



HAL
open science

A Calix[8]arene-Based Catalyst for Suzuki–Miyaura Couplings with Reduced Pd_Leaching

Erika Adhel, Axel Labattut, Timothée Naret, Diana Dragoe, Vincent Huc

► **To cite this version:**

Erika Adhel, Axel Labattut, Timothée Naret, Diana Dragoe, Vincent Huc. A Calix[8]arene-Based Catalyst for Suzuki–Miyaura Couplings with Reduced Pd_Leaching. *Catalysts*, 2022, 12 (10), pp.1098. 10.3390/catal12101098 . hal-03874243

HAL Id: hal-03874243

<https://cnrs.hal.science/hal-03874243>

Submitted on 27 Nov 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

Article

A Calix[8]arene-Based Catalyst for Suzuki–Miyaura Couplings with Reduced Pd_Leaching

Erika Adhel , Axel Labattut , Timothée Naret, Diana Dragoe and Vincent Huc *Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO), Université Paris-Saclay,
Rue du doyen Georges Poitou, FR91405 Orsay, France* Correspondence: vincent.huc@universite-paris-saclay.fr

Abstract: Pd-catalysed reactions are amongst the most important in current chemistry. Consequently, very reactive catalysts were developed during the last decades, allowing very high conversions at low catalytic rates. However, decreasing Pd leaching in final products without decreasing catalyst efficiency remains an unsolved issue, especially in the pharma industry. We recently showed that using calixarenes as platforms for Pd-based catalysts constitutes an efficient answer to this concern. In the present work, we show that using these calixarenic platforms in combination with suitably engineered ligands allows for an even more strongly decreased Pd leaching. It thus opens up interesting perspectives for the synthesis of new families of catalysts combining a very high reactivity and a very low Pd leaching in final products.

Keywords: catalysis; palladium; calixarene



Citation: Adhel, E.; Labattut, A.; Naret, T.; Dragoe, D.; Huc, V. A Calix[8]arene-Based Catalyst for Suzuki–Miyaura Couplings with Reduced Pd_Leaching. *Catalysts* **2022**, *12*, 1098. <https://doi.org/10.3390/catal12101098>

Academic Editors: Annaluisa Mariconda and Pasquale Longo

Received: 23 July 2022

Accepted: 14 September 2022

Published: 22 September 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Organometallic catalysis emerged as one of the most powerful synthetic tools during the last century. A broad scope of organic transformations can now be performed in excellent conditions regarding yields, selectivities and catalyst loading [1]. Among them, metal-catalysed C-C bond formation reactions are of central importance, and Pd chemistry offers highly efficient systems in this regard [2–7].

Despite this well documented efficiency, these catalysts are still suffering from drawbacks, especially regarding industrial applications. Indeed, along with cost considerations, the reactivity of a given catalyst (i.e., the amount of Pd to be used for a given transformation) is not the only criterion to be taken into account. Indeed, metal leaching is observed during all Pd-catalysed reactions. This may originate from both catalyst decomposition and activation processes [8], or from the intrinsic solubility of the catalyst used. This could result in final products being contaminated with Pd. This issue turns out to be critical in the pharma industry, where toxicity concerns are of paramount importance. Here, the amount of Pd in active principles is severely constrained (in some cases less than 1 ppm [9]). Post-process removal of metal traces is thus commonly used (often using active carbons or metal scavengers).

These considerations led to the development of supported catalysts [10–15], where the active species are grafted onto solid organic [16,17] or inorganic [18,19] supports. This considerably reduces metal leaching, but also usually decreases the activity of the catalyst, due to its reduced accessibility.

Recently, we described new calixarene-supported catalysts [20,21]. Calix[8]arenes were functionalised by imidazole-derived ligands, that were subsequently converted to carbenes and used for the anchoring of different Pd complexes.

PEPSI-type (Figure 1, Cat. 1, Cat. 2, Cat. 3) or Pd (cinnamyl) complexes (Figure 1, Cat. 4) were obtained in this way. All these calixarene-supported catalysts demonstrated their efficiency for Suzuki–Miyaura [22–27] and Buchwald [28] catalysis, allowing for both

high activities and low metal leaching to be achieved at once. Even if low metal leaching values are observed using calixarenes-supported catalysts [22–28], obtaining even lower values is still required in some cases, and is always an important target by itself.

