Green Chemistry

Accepted Manuscript

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Green Chemistry

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Carbon-supported iron-ionic liquid: an efficient and recyclable catalyst for benzylation of 1,3-dicarbonyl compounds with alcohols

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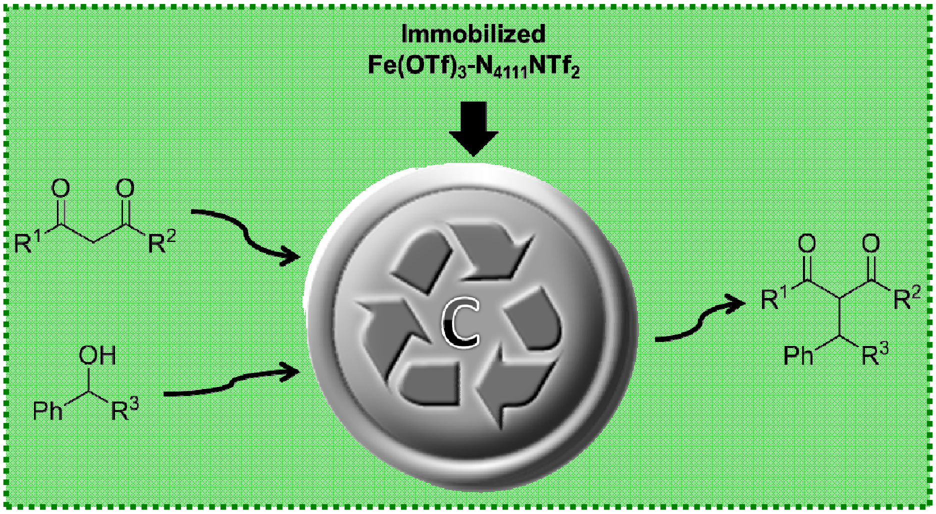
Combining chemical strategies: a robust, heterogeneous and recyclable catalytic system: iron-ionic liquid/carbon material as solid Lewis acid for direct benzylation of 1,3-dicarbonyl compounds with alcohols.



Carbon-supported iron-ionic liquid: an efficient and recyclable catalyst for benzylation of 1,3-dicarbonyl compounds with alcohols

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Abstract

The effect of the addition of ILs with non-coordinating anions on the iron-catalyzed benzylation of 1,3-dicarbonyl compounds with alcohols under solvent free conditions have been evaluated. Among them, the presence of those with the bistriflimide anion was found to be crucial to the selectivity towards the benzylated product in the homogenous reaction. Therefore, the catalytic activity of the $Fe(OTf)_3$-$N_{4111}NTf_2$ combination supported on carbon materials with different textural and chemical surface properties has been studied. In the heterogeneous phase, the reaction selectivity was also enhanced by the addition of the IL. However, substantial differences between the activities of the different Fe-IL/carbon material catalytic systems were observed, indicating the influence of the carbon support properties. As regards selectivity, the best results were obtained by using the carbon supports with low microporosity. Moreover, the presence of oxygen functional groups on the surface of the carbon surface improved the catalyst recycling.

Introduction

In the last decade, iron salts have emerged as powerful Lewis acid catalysts for organic synthesis.[1] An example is the carbon-carbon bond formation in the reaction between an active methylene compound and an alcohol. Direct substitution of a hydroxyl group is an attractive salt-free and atom-economic process with water being the only by-product. However, due to the poor leaving ability of this functional group, harsh reaction conditions and large amount of expensive, toxic and moisture sensitive reagents are required. These drawbacks can be solved through the use of catalytic amounts of $FeCl_3$ or $Fe(ClO_4)_3$.[2,3] Moreover, iron salts are inexpensive, easy to handle and environment-friendly.

Ionic liquids (ILs) are another topic of great attention in chemistry because of a number of interesting tailored properties.[4] Specifically the use of ILs in catalysis allows the recycling of the catalysts, and in many cases, improves dramatically their activities. For example, Lewis acidic metal salts often become much more reactive in ILs containing non-coordinating anions as a result of anion exchange between the Lewis acid and the IL.[5] Consequently, more electrophilic Lewis acidic species generated *in situ* accelerate the catalytic reactions. Additionally, because of the polar nature of ILs, the activation barrier of the reactions can be reduced by the stabilization of the polar transition states or reaction intermediates. However, the immobilization of catalysts in ILs usually brings about mass transfer limitations and cumbersome work-up procedures due to the high viscosity of many ILs. These drawbacks can be overcome by supporting both the catalyst and the IL on the surface of a solid. Supported Ionic Liquid Phase Catalysts (SILPC) combine the benefits of ILs and heterogeneous catalysts, such as flexibility, good solubility of the catalytically active species, as well as ease of handling, separation and recycling.[6] Generally, SILPC are composed of three elements: a porous solid support, an IL (a small amount of IL is dispersed on the support surface) and the active catalyst.

