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Synthesis, characterization and X-ray structures of *N*-heterocyclic carbene palladium complexes based on calix[4]arenes: highly efficient catalysts towards Suzuki–Miyaura cross-coupling reactions

Hui Ren [a], Yong Xu [b], Erwann Jeanneau [a], Isabelle Bonnamour [a,*], Tao Tu [b,*], Ulrich Darbost [a,*]

[a] *ICBMS UMR CNRS 5246, Equipe Chimie Supramoléculaire Appliquée, Université de Lyon, Université Lyon 1, 43 Boulevard du 11 Novembre 1918, F-69622, Villeurbanne, France*
[b] *Department of Chemistry, Fudan University, 220 Handan Road, 200433 Shanghai, China*

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ABSTRACT

A new series of calix[4]arene supported *N*-heterocyclic carbene palladium complexes were developed and fully characterized. A mono-substituted calix[4]arene was prepared through conventional procedures, following with the attachment of imidazolyl derivative groups to compose the precursors of novel NHCs ligands. Undergoing the alkylation with *n*-butylbromide and corresponding metallation with palladium and pyridine, original complexes were obtained. After a full characterization in solution and solid state, the evaluation of catalytic activity was taken out in Suzuki–Miyaura cross-coupling reactions, which revealed good performances.

1. Introduction

N-Heterocyclic carbenes (NHCs) and their transition metal complexes have attracted increasing attention in recent years,[1] due to their wide applications in catalysis and material sciences. Numerous NHC transition metal complexes were developed until now, including metals such as Co,[2] Pd,[3] Cu[4] and Ni.[5] Among them, complexes composed with NHCs and Pd constituted one of the prominent representatives owing to their robustness against air, moisture and heat, which also exhibited excellent catalytic activities in cross-coupling reactions.[3c–l]

From the point of view of coordination chemistry, the calix[4]arene skeleton displays essential advantages. Indeed, attaching a set of podand arms on calixarene skeleton, leads to an attractive platform for the design of sophisticated coordination spheres.[6] Moreover, the calixarene core displays essential advantages features such as preorganization,[7] flexibility[8] and its bulkiness skeleton,[9] as well as its widely tolerance of functional groups and metals. As a consequence, by tethering particular transition metals on such structure, the new series compounds were predicted to be potential candidates as supramolecular catalysts. Thanks to an interaction through the space, the presence of a well-defined cavity near the catalytic centre could induce selectivity in the reaction. Furthermore, the calixarene scaffold could be used to introduce specific features like chirality, fluorescence or hydro solubilizating groups, which can be useful for the design of versatile catalysts.

Following our recent research on developing novel metal complexes and their potential application in catalysis and material sciences,[3k,5b,10a–f,11] NHCs were prior selected to introduce into the calix[4]arene skeleton for novel catalysts owe to their impressive appearance in cross-coupling reactions, such as Suzuki coupling, Heck and amination reactions, even at low catalyst loadings. To the best of our knowledge, there is only a few examples of calixarene supported NHC ligands described in the literature,[4c,12] some of them displaying good catalytic activities towards Suzuki coupling reactions. Complementary studies were carried out by Dominique Matt.[13] In his research, imidazole was introduced to calix[4]arene skeleton as a precursor of NHCs. Ultimately, a series of ligands with direct combination between the upper rim of calix[4]arene and NHCs through one of the nitrogen atoms was reported.[13d,e] The evaluation of catalytic activity indicated that those compounds display good performances as catalyst in Suzuki cross-coupling reactions.

* Corresponding authors. E-mail address: Ulrich.darbost@univ-lyon1.fr (U. Darbost).

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Despite the calix[4]arene cavity, adopting a well-defined cone conformation, it was demonstrated that there was no supramolecular effect involved with the reported complexes. Indeed, due to bulkiness reasons, NHC complexes are constrained in an 'out' conformation, meaning that the PdX_2L moiety is oriented towards the outside of the cavity.

