investigated in the acylation of amines into the corresponding amides derivatives. By our procedure, both aliphatic and aromatic amines with activating and deactivating groups were transformed into the corresponding acetamides derivatives in good yields under the identical reaction conditions (Table 4). It is significant to note that in these reactions, acid anhydrides were preferred over acid chlorides because amines reacted very rapidly with acid chlorides at room temperature, which makes it difficult to monitor the reactions. The conversion of aniline into acetanilide on a 100-mmol scale (Table 4, entry 1) proceeded just as well as the 1-mmol scale reaction. All the amines reacted very rapidly within 10–40 min with acid anhydrides. Acylation of aromatic amines containing both electron-donating as well as electron-deficient groups (Table 4, entries 1–13, 15 and 16) and aliphatic amines (Table 4, entries 14, 18, 21 and 22) were efficient and fast. The strongly deactivated nitro- and cyanoanilines afforded the corresponding acetamides within 15–20 min, respectively in excellent yields (Table 4, entries 2, 4 and 5). This procedure also was successfully used for synthesis of bis-amides **55** as potential HIV-1 integrase

Table 5. Fe/SWCNTs (2.8 mol%, 0.04 g) catalyzed acylation of aromatic acids (1.0 mmol) using benzoyl chlorides (1.0 mmol).

Entry	Substrate	Acylation reagent[a]	Products		Time [min]	Yield [%][b]
1				**62**	85	90
2				**63**	58	90
3				**64**	60	86
4				**65**	75	86
5				**66**	100	84
6				**67**	90	81
7				**68**	80	81
8				**69**	100	90
9				**70**	90	89

[a] Acylation reagent (1 equiv.) for each OH function was used.
[b] Isolated yields.

inhibitors affording 91% yield at 90 °C within 15 min while the reaction between two moles of aniline and diethyl malonate at 185 °C after 5.5 h produced product **55** in 72% yield (Table 4, entry 17).[14] An important feature of this procedure is the survival of a variety of functional groups such as ethers, nitro, hydroxy, halides, cyanide groups, etc. under the reaction conditions. Acid-sensitive substrates such as 4-cyanoaniline[11g,h] also reacted in high yield without the formation of any side product (Table 4, entries 5 and 20).

The reactions of amines with acetic anhydride were so fast in comparison to those of the phenols and acids that the selective protection of an amine in the presence of phenols and benzoic acids appeared to be a distinct possibility (Table 4, entries 7, 9 and 10). It is noteworthy that coumaryl azacrown ethers can be acylated by the present method indicating mildness of the reaction conditions (Table 4, entries 14 and 18).

Fe/SWCNTs-Catalyzed Acylation of Carboxylic Acids

Another remarkable characteristic of this method is that aromatic acids with activating and deactivating groups as well as alcohols, phenols and amines were transformed into the corresponding anhydride derivatives in good yields under the reaction conditions (Table 5).

Acid anhydrides are one of the most important classes of reagents used in organic synthesis. They are the preferred reactive acid derivatives for the preparation of amides, esters and peptides.[15] Furthermore, the use of acid anhydrides does not require any acid scavengers unlike the case with acid chlorides.

Investigation of Reusability of Fe/SWCNTs

Next, the reusability of Fe/SWCNTs was investigated. After the first use of Fe/SWCNTs in the acetylation of benzyl alcohol (Table 3, entry 33), the recovered catalyst was successfully used in 10 subsequent runs without any significant loss in the catalytic activity under similar experimental conditions (Table 6). No pretreatment step was used, although the recovered catalyst was washed with 10 mL of ethyl acetate to remove traces of the previous reaction mixture and dried before the next cycle.

Table 6. Reusability of Fe/SWCNTs (2.8 mol%, 0.04 g) in the acetylation of benzyl alcohol (1.0 mmol) with acetyl chloride (1.0 mmol).

Run no.	1	2	3	4	5	6	7	8	9	10
Yield [%][a]	97	97	97	97	96	96	94	94	90	90
Time [min]	10	10	10	10	15	15	15	15	20	25

[a] Isolated yields.

Comparison of the Catalytic Efficiency of Fe/SWCNTs with Literature Methods

A comparison of the catalytic efficiency of Fe/SWCNTs with selected previously known catalysts is collected in Table 7 to demonstrate that the present protocol is indeed superior to several of the other protocols.

The Fe/SWCNTs-catalyzed acylation of 2-naphthol with a stoichiometric amount of CH_3COCl proceeded smoothly at 25 °C and after 10 min the desired compound was obtained in 93% yield, while the use of Al_2O_3 for the preparation of same product requires a considerably prolonged reaction time (16 h) (Table 7, entry 1).

Additionally, the present protocol is effective in causing complete acetylation of 1-naphthol in less than 8 min. The same transformation requires 12 h for completion by using zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) as catalyst (Table 7, entry 2).

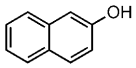
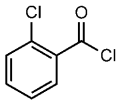
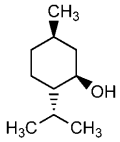
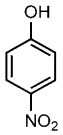
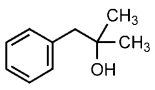
Using the present protocol the acylation of menthol is completed in less than 20 min with an 83% isolated yield. Most of the other listed methodologies suffer from limitations such as prolonged reaction times (e.g., $HBFO_4/SiO_2$), elevated temperatures (e.g., yttria–zirconia-based Lewis acid), excess reagents [e.g., $Bi(OTf)_3$] or use of hazardous materials (e.g., $DMAP/Et_3N/CH_3CN$) (Table 7, entry 3).

