Synthesis of β-aryl ketones by Heck arylation of allylic alcohols catalysed by a MCM-41-supported bidentate nitrogen palladium complex

Yixiang Huang[a], Pingping Wang[b], Jiaqin Liu[a] and Mingzhong Cai[a]*

[a]*Department of Chemistry, Jiangxi Normal University, Nanchang 330022, P. R. China*

[b]*Department of Chemistry, Jiujiang University, Jiujiang 332000, P. R. China*

The Heck arylation reaction of aryl iodides with allylic alcohols catalysed by an mesoporous silica (MCM-41)-supported bidentate nitrogen palladium complex [MCM-41-2N-Pd(OAc)$_2$] proceeded smoothly in the presence of tetrabutylammonium chloride (TBAC) in DMF to afford β-aryl ketones in good to excellent yields. This heterogeneous palladium catalyst can be recovered by simple filtration and reused several times without any decrease in activity.

Keywords: supported catalyst, Heck arylation, bidentate nitrogen palladium complex, β-aryl ketone, heterogeneous catalysis, MCM-41

β-Aryl ketones are important intermediates in organic synthesis[1–4] and, therefore, the development of efficient synthetic methods is of significant interest. Although the palladium-catalysed arylation of allylic alcohols with aryl iodides or bromides has been applied for the synthesis of these compounds,[5–10] a mixture of carbonyl compounds and substituted allylic alcohols is usually obtained since these arylation reactions are poorly regioselective.[11–13] Recently, Calo *et al.*[14] described Heck arylation reactions of aryl bromides and activated aryl chlorides with allylic alcohols catalysed by a palladium-benzothiazole carbene complex in molten tetrabutylammonium bromide (TBAB) as solvent, good to excellent yields and high regioselectivity were obtained. Unfortunately, the yield dropped seriously with recycling of the catalyst and ionic liquid. It is well known that homogeneous palladium catalysts are expensive and air sensitive, which limits their industrial applications and it is difficult to recycle and reuse these homogeneous catalysts due to their low stability toward oxidation.[15,16] In contrast, heterogeneous catalysts can be easily separated from reaction mixtures by simple filtration and reused in successive reactions provided that the active sites have not become deactivated. The high costs of the transition-metal catalysts coupled with toxic effects associated with many transition metals has led to an increased interest in immobilising catalysts onto a support. Heterogeneous catalysis also helps to minimise wastes derived from reaction work-up, contributing to the development of green chemical processes.[17–21] So far, supported palladium catalysts have successfully been used for the Heck reaction.[22–26] In spite of the significant advances in this area, there are very few reports that employ the heterogeneous palladium complexes as catalysts for the Heck arylation reaction of allylic alcohols with aryl halides.

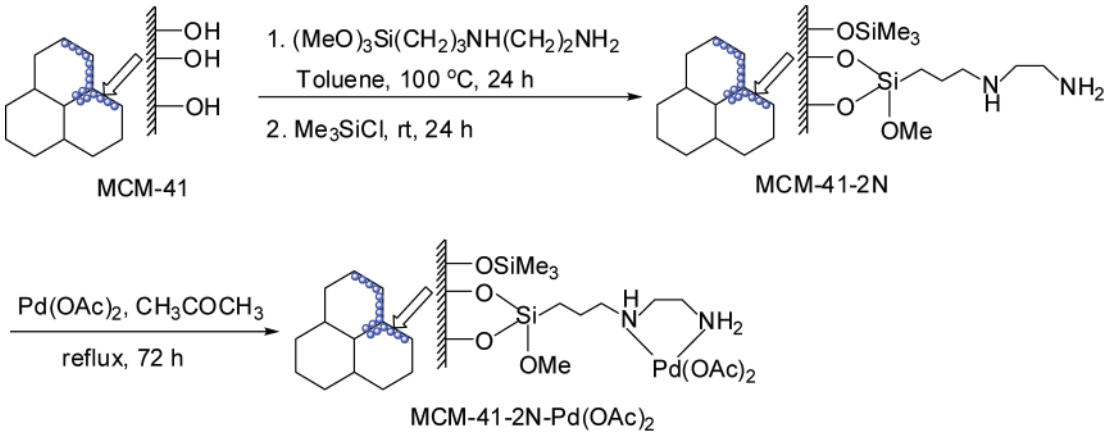
Developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilisation of homogeneous catalysts.[27] MCM-41 has a regular pore diameter of *ca* 5 nm and a specific surface area > 700 m^2 g^{-1}.[28] Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach to the surface of the channel.[29–31] It is generally accepted that high surface area of a heterogeneous catalyst results in high catalytic activity. Considering the fact that the MCM-41 support has an extremely high surface area and the catalytic palladium species is anchored on the inner surface of the mesopore of the MCM-41 support, we expect that a MCM-41-immobilised palladium catalyst will exhibit high activity and good reusability. To date, some palladium complexes on functionalised MCM-41 supports have been prepared and successfully used in Heck reactions.[32–35] However, to the best of our knowledge, no Heck arylation of allylic alcohols with aryl halides catalysed by an MCM-41-supported palladium complex has been reported. In continuing our efforts to develop greener synthetic pathways for organic transformations, our new approach, described in this paper, was to design and synthesise an MCM-41-supported bidentate nitrogen palladium complex, which was used as an effective heterogeneous palladium catalyst for the Heck arylation of allylic alcohols with aryl iodides.

