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Suzuki Cross-Coupling Reaction of Sterically Hindered Aryl Boronates with 3-Iodo-4-methoxybenzoic Acid Methylester

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Abstract—The cross-coupling reaction of 3-iodo-4-methoxybenzoic acid methylester with sterically hindered arylboronic esters and especially 5,5-dimethyl-2-mesityl-1,3,2-dioxaborinane, is reported. The optimisation of the process in order to obtain biaryls in good yield by using anhydrous benzene at reflux and sodium phenoxide in the presence of 0.06 equiv. of $Pd(PPh_3)_4$ is described. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

A large number of precursors to drugs, polymers, liquid crystals as well as ligands for organo-metallic chemistry possess a biaryl structure. Therefore, numerous catalytic methods devoted to the preparation of biaryls by cross-coupling reactions have been developed over the last two decades. One of the most useful approaches, commonly referred as Suzuki coupling,[1] is based on Pd(0) catalysed cross-coupling reactions of various organoboron derivatives with aryl halides, triflates or diazonium salts under basic conditions. The original procedure, using $Pd(PPh_3)_4$ and aqueous Na_2CO_3 in benzene at reflux gives good yields with many substituted arylboronic acids.[1c] In general, cross-coupling reactions of organobon derivatives with organic halides are believed to process through a catalytic cycle[1d,1f,1g,1j,1k,1l,2] related to the cycles proposed for the cross-couplings induced by other metals such as Mg,[3] Zn[4] and Sn.[5] However, a particularity of the Suzuki cross-coupling reaction is that it proceeds only in the presence of bases.[1a,2] One of the admitted possibilities is that the catalytic cycle includes a step in which the base is introduced in the coordination sphere of palladium since the formation of Ar-PdL_2-OR from Ar-PdL_2-X is known to accelerate the transmetalation step.[1b,2a,6]

Another important feature of the Suzuki coupling reaction, in the usual conditions, must be emphasized. Arylboronic acids which are sterically hindered generally give low yields and hydrolytic deboronation of the C–B bond predominates.[7] Furthermore, both electron-withdrawing and electron-attracting groups could, at least, in some cases, accelerate the protonolysis.[7b,8] One of the alternative is to replace the boronic acids by the corresponding esters. This allows the use of anhydrous conditions in which no protonolysis occurs, enabling the synthesis of hindered biaryls in good yields.[1e,7b,9] However, until now, no systematic investigation of the cross-coupling reaction of hindered arylboronic esters seems to have been published.

Therefore, since in literature, *ortho–ortho′* tetrasubstituted biaryls could not be prepared in acceptable yields,[7b,7d,8c] we decided to focus our efforts on the Suzuki coupling of sterically hindered arylboronic esters **2**–**8** with a substituted anisic acid derivative **1** (Scheme 1). The other retrosynthetic possibility: the coupling of an hindered aromatic halide with a boronic ester seemed less favourable. Among the various boronic esters, mostly cyclic, already used in literature for coupling reactions, we chose 1,2,3-dioxaborinanes,[10] since 2,2-dimethyl-1,3-propanediol is known to give easily crystallised acetals.

Results and Discussion

In a first set of experiments, the coupling reaction of **1** with the unsubstituted boronic ester **2** and the two *ortho*-substituted 5,5-dimethyl-2-aryl-1,3,2-dioxaborinanes **3** and **4** (Table 1, entries 1 to 3) was studied. The two latter reactions of **1** were conducted using conditions already reported in literature,[9] i.e. $Pd(Ph_3)_4$ as catalyst, Tl_2CO_3 as base, benzene at reflux as solvent. It appeared that the cross-coupling reaction occurred in high yields and no trace of protonolysis could be observed. A prolonged reaction time was required

Keywords: Suzuki cross-coupling reaction; hindered arylboronic esters; biaryls.

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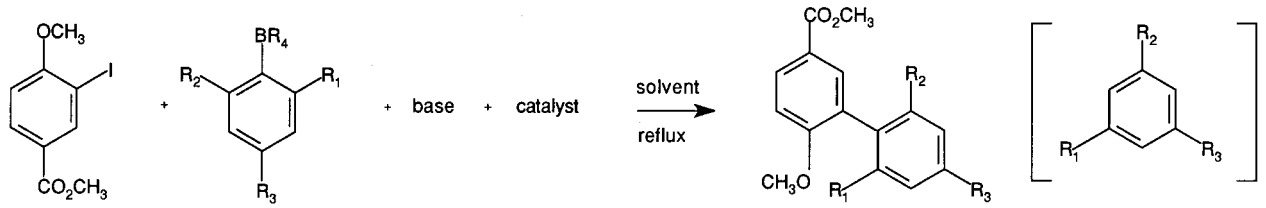


1

2 $R_1 = R_2 = R_3 = H$, $R_4 = -(OCH_2\text{-}C(CH_3)_2\text{-}CH_2O)-$
3 $R_1 = OMe$, $R_2 = R_3 = H$, $R_4 = -(OCH_2\text{-}C(CH_3)_2\text{-}CH_2O)-$
4 $R_1 = OPr$, $R_2 = R_3 = H$, $R_4 = -(OCH_2\text{-}C(CH_3)_2\text{-}CH_2O)-$
5 $R_1 = R_2 = R_3 = CH_3$, $R_4 = -(OCH_2\text{-}C(CH_3)_2\text{-}CH_2O)-$
6 $R_1 = R_2 = R_3 = i\text{Pr}$, $R_4 = (OBu)_2$
7 $R_1 = R_2 = R_3 = OMe$, $R_4 = -(OCH_2\text{-}C(CH_3)_2\text{-}CH_2O)-$
8 $R_1 = R_2 = R_3 = O\text{i}Pr$, $R_4 = -(OCH_2\text{-}C(CH_3)_2\text{-}CH_2O)-$

