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A new thioglycolic ester β-cyclodextrin/$PdCl_2$ in water: An accessible catalyst for the Suzuki-Miyaura coupling reaction

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ABSTRACT

A novel, easily prepared and accessible water-soluble supramolecular catalyst for the Suzuki-Miyaura C—C coupling reaction was synthesized and characterized by FTIR, NMR, XRD, SEM, and HR-TEM. An inexpensive Pd (II) source added to the resulting aqueous solution of thioglycolic ester β-cyclodextrin (1-TGA-SH-β-CD/$PdCl_2$) showed Pd nanoclusters and efficient catalytic activity for Suzuki-Miyaura C—C coupling reactions of aryl halides with aryl boronic acids, employing K_2CO_3 as base, in an environmentally benign aqueous solution prepared in open flasks. Organic aryl halides including chlorides can produce moderate to excellent yields with aryl boronic acids and a small catalytic amount (0.01 mol%) of 1-TGA-SH-β-CD/$PdCl_2$. This hydro-soluble catalyst stock solution was stable for long periods (more than three months) and could be reused in two runs until showing loss of catalytic activity. Some experiments to understand the mechanism were performed, with the results suggesting incorporation of aryl halide in the catalytic cavity.

1. Introduction

In modern organic synthesis, C—C bond formation certainly is one of the most useful synthetic transformations. Among the most important C—C palladium coupling methods, we can highlight the Suzuki-Miyaura cross-coupling reaction, which is one of the reactions that has revolutionized the pharmaceutical and agrochemical industries, such as for synthesis of the anticancer drug Taxol® (Daneshafruz et al., 2022; Koshvandi et al., 2018; Miyaura & Suzuki, 1979, 1995; Suzuki, 1999). The unique advantages of organoborane reagents, including their low toxicity, high stability, and effortless introduction in various substrates, have been widely recognized, spurring expansion of research. Furthermore, their use has become a prominent strategy for the synthesis of biaryl compounds (Yang et al., 2016). Their uses in the synthesis and preparation of new materials, such as fine chemicals and pharmaceuticals, have also been reported (Heravi & Hashemi, 2012; Koshvandi et al., 2018).

In the Suzuki-Miyaura cross-coupling reaction, normally phosphine ligands are employed for the complexation and activation of the palladium species. However, these standard conditions lead to air and moisture sensitivity, limiting the recyclability of the palladium or catalyst, and leaving unwanted residues, meaning the overall process is not sustainable. These limitations have been motivating the development of efficient, selective and recyclable palladium catalysts for the Suzuki-Miyaura reaction (Molnár, 2011). Thus, many systems have been developed to immobilize Pd catalysts, from inorganics like silica (Sharma & Singh, 2014) and carbon (Taylor & Felpin, 2007), to organics such as polymers (Duan et al., 2015) in polymer-coated nanoparticles (Bortolotto et al., 2015).

Among these catalytic systems, cyclodextrins (CDs) have recently attracted strong attention for Suzuki–Miyaura coupling, in harmony with the green chemistry premises, which in this context are: i) to use

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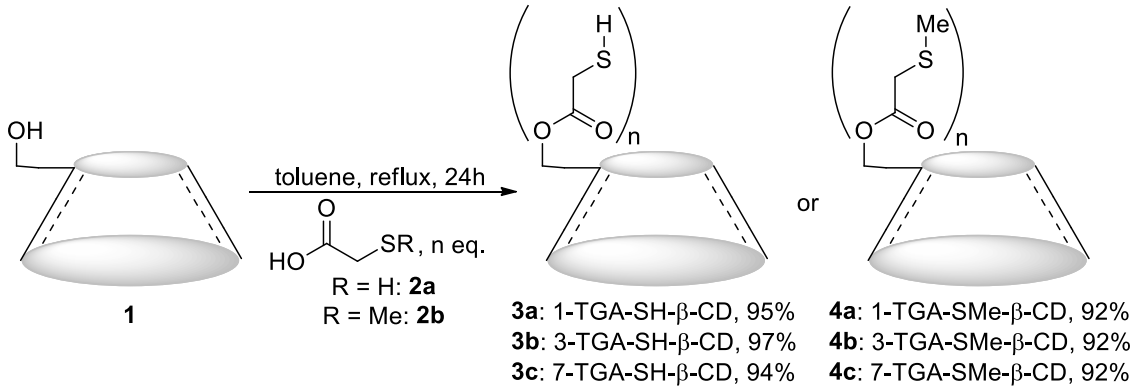


Scheme 1. Synthesis of ligands **3a-3c** and **4a-4c**.

environmentally friendly solvents; ii) to reduce the quantity of Pd; and iii) to improve efficiency and recycling (Kanchana et al., 2020). CDs are well-known cyclic oligosaccharides composed of D-glucopyranoside units (glucose) linked by α-1,4-glycosidic bonds (Steed & Atwood, 2022). In particular, β-CD **1** is composed of 7 units of glucose, and is the most accessible, lowest-priced, and generally the most useful CD (Del Valle, 2004). With a polar hydrophilic outer surface and a hydrophobic non-polar inner cavity, β-CD **1** has shown great potential as an environmentally friendly medium for catalytic processes. β-CD **1** has been used in the native form as ligand with palladium as a catalyst in an aqueous system (Kaboudin et al., 2016), but its use in modified form is more common: as a carbene-ligand (Guitet et al., 2013), ionic-ligand (Kairouz & Schmitzer, 2014; Khan & Pitchumani, 2016), or as a nitrogenated-ligand (Guo et al., 2017; Luo et al., 2018; Shinde et al., 2019; Zhang et al., 2013; Zhou et al., 2018). Sulfur-containing modifications are rare, and as far as we are aware, there is only one example of the synthesis of CD-capped palladium nanoparticles for use as heterogeneous catalysts for the Suzuki-Miyaura reaction. This catalyst consists of Pd nanoparticles prepared using sodium borohydride as reductant and perthiolated β-CD as capping agent, where 1 mol% of catalyst was used in acetonitrile under nitrogen (Strimbu et al., 2003). Few works have described the green synthesis of metallic nanoparticles using functionalized CDs as both capping and reduction agents (Guo et al., 2016). Thus, due to the greater catalytic efficiency of modified CDs and the absence of derivatizations that employ sulfur as a coordination atom of palladium, we now report the use of thioglycolic acid (TGA-SH) as a novel thiol-ester β-CD derivative for use as a ligand or even reducing/stabilizing agent of Pd(II). TGA-SH has already been used as stabilizing agent of CdTe quantum dots (Jhonsi & Renganathan, 2010), but it is not a ligand normally used when palladium is the metal to be coordinated. We also based our choice on the fact that although elemental sulfur is known to poison the catalyst in the Suzuki-Miyaura reaction (Liu et al., 2018), sulfur derivatives have not been proven to inhibit cross-coupling (Mai et al., 2019). Our hypothesis was that an easy and cheap method to obtain a novel sulfur-containing CD derivative using CD and TGA-SH for esterification, followed by addition of $PdCl_2$, as a cheap source of Pd, would produce an efficient water-soluble catalyst for the Suzuki-Miyaura cross-coupling reaction. In order to expand our investigation, thioglycolic acid was methylated (TGA-SMe), the equivalents of ligands to CD were varied (1, 3 and 7 equivalents), and an aryl compound modulated for possible insertion in the cavity of the catalyst was tested. Catalyst recyclability was also evaluated.