The textural properties of mesoporous materials, such as a large surface area to disperse the active phases and a proper pore size distribution to facilitate the diffusion of reactants and products, make them very attractive as catalyst supports. Carbon materials have been scarcely studied even though showing some advantages over other traditional catalyst support like silica, alumina, metal oxides or polymers.[7] These materials have high corrosion resistance, good thermal and mechanical stability, ease of handling, and low cost of manufacture. Furthermore, chemical properties of the surface can be modified to control polarity, hydrophobicity and acid-base character. Recently, mesoporous carbon materials have been successfully employed in our research group as support for different types of catalyst, namely Ru and Pd nanoparticles,[8] ILs derived from choline and amino acids [9] and lipases CALA and CALB.[10]

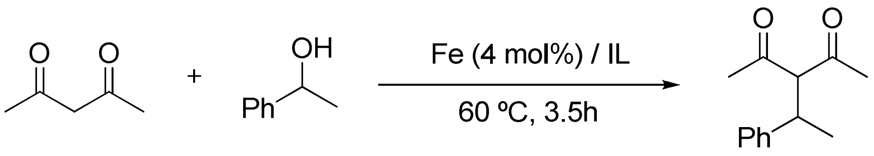
Results and discussion

Based on the background above described, the effect of the addition of ILs with non-coordinating anions on the iron-catalyzed benzylation of 1,3-dicarbonyl compounds with alcohols under solvent free conditions have been evaluated in this work. Different mesoporous carbon materials have been tested as support for the immobilization of Fe-IL catalysts. The influence of the textural and surface chemical properties of the carbon materials on the catalytic activity of the supported Fe-IL has also been discussed. Furthermore, the recyclability and substrate scope of the carbon-supported Fe-IL systems have also been studied.

The reaction between acetylacetone (**1a**) and 1-phenylethanol (**2a**) in a homogeneous phase using $FeCl_3$, $Fe(ClO_4)_3$ or $Fe(OTf)_3$ as metal source, different ionic liquids (ILs) and reaction conditions was firstly investigated (Table 1). The selected ILs were 1-butyl-3-methylimidazolium cation (BMIM) with different non-coordinating anions (PF_6, BF_4, OTf and NTf_2) and butyltrimethylammonium bis(trifluoromethylsulfonyl)imide ($N_{4111}NTf_2$) whose apparent degree of dissociation is larger than the corresponding IL with an aromatic cation.[11]

Most of the catalytic combinations promote the formation of 3-(1-phenylethyl)pentane-2,4-dione (**3a)** to some extent. Apart from the desired product, relatively high amounts of bis(diphenylmethyl) ether (**4a**) and, in a low quantity (0-10%), styrene (**5**), 4-phenylpentan-2-one (**6a**),[12] 1-phenylethyl acetate (**7a**) and some oligomers derived from styrene (**8**) were also detected (see Scheme S1 and Table S1 in the *Supporting Information* for more details).[13] As seen in Table 1, the best results were obtained when less-nucleophilic, i.e. more Lewic acidic, counter-anions of the metal salt (perchlorate and triflate) and the IL (bistriflimidate) were used (entries 2 and 8). The addition of ILs with bistriflimide anion was crucial to the selectivity towards the benzylated product (**3a**) (entry 1). However, any general trend was observed as regards the cation of the IL. Therefore, the formation of $Fe(ClO_4)_x(NTf_2)_{3-x}$ or $Fe(OTf)_x(NTf_2)_{3-x}$ appears to be the most catalytically active iron species.[5] Moreover, the catalyst selectivity was observed to improve by increasing the amount of IL (entries 3-4 and 7-8).