The novel MCM-41-supported bidentate nitrogen palladium complex [MCM-41-2N-Pd(OAc)$_2$] was conveniently synthesised from commercially available and inexpensive 3-(2-amin oethylamino)propyltrimethoxysilane by immobilisation on MCM-41, followed by reaction with palladium acetate in acetone (Scheme 1). The X-ray powder diffraction (XRD) analysis of the MCM-41-2N-Pd(OAc)$_2$ indicated that, in addition to an intense diffraction peak (100), two higher order peaks (110) and (200) with lower intensities were detected and therefore the chemical bonding procedure did not diminish the structural ordering of the MCM-41.

Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterise the MCM-41-supported bidentate nitrogen palladium complex. The N: Pd mole ratio of the MCM-41-2N-Pd(OAc)$_2$ was determined to be 6.22. The XPS data for MCM-41-2N-Pd(OAc)$_2$, MCM-41-2N, Pd(OAc)$_2$ and metal Pd are listed in Table 1. It can be seen that the binding energies of Si_{2p} and O_{1s} of MCM-41-2N-Pd(OAc)$_2$ are similar to those of MCM-41-2N. However, the difference of N_{1s} binding energies between MCM-41-2N-Pd(OAc)$_2$ and MCM-41-2N is 1.2 eV. The binding energy of $Pd_{3d5/2}$ in MCM-41-2N-Pd(OAc)$_2$ is 0.7 eV less than that in Pd(OAc)$_2$, but 2.1 eV larger than that in metal Pd. These results show that a coordination bond between N and Pd is formed in MCM-41-2N-Pd(OAc)$_2$.

In order to test the catalytic activity of the MCM-41-2N-Pd(OAc)$_2$, the arylation reactions of allylic alcohols with aryl iodides were investigated (Scheme 2). The reaction of but-3-en-2-ol (1.5 equiv.) with iodobenzene was chosen as a model reaction, and the influences of various reaction parameters such as base, the additive (TBAC) quantity, and palladium catalyst quantity on the reaction were tested. The results are summarised in Table 2. For the bases evaluated, $NaHCO_3$ was found to be the most effective (entry 3). The organic bases such as Bu_3N and DBU and other inorganic bases were less effective. We then investigated the influence of the additive (TBAC) quantity on the arylation reaction. It was found that the additive (TBAC) quantity had an important influence on the arylation reaction owing to the efficient controlling of regioselectivity. When 1.0 equiv. TBAC was used as the additive, a high yield of 4-phenylbutan-2-one was formed due to high regioselectivity (entry 3). Increasing further the additive

* Correspondent. E-mail: caimzhong@163.com



Scheme 1

Table 1 XPS data for MCM-41-2N-Pd(OAc)$_2$, MCM-41-2N, Pd(OAc)$_2$ and metal Pd[a]

Sample	$Pd_{3d5/2}$	N_{1s}	Si_{2p}	O_{1s}
MCM-41-2N-Pd(OAc)$_2$	337.5	400.8	103.3	533.1
MCM-41-2N		399.6	103.2	533.2
Pd(OAc)$_2$	338.2			
Metal Pd	335.4			