2. Experimental section

2.1. Materials

β-Cyclodextrin 97 %, palladium dichloride 99 %, 4-methoxy-phenyl boronic acid (AR), 4-byphenyl boronic acid 95 %, 3-pyridinyl boronic acid 95 %, thioglycolic acid 98 %, methyl iodide 99 %, 4′-bromoacetophenone 98 %, 1-bromo-4-chlorobenzene (AR), chlorobenzene (AR) and toluene (AR) were purchased from Sigma-Aldrich. 4-Tolyl boronic acid (AR) and phenyl boronic acid (AR) were provided by Oakwood Chemical. 4′-Iodoacetophenone 98 % was purchased from TCI America. DMSO-d_6 (99.9 % D) and $CDCl_3$ (99.9 % D) were provided by CIL. 4-Bromoacetanilide was synthesized from acetanilide and bromine in acetic acid. All other materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to standard methods.

2.2. Methods

2.2.1. Synthesis of methyl-thioglycolic acid *2b*

The methylation of thioglycolic acid was adapted from the method described by Liu et al. (2014). To a 0.4 mol L^{-1} NaOH solution (40 mL), 10 mL of ethanol and 20 mmol of thioglycolic acid were added. The solution was stirred for 1 h and then 24 mmol of methyl iodide was added, and the mixture was stirred for 2 h. After the reaction time, the mixture was acidified with a 6.0 mol L^{-1} hydrochloric acid solution, until reaching a pH range of 2–3. The product was extracted with ethyl acetate, washed with saturated NaCl solution, dried over anhydrous sodium sulfate, filtered and concentrated in a vacuum. The **2b** product was vacuum distilled in a Kugelrohr distillation system, furnishing 1.33 g of product (63 % yield).

2.2.2. Synthesis of ligands

The thiol-ester β-CD ligands were obtained by a method adapted from the literature (Bourgeat-Lami & Guyot, 1997). The β-CD **1** was esterified with thioglycolic acid **2a** and methylated thioglycolic acid **2b** according to Scheme 1. The β-CD (0.5 mmol) was dissolved in 10 mL of toluene and refluxed until the water was removed with the aid of 3A molecular sieves added to the reflux condenser. Acid **2a** or **2b** was added in three different proportions (1, 3 and 7 equivalents; 0.5 mmol, 1.5 mmol and 3.5 mmol, respectively) in different systems, and the reactions were carried out by reflux for 24 h through 3A molecular sieves. The solvent was removed by a rotary evaporator, the product was then washed with 10 mL of ice-cold acetone and centrifuged 3 times to remove unreacted **2a** or **2b**. The material was transferred to a Petri dish and dried in a vacuum oven at 60 °C for 1 h to remove the acetone. White products were obtained with yields above 90 %.

2.2.3. Catalyst synthesis

The catalysts were obtained according a previously described method (Zhou et al., 2018). In a flask with degassed water, the ligand and palladium dichloride were mixed in a molar ratio of 2:1. Ligands **3a-3c** and **4a** (0.0334 mmol) were dissolved in H_2O (16.7 mL), and palladium dichloride (0.0167 mmol) was added. The mixture was stirred for 20 min at 100 °C (oil bath temperature) under argon reflux. After the

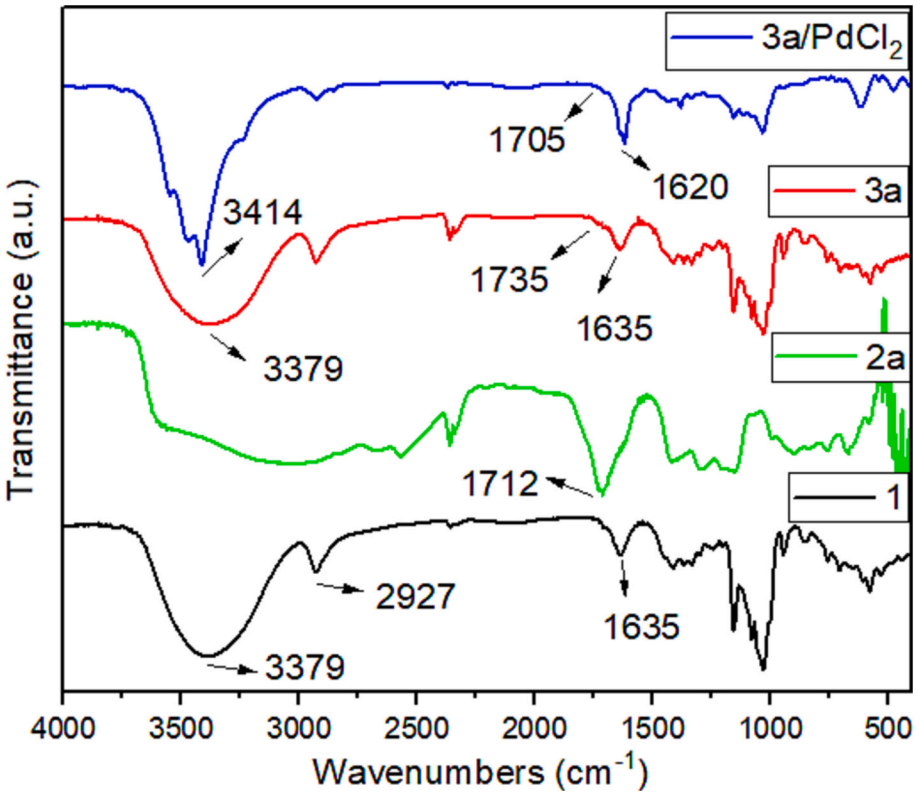


Fig. 1. FTIR spectra of β-CD **1**, thioglycolic acid **2a**, 1-TGA-SH-β-CD **3a** and **3a**/$PdCl_2$.

reaction time, the solution was cooled, and the catalyst solution was stored protected from light in a covered flask (Pd concentration 0.001 mmol mL^{-1}). For NMR, SEM and MET analyses, an aliquot of the **3a**/$PdCl_2$ catalyst was lyophilized in a Christ Alpha 1-4LD Plus freeze dryer, yielding a yellowish powder. For the other analyses, the catalyst was used in an aqueous solution.

2.2.4. General procedure for the Suzuki-Miyaura coupling reaction

A screw cap flask equipped with a magnetic stir bar was charged with aryl halide (0.5 mmol), aryl boronic acid (0.75 mmol), catalyst **3a**/$PdCl_2$ 0.01 mol%, K_2CO_3 (0.75 mmol) and water (5 mL) at 100 °C (oil bath temperature) for four hours. After the reaction, the aqueous phase was extracted with ethyl acetate (3 × 10 mL). Then the combined organic layers were dried over anhydrous Na_2SO_4, concentrated under vacuum and purified by column chromatography.