Table 1 Iron-catalyzed reaction of acetylacetone (**1a**) and 1-phenylethanol (**2a**)[a, b, c]



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

Entry	Iron source	IL	Conv. (%)[d]	Yield (%)[e]
1	$Fe(OTf)_3$	-	100	23
2	$Fe(ClO_4)_3.xH_2O$	BMIM NTf_2	100	**97**
3	$Fe(OTf)_3$	BMIM NTf_2	100	67
4	$Fe(OTf)_3$	BMIM NTf_2[f]	100	78
5	$FeCl_3.6H_2O$	BMIM NTf_2	100	48
6	$Fe(ClO_4)_3.xH_2O$	N_{4111} NTf_2	100	69
7	$Fe(OTf)_3$	N_{4111} NTf_2	100	79
8	$Fe(OTf)_3$	N_{4111} NTf_2[f]	100	**86**
9	$FeCl_3.6H_2O$	N_{4111} NTf_2	100	44
10	$Fe(ClO_4)_3.xH_2O$	BMIM OTf	100	46
11	$Fe(OTf)_3$	BMIM OTf	100	22
12	$FeCl_3.6H_2O$	BMIM OTf	100	15
13	$Fe(ClO_4)_3.xH_2O$	BMIM BF_4	58	5
14	$Fe(OTf)_3$	BMIM BF_4	80	10
15	$FeCl_3.6H_2O$	BMIM BF_4	13	0
16	$Fe(ClO_4)_3.xH_2O$	BMIM PF_6	96	13
17	$Fe(OTf)_3$	BMIM PF_6	100	24
18	$FeCl_3.6H_2O$	BMIM PF_6	91	13

[a] Selected data from the optimization of the reaction conditions. [b] *General reaction conditions*: 0.5 mmol of **2a**; 4 equiv. of **1a**; 4 mol% Fe; 77 mg of IL; 60 ºC for 3.5 h. [c] After 3.5 h the yields of bis(diphenylmethyl) ether (**4a**) and styrene (**5**) were lacking or remained constant as determined by GC. See Scheme S1 and Table S1 (*Supporting information)* for more details. [d] GC conversion of **2a**. [e] GC yield of **3a**. [f] 100 mg of IL was used.

On the basis of these results, to evaluate the catalytic activity of Fe-IL systems in heterogeneous phase, $Fe(OTf)_3$ was selected as the iron source to avoid the explosiveness of perchlorate salt [14] and $N_{4111}NTf_2$ as IL. Therefore, the $Fe(OTf)_3$-$N_{4111}NTf_2$ combination was immobilized on four carbon materials (MB-0, MB-LTA, MB-2000 and MB-2000-LTA) by an impregnation method, and they were employed as catalysts for the model reaction. For comparison, the catalytic activity of $Fe(OTf)_3$ supported on MB-2000 and MB-2000-LTA was also studied.

Before discussing the results of the catalytic activity of the carbon-supported Fe-IL systems, the textural parameters (surface area and pore volume) and surface chemical analyses (total oxygen) of the carbon materials supports (Table 2) are briefly considered. The starting MB shows relatively high micro- and mesoporous volumes (MB-0). Heating treatment of MB-0 at 2000 ºC remarkably reduced the BET surface area, mainly at expense of the micropore volume, and the surface oxygen (MB-2000). Plasma oxidation treatment (LTA) of MB-0 and MB-2000 did not significantly affect the textural parameters; however, the amount of oxygen on the surface increased drastically (MB-LTA and MB-2000-LTA).

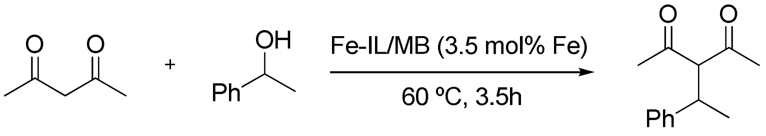
Table 2 Textural parameters and XPS oxygen analysis of the carbon materials

Material	S_{BET} (m^2g^{-1})	V_t (cm^3g^{-1})	VDR_{N2} (cm^3g^{-1})	V_{MESO} (cm^3g^{-1})[a]	Micro (%)[b]	O (at.%)
MB-0	1294	1.141	0.506	0.635	44	5.0
MB-LTA	1251	1.111	0.490	0.621	44	25.8
MB-2000	211	0.676	0.081	0.595	12	1.0
MB-2000-LTA	223	0.719	0.083	0.636	12	32.9

[a] Mesopore volume : $V_t - VDR_{N2}$. [b] Percentage of micropore volume (VDR_{N2}) over the total N_2 pore volume V_t (at $p/p^0 = 0.99$).