As a further example, *p*-nitrophenol was acetylated efficiently with the use of Fe/SWCNTs, while *p*-nitrophenol did not produce any desired product in the presence of Al_2O_3.[16a] On the other hand, although the acetylation of this substrate under cobalt(II) salen complex is equally effective, however, it requires the use of a large excess (5 equiv.) of acetic anhydride to provide the corresponding acetate[8k] (Table 7, entry 4).

It was also observed that the present methodology is suitable for the acylation of tertiary alcohols. The acetylation of tertiary alcohols is considered as one of the most difficult transformations due to the large steric hindrance around the tertiary hydroxy group.[16f] The present protocol allows the acetylation of a tertiary alcohol such as 2-methyl-1-phenylpropan-2-ol at 25 °C in 80% yield. It is of interest to note that no elimination adducts were observed.

Applying $ZnCl_2$ and DMAP as catalyst for the same substrate requires the use of 10 equivalents of acylating reagent and more than 20 h for completion. When the acetylation of 2-methyl-1-phenylpropan-2-ol was performed in the presence of pyridinium *p*-toluenesulfonate (PPTS) no reaction was observed and the starting alcohol remained unaffected.[16i] (Table 7, entry 5).

Table 7. Comparison of protocols for the acylation of 2-naphthol, 1-naphthol, menthol, 4-nitrophenol and 2-methyl-1-phenylpropan-2-ol.

Entry	Substrate	Reagent/catalyst	Solvent	Acylating agent (equiv.)	Time [min]	Temperature [°C]	Yield [%]	Ref.
1		$Zn(ClO_4)_2{\cdot}6H_2O$	solvent-free	$(CH_3CO)_2O$ (1)	10	25–30	90	[2e]
		$ZrOCl_2\ 8H_2O$	CH_2Cl_2	PhCOCl (5)	1260	25	98	[16b]
		Al_2O_3	solvent-free	CH_3COCl (1)	960	25	90	[16a]
		$ZnCl_2$-SiO_2	CH_3CN	$(CH_3CO)_2O$ (1)	390	80	83	[16d]
		ZnO	solvent-free	CH_3COCl (1)	30	25	91	[8c]
		Fe/SWCNTs	solvent-free	CH_3COCl (1)	10	25	93	–
2		ZnO	solvent-free	CH_3COCl (1)	120	60	86	[16e]
		$ZrOCl_2\ 8H_2O$	CH_2Cl_2	CH_3COCl (2)	720	25	97	[16b]
		Fe/SWCNTs	solvent-free	CH_3COCl (1)	8	25	95	–
		$InCl_3$	neat	$(CH_3CO)_2O$ (1)	45	25	70	[5e]
		$HBFO_4/SiO_2$	solvent-free	$(CH_3CO)_2O$ (1)	360	25	83	[16c]
		$HClO_4/SiO_2$	solvent-free	CH_3CO_2H (2)	360	25	97	[7e]
3		$Bi(OTf)_3$	Neat	$(CH_3CO)_2O$ (5)	90	reflux	97	[16f]
		DMAP/Et_3N	CH_3CN	$(CH_3CO)_2O$ (1.5)	55	0	75	[16f]
		yttria-zirconia-based Lewis acid	solvent-free	CH_3CO_2H (1)	180	125	91	[16 g]
		ZnO	solvent-free	PhCOCl (1)	60	25	84	[8c]
		Fe/SWCNTs	solvent-free	CH_3COCl (1)	20	25	83	–
		$ZrOCl_2\ 8H_2O$	CH_2Cl_2	CH_3COCl (1.5)	360	25	97	[16b]
		$HClO_4/SiO_2$	solvent-free	$(CH_3CO)_2O$ (1)	480	25	90	[7e]
		$Zn(ClO_4)_2{\cdot}6H_2O$	solvent-free	$(PhCO)_2O$ (1)	2	80	100	[2e]
		cobalt(II) salen complex	neat	$(CH_3CO)_2O$ (5)	45	50	99	[8k]
		Al_2O_3	solvent-free	PhCOCl (1)	–	–	–	[16a]
4		Fe/SWCNTs	solvent-free	CH_3COCl (1)	12	25	90	–
		$ZnCl_2$	CH_2Cl_2	$(CH_3CO)_2O$ (10)	1200	25	90	[16f]
5		DMAP	pyiridine	$(CH_3CO)_2O$ (10)	1440	25	60	[16f,h]
		pyridinium *p*-toluenesulfonate (PPTS)		$(CH_3CO)_2O$ (1)	2	MW	0	[16i]
		Fe/SWCNTs	solvent-free	CH_3COCl (1)	60	25	80	–

Conclusions

In conclusion, we have demonstrated a new, efficient, chemoselective and simple procedure for the acetylation of alcohols, phenols, amines, and carboxylic acids by use of a catalytic amount of Fe/SWCNTs as catalyst at room temperature under very mild conditions. No competitive Fries rearrangement was observed for phenolic substrates.[13a,d] Furthermore, an alcohol can be acylated in the presence of phenols with very high selectivity. Secondary and tertiary alcohols did not experience any competitive dehydration. The significant features of this method include its ease of operation, high efficiency, mild conditions and chemoselectivity,

which may prove widely useful in organic synthesis. The catalyst is also suitable for large-scale acetylation, and it is useful for industrial applications. Current efforts in our research group are aimed to expand the application of Fe/SWCNTs for catalyzed organic reactions.