2.2.5. Large-scale Suzuki-Miyaura coupling reaction

A screw cap flask equipped with a magnetic stirring bar was charged with **6a'** (5.0 mmol), aryl boronic acid **5a** (7.5 mmol), catalyst **3a**/$PdCl_2$ 0.01 mol%, K_2CO_3 (7.5 mmol) and water (50 mL) at 100 °C (oil bath temperature) for four hours. After the reaction, the aqueous phase was extracted with ethyl acetate (3 × 10 mL). Then the combined organic layers were dried over anhydrous Na_2SO_4, concentrated under vacuum and purified by column chromatography, leading to 885.5 mg of **7aa'** biaryl compound (84 % yield).

*2.2.6. Recyclability of **3a**/$PdCl_2$ catalyst*

Investigation of recyclability and reuse of the catalyst was performed using the model reaction with **6a'**, **5a** and **3a**/$PdCl_2$ catalyst. The same concentrations cited in the general procedure for the Suzuki coupling reaction (item 2.2.4.) were used. When the reaction was complete, the aqueous reaction mixture was extracted with ethyl acetate (3 × 10 mL) to remove the product and the remaining aqueous phase was then loaded again with 4-bromo-acetophenone **6a'** and 4-methylphenyl boronic **5a** for the next reaction cycle. All told, there were four reaction cycles, until total loss of catalyst activity.

*2.2.7. Synthesis of biaryl flavonoid **11***

*2.2.7.1. Synthesis of 8-iodo-5,7-dimethoxyflavone **9**.* i) To a stirred solution of chrysin **8** (0.902 g, 3.54 mmol) in dry DMF (15 mL), K_2CO_3 (1.503 g, 10.8 mmol) and CH_3I (859.7 mg, 6.08 mmol) were added. After this addition, the mixture was stirred for 18 h at room temperature. The reaction mixture was then diluted with CH_2Cl_2 (45 mL) and poured into aqueous HCl (1 M) (15 mL). The organic layer was separated, washed with H_2O (3 × 40 mL) and dried over Mg_2SO_4. After concentration to dryness under reduced pressure, the crude product was purified by column chromatography on silica (ethyl acetate 100 %) to afford the known compound 5,7-dimethoxyflavone (945 mg, 99 %) as a white solid. ii) To a stirred solution of dialkylated chrysin (400 mg, 1.42 mmol) in dry DMF (6 mL), NIS (414.4 mg, 1.84 mmol) was added portion-wise. After the addition, the mixture was stirred for 10 h at 70 °C. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and poured into a saturated sodium bicarbonate solution (10 mL). The organic layer was separated, washed with H_2O (3 × 15 mL), dried over Mg_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica (ethyl acetate 100 %) to afford compound **9** (458.4 mg, 79 %) as a white solid.

*2.2.7.2. Synthesis of 8-iodo-5,7-dibenzyloxyflavone **10**.* i) Benzyl chloride (1.81 mL, 158 mmol, 4.0 equiv.) and K_2CO_3 (2.2 g, 159 mmol, 4.0 equiv.) were added to a solution under stirring of chrysin **8** (1 g, 3.93 mmol) in DMF (6 mL). The resulting suspension was stirred at 70 °C for 4 days under an argon atmosphere. After cooling, the solution was acidified to pH 1 with 1 M HCl (30 mL) and extracted with ethyl acetate (25 mL). The solution was left under stirring for 10 min before the resulting precipitate was filtered off and washed with ethyl acetate (50

mL) to give 5,7-dibenzyloxyflavone as an off white solid, pure enough for the next step (1.631 g, 95 %). ii) This compound was synthesized by the same procedure as for the synthesis of compound **9** from 5,7-dimethoxyflavone (500.2 mg, 1.15 mmol). Purification of the crude product by column chromatography on silica (petroleum ether/ethyl acetate 3:7) yielded compound **10** (555.9 mg, 86 %) as a yellow solid.

*2.2.7.3. Synthesis of 5,7-dimethoxy-8-phenylflavone **11**.* A screw cap flask equipped with a magnetic stir bar was charged with flavonoid halide **9** (82.0 mg, 0.2 mmol), phenyl boronic acid **5b** (36.6 mg, 0.3 mmol), catalyst **3a**/$PdCl_2$ (0.01 mol%), K_2CO_3 (41.4 mg, 0.3 mmol) and water (5 mL) at 100 °C (oil bath temperature) for 18 h. After the reaction, the aqueous phase was extracted with ethyl acetate (3 × 10 mL). Then the combined organic layers were dried over anhydrous Na_2SO_4, concentrated under vacuum, and purified by column chromatography (ethyl acetate/methanol 10 %), yielding compound **11** (60.2 mg, 84 %) as a white solid.

2.3. Analyses

Nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were acquired with a Bruker Avance III spectrometer, operating at frequencies of 400 and 500 MHz for ^{1}H and 100 and 125 MHz for ^{13}C, using DMSO-d_6, $CDCl_3$ as solvent. Tetramethylsilane (TMS) was used as internal standard. The multiplicity of signals is abbreviated as follows: d = doublet, m = multiplet, s = singlet. NMR solvents with purity of at least 99.8 % were used. Developed plates were visualized using UV light at 254 nm and 365 nm. High-resolution mass spectra were acquired using an Agilent 6520 Q-TOF mass spectrometer with electron spray ionization (ESI) (QqTOF/MSMicrotof-QII models). Fourier-transform infrared spectroscopy (FTIR) was performed with KBr pellets (solid samples) and NaCl saddle (oils and liquids) using a Shimadzu IRAffinity-1 FTIR device. The thermogravimetric analyses were performed with Shimadzu TGA-60H analyzer, using a nitrogen atmosphere (50 mL min^{-1}), with a heating rate of 10 °C min^{-1} from 25 °C to 800 °C and 5 mg of sample. Melting points were determined with a Thermo Fisher IA9000 Digital Melting Point apparatus. X-ray diffractograms were obtained using a Shimadzu XRD-6000 diffractometer, operating with CuKα radiation at 40 kV and 30 mA, along with a graphite monochromator, from 1.4 to 80° (2θ) scan range, at a scanning rate of 2°min^{-1}. Morphological analyses were performed using a Hitachi S-3400 N scanning electron microscope and Jeol USA JSM-6510LV scanning electron microscope. The transmission microscopic images were obtained using a Jeol JEM-2100 microscope operating at 200 kV.

3. Results and discussion

3.1. Synthesis of ligands

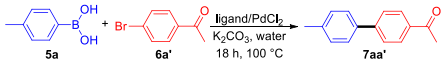
Our simple one-step strategy for synthesis of thioglycolate ligands is schematized in Fig. 1, which summarizes the derivatives with their respective yields.