9 $R_1 = R_2 = R_3 = H$
10 $R_1 = OMe$, $R_2 = R_3 = H$
11 $R_1 = OPr$, $R_2 = R_3 = H$
12 $R_1 = R_2 = R_3 = CH_3$
13 $R_1 = R_2 = R_3 = i\text{Pr}$

14 $R_1 = R_2 = R_3 = CH_3$

Scheme 1.

for the sterically hindered mesitylene derivative **5** (entry 4). This is in agreement with previous studies from Thomson et al. who reported the slow rate of coupling reaction of *ortho–ortho′* disubstituted arylboronic acids.[11]

Then, in an attempt to accelerate the reaction and eventually to use less toxic conditions, we screened, not only different solvents but also a variety of bases on the coupling reaction of **1** with **5**.

Solvent effect

Among the eight solvents screened (entries 4 to 13), the reactions were best conducted in benzene. Astonishingly, the yield of the coupling reaction decreased to 47% in toluene. Nevertheless, the use of the less toxic solvents THF, DMF or DME could be considered as alternatives. Furthermore, a propensity to protonolysis with formation of **14** was evident when the reaction conditions were not strictly anhydrous. This result was not unexpected since, in our hands, the coupling reaction of mesitylene boronic acid with **1** under the usual Suzuki conditions (aqueous Na_2CO_3, $Pd(PPh_3)_4$, toluene/ethanol) afforded a yield of biaryl of only 6%. Therefore, we chose to run our reaction in strictly anhydrous conditions using a Dean–Stark apparatus, with benzene as solvent.

Amount and nature of the base

It has been suggested that the overall stoichiometry of the cross-coupling reaction between a boronic acid and an aryl halide requires one equivalent of water and two equivalents of base: one mole of base is needed to activate the boronic acid and the other to neutralise the formed boric acid.[2c] We found that the minimal amount of Tl_2CO_3 required for the coupling reaction of **1** with the boronic ester **5**, was 0.5 molar equivalent (if CO_2 is formed, this corresponds to one equivalent of base) (Table 2). In the presence of smaller amount of base, unconsumed **1** was recovered. Nevertheless, an excess of base could be employed with no negative effect on the yield. We observed a significant formation of CO_2 during the coupling reaction (see Experimental). This allows us to write the tentative equation shown in Scheme 2.

During our initial efforts, a yield of 96% was achieved using Tl_2CO_3 (Table 1). Unfortunately this base is highly toxic and therefore unsuitable for larger scale processes. Therefore, the effect of a large range of mineral and organic bases (Table 3) was examined.

Thallium (I) salts were successfully used by Kishi et al. for the coupling reaction of 1-alkenylboronic acid with iodoolefins in THF.[12] Suzuki et al. have reported, in

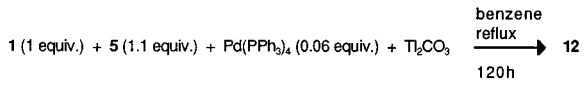
Table 1. Coupling reaction of **1** with arylboronic esters **2** to **5**

1 (1 equiv.) + **2-5** (1.2 equiv.) + Tl_2CO_3 (1.2 equiv.) + $Pd(PPh_3)_4$ (0.06 equiv.) $\xrightarrow[\text{reflux}]{\text{solvent}}$ **9-12**

Entry	Substrates	R1	R2	R3	Products	Solvent	Time (h)	Yield %
1	**2**	H	H	H	**9**	THF	6	97
2	**3**	OMe	H	H	**10**	Benzene	30	97
3	**4**	OPr	H	H	**11**	Benzene	30	99
4	**5**	Me	Me	Me	**12**	Benzene	90–100	96
5	**5**	Me	Me	Me	**12**	$ClCH_2CH_2Cl$	90–100	81.5
6	**5**	Me	Me	Me	**12**	THF	90–100	72
7	**5**	Me	Me	Me	**12**	DMF[a]	90–100	70
8	**5**	Me	Me	Me	**12**	DME	90–100	69
9	**5**	Me	Me	Me	**12**	1,4-dioxane	90–100	65
10	**5**	Me	Me	Me	**12**	C_6H_{12}	90–100	65
11	**5**	Me	Me	Me	**12**	CH_3CN	90–100	62.5
12	**5**	Me	Me	Me	**12**	$C_6H_5CH_3$	90–100	47
13	**5**	Me	Me	Me	**12**	CCl_4	90–100	16

[a] Reaction run at 110°C.