Experimental Section

Instrumentation, Analyses and Starting Materials

General information: NMR spectra were recorded on a Bruker Avance DPX-250 (^{1}H NMR 250 MHz and ^{13}C NMR 62.9 MHz) spectrometer in pure deuterated solvents with tetramethylsilane as an internal standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hz. The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. IR spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. Mass spectra were determined on a Shimadzu GCMS-QP 1000 EX instrument at 70 or 20 eV. Melting points were determined in open capillary tubes in a Büchi-535 circulating oil melting point apparatus. Scanning electron micrographs were observed by SEM instrumentation (XL-30 FEG SEM, Philips, at 20 KV). Transmission electron microscopy (TEM, CN-10, Philips, at 100 KV) was used for observation of TEM images. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/UV254 plates or by a Shimadzu gas chromatograph (GC-10 A) instrument with a flame ionization detector using a column of 15% Carbowax 20M Chromosorb-w acid washed 60–80 mesh. Column chromatography was carried out on short columns of silica gel 60 (70–230 mesh) in glass columns (2–3 cm diameter) using 15–30 gram of silica gel per one gram of crude mixture. Chemical materials were either prepared in our laboratories or were purchased from Fluka, Aldrich and Merck Companies.

The following compounds obtained in this paper are known compounds: 2-bromophenyl acetate[8k] (**1**), 2-methoxyphenyl acetate[18] (**2**), 2-nitrophenyl acetate[19] (**3**), 2,4-dimethylphenyl acetate[20] (**4**), 3-tolyl acetate[21] (**5**), 3,5-dimethylphenyl acetate[22] (**6**), 3-fluorophenyl acetate[23] (**7**), 4-benzylphenyl acetate[24] (**8**), 4-bromophenyl acetate[25a] (**9**), 4-chlorophenyl acetate[25b] (**10**), 4-*tert*-butylphenyl acetate[8i] (**11**), 4-nitrophenyl acetate[26] (**12**), naphthalen-1-yl acetate[6e] (**13**), naphthalen-2-yl acetate[27] (**14**), phenyl acetate[6e] (**15**), 8-hydroxy-9,10-dioxo-9,10-dihydroanthracen-1-yl acetate[28] (**16**), 4-methoxyphenyl acetate[29] (**17**), (4-chlorophenyl)(diethoxyphosphoryl)methyl acetate[30a] (**18**), (diethoxyphosphoryl)(*p*-tolyl)methyl acetate[30a] (**19**), (diethoxyphosphoryl)(*m*-tolyl)methyl acetate[30a] (**20**), (diethoxyphosphoryl)(phenyl)methyl acetate[30a] (**21**), acetic acid 10,13-dimethyl-17-octyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl ester[31] (**22**), acetic acid 2-oxo-1,2-diphenylethyl ester[30b] (**23**), (1*R*,2*R*,5*R*)-2-isopropyl-5-methylcyclohexyl acetate[32] (**24**), 1-phenylethyl acetate[33] (**25**), benzyl acetate[32] (**26**), 2-nitrobenzyl acetate[34] (**27**), acetic acid dodecyl ester[35] (**28**), 2-methyl-1-phenylpropan-2-yl acetate[32] (**29**), 4-methoxyphenyl benzoate[36] (**30**), 4-chlorophenyl benzoate[36] (**31**), dodecyl benzoate[37] (**32**), 4-methoxyphenyl 2-chlorobenzoate[38] (**33**), 4-methoxyphenyl 2-phenylacetate[39] (**34**), 4-methoxyphenyl 4-methylbenzoate[40] (**35**), phenyl 2-chloroacetate[41] (**36**), 4-methoxyphenyl thiophene-2-carboxylate[42] (**37**), 3,6,9,12-tetraoxa-18-azabicyclo[12.3.1]octadeca-1(18),14,16-triene-2,13-dione[43] (**38**), *N*-phenylacetamide[26] (**39**), *N*-(2-cyanophenyl)-acetamide[44] (**40**), *N*-(4-bromophenyl)acetamide[43] (**41**), *N*-(4-nitrophenyl)acetamide[26] (**42**), *N*-(4-cyanophenyl)acetamide[45] (**43**), *N*-(2-chlorophenyl)acetamide[46] (**44**), *N*-(3-hydroxyphenyl)acetamide[47a] (**45**), *N*-(4-acetylphenyl)acetamide[47b] (**46**), 2-acetamidobenzoic acid[48] (**47**), 5-acetamido-2-hydroxybenzoic acid[49] (**48**), *N*-(3-bromophenyl)acetamide[50] (**49**), *N*-*o*-tolylacetamide[51] (50), *N*,*N*-diphenylacetamide[26] (**51**), *N*-phenylhexanamide[52] (**53**), *N*-phenylcyclohexanecarboxamide[53] (**54**), *N*,*N*′-diphenylmalonamide[14] (**55**), *N*-phenylbenzamide[54] (**57**), *N*-(4-cyanophenyl)benzamide[55] (**58**), *N*-butylbenzamide[56a] (**59**), morpholin-4-yl-phenylmethanone[47b] (**60**), *N*-benzylacetamide[56b] (**61**), benzoic anhydride[57a] (**62**), 4-nitrophenyl phenyl anhydride[57b] (**63**), 2-chlorophenyl phenyl anhydride[58] (**64**), 4-chlorophenyl phenyl anhydride[59a] (**65**), 4-methylphenyl phenyl anhydride[59b] (**66**), 2-naphthyl phenyl anhydride[60] (**67**), 4-methoxyphenyl 4-nitrophenyl anhydride[60] (**68**), *p*-methoxybenzoic anhydride[59] (**69**), 4-nitrophenyl anhydride[59] (**70**)

