DOI: 10.1002/adsc.201000319

Catalytic Friedel–Crafts Acylation and Benzoylation of Aromatic Compounds Using Activated Hematite as a Novel Heterogeneous Catalyst

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

[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
[b] Department of Chemistry, Shiraz University of Technology, Shiraz 75555-313, Iran

Received: April 26, 2010; Revised: October 12, 2010; Published online: November 17, 2010

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201000319.

Abstract: Catalytic Friedel–Crafts acylation of benzene and unactivated benzenes such as chlorobenzene and nitrobenzene have been successfully carried out using activated hematite (α-Fe_2O_3) as a new, heterogeneous and green catalyst. Sonication of neat α-Fe_2O_3 in a water bath under air atmosphere at room temperature followed by heating at 200 °C, dramatically increase the activity of α-Fe_2O_3. With the catalyst loading as low as 5.0 mol%, a wide variety of benzene derivatives were easily converted into the corresponding acylated products in a clean and high-yielding acylation reaction. It was found that the activated α-Fe_2O_3 could be efficiently recycled and reused several times by simple washing with ethyl acetate, this cannot be attained with most of the traditional catalysts.

Keywords: activated hematite; aromatic compounds; Friedel–Crafts acylation; heterogeneous catalysis; solvent-free reaction

Introduction

The Friedel–Crafts (FC) acylation reaction produces aromatic ketones, which are important intermediates in a wide variety of fields including manufacturing of fine chemicals and pharmaceuticals such as naproxen[1b] and ibuprofen,[1e] dyes, fragrances and agrochemicals.[1a–f]

Friedel–Crafts acylation reactions represent one of the greatest challenges to green chemistry.[1g–h] Traditional methods generally employ large quantities of hazardous soluble Lewis acids, (e.g., $AlCl_3$, $TiCl_4$, and $FeCl_3$) or strong mineral acids (e.g., HF), which are destroyed in the course of work-up giving poor resource utilization and large volumes of waste.[2] Considering the ecological and economical problems associated with waste management in most countries, the design of safe and environmentally acceptable processes for FC reactions is of increasing interest;[1f,3] thus, the development of truly catalytic alternatives is highly desirable and constitutes a field of current interest.

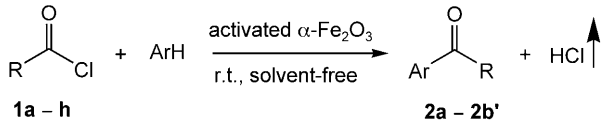
In order to solve the aforementioned problems, some catalytic Friedel–Crafts acylations have been developed. Lanthanide triflates,[4] $TiCl(Otf)_3$-TfOH,[5a] Re-$Br(CO)_5$,[5b] $LiClO_4$-acyl hydride complex,[6] $FeCl_3$ over K10,[7a] perfluorinated nafion-modified SBA-15,[7b] clay catalysts,[8] inorganic solids,[9] or solid acids,[10] HZSM-5 zeoilte,[11] metal oxide-promoted sulphated zirconia,[12a] ZnO,[12b] aluminium metal powder,[12c] $In(Br)_3$ using dimethylchlorosilane,[13] P_2O_5/Al_2O_3,[14a] and MoO_2Cl_2,[14b] have already been reported as catalysts for Friedel–Crafts acylations. Although some catalysts which complete the acylation reaction have been reported,[15] usually the conventional catalysts suffer from drawbacks in terms of requirement of more than stoichiometric quantities.[12c,16] Moreover, some recipes are based on highly moisture-sensitive reagents such as, $Bi(OTf)_3$,[17a] $TiCl(OTf)_3$,[5a] $SiCl_4$·$AgClO_4$[17b] and $SbCl_5$[17c] which are difficult to handle and require rigorously anhydrous reaction media. Therefore, the development of more efficient and easy handling catalysts is in strong demand.

Among many others, we have recently demonstrated that heterogeneous reagent systems have several

advantages such as simplicity in handling, mild reaction conditions, environmentally safe disposal and the minimization of chemical wastes compared to their homogeneous phase counterparts.[18] The above facts encouraged us to investigate a heterogeneous system for the Friedel–Crafts acylation of aromatic compounds.

As a part of our ongoing research projects to develop new synthetic methodologies, particularly with a potential for using metal oxides,[12b] we have been interested in iron oxide (Fe_2O_3 or hematite) as an inexpensive, high corrosion resistive and commercially available inorganic solid as a potential reaction catalyst. It is worth mentioning that α-Fe_2O_3 has attracted considerable attention due to its wide applications in diverse fields such as transistors,[19a] catalysis,[19b,c] photoelectrolysis reactors,[19d,e] batteries,[19f,g] magnetic storages,[19h] gas sensors,[19i,j] and as drug carriers for magnetically guided drug delivery etc.[19k,l,m]

Herein we wish to report that activated α-Fe_2O promoted the convenient, simple and selective Friedel–Crafts acylation of benzene and unactivated benzenes under solvent-free conditions, as shown in Scheme 1.



Scheme 1.

Results and Discussion

In order to establish the most convenient catalyst, we used eight commercially available metal oxides (CuO, NiO, CoO, Cr_2O_3, Mn_2O_3, SnO, ZnO, α-Fe_2O_3) for the study of Friedel–Crafts acylation reactions. The acylation of chlorobenzene was used as a model reaction to compare the catalytic ability of each metal oxide.

In a typical reaction, metal oxide was added to a mixture of acetyl chloride (**1a**) (1.0 mmol) and chlorobenzene (1.0 mmol). The reaction was performed at room temperature under solvent-free conditions (Scheme 2).

It was observed that all of the investigated metal oxides were able to catalyze the FC acylation (Table 1), while the reaction performed in the absence of the catalysts, resulted in the formation of no product (Table 1, entry 1). α-Fe_2O_3 demonstrated the greatest activity among the eight catalysts tested, affording quantitative conversion within 15 min, with 91% yields; while CuO, NiO, CoO, Cr_2O_3, Mn_2O_3 displayed reduced activity, and afforded 15 min conversions of 50, 55, 59, 56 and 59%, respectively, as evidenced by ^{1}H NMR as of the crude product (Table 1). SnO was least active, producing a 15 min conversion of only 28%.

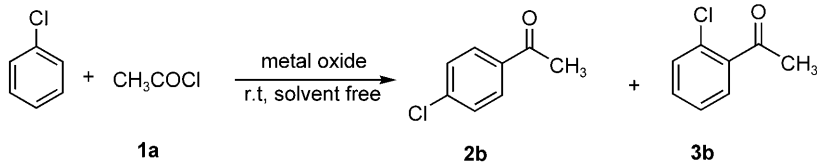
As shown in the Table 1, α-Fe_2O_3 was found to be the most effective catalyst in terms of reaction rate, selectivity and isolated yield of product (Table 1, entry 9). Results in Table 1 indicate that the optimal metal oxide loading for achieving the highest yield is 5.0 mol% of α-Fe_2O_3.

Later, the effects of a variety of conditions for increasing the catalytic activity of α-Fe_2O_3 were investigated (Table 1, entries 10–15). As is obvious from entry 15 of Table 1, the best result was obtained with the activating use of ultrasound (650 kHz) radiation of neat α-Fe_2O_3 in a water bath under an air atmosphere at room temperature for 1.0 h followed by heating the solid powder at 200 °C for 72 h.

The reactivity and regioselectivity of the activated α-Fe_2O_3 as catalyst in the acylation of chlorobenzene under solvent-free condition compares favorably with those observed in various solvents. Solvents having strong coordination ability such as 1,4-dioxane and THF gave no products (Table 2, entries 1 and 2).

In fact, under solvent-free conditions, the ketone was obtained quantitatively within 5.0 min with an excellent *o*/*p* ratio of 2/98. In contrast, in CH_2Cl_2 and $CHCl_3$, lower conversions and *o*/*p* ratios were obtained (Table 2, entries 3, 4), and the reaction required much longer time periods to go to completion and led to two ketones with an *o*/*p* ratio of 20/80 and 15/85, respectively. In the case of use of toluene as a non-polar solvent, the desired ketone was obtained quantitatively within 120 min with an *o*/*p* ratio of 8/92 in 60% yields along with 30% of acylated toluene (Table 2, entry 9). Solvent studies indicated that the solvent-free condition serves as the most suitable system for the FC reaction using 5.0 mol% of the activated α-Fe_2O_3 (Table 2, entry 12).

Encouraged by our preliminary results, the activated α-Fe_2O_3 was subsequently used to catalyze a range



Scheme 2.

Table 1. Investigation of the activity of various metal oxides on the synthesis of 1-(4-chlorophenyl)ethanone from chlorobenzene (1.0 mmol), acetyl chloride **1a** (1.0 mmol) under solvent-free conditions at room temperature.