Table 2. Influence of base amount on the yield of the reaction



Base (mol. equiv.)	Time (h)	Yields %
2.12	120	94
0.53	120	96
0.28	168	54

addition, the promotion of the coupling reaction of alkylboronic esters with 1-alkenyl and aryl halides in the presence of thallium salts in a mixture THF/H_2O.[13] Thallium (I) is thought to remove halide as TlX, producing PdOH species that accelerates the transmetalation.[14] However, Sniekus et al., in 1994, reported that Tl_2CO_3 was inefficient for the coupling of arylboronate esters with an aryl iodide in THF.[15] We found that he coupling reaction of **1** with **5** in benzene readily proceeded using Tl_2CO_3 but failed using other thallium salts (entries 2–4). Using TlOH, the main product resulted in the reduction of **1** (entry 2). Suzuki et al. has already described such a reduction during the cross coupling reaction of (*E*)-1-hexenylborane with (*E*)-β-styrylbromide.[2a]

Pb(II) as PbO and $PbCO_3$, Bi(III) as $Bi_2O_2CO_3$ have the same $d^{10}s^2$ configuration as Tl(I) salts. Therefore, the use of these salts seemed to be particularly attractive. Unfortunately, the coupling reaction proceeded, at best, only in very low yields (entries 5 to 7).

Since Chang et al. described that, using carbonates as base, the cross-coupling reaction rate were strongly dependent of the nature of the cation,[16] we tried Ag_2CO_3, Cs_2CO_3 and Na_2CO_3 (entries 8–10). The excellent yield achieved with the former should be emphasized. It is consistent with the literature, indicating that the reductive elimination of halide is enhanced when a sparingly soluble salt is formed.[12]

In literature, couplings of hindered boronic esters were often promoted by K_3PO_4 in DMF.[7b,15,17] (In our hands, we obtained under these conditions a 60% yield.) In benzene at reflux, K_3PO_4 and Ag_3PO_4 were ineffective (entries 12–13).

$Ba(OH)_2$ both in benzene and DME was used in sterically demanding coupling reactions and good yields of product were often obtained[1e,1i,7b] (see, however, Ref. 16). Unfortunately, the coupling reaction of **1** with **5** in benzene proceed with only 5% yield (entry 14).

Our experiments clearly highlight the importance of both the nature of the cation and the strength of the base in the course of the cross-coupling reaction. Smith et al. have

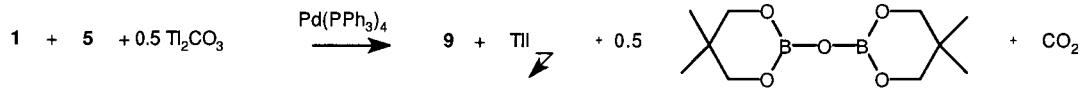
Table 3. Effect of different bases on the cross-coupling reaction

Entry	Base	Yield %
1	Tl_2CO_3	96
2	TlOH	19[a]
3	TlOEt	7.5[b]
4	TlOAc	0
5	PbO	16
6	$PbCO_3$	0
7	$Bi_2O_2CO_3$	0
8	Ag_2CO_3	97
9	Cs_2CO_3	46
10	Na_2CO_3	0
11	Ag_2O	67[c]
12	Ag_3PO_4	9
13	K_3PO_4	6
14	$Ba(OH)_2,H_2O$	5
15	BaO	5
16	NaOMe	60[d]
17	NaOH	27
18	AgOAc	0
19	Hünig'base	0
20	$NaOC_6H_5$	80
21	KOC_6H_5	79
22	NaO–(4-*t*Bu–C_6H_4)	80
23	NaO–(4-CH_3–C_6H_4)	80
24	NaO–(2-CH_3–C_6H_4)	63.5
25	NaO–(3-CH_3–C_6H_4)	60.5
26	NaO–(4-Cl–C_6H_4)	62
27	NaO–(2-Cl–C_6H_4)	10
28	NaO–(3-NO_2–C_6H_4)	20
29	NaO–(4-NO_2–C_6H_4)	5
30	NaO–(2-NO_2–C_6H_4)	0
31	$CsOC_6H_5$	60
32	$LiOC_6H_5$	22

[a] Presence of 45% 4-methoxybenzoic acid methylester.
[b] Presence of 43% 4-methoxybenzoic acid ethylester.
[c] Presence of 13% 4-methoxybenzoic acid methylester.
[d] Presence of 22% 4-methoxybenzoic acid methylester.

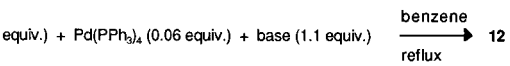
already claimed that, for boronic acids, a base of sufficient strength was needed to form the boronate anion, allowing, therefore, the transmetalation step to occur.[2c] The major influence of pH, in cross coupling reactions, has also been demonstrated in detail.[18] Charette et al. recommended strong base for the cross-coupling of boronate esters with iodocyclopropane.[19] It's worth noting that ethoxide, methoxide and hydroxide are commonly used for the Suzuki coupling reaction of arylboronic acids.[1f]

We concentrated then on the use of phenoxides: sodium phenoxide having been already successfully tested by Suzuki for the cross coupling of (*Z*)1-hexylboranes with (*E*)-β-styrylbromide.[2a] Phenoxides are cheap and easy to prepare. The results indicated that the use of sodium or potassium phenoxide, sodium *p*-*t*Bu- or *p*-methylphenoxides led to the desired biaryl compound in good



Scheme 2.

Table 4. Influence of the reaction time on the cross-coupling reaction



Base	Time(h)	Yield %
Tl_2CO_3	21	36
Tl_2CO_3	30	50
Tl_2CO_3	48	88.5
Tl_2CO_3	100	96
PhONa	24	7.5
PhONa	48	10
PhONa	50	21
PhONa	70	29
PhONa	72	43
PhONa	79	47
PhONa	87	80
PhONa	118	80

yields (entries 20 to 23), while phenates of weaker basicity were less effective (entries 28 to 30). Compared to the *p*-isomers the use of sterically hindered *ortho*-substituted phenoxides gave lower yields suggesting that the transmetalation step was sensitive to the steric hindrance of the base (entries 24, 27, 30). Replacement of Tl_2CO_3 by sodium phenoxide required a longer reaction time (Table 4). This could be explained by differences in the nucleophilicities of the bases which can delay the transmetalation step.