Synthesis of Fe/SWCNTs

In this study, Fe/SWCNTs were synthesized by the chemical vapor disposition (CVD) method *via* deposition of carbon vapors at high temperature (1300 °C) inside a quartz tube in a thermal furnace under an inert atmosphere of argon. Acetylene was selected as the source of SWCNTs. Carbon vapors were then deposited on iron nanoparticles, synthesized with the CVD method [17] through the decomposition of ferrocene (~14% molar percentage).

The synthesized Fe/SWCNTs were then purified from any amorphous carbon or bulky nanomaterials such as fullerenes, and activated carbon in an on-line system by a hydrogen and oxygen etching process, ultraviolet (UV) and microwave irradiaton. The amounts of iron nanoparticles doped on SWCNTs were controlled by optimization of the concentration of ferrocene and the flow rate of argon.

General Procedure for Solvent-Free and Rapid Acetylation of Phenols, Alcohols, Carboxylic Acids and Amines with Acid Chlorides or Acid Anhydrides using Fe/SWCNTs

To a mixture of Fe/SWCNTs, (0.04 g, 2.8 mol%) and an acid chloride or anhydride (1.0 mmol), alcohol, phenol or amine or carboxylic acid (1.0 mmol) was added. The reaction mixture was stirred with a mechanical stirrer for a certain period of time as required to complete the reaction (monitored by TLC) at room temperature. The solid mass (Fe/SWCNTs) was then eluted with ethyl acetate (20 mL), and the ethyl acetate extract was then washed with an aqueous solution of sodium bicarbonate and dried over anhydrous sodium sulfate. Evaporation of solvent furnished, in practically pure form, the corresponding product. The identity of these compounds was easily established by comparison of their ^{1}H NMR spectra with those of authentic samples.

7-Acetyl-16-methyl-5,6,7,8,9,10-hexahydro-2*H*,18*H*-chromeno[7,8-*b*][1,4,7,10,13]dioxatriazacyclopentadecine-3,11,18(4*H*,12*H*)-trione (52): Compound **52** was obtained as colourless solid; yield: 89%, after purification by plate chromatography, eluted with *n*-hexane/ethanol (10/3). Compound **52**: mp 278–280 °C; IR (KBr); $\upsilon = 3403$, 3373, 2938, 1715, 1674, 1640, 1606, 1535, 1109, 1020, 560 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.00$–2.20 (m, 3H), 2.40 (d, 3H, $J =$ 1.0 Hz), 3.38–3.72 (m, 8H), 4.560–4.78 (m, 4H), 6.21 (s, 1H), 6.84 (d, 1H, $J = 8.2$ Hz), 6.9 (s, 1H), 7.37(d, 1H, $J = 8.2$ Hz), 8.16 (s, 1H); ^{13}C NMR (62.9 MHz, DMSO-d_6): $\delta = 18.2$, 21.6, 22.2, 45.5, 46.5, 49.06, 49.8, 68.3, 72.8, 73.3, 109.7, 110.1, 111.9, 120.9, 137.7, 149.1, 151.8, 153.5, 165.7, 167.1, 168.8, 171.5; MS: *m*/*z* (%) = 419 ($M^+ + 2$, 1.6), 418 ($M^+ + 1$, 3.7), 417 (M^+, 4.6), 374 (4.8), 346 (6.4), 306 (34.9), 249 (22.7), 232 (30.1), 205 (38.4), 176 (13.4), 155 (24.1), 113 (55.7), 85 (80.2), 56 (100.0); anal. calcd. for $C_{20}H_{23}N_3O_7$ (417.15): C 57.55, H 5.55; found: C 57.51, H 5.58.

7-Benzoyl-16-methyl-5,6,7,8,9,10-hexahydro-2*H*,18*H*-chromeno[7,8-*b*][1,4,7,10,13]dioxatriazacyclopentadecine-3,11,18(4*H*,12*H*)-trione (56): Compound **56** was obtained as colourless solid; yield: 87%, after purification by plate chromatography, eluted with *n*-hexane/ethanol (10/3). Compound **56**: mp 278–280 °C; IR (KBr): $\upsilon = 3515$, 3423, 3226, 1741, 1694, 1664, 1622, 1602, 1368, 1219, 1105, 1100, 843, 554 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.43$ (d, 3H, $J =$ 1.0 Hz), 3.64–3.75 (m, 8H), 4.37 (s, 2H), 4.85 (s, 2H), 6.20 (s, 1H), 6.88 (d, 1H, $J = 8.75$ Hz), 7.26–7.43 (m, 7H), 8.07 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 18.8$, 30.9, 37.1, 67.9, 73.6, 108.6, 113.4, 116.2, 120.7, 121.4, 126.5, 130.1, 135.5, 152.3, 166.6, 174.8; MS: *m*/*z* (%) = 480 ($M^+ + 1$, 1.5), 479 (M^+, 2.0), 422 (0.8, 1.4), 396 (3.0), 374 (3.8), 345 (3.1), 306 (3.3), 287 (4.4), 249 (6.1), 232 (7.5), 173 (15.3), 105 (100.0), 77 (49.8), 56 (32.7); anal. calcd. for $C_{25}H_{25}N_3O_7$ (479.17): C 62.62, H 8.26; found: C 62.65, H 8.21.