Entry	Catalyst	Mmol of catalyst	Conversion[a] [%]	Time [min]	*o*/*p* [%][c]
1	–	–	0	5	0
			0	15	0
2	CuO	0.05	50	15	8/98
		0.20	41	30	10/90
3	NiO	0.05	55	15	2/98
		0.20	49	30	5/95
4	CoO	0.05	59	15	6/94
		0.20	48	40	8/94
5	Cr_2O_3	0.05	56	15	3/97
		0.20	41	45	9/91
6	Mn_2O_3	0.05	59	15	4/96
		0.20	39	60	11/89
7	SnO	0.05	28	15	10/90
		0.20	20	40	15/85
8	Commercial ZnO[12b]	0.05	60	30	2/98
		0.20	78	15	4/96
		0.50	85	10	4/96
9	α-Fe_2O_3	0.05	91	15	3/97
		0.10	90	20	3/97
		0.15	86	30	4/69
		0.20	85	35	4/96
10	α-Fe_2O_3/heating for 1 day at 100 °C	0.05	92	15	3/97
11	α-Fe_2O_3/heating for 3 days at 200 °C	0.05	94	13	3/97
12	α-Fe_2O_3/sonication (650 kHz)/1 h	0.05	91	13	3/97
13	α-Fe_2O_3/microwave irradiation/300 W/15 min	0.05	93	12	4/96
14	α-Fe_2O_3/microwave irradiation/300 W/15 min and then heating for 3 days at 200 °C	0.05	93	10	3/97
15	α-Fe_2O_3/sonication (650 kHz)/1 h and then heating for 3 days at 200 °C	0.05	95	5	2/98
16	γ-Fe_2O_3	0.05	70	15	3/97

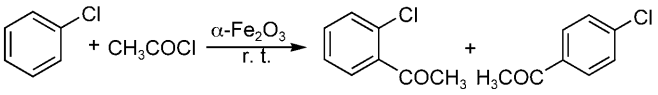
[a] Conversion of acetyl chloride, measured by ^{1}H NMR.
[b] *ortho*/*para* ratio measured by GC.

of Friedel–Crafts acylation reactions under solvent-free conditions (Table 3). All activated and unactivated aromatic compounds reacted very rapidly with a variety of acid chlorides along with a catalytic amount of activated α-Fe_2O_3 within 5–85 min at room temperature

The analysis of the results showed that the highest yields were obtained with substrates bearing electron-donating groups such as alkoxy substituents on the aromatic ring (Table 3, entries 6, 7 and 22-2-8). It is indeed gratifying to note that the reaction conditions are mild enough since they do not induce any dealkylation of an ether group located at an *ortho* position to the introduced acyl group (Table 3, entry 7) as observed in the acylation reaction with carboxylic acid catalyzed by BF_3.[20]

The acylation of alkyl-substituted benzenes such as toluene is more difficult, and some of the methods reported in the literature are not applicable to this substrate or give poor yields of ketone.[21] Under our catalytic conditions, the acylation of toluene afforded a mixture of *ortho*/*para*-regioisomers with a high *para*-selectivity (Table 3, entry 5), and acylation of *o*-xylene gave the corresponding ketone in excellent yield (Table 3, entry 8). Mesitylene was also reacted with acetyl chloride in the presence of activated α-Fe_2O_3 in excellent yield (Table 3, entry 9). Obviously, the methoxy group of anisole has a stronger activating effect on the aromatic system than the three methyl groups of mesitylene. Thus, the acylation of anisole is completed after 5 min in 98% yield, whereas the complete acylation of mesitylene requires a reaction time of 10 min, affording the desired product in 96% yield (Table 3, entry 6 *vs.* 9). Acylation occurs exclusively at the position *para* to OMe, Me, and Cl substituents for all of the compounds studied, in almost quantitative yields. However, in cases where the *para* positions are blocked, the acyl group is introduced in the *ortho* position (Table 3, entries 7 and 17).

Table 2. Investigation of various solvents effect on the synthesis of 1-(4-chlorophenyl) ethanone from chlorobenzene (1.0 mmol), acetyl chloride **1a** (1.0 mmol), activated α-Fe_2O_3 (0.05 mmol) at room temperature.



1a **2b** **3b**

Entry	Solvent	Conversion[a] [%]	Time [min]	*o*/*p*[b]
1	1,4-dioxane	0	120	0
2	THF	0	120	0
3	chloroform	40	130	15/85
4	dichloromethane	50	120	20/80
5	acetonitrile	10	120	5/95
6	EtOAc	15	120	6/94
7	xylene	30	120	7/93
8	water	10	120	90/10
9	toluene	60	120	8/92[c]
10	DMF	10	120	20/80
11	diethyl ether	5	120	10/90
12	–	95	5.0	2/98

[a] Conversion of acetyl chloride, measured by ^{1}H NMR.
[b] *ortho*/*para* ratio measured by GC.
[c] Acylated toluene was obtained in 30% yield.

The acylation of anthracene with acetyl chloride seemed to be more difficult to perform (Table 3, entries 10 and 11). Our attempt to prepare 9,10-diacetylanthracene (**2k**) using the activated α-Fe_2O_3 for direct FC acylation, after vigorous stirring of reaction at 80 °C, resulted the corresponding diacylated product in only 54% yield (Table 3, entry 11).

In the case where the aromatic ring is fused to a crown ether, a potential difficulty is apparent. The Lewis acid catalyst and/or the reactive electrophilic intermediate may be complex and consequently deactivated by the crown ether.[22] Interestingly, our procedure is good enough for the acylation of crown ethers such as benzo-18-crown-6 and dibenzo-18-crown-6 (Table 3, entries 13 and 14), producing the corresponding acylated products in excellent yield. Diacylation of dibenzo-18-crown-6 lead to two isomeric products, which could not be separated with recrystallization.

The acylation of ferrocene with acetyl chloride (**1a**) was also studied in the presence of activated α-Fe_2O_3, it proceeded with highly chemoselectively and furnished monoacylated ferrocene in 64% yield (Table 3, entry 15).

The presence of NO_2 as a strong electron-withdrawing group on the aromatic ring reduced the yield of the acylation reaction, so that the corresponding ketone was isolated in 69% yield (Table 3, entry 4).

An important feature of this procedure is the survival of a variety of functional groups such as ethers, nitro, amide, cyanide, etc. under the reaction conditions. Acid-sensitive substrates such as acetamide also reacted in high yields without the formation of any side products (Table 3, entry 19).

Although the benzoylation of chlorobenzene led to 80% conversion after 20 min in the presence of activated α-Fe_2O_3, the benzoylation of activated aromatics yielded the ketones in excellent yields (Table 3, entries 22–27).

To establish the generality and applicability of this method, the FC acylation of anisole with different acyl chlorides was investigated. The reaction with 2-chlorobenzoyl chloride produced a mixture of isomers with an *o*/*p* ratio of 2/98 in 90% yield (Table 3, entry 23). Similarly, acylation of anisole with *p*-toluoyl and 2-phenylacetyl chloride afforded exclusively the *para*-isomers in 95% and 91% yields, respectively (Table 3, entries 24 and 25), indicating a high selectivity with these acyl chlorides. In contrast, the reaction between anisole and benzoyl chloride was regioselective, yielding to the *para*-isomer (Table 3, entry 22).

Furthermore, we have elaborated our study with heteroaroyl chlorides such as thiophenyl chloride to establish their reactivity with anisole. This study disclosed that this procedure is also good enough for the preparation of the corresponding 2-acylated product in excellent yield (Table 3, entry 26). Finally, the acylation reaction of diaroyl chlorides such as isophthaloyl dichloride and anisole was studied. It was found that the reaction undergoes acylation predominantly at the *para*-position (Table 3, entry 27). To access the feasibility of applying this method on a preparative scale, we carried out the reaction of anisole with acetyl chloride on a 100-mmol scale in the presence of the heterogeneous catalyst (Table 3, entry 6). As expected, the reaction proceeded similarly to the case with a smaller scale, and the desired product was obtained in 98% isolated yield in 5 min.

The effects of activation process applied on the initial powder of α-Fe_2O_3 were evaluated by measuring the active surface area of the catalyst *via* the nitrogen adsorption method using a home-made thermogravimetric analysis (TGA) instrumentation system, and the results are shown in Figure 1.

The active surface areas, measured according to the Knudsen equation[23a], were as follows: 1.18E+2 m^2 kg^{-1} for initial α-Fe_2O_3; 6.19E+2 m^2 kg^{-1} for α-Fe_2O_3 after sonication for 1 h; 7.02E+2 m^2 kg^{-1} for α-Fe_2O_3 after sonication (650 kHz) for 1 h and then heating for 3 days at 200 °C.