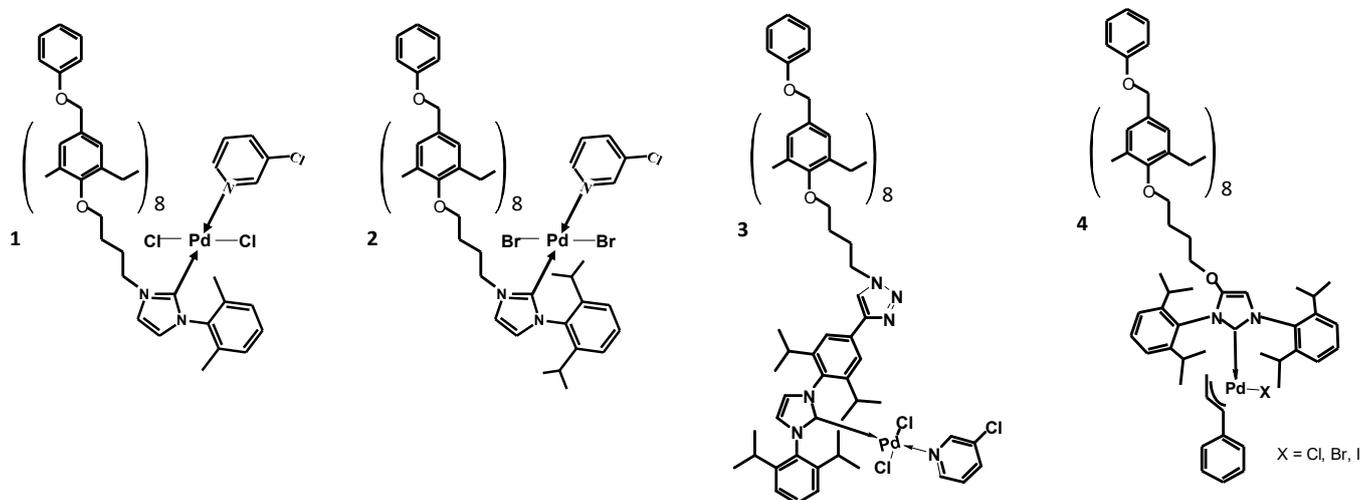
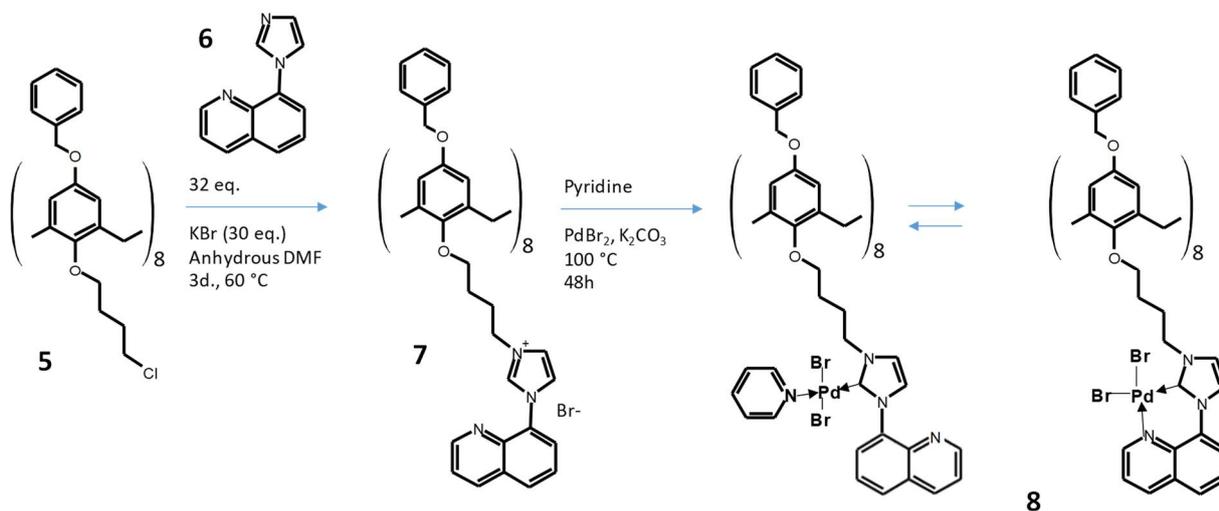


Figure 1. Previously described calix[8]arene-based catalysts.