Acknowledgements

We gratefully acknowledge the support of this work by the Shiraz University Research Council. We are also grateful to Mr. H. Sajedian Fard for helpful cooperation.

References

[1] a) T. W. Greene, P. G. M. Wuts, *Protective Groups in Organic Synthesis*, Wiley, New York, 3rd edn., **1999**; b) J. R. Hanson, *Protecting Groups in Organic Synthesis*, Blackwell Science Inc., Malden, MA, 1st edn., **1999**.

[2] a) A. K. Chakraborti, L. Sharma, M. K. Nayak, *J. Org. Chem.* **2002**, *67*, 2541–2547; b) A. K. Chakraborti, M. K. Nayak, L. Sharma, *J. Org. Chem.* **2002**, *67*, 1776–1780; c) A. K. Chakraborti, L. Sharma, U. Sharma, *Tetrahedron* **2001**, *57*, 9343–9346; d) A. K. Chakraborti, M. K. Nayak, L. Sharma, *J. Org. Chem.* **1999**, *64*, 8027–8030; e) S. R. Gulhane, A. K. Chakraborti, *J. Mol. Catal. A: Chem.* **2007**, *264*, 208–213.

[3] J. S. Carey, D. Laffan, C. Thomson, M. T. Williams, *Org. Biomol. Chem.* **2006**, *4*, 2337–2347.

[4] a) E. Vedejs, S. T. Diver, *J. Am. Chem. Soc.* **1993**, *115*, 3358–3359; b) E. Vedejs, N. S. Bennett, L. M. Conn, S. T. Diver, M. Gingras, S. Lin, P. A. Oliver, M. J. Petrson, *J. Org. Chem.* **1993**, *58*, 7286–7288.

[5] a) J. Iqbal, R. R. Srivastava, *J. Org. Chem.* **1992**, *57*, 2001–2007; b) S. Chandrasekhar, T. Ramaeshandar, M. Takhi, *Tetrahedron Lett.* **1998**, *39*, 3263–3266; c) R. H. Baker, F. G. Bordwell, *Org. Synth.* **1995**, *3*, 141–142; d) A. K. Chakraborti, R. Gulhane, *Synlett* **2004**, 627–630; e) A. K. Chakraborti, R. Gulhane, R. *Tetrahedron Lett.* **2003**, *44*, 6749–6753; f) F. Shirini, M. A. Zolfigol, M. Abedini, *Monatsh. Chem.* **2004**, *135*, 279–282; g) J. W. J. Bosco, A. K. Saikia, *Chem. Commun.* **2004**, 1116–1117; h) J. W. J. Bosco, A. Agrahari, A. K. Saikia, *Tetrahedron Lett.* **2006**, *47*, 4065–4068; i) P. Phukan, *Tetrahedron Lett.* **2004**, *45*, 4785–4587; j) R. H. Tale, R. N. Adude, *Tetrahedron Lett.* **2006**, *47*, 7263–7265; k) M. M. Heravi, K. F. Behbahani, F. F. Bamoharram, *J. Mol. Catal. A J. Mol. Catal. A: Chem.* **2006**, *253*, 16–19.

[6] a) K. Ishihara, M. Kubota, H. Kurihara, H. Yamamoto, *J. Org. Chem.* **1996**, *61*, 4560–4667; b) A. Orita, C. Tanahashi, A. Kakuda, J. Otera, *Angew. Chem.* **2000**, *112*, 2999–3001; *Angew. Chem. Int. Ed.* **2000**, *39*, 2877–2879; c) P. Saravanan, V. K. Singh, *Tetrahedron Lett.* **1999**, *40*, 2611–2614; d) K. K. Chauhan, C. G. Frost, I. Love, D. Waite, *Synlett* **1999**, 1743–1744; e) A. Kamal, M. A. Khan, S. K. Reddy, V. V. Srikant, T. Krishnaji, *Tetrahedron Lett.* **2007**, *48*, 3813–3818; f) R. Dalpozzo, A. De Nino, L. Maiuolo, A. Procopio, M. Nardi, G. Bartoli, R. Romeo, *Tetrahedron Lett.* **2003**, *44*, 5621–5624; g) R. Alleti, M. Perambudura, S. Samantha, V. P. Reddy, *J. Mol. Catal. A: Chem.* **2005**, *226*, 57–59; h) A. Procopio, R. Dalpozzo, A. D. Nino, L. Maiuolo, B. Russo, G. Sindona, *Adv. Synth. Catal.* **2004**, *346*, 1465–1670.