It is believed that the contaminant adsorption capacity of an adsorbent is largely determined by the surface area available for adsorption[23b] and nitrogen adsorption of the initial and activated α-Fe_2O_3 show that high specific surface areas were directly prepared

Table 3. Catalytic FC acylation catalyze by activated α-Fe_2O_3.[a]

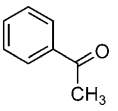
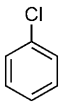
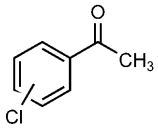
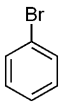
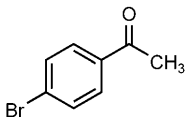
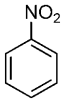
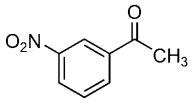
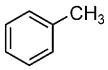
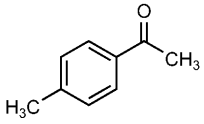
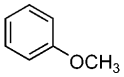
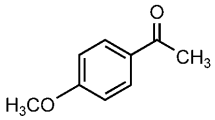
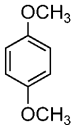
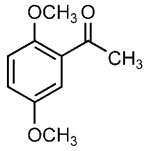
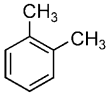
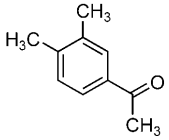
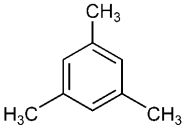
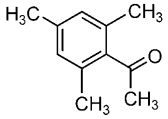
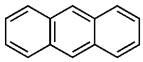
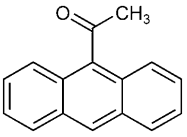
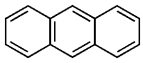
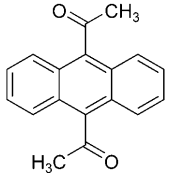
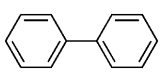
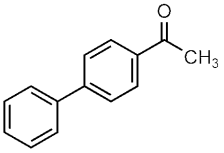
Entry	Substrate	Acylation reagent		Product		Time [min]	Yield [%][b]	(*o*/*p*)[c]
1		CH_3COCl	**1a**		**2a**	10	98	0/100
2		CH_3COCl	**1a**		**2b**	5	95	2/98
3		CH_3COCl	**1a**		**2c**	10	89	0/100
4		CH_3COCl	**1a**		**2d**	15	69[d]	–
5		CH_3COCl	**1a**		**2e**	8	96	0/100
6		CH_3COCl	**1a**		**2f**	5	98[e]	0/100
7		CH_3COCl	**1a**		**2g**	5	96[f]	–
8		CH_3COCl	**1a**		**2h**	8	96	0/100
9		CH_3COCl	**1a**		**2i**	10	96	–
10		CH_3COCl	**1a**		**2j**	70	83[i]	–
11		CH_3COCl	**1a**		**2k**	85	54[g]	–
12		CH_3COCl	**1a**		**2l**	12	94	0/100

Table 3. (Continued)

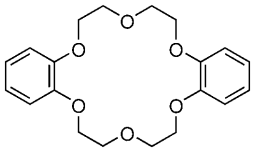
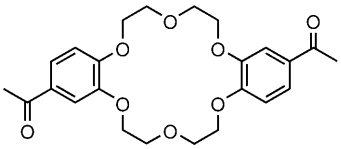
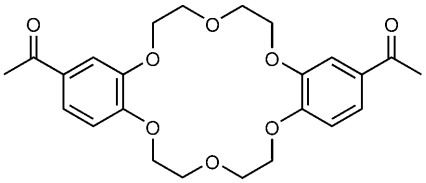
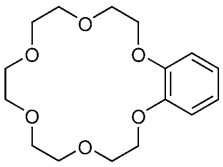
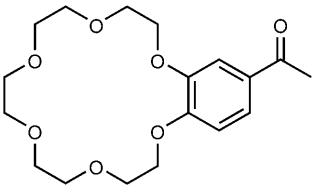
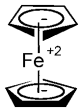
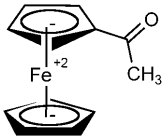
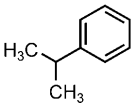
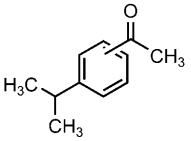
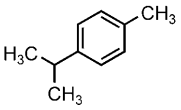
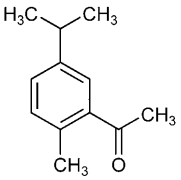
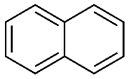
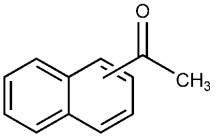
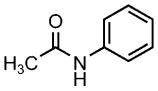
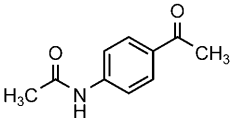
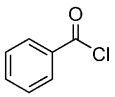
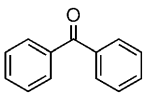
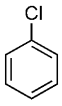
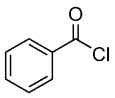
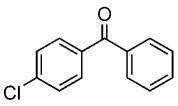
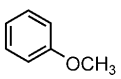
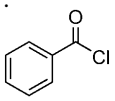
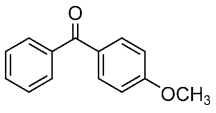
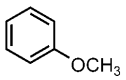
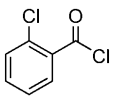
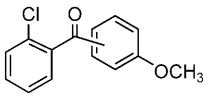
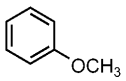
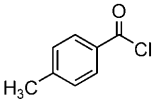
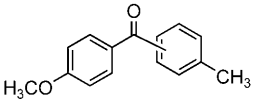
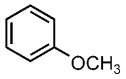
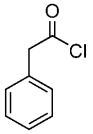
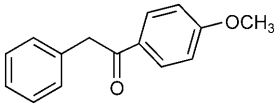
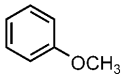
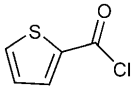
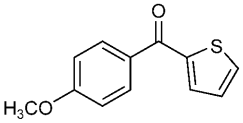
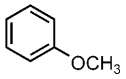
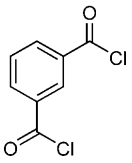
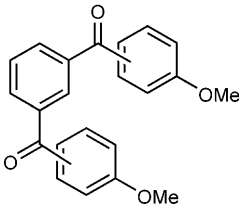
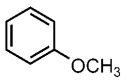
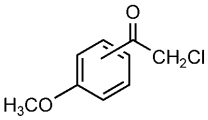
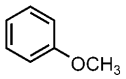
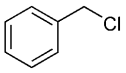
Entry	Substrate	Acylation reagent		Product		Time [min]	Yield [%][b]	(*o*/*p*)[c]
13		CH_3COCl	**1a**	 	**2m**	45	89[h]	–
14		CH_3COCl	**1a**		**2n**	30	87	–
15		CH_3COCl	**1a**		**2o**	60	64[g]	–
16		CH_3COCl	**1a**		**2p**	10	93	2/98
17		CH_3COCl	**1a**		**2q**	10	89[d]	–
18		CH_3COCl	**1a**		**2r**	10	88	2/98
19		CH_3COCl	**1a**		**2s**	15	81	0/100
20			**1b**		**2t**	18	94	–
21			**1b**		**2u**	20	80	0/100
22			**1b**		**2v**	10	95	0/100

Table 3. (Continued)

Entry	Substrate	Acylation reagent		Product		Time [min]	Yield [%][b]	(*o*/*p*)[c]
23			**1c**		**2w**	15	90	2/98
24			**1d**		**2x**	10	95	2/98
25			**1e**		**2y**	10	91	0/100
26			**1f**		**2z**	20	92	0/100
27			**1g**		**2a′**	20	90	3/97
28		$ClCH_2COCl$	**1h**		**2b′**	15	91	17//83
29			**1i**	no reaction				

[a] For general reaction conditions, see Experimental Section.
[b] 100% *para* product unless stated otherwise.
[c] The ratio of *ortho-/para*-isomers was determined by ^{1}H NMR and GC.
[d] Only *meta* isomer obtained under identical reaction conditions.
[e] The reaction was carried out on a 100 mmol scale. **Caution**: the anisole (100 mmol) was added into a mixture of activated α-Fe_2O_3 (0.2 g, 5 mmol,) and benzoyl chloride (100 mmol) in small portions.
[f] The acyl group is introduced in the *ortho* position.
[g] The reaction was carried out at 80 °C.
[h] Two isomeric products were obtained from diacylation of dibenzo-18-crown-6.
[i] Monoacylated product was obtained under identical reaction condition.

due to the sonication of neat α-Fe_2O_3 and then heating the solid powder at 200 °C.