Substantial differences between the catalytic activity of the supported Fe(OTf)$_3$-N$_{4111}$NTf$_2$ systems were observed, indicating a significant influence of the carbon materials properties (Table 3). Thus, whereas Fe(OTf)$_3$-N$_{4111}$NTf$_2$/MB-0 and Fe(OTf)$_3$-N$_{4111}$NTf$_2$/MB-LTA did not catalyze the formation of **3a**, the reaction proceeded smoothly in the presence of Fe(OTf)$_3$-N$_{4111}$NTf$_2$/MB-2000 and Fe(OTf)$_3$-N$_{4111}$NTf$_2$/MB-2000-LTA leading to almost quantitative yields of **3a**. J. J. Rodríguez *et al.* found that depending on the available pores in a solid support, ILs tend to fill micropores firstly, then mesopores and lately macropores.[15] Consequently, the access of the substrate molecules to the catalyst on MB-0 and MB-LTA was more limited compared to MB-2000 and MB-2000-LTA that presented lower microporosity (Table 3). In heterogeneous phase, the selectivity of the formation of **3a** was also enhanced by the addition of the IL, although to a lesser extent (entries 5 and 6). It should be also remarked that the catalyst loading in the heterogeneous reaction was lower than in the homogeneous one. Therefore, the addition of N$_{4111}$NTf$_2$ and its subsequent immobilization on an appropriate carbon support improved drastically the selectivity of Fe(OTf)$_3$ towards benzylated product, from 23 to 98% of yield (entries 1 and 8, Table 1 and entry 3, Table 3).

Table 3 Catalytic activity of carbon-supported Fe(OTf)$_3$-N$_{4111}$NTf$_2$ and Fe(OTf)$_3$ systems.[a,d]



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

Entry	Catalyst	Conv. (%)[b]	Yield (%)[c]
1	Fe(OTf)$_3$-N$_{4111}$ NTf$_2$/MB-0	58	4
2	Fe(OTf)$_3$-N$_{4111}$ NTf$_2$/MB-LTA	53	4
3	Fe(OTf)$_3$-N$_{4111}$ NTf$_2$/MB-2000	100	**98**
4	Fe(OTf)$_3$-N$_{4111}$ NTf$_2$/MB-2000-LTA	100	**96**
5	Fe(OTf)$_3$/MB-2000	100	65
6	Fe(OTf)$_3$/MB-2000-LTA	100	86

[a] *General reaction conditions*: 0.5 mmol of **2a**; 4 equiv. of **1a**; 286 mg of Fe(OTf)$_3$-N$_{4111}$NTf$_2$/MB (35 wt% IL; 3.5 wt% iron salt) (3.5 mol% Fe); 60 ºC for 3.5 h. [b] GC conversion of **2a**. [c] GC yield of **3a**. [d] See Table S2 in *Supporting Information* for secondary products yield.

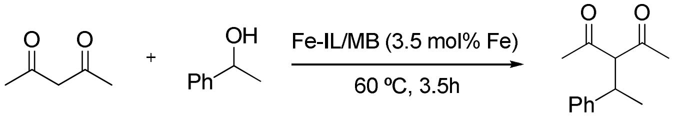
To reinforce the advantage of these heterogeneous catalyst systems, the recyclability of Fe(OTf)$_3$-IL/MB-2000 and Fe(OTf)$_3$-IL/MB-2000-LTA was studied. In first attempts, second runs of both provided high conversions of alcohol **2a**, but low selectivity for benzylated product **3a**. Therefore, it was decided to quantify the amount of iron supported after the first cycle of the reaction by ICP-MS. As shown by the data collected in Table 4, ICP-MS analyses of carbon supports obtained after ether work-up revealed that, in both cases, most of the Fe(OTf)$_3$-N$_{4111}$NTf$_2$ was dissolved in the organic phases. However, when the heterogeneous catalyst systems were washed with Et_2O or Hexane, most of the catalyst remained on the support. Consequently, removing the 1,3-dicarbonyl compound is necessary for avoiding losing catalyst during the reaction work-up.[16] Thus, this strategy was used in recycling experiments. The results, summarized in Table 5, are in agreement with ICP-MS analyses. Therefore, $Fe(OTf)_3$-$BMIMNTf_2$, a bit more soluble in Et_2O, supported on MB-2000 and MB-2000-LTA could be used without loss of activity for only two cycles (entries 2 and 4, Table 5). The best results were obtained with $Fe(OTf)_3$-$N_{4111}NTf_2$/MB-2000-LTA that could be employed without loss of activity and without harsher reaction conditions for 4 runs (entry 3, Table 5). This catalytic system supported on MB-2000 afforded moderated yields of **3a** in the third cycle (entry 1, Table 5). The difference observed between $Fe(OTf)_3$-$N_{4111}NTf_2$ supported on these two carbon materials is linked to the surface properties. Probably, oxygen containing functional groups on MB-2000-LTA would help to retain the iron salt-IL on the carbon surface.

