Regiospecific synthesis of functionalised 1,3-diarylisobenzofurans *via* palladium- and rhodium-catalysed reaction of boronic acids with *o*-acylbenzaldehydes under thermal or microwave activation†

Jérôme Jacq, Bernard Bessières, Cathy Einhorn and Jacques Einhorn*

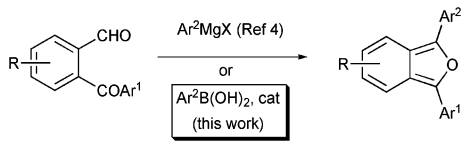
Received 11th May 2010, Accepted 23rd July 2010
DOI: 10.1039/c0ob00110d

Variously substituted 1,3-diarylisobenzofurans have been regiospecifically prepared *via* palladium- and rhodium-catalysed reaction of functionalised boronic acids onto *o*-acylbenzaldehydes. Rhodium catalysis has furthermore been improved using microwave activation. Thus, isobenzofurans containing aryl groups substituted by halogens, unprotected amine, alcohol and even aldehyde groups, have been obtained directly in good to satisfactory yields. Divergent results have been observed when palladium-, rhodium- and MW-activated rhodium-catalysis was applied to the reaction of phenylboronic acid with an iodinated *o*-acylbenzaldehyde, leading principally to Suzuki coupling product and/or to iodinated isobenzofuran.

Introduction

Benzo[*c*]furans (or isobenzofurans) constitute a class of heterocyclic compounds behaving as highly reactive dienes,[1] their Diels–Alder reaction with dienophiles for the synthesis of natural and non-natural products being well documented.[2] We became interested in the synthesis of variously functionalised 1,3-diarylisobenzofurans, as precursors of functional *N*-hydroxyphthalimide analogues possessing interesting catalytic and biological properties.[3] In this context, we have recently developed a fairly general synthesis of functionalised 1,3-diarylisobenzofurans.[4] Our approach was based on chemoselective addition of aryl Grignard reagents to the aldehyde function of *o*-aroylbenzaldehydes, themselves readily obtained by lead(IV) acetate oxidation of *N*-aroylhydrazones of salicylaldehydes (Kotali reaction).[5] This method allows the synthesis of 1,3-diarylisobenzofurans bearing a broad diversity of functional groups, including nitro, halogen, methoxy and ester groups, at any position of the 1,3-diarylisobenzofuran backbone. It is also totally regiospecific, as the position of each functional group is directly related to its original position on the *N*-aroylhydrazide-, salicylaldehyde-, or Grignard reagent aromatic rings. Noteworthy, it allows straightforward functionalisation of the central carbocycle of the isobenzofuran core, leading to previously unknown isobenzofuran derivatives.

Although functional aryl Grignard reagents, including highly functionalised ones described by Knochel,[6] can be used without difficulties, some limitations still remain related to the high reactivity and/or low stability of some Grignard reagents, making necessary protection of some functional groups and/or careful control of the reaction conditions. Consequently, we became interested in replacing Grignard reagents by other organometallic species able to overcome the susmentioned limitations. In this context, boronic acids possess ideal features such as low toxicity, ease of manipulation and very high functional groups tolerance (Scheme 1). Moreover, a broad diversity of aryl- and heteroarylboronic acids are now commercially available. Boronic acids do not add spontaneously to aldehydes or ketones, but they do so using catalytic systems involving various transition metal complexes.[7]

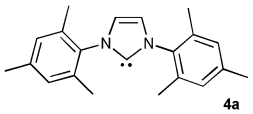


Scheme 1 Synthesis of 1,3-diarylisobenzofurans from *o*-acylbenzaldehydes *via* Grignard *vs.* boronic acid addition.

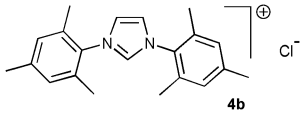
Herein we report a new approach to 1,3-diarylisobenzofurans *via* palladium and rhodium catalysed reaction of arylboronic acids with *o*-ketoaldehydes resulting from the Kotali reaction, associated or not with microwave activation.

Results and discussion

Among various catalytic activation methods for arylboronic addition to carbonyl compounds, we choose two of them, owing to their efficiency, broad scope and convenience: catalysis by palladium(II) chloride in the presence of tri-1-naphthylphosphine reported by Wu and Cheng,[7o] and catalysis by rhodium(III) chloride in the presence of an *N*-heterocyclic carbene **4a** ligand formed *in situ* from imidazolium salt **4b**, as reported by Fürstner.[7h]



4a



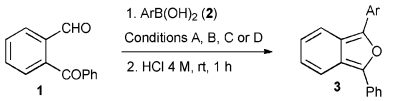
4b

In our first experiment, *o*-benzoylbenzaldehyde **1** was reacted with 2 equiv of phenylboronic acid **2a** in the presence of 5 mol% $PdCl_2$, 5 mol% P(1-Nap)$_3$ and 3 equiv of K_2CO_3 in THF at 60 °C for 24 h. After acidic treatment,[8] 1,3-diphenylisobenzofuran

Synthèse et Réactivité en Chimie Organique (SERCO) Département de Chimie Moléculaire (DCM) UMR-5250, ICMG FR-2607, CNRS Université Joseph Fourier, BP-53, 38041, Grenoble Cedex 9, France. E-mail: Jacques.Einhorn@ujf-grenoble.fr; Fax: (+33)4-7651-4836; Tel: (+33)4-7651-4839

† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of all new compounds. See DOI: 10.1039/c0ob00110d

Table 1 Synthesis of 1,3-diarylisobenzofurans *via* palladium- and rhodium-catalysed reaction of boronic acids with ketoaldehyde **1**



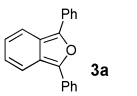
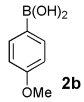
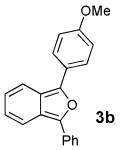
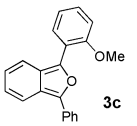
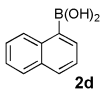
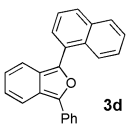
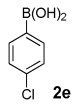
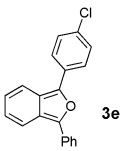
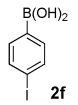
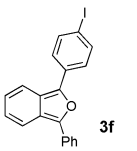
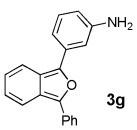
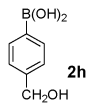
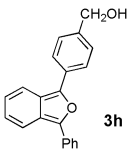
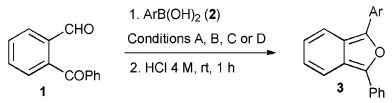
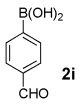
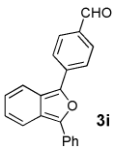
Entry	Boronic acid	Conditions[a]	Isobenzofuran	Yield (%)[b]
1	 **2a**	A[c]	 **3a**	90
2		B[d]		89
3	 **2b**	A	 **3b**	95
4		B		92
5	 **2c**	A[e]	 **3c**	(93)
6		B[f]		(20)
7		C		62 (90)
8	 **2d**	A[e]	 **3d**	(96)
9		B[f]		(20)
10		C		60 (92)
11	 **2e**	C	 **3e**	96
12	 **2f**	A	 **3f**	—
13		B		88
14		D		(10)
15	 **2g**	A	 **3g**	—
16		B		(25)
17		C		36 (90)
18		D		—
19	 **2h**	A[e]	 **3h**	(28)
20		B[f]		(25)
21		C		90 (96)
22		D		(3)