The lattice model in Figure 2 shows the geometry of the α-Fe_2O_3 surface. Each of the cations inside the Fe_2O_3 matrix is five-fold coordinated, in contrast to the three-fold coordination on the surface; zig-zag rows of oxygen anions separate the neighboring cations. The relative area of Fe^{3+} and Fe^{2+} valence states in α-Fe_2O_3 was estimated to be 4:1.[24a] Unit surface meshes that correspond to observed LEED (low energy electron diffraction) patterns are indicated.[24a]

In this study, the effects of different processes were studied to distinguish the mechanism of the behavior of α-Fe_2O_3. For this purpose, the responsibility of chloride ion was studied in detail. It was evidenced that in the absence of a chlorinating agent, for example, when using an acid anhydride as the reagent and α-Fe_2O_3 as the catalyst, the acylation does not occur. Whereas the reaction occurs rapidly when bubbling HCl gas, revealing that the true catalytic effect of α-Fe_2O_3 is strongly dependent on the presence of chloride. This implies that the chloride ion is generated *in situ* during the acylation of aromatic or aliphatic acid

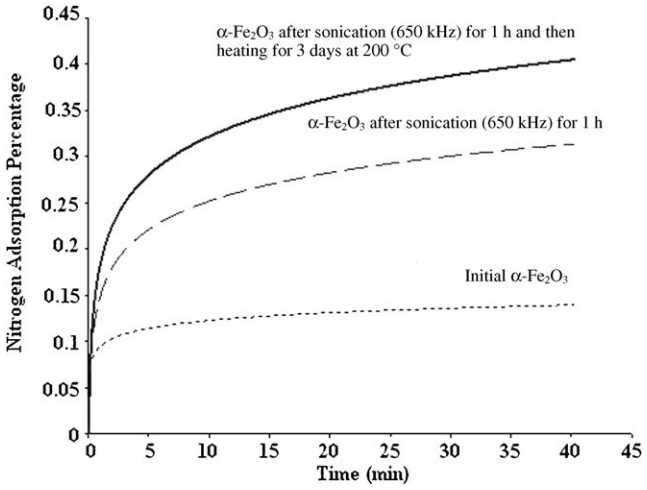


Figure 1. Nitrogen adsorption percentage of initial and activated α-Fe_2O_3.

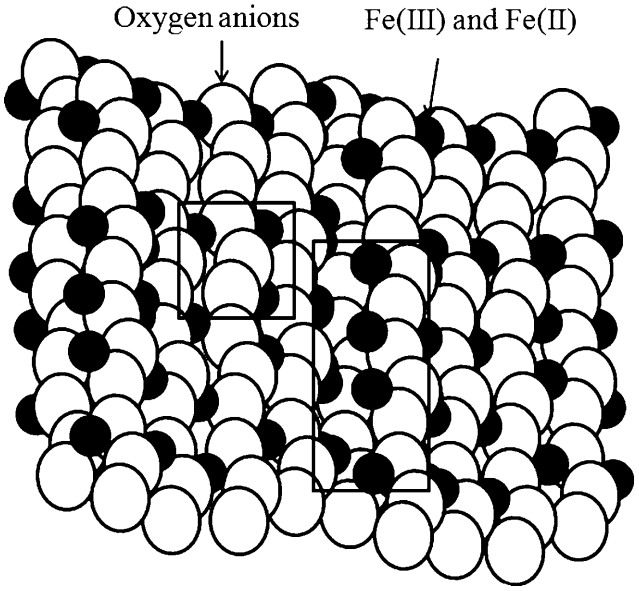


Figure 2. Model of the α-Fe_2O_3 surface.

chloride or *via* purging of the acid chloride during the acylation of aromatic compounds with acid anhydrides. One hypothesis is that the acylation process is homogenously catalyzed by small amounts of leached $FeCl_3$. The α-Fe_2O_3-leached $FeCl_3$, may be generated *in situ* by the reaction of α-Fe_2O_3 with acid chloride and hydrogen chloride. Since the formation of $FeCl_3$ from α-Fe_2O_3 and hydrogen chloride is endothermic, the probability of the formation of $FeCl_3$ under the conditions of acylation (room temperature) is low in this experiment. Also, for further confidence about the lack of responsibility of the $FeCl_3$ in the acylation process, the stability of α-Fe_2O_3 was studied under the conditions of liquid phase oxidations with *tert*-butyl hydrogen peroxide (TBHP) according to the Sheldon test.[24b] The results of Sheldon tests revealed that the organic reaction takes place in micropores or at the outer surface of the α-Fe_2O_3. Therefore, $FeCl_3$ is not considered as a true catalyst in the synthesis of organic compounds during the acylation processes. The probable evidence for the corresponding catalyst is that, due to the availability of Fe(II) and Fe(III) ions on the outer surface of α-Fe_2O_3 , the *in situ* generated chloride during the acylation process is adsorbed on the micropores or at the outer surface of α-Fe_2O_3. This layer is considered as the first electrical layer providing negative electrical charge on the solid state catalyst. Also, the attractive interaction of the negatively charged catalyst with acylinum ion (positively charged) then results in the acylinum ion to form the secondary layer on the α-Fe_2O_3 surface. Therefore, this phenomenon precedes the acylation process (Figure 3). The adsorption behavior of chloride ion on α-Fe_2O_3 has already been investigated, providing a homogeneous electrical double layer in the reaction environment.[24c] The complexation constant (pK_{Cl}) of α-Fe_2O_3 in chloride solution has been evaluated as 5.21.[24d] The influence of the electric charge density on the surface of α-Fe_2O_3 is due to the adsorption process, providing a salting-out effect. This effect causes the organic products to be simply repelled from the surface of α-Fe_2O_3, causing protection of catalyst from any foreign species and regeneration of the catalyst after each use as catalyst in the synthesis of organic compounds. Therefore, α-Fe_2O_3 is the true catalyst in the acylation reaction.

It is noteworthy that α-Fe_2O_3 could be used for subsequent cycles of acylation without any loss of its catalytic activity. After the first use of activated α-Fe_2O_3 in the acetylation of anisole (Table 3, entry 6), the recovered catalyst was successfully used in 10 subsequent independent runs without any significant loss in catalytic activity under similar experimental conditions (Table 4). 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.

The literature reports for the FC acylation reactions of aromatic compounds with acid chlorides in the presence of various catalysts are listed in Table 5. The reaction in the presence of activated α-Fe_2O_3 as catalyst is also included. The results demonstrate that the present protocol is indeed superior to several of the other protocols. Anisole is completely acylated in less than 5 min at 25 °C in 98% isolated yield using the present protocol. Most of the other protocols listed take either longer time for completion or use high temperature.

The activated α-Fe_2O_3-catalyzed acylation of *o*-xylene with CH_3COCl at room temperature, afforded a 96% yield within 8 min while the *o*-xylene reacted

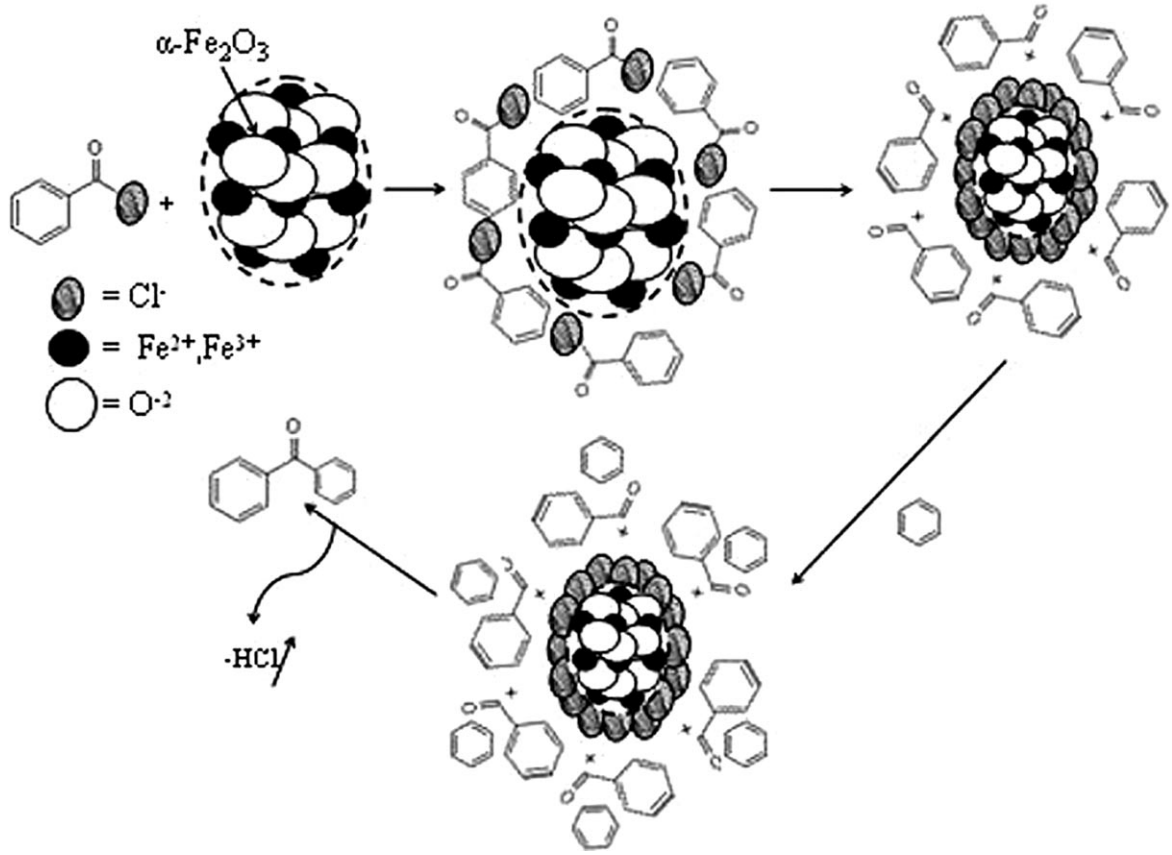


Figure 3. The mechanism proposed for FC acylation in the presence of α-Fe_2O_3

with CH_3COCl in the presence of indium in dioxane solvent with 40% yield within 2.5 h.