3.2. Characterization of ligands and catalysts

Fig. 1 shows the FTIR spectra in KBr pellets of pristine β-CD **1** and thioglycolic acid **2a** as well as **1** esterified with 1 equivalent of **2a** (**3a**), and finally the catalyst **3a**/$PdCl_2$ (1-TGA-SH-β-CD/$PdCl_2$). The spectra using other **1**:**2a** molar ratios (**3a-3c**), as well as methylated ligands (n-TGA-SMe-β-CD, **4a-4c**), are shown in the Supporting Information (Figs. 1S and 2S, respectively). As seen in Fig. 1, the spectrum of **1** presents a broad and intense band at 3379 cm^{-1} as well as bands at 2927 cm^{-1} and 1635 cm^{-1}, assigned to asymmetric stretching of the hydroxyl —OH group, asymmetric stretching of the —CH group and hydroxyl axial deformation, respectively (Egyed, 1990; Tammer, 2004). In the spectrum of **2a**, a band at 1712 cm^{-1} is assigned to asymmetric vibration of the —C═O group of carboxylic acid, and the shift of this band to higher frequencies is indicative of the esterification (Kondratenko et al., 2020). The **3a** ligand presents bands of 1 at 3379 cm^{-1} and 2927 cm^{-1}, indicating the molecular integrity of β-CD after synthesis and purification. The band at 1732 cm^{-1} is attributed to stretching vibrations of the —C═O group, contained in the ester bond, indicating that compound **2a** was successfully linked to the β-CD **1**. An increase in the intensity of this band is observed, indicating increasing molar ratio of **2a**:**1** (Fig. 1S) (Garavand & Tehrani, 2016; Parsamanesh et al., 2017). The spectrum of the **3a**/$PdCl_2$ catalyst showed a band shift referring to the —C═O group from 1732 cm^{-1} to 1705 cm^{-1}, suggesting interaction of this group with palladium, while the bands at 3417 cm^{-1} and 1620 cm^{-1} indicate possible interaction with the hydroxyl groups of **1** (Garavand & Tehrani, 2016; Kondratenko et al., 2020).

^{1}H and ^{13}C NMR spectra of **1** and β-CD functionalized with **2a** as well as with **2b** (**3a-3c** and **4a-4c**, respectively) are shown in the Supporting Information (Figs. 3S–16S). All ^{1}H NMR spectra show chemical shifts characteristic of **1** H-1 to -H-5. A peak at 2.08 ppm is assigned to the SH group, indicating that **1** was covalently linked to **2a** by esterification. After the functionalization of **1** with **2a**, the intensity of the peak at 4.43 ppm decreased as well as becoming broader, suggesting that deprotonation occurred at the hydroxyl at position 6 (OH-6) of β-CD (see Table 1S) (Garavand & Tehrani, 2016; Schneider et al., 1998). The

Table 1
Optimization of catalysts in the Suzuki-Miyaura cross-coupling reactions.[a]



Entry	Ligand	$PdCl_2$ (mol%)	Yield[b]
1	1-TGA-SH-β-CD (**3a**)	0.001	88%
2	1-TGA-SH-β-CD (**3a**)	0.01	95%
3	1-TGA-SH-β-CD (**3a**)	0.5	81%
4	1-TGA-SH-β-CD (**3a**)	1.0	83%
5	1-TGA-SMe-β-CD (**4a**)	0.001	82%
6	1-TGA-SMe-β-CD (**4a**)	0.01	92%
7	1-TGA-SMe-β-CD (**4a**)	0.5	74%
8	1-TGA-SMe-β-CD (**4a**)	1.0	65%
9	3-TGA-SH-β-CD (**3b**)	0.001	80%
10	3-TGA-SH-β-CD (**3b**)	0.01	88%
11	3-TGA-SH-β-CD (**3b**)	0.5	81%
12	3-TGA-SH-β-CD (**3b**)	1.0	78%
13	7-TGA-SH-β-CD (**3c**)	0.001	89%
14	7-TGA-SH-β-CD (**3c**)	0.01	90%
15	7-TGA-SH-β-CD (**3c**)	0.5	87%
16	7-TGA-SH-β-CD (**3c**)	1.0	79%
17	1-TGA-SH-β-CD[c] (**3a**)	0.01	80%
18	β-CD (**1**)	0.01	73%
19	**1-TGA-SH-β-CD[d] (3a)**	**0.01**	**98%**
20	1-TGA-SH-β-CD (**3a**)	None	0%
21	1-TGA-SH-β-CD[e] (**3a**)	0.001	87%
22	None	0.01[f]	76%

a) Reaction conditions: 4-bromoacetophenone (0.5 mmol), 4-methylphenyl boronic acid (0.75 mmol); K_2CO_3 (0.75 mmol), catalyst/concentration (see Table) and degassed water (5 mL) were stirred under argon for 18 h at 100 °C (oil bath temperature); b) isolated yield; c) aqueous catalyst solution prepared with 1:1 equivalents of ligand and $PdCl_2$; d) non-degassed water; e) 1 % *v*/v of TPGS-750 M; f) only $PdCl_2$ was employed.

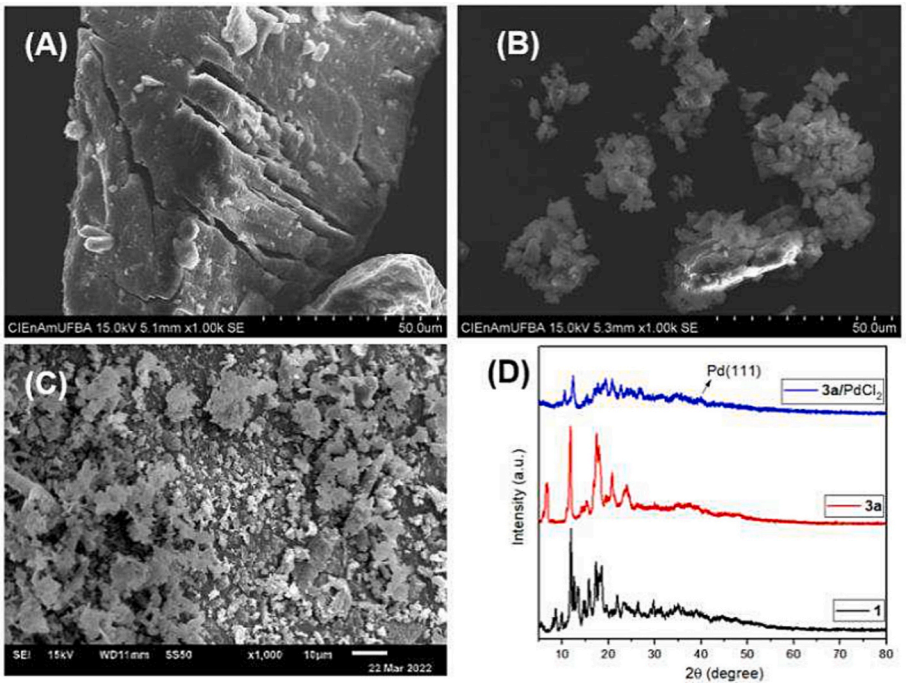


Fig. 2. SEM images of **1** (A), **3a** (B), catalyst **3a**/$PdCl_2$ (C) and XRD of **1**, **3a** and **3a**/$PdCl_2$ (D).

