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ARTICLE

Palladium(II) Oxide Impregnated on Magnetite as Catalyst for the Synthesis of 4-Arylcoumarins via a Heck-arylation/cyclization process

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Heck-arylation/cyclization has been achieved using the heterogeneous palladium(II) oxide impregnated on magnetite catalyst (2.5 mol%), using a lower catalyst loading than that reported for similar processes. Ethanol was used as non-toxic and bio-renewable solvent. Good yields are afforded using a broad range of substrates (40-98 %). The catalyst could be partially recycled and analyses confirmed the almost total reduction of palladium(II) oxide to palladium(0) as well as iodine poissoning effect as the main barrier to complete recyclability.

Introduction

The Heck reaction[1] is a powerful and general synthetic method used in Organic Chemistry to construct compounds by C-C bond formation. Its synthetic flexibility and compatibility with most organic functional groups makes it one of the most explored reaction promoted by palladium.[2] Some efforts have been devoted to improving the efficiency of this reaction, and recently, iodonium salts[3] have been extensively studied as arylation agent to replace aryl halides or triflates in the Heck reaction. They are appealing coupling partners as they display different reactivity profiles to halides, are highly reactive yet air- and moisture-stable, and can be easily prepared in one step from commercially available starting materials.[4,5]

Coumarins[6] are important structural motifs in natural compounds and exhibit broad biological activity. Particularly, 4-aryl derivatives constitute a subgroup of flavonoids that have received considerable attention, as they display important biological activities such as anti-HIV, antimalarial, antibacterial and cytotoxic properties. Classical synthetic approaches for the synthesis of 4-arylcoumarins are based on Knoevenagel condensation,[7] cross-coupling reactions,[8] C-H bond activation,[9] von Pechman condensation,[10] among others.[11] In many cases, the reactions were performed under harsh reaction conditions and high temperatures. The loading of transition metal was, in many cases, very high (5-20 mol%).

Another methodology to obtain 4-arylcoumarins, that has been less studied, is the arylation/cyclization of *o*-hydroxylcinnamates. Initially, this approach was reported in 2005 using aryl halides in a molten *n*-Bu_4NOAc/*n*-Bu_4NBr mixture,[12] later on the approach was modified by the use of aryl diazonium salts in methanol.[13] Finally, diaryliodonium(III) salts have been successfully used to perform this transformation using dimethylformamide as solvent.[14] In all cases the reaction was performed with the help of high amounts of the homogeneous $Pd(OAc)_2$ (5-10 mol%) catalyst, giving moderate to good yields.

As a continuation of our project on the arylation of heterocycles,[15] herein, we reported the synthesis of 4-arylcoumarins using for the first time heterogeneous palladium(II) oxide impregnated on magnetite catalyst for the Heck-arylation/cyclization using diaryliodonium(III) salts. Ethanol as a non-toxic and bio-renewable solvent was used under mild reaction conditions.

Results and discussion

To start the study, (*E*)-ethyl 3-(2-hydroxyphenyl)acrylate (**1a**) and diphenyliodonium tetrafluoroborate (**2a**), using palladium impregnated on magnetite as catalyst,[16] was selected as the reaction model for the optimization (Table 1). Initially, the reaction was performed using different equivalents of compound **2a** (entries 1-3). Full conversion of the starting material was observed after 5 hours when 2 equivalents of the salt were used. This result could not be improved by increasing the amount of iodonium salt. After that, different loadings of palladium catalyst were tested (entries 4-7). Good yields were obtained with 2.5 mol% Pd, which could be slightly improved using higher amounts of metal. Then, a study of the solvent was performed (entries 8-15). A moderate yield was obtained in H_2O, but best results were observed in EtOH (entry 5). When the reaction was performed without solvent (entry 16) only traces of the product could be detected.

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Electronic Supplementary Information (ESI) available: [TEM images, ^{1}H-NMR and ^{13}C-NMR]. See DOI: 10.1039/x0xx00000x

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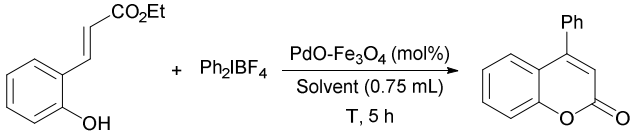
Table 1. Optimization of the reaction conditions.[a]

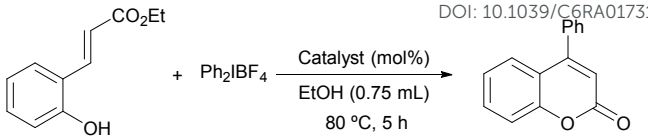


1a 2a 3a

Entry	PdO-Fe_3O_4 (mol%)	Solvent	T (ºC)	Yield (%)[b]
1	10	EtOH	60	99
2[c]	10	EtOH	60	54
3[d]	10	EtOH	60	99
4	1	EtOH	60	46
5	2.5	EtOH	60	86
6	5	EtOH	60	90
7	7.5	EtOH	60	99
8	2.5	Toluene	60	0
9	2.5	THF	60	0
10	2.5	H_2O	60	64
11	2.5	Dioxane	60	0
12	2.5	DCM	60	0
13	2.5	CH_3CN	60	34
14	2.5	DMF	60	48
15	2.5	DMSO	60	10
16	2.5	-	60	15
17	2.5	EtOH	RT	7
18	2.5	EtOH	80	99

[a] Reaction carried out using compounds **1a** (0.25 mmol), **2a** (0.5 mmol). [b] Yield determined by GC using 0.25 mmol of tridecane as internal standard. [c] Reaction carried out using compounds **1a** (0.25 mmol), **2a** (0.25 mmol). [d] Reaction carried out using compounds **1a** (0.25 mmol), **2a** (0.75 mmol).

Table 2. Optimization of the catalyst.[a]



1a 2a 3a

Entry	Catalyst (mol%)	Yield (%)[b]
1	PdO-Fe_3O_4 (2.5)	99
2	-	0
3	Nano-Fe_3O_4 (129.9)	11
4	Micro-Fe_3O_4 (129.9)	10
5	CoO-Fe_3O_4 (2.83)	17
6	NiO-Fe_3O_4 (2.06)	0
7	Ru_2O_3-Fe_3O_4 (2.64)	25
8	Rh_2O_3-Fe_3O_4 (2.52)	25
9	Ag_2O/Ag-Fe_3O_4 (2.50)	4
10	OsO_2-Fe_3O_4 (2.05)	8
11	IrO_2-Fe_3O_4 (2.10)	10
12	PtO/PtO_2-Fe_3O_4 (2.15)	17
13	Au_2O_3/Au-Fe_3O_4 (2.26)	0
14	PdO/Cu-Fe_3O_4 (3.06/1.79)	18
15	NiO/Cu-Fe_3O_4 (1.82/1.76)	7
16	WO_3-Fe_3O_4 (2.26)	25
17	CuO-Fe_3O_4 (2.34)	0
18	PdO (2.5)	79
19	$PdCl_2$ (2.5)	83
20	$Pd(OAc)_2$ (2.5)	76

[a] Reaction carried out using compounds **1a** (0.25 mmol), **2a** (0.5 mmol). [b] Yield determined by GC using 0.25 mmol of tridecane as internal standard.

To complete the optimization, different temperature were tried (entries 17-18). Only traces of product were detected at room temperature and full conversion of the starting material was observed at 80 °C.

Once the optimal conditions were determined, the reaction was submitted to a variety of catalysts, prepared by a simple impregnation protocol[17] (Table 2). The reaction without catalyst did not give any product (entry 2). The partial inactivity of the support was confirmed (entries 3 and 4), the role of magnetite is only to facilitate the easy separation of the reaction media through magnetic decantation.[18] Then, different metal oxides impregnated on magnetite (entries 5-17) were evaluated as catalyst, but the high activity displayed by the palladium catalyst could not be surpassed. With these results in hand, the reaction was carried out using different sources of palladium, (entries 18-20). All catalysts tested (homogeneous, as well as heterogeneous) failed to give similar or improved activities relative to palladium on magnetite (entry 1).

In order to establish the reusability of the catalyst, the standard reaction was repeated (Figure 1). When the reaction was completed, the catalyst was retained in the reaction vessel using a magnet and washed several times with ethanol. The vessel was then charged with a new set of reagents and the standard conditions were applied.