2. Results and Discussion

Towards that goal, a new calixarene-based catalyst was designed, where the carbenic ligand is associated with a quinoline group, able to form a stable chelate complex with palladium. This possibility is likely to more efficiently hold the Pd species inside the support, thus lowering metallic leaching. Its synthesis is outlined in Scheme 1.



Scheme 1. Synthesis of a calix[8]arene-based catalysts with added quinoline ligand (compound 8).

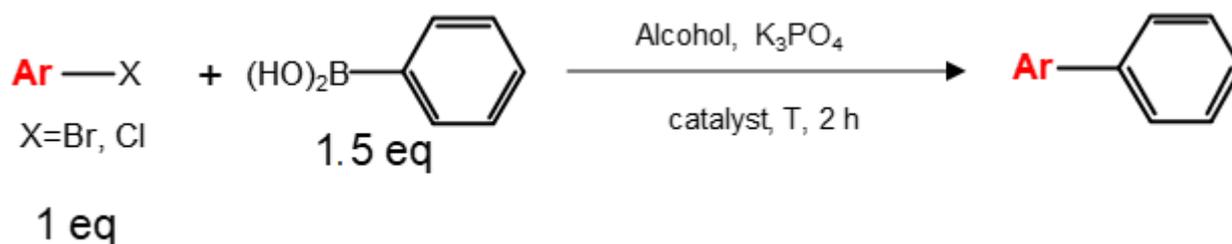
The strategy relies on the alkylation of the commercially available quinoline **6** by the chlorobutyl-functionalised calixarene **5** [22–28]. The resulting imidazolium salt **7** was first characterised by ^1H NMR spectroscopy (see Supplementary Materials), clearly evidencing the presence of the expected imidazolium protons, with the expected intensity. The signals appear quite broadened compared with **5**. This results from the increased crowding associated with the introduction of the quinolinium moieties, resulting in reduced conformational flexibility for the calixarenic macrocycle. However, the signals are sufficiently symmetric to confirm the full conversion of all the chlorobutyl moieties of **5** to imidazolium groups. An elemental analysis of this compound was provided by XPS analysis of a powdered sample.

It shows the presence of the expected elements. Interestingly, the N 1s/Cl 2p normalised ratio is 2.6, close to the expected value of 3 (see Supplementary Materials).

The imidazolium salt **7** is then metalated using palladium bromide in pyridine, resulting in the targeted catalyst, compound **8** [29,30]. ^1H NMR analysis shows the complete disappearance of the imidazolium protons, as expected. The signals appear as quite broadened, as observed for **7**, due to further reduced conformational flexibility. Interestingly, this broadening effect is more pronounced in CDCl_3 compared with $(\text{DMSO})\text{-d}_6$ (see Supplementary Materials). This could be indicative of the presence of aggregated species in the former solvent, due to its smaller dielectric constant. The signals observed in $(\text{DMSO})\text{-d}_6$, although broadened, are sufficiently symmetric to ensure that all the eight constituting units of the calixarenic core are metalated. Despite several attempts, we were not able to achieve mass spectrometry analyses, regardless of the technique used (ESI or MALDI). We believe that the highly apolar nature of the product along with its high molecular weight is not compatible with ESI-MS. Regarding MALDI-MS attempted analyses, it seems that an extensive reduction in the Pd^{2+} ions occurs, resulting in the decomposition of **8**. As reliable elemental analyses cannot be obtained with such large, empty molecules as our calix[8]arenes derivatives, the only option left to obtain accurate information on the composition is thus XPS. Common light elements analysis (C and O) is difficult, as they are widespread contaminants. However, reliable results are obtained for such elements as N, Br and Pd that do not suffer from such contamination problems. Accordingly, the measured N/Pd ratio for compound **8** is 2.7, close to the expected value of 3 (as pyridine is eliminated under the required UHV conditions for XPS analyses). In the same way, the observed Br/Pd ratio is 1.86, close to the expected value of 2.

