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Molecular sieves-supported palladium(II) catalyst: Suzuki coupling of chloroarenes and an easy access to useful intermediates for the synthesis of irbesartan, losartan and boscalid

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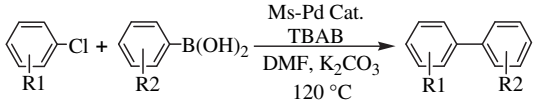
ABSTRACT

Palladium(II) chloride supported on 4 Å molecular sieves efficiently catalyzes the Suzuki coupling reactions of chlorobenzenes in presence of tetrabutylammonium bromide without any ligand. The useful intermediates for the synthesis of bioactive compounds such as irbesartan, and losartan have been prepared in one step following this reaction. The preparation of this catalyst is very simple. The FE-SEM image shows a cube shape ordered structure. The catalyst does not exhibit any nanoparticles as indicated by TEM. EDS and XPS demonstrate anchoring of Pd on molecular sieves in +2 oxidation state. This heterogeneous catalyst is stable, non-air sensitive and recyclable.

1. Introduction

The palladium-catalyzed cross-coupling reaction constitutes a major protocol for carbon–carbon bond formation. The Suzuki reaction represents a widely accepted methodology in modern organic synthesis for carbon–carbon bond formation providing an easy access to biaryls[1–14] that are highly useful in pharmaceuticals and fine chemicals.[15] However, usually expensive bromo- and iodobenzenes are employed in this coupling reaction, which restrict the wide use of this reaction in industry.[16,17] Thus, the demand of easily available and less expensive chlorobenzenes as substrates for this useful reaction is increasing for industrial applications. But, chlorobenzenes are less reactive and this makes this protocol a challenging task.[4–6] Significantly, the methods, which involved chlorobenzenes used mostly homogeneous Pd catalysts in presence of ligands.[6,7] However, the limitations of single use and tedious separation process from the product using homogeneous Pd complexes, posed a serious problem for industrial application.[18,19] The presence of heavy metal even in lowest level in pharmaceutical products is closely regulated. On the other hand, in general, the heterogeneous catalysts offer ease of separation of product, reusability of the catalyst and improved efficiency compared to their homogeneous counterparts.[20,21] Thus, heterogeneous supported catalysts are more desirable from industrial as well as environmental concern. In recent times, a few methods using heterogeneous Pd-catalysts for coupling of chlorobenzenes have been developed.[22–31] Those without using any ligand include Pd(II)-exchanged mesoporous sodalite and NaA zeolite,[22] layered double hydroxide supported nanopalladium,[23] ordered mesoporous Pd/silica-carbon,[24] mercaptopropyl-modified mesoporous silica,[25] hydroxyapatite-bound palladium complex[26] and palladium nanoparticles supported on polyaniline nanofibres.[27] A few methods using ligands are also available.[12,28,29] Although these procedures are quite satisfactory, majority of them did not address adequate reactions of substituted chlorobenzenes and in addition, the catalyst syntheses are often time consuming, tedious and they require expensive starting materials. We report here a very simple procedure using an easily accessible 4 Å molecular sieves-supported palladium(II) as catalyst for Suzuki coupling of chlorobenzenes in absence of any ligand (Scheme 1).



Scheme 1. Suzuki coupling of chlorobenzenes.

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2. Results and discussion

The catalyst was prepared by stirring a solution of $PdCl_2$ in acetone with commercially available molecular sieves for 48 h at room temperature. A pale yellow solid material was obtained and this was filtered and washed with acetone five times to remove any unreacted $PdCl_2$. This material was then dried in the oven at 80 °C for 2 h to provide the palladium immobilized molecular sieves as an easy flowing yellow powder.