Benzoylation of anisole with 1.0 equivalent of 4-methylbenzoyl chloride afforded 95% yields in 10 min in the presence of activated α-Fe_2O_3 under solvent-free conditions, while MoO_2Cl_2 requires long time (20 h) for completion and the reaction carried out under reflux conditions affording 85% yield.

By using the present protocol, benzene is completely acylated within 10 min at 25 °C in 98% isolated yield, while benzene when reacted with CH_3COCl in the presence of $SbCl_5$-TBEA[25] in nitromethane solvent afforded a 37% yield within 2 h.

Conclusions

In conclusion, we have developed an activated α-Fe_2O_3-catalyzed FC acylation of aromatic compounds with acid chlorides under mild conditions, which has added a new catalyst for this class of reactions. The advantages of this environmentally benign and safe protocol include simple reaction set-up without requiring specialized equipment, very mild reaction conditions, high efficiency and high selectivity, very short reaction times, and the elimination of solvent.

Table 4. Reusability of activated α-Fe_2O_3 in the acetylation of anisole with acetyl chloride.

Run no.	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
Yield [%][a]	98	98	97	97	96	95	94	93	90	90
Time [min]	10	10	10	10	15	15	15	15	35	30

[a] Isolated yield.

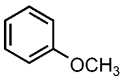
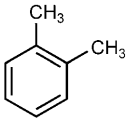
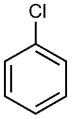
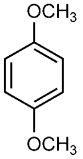
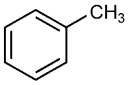
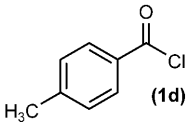
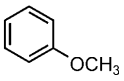
These advantages indicate the potential usefulness of this class of catalysts for future studies and their applications in the fields of organic synthesis, industrial production, and green chemistry.

Experimental Section

Instrumentation, Analyses and Starting Material

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. IR spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. Elemental analyses were obtained using a Thermofinnigan Flash-Ea 1112 series apparatus.

Table 5. Comparison of protocols for the FC acylation of aromatic compounds.

Entry	Acid chloride	Aromatic compound		Conditions	Catalysts	Yields [%]	Time [min]
1	CH_3COCl (**1a**)		**8**	$MeNO_2$/50 °C	$Sc(OTf)_3LiClO_4$[4]	90	60
				benzene/reflux	Graphite[26]	89	480
				$MeNO_2$/120 °C	$BnNEt_3(SbCl_5)_2Cl$[27]	96	120
				solvent-free/r.t.	activated α-Fe_2O_3	98	5
2	CH_3COCl (**1a**)		**2**	dioxane/100 °C	In[21b]	40	2.5 h
				$MeNO_2$/120 °C	$SbCl_5$-TBEA[25]	90	30
				solvent free/r.t.	activated α-Fe_2O_3	96	8
3	CH_3COCl (**1a**)		**9**	dioxane/100 °C	In[21b]	–	5 h
				solvent free/r.t.	activated α-Fe_2O_3	93	12
4	CH_3COCl (**1a**)		**4**	CH_3CN/r.t.	SmI_3[28]	59	3 h
				solvent free/r.t.	activated α-Fe_2O_3	96	5
5	CH_3COCl (**1a**)		**7**	dioxane/100 °C	In[21b]	21	2.5 h
				$MeNO_2$/120 °C	$SbCl_5$-TBEA[25]	82	60
				solvent free/r.t.	activated α-Fe_2O_3	96	8
6			**8**	reflux/20 h	MoO_2Cl_2[14b]	85	20 h
				solvent free/r.t.	activated α-Fe_2O_3	95	10
7	CH_3COCl (**1a**)		**10**	$MeNO_2$/120 °C	$SbCl_5$-TBEA[25]	37	120
				150 °C	[Emim][NTf2]/Bi_2O_3[1f]	62	24 h
				solvent free/r.t.	activated α-Fe_2O_3	98	10

Melting points were determined in open capillary tubes in a Büchi-535 circulating oil melting point apparatus. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates. 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 grams of silica gel per one gram of crude mixture. Chemical materials were purchased from Fluka, Aldrich and Merck. The used activated carbon was also purchased from Merck (Atr. No. 9631, 0.3-.05 mm).

General Procedure for Preparation of Activated α-Fe_2O_3

Activated α-Fe_2O_3 can be simply prepared by the sonication (650 kHz) of neat α-Fe_2O_3 in a water bath under an air atmosphere at room temperature for 60 min. After sonication of neat α-Fe_2O_3, the solid powder was kept at 200 °C for 72 h. Activated α-Fe_2O_3 was thus obtained.

General Procedure for a Facile and Rapid Friedel–Crafts Acylation and Benzoylation of Aromatic Compounds in Solvent-Free Conditions by Activated α-Fe_2O_3 as a New, Highly Efficient, and Reusable Catalyst

To a mixture of activated α-Fe_2O_3 (dry powder, 0.01 g, 0.05 mmol) and acid chloride (1.0 mmol), the aromatic compound (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 α-Fe_2O_3 was then separated from the organic solution *via* addition of several drops of hydrogen peroxide (3.0 M) to oxidize chloride ion and induce precipitation of the catalyst from the organic solution. The solid mass (α-Fe_2O_3) 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 the solvent and purification by silica gel column chromatography using petroleum ether as solvent provided the pure product. The identity of these compounds was easily established by comparison of their ^1H NMR and ^{13}C NMR spectra with those of authentic samples.

Acetophenone[27] (2a): Compound **2a** was obtained in 98% yield; mp 20 °C; IR (neat): $\nu = 1681\ cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.60$ (s, 3H), 7.44–7.48 (m, 2H), 7.54–7.58 (m, 1H), 7.95 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 26.9, 127.7, 128.7, 133.5, 137.6, 197.9$.

1-(4-Chlorophenyl)ethanone[29] (2b): Compound **2b** was obtained in 95% yield; mp 18 °C; IR (neat): $\nu = 1681\ cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.58$ (s, 3H), 7.42 (d, 2H, $J = 8.8$ Hz), 7.88 (d, 2H, $J = 8.8$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 26.3, 128.7, 129.3, 130.1, 139.9, 196.5$.

4-Bromoacetophenone[29] (2c): Compound **2c** was obtained as a white solid in 89% yield; mp 48–52 °C. IR (KBr): $\nu = 1670\ cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.54$ (s, 3H), 7.60 (d, 2H, $J = 8.8$ Hz), 7.81 (d, 2H, $J = 8.8$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 26.9, 128.7, 130.2, 132.3, 136.3, 196.9$.

1-(3-Nitrophenyl)ethanone[29] (2d): Compound **2d** was obtained as a yellow solid in 69% yield; mp 76–79 °C; IR (KBr): $\nu = 1689, 1523, 1344\ cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.65$ (s, 1H), 7.71–7.67 (m, 3H), 8.01 (d, 1H, $J = 7.7$ Hz), 8.24 (d, 1H, $J = 7.7$ Hz), 8.70 (d, 1H, $J = 2.0$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 27.1, 123.6, 127.8, 130.3, 134.1, 138.7, 148.9, 199.5$

1-*p*-Tolylethanone[29] (2e): Compound **2e** was obtained in 96% yield; IR (neat), $\nu = 1677\ cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.41$ (s, 3H), 2.57 (s, 3H), 7.25(d, 2H, $J = 8.0$ Hz), 7.85 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.2, 26.4, 125.5, 128.3, 129.1, 133.8, 134.6, 143.8, 198.2$.

4-Methoxyacetophenone[29] (2f): Compound **2f** was obtained as a white solid in 98% yield; mp 36–39 °C; IR (KBr): $\nu = 1664\ cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.54$ (s, 3H), 3.86 (s, 3H), 6.92(d, 2H, $J = 8.8$ Hz), 7.93 (d, 2H, $J = 8.8$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 26.2, 55.4, 119.6, 130.2, 130.5, 163.4, 196.8$.