Table 1 *(Contd.)*



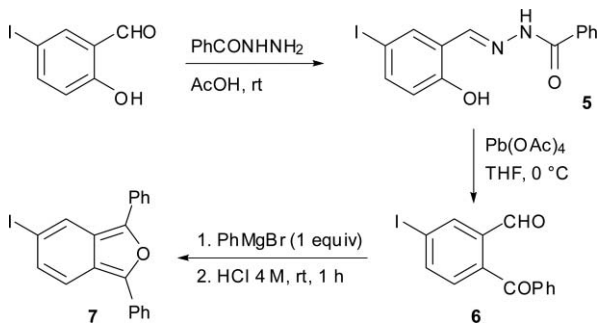
Entry	Boronic acid	Conditions[a]	Isobenzofuran	Yield (%)[b]
23	 **2i**	A[g]	 **3i**	(18)
24		B[g]		(16)
25		C[g]		33 (45)
26		D[g]		(4)

[a] Conditions A: Boronic acid (2 equiv), 10 mol% $PdCl_2$, 10 mol% P(1-Nap)$_3$, K_2CO_3 (3 equiv), THF at 60 °C for 24 h. Conditions B: Boronic acid (2 equiv), 2 mol% $RhCl_3 \cdot 3H_2O$, 2 mol% **4b**, MeONa (1 equiv), DME/H_2O 4 : 1 at 90 °C for 24 h. Conditions C: as conditions B, replacing heating by MW irradiation (150 W) at 150 °C for 20 min. Conditions D: as conditions A, replacing heating by MW irradiation (150 W) at 150 °C for 20 min. [b] Isolated yield; yields determined by ^{1}H NMR of the crude using an internal standard are given in parentheses. [c] 5 mol% of catalyst and ligand. [d] 1 mol% of catalyst and ligand. [e] 20 mol% of catalyst and ligand. [f] 4 mol% of catalyst and ligand. [g] One equiv of boronic acid.

3a was isolated in 90% yield (entry 1, Table 1). An experiment was next performed using the conditions reported by Fürstner: **1** was reacted with 2 equiv of phenylboronic acid **2a** in the presence of 1 mol% $RhCl_3$, 1 mol% NHC precursor **4b** and 1 equiv of MeONa in DME/water. Heating at 90 °C for 24 h was necessary to obtain complete conversion of the starting material and isobenzofuran **3a** was obtained in 89% yield after acidic workup (entry 2, Table 1). Using 4-methoxyphenylboronic acid **2b**, complete conversions required twofold amounts of catalysts and ligands: thus isobenzofuran **3b** was obtained in 95% yield using 10 mol% $PdCl_2$ and P(1-Nap)$_3$ and in 92% yield using 2 mol% $RhCl_3$ and imidazolium salt **4b** (entries 3–4, Table 1). We next examined the case of more sterically hindered 2-methoxyphenylboronic acid **2c**. With 10 mol% catalyst and ligand, palladium catalysed reaction of **2c** (2 equiv) with **1** at 60 °C furnished isobenzofuran **3c**, but large amounts of unreacted starting materials remained even after prolonged reaction times. Good conversions were observed when 20 mol% $PdCl_2$ and P(1-Nap)$_3$ were used, yielding 93% (NMR calculated) of **3c** after 24 h. Rhodium catalysis was even more sluggish: using 4 mol% of both $RhCl_3$ and imidazolium salt **4b**, only 20% of isobenzofuran **3c** was formed after 24 h reaction at 90 °C. Gratifyingly, microwave activation had a dramatic effect on this reaction: using 2 mol% of $RhCl_3$ and imidazolium salt **4b** and submitting the reaction medium to microwave irradiation for 20 min (150 °C, 150 W power) gave isobenzofuran **3c** in 90% yield.[9] Due to air oxidation, **3c** was obtained in only 62% after column chromatography purification (entries 5–7, Table 1). Similar trends were found with 1-naphthylboronic acid **2d** (entries 8–10, Table 1). We next examined the case of arylboronic acids bearing various sensitive functional groups. Microwave activated rhodium-catalysed reaction using 4-chlorophenylboronic acid **2e** gave isobenzofuran **3e** in 96% yield (entry 11, Table 1). With 4-iodophenylboronic acid **2f**, palladium catalysis failed to give the expected product, whereas rhodium catalysis under classical activation gave iodinated isobenzofuran **3f** in 88% yield. Considering the complete failure of palladium catalysis in this case, the reaction was attempted using microwave heating.[9] A poor yield of 10% of isobenzofuran **3f** was obtained after 20 min irradiation (150 °C, 150 W power) (entries 12–14,

Table 1). With boronic acid bearing a free amino group **2g**, palladium catalysis failed, both under classical conditions and MW activation, whereas rhodium catalysis gave air-sensitive isobenzofuran **3g** in 25% calculated yield under classical activation and in 90% calculated yield under MW activation (36% isolated yield), (entries 15–18, Table 1). The case of a free hydroxymethyl functionalised boronic acid **2h** was also examined. Isobenzofuran **3h** has been obtained in resp 28, 25, 96 and 3% yields (NMR calculated) *via* palladium-, rhodium-, MW-activated rhodium- and MW-activated palladium catalysis (entries 19–22, Table 1). Experiment of entry 21 gave **3h** in 90% isolated yield. We next examined the highly challenging case of an aldehyde functionalised boronic acid **2i**. To our delight, isobenzofuran **3i** bearing a free aldehyde group was formed in respectively 18, 16, 45 and 4% yields (NMR calculated) *via* palladium-, rhodium-, MW-activated rhodium- and MW-activated palladium catalysis (entries 23–26, Table 1). Isobenzofuran **3i** was isolated in 33% yield from the experiment reported in entry 25. The obtention of **3i** is remarkable as it requires the reaction of ketoaldehyde **1** with an organometallic species bearing itself a free aldehyde function.

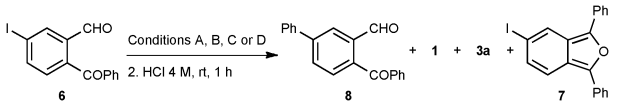
We were also interested in the synthesis of isobenzofurans iodinated on the central carbocycle. Ketoaldehyde **6** is readily available in 68% overall yield from 5-iodosalicylaldehyde[10] *via* lead(IV) acetate oxidation of its *N*-benzoylhydrazide **5**. The reaction of phenylmagnesium bromide with **6** gave isobenzofuran **7** in 75% isolated yield (Scheme 2).



Scheme 2 Synthesis of iodinated isobenzofuran **6** *via* a Kotali reaction/Grignard addition sequence.