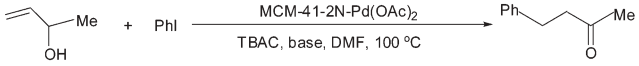
[a]The binding energies are referenced to C_{1s} (284.6 eV) and the energy differences were determined with an accuracy of ± 0.2 eV.

quantity did not enhance the yield of 4-phenylbutan-2-one (entry 9). The amount of supported palladium catalyst was also screened and 0.6 mol% loading of palladium was found to be optimal; a lower yield was observed and a longer reaction time was required when the amount of the catalyst was decreased (entry 10). Increasing the amount of palladium catalyst could shorten the reaction time, but did not increase the yield of 4-phenylbutan-2-one (entries 11 and 12). Thus, the optimised reaction conditions for this arylation reaction are MCM-41-2N-Pd(OAc)$_2$ (0.6 mol%) in DMF with $NaHCO_3$ as base and TBAC as the additive at 100 °C under Ar for 7h (entry 3).

With this promising result in hand, we started to investigate the range of both allylic alcohols and aryl iodides under the optimised conditions, and the results are summarised in Table 3. As shown in Table 3, the arylation reactions of but-3-en-2-ol with a variety of aryl iodides proceeded smoothly under mild conditions affording the corresponding 4-arylbutan-2-ones **3a–i** in good to excellent yields (entries 1–9). Both electron-donating and electron-withdrawing groups were well tolerated and the reactivity of aryl iodides with electron-withdrawing groups was higher than that of aryl iodides with electron-donating groups. The sterically hindered aryl iodides such as 2-methoxyiodobenzene and 2-trifluoromethyliodobenzene could also react with but-3-en-2-ol to afford the corresponding arylation products **3c** and **3i** in good yields (entries 3 and 9). The arylation reaction of the other secondary allylic alcohols such as pent-4-en-3-ol with aryl iodides under the same conditions also proceeded smoothly to give the desired arylation products in good to excellent yields (entries 10 and 11). However, when primary allylic alcohols such as allyl alcohol were used as the substrates under the same reaction conditions, low conversion was observed and a complicated mixture of carbonyl compounds and substituted allylic alcohols was formed. We also investigated the arylation of secondary allylic alcohols with aryl bromides, but the aryl bromides were not reactive under the conditions optimised for aryl iodides.

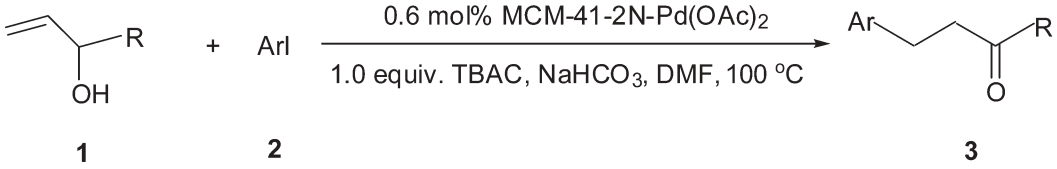
In order to determine whether the catalysis was due to the MCM-41-2N-Pd(OAc)$_2$ complex or to a homogeneous palladium complex that comes off the support during the reaction and then returns to the support at the end, we performed the hot filtration test.[36] We focused on the arylation reaction of but-3-en-2-ol with 4-nitroiodobenzene. We filtered off the MCM-41-2N-Pd(OAc)$_2$ complex after 1h of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (100 °C) in order to avoid

Table 2 Reaction condition screening for the arylation reaction of but-3-en-2-ol (1.5 equiv.) with iodobenzene[a]



Entry	TBAC quantity /mol%	Base	Pd quantity /mol%	Time /h	Yield[b] /%
1	100	Bu_3N	0.6	12	75
2	100	DBU	0.6	14	62
3	100	$NaHCO_3$	0.6	7	93
4	100	Na_2CO_3	0.6	12	73
5	100	Cs_2CO_3	0.6	12	69
6	20	$NaHCO_3$	0.6	10	43
7	50	$NaHCO_3$	0.6	10	71
8	80	$NaHCO_3$	0.6	10	86
9	120	$NaHCO_3$	0.6	7	92
10	100	$NaHCO_3$	0.3	18	87
11	100	$NaHCO_3$	1.0	5	93
12	100	$NaHCO_3$	1.5	3	92

[a]Reaction conditions: iodobenzene (1.0 mmol), but-3-en-2-ol (1.5 mmol), base (2.5 mmol) in DMF (1.0 mL) at 100 °C under Ar.
[b]Isolated yield.