The Energy Dispersive Spectra (EDS) of this material showed the presence of both palladium and chloride in the atomic ratio of approximately 1:2 indicating Pd in the +2 oxidation state. The X-ray Photoelectron Spectroscopy (XPS) exhibited two peaks for Pd at 337 eV and 343 eV. The deconvoluted photoelectron spectrum showed further splitting of these peaks (Fig. 1). The $3d_{5/2}$ peaks at 336.1 eV and 337.5 eV for lattice bound Pd^{+2} are in good agreement with the reported values of 336.3–336.9 eV for Pd^{+2} in PdO[32] and 337.1 eV for Pd^{+2} in ZnO.[33] The Transmission Electron Microscopic (TEM) image did not demonstrate the presence of any nanoparticles. The Field Emission Scanning Electron Microscopic (FESEM) image showed a cube shape ordered structure having edge length of 200 nm—on a rough surface. No shape or phase transition was observed before and after anchoring of $PdCl_2$ (Fig. 2). Thus, we speculate a structure like Figure 3 for our molecular sieves-supported $PdCl_2$.[34]

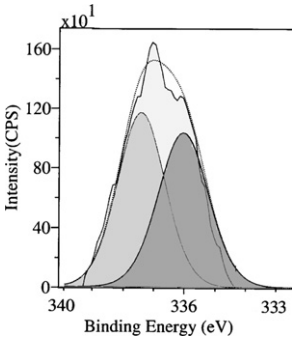


Figure 1. XPS of MS-Pd catalyst.

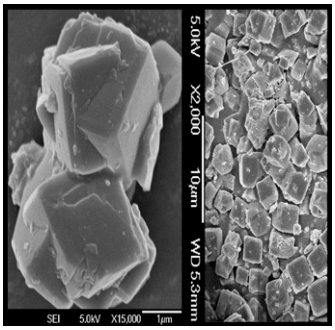


Figure 2. SEM of MS-Pd catalyst.

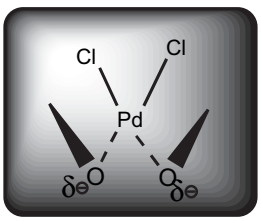
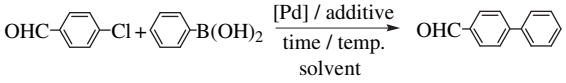


Figure 3. Proposed surface structure around Pd in MS-Pd catalyst.

To optimize the reaction conditions, a series of experiments were carried out with variation of solvent, base, reaction temperature and time for a representative reaction of 4-chlorobenzaldehyde and phenyl boronic acid, as illustrated in Table 1. The best result was obtained using 0.05 mol % of palladium catalyst, 10 mol % of tetrabutylammonium bromide (TBAB) and 1.2 equiv of K_2CO_3 in DMF at 120 °C (Table 1, entry 9).

Table 1
Standardization of reaction conditions



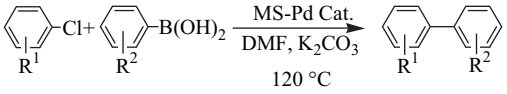
Entry	Solvent	Base	Additive	Temp (°C)	Time (h)	Yield[a] (%)
1	Dioxane/H_2O	Cs_2CO_3	—	100	24	20
2	Toluene	Cs_2CO_3	—	110	24	10
3	DMF	K_3PO_4	—	120	24	30
4	DMF	NaOAc	—	120	24	20
5	DMF	K_2CO_3	—	120	24	32
6	DMF	KF	—	120	24	20
7	DMF	K_2CO_3	—	120	24	45
8	DMF	K_2CO_3	TBAB	120	24	99
9	**DMF**	**K_2CO_3**	**TBAB**	**120**	**16**	**98**
10	DMF	K_2CO_3	TBAB	120	8	60
11	DMF	K_2CO_3	TBAB	120	16	25
12	H_2O	K_2CO_3	TBAB	100	16	25
13	DMF	K_2CO_3	KBr	120	16	30
14	DMF	KOH	TBAB	120	16	10
15	DMF	K_2CO_3	CTAB	120	16	95
16	DMF	K_2CO_3	SDS	120	16	93
17	DMF	K_2CO_3	TBAI	120	16	90

[a] Yields refer to those of pure products characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopic data.