Contrastingly, the implementation of palladium- and rhodium-catalysed reaction of phenylboronic acid with ketoaldehyde **6** led to some surprising results, reported in Table 2. ^{1}H NMR analysis of the crude product after palladium catalysis gave a 12 : 88 ratio of starting **6** and 5-phenyl-2-benzoylbenzaldehyde **8**, resulting from a Suzuki coupling reaction between boronic acid **2a** with iodo compound **6** (entry 1, Table 2). Rhodium catalysis under classical heating gave a 52 : 47 : 1 ratio of starting **6**, coupling product **8**[11] and de-iodinated compound **1** (entry 2, Table 2). The reaction went to completion when twice the amount of catalyst and ligand were used and the reaction carried on for 48 h. A 97 : 3 ratio of **8** and **1** was determined and **7** was obtained in 74% isolated yield after purification (entry 3, Table 2). The results where dramatically different using rhodium-catalysis with MW activation: reaction at 150 °C for 20 min led to a total consumption of starting **6** and to a 43 : 57 mixture of de-iodinated and iodinated isobenzofuran **3a** and **7** (entry 4, Table 2). Reducing the reaction

Table 2 Palladium- and rhodium-catalysed reaction of phenylboronic acid with ketoaldehyde **6**



Entry	Conditions[a]	T/°C	Time/h	Ratio of products[b]				
				6	**8**	**1**	**3a**	**7**
1	A	60	24 h	12	88	—	—	—
2	B	90	24 h	52	47	1	—	—
3	B[c]	90	48 h	—	97[d]	3	—	—
4	C	150	20 min	—	—	—	43	57
5	C	90	20 min	62	—	—	—	38
6	C	90	80 min	25	4	1	—	70[e]
7	D	150	20 min	38	48	—	—	14
8	D	90	20 min	48	42	—	—	10
9	D	90	80 min	42	49	—	—	9

[a] Condition A: Boronic acid (2 equiv), 10 mol% $PdCl_2$, 10 mol% P(1-Nap)$_3$, K_2CO_3 (3 equiv) in THF. Condition B: Boronic acid (2 equiv), 2 mol% $RhCl_3 \cdot 3H_2O$, 2 mol% **4b**, MeONa (1 equiv) in DME/H_2O 4 : 1. Condition C: as condition B, replacing heating by MW irradiation. Condition D: as condition A, replacing heating by MW irradiation. [b] Determined by ^{1}H NMR. [c] Reaction performed with 3 equiv MeONa. [d] Isolated in 74% yield. [e] Isolated in 68% yield.

temperature to 90 °C led to an uncomplete reaction but with iodinated isobenzofuran **7** as the sole product (entry 5, Table 2). At last, when MW irradiation was carried on for 80 min at 90 °C, a 25 : 4 : 1 : 70 ratio of starting **6**, coupling product **8**, ketoaldehyde **1** and isobenzofuran **7** was determined, and isobenzofuran **7** was isolated in 68% yield (entry 6, Table 2). Comparison between experiments reported in entries 3 and 6 is particularly intriguing: they only differ in their heating method (classical *vs.* MW heating), yet their outcome is completely different: classical heating gives almost exclusively Suzuki-type coupling product **8**, whereas MW favours almost exclusively addition of the boronic acid to the aldehyde function of **6**, yielding isobenzofuran **7** without affecting the carbon-iodine bond.

The explanation for this selectivity switch might be ascribed to the formation of different catalytic species from the initial $RhCl_3$/NHC mixture according to the heating process.[12] Thus the catalyticaly active hydroxorhodium(I) species (L_nRh^I–OH)[13] for the addition on carbonyls would be preferentially formed under MW irradiation whereas the active L_nRh^I–Cl species for the Suzuki cross coupling,[11e,11m] would be produce mostly under classical heating. This hypothesis would also explain the yield enhancement reported in Table 1 (entries 6–7, 9–10, 16–17, 20–21 and 24–25). Considering this remarkable switching involving rhodium catalysis, we also examined the case of MW-activated palladium catalysis. Irradiation for 20 min at 150 °C (150 W power) resulted in a 38 : 48 : 14 ratio of starting **6**, Suzuki coupling compound **8** and iodinated isobenzofuran **7** (entry 7, Table 2). Similar ratios were obtained from experiments performed at 90 °C for 20 and 80 min (entries 8–9, Table 2). Thus, in the case of palladium catalysis, no complete reversal of the reaction outcome was observed. Nevertheless, whereas classical heating gave Suzuki coupling compound **8** as the sole reaction product, some iodinated isobenzofuran **7** was also formed under MW.

Conclusions

The present report describes a new regiospecific synthesis of functionalised 1,3-diarylisobenzofurans *via* palladium- and rhodium-catalysed reaction of arylboronic acids with readily available *o*-aroylbenzaldehydes. Rhodium catalysis has furthermore been improved using microwave activation. Whereas in simple cases, palladium-, rhodium- and MW activated rhodium-catalysis all lead to excellent yields of isobenzofuranes, larger differences between the three methods appear with sterically hindered boronic acids or when sensitive functional groups are present. In the last case, MW activated rhodium-catalysis is of particular interest, as it allows the presence of free amino-, hydroxymethyl- and even aldehyde functions, giving the corresponding isobenzofurans in satisfactory to good yields, thus avoiding tedious protection-deprotection sequences. In comparison, MW irradiation had much less effect on palladium catalysed reactions. Dramatic differences in the reaction outcome using rhodium- *vs.* MW activated rhodium-catalysis have also been evidenced when phenylboronic acid was reacted with a iodinated *o*-benzoylbenzaldehyde, making questionable whether or not the same catalytic species are formed in both conditions. Further experiments will be undertaken in order to gain more evidences on these points.

Experimental

General

Commercial reagents were used without further purification unless otherwise stated. Solvents were dried prior to use according to standard methods. Reactions were monitored by thin layer chromatography (TLC) using commercial aluminium-backed silica gel plates. Plates were visualized under UV light (254 nm), followed by heating the plate after treatment with a 10% ethanolic solution of phosphomolybdic acid. Column chromatography were performed over silica gel 60 (40–60 mesh). Elemental analysis were performed at the microanalysis service of the Département de Chimie Moléculaire, Grenoble, France. Melting points were recorded on a Büchi B35 apparatus and are uncorrected. IR spectra were recorded on a Nicolet Impact-400 Fourier transform IR spectrometer (FTIR), using ATR (Attenuated Total Reflection) for solid compounds and the data are reported in reciprocal centimetres (cm^{-1}).^{1}H NMR Spectra (300 or 400 MHz), ^{13}C NMR spectra (75 or 100 MHz) were recorded on either a Bruker Advance 300 or Advance 400 spectrometers. Chemical shifts are given in ppm (d) and were referenced to the internal solvent signal or to TMS used as an internal standard. Low Resolution Mass Spectra (LRMS) were recorded on a Brücker Esquire 3000 plus (ESI) or a ThermoFinnigan PolarisQ ion-trap spectrometer, using DCI. High Resolution Mass Spectra (HRMS) were recorded on Thermoquest Orbitrap spectrometer at the LCOSB, UMR 7613, Université Pierre et Marie Curie, Paris. Microwave irradiation were performed on a monomode CEM Discover apparatus. (0–20 bar operating pressure, 15–300W power range from a 2.45 MHz magnetron). The reactions were carried out in a 5 mL vial equipped with a magnetic stirrer and the temperature was monitored by an internal IR sensor. The samples were irradiated at a maximum power of 150 W, and when the set temperature was reached (usually in less than 2 min), the irradiation power was temperature controlled for the duration of the experiment.