With the aim to evaluate the influence of changing the nature of the *N*-heterocyclic carbene on the conformation and also on the catalytic activity, new calix[4]arene-supported NHCs palladium complexes were developed and investigated. The new compounds were synthesized, fully characterized and their potential catalytic activities towards Suzuki–Miyaura cross-coupling reactions were also evaluated at low catalyst loadings.

2. Results and discussion

2.1. Synthesis and characterization

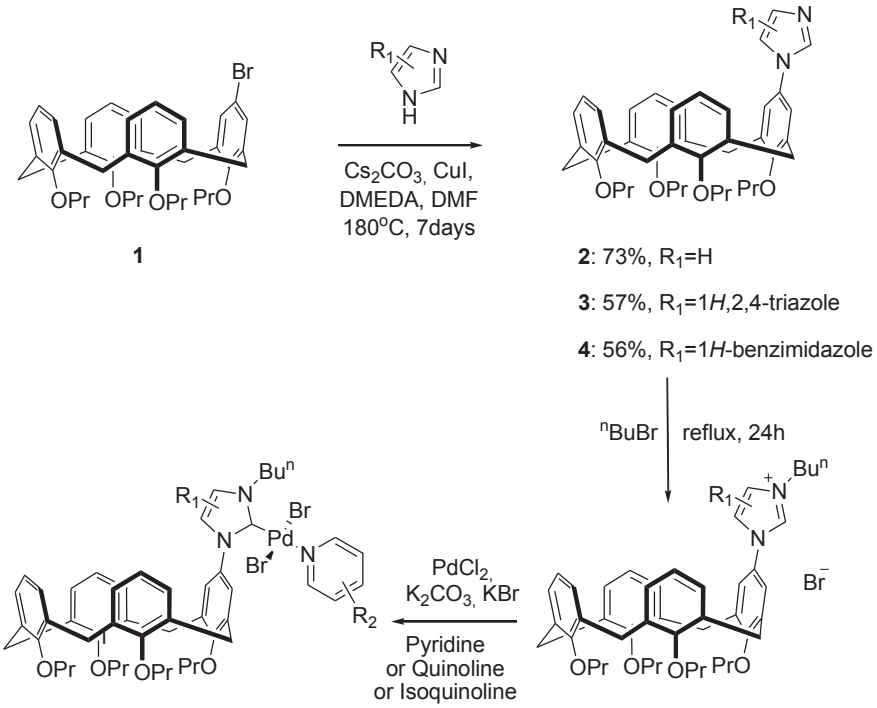
As illustrated in Scheme 1, a series of calix–NHC palladium complexes were prepared in three steps. The starting monobromide calix[4]arene **1**, a key intermediate, was obtained in a 79% overall yield according to literature procedure.[13a] Then, an Ullmann type coupling in the presence of CuI/DMEDA and Cs_2CO_3 in DMF, allows to introduce imidazolyl, triazolyl and benzimidazolyl groups on the wide rim of the calix[4]arene. The original compounds **2**, **3** and **4** were, respectively, synthesized in 73%, 57% and 56% yields and were alkylated with *n*-BuBr in excess, resulting in salts **2a** (88% yield), **3a** (40% yield) and **4a** (87% yield), respectively.

The NMR analysis was implemented after cross-coupling reactions with imidazole derivatives. The resonances of significant protons NCHN from imidazole attest that the new precursors of NHCs ligands were obtained. After subsequent alkylation, characteristic peaks in range of 11.86–10.47 ppm showed up corresponding to active protons, which is a convincing proof of formation of bromides. Finally NHC palladium complexes were obtained using conventional procedures: reaction of calixarenes **2a**–**4a** with $PdCl_2$ in pyridine at 80 °C in presence of K_2CO_3 and KBr afforded the NHC complexes **2b**–**4b** (in 97%, 56% and 87% yields, respectively). In addition, the reaction of **2a** with quinoline or isoquinoline in dioxane in the same conditions gave the NHC complexes **2c** (41%) and **2d** (74%), respectively. All those new structures were purified through chromatography and characterized through 1D NMR such as: ^{1}H NMR, ^{13}C NMR and 2D NMR including: COSY, HSQC, NOESY as well as HRMS.