1 **2** **3**

Scheme 2

Table 3 Heterogeneous arylation reaction of allylic alcohols with aryl iodides[a]

Entry	R	Ar	Time/h	Product	Yield/%[b]
1	Me	Ph	7	**3a**	93
2	Me	3-$CH_3C_6H_4$	8	**3b**	90
3	Me	2-$CH_3OC_6H_4$	12	**3c**	87
4	Me	4-ClC_6H_4	5	**3d**	94
5	Me	4-$CH_3COC_6H_4$	5	**3e**	96
6	Me	4-$CH_3OC_6H_4$	9	**3f**	87
7	Me	4-$NO_2C_6H_4$	4	**3g**	98
8	Me	4-BrC_6H_4	6	**3h**	92
9	Me	2-$CF_3C_6H_4$	12	**3i**	78
10	Et	4-$NO_2C_6H_4$	4	**3j**	95
11	Et	2-$CH_3OC_6H_4$	12	**3k**	85

[a] Reaction conditions: **1** (1.5 mmol), **2** (1.0 mmol), MCM-41-2N-$Pd(OAc)_2$ (0.6 mol%), TBAC (1.0 equiv.), $NaHCO_3$ (2.5 mmol) in DMF (1.0 mL) at 100 °C under Ar.
[b] Isolated yield.

possible recoordination or precipitation of soluble palladium upon cooling. We found that, after this hot filtration, no further reaction was observed. This result suggests that the palladium catalyst remains on the support at elevated temperatures during the reaction and points to a process of a heterogeneous nature.

For a heterogeneous transition-metal catalyst, it is important to examine its ease of separation, recoverability and reusability. This heterogeneous palladium catalyst can be easily recovered by a simple filtration of the reaction solution. We also investigated the possibility of reusing the catalyst by using the arylation reaction of but-3-en-2-ol with 4-nitroiodobenzene. After carrying out the reaction, the catalyst was separated by simple filtration and washed with distilled water, EtOH, and Et_2O. After being air-dried, it can be reused directly without further purification. The recovered palladium catalyst was used in the next run, and almost consistent activity was observed for six consecutive cycles (Table 4, entries 1–6). In general, the continuous recycle of resin-supported palladium catalysts is difficult owing to leaching of the palladium species from the polymer supports, which often reduces their activity within a five-recycle run. The high stability and excellent reusability of the catalyst may result from the chelating action of the bidentate 2-aminoethylamino ligand on palladium and the mesoporous structure of the MCM-41 support. The result is important from a practical point of view. The high catalytic activity, excellent reusability and the easy accessibility of the MCM-41-2N-$Pd(OAc)_2$ complex make it a highly attractive heterogeneous palladium catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

In summary, we have developed a novel, practical and economic catalyst system for the arylation reaction of allylic alcohols with aryl iodides by using an MCM-41-supported bidentate nitrogen palladium complex as catalyst with TBAC as an additive in DMF. This novel heterogeneous palladium catalyst can be very conveniently prepared by a simple two-step procedure from commercially available and cheap reagents and recycled by a simple filtration of the reaction solution and used for at least six consecutive trials without any decrease in activity. The heterogeneous arylation reaction of allylic alcohols with aryl iodides catalysed by the MCM-41-2N-$Pd(OAc)_2$ complex provides a better and practical procedure for the synthesis of a variety of β-aryl ketones.

Table 4 Arylation of but-3-en-2-ol with 4-nitroiodobenzene catalysed by recycled catalyst[a]

Cycle	Yield/%[b]	Cycle	Yield/%[b]
1	98	2	97
3	96	4	97
5	96	6	95

[a] Reaction conditions: 4-nitroiodobenzene (1.0 mmol), but-3-en-2-ol (1.5 mmol), MCM-41-2N-$Pd(OAc)_2$ (0.6 mol%), TBAC (1.0 mmol), $NaHCO_3$ (2.5 mmol) in DMF (1.0 mL) at 100 °C for 4h under Ar.
[b] Isolated yield.