The corresponding product was obtained with a 39 % yield after the first cycle indicating that the catalytic activity of the catalyst has been affected by the first reaction.

As a consequence of the non-recyclability of the catalyst, some investigative studies were performed. X-Ray Photoelectron Spectroscopy (XPS) analyses of the catalyst showed a change in the oxidation state [palladium(II) oxide to palladium(0)] after completion of the reaction.

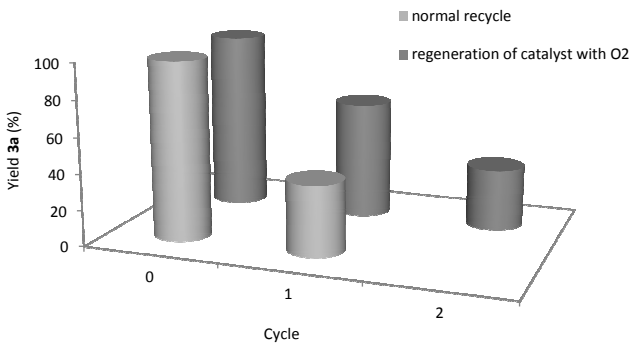


Figure 1. Recycling of the PdO-Fe_3O_4 catalyst.

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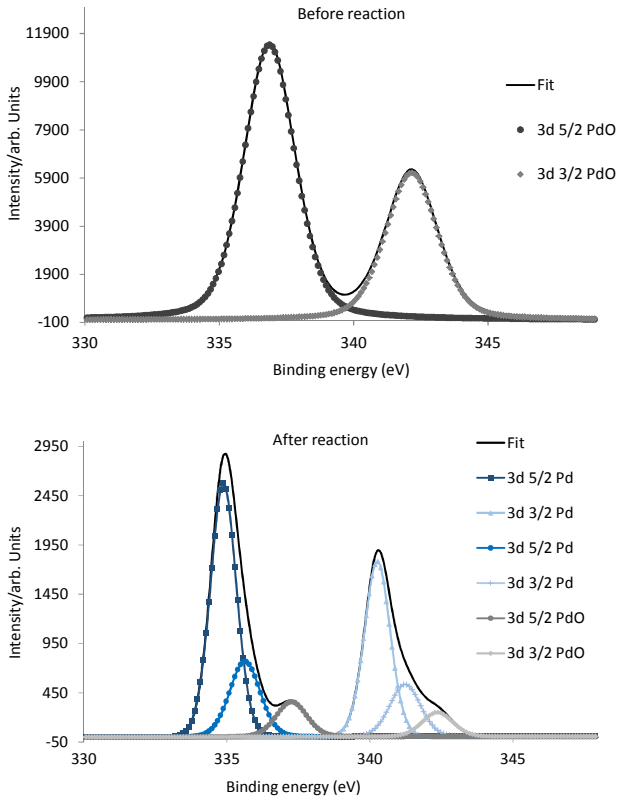

Figure 2. XPS of the fresh and recycled palladium catalyst.

The XPS spectra of the post-reaction sample showed, after deconvolution, four peaks at 334.9, 335.7, 340.3 and 341.3 eV, which correspond to the binding energies of Pd $3d_{5/2}$ and Pd $3d_{3/2}$, and two more peaks that have the same binding energy than the starting palladium(II) oxide nanoparticles, with a relative area of 4% (Figure 2). Furthermore, Transmission Electron Microscopy (TEM) analyses were carried out. We observed a high sinterization of the palladium nanoparticles as well dissociation of the palladium from the support after completion of the reaction (see Supporting Information). The initial size range of the starting PdO nanoparticles was 2-4 nm (Figure 3) but increased to 14-16 nm after the reaction. The phenomenon of leaching was studied by inductively coupled plasma mass spectrometry (ICP-MS). Here, the reaction mixture was filtered at high temperature after completion of the reaction and the homogeneous solution was tested. Only 3.64 % of the initial palladium was present in solution. More importantly, no progress of the reaction was observed in the filtrate after the filtration, providing further evidence of the heterogeneous nature of the reaction.

Finally, a modified hot filtration test was performed. Thus after the standard reaction, the mixture was decanted with the aid of a magnet, while hot, and a mixture of **1c** (0.25 mmol) and **2a** (0.5 mmol) dissolved in 0.75 mL of ethanol, was added to the filtrate. After five hours at 80 °C, starting reagents **1c** and **2a** were recovered unchanged.

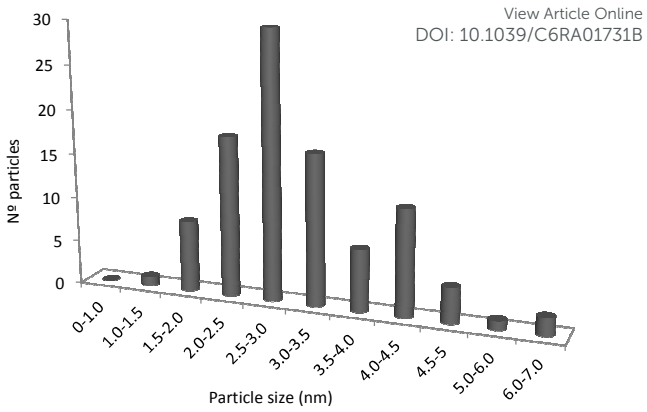

Figure 3. Particle size distribution of fresh catalyst.

The TPR and TPO analyses of Fe_3O_4, fresh and recycled catalyst were carried out (see Supporting Information). Previously to analyses, the samples were pre-treated by heating at 200 ºC under Argon atmosphere to be sure that all the organic material was removed. Then, the samples were heated to 900 ºC at 10 ºC/min in the corresponding atmosphere [TPR was performed with a mixture Ar/H_2 (1.8 %), and TPO with a mixture Ar/O_2 (3%)].

In the case of differential thermogravimetric analysis under reductive atmosphere (Figure 4a), when the temperature reached 100 ºC only the fresh catalyst sample showed a consumption of hydrogen and an emergence of H_2O, what it could be assigned to the reduction from PdO to Pd(0).

At 300 ºC a new consumption of H_2 could be observed and it seems to be due to the reduction of superficial magnetite. In the case of both magnetite support and recycled catalyst, only this last consumption of hydrogen was detected. It should be pointed out that in the case of the supported catalyst the reduction of superficial magnetite took places at lower temperatures, probably by the influence of the supported palladium. From the data of differential thermogravimetric analysis under reductive atmosphere it could be calculated the expected weight losing due to a PdO to Pd(0) transformation, with this figure being slightly higher than the nominal palladium. This could be due to the reduction through a spill-over of hydrogen to the support of magnetite units that are in intimate contact with palladium.

In the case of differential thermogravimetric analysis under oxidative atmosphere, only the recycled sample showed a weight losing at about 400 ºC (Figure 4b). The mass analysis showed the loss of CO_2 and then iodine in the case of recycled catalyst (Figure 5). The emergence of CO_2 should be associated to organic compounds strongly bounded to the catalyst surface; meanwhile the emergence of iodine could be a hindered proof of the poisoning of palladium species by this element.

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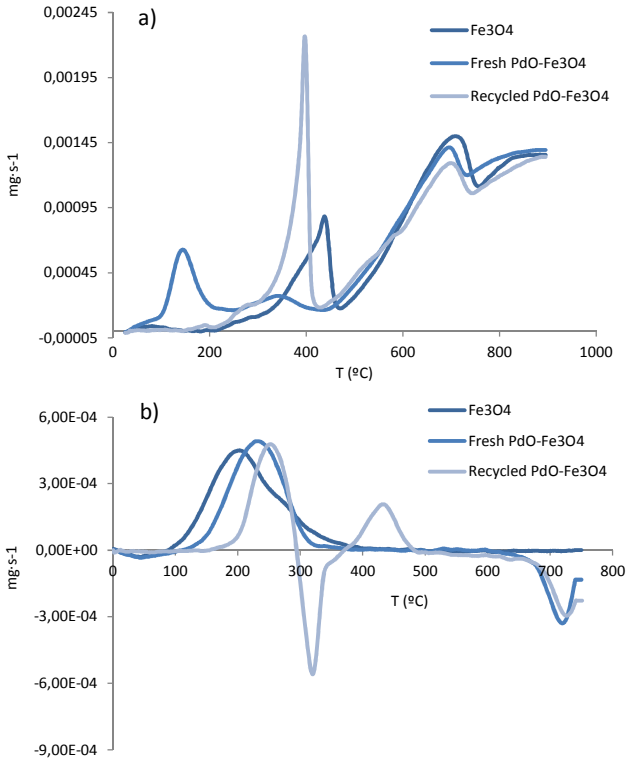

Figure 4. Differential thermogravimetric curves of Fe_3O_4 support, fresh and recycled catalyst with: a) reductive atmosphere, b) oxidative atmosphere.