2.2. Conformational study

The ^{13}C NMR spectra of all the calixarene derivatives **2**–**4** and **2a**–**4a** indicated that $ArCH_2Ar$ signals appeared at the range 32.3–30.8 ppm and their ^{1}H NMR spectra revealed two AB patterns for the diastereotopic $ArCH_2Ar$ protons, both observations demonstrating that the backbone of these calixarene derivatives are in *cone* conformation. Its interesting to note that particular resonances around 10 ppm demonstrate the presence of acidic protons in **2a**–**4a**, which conduces to the composition of NHCs.

New complexes **2b**, **3b** and **4b** were fully characterized. All resonances were well attributed with the contribution of 1D and 2D



Scheme 1. Synthesis of palladium complexes **2b**–**2d**, **3b** and **4b**.

NMR (see details in Supplementary data). The ^{13}C NMR spectra of complexes **2a**–**4a** show ArCH_2Ar signals presence in the range of 32.0–29.7 ppm. In parallel, two AB patterns for the diastereotopic ArCH_2Ar protons appear in their ^1H NMR spectra. Both phenomena indicated that the scaffold of calixarenes is in cone conformation. The signals range in 8.9–8.8 ppm corresponding to *ortho*-protons from pyridine, the chelation between palladium and pyridine was attested (Fig. 1). Through a NOESY experiment, it was also implied that there is no correlation between pyridine and the skeleton of calixarene, which suppose that no spatial interaction between those moieties exist among **2b**, **3b** and **4b**, indicating that all three complexes are constrained in an 'out' conformation.

To our knowledge, those X-ray structures are the first examples of crystallized monomeric calix–NHC–Pd complexes. In the solid state, both the calixarene parts of complexes **2b** and **4b** display a cone conformation, correlating with the observation made through NMR analysis in solution media. The metallic centre adopts a *trans* stereochemistry, with the following remarkable distances: (respectively for **2b** and **4b**) Pd–C 1.95(0) and 1.95(5), Pd–N 2.09(5) and 2.08(3), Pd–Br 2.44(9)/2.42(0) and 2.44(3)/2.43(4). This coordination fashion is classical and similar to the examples described previously by D. Matt et al.[13] In the case of **4b**, its interesting to notice that the NHC moiety of the edifice has a different orientation through space compared to the **2b** complex. Indeed, the dihedral