This, in turn, also confirms the full conversion of **5** to the octa(imidazolium) salt **7** at the previous step. Full synthetic details are provided in the Supplementary Materials, along with the characterisations of all these compounds. Regarding the structure of **8**, it can reasonably be assumed that the presence of the quinoline ligand may favour its occurrence as a chelated specie. However, signals associated with the pyridine ligand are still observed on its ^1H NMR spectra, but their intensity is lower than expected for a 1:1 Pd:pyridine complex. This shows that compound **8** probably exists as two species in equilibrium (Scheme 1). Note that the chelating effect of the large, coordinating aromatic quinoline ligand may also be effective at stabilising the different $\text{Pd}^{\text{II}}/\text{Pd}^{(0)}$ intermediates involved in the catalytic cycle.

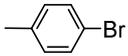
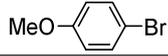
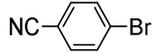
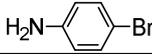
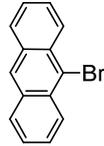
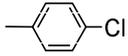
An evaluation of the reactivity of **8** in the Suzuki–Miyaura coupling of a representative scope of aryl halides was performed (Scheme 2).



Scheme 2. Conditions used for reactivity evaluation of compound **8**.

Its activity was compared with a reference catalyst (Cat. 2, Figure 1). The results are reported in Table 1.

Table 1. Compared results obtained with compound 8 and the reference catalyst 2.

Halide	Catalyst	Pd (mol%)	T (°C)	Solvent	Conversion (%) a,b
	Cat. 2	0.001	80	EtOH	93
	8	0.5	80	EtOH	95
	8	0.5	100	n-BuOH	100
	Cat. 2	0.05	80	EtOH	97
	8	2	80	EtOH	76
	Cat. 2	0.05	80	EtOH	>99 ^c
	8	2	80	EtOH	95
	8	1	80	EtOH	100
	8	0.5	80	EtOH	96
	8	0.1	80	EtOH	90
	Cat. 2	0.01	80	EtOH	>99
	8	0.1	80	EtOH	>99
	Cat. 2	0.1	80	EtOH	>99 ^d
	8	0.1	80	EtOH	>99
	Cat. 2	2	80	EtOH	57
	8	0.5	80	EtOH	4
	8	0.5	100	n-BuOH	15

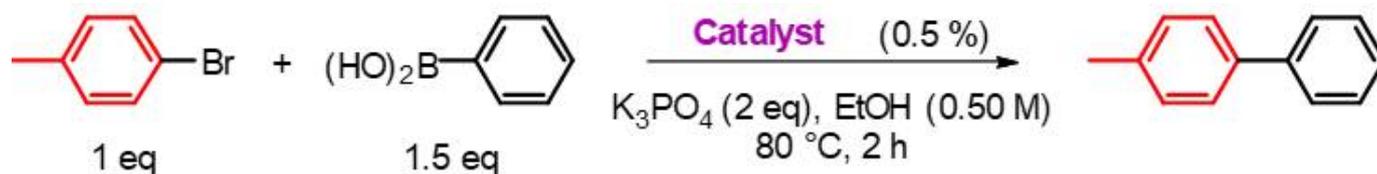
^a Aryl halide (1 eq, 0.50 M), phenylboronic acid (1.5 eq), K₃PO₄ (2 eq), compound 8, argon. ^b Determined by GC. ^c 27 °C. ^d 0.25 M.

The conditions used for these experiments are directly inspired by our previous studies [11–16], with alcohols being used as green solvents.

In these experiments, a high selectivity towards the expected couplings products was obtained, with only small amounts of dehalogenated or deborylated by-products observed. The performances of compound 8 are lower than the reference catalyst Cat. 2 (Figure 1). This was expected, as the presence of the quinoline, acting as an auxiliary ligand, tends to stabilise coordinatively unsaturated Pd species, thus reducing the overall reactivity.

However, the performances of compound 8 are still interesting, as full conversions with a broad panel of substrates are still observed at relatively low catalyst loadings.

With these results in hand, the Pd leaching of compound 8 was measured (and compared with the same reference catalyst as before) using the model reaction shown in Scheme 3.

**Scheme 3.** The reference reaction used for compared leaching evaluation.

The crude reaction media was directly filtered using a filter paper, and the filtrate was mineralized by refluxing in concentrated nitric acid [11].

The results are shown in Table 2.

Table 2. Comparative leaching measurement of Cat. 2 and compound 8.