Table 4 ICP-MS analyses of Iron [a]

	$Fe(OTf)_3$-$N_{4111}NTf_2$		$Fe(OTf)_3$-$BMIMNTf_2$	
	MB-2000	MB-2000-LTA	MB-2000	MB-2000-LTA
Freshly prepared	0.35	0.34	0.32	0.35
Washed with Et_2O[b]	0.25	0.22	0.18	0.21
Washed with Hexane [b]	0.35	0.31	0.34	0.33
After reaction and work-up with Et_2O	0.09	0.07		

[a] Percentage of iron. [b] 286 mg of catalyst supports were washed with 3 x 5 mL of solvent, filtered and dried under reduced pressure prior to elemental analyses

Table 5 Recycling study of Fe-IL catalysts supported on carbon materials [a, c]



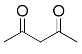
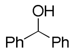
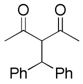
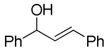
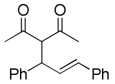
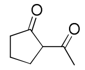
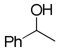
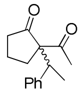
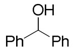
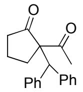
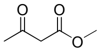
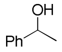
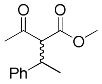
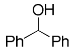
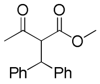
1a **2a** **3a**

Entry	Carbon support	Fe-IL	Run	Yield (%)[b]
1	MB-2000	$Fe(OTf)_3$-$N_{4111}NTf_2$	1	98 (100)
			2	96 (100)
			3	72(100)
			4	50 (98)
2		$Fe(OTf)_3$-$BMIMNTf_2$	1	96 (100)
			2	93 (100)
			3	52 (99)
3	MB-2000-LTA	$Fe(OTf)_3$-$N_{4111}NTf_2$	1	96 (100)
			2	95 (100)
			3	92 (100)
			4	93 (100)
			5	47 (99)
4		$Fe(OTf)_3$-$BMIMNTf_2$	1	95 (100)
			2	97 (100)
			3	56 (100)

[a] General reaction conditions: 0.5 mmol of 2a; 4 equiv. of 1a; 286 mg of $Fe(OTf)_3$-$N_{4111}NTf_2$/MB (35 wt% IL; 3.5 wt% iron salt) (3.5 mol% Fe); 60 ºC for 3.5 h. 1a was removed under reduced pressure before reaction mixture work-up. [b] GC yield of 3a. GC conversion of 2a in brackets. [c] See Table S3 in *Supporting Information* for secondary products yield.

Having these efficient experimental conditions in hand, we studied the scope of the reaction regarding both coupling partners, the 1,3-dicarbonyl compound (**1**) and the alcohol (**2**), using $Fe(OTf)_3$-$N_{4111}NTf_2$/MB-2000-LTA as catalytic system. Representative examples are reported in Table 6.

Table 6 Catalytic activity of Fe(OTf)$_3$-N$_{4111}$NTf$_2$/MB-2000-LTA in the reaction of 1,3-dicarbonyl compounds (**1**) and alcohols (**2**)[a]

Entry	Nucleophile (**1**)	Alcohol (**2**)	Product (**3**)	Time (h)	Yield (%)
1	 **1a**	 **2b**	 **3b**	3.5	99 (100)
2		 **2c**	 **3c**	3.5	99 (100)
3	 **1b**	 **2a**	 **3d**	3.5	45 (74)[c, d]
4		 **2b**	 **3e**	24	99 (100)
5	 **1c**	 **2a**	 **3f**	24	47 (100)[c, d]
6		 **2b**	 **3g**	24	98 (100)

[a] *General reaction conditions*: 0.5 mmol of **2a**; 4 equiv. of **1a**; 286 mg Fe(OTf)$_3$-N$_{4111}$NTf$_2$/MB-2000-LTA (35 wt% IL; 3.5 wt% iron salt) (3.5 mol% Fe); 60 ºC. [b] GC yield of **3a**. GC conversion of **2a** is shown in brackets. [c] Mixture of diastereomers ≈ 1:1, determined by ^{1}H NMR analysis. [d] Secondary products are shown in Scheme S2 (*Supporting information*).