Eventually, at this stage, our study clearly emphasizes the use of sodium or potassium phenoxides as efficient, convenient, cheap and non-toxic bases for a successful coupling reaction.

Nature and amount of catalyst

A great variety of palladium (0) catalysts has been commonly used for cross-coupling reactions between arylboronic acids and arylhalides.[1f,1n] Our attempts to replace $Pd(PPh_3)_4$ in the coupling reaction of **1** with **5** by of other palladium catalyst were unsuccessful (Table 5). The cross-coupling reaction with $Pd(OAc)_2$ gave a reaction mixture contaminated by Pd(0). This suggest that triphenylphosphine reduces the divalent palladium from the complex $Pd(OAc)_2(PPh_3)_4$ as Jutand et al. reported.[20]

The minimum amount of $Pd(PPh_3)_4$ required to complete the reaction in four days was 0.06 equiv.

Besides, the addition of triphenylphosphine to the catalyst had a negative effect on the reaction. With $Pd(PPh_3)_4$ (0.06 equiv.), the yield dropped from 80% to 30% in the presence of 0.12 equiv. of PPh_3 and from 45% to 37% in the case of $PdCl_2$(dppf). This phosphine inhibition in Suzuki aryl–aryl coupling between boronic acids and aryl halides has already been observed by Wallow and Novak.[18a]

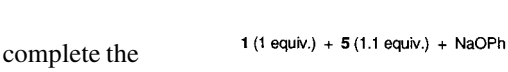
More hindered boronic esters

The coupling reaction of **1** with di-*n*-butyl 2,4,6-triisopropylphenylboronate **6** using Tl_2CO_3 and $Pd(PPh_3)_4$ in benzene at reflux, i.e. our initial conditions affording an almost quantitative yield for **5**, led to a much lower yield in coupling product **13** (11%). No further evolution could be observed after seven days. The reduction of **1** to 4-methoxybenzoic acid methylester was observed and unchanged ester **6** was recovered.

Attempts to couple **1** either with 5,5-dimethyl-2-(2,4,6-trimethoxyphenyl)-1,3,2-dioxaborinane **7** or with 5,5-dimethyl-2-(2,4,6-triisopropoxyphenyl)-1,3,2-dioxaborinane **8** failed, leading only to deboronated derivatives. Moreover, the coupling reaction of **5** with iodomesitylene gave no reaction which was expected according to previous Suzuki's results.[7b]

Using Ag_2CO_3 as a base, the cross-coupling reaction of 5,5-dimethyl-2-(2-formylphenyl)-1,3,2-dioxaborinane with iodomesitylene gave 30.5% yield of the expected biaryl product, whereas using sodium phenoxide as base, it gave only 3% yield. These low yields of cross-coupling were not unexpected since the 2-formyl group is known to accelerate the rate of protonolysis.[8a,8b] However, Suzuki et al. reported a 73% yield in coupling the 2-(2-formylphenyl)-1,3,2-dioxaborinane with iodomesitylene.[7b]

Table 5. Influence of nature and amount of catalysts on the cross-coupling reaction



Catalysts	Catalyst (mol equiv.)	Yield %
$Pd(PPh_3)_4$	0.007	25
$Pd(PPh_3)_4$	0.01	35
$Pd(PPh_3)_4$	0.03	52.5
$Pd(PPh_3)_4$	0.044	65.5
$Pd(PPh_3)_4$	0.06	80
$Pd(PPh_3)_4$	0.1	80
Pd/C	0.06	10
Pd/alumine	0.06	0
$Pd/BaSO_4$	0.06	0
$Pd(Oac)_2$	0.06	9
$PdCl_2$dppf[a]	0.06	45
$PdCl_2$dppb[b]	0.06	42
$PdCl_2$dppp[c]	0.06	48
$PdCl_2(CH_3CN)_2$	0.06	26.5
$PdCl_2(C_6H_4CN)_2$	0.06	25.5

[a] dppf: 1,1′ bis(diphenylphosphino)ferrocene.
[b] dppb: 1,1′ bis(diphenylphosphino)butane.
[c] dppp: 1,1′ bis(diphenylphosphino)propane.

Conclusion

Although numerous examples of Suzuki cross-couplings to form hindered biphenyls from aryl iodides or bromides have been reported.[8c,7d,15,17,21] Unfortunately, these reactions are often problematic. As for us, we coupled in high yields sterically hindered boronic esters with 3-iodo-4-methoxybenzoic acid methylester using 0.06 equiv. of $Pd(PPh_3)_4$ as catalyst. Sodium phenoxide proved to be an efficient base and silver carbonate was a useful alternative to the toxic thallium carbonate. As it could be expected, we did not succeed in synthesising *ortho–ortho′* tetrasubstituted biaryls.