We also prepared a few molecular sieves-supported catalysts using $Pd(OAc)_2$, $Pd(NO_3)_2$, Na_2PdCl_4 and these were tested for this reaction. However, no significant activity (less than 10% yield using $Pd(OAc)_2$ and Na_2PdCl_4 supported catalysts) was observed with these catalysts. The maximum yield of product (40%) was obtained using the one containing $Pd(NO_3)_2$. Thus, the catalyst using $PdCl_2$ provides the best result for this reaction. To the best of our knowledge this Ms-Pd(II) catalyst is developed by us for the first time, although a very recent communication reported a similar molecular sieves-supported Pd(0) catalyst for hydrogenation.[35]

Several substituted chlorobenzenes underwent cross-coupling reactions with phenyl boronic acids by this procedure to produce the corresponding biaryls. The results are reported in Table 2. Both

Table 2
Suzuki coupling of chroloarenes catalyzed by molecular sieves-supported palladium catalyst

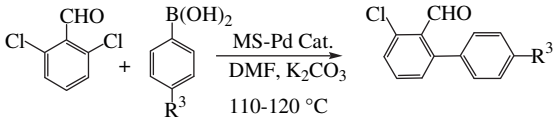


Entry	R^1	R^2	Time (h)	Yield[a] (%)
1	H	H	18	84
2	2-CHO	H	16	92
3	4-CHO	H	16	98
4	4-COMe	H	18	90
5	2-CN	H	16	98
6	4-CN	H	12	98
7	3-Me	H	22	75
8	4-Ph	H	20	83
9	4-OMe	H	24	73
10	4-CF_3	H	14	94
11	4-F	H	18	90
12	2-NO_2	H	14	92
13	4-NO_2	H	13	98

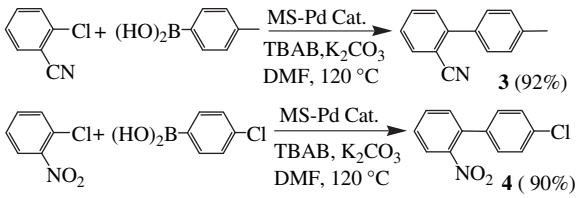
[a] Yields refer to those of purified products characterized by spectroscopic data.

electron withdrawing and electron donating substituents on the aromatic ring are compatible with this reagent and uniformly high yields are obtained in all these reactions. The chlorobenzenes bearing useful functionalities such as –CHO, COMe, CN, NO_2 led to the corresponding functionalized biaryls, which are of much potential for further manipulation to important molecules.

Significantly, 2,6-dichlorobenzaldehyde underwent selective monocoupling with substituted boronic acids to provide the corresponding products (Scheme 2), which is usually difficult to achieve.[10,11] The 4′-methyl-biphenyl-2-carbonitrile **3**, obtained in 92% yield by the coupling of 2-cyano-1-chlorobenzene and tolylboronic acid (Scheme 3), is used as a key intermediate in the synthesis of angiotensin II receptor antagonists such as irbesartan and losartan used for the treatment of hypertension.[36,37] Earlier, this carbonitrile **3** was reported to be prepared by three steps in 60% overall yield.[38] Another coupled product **4**[39] (Scheme 3) is also an intermediate to the synthesis of boscalid, a useful agrochemical. To the best of our knowledge, this is the first report for the synthesis of these important compounds **3** and **4** by direct Suzuki coupling of chlorobenzenes using heterogeneous supported catalyst under ligand free condition.



Scheme 2. Selective mono arylation of dichloro compound.



Scheme 3. Synthesis of a couple of useful intermediates.

In general, the reactions are very clean and high yielding with a reasonably good TON (1660–1960). Several sensitive functionalities CHO, COMe, CN, OMe, NO_2, and CF_3 are compatible with this procedure. The catalyst is thermal-, air- and moisture stable and thus, there is no need to use the fresh catalyst in every reaction. In fact, the catalyst can be stored for a few months without any depreciation.

The catalyst is highly heterogeneous and no appreciable dissolved palladium is available in the filtrate to carry out the reaction. This was established by an experiment where the catalyst was filtered off after 50% conversion (1H NMR) and the reaction was continued with the filtrate for another 7 h. No increase in the amount of product was observed beyond 50%, as determined by ^{1}H NMR. The catalyst is recyclable upto five times without appreciable loss of activity as illustrated in Figure 7.