Guided by the previously mentioned XPS, as well as TPR and TPO analysis, we attribute the deactivation of the catalyst to an almost complete reduction of the nanoparticles of palladium(II) oxide to palladium(0), the associated morphologic changes and the poisoning by iodine species.

Thus in an attempt to recycle the catalyst, post reaction particles of palladium(II) were subjected to oxygen (bubbling O_2) (see Figure 1). Using this protocol, the results obtained for the recycling of the catalyst were improved but did not reach the initial catalyst activity. Other oxidants tested (e.g. *t*-BuOOH or I_2) gave poorer results.

Once the best conditions were established, the scope of the reaction was evaluated (Table 3). Moderate yields could be obtained using symmetrical bis(4-fluorophenyl)iodonium tetrafluoroborate (entry 2). Better results were observed, with symmetrical bis(4-methoxyphenyl)iodonium tetrafluoroborate giving 77 % yield (entry 3). Chemoselective Heck-arylation/cyclization reactions were performed by introducing a non-transferable aryl group such as 1,3,5-triisopropylphenyl (TRIP). Good results were observed with substrates bearing electron-withdrawing and sterically hindered electron-donating groups (entries 4 and 5).

Then various substituted *o*-hydroxyphenylacrylates were tested (entries 6-8). Better results were found with the sterically hindered (*E*)-ethyl 3-(3,5-di-*tert*-butyl-2-hydroxyphenyl)acrylate. The presence of electron-withdrawing groups at 5-position in the aromatic ring of the acrylate seemed to negatively affect the reaction.

The use of substituted acrylates and diaryliodonium tetrafluoroborates gave very good yields in all the cases (entries 9-11). To finish with the study, different diaryliodonium trifluoromethanesulfonates were tested, which gave moderate to good results (entries 12-14). In the case of phenyl(2,4,6-triisopropylphenyl)iodonium trifluoromethanesulfonate (entry 12) the expected product 3a was obtained with a lower yield than that obtained with the previously tested diphenyliodonium tetrafluoroborate (entry 1). Others aryl sources were ineffective in similar reactions.[19]

Once the scope of the reaction was evaluated, the possible pathway of the process was studied. The reaction could occur through a cyclization reaction followed by arylation[20] or through a Heck-arylation reaction and subsequent cyclization. To check if the reaction took place following the first process, the cyclization reaction of (*E*)-ethyl 3-(2-hydroxyphenyl)acrylate (**1a**) using ethanol at 80 °C was tested. Here the starting material was recovered unchanged. We gained access to the cyclised product using an *n*-Bu_3P mediated reaction.[6] When the resulting 2*H*-chromen-2-one was treated with salt **2a** and PdO-Fe_3O_4 under standard conditions, only starting chromenone was recovered. These results suggest that the cyclization/arylation pathway is unlikely. To further study if the Heck-arylation reaction took place first, followed by cyclization (Scheme 1), some acrylates **4**, no longer possessing the required –OH group needed for cyclisation, were tested under the optimal reaction conditions (Table 4). Using two equivalents of **2a**, a 3:1 mixture of the mono- and di-substituted products **5** were obtained in good yield (entry 1).

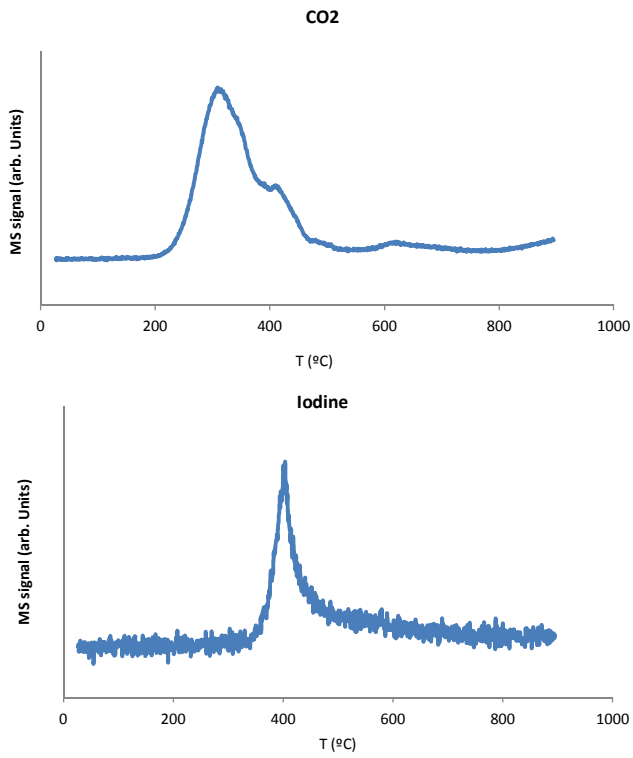

Figure 5. MS analysis of CO_2 and iodine on recycled PdO-Fe_3O_4 catalyst.

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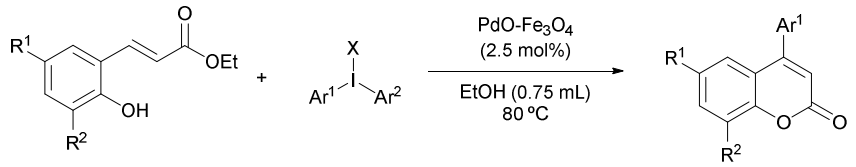
Table 3. Scope of the reaction[a]

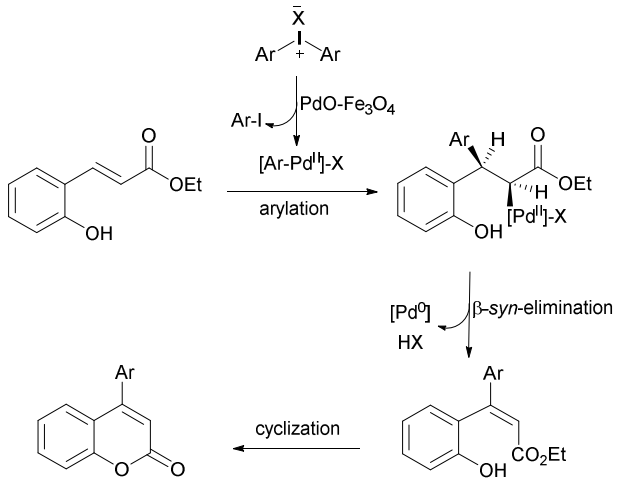


1 2 3

Entry	R^1	R^2	X	Ar^1	Ar^2	Nº	Yield (%)[b]
1	H	H	BF_4	Ph	Ph	**3a**	98
2	H	H	BF_4	4-FC_6H_4	4-FC_6H_4	**3b**	40
3	H	H	BF_4	4-$MeOC_6H_4$	4-$MeOC_6H_4$	**3c**	77
4	H	H	BF_4	4-ClC_6H_4	TRIP	**3d**	64
5	H	H	BF_4	2-MeC_6H_4	TRIP	**3e**	55
6	F	H	BF_4	Ph	Ph	**3f**	72
7	*t*Bu	*t*Bu	BF_4	Ph	Ph	**3g**	97
8	Br	OMe	BF_4	Ph	Ph	**3h**	56
9	F	H	BF_4	4-$MeOC_6H_4$	4-$MeOC_6H_4$	**3i**	70
10	*t*Bu	*t*Bu	BF_4	4-FC_6H_4	4-FC_6H_4	**3j**	79
11	Br	OMe	BF_4	4-FC_6H_4	4-FC_6H_4	**3k**	95
12	H	H	OTf	Ph	TRIP	**3a**	66
13	H	H	OTf	4-MeC_6H_4	4-MeC_6H_4	**3l**	52
14	Br	OMe	OTf	4-MeC_6H_4	4-MeC_6H_4	**3m**	91

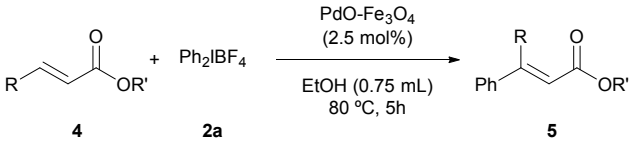
[a]Reaction carried out using compounds **1** (0.25 mmol) and **2** (0.5 mmol). [b]Isolated yield after column chromatography.