Experimental

All chemicals were reagent grade and used as purchased. DMF was dried and distilled before use. The products were purified by flash chromatography on silica gel. Mixture of EtOAc and hexane are generally used as eluent. All coupling products were characterised by comparison of their spectra and physical data with authentic samples. IR spectra were determined on a Perkin-Elmer 683 instrument. ^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR spectra (100 MHz) were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ as solvent. Palladium content was determined with an inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation) instrument. X-ray powder diffraction was obtained on a Damx-rA (Rigaka) instrument. X-ray photoelectron spectra was recorded on an XSAM 800 (Kratos) instrument. Microanalyses were recorded by using a Yanaco MT-3 CHN microelemental analyser. The mesoporous material MCM-41 was easily prepared according to a literature procedure.[37]

Synthesis of MCM-41-2N: A solution of 3-(2-aminoethylamino)propyltrimethoxysilane (1.54 g) in dry chloroform (18 mL) was added to a suspension of the MCM-41 (2.2 g) in dry toluene (180 mL). The mixture was stirred for 24h at 100 °C. Then the solid was filtered and washed by $CHCl_3$ (2 × 20 mL), and dried under reduced pressure at 160 °C for 5h. The dried white solid was then soaked in a solution of Me_3SiCl (3.1 g) in dry toluene (100 mL) at room temperature under stirring for 24h. Then the solid was filtered, washed with acetone (3 × 20 mL) and diethyl ether (3 × 20 mL), and dried under reduced pressure at 120 °C for 5h to obtain 3.49 g of hybrid material MCM-41-2N. The nitrogen content was found to be 1.84 mmol g^{-1} by elemental analysis.

Preparation of MCM-41-2N-Pd(OAc)$_2$: In a small Schlenk tube, the hybrid material MCM-41-2N (2.03 g) was mixed with $Pd(OAc)_2$ (0.137 g, 0.61 mmol) in dry acetone (50 mL). The mixture was refluxed for 72h under an argon atmosphere. The solid product was filtered by suction, washed with acetone, distilled water and acetone successively and dried at 70 °C/26.7 Pa under Ar for 5h to give 2.12 g of a light yellow palladium complex [MCM-41-2N-$Pd(OAc)_2$]. The nitrogen and palladium content was found to be 1.68 mmol g^{-1} and 0.27 mmol g^{-1}, respectively.

Synthesis of β-aryl ketones; general procedure

An oven-dried Schlenk tuble equipped with a magnetic stirring bar was charged with MCM-41-2N-$Pd(OAc)_2$ (22 mg, 0.006 mmol Pd), aryl iodide (1.0 mmol), allylic alcohol (1.5 mmol), TBAC (1.0 mmol), and $NaHCO_3$ (2.5 mmol) followed by anhydrous DMF (1 mL) under Ar. The reaction mixture was stirred in an oil bath at 100 °C for 4–12h. The mixture was cooled to room temperature, diluted with diethyl ether (30 mL) and filtered. The MCM-41-2N-$Pd(OAc)_2$ complex was washed with distilled water (2 × 5 mL), EtOH (2 × 5 mL), and Et_2O (2 × 5 mL) and reused in the next run. The filtrate was washed with water (2 × 10 mL) and dried over anhydrous magnesium sulfate. The solvent was removed and the residue was purified by flash column chromatography on silica gel (hexane–ethyl acetate = 10:1).

4-Phenylbutan-2-one: Oil.[14] IR (film): ν (cm^{-1}) 3020, 2925, 1717, 1610, 1449, 1365, 910, 696; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.28 (m, 2H), 7.24–7.20 (m, 3H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 207.9, 141.0, 128.5, 128.3, 126.1, 45.2, 30.1, 29.8.

4-(3-Methylphenyl)butan-2-one: Oil.[7] IR (film): ν (cm^{-1}) 3016, 2922, 1716, 1609, 1365, 1160, 779, 699; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (t, *J* = 7.2 Hz, 1H), 7.02–6.96 (m, 3H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.32 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 208.0, 141.0, 138.1, 129.1, 128.4, 126.9, 125.3, 45.3, 30.1, 29.7, 21.4.

4-(2-Methoxyphenyl)butan-2-one: Oil. IR (film): ν (cm^{-1}) 3023, 2926, 1726, 1683, 1608, 1456, 1097, 781, 701; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21–7.12 (m, 2H), 6.89–6.83 (m, 2H), 3.82 (s, 3H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ 208.7, 157.4, 130.0, 129.3, 127.5, 120.5, 110.2, 55.2, 43.7, 29.9, 25.0. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.87; H, 7.75%.