To determine the active catalytic species and understand reaction mechanism we carried out time dependent XPS, EDX, and TGA-MS experiments with our molecular sieves—supported Pd-catalyst. Deconvoulated XPS studies (Fig. 4) indicated the presence of Pd(II) in the fresh as well as in recovered catalyst after the reaction. The $3d_{5/2}$ peaks at 337.5 eV for lattice bound Pd(II) disappeared with the progress of the reaction and a new peak at 335.1 eV appeared indicating the conversion of Pd(II) to Pd(0)[40] during the reaction. For better understanding of the nature of this reaction a separate experiment was performed by treatment of iodobenzene and recovered catalyst in DMF at 100 °C for 6 h. The

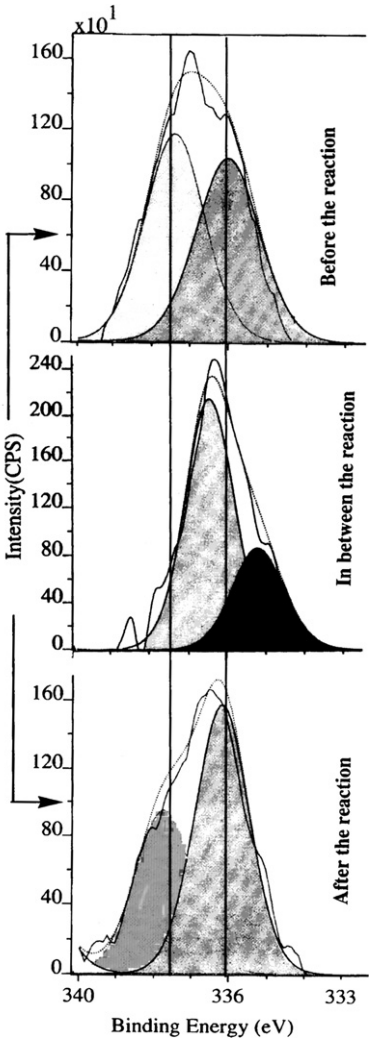


Figure 4. Deconvoluted XPS of MS-Pd catalyst.

XPS spectra of the reaction residue (Fig. 5) exhibit one peak centered at 287.7 eV for Pd–C bond and another one centered at 620.5 indicating Pd–I bond (Fig. 6). The TGA-Ms of the same exhibited *m*/*z* values at 77 and 127 amu corresponding to Ph and I species. As no peak (*m*/*z* value) corresponding to PhI was observed, it may be assumed that the pyrolysis products were generated from PhPdI. All these information suggest that a cycle involving Pd(II) to Pd(0) and then back to Pd(II) is a possibility. Thus, we propose that Pd(II) anchored on MS-Pd catalyst is reduced to Pd(0) by phenyl boronic

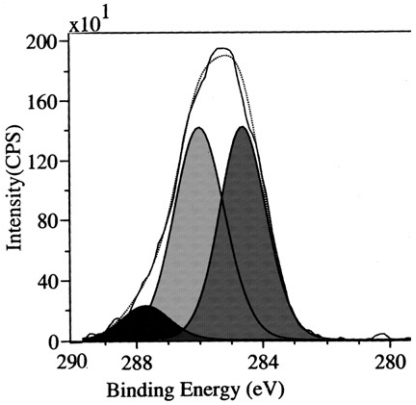


Figure 5. XPS Survey Scan of MS-Pd during reaction for C 1s orbital.

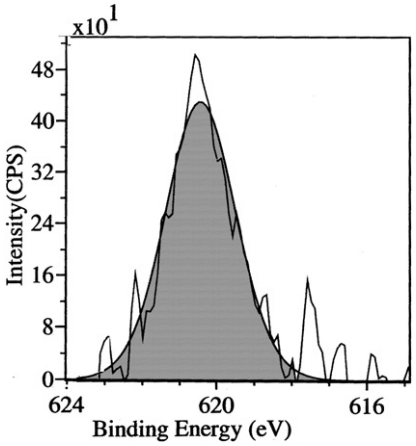
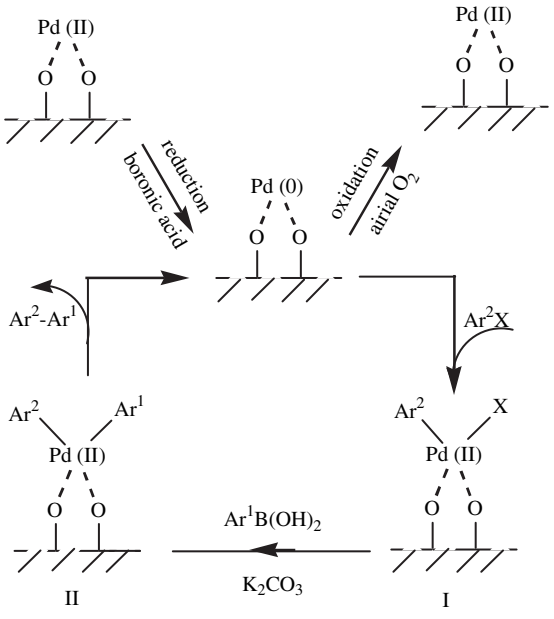