With these results in hand, the reaction was repeated with only one equivalent of the salt **2a**. A lower amount of the di-substituted product **5b** was obtained, along with concomitant improvement in the yield of **5a** (entry 2). Then, methyl cinnamate (**4b**) was tested and a 68 % yield of **5c** was obtained (entry 3). To finish with the study of the Heck-arylation, different substituents at the 4-possition of the aromatic ring of starting cinnamate were used, obtaining a *ca.* mixture 1:1 of *Z*/E isomers in good yields (entries 4 and 5).



Scheme 1. Possible mechanism of the reaction.

Table 4. Heck-arylation reaction[a]



4 2a 5

Entry	R	R'	Nº	Yield (%)[b]
1	H	Et	**5a**	76 (23)[c]
2[d]	H	Et	**5a**	86 (13)[c]
3	Ph	Et	**5b**	68
4	4-MeC_6H_4	Me	**5c**	71 (Z/E 0.95/1)
5	4-$MeOC_6H_4$	Me	**5d**	69 (Z/E 1/0.8)

[a]Reaction carried out using compounds **4** (0.25 mmol) and **2a** (0.5 mmol). [b]Isolated yield after bulb-to-bulb distillation. [c]Isolated yield of compound **5b**. [d]Reaction carried out using compounds **4** (0.25 mmol) and **2a** (0.25 mmol).

Experimental

General

Solvents and reagents were used as obtained from commercial sources and without purification. ^{1}H NMR (400 MHz) spectra and ^{1}H NMR (300 MHz) spectra were recorded on Bruker Avance 400 and Bruker Avance 300 NMR spectrometers respectively in proton coupled mode. ^{13}C NMR (150 MHz) spectra and ^{13}C NMR (75.5 MHz) spectra were recorded on Bruker Avance 400 and Bruker Avance 300 NMR spectrometers respectively in proton decoupled mode at 20 °C in deuterated chloroform using tetramethylsilane as internal standard; chemical shifts are given in δ (parts per million) and

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coupling constants (*J*) in Hertz. Low-resolution mass spectra were recorded on a Waters Quattro Micro triple quadropole instrument in electrospray ionisation (ESI) mode using 50 % acetonitrile-water containing 0.1 % formic acid as eluent; samples were made up in acetonitrile. High resolution precise mass spectra (HRMS) were recorded on a Waters LCT Premier Tof LC-MS instrument in electrospray ionisation (ESI) mode using 50 % acetonitrile-water containing 0.1 % formic acid as eluent; samples were made up in acetonitrile. Infrared spectra were measured as pressed potassium bromide (KBr) for solids or thin films on sodium chloride plates for liquids on a Perkin-Elmer FT-IR spectrometer. Melting points were obtained with a Reichert Thermovar apparatus. XPS analyses were carried out on a VG-Microtech Mutilab. TEM images were obtained on a JEOL, model JEM-2010 equipped with an X-ray detector OXFORD INCA Energy TEM 100 for microanalysis (EDS). XRF analyses were obtained on a PHILIPS MAGIX PRO (PW2400) X-ray spectrometer equipped with a rhodium X-ray tube and a beryllium window. BET isotherms were carried out on an AUTOSORB-6 (Quantachrome), using N_2. The chromatographic analyses (GLC) were determined with a Hewlett Packard HP-5890 instrument equipped with a flame ionization detector and 12 m HP-1 capillary column (0.2 mm diam, 0.33 mm film thickness, OV-1 stationary phase), using nitrogen (2 mL/min) as a carrier gas, $T_{injector}$ = 275 ºC, $T_{detector}$ = 300 ºC, T_{column} = 60 ºC (3 min) and 60-270 ºC (15 ºC/min), *P* = 40 kPa. Thin layer chromatography (TLC) was carried out on Schleicher & Schuell F1400/LS 254 plates coated with a 0.2 mm layer of silica gel; detection by UV_{254} light, staining with phosphomolybdic acid [25 g phosphomolybdic acid, 10 g $Ce(SO_4)_2$ 4 H_2O, 60 mL of concentrated H_2SO_4 and 940 mL H_2O]. Column chromatography was performed using silica gel 60 of 40-63 mesh. The ICP-MS analyses were carried out on a Thermo Elemental VGPQ-ExCell spectrometer. TG-DTA analysis were carried out on a METTLER TOLEDO equipment, model TGA/SDTA851e/LF/1600, and EM analysis on a PFEIFFER VACUUM, model THERMOSTAR GSD301T.

Synthetic procedures

General procedure for the preparation of impregnated palladium on magnetite catalyst: To a stirred solution of $PdCl_2$ (177 mg, 1 mmol), KCl (1 g, 13 mmol, to increase the palladium solubility) in deionized water (120 mL) was added Fe_3O_4 (4 g, 17 mmol, powder <5 mm, BET area: 9.86 m^2/g). After 10 min at room temperature, the mixture was slowly basified with NaOH (1 M) until pH around 13. The mixture was stirred during 1 day at room temperature in air. After that, the catalyst was filtered and washed with deionized water (3 x 10 mL). The solid was dried at 100 ºC during 24 h in a standard glassware oven, obtaining the expected catalyst: incorporation of palladium of 3.0 % according to XRF; by XPS the palladium on the surface was determined as 24.8 %; the BET area surface was 13.6 m^2/g. The molar ratio of catalyst $PdO:Fe_3O_4$ was 6.3:100.

General procedure for the preparation of acrylates: To a solution of the corresponding 2-hydroxybenzaldehyde (5 mmol) in THF (30 mL) was added ethyl 2-(diethoxyphosphoryl)acetate (5.2 mmol) and DBU (5.1 mL). The solution was stirred at room temperature overnight. The resulting mixture was quenched with water and extracted with AcOEt (3 × 5 mL). The organic phases were dried over $MgSO_4$, followed by evaporation under reduced pressure to remove the solvent. The product was usually purified by chromatography on silica gel (hexane/ethyl acetate) to give the corresponding products **1**. Physical and spectroscopic data follow:

(*E*)-Ethyl 3-(2-hydroxyphenyl)acrylate (1a).[13] White solid; m.p. = 83-86 ºC (Hexane/AcOEt); IR (ATR): ν 3375, 1675, 1601, 1459, 1249, 1036 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.36 (3H, t, *J* = 7.1 Hz), 4.30 (2H, q, *J* = 7.1 Hz), 6.62 (1H, d, *J* = 16.2 Hz), 6.85-6.95 (3H, m), 7.20-7.25 (1H, m), 7.45-7.50 (1H, m), 8.02 (1H, d, *J* = 16.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 14.3, 60.8, 116.4, 118.1, 120.5, 121.6, 129.2, 131.4, 140.9, 155.6, 168; MS (EI) m/z (%): 192 (M^+, 7), 147 (15), 146 (69), 118 (100), 91 (20), 90 (18), 89 (21).

(*E*)-Ethyl 3-(5-fluoro-2-hydroxyphenyl)acrylate (1b).[21] White solid; m.p. = 114-115 ºC (Hexane/AcOEt); IR (KBr): ν 3431, 1685, 1629, 1508, 1445, 1372, 1335, 1264, 1199 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.35 (3H, t, *J* = 7.1 Hz), 4.30 (2H, q, *J* = 7.1 Hz), 6.59 (1H, d, *J* = 16.2 Hz), 6.82 (1H, dd, $^3J_{(H,H)}$ = 8.9 Hz, $^4J_{(H,F)}$ = 4.6 Hz), 6.94 (1H, ddd, $^3J_{(H,H)}$ = 8.8 Hz, $^3J_{(H,F)}$ = 7.8 Hz, $^4J_{(H,H)}$ = 8.8 Hz), 7.10-7.20 (2H, m), 8.03 (1H, d, *J* = 15.7 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 14.2, 61.0, 114.3 (d, $^2J_{(C,F)}$= 23.3 Hz), 117.4 (d, $^3J_{(C,F)}$= 8.0 Hz), 118.1 (d, $^2J_{(C,F)}$= 23.5 Hz), 119.1, 122.6 (d, $^3J_{(C,F)}$= 7.5 Hz), 139.8 (d, $^4J_{(C,F)}$= 2.2 Hz), 151.7 (d, $^4J_{(C,F)}$= 1.9 Hz), 156.7 (d, $^1J_{(C,F)}$= 238.4 Hz), 168.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ -123.9 (m).