General methods for the Pd– and Rh– catalysed reactions

Condition A. A 10 mL vial was charged with $PdCl_2$ (4.4 mg, 0.025 mmol, 10 mol%), tri-1-naphthylphosphine (10.3 mg, 0.025 mmol, 10 mol%), arylboronic acid **2** (0.5 mmol, 2 equiv), *o*-acylbenzaldehyde (0.25 mmol, 1 equiv), K_2CO_3 (135 mg, 0.75 mmol, 3 equiv), and THF (2.5 mL). The reaction vial was purged with argon and sealed. The mixture was heated at 65 °C for 24 h. The resulting mixture was cooled to room temperature. An aqueous solution of HCl (4 M, 1 mL) was slowly added. The mixture (under argon) was stirred for 1h, then extracted several times with ether. The combined organic extracts were washed with a saturated solution of $NaHCO_3$, with brine and dried over Na_2SO_4 and the solvent was removed under reduced pressure. Yields were determined from the crude product by ^{1}H NMR. Isolated yields were determined after purification by column chromatography.

Condition B. A mixture of arylboronic acid **2** (0.5 mmol, 2 equiv), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (2.1 mg, 0.005 mmol, 2 mol%), sodium methoxide (13.5 mg, 0.25 mmol, 1 equiv), *o*-acylbenzaldehyde (0.25 mmol, 1 equiv) and $RhCl_3{\cdot}3H_2O$ (1.3 mg, 0.005 mmol, 2 mol%) in DME (2.0 mL) and water (0.5 mL) was heated at 90 °C in a sealed vial for 24 h. The resulting mixture was cooled to room temperature. An aqueous solution of HCl (4 M, 1 mL) was slowly added. The mixture (under argon) was stirred for 1h, then extracted several times with ether. The combined organic extracts were washed with a saturated solution of $NaHCO_3$, with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. Yields were determined from crude products by ^{1}H NMR. Isolated yields were determined after purification by column chromatography.

Condition C. A mixture of arylboronic acid **2** (0.5 mmol, 2 equiv), 1,2-bis(2,6-diisopropylphenyl)imidazolium chloride (2.1 mg, 0,005 mmol, 2 mol%), sodium methoxide (13.5 mg, 0.25 mmol, 1 equiv), *o*-acylbenzaldehyde (0.25 mmol, 1 equiv) and $RhCl_3{\cdot}3H_2O$ (1.3 mg, 0.005 mmol, 2 mol%) in DME (2.0 mL) and water (0.5 mL) were charged in a 5 mL microwave vial. The mixture was heated at 150 °C for 20 min (150 W). The resulting mixture was cooled to room temperature. An aqueous solution of HCl (4 M, 1 mL) was slowly added. The mixture (under argon) was stirred for 1h, then extracted several times with ether. The combined organic extracts were washed with a saturated solution of $NaHCO_3$, with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. Yields were determined from crude products by ^{1}H NMR. Isolated yields were determined after purification by column chromatography.

Condition D. A mixture of arylboronic acid **2** (0.5 mmol, 2 equiv), *o*-acylbenzaldehyde (0.25 mmol, 1 equiv), $PdCl_2$ (4.4 mg, 0.025 mmol, 10 mol%), tri-1-naphthylphosphine (10.3 mg, 0.025 mmol, 10 mol%), K_2CO_3 (135 mg, 0.75 mmol, 3 equiv), and THF (2.5 mL). were charged in a 5 mL microwave vial. The vial was purged with argon and sealed. The mixture was heated at 150 °C for 20 min (150 W). The resulting mixture was cooled to room temperature. An aqueous solution of HCl (4 M, 1 mL) was slowly added. The mixture (under argon) was stirred for 1h,

then extracted several times with ether. The combined organic extracts were washed with a saturated solution of $NaHCO_3$, with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. Yields were determined from crude products by ^1H NMR. Isolated yields were determined after purification by column chromatography.

1,3-Diphenylbenzo[c]furan (***3a***). Yellow solid; mp 127–128 °C (from ethyl acetate–pentane) [lit.[14] 129–131 °C]; δ_H ($CDCl_3$, 300 MHz) 7.03 (dd, J = 6.9, 2.9 Hz, 2H), 7.28 (t, J = 7.4 Hz, 2H), 7.47 (t, J = 7.8 Hz, 4H), 7.84, (dd, J = 6.9, 2.9 Hz, 2H), 7.95 (d, J = 7.3 Hz, 4H). δ_C ($CDCl_3$, 75 MHz) 120.3, 122.3, 125.0, 125.3, 127.0, 129.1, 131.9, 144.0.

1-(4-Methoxyphenyl)-3-phenylbenzo[c]furan (***3b***). Purification by flash chromatography, using dichloromethane as eluant, gave a yellow solid; mp 92 °C [lit.[15] 95 °C]; δ_H ($CDCl_3$, 300 MHz) 3.88 (s, 3H), 6.95–7.05 (m, 4H), 7.25–7.30 (m, 1H), 7.45–7.50 (m, 2H), 7.77–7.81 (m, 2H), 7.83–7.95 (m, 4H). δ_C ($CDCl_3$, 75 MHz) 55.5, 114.6, 120.2, 120.4, 121.2, 122.2, 124.7, 124.9, 125.3, 126.5, 126.7, 129.3, 132.0, 143.0, 144.3, 159.0.

1-(2-Methoxyphenyl)-3-phenylbenzo[c]furan (***3c***). Purification by flash chromatography, using dichloromethane as eluant, gave a green-yellow oil; ν_{max} (film) 3056, 2929, 2834, 1597, 1579, 1491, 1465 1246, 1180, 1023, 753; δ_H ($CDCl_3$, 300 MHz) 3.92 (s, 3H), 6.89–7.11 (m, 4H), 7.22–7.35 (m, 2H), 7.45 (m, 2H), 7.66 (d, J = 8.7 Hz, 1H), 7.75 (dd, J = 7.7, 1.7 Hz, 1H), 7.80 (d, J = 8.7 Hz, 1H), 7.91–7.94 (m, 2H); δ_C ($CDCl_3$, 75 MHz) 55.7, 111.8, 119.7, 121.1, 122.0, 123.6, 123.8, 124.9, 125.1, 126.7, 129.0, 129.1, 129.8, 132.1, 134.4, 142.2, 144.4, 156.1; m/z (CI^+) 301 ($[M+H]^+$, 100), 317 ($[M+CH_5]^+$, 30); HRMS (ESI) m/z: calcd for $C_{21}H_{16}O_2$: 300.11448 $[M]^+$; found: 300.11485.