1-(2,5-Dimethoxyphenyl)ethanone[28] (2g): Compound **2g** was obtained as a yellow oil in 96% yield; IR (neat): $\nu =$ 3003, 2994, 2944, 1673, 1608, 1258 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.35$ (s, 3H), 3.79 (s, 6H), 6.91 (d, 1H, $J = 9.2$ Hz), 7.03 (d, 1H, $J = 9.1$ Hz), 7.29 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.1, 55.5, 56.0, 113.2, 113.7, 114.4, 120.4, 122.3, 205.5$

1-(3,4-Dimethylphenyl)ethanone (2h): Compound **1h** was obtained as a yellow oil in 96% yield;[30] bp 176 °C; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.28$ (s, 6H), 2.54 (s, 3H), 7.25 (d, 1H, $J = 7.7$ Hz), 7.57–7.70 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 19.7, 19.9, 25.5, 126.1, 128.1, 129.8, 135.1, 136.8, 141.7, 198.1$.

1-Mesitylethanone (2i): Compound **2i** was obtained as a yellow oil in 96% yield;[31] IR (neat): $\nu = 1705\ cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.03$ (s, 6H), 2.13 (s, 3H), 2.27(s, 3H), 6.68(s, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta =$ 19.1, 20.5, 32.3, 126.3, 128.9, 132.3, 138.3, 139.9, 208.5.

1-(Anthracen-10-yl)ethanone[32] (2j): Compound **2j** was obtained as a yellow solid in 83% yield; mp 75–76 °C; IR (KBr): $\nu = 2921, 1676, 1121, 695\ cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.84$ (s, 3H), 7.50–7.58 (m, 4H), 7.87 (m, 2H), 8.06 (m, 2H), 8.52 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 33.8, 124.3, 125.5, 126.6, 126.7, 128.2, 128.8, 131.0, 136.7, 208.1$.

9,10-Diacetylanthracene[33] (2k): Compound **2k** was obtained as an orange solid in 54% yield; mp 248.5–249.5 °C; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.8$ (s, 6H), 7.5–7.7 (dd, 4H, $J_1 = 9.0$ Hz, $J_2 = 2.5$ Hz), 7.8–8.0 (dd, 4H, $J_1 = 9.0$ Hz, $J_2 = 2.5$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 33.8, 124.9, 126.8, 125.9, 138.3, 207.4$; anal. calcd. for $C_{18}H_{14}O_2$: C 82.21, H 5.37; found: C 82.42, H 5.38.

1-(Biphenyl-4-yl)ethanone[34a] (2l): Compound **2l** was obtained as a white solid in 94% yield; mp 121–123 °C; IR (KBr): $\nu = 1680, 1601\ cm^{-1}$; H NMR (250 MHz, $CDCl_3$): $\delta =$ 2.62 (s, 3H), 7.38–7.94 (m, 2H), 7.60–7.63 (m, 2H), 7.66–7.69 (m, 3H), 8.00–8.03 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 26.6, 127.2, 127.3, 128.9, 129.0, 135.8, 139.8, 145.7, 197.7$; MS: m/z (%) = 196 (M^+, 45), 181 ($M^+ - 15$, 100), 153 (36), 152 (54), 151 (20), 76 (65).

1,1′-(6,7,9,10,17,18,20,21-Octahydrodibenzo[*b,k*]-[1,4,7,10,13,16]hexaoxacyclooctadecine-2,13-diyl)diethanone (3l) and 1,1′-(6,7,9,10,17,18,20,21-octahydrodibenzo[*b,k*]-[1,4,7,10,13,16]hexaoxacyclooctadecine-2,14-diyl)diethanone[34b] (2m): Compound **2m** was obtained as a white solid in 89% yield; a mixture of isomers was obtained; mp 195–204 °C; IR (KBr): $\nu = 2945, 1670, 1596, 1516, 1429, 1360, 1271, 1212, 1130, 1057, 953, 595\ cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.53$ (s, 3H), 4.01–4.15 (m, 4H), 4.20–4.25 (m, 4H), 6.91 (1H, d, $J = 7.7$ Hz), 7.47–7.80 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 26.18, 68.2, 68.3, 69.3, 69.4, 69.5, 110.9, 111.2, 123.3, 123.4, 130.4, 148.3, 152.7, 196.8$.

1-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)ethanone[34c] (2n): Compound **2n** was obtained as a white solid in 87% yield; mp 93–94 °C; IR (KBr): $\nu = 2926, 1669, 1595, 1513, 1431, 1362, 1274, 1212, 1130, 940, 595\ cm^{-1}$; H NMR (250 MHz, $CDCl_3$): $\delta = 2.54$ (s, 3H), 3.75–3.77 (m, 12H), 3.90–3.95 (m, 4H), 4.16–4.20 (m, 4H), 6.86 (1H, d, $J = 8.2$ Hz), 7.49–7.58 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 26.2, 68.6, 68.9, 66.2, 69.4, 70.2, 70.38, 7.16, 89.9, 111.6, 112.6, 123.5, 124.8, 153.4, 199.8$.

Acetylferrocene (2o): Compound **2o** was obtained as an orange crystalline solid in 64% yield; mp 79–81 °C (lit.[35] 84–86 °C); IR (KBr): $\nu = 3116, 1645, 1456, 1281\ cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.39$ (s, 3H), 5.20 (s, 5H), 4.50 (t, 2H, $J = 2.0$ Hz), 4.77 (t, 2H, $J = 2.0$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 27.3, 69.4, 72.2, 79.1, 201.5$.

1-(4-Isopropylphenyl)ethanone[36] (2p): Compound **2p** was obtained as a yellow oil in 93% yield; IR (neat): $\nu =$ 1690 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.21$(d, J=7.5 Hz, 6H), 2.52 (s, 3H), 2.90 (m, 1H), 7.24 (d, 2H, $J =$ 8.4 Hz), 7.297.24 (d, 2H, $J = 8.4$ Hz).

1-(5-Isopropyl-2-methylphenyl)ethanone[37a] (2q): Compound **2q** was obtained as a yellow oil in 89% yield; IR (neat): $\nu = 1685\ cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.25$ (d, , 6H, $J = 7.0$ Hz), 2.47 (s, 3H), 2.57 (s, 3H), 2.91 (m, 1H), 7.15 (d, 1H, $J = 7.9$ Hz), 7.24(dd, 1H, $J_1 = 7.9$ Hz, $J_2 =$ 1.8 Hz) 7.50 (d, , 1H, $J = 1.8$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.1, 23.9, 29.6, 33.7, 127.3, 129.5, 132.0, 135.5, 137.8, 146.3, 202.1$; anal. calcd. for $C_{12}H_{16}O$: C 81.77, H 9.15; found: C 81.90, H 9.24.

1-(Naphthalen-2-yl)ethanone[37a] (2r): Compound **2r** was obtained as a white solid in 88% yield; mp 53–56 °C; IR (KBr); $\nu = 1670\ cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.72$ (s, 3H), 7.42–7.58 (m, 3H), 7.86–8.01 (m, 3H), 8.46 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 29.9, 124.3, 127.2, 128.2, 128.8, 128.9, 130.0, 130.6, 135.0, 136.0$, and 198.4.

***N*-(4-Acetylphenyl)acetamide[37b] (2s):** Compound **2s** was obtained as a white solid in 81% yield; IR (KBr): $\nu = 3296$, 1674, 1590, 1530, 1263, 1181, 854 cm^{-1};^1H NMR (250 MHz,

$CDCl_3$): $\delta = 2.22$ (s, 3H); 2.58 (s, 3H), 7.57 (d, 2H, $J =$ 8.7 Hz), 7.83 (d, 2H, $J = 8.7$ Hz), 8.22 (br, s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 23.6$, 55.1, 114.0, 121.5, 131.7, 155.7, 168.8.

Diphenylmethanone (2t): Compound **2t** was obtained as a white solid in 94% yield; mp 47–49 °C; IR (KBr): $\nu =$ 1658 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 7.46$ (t, 4H, $J =$ 7.8 Hz), 7.57 (t, 2H, $J = 7.3$ Hz), 7.79 (d, 4H, $J = 8.1$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 128.2$, 130.0, 132.3, 137.5, 196.7.

(4-Chlorophenyl)(phenyl)methanone (2u): Compound **2u** was obtained as a white solid in 80% yield; mp 75–77 °C (lit.[38] 74–76 °C); IR (KBr): $\nu = 1650$ cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 7.36$–7.42 (m, 4H), 7.52 (t, 1H, $J =$ 7.4 Hz), 7.65–7.70 (m, 4H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 128.3$, 128.5, 129.8, 131.4, 132.6, 135.7, 137.1, 138.8, 195.4

4-Methoxyphenyl)(phenyl)methanone[38] (2v): Compound **2v** was obtained as a white solid in 95% yield; mp 58–63 °C; IR (KBr): $\nu = 1650$ cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta =$ 3.76 (s, 3H), 6.84–6.86 (d, 2H, $J = 8.8$ Hz), 7.34–7.47 (m, 3H), 7.63- 7.65 (d, 2H, $J = 8.3$ Hz), 7.73–7.74 (d, 2H, $J =$ 8.8 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 55.4$, 113.4, 128.1, 129.6, 130.0, 131.8, 132.4, 138.1, 163.1, 195.4.