(*E*)-Ethyl 3-(3,5-di-*tert*-butyl-2-hydroxyphenyl)acrylate (1c).[14] Pale yellow solid; m.p. = 120-122 ºC (Hexane/AcOEt); IR (ATR): ν 1684, 1621, 1471, 1441, 1289, 1186 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.30 (9H, s), 1.33 (3H, t, *J* = 7.1 Hz), 1.44 (9H, s), 4.27 (2H, q, *J* = 7.1 Hz), 5.84 (1H, br s), 6.44 (1H, d, *J* = 15.8 Hz), 7.33 (1H, d, *J* = 2.4 Hz), 7.36 (1H, d, *J* = 2.4 Hz), 8.09 (1H, d, *J* = 15.8 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 14.3, 29.9 (3C), 31.4 (3C), 34.3, 34.8, 60.7, 118.7, 121.8, 122.3, 126.6, 136.5, 140.6, 142.7, 151.4, 167.5; MS (EI) m/z (%): 304 (M^+, 7), 244 (16), 243 (100).

(*E*)-Ethyl 3-(5-bromo-2-hydroxy-3-methoxyphenyl)acrylate (1d). White solid; m.p. = 97-99 ºC (Hexane/AcOEt); IR (ATR): ν 1734, 1701, 1630, 1359, 1260, 1172 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.33 (3H, t, *J* = 7.1 Hz), 3.91 (3H, s), 4.26 (2H, q, *J* = 7.1 Hz), 6.11 (1H, s), 6.55 (1H, d, *J* = 16.2 Hz), 6.95 (1H, d, *J* = 2.2 Hz), 7.22 (1H, d, *J* = 2.2 Hz), 7.85 (1H, d, *J* = 16.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 14.3, 56.4, 60.5, 111.5, 114.8, 120.3, 122.2, 123.0, 137.9, 144.3, 147.4, 167.1; MS (EI) m/z (%): 302 (M^++2, 18), 300 (M^+, 21), 281 (18), 257 (17), 256 (100), 255 (24), 254 (98), 226 (16), 208 (69), 148 (16), 133 (13), 105 (27), 77 (15), 76 (11); HRMS calcd. (%) for $C_{12}H_{13}BrO_4$: 299.9997; found: 299.9990.

General prodecure for the preparation of the diaryliodonium salts: The diaryliodonium salts were prepared following the procedures previously described.[4,5]

Diphenyliodonium tetrafluoroborate (2a).[5b] *m*-CPBA (24 mmol, 5.120 g) was dissolved in CH_2Cl_2 (80 mL). To the solution was added iodobenzene (21.6 mmol, 2.48 mL) followed by slow addition of

$BF_3{\cdot}OEt_2$ (54.4 mmol, 6.8 mL) at room temperature. The resulting yellow solution was stirred at room temperature for 30 min and then cooled to 0 ºC and $PhB(OH)_2$ (24 mmol, 2.960 g) was added. After 15 min of stirring at room temperature, the crude mixture was applied on a silica plug (20 g) and eluted with CH_2Cl_2 (2 x 100 mL) followed by CH_2Cl_2/MeOH (2 x 100 mL). The latter solution was concentrated and diethyl ether (40 mL) was added to the residue to induce precipitation. The solution was allowed to stir for 15 min, and then the solid was filtered and washed several times with diethyl ether and then dried *in vacuo*. White solid; m.p. = 133-135 ºC (Et_2O); IR (KBr): ν 1560, 1471, 1444, 1287, 1053, 985 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 7.54 (4H, t, *J* = 7.6 Hz), 7.68 (2H, t, *J* = 7.4 Hz), 8.25 (4H, d, *J* = 7.3 Hz); ^{13}C-NMR (75 MHz, DMSO-d_6): δ 116.4 (2C), 131.7 (4C), 132.0 (2C), 135.1 (4C); ^{19}F NMR (282 MHz, DMSO-d_6): δ -148.2 (br. s), -148.3 (dd, . *J* = 2.3, 1.2 Hz).

Bis(4-methoxyphenyl)iodonium tetrafluoroborate (2b).[5b] *m*-CPBA (6 mmol, 1.280 g) was dissolved in CH_2Cl_2 (20 mL). To the solution was added 1-iodo-4-methoxybenzene (5.4 mmol, 1.264 g). The mixture was placed then on a pre-heated oil bath at 80 ºC and stirred for 10 min. The mixture was cooled at -78 ºC. A 0 ºC cooled mixture of $BF_3{\cdot}OEt_2$ (13.6 mmol, 1.7 mL) and 4-methoxybenzeneboronic acid (6 mmol, 912 mg) in 20 mL of CH_2Cl_2 was added dropwise. The resulting solution was stirred at -78 ºC for 30 min Then was allowed to warm to room temperature and was applied on a silica plug (12 g) and eluted with CH_2Cl_2 (2 x 50 mL) followed by CH_2Cl_2/MeOH (2 x 50 mL). The latter solution was concentrated and diethyl ether (40 mL) was added to the residue to induce precipitation. The solution was allowed to stir for 15 min, and then the solid was filtered and washed several times with diethyl ether and then dried in vacuo. Grey solid; m.p. = 177-180 ºC (Et_2O); IR (KBr): ν 1572, 1487, 1441, 1406, 1302, 1258, 1177, 1062, 1022, 825 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 3.80 (6H, s), 7.07 (4H, d, *J* = 9.2 Hz), 8.13 (4H, d, *J* = 9.1 Hz); ^{13}C-NMR (75 MHz, DMSO-d_6): δ 55.7 (2C), 105.9 (2C), 117.3 (4C), 136.8 (4C), 161.8 (2C); ^{19}F NMR (282 MHz, DMSO-d_6): δ -148.2 (br. s), -148.3 (dd, *J* = 2.3, 1.1 Hz).

Bis(4-fluorophenyl)iodonium tetrafluoroborate (2c).[14] *m*-CPBA (2.9 mmol, 610 mg) was dissolved in CH_2Cl_2 (10 mL). To the solution was added 1-fluoro-4-iodobenzene (2.6 mmol, 300 µL) followed by slow addition of $BF_3{\cdot}OEt_2$ (6.5 mmol, 802 µL) at room temperature. The resulting solution was stirred at room temperature for 30 minutes and then cooled at 0 ºC, and 4-(fluorophenyl)boronic acid (2.9 mmol, 406 mg) was added. After 15 min of stirring at room temperature, the crude mixture was applied on a silica plug (20 g) and eluted with CH_2Cl_2 (2 x 100 mL) followed by CH_2Cl_2/MeOH (2 x 100 mL). The latter solution was concentrated and diethyl ether (40 mL) was added to the residue to induce precipitation. The solution was allowed to stir for 15 min, and then the solid was filtered and washed several times with diethyl ether and then dried *in vacuo*. White solid; m.p. = 97-98 ºC (Et_2O); IR (ATR): ν 1576, 1479, 1232, 1034, 996, 827 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 7.40-7.45 (4H, m), 8.30-8.35 (4H, m); ^{13}C-NMR (75 MHz, DMSO-d_6): δ 111.2 (2C), 119.36 (4C, d, $^2J_{(C,F)}$ = 22.8 Hz), 138.00 (4C, d, $^3J_{(C,F)}$ = 9.0 Hz), 163.99 (2C, d, $^1J_{(C,F)}$ = 251.4 Hz).