1-(1-Naphthyl)-3-phenylbenzo[c]furan (***3d***). Purification by flash chromatography, using dichloromethane as eluant, gave a yellow oil;[16] δ_H ($CDCl_3$, 300 MHz) 7.01–7.11 (m, 2H), 7.31–7.36 (m, 1H), 7.49–7.62 (m, 6H), 7.86–8.04 (m, 6H), 8.41–8.45 (m, 1H). δ_C ($CDCl_3$, 75 MHz) 120.0, 120.5, 121.7, 124.1, 124.8, 125.5, 125.6, 126.3, 126.8, 127.0, 127.5, 128.6, 128.8, 129.1, 129.7, 131.2, 132.0, 134.4, 144.6, 144.8.

1-(4-Chlorophenyl)-3-phenylbenzo[c]furan (***3e***). Purification by flash chromatography, using dichloromethane as eluant, gave a yellow solid; mp 113 °C [lit.[17] 111–112 °C]; δ_H ($CDCl_3$, 400 MHz) 7.00–7.04 (m, 1H), 7.28–7.57 (m, 5H), 7.60–7.70 (m, 4H) 7.79–7.93 (m, 3H). δ_C ($CDCl_3$, 75 MHz) 119.8, 120.3, 124.9, 125.2, 125.6, 125.8, 127.1, 128.4, 129.0, 130.4, 130.6, 131.1, 133.1.

1-(4-Iodophenyl)-3-phenylbenzo[c]furan (***3f***). Purification by flash chromatography, using cyclohexane/EtOAc (9/1) as eluant, gave a yellow solid; mp 135–137 °C (from ethyl acetate–pentane) [lit.[4] 135–137 °C]; δ_H ($CDCl_3$, 300 MHz) 7.01–7.08 (m, 2H), 7.29–7.35 (m, 1H), 7.47–7.52 (m, 2H), 7.66–7.69 (m, 2H), 7.76–7.87 (m, 4H), 7.92–7.96 (m, 2H).). δ_C ($CDCl_3$, 75 MHz) 91.8, 119.9, 120.4, 122.3, 122.7, 125.0, 125.3, 125.7, 126.2, 127.3, 129.1, 131.1, 131.5, 138.0, 142.7, 144.4.

1-(3-Aminophenyl)-3-phenylbenzo[c]furan (***3g***). Purification by flash chromatography, using dichloromethane as eluant, gave a green oil;[18] δ_H ($CDCl_3$, 300 MHz) 3.75 (br s, 2H), 6.61–6.65 (m, 1H), 6.99–7.02 (m, 2H), 7.25–7.37 (m, 4H), 7.45–7.50 (m, 2H), 7.81–7.84 (m, 2H), 7.92–7.95 (m, 2H).). δ_C ($CDCl_3$, 75 MHz) 111.4, 114.2, 115.7, 120.3, 120.5, 122.3, 124.9, 125.1, 125.3, 126.9, 129.1, 130.0, 131.9, 132.7, 143.7, 144.2, 147.0.

1-(4-Hydroxymethylphenyl)-3-phenylbenzo[c]furan (***3h***). Purification by flash chromatography, using dichloromethane as eluant, gave a yellow solid; mp 116 °C. ν_{max} (film) 3337, 3032, 2918, 2873, 1624, 1559, 1497, 1449, 1293, 1212, 1005, 970, 760; δ_H ($CDCl_3$, 300 MHz) 1.66 (bs, 1H), 4.74 (s, 2H), 6.99–7.05 (m, 2H), 7.30 (tt, J = 7.4, 1.3 Hz, 1H), 7.45–7.50 (m, 4H), 7.80–7.85 (m, 2H), 7.92–7.96 (m, 4H); δ_C ($CDCl_3$, 75 MHz) 65.3, 120.26, 120.34, 122.27, 122.32, 124.9, 125.0, 125.30, 125.35, 127.1, 127.7, 129.1, 131.2, 131.8, 139.5, 143.7, 144.0; m/z (CI^+) 301 ($[M+H]^+$, 100), 317 ($[M+CH_5]^+$, 30); HRMS (ESI) m/z: calcd for $C_{21}H_{16}O_2$: 300.11448 $[M]^+$; found: 300.11477.

1-(4-Formylphenyl)-3-phenylbenzo[c]furan (***3i***). Purification by flash chromatography, using dichloromethane as eluant, gave an orange–red oil; ν_{max} (film) 3050, 2922 2827, 2741, 1692, 1593, 1560, 1449, 1304, 1217, 1164, 834, 817, 743; δ_H ($CDCl_3$, 300 MHz) 7.06–7.17 (m, 2H), 7.33–7.38 (m, 1H), 7.51–7.54 (m, 2H), 7.90 (dd, J = 9.7, 1.2 Hz, 2H), 7.94–7.99 (m, 4H), 8.06–8.09 (m, 2H), 9.99 (s, 1H); δ_C ($CDCl_3$, 75 MHz) 120.0, 120.8, 122.7, 124.4, 124.5, 125.5, 125.6, 126.9, 128.0, 129.7, 130.6, 131.2, 134.1, 137.0, 142.3, 146.2, 191.4; m/z (CI^+) 299 ($[M+H]^+$, 100), 315 ($[M+CH_5]^+$, 20), 327 ($[M+C_2H_5]^+$, 15); HRMS (ESI) m/z: calcd for $C_{21}H_{14}NaO_2$: 321.08860 $[M+Na]^+$; found: 321.08883.

5-Iodosalicylaldehyde N-*benzoylhydrazone* (***5***). Benzohydrazide (3.41 g, 20 mmol)) was added at room temperature to a solution of 5-iodosalicylaldehyde (4.96 g, 20 mmol) in acetic acid (60 mL). The reaction mixture was stirred for 15 min then poured into cold water (15 mL). The resulting solid was filtered, washed with water, triturated with pentane, filtered and dried under vacuum to give **5** as a white solid (6.73 g, 18.4 mmol, 92%); mp 193 °C; ν_{max} (ATR) 3447, 3385, 3198, 3026, 1640, 1612, 1602, 1577, 1473, 1351, 1295, 1186, 1084, 972, 921, 693; δ_H (DMSO-d_6, 300 MHz) 6.78 (d, J = 8.6 Hz, 1H), 7.51–7.61 (m, 4H), 7.93–7.95 (m, 3H), 8.59 (s, 1H), 11.28 (s, 1H), 12.16 (s, 1H); δ_C (DMSO-d_6, 75 MHz) 81.2, 119.0, 121.9, 127.6, 128.5, 132.0, 132.8, 136.4, 139.3, 145.7, 157.0, 163.0; m/z (CI^+) 377 ($[M+H]^+$, 100), 389 ($[M+Na]^+$, 100); Anal. calcd for $C_{14}H_{11}IN_2O_2$, $1H_2O$: C, 43,77; H, 3.41, N, 7.29. Found: C, 44.02; H, 3.59, N, 7.55.