Catalyst	Conv.	Pd (ppm)
Cat. 2	99%	50
8	95%	12.5

Very high conversions (>90%) were observed for both catalysts.

To insure accurate comparisons, the protocol used for leaching evaluation was the same for both catalysts, regarding (i) filtration, (ii) mineralisation, and (iii) ICP-MS analyses of residual Pd [11–16].

Delightfully, we observed that the leaching of compound **8** is four times lower than the one observed for the reference catalyst **2**, 99.62% of the initial Pd content being retained in the catalyst. Thus, although the presence of the quinoline ligand decreases the reactivity of compound **8**, it also strongly reduces its release of Pd species. This is probably due to their trapping by coordination. Note that the electron-deficient, pi-extended structure of the quinoline moiety is also likely to favour strong stacking interactions with Pd nanoparticles (commonly observed at the end of Suzuki–Miyaura coupling reactions), keeping them inside the support and further reducing leaching values.

3. Materials and Methods

3.1. General

All the solvents were purchased from TCI and Aldrich as anhydrous, and used as received. Compound **5** was purchased from NOVECAL (Orsay, France: <https://www.novecal.com/>, accessed on 22 July 2022). Compound **6** was purchased from CHEMIELIVA (JiangBei, Chongqing, China) and used as received.

3.2. Synthesis of the Imidazolium Salt **7**

In a Schlenk flask equipped with a magnetic stirring bar and flushed with argon, compound **5** (250 mg, 0.1 mmol), **6** (1.2 g, 6.61 mmol) and sodium bromide (1.74 g, 14.6 mmol) were introduced and dry DMF (6 mL) was then added under argon. The reaction mixture was stirred at 60 °C under argon for 3 days. Then, 4 mL of DCM were added and the mixture was filtered over a Celite pad. The filtrate was evaporated under vacuum and the residue was dissolved in DCM and precipitated with Et₂O. The solid was filtrated and washed with Et₂O affording the imidazolium salt **7** as a white solid (136 mg, 31%).

¹H NMR (300 MHz, CDCl₃): δ = 10.51 (s, 8H); 8.80 (s, 8H); 7.73–8.40 (m, 32H); 7.35–7.71 (m, 16H); 7.19 (bs, 40H); 6.42 (bs, 16H); 4.21–4.96 (m, 32H); 3.39–4.21 (m, 32H); 1.48–2.43 (m, 40H).

¹³C NMR (100.4 MHz, CDCl₃): δ = 159.6 (N=(CH)-N)⁺_{imidazolium}; 154.23, 152.20 (quaternary C_{ar}-O); 139.6, 138.4 ArC-H_{pyridine/quinoline}; 130–123 ArC-H.

3.3. Synthesis of Compound **8**

In a Schlenk flask equipped with a magnetic stirring bar and flushed with argon, compound **7** (552 mg, 0.127 mmol), palladium bromide (100 mg, 1.43 mmol) and potassium carbonate (763 mg, 5.1 mmol) were introduced and pyridine (4 mL) was added under argon. The reaction mixture was stirred at 100 °C under argon for 24 h. DCM (20 mL) was added and the mixture was centrifuged. The mixture was filtrated and evaporated under vacuum. The residue was dissolved in DCM and precipitated with Et₂O. The solid was filtrated and washed with Et₂O affording a yellow solid after drying under vacuum (296 mg, 40%).

¹H NMR

(300 MHz, DMSO-d₆): δ (ppm) = 8.74–9.01 (m, 8H), 8.40–8.66 (m, 24H), 8.10–8.22 (m, 8H), 7.49–7.94 (m, 32H), 7.18–7.47 (m, 3H), 6.87–7.15 (m, 5H), 6.52 (bs, 2H), 4.58 (bs, 4H), 3.67–4.16 (m, 4H), 2.39–1.64 (m, 5H).