[7] a) Y. Nakae, I. Kusaki, T. Sato, *Synlett* **2001**, 1584–1586; b) J. K. Kondasamy, D. K. Chaand, *J. Mol. Catal. A: Chem.* **2006**, *255*, 275–282; c) G. Bartoli, M. Bosco, R. Dalpozzo, E. Marcantoni, M. Massaccesi, S. Rinaldi, L. Sambri, *Synlett* **2003**, 39–42; d) M. M. Heravi, F. K. Behbahani, R. H. Shoar, H. A. Oskooie, *Catal. Commun.* **2006**, *7*, 136–139; e) A. K. Chakraborti, F. K. Gulhane, *Chem. Commun.* **2003**, 1896–1897; f) A.-X. Li, T.-S. Li, T.-H. Ding, *Chem. Commun.* **1997**, 1389–1390.

[8] a) A. Khazaei, A. Rostami, Z. Tanbakouchian, Z. Zinati, *Catal. Commun.* **2006**, *7*, 214–217; b) T. S. Reddy, M. N. Narasimhulu, K. Suryakiran, C. Mahesh, K. Ashalatha, Y. Venkateswarlu, *Tetrahedron Lett.* **2006**, *47*, 6825–6829; c) M. Hosseini Sarvari, H. Sharghi, *Tetrahedron* **2005**, *61*, 10903–10907; d) P. Kumar, R. K. Pandey, M. S. Bodas, M. K. Dongare, *Synlett* **2001**, 206–209; e) M. A. Zolfigol, A. Khazaei, A. G. Choghamarani, A. Rostai, M. Hajjami, *Catal. Commun.* **2006**, *7*, 399–402; f) R. Kumareswaran, K. Pachamuthu, Y. D. Vakar, *Synlett* **2000**, 1652–1654; g) G. A. Grasa, T. Guveli, R. Singh, S. P. Nolan, *J. Org. Chem.* **2003**, *68*, 2812–2819; h) G. A. Grasa, R. M. Kissling, S. P. Nolan, *Org. Lett.* **2002**, *4*, 3583–3586; i) S. T. Kadam, S. S. Kim, *Synthesis* **2008**, 0267–0271; j) H. Firouzabadi, N. Iranpoor, S. Farahi, *J. Mol. Catal. A:*

Chem. **2008**, *289*, 61–68; k) F. Rajabi, *Tetrahedron Lett.* **2009**, *50*, 395–397; l) H. Nakatsuji, M. Morimoto, T. Misaki, Y. Tanabe, *Tetrahedron* **2007**, *63*, 12071–12080.

[9] a) J. C. Schumacher, *Perchlorates – Their Properties, Manufacture, and Use*, ACS Monograph Series, Reinhold, New York, **1996**; b) J. R. Long, *Chem. Health Safety* **2002**, *9*, 12–18.

[10] a) S. A. Forsyth, D. R. MacFarlane, R. J. Thompson, M. V. Itzstein, *Chem. Commun.* **2002**, 714–715; b) R. Dumeunier, I. E. Markó, *Tetrahedron Lett.* **2004**, *45*, 825–829; c) D. V. Sweet, *Registry of Toxic Effects of Chemical Substances*, *1985–1986*, U.S. Govt. Printing Office, Washington, DC, **1988**, p 3336; d) D. V. Sweet, *Registry of Toxic Effects of Chemical Substances*, *1985–1986*, U.S. Govt. Printing Office, Washington, DC, **1988**, p 4049; e) M. Mihara, T. Nakai, T. Iwai, T. Ito, T. Ohno, T. Mizuno, *Synlett* **2010**, 253–255.

[11] a) H. Sharghi, R. Khalifeh, M. M. Doroodmand, *Adv. Synth. Catal.* **2009**, *351*, 207–218; b) H. Sharghi, M. H. Beyzavi, A. Safavi, M. M. Doroodmand, R. Khalifeh, *Adv. Synth. Catal.* **2009**, *351*, 2391–2410; c) H. Sharghi, M. Aberi, M. M. Doroodmand, *Adv. Synth. Catal.* **2008**, *350*, 2380–2390; d) H. Sharghi, M. H. Beyzavi, M. M. Doroodmand, *Eur. J. Org. Chem.* **2008**, 4126–4138; e) H. Sharghi, M. Jokar, *Heterocycles* **2007**, 71, 2721–2733; f) H. Sharghi, M. Hosseini Sarvari, *Tetrahedron* **2003**, *59*, 3627–3633; g) H. Sharghi, M. Hosseini Sarvari, *Synth. Commun.* **2003**, *33*, 207–210; h) H. Sharghi, M. Hosseini Sarvari, *J. Org. Chem.* **2003**, *68*, 4096–4099; i) H. Sharghi, M. Jokar, *Can. J. Chem.* **2010**, *88*, 14–26; j) H. Sharghi, M. Hosseini Sarvari, *Synthesis* **2003**, 879–882; k) H. Sharghi, M. Hosseini-Sarvari, F. Moeini, *Can. J. Chem.* **2008**, *86*, 1044–1051; l) H. Sharghi, A. R. Salimi Beni, *Synthesis* **2004**, 2900–2904; m) H. Sharghi, O. Asemani, R. Khalifeh, *Synth. Commun.* **2008**, *38*, 1128–1136; n) H. Sharghi, F. Tamaddon, H. Eshghi, *Iran. J. Chem. Chem. Eng.* **2000**, *19*, 32- 36; o) H. Sharghi, B. Kaboudin, *J. Chem. Res. Synop.* **1998**, 628–629; p) H. Sharghi, M. Hosseini-Sarvari, F. Moeini, R. Khalifeh, A. Salimi Beni, *Helv. Chim. Acta* **2010**, *93*, 435–449.