Figure 6. XPS survey scan of MS-Pd during the reaction for I $3d_{5/2}$.

acid,[40] which then undergoes oxidative addition to aryl halide to generate the Pd(II) complex I. This species undergoes coupling with phenyl boronic acid to produce the intermediate II and finally it provides the biaryl product via the reductive elimination of Pd(II) to Pd(0), which, we believe, undergoes aerial oxidation to give back the Pd(II) catalyst,[22] as outlined in Scheme 4.



Scheme 4. Possible reaction pathway.

3. Conclusion

In conclusion, the present procedure using an inexpensive, stable and readily accessible molecular sieves-supported palladium catalyst, provides an efficient methodology for the Suzuki coupling of less reactive chloroarenes. The easy access to two important intermediates towards the synthesis of irbesartan and losartan, a hypertensive drug and boscalid, a useful agrochemical, by this protocol using chlorobenzenes is a significant achievement. To the best of our knowledge, we are not aware of any synthesis of these molecules using a ligand-free heterogeneous supported catalyst. The simple operation, easy recovery of catalyst. recyclability for a number of runs, excellent yields in all coupling reactions, compatibility with a variety of sensitive functionalities, and good TON (1660–1960) make this procedure attractive for industrial applications.

4. Experimental section

4.1. General

^{1}H NMR spectra were recorded on a 300 MHz spectrometer. The chemical shifts (δ) are reported in parts per million, using TMS as an internal standard and $CDCl_3$ as the solvent. The particle size and external morphology of the samples were observed on a JEOL 2010 Transmission Electron Microscope (TEM) at 200 kV and JEOL- JSM-6700R Field Emission Scanning Electron Microscope (FESEM). The samples were mounted on a copper grid by ultrasonication. X-ray Photoemission Spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg KR anode. The pressure in the spectrometer was about 10^{-9} Torr. For energy calibration, we have used the carbon 1s photoelectron line. The carbon 1s binding energy was taken to be 285.0 eV. Spectra were deconvoluted using the Sun Solaris based Vision 2 curve resolver. The location and the full width at half-maximum (fwhm) for a species was first determined using the spectrum of a pure sample. The location and fwhm of the products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible to within ±0.1 eV. Thermo Gravimetric Analysis-Mass Spectra (TGA-MS) thermograms were recorded on a Mettler-Toledo TGA/SDTA 821e instrument coupled to a Balzers Thermostar GSD 300T in the temperature range of 25–500 °C with a heating rate of 10 °C/min in a nitrogen atmosphere. Atomic absorption spectroscopy (AAS) analysis was carried out using palladium standards on Shimadzu AA-6300.

4.2. Preparation of MS-Pd catalyst

A mixture of a solution of $PdCl_2$ (15 mg, 0.084 mmol) in acetone (20 mL) and molecular sieves 4 Å (1 g) was stirred at room temperature (25–28 °C) for 48 h when a yellow solid appeared. This solid was then filtered and washed with acetone (5×20 mL) to remove any trace of unreacted $PdCl_2$. It was then dried in the oven at 80 °C for 2 h to provide an easy flowing pale yellow powder (980 mg). This molecular sieves-supported Pd catalyst (Pd content: 0.02 mmol g^{-1} determined by AAS) was used for all the reactions.

4.3. Heterogeneity tests

A mixture of MS-Pd (0.05 mol %), 4-chlorbenzaldehyde (140 mg, 1 mmol), phenyl boronic acid (145 mg, 1.2 mmol), K_2CO_3 (166 mg, 1.2 mmol), and TBAB (10 mol %) in DMF (2 mL) was stirred at 120 °C for 7 h. At this stage (50% conversion), the catalyst was filtered off and the experiment was continued with the filtrate for another 7 h in presence of K_2CO_3. There was no increase in the product concentration, as determined by the ^{1}H NMR analysis.