(300 MHz, CDCl₃): δ (ppm) = 8.82 (d, *o*-pyridine); 7.69 (t, *p*-pyridine); 7.26 (t, *m*-pyridine)–8.95 (m, *o*-quinoline), 7.87 (m, *p*-quinoline); 7.70 (m, *m*-quinoline); 8.6–8.8 (Ar quinoline); 7.2–6.80 (Ar benzyl), 6.2–6.8 (Ar-hydroquinone); 4.25–5 (Ar-CH₂-O-); 3.2–4.2 (Ar-CH₂-Ar/CH₂-O/CH₂-N+); 1.6–2.6 (-CH₂-CH₂-)

¹³C NMR (CDCl₃)

(100.62 MHz): δ (ppm) = 157.16 (*o*-pyridine); 154.5, 152.3 (quaternary C_{ar}-O); 148.4 (C_{carbene}-Pd); 138.61/125.59 (*p*-pyridine/*m*-quinoline); 136/121.8 (C-H carbene); 129.21 (*o*-quinoline); 121.7 (benzylic Ar); 51.35 (benzylic carbon).

3.4. General Protocol for Suzuki–Miyaura Couplings Using Catalyst 8

A 10 mL Schlenk-tube equipped with a magnetic stirring bar and a septum was loaded with the aryl halide derivative (1 mmol), the boronic acid (1.5 mmol), K_3PO_4 (2 mmol) and the catalyst (x mol% Pd). The mixture was dried under vacuum for 10 min and EtOH (anhydrous, 2 mL) and the aryl halide derivative (1 mmol) were then added under argon. The flask was flushed with three brief vacuum/argon cycles. The reaction mixture was subsequently stirred at 80 °C for two (or more) hours. The heterogeneous solution was then allowed to cool down to room temperature, filtered on a Whatman® grade 5 filter (rinsed with EtOH) and the filtrate was evaporated under reduced pressure. The residue was poured into water (20 mL) and extracted with DCM (3×20 mL). The combined organic layers were dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel, to afford the expected biaryl derivatives as pure products.

4. Conclusions

We disclose here a new calix[8]arene-supported Pd PEPPSI catalyst, where an additional quinoline ligand was added on the carbenic core. This new catalyst (along with all the synthetic intermediates) was fully characterised by NMR spectroscopy and XPS analysis.

The performances of this new catalyst were compared with those of previously described reference calix[8]arene-supported ones in Suzuki–Miyaura couplings. This comparison shows that the presence of the quinoline ligand reduces the reactivity, but the performances are still very interesting. Most importantly, it also strongly reduces Pd leaching in the final product. Thus, an important conclusion is that two leaching-reduction strategies can be combined: along with their intrinsically low leaching due to their calixarenic core [11–16], the performances of our previously developed calixarenic support can be further improved by engineering the ligands around the palladium.

This work opens interesting possibilities for the preparation of new families of calixarene-supported catalysts with even improved performances.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12101098/s1>, Figure S1: synthetic scheme of compound 8, Figure S2: 1H NMR spectrum of compound 7; Figure S3: ^{13}C NMR spectrum of compound 7; Figure S4: XPS spectrum of compound 7; Figure S5: 1H NMR spectrum of compound 8 (DMSO)- d_6 , Figure S6: 1H NMR spectrum of compound 8 (CDCl₃), Figure S7: ^{13}C NMR spectrum of compound 8; Figure S8: 2D COSY NMR spectrum of compound 8, Figure S9: 2D HSQC NMR spectrum of compound 8, Figure S10: 2D HMBC NMR spectrum of compound 8, Figure S11: XPS spectra of compound 8; Figure S12: XPS spectra of compound 8 Pd 3d; Figure S13: XPS spectra of compound 8 Br 3d.

Author Contributions: Investigation, E.A., A.L., T.N. and D.D.; supervision, PI of the project, writing and review and of the paper, V.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the French Ministry of research (PhD grant A.L.)

Data Availability Statement: All the experimental data are freely available from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Beller, M.; Bolm, C. *Transition Metals for Organic Synthesis*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2004; Volume 1, pp. 1–19.
2. Miyaura, N.; Yamada, K.; Suzuki, A. A new stereospecific cross-coupling by the palladium-catalyzed reaction of 1-alkenylboranes with 1-alkenyl or 1-alkynyl halides. *Tetrahedron Lett.* **1979**, *20*, 3437–3440. [[CrossRef](#)]
3. Johansson Seechurn, C.C.C.; Kitching, M.O.; Colacot, T.J.; Snieckus, V. Palladium-Catalyzed Cross-Coupling: A Historical Contextual Perspective to the 2010 Nobel Prize. *Angew. Chem. Int. Ed.* **2012**, *51*, 5062–5085. [[CrossRef](#)] [[PubMed](#)]
4. Magano, J.; Dunetz, J.R. Large-scale applications of transition metal-catalyzed couplings for the synthesis of pharmaceuticals. *Chem. Rev.* **2011**, *111*, 2177–2250. [[CrossRef](#)] [[PubMed](#)]