2-Benzoyl-5-iodobenzaldehyde (***6***). At room temperature, the appropriate hydrazone **5** (9.15 g, 25 mmol) was dissolved in tetrahydrofuran (200 mL, analytical grade). At 0 °C, lead tetraacetate (11.67 g, 25 mmol) was gradually added to the solution. The resulting mixture was stirred during 4 h at 0 °C. Progress of the reaction was monitored by the evolution of nitrogen. The solvent was removed under reduce pressure. Ethyl acetate (30 mL) was added to the residue. The suspension was filtered over celite. The organic layer was washed with a saturated solution of $NaHCO_3$, with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure. The oily residue was purified by flash column chromatography using dichloromethane as eluent to give **6** as a yellow solid (6.20 g, 18.5 mmol, 74%); mp 93–94 °C; ν_{max} (ATR) 3061, 2844, 2741, 1696, 1433, 1240, 1140, 920; δ_H ($CDCl_3$, 300 MHz) 7.27 (d, J = 8.0 Hz, 1H), 7.46–7.51 (m, 2H), 7.60–7.65 (m, 1H), 7.78–7.7.81 (m, 2H), 8.02 (dd, J = 8.0, 1.8 Hz, 1H), 8.35 (d, J = 1.8 Hz, 1H), 9.95 (s, 1H); δ_C ($CDCl_3$, 75 MHz) 97.1, 128.9, 130.1, 130.6, 134.0, 136.80, 136.84, 138.6, 140.5, 142.0, 189.1, 195.5; m/z (CI^+) 337 ($[M+H]^+$, 100); Anal. calcd for $C_{14}H_9IO_2$: C, 50.03; H, 2.70. Found: C, 50.01; H, 2.51.

1,3-Diphenyl-5-iodobenzo[c]furan (***7***). A dry and argon-flushed flask, equipped with a magnetic stirrer, was charged with **6**

(3.36 g, 10 mmol) in anhydrous tetrahydrofuran (40 mL). PhMgBr (6.33 mL, 1.58 M in THF, 10 mmol) was added dropwise at 0 °C and the resulted mixture was stirred at 0 °C. Progress of the reaction was monitored by TLC. When no starting material remained, an aqueous solution of HCl (4M, 20 mL) was slowly added at 0 °C. The mixture (still under argon) was warmed to room temperature and stirred for 1 h, then extracted several times with ether. The combined organic extracts were washed with a saturated solution of $NaHCO_3$, brine and dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product **7** was obtained as a yellow solid (3.01 g, 76% yield determined by ^{1}H NMR) of sufficient purity for synthetic purposes. Analytically pure samples were obtained after purification by flash chromatography (cyclohexane/ethyl acetate 9/1), gave product **7** as a yellow solid (2.96 g, 7.5 mmol, 75%); mp 127.5 °C; ν_{max} (ATR) 3056, 3024, 1597, 1527, 1484, 1447, 1279, 1202, 938, 787, 758; δ_H ($CDCl_3$, 400 MHz) 7.20 (d, J = 9.3, 1H), 7.30–7.34 (m, 2H), 7.47–7.51 (m, 4H), 7.59 (d, J = 9.2 Hz, 1H), 7.88–7.92 (m, 4H), 8.28 (s, 1H); δ_C ($CDCl_3$, 75 MHz) 90.8, 120.2, 121.8, 123.7, 125.0, 125.1, 127.5, 129.16, 129.18, 129.9, 131.19, 131.22, 133.5, 144.7, 153.7; m/z (CI^+) 270 ([M–I+H]$^+$, 50), 397 ([M+H]$^+$, 100); Anal. calcd for $C_{20}H_{13}IO$: C, 60.63; H, 3.31. Found: C, 60.81; H, 3.36.

2-Benzoyl-5-phenylbenzaldehyde (***8***). A mixture of phenyl boronic acid (61 mg, 0.5 mmol, 2 equiv), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (4.2 mg, 0,01 mmol, 4 mol%), sodium methoxide (30.5 mg, 0.75 mmol, 3 equiv), aldehyde **6** (84 mg, 0.25 mmol, 1 equiv) and rhodium chloride (2.6 mg, 0.01 mmol, 4 mol%) in DME (4 mL) and water (1 mL) was heated at 90 °C in a sealed tube for 24 h. The resulting mixture was cooled to room temperature; an aqueous solution of HCl (4M, 1 mL) was slowly added. The mixture (under argon) was stirred for 1h, then extracted several times with ether. The combined organic extracts were washed with a saturated solution of $NaHCO_3$, with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product **8** was obtained as colorless oil (70 mg, 97% of **8** and 3% of *o*-benzoylbenzaldehyde **1** determined by ^{1}H NMR). After purification by flash chromatography (dichloromethane), compound **8** was obtained as colourless oil (53 mg, 0.19 mmol, 74%); ν_{max} (ATR) 3059, 3032, 2923, 2851, 1770, 1694, 1659, 1596, 1448, 1279; δ_H ($CDCl_3$, 300 MHz) 7.44–7.54 (m, 5H), 7.59–7.63 (m, 2H), 7.67–7.70 (m, 2H), 7.84–7.88 (m, 3H), 8.26 (d, J = 1.8 Hz, 1H), 10.12 (s, 1H); δ_C ($CDCl_3$, 75 MHz) 127.3, 128.3, 128.7, 128.8, 129.7, 130.0, 130.2, 131.6, 133.8, 136.4, 137.3, 138.9, 139.9, 143.9, 190.7, 196.3; m/z (CI^+) 287 ([M+H]$^+$, 50), 309 ([M+Na]$^+$, 100); HRMS (ESI) m/z: calcd for $C_{20}H_{14}O_2Na$: 309.08860 [M+Na]$^+$; found: 309.08890.

Acknowledgements

Financial support from the CNRS and the Université Joseph Fourier (UMR 5250, FR-2607) and a fellowship award (to J. J.) from Cluster Chimie Durable et Chimie pour la Santé (Région Rhônes–Alpes) are gratefully acknowledged.

Notes and references

1 (*a*) W. Friedrichsen, *Adv. Heterocycl. Chem.*, 1980, **26**, 135; (*b*) W. Friedrichsen, *Adv. Heterocycl. Chem.*, 1999, **73**, 1; (*c*) P. G. Steel, *Sci. Synth.*, 2001, **10**, 87.

2 (*a*) R. Rodrigo, *Tetrahedron*, 1988, **44**, 2093; (*b*) O. Peters and W. Friedrichsen, *Trends Heterocycl. Chem.*, 1995, **4**, 217.

3 (*a*) C. Einhorn, J. Einhorn, C. Marcadal–Abbadi and J.-L. Pierre, *J. Org. Chem.*, 1999, **64**, 4542; (*b*) M. Nechab, D. N. Kumar, C. Philouze, C. Einhorn and J. Einhorn, *Angew. Chem., Int. Ed.*, 2007, **46**, 3080; (*c*) R. Prudent, V. Moucadel, M. Lopez Ramos, S. Aci, B. Laudet, L. Mouawad, C. Barette, J. Einhorn, C. Einhorn, J.-N. Denis, F. Schmidt, S. Roy, L. Lafanechère, J.-C. Florent and C. Cochet, *Mol. Cell. Biochem.*, 2008, **316**, 71.