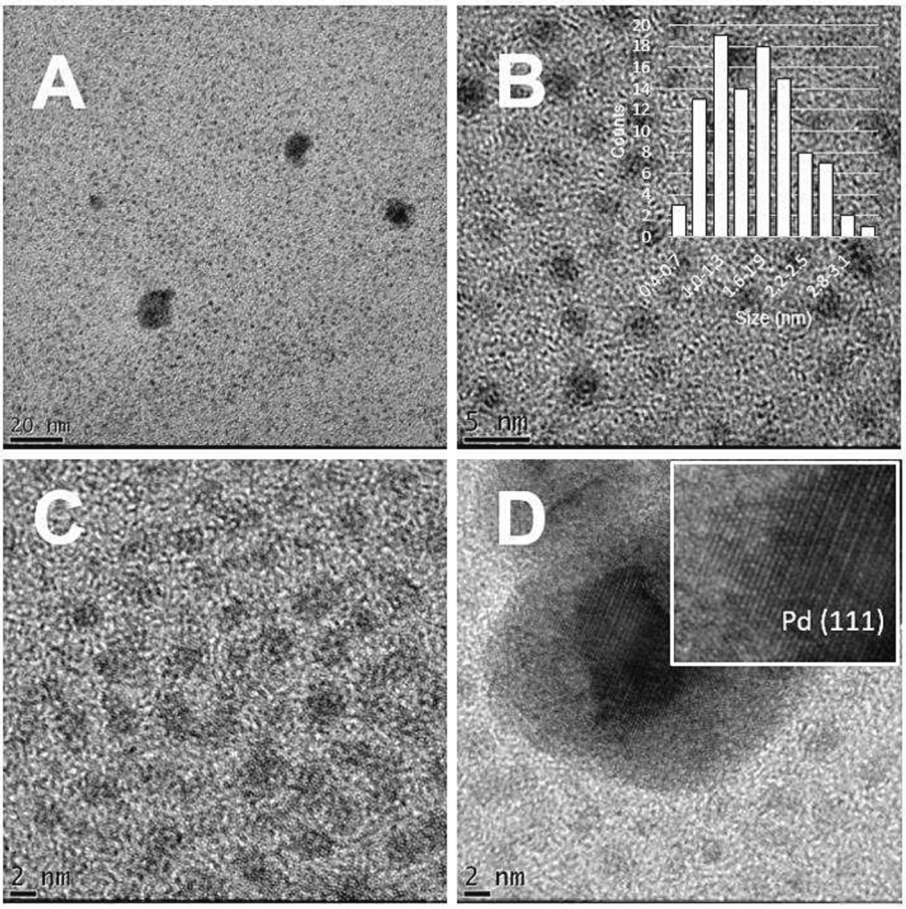


Fig. 3. (A-C) Representative TEM images of the catalyst **3a**/$PdCl_2$ at different magnifications. The inset in B shows the histogram of Fig. 4B–C (total number of particles measured = 100). (D) High resolution of a bigger particle (small population) showing the (111) crystalline planes of Pd in the inset.

formation of ligand **3a** was also corroborated by high-resolution mass spectroscopy (Figs. 19S–20S), which presented a peak at 1209.35 *m/z*.

The compounds of **1** esterified with methylated thioglycolic acid **2b** (Figs. 11S–16S, Supporting Information) had the peaks reported in Table S1 related to **1**. A decrease in peak intensity at 4.43 ppm was also observed, confirming the binding of **2b** to the structure of β-CD, preferentially by the primary hydroxyl in position 6. However, the peak referring to the protons of the methyl group was not detected. Structural confirmation was performed by ^{13}C NMR.

With respect to the ^{1}H NMR spectrum of the catalyst **3a**/$PdCl_2$ (Fig. 17S, Table 1), peaks of **1** with shifts of the hydroxyl groups 2 and 3 were seen. Signals at 2.08 ppm and 4.45 ppm, referring to the —SH and OH-6 groups, respectively, were missing, indicating coordination of Pd (II) or Pd binding with these groups. The ^{13}C NMR spectra of ligands **3a-3c** show two peaks, at 30.95 ppm and 171.96 ppm, which are attributed to the -CH_2-SH group and C═O of the ester carbonyl group, confirming that **1** was esterified with **2a**. The signal of **4a-4c** ligands at 32.84 ppm is attributed to the methyl group, confirming the methylation of thioglycolic acid, also showing peaks at 31.95 ppm and 171.96 ppm referring to the carbons of the groups —CH_2— and -C═O. The peaks in the region of 59.89 ppm to 101.90 ppm are attributed to the glycosylated β-CD structure (Schneider et al., 1998). The carbonyl peak in the ^{13}C NMR spectrum of the **3a**/$PdCl_2$ catalyst (see Table 2S) showed a downfield shift of 14.08 ppm; it changed from 171.96 ppm to 186.04 ppm.

The morphology at low magnification of **1**, **3a** and **3a**/$PdCl_2$ was investigated by scanning electron microscopy (SEM), which revealed large blocks related to **1** (Fig. 2A). As seen in Figs. 2B and 2C, **3a** and **3a**/$PdCl_2$ consist of smaller plates with irregular sizes with no well-defined geometric shapes, indicating materials with low crystallinity. This is in agreement with the XRD analysis shown in Fig. 2D. The diffraction peaks between $2\theta = 10.86$ and 22.70° of β-CD indicate its crystalline characteristic (Schiavo et al., 2016; Wang et al., 2011). Additional diffraction peaks and modification of the relative intensities of the existing ones in **1** are observed in the diffractogram of **3a**, suggesting changes in the crystal structure. As more thioglycolic acid and methyl thioglycolic acid chemically bind to the β-CD structure, the material becomes amorphous (Figs. 21S–22S), confirming the structural modification as proposed. For the **3a**/$PdCl_2$ catalyst, the diffraction peak intensities decrease considerably, suggesting a decrease in crystallinity. Furthermore, the characteristic peak of crystalline Pd(0) is detected at $2\theta = 40.1^{\circ}$, corresponding to the (111) plane (JCPDS card #46104). This may be related to nanoparticles of Pd, since it has low intensity and large width at half height value.

The **3a**/$PdCl_2$ catalyst was characterized by high-resolution transmission electron microscopy (HR-TEM) in order to identify the morphology of the possible nanoparticles obtained. The HR-TEM images, as seen in Fig. 3, revealed that most of the Pd particles are very small and quasi-spherical, with mean diameters of 1.62 nm. A small population of bigger particles (ca. 10 nm) was also visualized, and the mean interplanar distance of the palladium clusters was ~0.22 nm, in which the Pd lattice fringes were identified in the particles and assigned to the plane (111) of the Pd crystalline phase, as shown in Fig. 3D (Guo et al., 2016). This result corroborates our XRD analyses. Altogether, the characterization techniques indicated that **3a**/$PdCl_2$ consists of β-CD esterified with 1 equivalent of thioglycolic acid, which may act as reducing and stabilizing agent of $PdCl_2$ because nanoclusters and nanoparticles were visualized by TEM.