5. Torborg, C.; Beller, M. Recent Applications of Palladium-Catalyzed Coupling Reactions in the Pharmaceutical, Agrochemical, and Fine Chemical Industries. *Adv. Synth. Catal.* **2009**, *351*, 3027–3043. [CrossRef]
6. Han, F.-S. Transition-metal-catalyzed Suzuki-Miyaura cross-coupling reactions: A remarkable advance from palladium to nickel catalysts. *Chem. Soc. Rev.* **2013**, *42*, 5270–5298. [CrossRef]
7. Gildner, P.G.; Colacot, T.J. Reactions of the 21st Century: Two Decades of Innovative Catalyst Design for Palladium-Catalyzed Cross-Couplings. *Organometallics* **2015**, *34*, 5497–5508. [CrossRef]
8. Ananikov, V.P.; Beletskaya, I.P. Toward the Ideal Catalyst: From Atomic Centers to a “Cocktail” of Catalysts. *Organometallics* **2012**, *31*, 1595–1604. [CrossRef]
9. ICH Guideline Q3D (R1) on Elemental Impurities. Available online: https://www.ema.europa.eu/en/documents/scientific-guideline/international-conference-harmonisation-technical-requirements-registration-pharmaceuticals-human-use_en-32.pdf (accessed on 22 July 2022).
10. Wang, W.; Cui, L.; Sun, P.; Shi, L.; Yue, C.; Li, F. Reusable N-Heterocyclic Carbene Complex Catalysts and Beyond: A Perspective on Recycling Strategies. *Chem. Rev.* **2018**, *118*, 9843–9929. [CrossRef]
11. Lemay, M.; Pandarus, V.; Simard, M.; Marion, O.; Tremblay, L.; Béland, F. Synthesis of N-Hydroxypyrazin-2(1H)-ones via Selective O-Debenzylation of 1-Benzyloxypyrazin-2(1H)-ones Using Flow Methodology. *Top. Catal.* **2010**, *53*, 1059–1062. [CrossRef]
12. Jiang, X.; Sclafani, J.; Prasad, K.; Repic, O.; Blacklock, T.J. Pd–Smopex-111: A New Catalyst for Heck and Suzuki Cross-Coupling Reactions. *Org. Process Res. Dev.* **2007**, *11*, 769–772. [CrossRef]
13. Li, G.; Yang, H.; Li, W.; Zhang, G. Rationally designed palladium complexes on a bulky N-heterocyclic carbene-functionalized organosilica: An efficient solid catalyst for the Suzuki-Miyaura coupling of challenging aryl chlorides. *Green Chem.* **2011**, *13*, 2939–2947. [CrossRef]
14. Lee, D.-H.; Kim, J.-H.; Jun, B.-H.; Kang, H.; Park, J.; Lee, Y.-S. Macroporous Polystyrene-Supported Palladium Catalyst Containing a Bulky N-Heterocyclic Carbene Ligand for Suzuki Reaction of Aryl Chlorides. *Org. Lett.* **2008**, *10*, 1609–1612. [CrossRef] [PubMed]
15. Mennecke, K.; Kirschning, A. Immobilization of NHC-Bearing Palladium Catalysts on Polyvinylpyridine: Applications in Suzuki-Miyaura and Hartwig-Buchwald Reactions under Batch and Continuous-Flow Conditions. *Synthesis* **2008**, 3267–3272. [CrossRef]
16. Colacot, T.J. Palladium Based FibreCat and SMOPEX[®] as Supported Homogenous Catalyst Systems for Simple to Challenging Carbon-Carbon Coupling Reactions. *Top. Catal.* **2008**, *48*, 91–98. [CrossRef]
17. Colacot, T.J.; Carole, W.A.; Neide, B.A.; Harad, A. Tunable Palladium-FibreCats for Aryl Chloride Suzuki Coupling with Minimal Metal Leaching. *Organometallics* **2008**, *27*, 5605–5611. [CrossRef]