The appropriate iodoarene (5 mmol) was added to a stirred solution of *m*-CPBA (7.5 mmol, 1.6 g) in acetic anhydride (10 ml) and the solution was stirred for 1 h at room temperature after which 1,3,5-triisopropyl benzene (6.5 mmol, 1.32 mL) was added and the solution cooled to 0 ºC. Tetrafluoroboric acid (50 % aqueous, 10 mmol, 1.25 mL) was added over 15 min *via* syringe pump and the solution stirred at 0 ºC for 30 min before being allowed to warm to rt. After 6 h the solution was recooled to 0 ºC and water (100 mL) was slowly added with fast stirring. The solution was extracted with CH_2Cl_2 (2 x 50 ml) and the combined organic extracts dried ($MgSO_4$) and evaporated. The pure iodonium tetrafluoroborate salts were precipitated with Et_2O from a concentrated solution of hot CH_2Cl_2 and obtained by filtration followed by washed with generous amounts of Et_2O on the filter.

(4-Chlorophenyl)(2,4,6-triisopropylphenyl)iodonium tetrafluoroborate (2d).[16] White solid; m.p. = 180-181 ºC (Et_2O); IR (KBr): ν 1585, 1570, 1471, 1389, 1369, 1087, 1011, 817 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.26 (12H, d, *J* = 6.8 Hz), 1.29 (6H, d, *J* = 7.0 Hz), 2.79 (1H, hept, *J* = 6.9 Hz), 3.26 (2H, hept, *J* = 6.7 Hz), 7.20 (2H, s), 7.42 (2H, d, *J* = 8.9 Hz), 7.64 (2H, d, *J* = 8.9 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 23.6 (2C), 24.3 (4C), 32.4, 39.7 (2C), 108.6, 119.7, 125.5 (2C), 132.6 (2C), 133.9 (2C), 139.0, 152.7 (2C), 156.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ -146.7 (br. s), -146.8 (dd, *J* = 3.3, 1.6 Hz).

***o*-Tolyl(2,4,6-trisiopropylphenyl)iodonium tetrafluoroborate (2e).** White solid; m.p. = 154-155 ºC (Et_2O); IR (KBr): ν 1586, 1572, 1560, 1467, 1426, 1058, 979 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 1.21 (18H, 2 x d, *J* = 6.7 and 6.9 Hz, respectively), 2.63 (3H, s), 2.98 (1H, hept, *J* = 6.9 Hz), 3.31 (2H, hept, *J* = 6.9 Hz), 7.25-7.35 (3H, m), 7.50-7.60 (2H, m), 7.77 (1H, d, *J* = 7.9 Hz); ^{13}C-NMR (75 MHz, DMSO-d_6): δ 23.5 (2C), 24.0 (4C), 24.4, 33.3, 38.9 (2C), 119.4, 123.0, 124.8 (2C), 129.6, 132.0, 132.3, 135.4, 140.4, 151.1 (2C), 154.2. ^{19}F NMR (282 MHz, DMSO-d_6): δ -148.3 (br. s), -148.3 (dd, *J* = 2.3, 1.1 Hz); HRMS calcd. (%) for $C_{22}H_{30}I^+$: 421.1287; found: 421.1368.

Phenyl(2,4,6-triisopropylphenyl)iodonium trifluoromethanesulfonate (2f).[4a] 1,3,5-triisopropylbenzene (10 mmol, 2.38 mL) was added to a solution of iodobenzene (9 mmol, 1 mL) and *m*-CPBA (10 mmol, 2.64 g) in CH_2Cl_2 (40 mL). The solution was cooled to 0ºC. Trifluoromethanesulfonic acid (15 mmol, 1.31 mL) was added dropwise over 5 min and the mixture allowed to slowly warm to room temperature over 2 hours. The latter solution was concentrated and diethyl ether (40 mL) was added to the residue to induce precipitation. The solution was allowed to stir for 15 min, and then the solid was filtered and washed several times with diethyl ether and then dried *in vacuo*. White solid; m.p. = 169-170 ºC (Et_2O); IR (KBr): ν 1580, 1588, 1566, 1465, 1279, 1240, 1162, 1029, 881, 756 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 1.15-1.25 (18H, m), 2.90-3.05 (1H, m), 3.35-3.45 (2H, m), 7.32 (2H, s), 7.54 (2H, t, *J* = 7.5 Hz), 7.64 (1H, t, *J* = 7.4 Hz), 7.93 (2H, d, *J* = 7.3 Hz); ^{13}C-NMR (75 MHz, DMSO-d_6): δ 23.4 (2C), 23.9 (4C), 33.3, 38.6 (2C), 114.9, 123.0, 124.6 (2C), 131.7, 131.9 (2C), 133.9 (2C), 151.2 (2C), 154.2; ^{19}F NMR (282 MHz, DMSO-d_6): δ -77.8 (br. s), -148.3 (dd, . *J* = 2.3, 1.2 Hz).

Di-*p*-tolyliodonium trifluoromethanesulfonate (2g).[5a] *m*-CPBA (1.65 mmol, 285 mg) and 1-iodo-4-methylbenzene (1.5 mmol, 327 mg) were dissolved in CH_2Cl_2 (7 mL). Toluene (1.65 mmol, 176 µL) was added to the solution at room temperature followed by dropwise addition of TfOH (2 equiv.). The reaction mixture was

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stirred at room temperature during 10 minutes and subsequently concentrated under vacuum. Et_2O was added and the mixture was stirred at room temperature for 10 minutes to precipitate out an off-white solid. To ensure complete precipitation, the flask was stored in the freezer for at least 30 minutes before the solid was filtered off, washed with Et_2O and dried under vacuum. Grey solid; m.p. = 121-123 ºC (Et_2O); IR (ATR): ν 1481, 1242, 1156, 1024, 812, 796 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 2.33 (6H, s), 7.30-7.35 (4H, m), 8.05-8.10 (4H, m); ^{13}C-NMR (75 MHz, DMSO-d_6): δ 20.8 (2C), 113.0 (2C), 132.3 (4C), 135.0 (4C), 142.4 (2C).

General procedure for the synthesis of products 3: To a stirred solution of the corresponding acrylate **1** (0.25 mmol) in ethanol (0.75 mL) were added the corresponding diaryliodonium salt **2** (2 equiv) and PdO-Fe_3O_4 (25 mg, 2.5 mol% Pd). The mixture was stirred at 80 ºC for 5 h. The catalyst was removed by a magnet and the solvent was evaporated under reduced pressure. The corresponding products **3** were usually purified by chromatography on silica gel (hexane/ethyl acetate).

4-Phenyl-2*H*-chromen-2-one (3a).[14] White solid; m.p. = 98-100 ºC (Hexane/AcOEt); IR (KBr): ν 1737, 1607, 1558, 1444, 1367, 1247, 1181, 1115, 941, 884, 773, 744, 699 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.38 (1H, s), 7.20-7.30 (1H, m), 7.35-7.60 (8H, m); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 115.1, 117.3, 118.9, 124.1, 127.0, 128.4 (2C), 128.8 (2C), 129.6, 131.9, 135.2, 154.2, 155.6, 160.7; MS (EI) m/z (%): 222 (M^+, 100), 221 (M^+-1, 50), 194 (89), 166 (11), 165 (69), 164 (13), 163 (10), 139 (11); HRMS calcd. (%) for $C_{15}H_{11}O_2$: 223.0759; found: 223.0762.

4-(4-Fluorophenyl)-2*H*-chromen-2-one (3b).[14] White solid; m.p. = 128-130 ºC (Hexane/AcOEt); IR (ATR): ν 1724, 1605, 1507, 1190, 1158, 943, 840, 830 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.37 (1H, s), 7.20-7.30 (3H, m), 7.40-7.50 (4H, m), 7.57 (1H, ddd, *J* = 8.6, 7.3, 1.6 Hz respectively); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 115.3, 116.1 (2C, d, $^2J_{(C,F)}$= 21.8 Hz), 117.4, 118.9, 124.2, 126.7, 130.4 (2C, d, $^3J_{(C,F)}$= 8.4 Hz), 131.2 (d, $^4J_{(C,F)}$= 3.5 Hz), 132.0, 154.1, 154.6, 160.5, 163.5 (d, $^1J_{(C,F)}$= 250.2 Hz); MS (EI) m/z (%): 241 (M^++1, 11), 240 (M^+, 72), 239 (10), 213 (15), 212 (100), 207 (27), 184 (13), 183 (82).