[12] a) A. C. Dillon, T. Gennett, P. A. Parilla, J. L. Alleman K. M. Jones M. Heben *J. Mater. Res. Soc. Symp. Proc.* **2001**, *633*, A5.2.1–A5.2.6; b) M. S. Dresselhaus, A. Jorio, A. G. Souza Filho, G. Dresselhaus, R. Saito, M. A. Pimenta, *Mater. Res. Soc. Symp. Proc.* **2002**, *706*, Z7.1.1; c) J. E. Herrera, L. Balzano, F. Pompeo, D. E. Resasco, *J. Nanosci. Nanotechnol.* **2003**, *3*, 1–6; d) Y. Kobayashi, D. Takagi, Y. Ueno, Y. Homma, *Phys. E* **2004**, *24*, 26–31; e) H. R. Byon, H. Lim, H. J. Song, H. C. Choi, *Bull. Korean Chem. Soc.* **2007**, *28* , 2056–2060.

[13] a) H. Sharghi, H. Eshghi, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 135–139; b) S. K. De, *Tetrahedron Lett.* **2004**, *45*, 2919–2922; c) A. B. Khan, L. H. Choudhury, S. Ghosh, *Eur. J. Org. Chem.* **2005**, 2782–2787; d) H. Sharghi, B. Kaboudin, *J. Chem. Res. Synop.* **1998**, 628–629.

[14] M. Sechi, U. Azzena, M. P. Delussu, R. Dallocchio, A. Dessì, A. Cosseddu, N. Pala, N. Neamati, *Molecules* **2008**, *13*, 2442–2461.

[15] a) D. S. Tarbel, *Acc. Chem. Res.* **1969**, *2*, 296–300; b) J. Meienhofer, in: *The Peptides: Analysis, Synthesis and Biology*, (Eds.: E. Gross, J. Meienhofer), Academic Press, New York, **1979**, Vol. I, Chap 6, p 264.

[16] a) V. K. Yadav, K. G. Babu, *J. Org. Chem.* **2004**, *69*, 577–580; b) R. Ghosh, S. Maiti, A. Chakraborty, *Tetrahedron Lett.* **2005**, *46*, 147–151; c) A. K. Chakraborti, R. Gulhane, *Tetrahedron Lett.* **2003**, *44*, 3521–3525; d) R. Gupta, V. Kumar, M. Gupta, S. Paul, R. Gupta, *Indian J. Chem.* **2008**, *47B*, 1739–1743; e) F. Tamaddon, M. A. Amrollahi, L. Sharafat *Tetrahedron Lett.* **2005**, *46*, 7841–7844; f) A. Orita, C. Tanahashi, A. Kakuda, J. Otera *J. Org. Chem.* **2001**, *66*, 8926–8934; g) P. Kumara, R. K. Pandey, M. S. Bodas, S. P. Dagadeb, M. K. Dongare, A. V. Ramaswamy *J. Molec. Catal. A: Chem.* **2002**, *181*, 207–213; h) W. Steglich, G. Hofle, *Angew. Chem.* **1969**, *81*, 1001; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 981; i) J. C. Lee, S. J. Lee, J. S. Lee, *Bull. Korean Chem. Soc.* **2004**, *25*, 1295–1296.

[17] a) K. Hata, D. N. Futaba, K. Mizuno, T. Namati, M. Yumura, S. Ijima, *Science* **2004**, *306*, 1362–1364; b) G. Zhang, D. Mann, L. Zhang, A. Javey, Y. Li, E. Yenilmez, Q. Wang, J. P. Mcvittie, Y. Nishi, J. Gibbons, H. Dai et al., *Proc. Natl. Acad. Sci.* **2005**, *102*, 16141–16145.

[18] A. S. Paraskar. A. Sudalai, *Tetrahedron* **2006**, *62*, 4907–4916.

[19] S. P. P. Nanda, R. Guptaa, A. Loupyb, *Tetrahedron Lett.* **2002**, *43*, 4261–4265.

[20] D. C. Harrowven, R. F. Dainty, *Tetrahedron Lett.* **1996**, *37*, 7659–7660.

[21] A. P. Vásquez, A. Reyes, E. Linares, R. Bye, R. Mata, *J. Nat. Prod.* **2005**, *68*, 959–962.

[22] M. S. Newman, J. Landers, *J. Org. Chem.* **1977**, *42*, 2556–2559.

[23] R. Henning, R. Lattrell, H. J. Gerhards, M. Leven, *J. Med. Chem.* **1987**, *30*, 814–819.

[24] A. Singh, L. J. Andrews, R. M. Keefer, *J. Am. Chem. Soc.* **1962**, *84*, 1179–1185.

[25] a) A. Tavares, P. H. Schneider, A. A. Merlo, *Eur. J. Org. Chem.* **2009**, 889–897; b) J. Tong-Shou, *Synth. Commun.* **2006**, *36*, 1221–1227.

[26] K. Mogiliaiah, *Orient. J. Chem.* **2009**, *25*, 187–190 .

[27] R. K. Jeeva, *J. Mol. Catal. A: Chem.* **2007**, *276*, 230–234.