18. Greco, R.; Goessler, W.; Cantillo, D.; Kappe, C.O. Benchmarking Immobilized Di- and Triarylphosphine Palladium Catalysts for Continuous-Flow Cross-Coupling Reactions: Efficiency, Durability and Metal Leaching Studies. *ACS Catal.* **2015**, *5*, 1303–1312. [CrossRef]
19. Available online: <https://www.silicycle.com/products/functionalized-silica-gels> (accessed on 22 July 2022).
20. Homden, D.M.; Redshaw, C. The use of calixarenes in metal-based catalysis. *Chem. Rev.* **2008**, *108*, 5086–5130. [CrossRef]
21. Santoro, O.; Redshaw, C. Metallocalix [n] arenes in catalysis: A 13-year update. *Coord. Chem. Rev.* **2021**, *448*, 214173. [CrossRef]
22. Abdellah, I.; Kasongo, P.; Labattut, A.; Guillot, R.; Schulz, E.; Martini, C.; Huc, V. Benzyloxy-calix[8]arene: A new valuable support for NHC palladium complexes in C-C Suzuki-Miyaura couplings. *Dalton Trans.* **2018**, *47*, 13843–13848. [CrossRef]
23. Abdellah, I.; Martini, C.; Dos Santos, A.; Dragoe, D.; Guérineau, V.; Huc, V.; Schulz, E. Calix[8]arene as New Platform for Cobalt-Salen Complexes Immobilization and Use in Hydrolytic Kinetic Resolution of Epoxides. *Chem. Cat. Chem.* **2018**, *10*, 4761–4767. [CrossRef]
24. Peramo, A.; Abdellah, I.; Pecnard, S.; Mougín, J.; Martini, C.; Couvreur, P.; Huc, V.; Desmaële, D. A Self-Assembling NHC-Pd-Loaded Calixarene as a Potent Catalyst for the Suzuki-Miyaura Cross-Coupling Reaction in Water. *Molecules* **2020**, *25*, 1459. [CrossRef] [PubMed]
25. Labattut, A.; Fayssal, S.A.; Buendia, J.; Abdellah, I.; Huc, V.; Martini, C.; Schulz, E. Calixarene-supported Pd-NHC complexes as efficient catalysts for scalable Suzuki-Miyaura cross-couplings. *React. Chem. Eng.* **2020**, *5*, 1509. [CrossRef]
26. Labattut, A.; Abdellah, I.; Buendia, J.; Abifayssal, S.; Adhel, E.; Dragoe, D.; Martini, C.; Schulz, E.; Huc, V. Palladium PEPPSI-IPr Complex Supported on a Calix[8]arene: A New Catalyst for Efficient Suzuki-Miyaura Coupling of Aryl Chlorides. *Catalysts* **2020**, *10*, 1081. [CrossRef]
27. Fayssal, S.A.; Naret, T.; Buendia, J.; Labattut, A.; Huc, V.; Martini, C.; Schulz, E. Synthesis, Catalytic Activity and Comparative Leaching Studies of Calix[8]arene-Supported Pd-NHC Complexes for Suzuki-Miyaura Cross-Couplings. *Adv. Synth. Catal.* **2022**, *364*, 947–957. [CrossRef]
28. Abi Fayssal, S.; Naret, T.; Huc, V.; Buendia, J.; Martini, C.; Schulz, E. Benzyloxy-calix[8]arene supported Pd-NHC cinnamyl complexes for Buchwald-Hartwig C-N cross-couplings. *Catal. Sci. Technol.* **2021**, *11*, 5223–5231. [CrossRef]
29. Cui, X.; Li, J.; Zhang, Z.-P.; Fu, Y.; Liu, L.; Guo, Q.-X. Pd(quinoline-8-carboxylate)₂ as a Low-Priced, Phosphine-Free Catalyst for Heck and Suzuki Reactions. *J. Org. Chem.* **2007**, *72*, 9342–9345. [CrossRef]
30. Ingalls, E.L.; Holtzen, G.A.; Kaminsky, W.; Michael, F.E. Synthesis and structural characterization of palladium(II) complexes of chiral bidentate N-heterocyclic carbene-quinoline ligands. *J. Organomet. Chem.* **2017**, *832*, 9–11. [CrossRef]