3.3. Performance of catalysts in Suzuki-Miyaura cross-coupling

The coupling between 4-methylphenyl boronic acid (**5a**) and 4-bromo-acetophenone (**6a'**) was chosen as a model reaction for the evaluation of the prepared catalysts. The results are summarized in Table 1.

As shown in Table 1, the mono-modified **3a** and **4a** gave good to excellent yields for the model reaction, with slightly better results of non-alkylated ligand 1-TGA-SH-β-CD **3a** (compare entries 1–4 with 5–8). The screening of loading of catalyst indicated that the **3a**/$PdCl_2$ complex had highly efficient catalytic activity for Suzuki-Miyaura cross-coupling when the amount of catalyst was 0.01 mol% (95 % yield, see entry 2). Our screening also proved that higher content of β-CD ligands **3b** (entries 9–12) and **3c** (entries 13–16) led to a decrease in coupling performance. Interestingly, higher contents of catalyst (1.0 mol% of Pd) led to a decrease of the desired cross-coupling product, due to increasing amounts of a byproduct resulting from homo-coupling of boronic acid (4,4′-dimethyl-biphenyl). The performance decrease noted from the use of **3a** to **3b** or **3c** prompted us not to evaluate the **4b** and **4c** in the cross-coupling reaction, due to the inferior results already observed when comparing **4a** versus **3a** and the probable maintenance of the observed trend. The original (2:1) ligand:Pd molar ratio in the preparation of the aqueous catalyst solution proved to be essential, since only 80 % yield was obtained when (1:1) **3a**/$PdCl_2$ was employed (entry 17). Although **1** can be used as ligand without modification in the cross-coupling reaction, the yields were lower (73 %, entry 18). The coupling yields were also low when no ligand was employed (76 %, entry 22), highlighting the positive influence of our ligand **3a**, and did not improve with addition the surfactant TPGS-750 M (Lipshutz et al., 2011) (see entries 21 and 1). Finally, to our delight, an open-air flask can be used without any reduction in yield (entry 19).

Table 2
Optimization of conditions of the Suzuki-Miyaura cross-coupling reactions.[a]

Entry	Temperature	Time	Yield[b]
1	100 °C	1 h	83 %
2	100 °C	2 h	90 %
3	100 °C	4 h	98 %
4	100 °C	6 h	98 %
5	100 °C	18 h	98 %
6	80 °C	4 h	88 %
7	60 °C	4 h	80 %

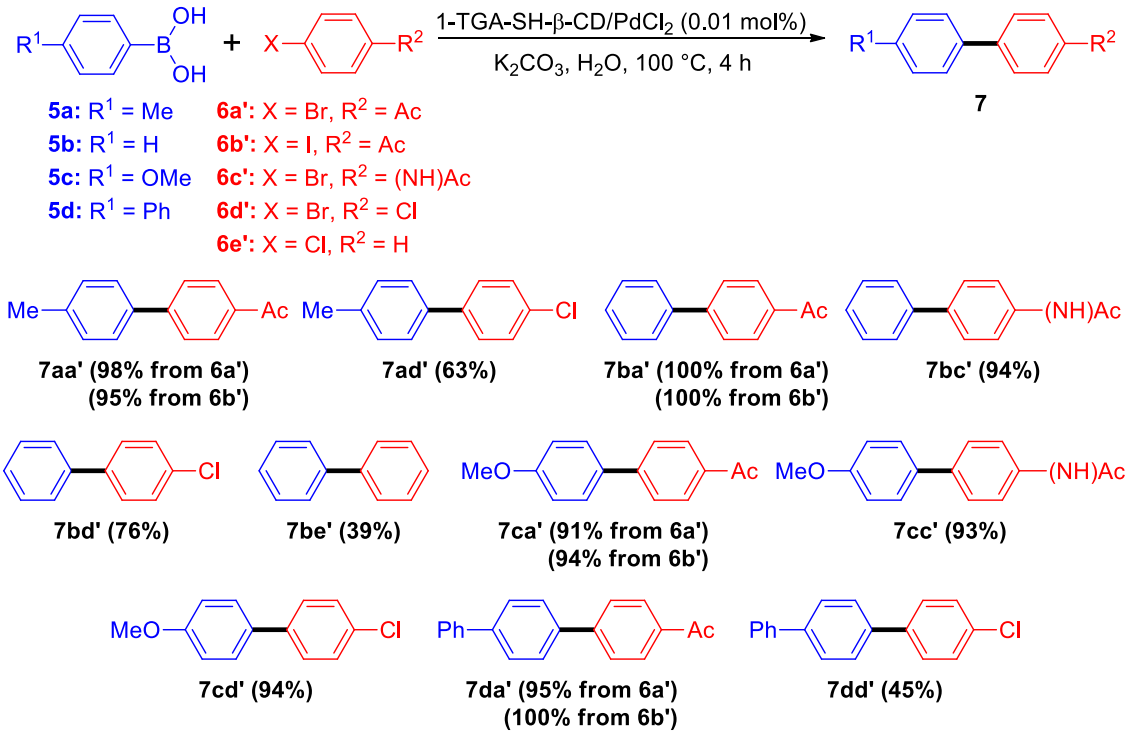
[a] Reaction conditions: 4′-bromoacetophenone (0.5 mmol), 4-methylphenyl boronic acid (0.75 mmol); K_2CO_3 (0.75 mmol), **3a**/$PdCl_2$ (0.01 mol%) and water (5 mL) were stirred in an open flask for the times and at the temperatures (oil bath) shown (see Table).
[b] Isolated yield.

With the best catalyst (**3a**/$PdCl_2$, 0.01 mol%), further optimization of the cross-coupling conditions was conducted (see Table 2). Initially, we observed the optimal reaction time, finding that the maximum yield was achieved with 4 h of reaction (entry 3). Subsequently, different temperatures were evaluated, and 100 °C (oil bath temperature) was selected as the most suitable. Finally, since we had already started our investigation by employing a cheap, safe, efficient, and available base (K_2CO_3) as well as a cheap source of palladium ($PdCl_2$), we did not evaluate changes in these two parameters.

3.4. Application of 1-TGA-SH-β-CD/$PdCl_2$ in Suzuki-Miyaura aqueous cross-coupling

The substrate scope of the catalytic system was explored with a series of phenyl boronic acids (**5a**: 4-methylphenyl; **5b**: phenyl; **5c**: 4-methoxyphenyl; and **5d**: 4-biphenyl) and aryl halides (**6a'**: 4-bromoacetophenone; **6b'**: 4-iodoacetophenone; **6c'**: 4-bromophenylacetamide; **6d'**: 4-chloro-bromobenzene; and **6e'**: chlorobenzene) under optimized conditions: 0.01 mol% of **3a**/$PdCl_2$ as catalyst and 1.5 equivalents of K_2CO_3 at 100 °C (oil bath temperature) for 4 h in 5 mL of water in an open flask (Scheme 2).