4-(4-Methoxyphenyl)-2*H*-chromen-2-one (3c).[14] White solid; m.p. = 123-126 ºC (Hexane/AcOEt); IR (KBr): ν 1731, 1605, 1509, 1451, 1367, 1296, 1245, 1176, 1030, 929, 831, 752 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.90 (3H, s), 6.35 (1H, s), 7.00-7.05 (2H, m), 7.20-7.30 (1H, m), 7.35-7.45 (3H, m), 7.50-7.60 (2H, m); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 55.4, 114.3 (2C), 114.6, 117.3, 119.2, 124.1, 127.0, 127.5, 129.9 (2C), 131.8, 154.2, 155.3, 160.8, 160.9; HRMS calcd. (%) for $C_{16}H_{13}O_3$: 253.0865; found: 253.0863.

4-(4-Chlorophenyl)-2*H*-chromen-2-one (3d).[14] White solid; m.p. = 180-182 ºC (Hexane/AcOEt); IR (KBr): ν 1733, 1606, 1557, 1482, 1445, 1404, 1365, 1253, 1191, 1093, 945, 842, 750 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.36 (1H, s), 7.15-7.30 (1H, m), 7.35-7.45 (4H, m), 7.50-7.60 (3H, m). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 115.4, 117.4, 118.7, 124.3, 126.7, 129.2 (2C), 129.8 (2C), 132.1, 133.6, 136.0, 154.2, 154.4, 160.4; HRMS calcd. (%) for $C_{15}H_{10}O_2Cl$: 257.0369; found: 257.0371.

4-(*o*-Tolyl)-2*H*-chromen-2-one (3e).[14] Colourless oil; IR (KBr): ν 1731, 1604, 1564, 1483, 1451, 1365, 1276, 1254, 929 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.16 (3H, s), 6.32 (1H, s), 7.07 (1H, dd, *J* = 7.9 Hz, ^4J = 1.6 Hz), 7.15-7.20 (2H, m), 7.30-7.35 (2H, m), 7.35-7.45 (2H, m), 7.53 (1H, ddd, *J* = 8.6, 7.2 Hz, ^4J = 1.6 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 19.7, 115.7, 117.1, 119.4, 124.3, 126.1, 126.9, 128.4, 129.2, 130.5, 131.9, 134.7, 135.3, 153.8, 156.1, 160.8; HRMS calcd. (%) for $C_{16}H_{13}O_2$: 237.0916; found: 237.0908.

6-Fluoro-4-phenyl-2*H*-chromen-2-one (3f).[22] White solid; m.p. = 127-129 ºC (Hexane/AcOEt); IR (KBr): ν 1732, 1564, 1481, 1446, 1428, 1360, 1263, 1247, 1179, 971, 826 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.42 (1H, s), 7.10-7.20 (1H, m), 7.20-7.30 (1H, m), 7.35-7.50 (3H, m), 7.50-7.60 (3H, m); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 112.5 (d, $^2J_{(C,F)}$= 25.2 Hz), 116.0, 118.8 (d, $^3J_{(C,F)}$= 8.4 Hz), 119.3 (d, $^2J_{(C,F)}$= 24.5 Hz), 119.9 (d, $^3J_{(C,F)}$= 8.6 Hz), 128.2 (2C), 129.0 (2C), 129.9, 134.6, 150.3 (d, $^4J_{(C,F)}$= 2.0 Hz), 154.7 (d, $^4J_{(C,F)}$= 2.7 Hz), 158.6 (d, $^1J_{(C,F)}$= 243.9 Hz), 160.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ -116.9 (m); HRMS calcd. (%) for $C_{15}H_{10}O_2F$: 241.0665; found: 241.0668.

6,8-Di-*tert*-butyl-4-phenyl-2*H*-chromen-2-one (3g).[14] White solid; m.p. = 181-183 ºC (Hexane/AcOEt); IR (ATR): ν 1720, 1568, 1362, 1250, 869, 766, 704 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.26 (9H, s), 1.56 (9H, s), 6.35 (1H, s), 7.32 (1H, d, *J* = 2.3 Hz), 7.40-7.45 (2H, m), 7.50-7.55 (3H, m), 7.61 (1H, d, *J* = 2.3 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 30.0 (3C), 31.3 (3C), 34.7, 35.2, 114.4, 118.6, 121.5, 127.1, 128.4 (2C), 128.7 (2C), 129.4, 136.1, 137.5, 146.1, 150.9, 156.8, 160.6; MS (EI) m/z (%): 334 (M^+, 22), 320 (23), 319 (100), 207 (55).

6-Bromo-8-methoxy-4-phenyl-2*H*-chromen-2-one (3h). White solid; m.p. = 181-183 ºC (Hexane/AcOEt); IR (ATR): ν 1726, 1554, 1461, 1443, 1358, 1259, 1209, 1167, 1085, 865, 699 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.98 (3H, s), 6.40 (1H, s), 7.16 (1H, d, *J* = 2.3 Hz), 7.20 (1H, d, *J* = 2.3 Hz), 7.40-7.45 (2H, m), 7.50-7.55 (3H, m). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 56.6, 116.4, 116.5, 116.8, 120.6, 120.7, 128.3 (2C), 129.0 (2C), 129.9, 134.8, 143.1, 148.3, 154.8, 159.4; MS (EI) m/z (%): 332 (M^++2, 91), 331 (M^++1, 19), 330 (M^+, 92), 304 (32), 302 (35), 281 (29), 208 (22), 207 (100), 163 (12), 152 (83), 151 (24), 150 (15), 102 (17), 76 (23), 73 (10); HRMS calcd. (%) for $C_{16}H_{11}BrO_3$: 329.9892; found: 329.9883.

6-Fluoro-4-(4-methoxyphenyl)-2*H*-chromen-2-one (3i).[23] White solid; m.p. = 162-164 ºC (Hexane/AcOEt); IR (KBr): ν 1718, 1610, 1565, 1510, 1478, 1431, 1361, 1253, 1176, 1120, 1036, 824 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.90 (3H, s), 6.39 (1H, s), 7.06 (2H, d, *J* = 8.8 Hz), 7.20-7.30 (2H, m), 7.35-7.45 (3H, m with d at 7.40, *J* = 8.8 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 55.4, 112.6 (d, $^2J_{(C,F)}$= 25.2 Hz), 114.5 (2C), 115.5, 118.8 (d, $^3J_{(C,F)}$= 8.4 Hz), 119.2 (d, $^2J_{(C,F)}$= 24.5 Hz), 120.1 (d, $^3J_{(C,F)}$= 8.5 Hz), 126.9, 129.8 (2C), 150.3 (d, $^4J_{(C,F)}$= 2.0 Hz), 154.5 (d, $^4J_{(C,F)}$= 2.7 Hz), 158.6 (d, $^1J_{(C,F)}$= 243.4 Hz), 160.5, 161.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ -117.1 (m); HRMS calcd. (%) for $C_{16}H_{12}O_3F$: 271.0770; found: 271.0758.

6,8-Di-*tert*-butyl-4-(4-fluorophenyl)-2*H*-chromen-2-one (3j). White solid; m.p. = 112-114 ºC (Hexane/AcOEt); IR (ATR): ν 1727, 1601, 1507, 1223 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.26 (9H, s), 1.56 (9H, s), 6.33 (1H, s), 7.20-7.30 (3H, m), 7.40-7.50 (2H, m), 7.61 (1H, d, *J* = 2.3 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 30.0 (3C), 31.3 (3C), 34.8, 35.3, 114.6, 115.9 (d, $^2J_{(C,F)}$= 21.8 Hz, 2C), 118.6, 121.2, 127.3, 130.4 (d, $^3J_{(C,F)}$= 8.3 Hz, 2C), 132.1 (d, $^4J_{(C,F)}$= 3.1 Hz), 137.7, 146.2, 150.9,

155.7, 160.4, 163.3 (d, $^{1}J_{(C,F)}$= 250.0 Hz); MS (EI) m/z (%): 330 (M^+, 23), 338 (23), 337 (100); HRMS calcd. (%) for $C_{23}H_{25}FO_2$: 352.1839; found: 352.1830.