Experimental

General

Et_2O, THF, toluene and benzene were freshly distilled from sodium/benzophenone, CCl_4, cyclohexane and dichloroethane from P_2O_5, CH_3CN from CaH_2 and TMEDA from KOH. A freshly opened DMF bottle was used. Residual water content has been measured with a Bizot and Constant apparatus. ^1H NMR (60 or 250 MHz) and ^{13}C NMR (62.9 MHz) spectra were measured in $CDCl_3$. Microanalyses were performed by the 'Service Central d'Analyse du C.N.R.S.'.

Halides compounds

3-Iodo-4-methoxybenzoic acid methyl ester **1** and monoiodomesitylene were prepared according to the literature.[22,23]

Palladium complexes

Pd/C, Pd/alumina, $Pd/BaSO_4$ and $Pd(OAc)_2$ were purchased from Fluka. The reported procedures were used to prepare $Pd(PPh_3)_4$,[24] $PdCl_2(C_6H_5CN)_2$ and $PdCl_2(CH_3CN)_2$,[25] $PdCl_2$(dppf), $PdCl_2$(dppb), $PdCl_2$(dppp).[26]

Bases

Lithium phenoxide, potassium phenoxide and the different sodium phenoxides were prepared according to literature.[27,28]

Cesium phenoxide. A sealed tube slightly notched containing cesium (1.99 g, 14.9 mmol) was fitted under N_2 in a P.V.C. tube. The sealed tube was broken and the pieces were quickly dropped into a solution of phenol (1.71 g, 18.1 mmol) in 25 ml of anhydrous hexane. The mixture was allowed to react under N_2. The pieces of glass were discarded. The solvent was evaporated and the resulting solid was heated at 60°C under vacuum (1 Torr) overnight to remove the traces of solvent and the excess of phenol.

Boronic acids

We obtained, according to the literature procedures, the phenylboronic acid,[29] the mesityleneboronic acid[30] and 2-formylbenzene boronic acid.[31]

2-Methoxyphenylboronic acid.[32] A solution of 2-bromoanisole (5 g, 26.7 mmol) in 50 ml of THF and a solution of *n*-butyllithium in hexane (1.6 M, 20 ml, 1.2 equiv.) were added simultaneously with vigorous stirring at −90°C under N_2 to 50 ml of THF. After 15 min at −90°C, trimethyl borate (6 ml, 2 equiv.) was rapidly added. The reaction mixture was stirred at −90°C for 1 h and at room temperature for an extra 1 h. The solvents were concentrated in vacuo. The colourless oil was poured into a mixture of ice and water (1:1). The mixture was acidified with HCl to pH 5–6 and extracted with Et_2O. The combined extracts were dried over $MgSO_4$ and concentrated in vacuo. The crude material was crystallised from *n*-hexane (2.4 g, 67%). mp=100°C. IR (KBr): 3500–3250, 3060–2960, 2830, 1595, 1570, 1480, 1460, 1340, 1160, 1105, 1090, 1050, 1020, 770, 750. ^1H NMR: 3.8 (3H, s), 6.7 (2H, s), 6.8–7.1 (2H, m), 7.4 (1H, ddd), 7.9 (1H, dd). Anal. calcd for $C_7H_9BO_3$ (151.96): C 55.33%, H 5.97%; found: C 55.57%, H 5.96%.

2-Isopropoxyphenylboronic acid.[33] This was prepared according to the procedure used for 2-methoxyphenylboronic acid, starting from 1-bromo-2-isopropoxybenzene[34] (5 g, 23 mmol), *n*-butyllithium (1.6 M, 17.23 ml, 1.2 equiv.) and trimethyl borate (5.17 ml, 2 equiv.). After crystallisation in hexane, the desired product was obtained as a colourless solid (2.93 g, 70%). mp=40–41°C. IR (KBr): 3500–3300, 3060–2870, 1595, 1570, 1470, 1440, 1400–1330, 1215, 1015, 950, 750. ^1H NMR: 1.4 (6H, d, J=6 Hz), 4.71 (1H, sept., J=6 Hz), 6.75 (2H, s), 6.8–7.1 (2H, m), 7.4 (1H, ddd, J=8; 7; 3 Hz), 7.9 (1H, dd, J=7; 2 Hz). Anal. calcd for $C_9H_{13}BO_3$ (180.01): C 60.05%, H 7.28%; found: C 60.06%, H 7.37%.

2,4,6-Trimethoxyphenylboronic acid. [7a] To a solution of 1,3,5-trimethoxybenzene (6.72 g, 40 mmol.) in 40 ml Et_2O, at −5°C, under N_2, were added with vigorous stirring, 6 ml of TMEDA and *n*-butyllithium in hexane (1.6 M, 30 ml, 1.2 equiv.). After 20 min, the mixture was cooled to −78°C and 30 ml of THF was slowly added. Then, trimethyl borate was added (9 ml, 2 equiv.). The reaction mixture was stirred at −78°C for 1 h and, then, 15 h at room temperature. The solvents were concentrated in vacuo. The colourless oil was dropped into a mixture of ice and water (1:1). The mixture was acidified with HCl 2 N to pH 5–6. This aqueous solution was extracted three times with chloroform. The combined extracts were dried over $MgSO_4$ and concentrated in vacuo. The crude material was treated with Et_2O and crystallised. The desired product was obtained as a colourless solid (5g, 60%). mp=107–109°C (mp=109°C[7a]). IR (KBr): 3540–3420, 3020–2900, 2840, 1605, 1575, 1465, 1410, 1340, 1290, 1220, 1205, 1120, 810, 755. ^1H NMR: 3.87 (3H, s), 3.9 (6H, s), 6.17 (2H, s), 7.00 (2H, s).