4-(4-Chlorophenyl)butan-2-one: Oil.[6] IR (film): ν (cm^{-1}) 2927, 1716, 1492, 1362, 1160, 1093, 811; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 2.86 (t, *J* = 7.4 Hz, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.8, 139.5, 131.8, 129.7, 128.6, 45.0, 30.2, 29.0.

4-(4-Acetylphenyl)butan-2-one: Oil.[8] IR (film): ν (cm^{-1}) 2926, 1715, 1680, 1607, 1414, 1359, 1269, 1076, 733; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 2.95 (t, *J* = 7.6 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.58 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.3, 197.8, 146.8, 135.3, 128.6, 128.5, 44.5, 30.1, 29.6, 26.5.

4-(4-Methoxyphenyl)butan-2-one: Oil.[9] IR (film): ν (cm^{-1}) 2937, 1714, 1612, 1514, 1370, 1247, 1178, 1036, 821; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 3.78 (s, 3H), 2.83 (t, *J* = 7.2 Hz, 2H), 2.73 (t, *J* = 7.2 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.6, 157.9, 133.0, 129.3, 113.9, 55.3, 45.5, 30.2, 28.9.

4-(4-Nitrophenyl)butan-2-one: Oil.[6] IR (film): ν (cm^{-1}) 2958, 1710, 1605, 1520, 1342, 1169, 1109, 857; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.7, 149.0, 146.5, 129.3, 123.8, 44.2, 30.1, 29.3.

4-(4-Bromophenyl)butan-2-one: Oil.[8] IR (film): ν (cm^{-1}) 2927, 1716, 1489, 1367, 1161, 1072, 1011, 808; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 2.84 (t, *J* = 7.4 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.4, 140.0, 131.5, 130.1, 119.9, 44.8, 30.1, 29.0.

4-(2-Trifluoromethylphenyl)butan-2-one: Oil. IR (film): ν (cm^{-1}) 2901, 1717, 1609, 1494, 1361, 1312, 1155, 1111, 1046, 916, 725; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.33–7.28 (m, 2H), 3.06 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.2, 139.8, 132.0, 131.1, 128.4 (q, $^1J_{CF}$ = 30 Hz), 126.3, 126.0 (q, $^2J_{CF}$ = 6 Hz), 123.2, 45.2, 29.8, 26.6. Anal. Calcd for $C_{11}H_{11}OF_3$: C, 61.11; h, 5.13. Found: C, 60.87; H, 5.32%.

1-(4-Nitrophenyl)pentan-3-one: Oil.[9] IR (film): ν (cm^{-1}) 2970, 1705, 1602, 1515, 1338, 1106, 855; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 3.02 (t, *J* = 7.4 Hz, 2H), 2.80 (t, *J* = 7.4 Hz, 2H), 2.44 (q, *J* = 7.4 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.6, 149.2, 146.4, 129.3, 123.7, 42.9, 36.1, 29.4, 7.7.

1-(2-Methoxyphenyl)pentan-2-one: Oil. IR (film): ν (cm^{-1}) 2976, 1714, 1602, 1495, 1362, 1244, 1221, 1029, 756; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21–7.12 (m, 2H), 6.89–6.83 (m, 2H), 3.82 (s, 3H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.42 (q, *J* = 7.2 Hz, 2H), 1.05 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.5, 157.4, 130.0, 129.4, 127.4, 120.5, 110.2, 55.2, 42.3, 36.0, 25.1, 7.8. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.69; H, 8.16%.

We thank the National Natural Science Foundation of China (20862008) for financial support.