4 J. Jacq, C. Einhorn and J. Einhorn, *Org. Lett.*, 2008, **10**, 3757.

5 (*a*) A. Kotali, I. S. Lafazanis and P. A. Harris, *Synthesis*, 2009, 836; (*b*) A. Kotali, I. S. Lafazanis and P. A. Harris, *Tetrahedron Lett.*, 2007, **48**, 7181; (*c*) A. Kotali, M. Papapetrou and V. Dimos, *Org. Prep. Proced. Int.*, 1998, **30**, 159; (*d*) A. Kotali, A. Koulidis, H.-M. Wang and L.-C. Chen, *Org. Prep. Proced. Int.*, 1996, **28**, 622; (*e*) A. Kotali, *Tetrahedron Lett.*, 1994, **35**, 6753; (*f*) R. M. Moriarty, B. A. Berglund and M. S. C. Rao, *Synthesis*, 1992, 318; (*g*) A. R. Katritzky, P. A. Harris and A. Kotali, *J. Org. Chem.*, 1991, **56**, 5049; (*h*) A. R. Katritzky and A. Kotali, *Tetrahedron Lett.*, 1990, **31**, 6790; (*i*) A. Kotali, U. Glaveri, E. Pavlidou and P. G. Tsoungas, *Synthesis*, 1990, 1172; (*j*) A. Kotali and P. G. Tsoungas, *Tetrahedron Lett.*, 1987, **28**, 4321; (*k*) for reviews see: A. Kotali, E. Kotali, I. S. Lafazanis and P. A. Harris, *Curr. Org. Chem.*, 2010, **7**, 62; (*l*) A. Kotali and P. A. Harris, *Org. Prep. Proced. Int.*, 2003, **35**, 583; (*m*) A. Kotali, *Curr. Org. Chem.*, 2002, **6**, 965.

6 P. Knochel, in *Handbook of Functionalized Organometallics*, Wiley-VCH, New York, 2005.

7 For rhodium catalysis see: (*a*) D. R. Snead, I. Ghiviriga, K. A. Abboud and S. Hong, *Org. Lett.*, 2009, **11**, 3274; (*b*) P. M. P. Gois, A. F. Trindade, L. F. Veiros, V. André, M. T. Duarte, C. A. M. Afonso, S. Caddick and F. G. N. Cloke, *Angew. Chem., Int. Ed.*, 2007, **46**, 5750; (*c*) R. B. C. Jagt, P. Y. Toullec, J. G. deVries, B. L. Feringa and A. J. Minnaard, *Org. Biomol. Chem.*, 2006, **4**, 773; (*d*) H.-F. Duan, J.-H. Xie, W.-J. Shi, Q. Zhang and Q.-L. Zhou, *Org. Lett.*, 2006, **8**, 1479; (*e*) J. Chen, X. Zhang, Q. Feng and M. Luo, *J. Organomet. Chem.*, 2006, **691**, 470; (*f*) M. Pucheault, S. Darses and J.-P. Genet, *Chem. Commun.*, 2005, 4714; (*g*) S. U. Son, S. B. Kim, J. A. Reingold, J. B. Carpenter and D. A. Sweigart, *J. Am. Chem. Soc.*, 2005, **127**, 12238; (*h*) A. Fürstner and H. Krause, *Adv. Synth. Catal.*, 2001, **343**, 343; (*i*) M. Ueda and N. Miyaura, *J. Org. Chem.*, 2000, **65**, 4450; (*j*) M. Sakai, M. Ueda and N. Miyaura, *Angew. Chem., Int. Ed.*, 1998, **37**, 3279; (*k*) for palladium catalysis see: T. Yamamoto, M. Iisuka, H. Takenaka, T. Ohta and Y. Ito, *J. Organomet. Chem.*, 2009, **694**, 1325; (*l*) A. Ju, B. Cheng, Y. Wu, J. Li and K. Wei, *Tetrahedron Lett.*, 2008, **49**, 5405; (*m*) M. Kuriyama, M. Shimazawa and R. Shirai, *J. Org. Chem.*, 2008, **73**, 1597; (*n*) G. D. Vo and J. F. Hartwig,, *Angew. Chem., Int. Ed.*, 2008, **47**, 2127; (*o*) C. Qin, H. Wu, J. Cheng, X. Chen, M. Liu, W. Zhang, W. Su and J. Ding, *J. Org. Chem.*, 2007, **72**, 4102; (*p*) A. Novodomskà, M. Dudicovà, F. R. Leroux and F. Colobert, *Tetrahedron: Asymmetry*, 2007, **18**, 1628; (*q*) T. Suzuki, T. Arao, S. Ishii, Y. Maeda, K. Kondo and T. Aoyama, *Tetrahedron Lett.*, 2006, **47**, 5789; (*r*) G. Liu and X. Lu, *J. Am. Chem. Soc.*, 2006, **128**, 16504; (*s*) T. Yamamoto, T. Ohta and Y. Ito, *Org. Lett.*, 2005, **7**, 4153; (*t*) for various transition metal catalysis see: H. Zheng, Q. Zhang, J. Chen, M. Liu, S. Cheng, J. Ding, H. Wu and W. Su, *J. Org. Chem.*, 2009, **74**, 943; (*u*) Y. Yamamoto, K. Kurihara and N. Miyaura, *Angew. Chem., Int. Ed.*, 2009, **48**, 4414; (*v*) Y.-X. Liao, C.-H. Xing, P. He and Q.-S. Hu, *Org. Lett.*, 2008, **10**, 2509; (*w*) L. Zhou, X. Du, R. He, Z. Ci and M. Bao, *Tetrahedron Lett.*, 2009, **50**, 406; (*x*) T. Zou, S.-S. Pi and J.-H. Li, *Org. Lett.*, 2009, **11**, 453.

8 Acidic treatment converts intermediate lactols into corresponding isobenzofurans *via* 1,4 water elimination: (*a*) W. Baker, J. F. W. Mc Omie, G. A. Pope and D. R. Preston, *J. Chem. Soc.*, 1961, 2965; (*b*) P. Courtot and D. H. Sachs, *Bull. Soc. Chim. Fr.*, 1965, 2259.

9 For MW activated Rh-catalysed reactions, see: (*a*) L. Garcia, A. Pla-Quintana, A. Roglans and T. Parella, *Eur. J. Org. Chem.*, 2010, 3407; (*b*) T. Morimoto, K. Yamasaki, A. Hirano, K. Tsutsumi, N. Nagawa, K. Kakiuchi, Y. Harada, Y. Fukumoto, N. Chatani and T. Nishioka, *Org. Lett.*, 2009, **11**, 1777; (*c*) A. Mondiere, G. Pousse, D. Bouyssi and G. Balme, *Eur. J. Org. Chem.*, 2009, 4225; (*d*) A. L. Jones and J. K. Snyder, *J. Org. Chem.*, 2009, **74**, 2907; (*e*) T. Abe, H. Takeda, Y. Takahashi, Y. Miwa, K. Yamada and M. Ishikura, *Heterocycles*, 2008, **75**, 2931; (*f*) W. Hang, F. Y. Kwong and A. S. C. Chan, *Synlett*, 2008, 1553; (*g*) H. W. Lee, L. N. Lee, A. S. C. Chan and F. Y. Kwong, *Eur. J. Org. Chem.*, 2008, 3403; (*h*) Y. Sumida, Y. Takada, S. Hayashi, K. Hirano, H. Yorimitsu and K. Oshima, *Chem.–Asian J.*, 2008, **3**,