(2-Chlorophenyl)(4-methoxyphenyl)methanone[39] (2w): Compound **2w** was obtained as a white solid in 90% yield; mp 79–80 °C; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 3.80$ (s, 3H). 6.86 (d, 2H, $J = 3.5$ Hz), 7.28–7.27 (m, 2H) 7.36 (d, 2H $J =$ 8.1 Hz), 7.71(d, 2H, $J = 9.0$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 55.5$, 113.8, 126.6, 129.7, 130.9, 131.6, 132.4, 134.1, 138.9, 164.1, 193.9.

(4-Methoxyphenyl)(4-methylphenyl)methanone (2x): Compound **2x** was obtained as a white solid in 95% yield; mp 85–87 °C (lit.[38] 88–89 °C); IR (KBr): $n = 1643$ cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.35$ (s, 3H), 3.80 (s, 3H), 6.87 (d, 2H, $J = 6.8$ Hz), 7.19 (d, 2H, $J = 7.8$ Hz), 7.59 (d, 2H, $J = 8.3$ Hz), 7.73 (d, 2H, $J = 6.8$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.5$, 55.3, 113.3, 128.8, 130.0, 132.4, 135.4, 142.5, 162.9, 195.3.

1-(4-Methoxyphenyl)-2-phenylethanone[40] (2y): Compound **2y** was obtained as a white solid in 91% yield; mp 74–76 °C; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 3.82$ (s, 3H), 4.16 (s, 2H), 6.83–6.88 (m, 2H), 7.16–7.25 (m, 5H), 7.89–7.94 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 45.3$, 55.45, 113.7, 114.3, 126.8, 128.6, 129.3, 129.9, 130.9, 132.4, 134.7, 196.1.

(4-Methoxyphenyl)(2-thienyl)methanone (2z): Compound **2z** was obtained as a white solid in 92% yield; mp 72–74 °C (lit.[38] 68–70 °C); IR (KBr): $\nu = 1628$ cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 3.78$ (s, 3H), 6.88 (d, 2H, $J = 8.8$ Hz), 7.03–7.06 (m, 1H), 7.53–7.59 (m, 2H), 7.80 (d, 2H, $J =$ 6.8 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 55.3$, 113.5, 127.7, 130.4, 131.4, 133.3, 133.9, 143.6, 162.9, 186.7.

1,3-Phenylenebis((4-methoxyphenyl)methanone)[38] (2a′): Compound **2a′** was obtained as a white solid in 90% yield; mp 136–138 °C; IR (KBr): $\nu = 1655$, 1599, 1507, 1310, 1252, 1160, 1025, 841, 750, 600 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 3.85$ (s, 6H), 6.93–6.95 (d, 4H, $J = 7.1$ Hz), 7.56–7.59 (t, 1H, $J = 7.8$ Hz), 7.80–7.82 (d, 4H, $J = 7.3$ Hz), 7.92–7.93 (d, 2H, $J = 7.6$ Hz), 8.05 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 55.4$, 113.6, 128.3, 129.5, 130.5, 132.5, 132.6, 138.3, 163.4, 194.6.

2-Chloro-1-(4-methoxyphenyl)ethanone[41] (2b′): Compound **2b′** was obtained as a white solid in 91% yield; mp 96–97 °C; IR (KBr): $\nu = 1693$ (C=O), 1599, 1513, 1266–1224 (CH_2Cl), 1173, 1021 (C-O), 845–820–781 (phenyl), 590 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 3.89$ (s, 3H, 1H), 4.66 (s, 2H, 1H), 6.97 (dd, 2H, $J_1 = 7.0$ Hz and $J_2 = 2.0$ Hz), 7.96 (dd, 2H, $J_1 = 7.0$ Hz and $J_2 = 2.0$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 40.5$, 45.6, 51.1, 55.5, 111.6, 114.1, 121.1, 130.9, 131.3, 134.8, 164.2, 172.2, 189.9.

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) B. S. Furniss, A. J. Hannaford, P. W. G. Smith, R. Tatchell, *Vogels Textbook of Practical Organic Chemistry*, 5th edn., England: Addison Wesley Longman Limited, **1989**, p 1006; b) P. J. Harrington, E. Lodewijk, *Org. Process Res. Dev.* **1997**, *1*, 72–76; c) G. Harvey, G. Mader, *Collect. Czech. Chem. Commun.* **1992**, *57*, 862–868; d) T. Fujisawa, K. Kondo, K. Sakai, U.S. Patent 4,266,067, **1981**; e) R. A. Sheldon, *Chemistry and Industry*, **1992**, 903–906; f) S. Gmouh, H. Yang, M. Vaultier, *Org. Lett.* **2003**, *5*, 2219–2222; g) G. Sartori, R. Maggi, *Chem. Rev.* **2006**, *106*, 1077–1104; h) G. Sartori, R. Maggi, *Advances in Friedel–Crafts Acylation Reactions Catalytic and Green Processes*, CRC Press Taylor & Francis Group, **2010**.

[2] a) G. A. Olah, *Friedel–Crafts and Related Reactions*; Wiley-Interscience, New York, **1963**; b) J. Ross, J. Xiao, *Green Chem.* **2002**, *4*, 129–133.

[3] M. Lancaster, *Green Chemistry: An Introductory Text*, The Royal Society of Chemistry: **2002**.

[4] See the following for leading references: a) A. Kawada, S. Mitamura, S. Kobayashi, *J. Chem. Soc. Chem. Commun.* **1993**, 1157–1158; b) S. Kobayashi, S. Nagayama, *J. Am. Chem. Soc.* **1998**, *120*, 2985–2986; c) A. Kawada, S. Mitamura, S. Kobayashi, *Synlett* **1994**, 545–546; d) S. Kobayashi, I. Komoto, *Tetrahedron* **2000**, *56*, 6463–6465; e) M. T. Reetz, D. Giebel, D. *Angew. Chem.* **2000**, 112, 2614–2617; *Angew. Chem. Int. Ed.* **2000**, *39*, 2498–2501.

[5] a) J. Izumi, T. Mukaiyama, *Chem. Lett.* **1996**, 739740; b) H. Kusama, K. Narasaka, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2379–2383.

[6] G. Bartoli, M. Bosco, E. Marcantoni, M. Massaceri, S. Rinaldi, L. Sambri, *Tetrahedron Lett.* **2002**, *43*, 6331–6334.

[7] a) S. G. Pai, A. R. Bajpai, A. B. Deshpande, S. D. Samant, *Synth. Commun.* **1997**, *27*, 2267–2273; b) F. Martinez, G. Morales, A. Martin, R. van Grieken *Appl. Catal. A: General* **2008**, *347*, 169–178.

[8] J. Farkes, S. Be Kassy, B. Agia, M. Hegeders, F. Figueras, *Synth. Commun.* **2000**, *30*, 2479–2485.

[9] T. W. Bastock, J. H. Clark, P. Landon, K. Martin, *J. Chem. Res. Synop.* **1994**, 104–105.