The reactions of 2,4-pentadione (**1a**) with diphenylmethanol (**2b**) and an allyl alcohol (**2c**) proceeded smoothly to give the benzylated products **3b** and **3c** with excellent yield and high selectivity (entries 1 and 2, Table 6). Benzylation of 1,3-difunctionalized compounds with higher pKa values (a cyclic β-diketone **1b** and a β-ketoester **1c**)[17] with diphenylmethanol (**2b**) afforded quantitative yields, but longer times of reaction were needed (entries 4 and 6, Table 6). The reactions with alcohol

2a were lack of selectivity, giving yields of 45 and 47% of the desired benzylated product **3d** and **3f**, respectively. In these cases, the carbocation generated from **2a** was too unstable to overcome higher activation energy barrier of the benzylation reaction with **1b** and **1c** (entries 3 and 5, Table 6).[3d]

Conclusions

Different strategies have been combined to achieve the benzylation of 1,3-difunctionalized compounds with alcohols by an efficient, economic and environment-friendly process. The developed catalyst system consists of immobilizing $Fe(OTf)_3$ solved in a minimal amount of $N_{4111}NTf_2$ on a mesoporous carbon material with suitable textural and surface chemical properties by an impregnation method, avoiding cumbersome procedures and large amount of by-products and solvent waste. This carbon-supported catalyst can be recycled without loss of activity and without harsher reaction conditions for 4 runs. Furthermore, the reactions can be carried out under air atmosphere and solvent-free conditions without any special precautions and the immobilized catalyst system can be stored for months in open air without loss of catalytic activity.

Experimental section

Mesoporous activated carbon spheres (MB-0), having a size distribution in the range of 500-1000 μm and derived from a phenolic resin, were used as starting support. MB-0 carbon material was heated at 2000 ºC under a flowing argon atmosphere for an hour in a electrical furnace, at a heating rate of 10 ºC/min (MB-2000). Oxidation of MB-0 and MB-2000 were carried out in a plasma reactor (MB-LTA and MB-2000-LTA). Batches of approx. 500 mg of carbon material were treated using oxygen excited by a radiofrequency power of 75 W for 10 min.

Surface area, pore volume and pore size distribution of MB-0, MB-2000, MB-LTA and MB-2000-LTA supports were derived from the N_2 adsorption–desorption isotherms performed at 77 K in a volumetric adsorption system. X-Ray Photoelectron Spectroscopy (XPS) surface chemical analyses of carbon supports were carried out using Mg Ka X-rays (1486.6 eV) at a power of 120 W and in a residual vacuum of 10^{-7} Pa. The atomic percentages (atom.%) of the different elements present in the approx. 10 nm upper layer were calculated from the survey spectra by considering the integrated areas of the main XPS peaks. Representative samples of mesoporous carbon supports (around 150 mg) were tested (more details about the carbon supports characterization are provided in *Supporting Information*).

For the preparation of the carbon-supported iron-ionic liquid catalyst, the corresponding ionic liquid (35 wt.%) and iron (III) triflate (3.5 wt%) dissolved in a minimal amount of acetone were mixed with the carbon support in a screw top vial. The mixture was shaken at room temperature for 2.5 h followed by a careful removal of the solvent in a rotary evaporator. Then, the heterogeneous catalyst was dried at 60 ºC in a vacuum oven for 2 h. Catalyst loading was evaluated from the Fe elemental content as analyzed by ICP-MS after wet digestion with aqua regia ($HCl:HNO_3$ 3:1) in a microwave reactor .

All reactions were carried out under air atmosphere without any special precautions. The reaction mixture in a flask was stirred at 60 ºC and 200 rpm, and monitored by CG. After completion, the crude reaction mixture was allowed to cool to room temperature and taken up in diethyl ether (3 x 5 ml). The combined organic extracts were dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure; if necessary, the residue was purified by flash chromatography on silica gel. In recycling experiments, it was necessary to remove 2,4-pentadione under reduced pressure before reaction work-up in Et_2O (3 x 5 ml) to avoid losing catalyst. Then, recovered catalyst was dried under reduced pressure and used in the next cycle of the reaction. The products are well known in the literature and were confirmed by GC-MS and ^{1}H NMR spectroscopic techniques.[18]

Acknowledgements

Financial support from Asturias Government PCTI (under Project IB09-002C2) is gratefully acknowledged. Patricia Moriel thanks the Spanish Research Council for Scientific Research (CSIC) for a JAE-Doc contract, co-funded by the European Social Fund (ESF).

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