4.4. General experimental procedure for cross-coupling reactions. representative procedure for coupling of 4-chlorobenzaldehyde and phenyl boronic acid (Table 2, entry 3)

A mixture of phenyl boronic acid (145 mg, 1.2 mmol), 4-chlorobenzaldehyde (140 mg, 1 mmol), MS-Pd catalyst (0.05 mol %, 25 mg of solid catalyst), tetrabutylammonium bromide (40 mg, 10 mol %), and K_2CO_3 (1.2 mmol, 170 mg) in DMF (2 mL) was heated at 120 °C for 18 h (TLC). The reaction mixture was extracted with dry Et_2O (3×10 mL), and the ether extract was washed with brine and water and dried (Na_2SO_4). Evaporation of solvent left the crude product, which was purified by column chromatography over silica gel [R_f 0.85 (hexane/ether 9:1)] to give biphenyl-4-carbaldehyde as

a white solid (178 mg, 98%). The spectroscopic data (IR, ^{1}H NMR, and ^{13}C NMR) are in good agreement with the reported values.

The MS-Pd catalyst was recovered and washed with water–acetone (1:1) (2×2 mL) and then once with acetone and dried in the oven for 2 h at 80 °C for next use. It was recycled for five times without any appreciable loss of activity (Fig. 7).

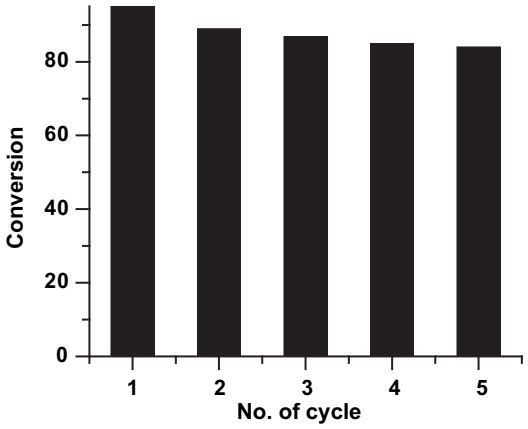


Figure 7. Recyclability chart.

This procedure was followed for all of the reactions listed in Table 2. Although the representative procedure was based on a 1 mmol scale, gram quantities also provided similar results.

Several of these products are known compounds and these were identified by comparison of their spectroscopic (IR, ^{1}H NMR, ^{13}C NMR) data with those reported.[12,27–29,31,38,39] The unknown compounds (compounds **1** and **2** in Scheme 2) were properly characterized by their spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, HRMS). The purity of all compounds was also checked by ^{1}H NMR, ^{13}C NMR, and elemental analysis.

*4.4.1. 3-Chloro-biphenyl-2-carbaldehyde (**1**).* Colorless liquid; R_f 0.8 (hexane/ether 9:1); IR (neat): 2862, 1703, 1585, 1450, 1201, 1045, 823, 790 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.32 (broad, 3H), 7.43–7.45 (m, 3H), 7.48–7.49 (m, 2H), 10.06 (s, 1H); ^{13}C NMR (75 MHz) δ 128.3, 128.5 (2C), 129.6 (3C), 130.2, 131.9, 132.7, 134.5, 137.9, 146.6, 191.1; *m*/*z* calcd for $[C_{13}H_9OCl+Na]^+$: 239.024, found: 239.027.

*4.4.2. 3-Chloro-4′-methyl-biphenyl-2-carbaldehyde (**2**).* Colorless liquid; R_f 0.85 (hexane/ether 9:1); IR (neat): 3059, 2854, 1699, 1585, 1448, 1201, 759, 702 cm^{-1}; ^{1}H NMR (300 MHz) δ 2.40 (s, 3H), 7.16–7.31 (m, 5H), 7.44–7.46 (m, 2H), 10.02 (s, 1H); ^{13}C NMR (75 MHz) δ 21.2, 129.2 (2C), 129.6 (3C), 130.0, 132.0, 132.7, 134.3, 134.9, 138.3, 146.7, 191.3; *m*/*z* calcd for $[C_{14}H_{11}OCl+Na]^+$: 253.039, found: 253.036.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found in the online version doi:10.1016/j.tet.2010.02.011.

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