2,4,6-Triisopropylphenylboronic acid. This was prepared according to the procedure used for 2,4,6-trimethoxyphenylboronic acid starting from 1-bromo-2,4,6-triisopropylbenzene[35] (6 g, 21 mmol), *n*-butyllithium (1.6 M, 15.75 ml, 1.2 equiv.) and trimethyl borate (4.72 ml, 2 equiv.). A yellow oil was obtained and was heated at reflux with 50 ml of water at 0°C; After crystallisation from hexane, the desired product was obtained as a

colourless solid (3 g, 57%). mp=159–161°C. IR (KBr): 3450–3200, 2980–2870, 1605, 1460, 1400–1250, 1055, 1025, 870. ^{1}H NMR: 1.24 (6H, d, *J*=6.8 Hz), 1.27 (12H, d, *J*=6.8 Hz), 2.9 (3H, m), 4.67 (2H, s), 7 (2H, s). Anal. calcd for $C_{15}H_{25}BO_2$ (248.18): C 72.60%, H 10.15%; found: C 72,67%, H 10.13%.

2,4,6-Triisopropoxyphenylboronic acid. This was prepared according to the procedure used for 2,4,6-trimethoxyphenylboronic acid starting from 1,3,5-triisopropoxybenzene (6.5 g, 26 mmol), *n*-butyllithium (1.6 M, 19.5 ml, 1.2 equiv.) and trimethyl borate (5.85 ml, 2 equiv.). After crystallisation from hexane, the desired product was isolated as colourless solid (5.6 g, 73%).mp=64°C (mp=64–65°C[36]), ^{1}H NMR: 1.35 (6H, d, *J*=6 Hz), 1.38 (12H, d, *J*=6 Hz), 4.56 (3H, sept., *J*=6 Hz), 6.08 (2H, s), 7.36 (2H, s).

Boronic esters

Dibutyl 2,4,6-triisopropylphenylboronate 6. 2,4,6-Triisopropylphenylboronic acid (500 mg, 2.02 mmol) in solution in 35 ml of *n*-butanol was stirred at reflux for one day according to the literature.[37] The evaporation under reduced pressure of the excess of alcohol yielded the desired product as a colourless oil (674 mg, 93%). IR (KBr): 2960–2860, 1605, 1460, 1405, 1360–1260, 870. ^{1}H NMR: 1.03 (6H, *J*=7.2 Hz), 1.37 (18H, d, *J*=6.7 Hz), 3.94 (4H, t, *J*=6.35 Hz), 7.06 (2H, s). Anal. calcd for $C_{23}H_{41}BO_2$ (360.39): C 76.65%, H 11.47%; found C 76.40%, H 11.32%.

General procedure for 2 to 5 and 7 to 8

In a flask equipped with a Dean–Stark apparatus and a condenser, boronic acid and 2,2-dimethyl-1,3-propanediol (1.2 equiv.) in THF (40 ml/g of boronic acid) was stirred at reflux. Evaporation under reduced pressure yield the crude boronic ester.[38]

5,5-Dimethyl-phenyl-1,3,2-dioxaborinane 2. This was prepared from phenylboronic acid (750 mg, 6.1 mmol) and 2,2-dimethyl-1,3-propanediol. After 4 h at reflux and evaporation, the crude material was cooled at −10°C and the desired product was isolated as a colourless solid (951 mg, 82%). mp=62°C (mp=62°C[36]). IR (KBr): 3060, 2960–2860, 1600, 1475, 1435, 1410, 1340–1285, 1250, 1130, 760, 695. ^{1}H NMR: 1.0 (6H, s), 3.7 (4H, s), 7.2–7.45 (3H, m), 7.7–7,9 (2H, m).

5,5-Dimethyl-2-(2-methoxyphenyl)-1,3,2-dioxaborinane 3. This was prepared from 2-methoxyphenylboronic acid (1 g, 6.58 mmol) and 2,2-dimethyl-1,3-propanediol. After 5 h at reflux and evaporation, the desired product was crystallised from hexane and isolated as a colourless solid (1.23 g, 86%). mp=41°C. IR(KBr): 3000–2890, 1600, 1485, 1475, 1430, 1340–1240, 1130, 1100, 1020, 770. ^{1}H NMR: 1.05 (6H, s), 3.75 (4H, s), 3.8 (3H, s), 6.8–7.7 (4H, m). Anal. calcd for $C_{12}H_{17}BO_3$ (220.08): C 65.49%, H 7.79%; found C 64.92%, H 8.12%.

5,5-Dimethyl-2-(2-isopropoxyphenyl)-1,3,2-dioxaborinane 4. This was prepared from 2-isopropoxyphenylboronic acid (2.5 g, 13.9 mmol) and 2,2-dimethyl-1,3-propanediol. After 6 h at reflux, the desired product was isolated as a colourless oil (2.75 g, 86%). IR (film): 3070–2890, 1600, 1575, 1480, 1440, 1415, 1380, 1335, 1315, 1240, 1135, 1110, 950, 755. ^{1}H NMR: 1.0 (6H, s), 1.3 (6H, d, *J*=6 Hz), 3.7 (4H, s), 4.4 (1H, sept., *J*=6 Hz), 6.75 (1H, m), 6.91 (1H, m), 7.25 (1H, ddd, *J*=7; 6; 2 Hz), 7.55 (1H, dd, *J*=8; 2 Hz). Anal. calcd for $C_{14}H_{21}BO_3$ (248.13): C 67.77%, H 8.53%; found C 67.35%, H 8.79%.