119; (*i*) E.-A. Jo, J.-A. Ahn and C.-H. Jun, *Bull. Korean Chem. Soc.*, 2007, **28**, 2020; (*j*) G. Palmisano, W. Bonrath, L. Boffa, D. Garella, A. Barge and G. Cravotto, *Adv. Synth. Catal.*, 2007, **349**, 2338; (*k*) Y. Yamamoto and H. Hayashi, *Tetrahedron*, 2007, **63**, 10149; (*l*) P. S. Iyer, M. M. O'Malley and M. C. Lucas, *Tetrahedron Lett.*, 2007, **48**, 4413; (*m*) C. G. Frost, S. D. Penrose, K. Lambshead, P. R. Raithby, J. E. Warren and R. Gleave, *Org. Lett.*, 2007, **9**, 2119; (*n*) J. C. Lewis, J. Y. Wu, R. G. Bergman and J. A. Ellman, *Angew. Chem., Int. Ed.*, 2006, **45**, 1589; (*o*) J.-A. Ahn, D.-H. Chang, Y. J. Park, Y. R. Yon, A. Loupy and C.-H. Jun, *Adv. Synth. Catal.*, 2006, **348**, 55; (*p*) S. W. Hadebe and R. S. Robinson, *Tetrahedron Lett.*, 2006, **47**, 1299; (*q*) V.-T. Giang, H. Lahrache, A. Loupy, I.-J. Kim, D.-H. Chang and C.-H. Jun, *Tetrahedron*, 2004, **60**, 5539; (*r*) M. Takahashi, K. Oshima and S. Matsubara, *Tetrahedron Lett.*, 2003, **44**, 9201; (*s*) A. Loupy, S. Chatti, S. Delamare, D.-Y. Lee, J.-H. Chung and C.-H. Jun, *J. Chem. Soc., Perkin Trans. 1*, 2002, 1280; (*t*) For MW activated Pd-catalysed reactions, see: B. Roberts, D. Liptrot and L. Alcaraz, *Org. Lett.*, 2010, **12**, 1264; (*u*) M. D. Crozet, L. Zink, V. Remusat, C. Curti and P. Vanelle, *Synthesis*, 2009, 3150; (*v*) W. Erb, L. Neuville and J. Zhu, *J. Org. Chem.*, 2009, **74**, 3109; (*w*) M. Al-Masum and S. Alam, *Tetrahedron Lett.*, 2009, **50**, 5201; (*x*) L. J. Goossen, B. Zimmermann, C. Linder, N. Rodriguez, P. P. Lange and J. Hartung, *Adv. Synth. Catal.*, 2009, **351**, 2667; (*y*) M. Andaloussi, J. Lindh, J. Saevmarker, P. J. R. Sjoeberg and M. Larhed, *Chem.–Eur. J.*, 2009, **15**, 13069; (*z*) T. N. Glasnov, S. Findenig and C. O. Kappe, *Chem.–Eur. J.*, 2009, **15**, 1001; (*aa*) H. Tsukamoto, T. Matsumoto and Y. Kondo, *J. Am. Chem. Soc.*, 2008, **130**, 388; (*bb*) A. Voutchkova, A. Coplin, N. E. Leadbeater and R. H. Crabtree, *Chem. Commun.*, 2008, 6312; (*cc*) L. Bai and J.-X. Wang, *Adv. Synth. Catal.*, 2008, **350**, 315; (*dd*) E. M. Beccalli, G. Broggini, M. Martinelli and S. Sottocornola, *Synthesis*, 2008, 136; (*ee*) M. Kalek, A. Ziadi and J. Stawinski, *Org. Lett.*, 2008, **10**, 4637: For a review on Pd-catalyzed reactions promoted by ultrasound and/or microwave irradiation, see: (*ff*) A. Barge, S. Tagliapietra, L. Tei, P. Cintas and G. Cravotto, *Curr. Org. Chem.*, 2008, **12**, 1588.

10 M. Toumi, F. Couty and G. Evano, *Angew. Chem., Int. Ed.*, 2007, **46**, 572.

11 In comparison with the numerous Pd- or Ni-catalyzed cross couplings of organic halides with organometallic species, Rh-catalyzed ones are few. See: (*a*) R. C. Larock and S. S. Hershberger, *J. Organomet. Chem.*, 1982, **225**, 31; (*b*) R. C. Larock, K. Narayanan and S. S. Hershberger, *J. Org. Chem.*, 1983, **48**, 4377; (*c*) P. A. Evans and D. Uraguchi, *J. Am. Chem. Soc.*, 2003, **125**, 7158; (*d*) P. A. Evans and D. K. Leahy, *J. Am. Chem. Soc.*, 2003, **125**, 8974; (*e*) K. Uemura, T. Satoh and M. Miura, *Org. Lett.*, 2005, **7**, 2229; (*f*) H. Yasui, K. Mizutani, H. Yorimitsu and K. Oshima, *Tetrahedron*, 2006, **62**, 1410; (*g*) J. Wu, L. Zhang and Y. Luo, *Tetrahedron Lett.*, 2006, **47**, 6747; (*h*) J. Wu, L. Zhang and K. Gao, *Eur. J. Org. Chem.*, 2006, 5260; (*i*) M. L. Kantam, S. Roy, M. Roy, B. Sreedhar, B. M. Choudary and R. L. De, *J. Mol. Catal. A: Chem.*, 2007, **273**, 26; (*j*) L. Zhang and J. Wu, *Adv. Synth. Catal.*, 2008, **350**, 2409; (*k*) J.-Y. Yu and R. Kuwano, *Angew. Chem., Int. Ed.*, 2009, **48**, 7217; (*l*) H. Takahashi, S. Inagaki, N. Yoshii, F. Gao, Y. Nishihara and K. Takagi, *J. Org. Chem.*, 2009, **74**, 3403; (*m*) S. Ejiri, S. Odo, H. Takahashi, Y. Nishimura, K. Gotoh, Y. Nishihara and K. Takagi, *Org. Lett.*, 2010, **12**, 1692.

12 For a discussion about a possible role of microwave in selectivity switches already observed on some chemical reactions, see: C. O. Kappe, *Chem. Soc. Rev.*, 2008, **37**, 1127.

13 K. Yoshida and T. Hayashi, in *Boronic Acids*, ed. D. G. Hall, Wiley-VCH, Weinheim, 1st edn, 2005, ch. 4, pp 171–205.

14 J. E. Baldwin and D. S. Johnson, *J. Org. Chem.*, 1973, **38**, 2147.

15 A. S. Paraskar, A. R. Reddy, A. Patra, Y. H. Wijsboom, O. Gidron, L. J. W. Shimon, G. Leitus and M. Bendikov, *Chem.–Eur. J.*, 2008, **14**, 10639.

16 P. Amaladass, N. S. Kumarand and A. K. Mohanakrishnan, *Tetrahedron*, 2008, **64**, 7992.

17 W. W. Zajac, Jr. and D. E. Pichler, *Can. J. Chem.*, 1966, **44**, 833.

18 F. Amat-Guerri, E. Lempe, E. A. Lissi, F. J. Rodriguez and F. R. Trull, *J. Photochem. Photobiol., A*, 1996, **93**, 49.