6-Bromo-4-(4-fluorophenyl)-8-methoxy-2*H*-chromen-2-one (3k). White solid; m.p. = 178-180 ºC (Hexane/AcOEt); IR (ATR): ν 1719, 1601, 1558, 1507, 1262, 1091, 835 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.98 (3H, s), 6.39 (1H, s), 7.11 (1H, d, *J* = 2.0 Hz), 7.21 (1H, d, *J* = 2.0 Hz), 7.25-7.30 (2H, m), 7.40-7.45 (2H, m); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 56.6, 116.2 (2C, d, $^{2}J_{(C,F)}$= 21.9 Hz), 116.5, 116.6, 116.9, 120.3, 120.6, 130.3 (2C, d, $^{3}J_{(C,F)}$= 8.4 Hz), 130.7 (d, $^{4}J_{(C,F)}$= 3.5 Hz), 143.1, 148.3, 153.7, 159.2, 163.6 (d, $^{1}J_{(C,F)}$= 250.7 Hz); MS (EI) m/z (%): 351 (M^++3, 18), 350 (M^++2, 100), 349 (M^++1, 21), 348 (M^+, 99), 323 (10), 322 (45), 321 (10), 320 (43), 279 (10), 277 (12), 184 (14), 181 (11), 171 (11), 170 (94), 169 (22), 120 (21), 85 (19); HRMS calcd. (%) for $C_{16}H_{10}BrFO_3$: 347.9797; found: 347.9786.

4-(*p*-Tolyl)-2*H*-chromen-2-one (3l).[14] Pale yellow solid; m.p. = 108-110 ºC (Hexane/AcOEt); IR (ATR): ν 3068, 1727, 1605, 1189, 940 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.46 (3H, s), 6.36 (1H, s), 7.20-7.25 (1H, m), 7.35-7.45 (5H, m), 7.50-7.60 (2H, m); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 21.3, 114.8, 117.3, 119.0, 124.0, 127.0, 128.4 (2C), 129.5 (2C), 131.8, 132.2, 139.9, 154.1, 155.7, 160.8; MS (EI) m/z (%): 237 (M^++1, 10), 236 (M^+, 92), 235 (M^+-1, 26), 221 (54), 209 (17), 208 (100), 207 (25), 179 (14), 178 (30), 176 (10), 165 (35), 152 (13), 89 (11), 76 (10), 63 (10).

6-Bromo-8-methoxy-4-(*p*-tolyl)-2H-chromen-2-one (3m). White solid; m.p. = 186-188 ºC (Hexane/AcOEt); IR (ATR): ν 1726, 1558, 1460, 1261, 1091 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.46 (3H, s), 3.98 (3H, s), 6.38 (1H, s), 7.15-7.30 (2H, m), 7.30-7.35 (4H, m); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 21.4, 56.6, 116.1, 116.4, 116.8, 120.7, 120.9, 128.3 (2C), 129.7 (2C), 131.9, 140.1, 143.1, 148.3, 154.9, 159.5; MS (EI) m/z (%): 347 (M^++3, 24), 346 (M^++2, 100), 345 (M^++1, 17), 344 (M^+, 95), 329 (13), 318 (32), 316 (36), 222 (12), 207 (22), 194 (10), 166 (35), 165 (56), 164 (13), 163 (10), 139 (10), 115 (16); HRMS calcd. (%) for $C_{17}H_{13}BrO_3$: 344.0048; found: 344.0029.

General procedure for the synthesis of products 5: To a stirred solution of the corresponding α,β-unsaturated ester **4** (0.25 mmol) in ethanol (0.75 mL) was added the corresponding diaryliodonium salt **2** (2 equiv) and PdO-Fe_3O_4 (25 mg, 2.5 mol% Pd). The mixture was stirred at 80 ºC for 5 h. The catalyst was removed by a magnet and the solvent was evaporated under reduced pressure. The corresponding products **5** were usually purified by bulb-to-bulb distillation.

Ethyl cinnamate (5a).[24] Colorless oil; IR (ATR): ν 1707, 1637, 1450, 1165, 1036, 765 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.33 (3H, t, *J* = 7.1 Hz), 4.26 (2H, q, *J* = 7.1 Hz), 6.43 (1H, d, *J* = 16.0 Hz), 7.35-7.40 (3H, m), 7.50-7.55 (2H, m), 7.69 (1H, d, *J* = 16.0 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 14.2, 60.4, 118.2, 127.9 (2C), 128.8 (2C), 130.1, 134.4, 144.5, 166.9; MS (EI) m/z (%): 176 (M^+, 31), 148 (13), 147 (16), 132 (11), 131 (100), 103 (44), 102 (12), 77 (28), 51 (10).

Ethyl 3,3-diphenylacrylate (5b).[25] Brown oil; IR (ATR): ν 1719, 1617, 1574 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.1 (3H, t, *J* = 7.1 Hz), 4.05 (2H, q, *J* = 7.1 H), 6.36 (1H, s), 7.20-7.40 (2H and 8H respectively, 2m); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 13.9, 60.0, 117.5, 127.8 (2C), 128.0, 128.2 (2C), 128.3 (2C), 129.1 (2C), 129.3, 139.0, 140.8, 156.4, 166.1; MS (EI) m/z (%): 253 (M^++1, 15), 252 (M^+, 83), 251 (M^+-1, 18), 223 (15), 211 (28), 208 (12), 207 (73), 180 (45), 179 (60), 178 (100), 177 (16), 176 (21), 165 (20), 152 (27), 151 (13), 105 (18), 77 (18).

(*E/Z*)-Methyl 3-phenyl-3-(*p*-tolyl)acrylate (5c).[2] Pale yellow oil; IR (ATR): ν 1721, 1608, 1509, 1492, 1263, 1160, 1150, 815 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.35 (3H, s), 2.39 (3H, s), 3.60 (3H, s), 3.63 (3H, s), 6.32 (1H, s), 6.35 (1H, s), 7.10-7.40 (18H, m); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 21.2, 21.3, 51.2 (2C), 115.8, 116.4, 127.8 (2C), 128.0, 128.1, 128.8 (2C), 128.3 (2C), 128.4 (2C), 128.6 (2C), 129.0 (4C), 129.1 (2C), 129.4, 135.7, 137.9, 138.1, 139.0, 139.7, 141.1, 157.1, 157.4, 166; MS (EI) m/z (%): 253 (M^++1, 17), 252 (M^+, 100), 251 (M^+-1, 35), 222 (16), 221 (97), 194 (13), 193 (29), 192 (14), 191 (19), 189 (15), 179 (16), 178 (57), 165 (17), 115 (23).

(*E/Z*)-Methyl 3-(4-methoxyphenyl)-3-phenylacrylate (5d).[26] Pale yellow oil; IR (ATR): ν 2843, 1719, 1601, 1509, 1247, 1160, 1147, 1031, 831 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.60 (s, 3H), 3.64 (s, 3H), 3.81 (s, 3H), 3.85 (s, 3H), 6.28 (s, 1H), 6.32 (s, 1H), 6.84 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 7.15-7.40 (m, 14H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 51.2 (2C), 55.2, 55.4, 113.2, 113.8, 114.6, 116.2, 127.9 (2C), 128.1 (2C), 128.3 (2C), 128.6 (2C), 129.0 (2C), 129.4 (2C), 129.8 (2C), 130.9 (2C), 133.1, 139.0, 141.5, 153.9, 156.9, 157.1, 159.8, 160.8, 166.6 (2C); MS (EI) m/z (%): 269 (M^++1, 12), 268 (M^+, 100), 267 (M^+-1, 13), 238 (13), 237 (71), 210 (16), 209 (15), 195 (11), 194 (16), 178 (10), 166 (16), 165 (50), 135 (21).

Conclusions

In conclusion, we have demonstrated that palladium(II) oxide impregnated on magnetite is a cheap, selective, versatile and very active catalyst for the Heck-arylation/cyclization reaction of o-hydroxyphenylacrylates and diaryliodonium salts using ethanol, as non-toxic and bio-renewable solvent. This is the first report of this reaction using a heterogeneous palladium catalyst and with the lowest amount ever used (2.5 mol%). The magnetic properties of the catalyst allow its separation from the reaction media very easily, not being possible the recyclability of the same, due to the practically total reduction of the palladium(II) oxide, the sinterization of the same particles on the surface of the magnetite and iodine species poisoning.

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