4-Bromo and 4-iodoacetophenone (**6a'** and **6b'**, respectively) yielded the same products with all four different boronic acids, producing similar excellent yields. When the *N*-acetamido aryl substituent was present, some limitations were observed (only **7bc'** and **7 cc'** were obtained). Our method showed high chemo selectivity to aryl bromine over



Scheme 2. Synthesis of **7aa'-7dd'** biaryl compounds by aqueous Suzuki-Miyaura cross-coupling reactions (yields refer to isolated products).

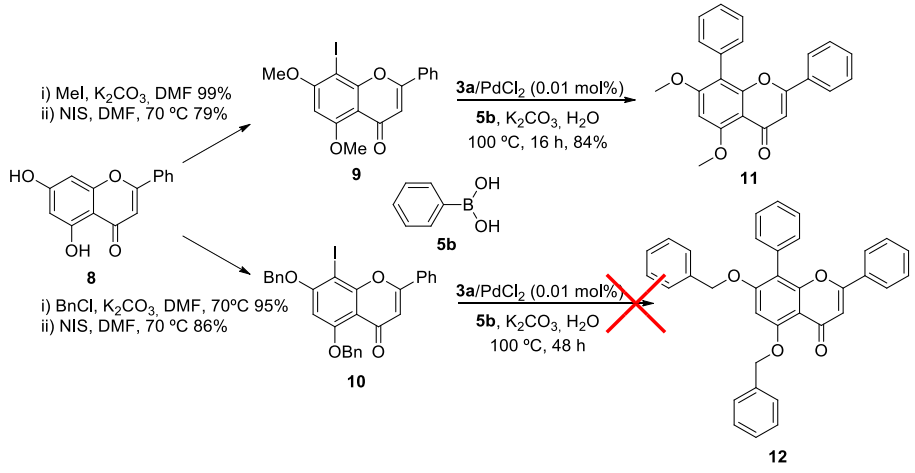
Table 3
Reusability test of **3a**/$PdCl_2$ (0.01 mol%) catalyzed cross-coupling of 4′-bromoacetophenone **6a'** (0.5 mmol), 4-methylphenyl boronic acid **5a** (0.75 mmol) in the presence of K_2CO_3 (0.75 mmol) at 100 °C (oil bath temperature) for 4 h in 5 mL of water in an open flask.

Product	Yield (1st run)	2nd run	3rd run	4th run
7aa'	98	98	48	0

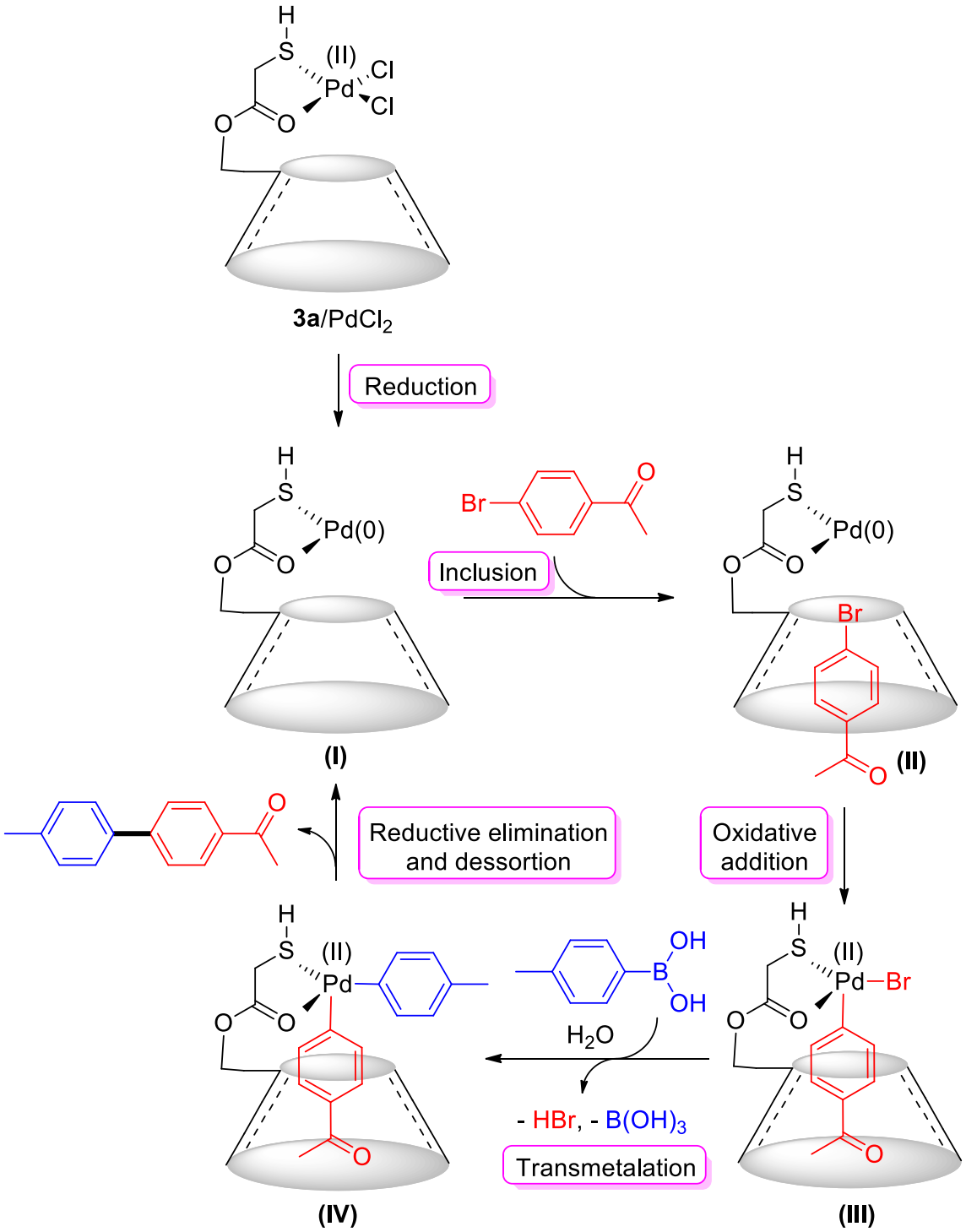
chloride, with moderate to excellent yields (45–95 % yield, compounds **7xd'**). Accordingly, only phenyl boronic acid **5b** furnished the coupling product **7be'** with chlorobenzene **6e'** in low yield (39 %), being unreactive with all other boronic acids employed.

To investigate the practical application of our aqueous catalytic system in the Suzuki–Miyaura cross-coupling reaction, we conducted a gram-scale reaction of **6a'** (995.2 mg, 5.0 mmol) with **5a** in the presence of 0.01 mol% of **3a**/$PdCl_2$ catalyst, and isolated 885.5 mg of the desired product **7aa'** with 84 % yield.