[28] M. I. Mzhelskay, I. D. Ivanchikov, N. E. Polyakov, A. A. Moroz, M. S. Shvartsberg, *Russ. Chem. Bull. Int. Ed.* **2005**, *53*, 2798–2804.

[29] A. K. Chakraborti, S. V. Chankeshwara, *J. Org. Chem.* **2009**, *74*, 1367–1370.

[30] a) H. Firouzabadi, N. Iranpoor, S Sobhani, Z Amoozgar, *Synthesis* **2004**, 1771–1774; b) Y. Hiroshi, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3153–3159.

[31] H. Eshghi, P. Shafieyoon, *J. Chem. Res.* **2004**, *12*, 802–805.

[32] M. Barbero, S. Cadamuro, S Dughera, P. Venturello. *Synthesis* **2008**, 3625–3632.

[33] S. V. Pansare, M. G. Malusare, A. N. Rai, *Synth. Commun.* **2000**, *30*, 2587–2592.

[34] P. J. Serafinowski, P. B. Garland, *J. Am. Chem. Soc.* **2003**, *125*, 962–965.

[35] L. Brinchi, R. Germani, G. Savelli, *Tetrahedron Lett.* **2003**, *44*, 2027–2029.

[36] S. Hashimoto, I. Furukawa, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2227–2228.
[37] I. Kubo, K. Fujita, K. Nihei, K. Masuoka. *Bioorg. Med. Chem.* **2003**, *11*, 573–580.
[38] M. D. Bhavasar, *Man-Made Text. India* **1989**, *32*, 8–11.
[39] R. Martin, *Monatsh. Chem.* **1981**, *112*, 1155–1163.
[40] H. Neuvonen, K. Neuvonen, P. Pasanen, *J. Org. Chem.* **2004**, *69*, 3794–3800.
[41] H. Neuvonen, K. Neuvonen, P. Pasanen, *J. Org. Chem.* **2002**, *67*, 6995–7003.
[42] C. K. Lee, J. S. Yu, H. J. Lee, *J. Heterocycl. Chem.* **2002**, *39*, 1207–1217.
[43] H. Sharghi, M. Hosseini Sarvari, *Synthesis* **2003**, 879–882.
[44] B. H. Kim, R. Han, F. Piao, Y. M. Jun, W. Baik, B. M. Lee, *Tetrahedron Lett.* **2003**, *44*, 77–79.
[45] Y. Ren, W. Wang, Sh. Zhao, X. Tian, J. Wang, W. Yin, L. Cheng, *Tetrahedron Lett.* **2009**, *50*, 4595–4597.
[46] X. Wan, Z. Ma, B. Li, K. Zhang, K. Cao, S. Zhang, Z. Shi, *J. Am. Chem. Soc.* **2006**, *128*, 7416–7417.
[47] a) H. S. Prasad, G. R. Srinivasa, D. Channe Gowda, *Synth. Commun.* **2005**, *35*: 1189–1195; b) D. Wei, C. Chen, L. Min. Z. Yan, L. Lei, G. Qing-Xiang, *Chin. J. Chem.* **2005**, *23*, 1241–1246.
[48] E. B. Pedersen, *Tetrahedron* **1977**, *33*, 217–220.
[49] M. Zou, H. Okamoto, G. Chang, X. Hao, J. Sun, F. Cui, K. Danjo, *Eur. J. Pharm. Biopharm.* **2005**, *59*, 155–160.
[50] H. Y. Choi, D. Y. Chi, *J. Am. Chem. Soc.* **2001**, *123*, 9202–9203.
[51] I. Cepanec, M. Litvic, J. Udikovic, I. Pogorelic, M. Lovric, *Tetrahedron* **2007**, *63*, 5614–5621.
[52] J. Suribabu, *J. Org. Chem.* **2009**, *74*, 1971–1976.
[53] L. Li, F. Xu, Y. Zhang, Q. Shen, *J. Org. Chem.* **2009**, *74*, 2575–2577.
[54] J. Wang, J. Li, F. Xu, Q. Shen, *Adv. Synth. Catal.* **2009**, *351*, 1363–1370.
[55] X. Wu, L. Hu, *J. Org. Chem.* **2007**, *72*, 765–774.
[56] a) D. P. Curran, S. Dandapani, S. Werner, M. Matsugi, *Synlett* **2004**, 1545–1548; b) M. Shi, S. C. Cui, *Synth. Commun.* **2005**, *35*, 2847–2858.
[57] a) J. J. Kim, Y. D. Park, W. S. Lee, S. D. Cho, Y. J. Yoon, M. Zou, H. Okamoto, *Synthesis* **2003**, 1517–1520; b) K. Kikukawa, K. Kono, K. Nagiira, F. Wad, T. Matsuda, *Tetrahedron Lett.* **1980**, *21*, 2877–2878.
[58] Y. Watanabe, M. Yamashita, T. A. Mitsudo, M. Igami, *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2490–2491.
[59] a) A. R. Hajipour; G. Mazloumi, *Synth. Commun.* **2002**, *32*, 23–30; b) B. C. Lee, J. H. Yoon, C. J. Gyulee, *J. Phys. Org. Chem.* **1994**, *7*, 273–279.
[60] J. M. Zeavin, A. M. Fisher. *J. Am. Chem. Soc.* **1932**, *54*, 3738–3742.