5,5-Dimethyl-2-(2,4,6-trimethylphenyl)-1,3,2-dioxaborinane 5. This was prepared from 2,4,6-trimethylphenylboronic acid (1 g, 6.1 mmol) and 2,2-dimethyl-1,3-propanediol. After 6 h at reflux and evaporation, the desired product was crystallized from water and isolated as a colourless solid (900 mg, 64%). mp=39–40°C. IR (KBr): 2960–2870, 1610, 1470, 1425, 1410, 1370, 1320, 1290, 1240, 1165, 1105, 845. ^{1}H NMR: 1.1 (6H, s), 2.25 (3H, s), 2.37 (6H, s), 3.79 (4H, s), 6.78 (2H, s). Anal. calcd for $C_{14}H_{21}BO_2$ (232.13) C 72.44%, H 9.12%; found C 72.80%, H 9.34%.

5,5-Dimethyl-2-(2,4,6-trimethoxyphenyl)-1,3,2-dioxaborinane 7. This was prepared from 2,4,6-trimethoxyphenylboronic acid (1 g, 4.7 mmol) and 2,2-dimethyl-1,3-propanediol. After 9 h at reflux and evaporation, the desired product was crystallized from Et_2O and isolated as a colourless solid (990 mg, 75%). mp=99–101°C. IR (KBr): 3000–2880, 2835, 1600, 1580, 1475, 1450, 1405, 1310, 1285, 1250, 1220, 1200, 1150, 1130, 810. ^{1}H NMR: 1.1 (6H, s), 3.8 (13H, s), 6.1 (2H, s). Anal. calcd for $C_{14}H_{21}BO_5$ (280.13): C 60.03%, H 7.56%; found C 59.88%, H 7.56%.

5,5-Dimethyl-2-(2,4,6-triisopropoxyphenyl)-1,3,2-dioxaborinane 8. This was prepared from 2,4,6-triisopropoxyphenylboronic acid (1 g, 3.4 mmol) and 2,2-dimethyl-1,3-propanediol. After 8 h at reflux and evaporation, the desired product was crystallized from hexane and isolated as a colourless solid (1.06 g, 80%). mp=48–49°C. IR (KBr): 2970–2860, 1595, 1570, 1475, 1420, 1370, 1330, 1320, 1290, 1110, 1025. ^{1}H NMR: 1.08 (6H, s), 1.28 (18H, d, *J*=6 Hz), 3.72 (4H, s), 4.44 (3H, sept, *J*=6 Hz), 6.03 (2H, s). Anal. calcd for $C_{20}H_{33}BO_5$ (364.29) C 65.94%, H 9.13%; found C 65.53%, H 9.22%.

5,5-Dimethyl-2-(2-formylphenyl)-1,3,2-dioxaborinane. This was prepared from 2-formylbenzeneboronic acid[39] (500 mg, 3.3 mmol) and 2,2-dimethyl-1,3-propanediol. After 24 h at reflux and evaporation, the desired product was crystallized from hexane and isolated as a colourless solid (725 mg, 99%). mp=122.6°C. IR (KBr): 2932, 1694, 1478, 1415, 1303, 1247, 1133.^{1}H NMR: 1.08 (6H, s), 3.82 (4H, s), 7.50–7.60 (2H, m), 7.8 (1H, dd, *J*=8.5; 1.55 Hz), 7.91 (1H, dd, *J*=7.77; 1.72 Hz), 10.46 (1H,s). ^{13}C NMR: 21.9 (2q), 31.75 (s), 72.54 (2t), 128.34 (d), 129.91 (d), 132.96 (d), 133.84 (s), 134.28 (d), 140.83 (s), 194.96 (d).

Coupling reaction

General procedure. In a flask equipped with a Dean–Stark apparatus and a condenser, 3-iodo-4-methoxybenzoic acid methylester **1** (100 mg, 0.34 mmol.), arylboronic ester (1.1 equiv.), catalyst (0.06 equiv.) and base (1.1 equiv.) were suspended in 20–25 ml of solvent and were stirred at

reflux under N_2 for 90–100 h. The suspension was filtered through Celite and a solution of HCl 2N was added to the filtrate with stirring. The organic layer was washed with water. The aqueous layers were extracted twice with CH_2Cl_2. The organic phases were then washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The coupling product **9**–**13** was isolated by chromatography on silicagel (petroleum ether/ethyl acetate) and further crystallised from ethanol.

Methyl 6-methoxybiphenyl-3-carboxylate 9. Mp=90°C. IR (KBr): 3060–2950, 2840, 1710, 1600, 1460, 1435, 1310, 1230, 1140, 1015, 770, 725. ^{1}H NMR: 3.87 (3H, s), 3.89 (3H, s), 7.3–7.55 (5H, m), 7.00 (1H, d, *J*=9.2 Hz), 8.01 (1H, d, *J*=2.2 Hz), 8.03 (1H, dd, *J*=9.2; 2.2 Hz). ^{13}C NMR: 51.92 (q), 55.77 (q), 110.6 (d), 122.7 (s), 127.35 (d), 128.09 (2d), 129.52 (2d), 130.61 (s), 130.76 (d), 132.45 (d), 137.54 (s), 160.20 (s), 166.89 (s). Anal. calcd for $C_{15}H_{14}O_3$ (242.28): C 74.36%, H 5.82%; found: C 74.18%, H 5.98%.