Recycling of the metal catalysts was performed, in which our catalytic system could be recycled and reused without significant loss of catalytic activity two times after extraction of the products with ethyl acetate (Table 3). The reaction yield dropped to 48 % in the third run and was inactive in the fourth attempt. It is noteworthy that we did not observe decomposition to form palladium black in the aqueous phase, which suggests effective stabilization of the catalyst by the ligand **3a,** making recycling feasible (Kaboudin et al., 2016). Evidence of catalyst decomposition to palladium black was only observed when high-content sulfur ligands (**3b** or **3c**, and **4b** or **4c**) were used and in stock solutions after cooling with a few days of storage.



Scheme 3. Syntheses of aryl halides **9** and **10** and their coupling reactions with boronic acid **5b**.



Scheme 4. Proposed mechanism of Suzuki-Miyaura cross-coupling using **3a**/$PdCl_2$ complex as catalyst.

3.5. Proposed mechanism of the Suzuki-Miyaura cross-coupling reaction employing 1-TGA-SH-β-CD/$PdCl_2$ aqueous catalyst

The proposed mechanisms of the aqueous Suzuki-Miyaura cross-coupling reaction mediated with derivatives or pristine β-CD as ligands to the palladium species are controversial. In 2016 Pitchumani and co-workers proposed that the Pd(II)@Pyr:β-CD catalyst acts by an initial Pd (0) active complex (not shown), and both aryl halide and boronic acid are inserted into the catalyst cavity during the coupling (Khan & Pitchumani, 2016). The normal sequence of oxidative addition, transmetalation and reductive elimination steps were respected. In the same year, Jung and coworkers proposed that synthesized DACH-Pd-β-CD recognizes aryl halide, which is then inserted into the cavity (Guo et al., 2017). Then the aryl halide was again reacted with Pd(0), and it was suggested that boronic acid approaches and coordinates within the cavity to form a diaryl complex. A similar suggestion was described in 2019 by Jung and coworkers, who used a modified amino-chain β-CD as ligand to the palladium (Shinde et al., 2019). When pristine β-CD was coordinated with $Pd(OAc)_2$ for a Suzuki–Miyaura cross-coupling reaction in continuous flow, Hartman and Liu suggested that approach and coordination of species occurred outside the cavity (Liu & Hartman, 2019). Despite this divergence over the influence of the catalyst, the

sequence of oxidative addition, transmetalation and reductive elimination involving Pd(0)-Pd(II) species was maintained, with a third-order reaction in the oxidative addition step. Finally, recently Lin and co-workers suggested that the reaction may occur by an unusual Pd(II)/Pd (IV) center when a picolinamide-modified β-CD/Pd(II) complex is employed (Luo et al., 2018). Additionally, the authors described a possible competitive affinity of reactants with the cavity (approach inside or from outside the catalyst), as well as a flexible position of palladium (on top of or outside the cavity).

Taking into account the variety of suggestions in the literature, we decided to carry out some experiments to help determine the relationship between reactants/catalyst affinity/cavity and reaction mechanism. For this, we envisaged a coupling reaction employing an aryl halide that could be modulated to enter or not into the cavity of the catalyst by simple chemical modification. A possible coupling partner would be chrysin **8**. Its transformation to methyl and benzyl ethers, followed by iodination at the C8 position (to yield **9** and **10**, respectively), would provide two flavonoid halides with different steric hindrances for insertion into the catalyst cavity (estimated from 0.60 to 0.70 nm) because of the difference in volume of their substituents. These compounds were synthesized by methylation of chrysin **8** (99 % yield), followed by selective iodination at the C8 position (Lu et al., 2013) with 79 % yield, producing aryl iodide **9**, and by benzylation of **8** (Caldwell et al., 2006) with 95 % yield, followed by iodination (86 % yield) under the same conditions, leading to **10** (Scheme 3). The use of these halides led to distinct results in the aqueous Suzuki-Miyaura cross-coupling reaction: while the smaller and narrower dimethyl halide **9** provided the biaryl product **11** with 84 % yield under standard conditions after 16 h of reaction. The broader dibenzyl halide **10** did not react, even after 48 h, and biaryl compound **12** was not obtained. These results strongly suggest that for the reaction to occur, the insoluble halide must be wrapped by the catalyst, so that it can complex with palladium and continue in the catalytic cycle to the reaction with boronic acid.

Based on these results, we suggest a mechanism based on a few assumptions: i) normal catalytic cycle involving Pd(0)-Pd(II) species; ii) inclusion of the aryl halide within catalyst cavity; and iii) an outside approach of the water-soluble boronic acid (Martin & Buchwald, 2008). In our proposed mechanism (Scheme 4), at first, the chlorines coupled to the Pd(II) center of **3a**/$PdCl_2$ are eliminated to form an activated catalytic Pd(0) complex (I). This step can also be promoted by nanoclusters of Pd(0). Inclusion of aryl halides within the cavity led to inclusion complex (II), which underwent an oxidative addition to the palladium center, leading to the intermediate (III). Next, with the progress of transmetalation, the diaryl complex (IV) is formed. Finally, the desired reductive elimination proceeded, and the cross-coupled biaryl product was released from the cavity.

4. Conclusion

In conclusion, we designed and synthesized the first examples of novel thioglycolate β-CD derivatives added to $PdCl_2$ and their application as efficient catalysts for an aqueous Suzuki-Miyaura cross-coupling reaction in an open-air flask. The derivatives and their systems with Pd (II) addition were characterized by NMR, FTIR, XRD, SEM, and HR-TEM. Among these ligands, 1-TGA-SH-β-CD **3a** afforded the best catalytic performance when complexed with $PdCl_2$. The **3a**/$PdCl_2$ samples showed excellent activity in the Suzuki–Miyaura cross-coupling reaction and the yields of the most desired products ranged from moderate to excellent (63–100 %). The advantages of this catalyst complex arise from its easy and simple preparation and storage, catalytic efficacy (0.01 mol%) under mild reaction conditions, and environmental benefits of the use of water as solvent. Meanwhile, a putative mechanism for aqueous **3a**/$PdCl_2$ catalyzed Suzuki-Miyaura cross-coupling reaction is suggested, based in the controlled experiments. Consequently, these novel thioglycolate β-CD derivatives as ligands will open the way to challenging novel designs of new water-soluble catalyst systems with potential synthetic utility in cross-coupling reactions.

CRediT authorship contribution statement

Viviane Costa de Souza: methodology, validation, investigation, **Gabriel dos Santos Ramos**: validation, investigation. **Juliana Lago Leite**: methodology. **Mauricio Brandão dos Santos**: formal analysis. **Larissa Otubo**: formal analysis. **Zaine Teixeira Camargo**: conceptualization, writing review & editing, supervision. **Mauricio Moraes Victor**: conceptualization, writing review & editing, supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbpol.2022.120271.

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