Received 12 January 2013; accepted 9 March 2013
Paper 1301719 doi: 10.3184/174751913X13668131126257
Published online: 12 June 2013

References

1 J.C. Dearden and R.M. Nicholson, *J. Pharm. Pharmacol.*, 1984, **36**, 713.
2 S. Ducki, J.A. Hadfield, L.A. Hepworth, N.J. Lawrence, C.-Y. Liu and A.T. McGown, *Bioorg. Med. Chem. Lett.*, 1997, **7**, 3091.
3 Y.V.S.N. Murthy, Y. Meah and V. Massey, *J. Am. Chem. Soc.*, 1999, **121**, 5344.
4 Y.-X. Liao, C.-H. Xing, M. Israel and Q.-S. Hu, *Org. Lett.*, 2011, **13**, 2058.
5 J.B. Melpolder and R.F. Heck, *J. Org. Chem.*, 1976, **41**, 265.
6 A.J. Chalk and S.A. Magennis, *J. Org. Chem.*, 1976, **41**, 273.
7 W. Smadja, S. Czernecki, G. Ville and C. Georgoulis, *Organometallics*, 1987, **6**, 166.
8 D. Basavaiah and K. Muthukumaran, *Tetrahedron*, 1998, **54**, 4943.
9 S. Bouquillon, B. Ganchegui, B. Estrine, F. Henin and J. Muzart, *J. Organomet. Chem.*, 2001, **634**, 153.
10 L. Bagnell, U. Kreher and C.R. Strauss, *Chem. Commun.*, 2001, 29.
11 I.P. Beletskaya and A.V. Cheprakov, *Chem. Rev.*, 2000, **100**, 3009.
12 T.J. Jeffery, *J. Chem. Soc., Chem. Commun.*, 1991, 324.
13 S.-K. Kang, H.-W. Lee, S.-B. Jiang, T.-H. Kim and S.-J. Pyun, *J. Org. Chem.*, 1996, **61**, 2604.
14 V. Calo, A. Nacci, A. Monopoli and M. Spinelli, *Eur. J. Org. Chem.*, 2003, 1382.
15 Q. Fan, X. Li and A.S.C. Chan, *Chem. Rev.*, 2002, **102**, 3385.
16 C.E. Song, *Chem. Commun.*, 2004, 1033.
17 M. Poliakoff, J.M. Fitzpatrick, T.R. Farren and P.T. Anastas, *Science*, 2002, **297**, 807.
18 A. Kirschnig, H. Monenschein and R. Wittenberg, *Angew. Chem., Int. Ed.*, 2001, **40**, 650.
19 B. Clapham, T.S. Reger and K.D. Janda, *Tetrahedron*, 2001, **57**, 4637.
20 N.E. Leadbeater and M. Marco, *Chem. Rev.*, 2002, **102**, 3217.
21 L. Yin and J. Liebscher, *Chem. Rev.*, 2007, **107**, 133.
22 P.-W. Wang and M.A. Fox, *J. Org. Chem.*, 1994, **59**, 5358.
23 M.-Z. Cai, C.-S. Song and X. Huang, *Synthesis*, 1997, 521.
24 S.I. Khan and M.W. Grinstaff, *J. Org. Chem.*, 1999, **64**, 1077.
25 K. Yu, W. Sommer, J.M. Richardson, M. Week and C.W. Jones, *Adv. Synth. Catal.*, 2005, **347**, 161.
26 J.H. Clark, D.J. Macquarrie and E.B. Mubofu, *Green Chem.*, 2000, **2**, 53.
27 C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli and J.S. Beck, *Nature*, 1992, **359**, 710.
28 J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins and J.L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
29 W. Zhou, J.M. Thomas, D.S. Shephard, B.F.G. Johnson, D. Ozkaya, T. Maschmeyer, R.G. Bell and Q. Ge, *Science*, 1998, **280**, 705.
30 T. Maschmeyer, F. Rey, G. Sankar and J.M. Thomas, *Nature*, 1995, **378**, 159.
31 C.-J. Liu, S.-G. Li, W.-Q. Pang and C.-M. Che, *Chem. Commun.*, 1997, 65.
32 P.C. Mehnert, D.W. Weaver and J.Y. Ying, *J. Am. Chem. Soc.*, 1998, **120**, 12289.
33 H. Yang, G. Zhang, X. Hong and Y. Zhu, *J. Mol. Catal. A*: *Chem.*, 2004, **210**, 143.
34 C. Gonzalez-Arellano, A. Corma, M. Iglesias and F. Sanchez, *Adv. Synth. Catal.*, 2004, **346**, 1758.
35 F. Alonso, I.P. Beletskaya and M. Yus, *Tetrahedron*, 2005, **61**, 11771.
36 H.E.B. Lempers and R.A. Sheldon, *J. Catal.*, 1998, **175**, 62.
37 M.H. Lim and A. Stein, *Chem. Mater.*, 1999, **11**, 3285.