Methyl 6,2′-dimethoxybiphenyl-3-carboxylate 10. Mp=93°C. IR (KBr): 3040–2940, 2840, 1710, 1610, 1590, 1460, 1430, 1310, 1295, 1240, 1135, 1115, 1030, 1015, 770, 745. ^{1}H NMR: 3.76 (3H, s), 3.82 (3H, s), 3.87 (3H, s), 6.97 (1H, d, *J*=8.7 Hz), 6.99–7.05 (2H, m), 7.22 (1H, dd, *J*=7.5; 1.8 Hz), 7.35 (1H, ddd, *J*=7.5; 7.6; 1.8 Hz), 7.94 (1H, d, *J*=2.2 Hz), 8.04 (1H, dd, *J*=8.7; 2.2 Hz). ^{13}C NMR: 51 (q), 55.69 (q), 55.81 (q), 110.33 (d), 111.07 (d), 120.41(d), 122.22 (s), 126.84 (s), 127.8 (s), 129.02 (s), 130.87 (s), 131.31 (d), 133.08 (d), 157.02 (s), 160.87 (s), 166.97 (s). Anal. calcd for $C_{16}H_{16}O_4$ (272.30): C 70.58%, H 5.92%; found: C 70.50%, H 5.94%.

Methyl 6-methoxy-2′-isopropoxybiphenyl-3-carboxylate 11. Mp=106°C. IR (KBr): 3000–2900, 2830, 1705, 1605, 1590, 1480, 1445, 1295, 1240, 1110, 1025, 1010, 950, 760. ^{1}H NMR: 1.17 (6H, d, *J*=6 Hz), 3.84 (3H, s), 3.9 (3H, s), 4.42 (1H, sept, *J*=6 Hz), 6.93–7.2 (2H, m), 6.95 (1H, d, *J*=8.6 Hz), 7.21–7.33 (2H, m), 7.94 (1H, d, *J*=2.2 Hz), 8.04 (1H, dd, *J*=8.6; 2.2 Hz). ^{13}C NMR: 22.03 (2 q), 51.79 (q), 55.59 (q), 70.55 (d), 109.99 (d), 114.25 (d), 120.38 (d), 122.03 (s), 128.22 (s), 128.26 (s), 128.79 (d), 130.64 (s), 131.47 (s), 133.21 (d), 155.46 (s), 160.88 (s), 167.07 (s). Anal. calcd for $C_{18}H_{20}O_4$ (300.36): C 71.98%, H 6.71%; found: C 72.04%, H 6.60%.

Methyl 6-methoxy-2′,4′,6′-trimethylbiphenyl-3-carboxylate 12. Mp=156–159°C. IR (KBr): 3020, 2950, 2930, 2860, 1710, 1600, 1440, 1260, 1240, 1020, 780, 640. ^{1}H NMR: 1.99 (6H, s), 2.35 (3H, s), 3.82 (3H, s), 3.89 (3H,s), 6.96 (2H, s), 7.08 (1H, d, *J*=8.7 Hz), 7.77 (1H, d, *J*=2.2 Hz), 8.08 (1H, dd, *J*=8.6; 2.1 Hz). ^{13}C NMR: 20.24 (2q), 21.07 (q), 51.76 (q), 55.60 (q), 110.25 (d), 122.58 (s), 127.97 (d), 129.46 (s), 130.68 (d), 132 (d), 134.12 (s), 136.29 (s), 160.53 (s), 168.90 (s). Anal. calcd for $C_{18}H_{20}O_3$ (284.36): C 76.03%, H 7.09%; found: C 75.84%, H 7.10%.

Methyl 6-methoxy-2′,4′,6′-triisopropylbiphenyl-3-carboxylate 13. ^{1}H NMR: 1.06 (6H, d, *J*=6.9 Hz), 1.30 (6H, d, *J*=6.9 Hz), 2.48 (2H, sept, *J*=6.9 Hz), 2.95 (1H, sept, *J*=6.9 Hz), 3.78 (3H, s), 3.87 (3H, s), 6.98 (1H, d, *J*=8.63 Hz), 7.06 (2H, s), 7.78 (1H, d, *J*=2.24 Hz), 8.06 (1H, dd, *J*=2.24; 8.63 Hz). ^{13}C NMR: 23.84 (q), 24.04 (q), 24.24 (q), 30.65 (2d), 34.19 (d), 51.85 (q), 55.46 (q), 109.97 (d), 120.61 (2d), 122.22 (s), 129.37 (s), 130.63 (d), 132.00 (s), 133.16 (d), 146.67 (2s), 148.02 (s), 167.00 (s).

Detection of a CO_2 emission

The coupling reaction of **1** and **2** was carried out as previously described, however using 700 mg (2.4 mmol) of iodoaromatic **1**. A slow stream of N_2 was intermittently passed through the reaction vessel to a wash bottle containing lime water. After 4 days of reaction, 32 mg (0.32 mmol i.e. 27% of the theoretical amount) of calcium carbonate could be recovered by centrifugation of the lime water. When a similar experiment was run without $Pd(Ph_3)_4$, no coupling reaction could be observed and less than 1 mg of $CaCO_3$ was formed. Therefore, we have not attempted by further experiments to quantitatively recover the CO_2 formed during the coupling reaction.

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