[10] B. Chiche, A. Finiels, G. Gauthier, P. Geneste, *J. Org. Chem.* **1986**, *51*, 2128–2130.
[11] Q. L. Wang, Y. Ma, X. Ji, H. Yan, Q. Qui, *J. Chem. Soc. Chem. Commun.* **1995**, 2307–2308.
[12] a) M. Signoretto, A. Torchiaro, A. Breda, F. Pinna, G. Cerrato, C. Morterra *Appl. Catal. B: Environmental*, **2008**, *84*, 363–371; b) M. Hosseini Sarvari, H. Sharghi, *J. Org. Chem.* **2004**, *69*, 6953–6956; c) M. Gopalakrishnan, P. Sureshkumar, V. Kanagarajan, J. Thanusu, *Catal. Commun.* **2005**, *6*, 753–756.
[13] Y. Nishimoto, S. A. Babu, M. Yasuda, A. Baba, *J. Org. Chem.* **2008**, *73*, 9465–9468.
[14] a) A. R. Hajipour, A. Zarei, L. Khazdooz, A. E. Ruoho, *Synth. Commun.* **2009**, *39*, 2702–2722; b) R. G. d. Noronha, A. C. Fernandes, C. C. Romao, *Tetrahedron Lett.* **2009**, *50*, 1407–1410.
[15] a) D. E. Pearson, C. A. Buehler, *Synthesis* **1972**, 533–542; b) F. Effenberger, G. Epple, *Angew. Chem.* **1972**, *84*, 295–296; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 300–301; c) M. Hino, K. Arata, *Chem. Lett.* **1978**, 325–326; d) K. Nomiya, Y. Sugaya, S. Sasa, M. Miwa, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2089–2090; e) T. Yamaguchi, A. Mitoh, K. Tanabe, *Chem. Lett.* **1982**, 1229–1232; f) T. Mukaiyama, H. Nagaoka, M. Ohshima, M. Murakami, *Chem. Lett.* **1986**, 165–168; g) B. Chiche, A. Finiels, C. Gauthier, P. Geneste, *J. Org. Chem.* **1986**, *51*, 2128–2130; h) F. Effenberger, D. Steegmtiller, *Chem. Ber.* **1988**, *121*, 117–123; i) F. Effenberger, D. Steegmtiller, V. Null, T. Ziegler, *Chem. Ber.* **1988**, *121*, 125–130; j) G. A. Olah, O. Farooq, S. Morteza, F. Farnia, J. A. Olah, *J. Am. Chem. Soc.* **1988**, *110*, 2560–2565; k) T. Mukaiyama, T. Ohno, T. Nishimura, S. Suda, S. Kobayashi, *Chem. Lett.* **1991**, 1059–1062; l) T. Harada, T. Ohno, S. Kobayashi, T. Mukaiyama, *Synthesis* **1991**, 1216–1220; m) T. Mukaiyama, K. Suzuki, S. J. Han, S. Kobayashi, *Chem. Lett.* **1992**, 435–438; n) A. Cornelis, P. Laszlo, S. Wang, *Tetrahedron Lett.* **1993**, *34*, 3849–3852; o) K. Suzuki, H. Kitagawa, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3729–3734; p) S. Pivsa-Art, K. Okuro, M. Miura, S. Murata, M. Nomura, *J. Chem. Soc. Perkin Trans. 1* **1994**, 1703–1707; q) J. Izumi, T. Mukaiyama, *Chem. Lett.* **1996**, 739–740; r) K. Mikami, O. Kotera, Y. Motoyama, H. Sakaguchi, M. Maruta, *Synlett* **1996**, 171–172.
[16] G. A. Olah, *Angew. Chem.* **1993**, *105*, 70–71; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*,767–788.
[17] a) Y. Matsushita, K. Sugamoto, T. Matsui, *Tetrahedron Lett.* **2004**, *45*, 4723–4727; b) K. Suzuki, H. Kitagawa, T. T. Mukaiyama, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3729–3734; c) T. Mukaiyama, K. Suzuki, J. K. Han, S. Kobayashi, *Chem. Lett.* **1992**, 435–438.
[18] 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**, *1*, 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.
[19] a) Z. Y. Fan, X. G. Wen, S. H. Yang, J. G. Lu, *Appl. Phys. Lett.* **2005**, *87*, 13113–13123; b) F. Shi, M. K. Tse, M. M. Pohl, A. Bruckner, S. M. , M. Beller, *Angew. Chem.* **2007**, *119*, 9022–9024; *Angew. Chem. Int. Ed.* **2007**, *46*, 8866–8868; c) R. W. Tuttle, A. Chowdury, E. T. Bender, R. D. Ramsier, J. L. Rapp, M. P. Espe, *Appl. Surf. Sci.* **2008**, 254, 4925–4929; d) A. Kay, I. Cesar, M. Gratzel, *J. Am. Chem. Soc.* **2006**, *128*, 15714–15721; e) I. Cesar, A. Kay, J. A. G. Martinez, M. Gratzel, *J. Am. Chem. Soc.* **2006**, *128*, 4582–4583; f) J. Chen, L. N. Xu, W. Y. Li, X. L. Gou, *Adv. Mater.* **2005**, *17*, 582–586; g) B. T. Hang, H. Hayashi, S. H. Yoon, S. Okada, J. I. Yamaki, *J. Power Sources*, **2008**, *178*, 393–401; h) T. Ninjbadgar, S. Yamamoto, T. Fukuda, *Solid State Sci.* **2004**, *6*, 879–885; i) Z. Y. Li, H. N. Zhang, W. Zheng, W. Wang, H. M. Huang, C. Wang, A. G. MacDiarmid, Y. Wei, *J. Am. Chem. Soc.* **2008**, *130*, 5036–5037; j) M. S. Tong, G. R. Dai, D. S. Gao, *Appl. Surf. Sci.* **2001**, *171*, 226–230; k) T. P. Raming, A. J. A. Winnubst, C. M. Kats, P. A. Philipse, *J. Colloid Interface Sci.* **2002**, *249*, 346–350; l) L. S. Zhong, J. S. Hu, H. P. Liang, A. M. Cao, W. G. Song, L. J. Wan, *Adv. Mater.* **2006**, *18*, 2426–2431; m) P. P. Sarangi, B. Naik, N. N. Ghosh, *Powder Technol.* **2009**, *192* , 245–249.
[20] G. P. Schiemenz, U. Schmidt, *Justus Liebigs Ann. Chem.* **1976**, 1514–1519.
[21] a) S. Arai, Y. Sudo, A. Nishida, *Tetrahedron* **2005**, *61*, 4639–4642; b) D. O. Jang, K. S. Moon, D. H. Cho, J. G. Kim, *Tetrahedron Lett.* **2006**, *47*, 6063–6066.
[22] W. W. Parish, P. E. Stott, C. W. McCausland, J. S. Bradshaw, *J. Org. Chem.* **1978**, *43*, 4577–4581.
[23] a) C. N. Satterfild, *Mass Transfer in Heterogeneous Catalysis*, MIT Press, Cambridge, Mass., **1970**; b) P. Wang, I. M. C. Lo, *Water Res.* **2009**, *43*- 3727–3734.
[24] a) R. J. Lad, V. E. Henrich, *Surf. Sci.* **1988**, *193*, 81–93; b) H. E. B. Lempers, R. A. Sheldon, *J. Catal.* **1998**, *175*, 62–69; c) W. Janusz, .A. Sworska, J. Szczypa, *Coll. Surf. A: Phys. Eng. Asp.***1999**, *149*, 421–426; d) J. A. Davis, R. O. James, J. O. Leckie, *J. Colloid Interface Sci.* **1978**, *63*, 480.
[25] A. P. Huang, X. Y. Liu, L. H. Li, X. L. Wu, W. M. Liu, Y. M. Liang, *Chin. Chem. Lett.* **2004**, *15*, 1415–1418.
[26] M. Kodomari, Y. Suzuki, K. Yoshida, *Chem. Commun.* **1997**, 1567–1569.
[27] A Huang, X. Liu, L. Li, X. Wu, W. Liu, Y. Liang, *Adv. Synth. Catal.* **2004**, *346*, 599 –602.
[28] X. Chen, M. Yu, M. Wang, *J. Chem. Res.* **2005**, 80–81.
[29] J. Ruan, X. Li, O. Saidi, J. Xiao . *J. Am. Chem. Soc.* **2008**, *130*, 2424–2425.

[30] M. Hosseini Sarvari. H. Sharghi. *Helv. Chim. Acta* **2005**, *88*, 2282–2287.
[31] W. R. Bergmark, C. Barnes, J. Clark, S. Paparian, S. Marynowski, *J. Org. Chem.* **1985**, *50*, 5612–5615.
[32] J. C. C. Atherton, S. Jones, *J. Chem. Soc. Perkin Trans. 1* **2002**, 2166–2173.
[33] F. Duerr, Y. S. Chung, A. W. Czarnik, *J. Org. Chem.* **1988**, *53*, 2120–2122.
[34] a) E. Alacid, N. Carmen, *Org. Lett.* **2008**, *10*, 5011–5014; b) N. Zh. Saifullina, A. K. Tashmukhamedova, *Chem. Heterocycl. Comp.* **2005**, *41*, 973–976, c) D. E. Fenton, D. Parkin, R. F. Newton, *J. Chem. Soc. Perkin Trans. I*, **1981**, 449–454.
[35] C. R. Hauser and J. K. Lindsay, *J. Org. Chem.* **1957**, *22*, 482–485.
[36] F. Chen, A. Liu, Q. Yan, M. Liu, D. Zhang, L. Shao, *Synth. Commun.* **1999**, *29*, 1049–1056.
[37] a) R. Ballini, L. Barboni, G. Bosica. *J. Org. Chem.* **2000**, *65*, 6261–6263; b) D. Wei, C. Chen, L. Min. Z. Yan, L. Lei, G. Qing-Xiang. *Chin. J. Chem.* **2005**, *23*, 1241–1246.
[38] M. L. N. Rao, V. Venkatesh. D. Banerjee. *Tetrahedron* **2007**, *63*, 12917–12926.
[39] B. Xin, Zhang, Y. Chenga, *Synthesis* **2007**, 1970–1978.
[40] A. Takemiya, J. F. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 14800–14801.
[41] M. Yoshimatsu, M. Sakai, E. Moriura, *Eur. J. Org. Chem.* **2007**, 498–507.