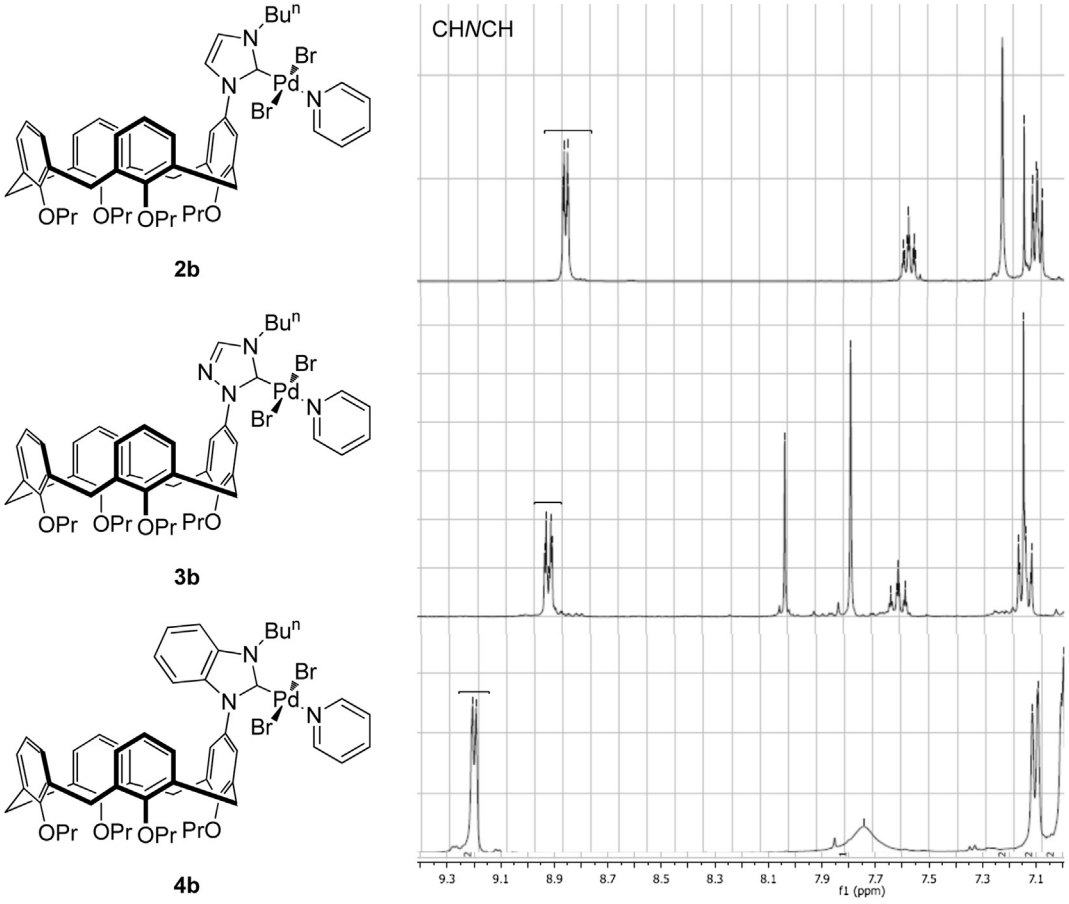


Fig. 1. Triple display of partial ^1H NMR spectra (400 MHz, $CDCl_3$) of complexes **2b**, **3b** and **4b**.

2.3. X-ray structures

Among many attempts of crystallisation, single crystals of the compound **2b** and **4b** were obtained. An X-ray analysis revealed the structures of the two monomeric species and confirmed the conclusions of solution analysis regarding the expected 'out' conformation (Fig. 2).

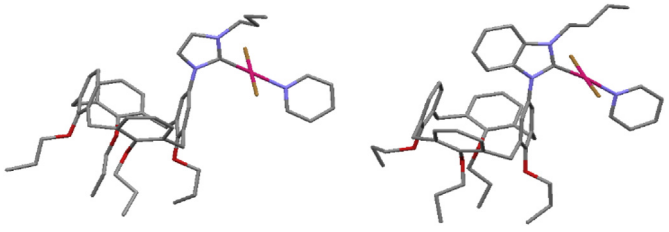
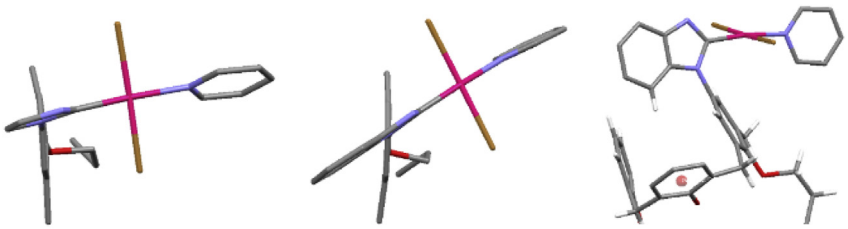


Fig. 2. X-ray structures of **2b** (left) and **4b** (right). Solvent of crystallization and counter anions were omitted for clarity.

angle CAr_{calix}–N_{Im}–C_{Im}–C_{Im} of **4b** is much more closed (52.3(4)°) than the corresponding angle of **2b** (82.5(8)°) (see Fig. 3). This observation could be rationalized with the establishment of a weak C–H…π interaction between the benzimidazole and the proximal aromatic ring of the calixarene H-Centroid 3.54(1). The lack of this interaction in the case of **2b**, leads the PdX_2L being oriented as far as possible from the calixarene, that is to say at almost a right angle.

2.4. Suzuki–Miyaura cross-coupling

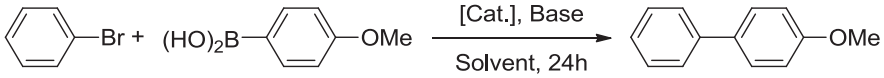
To study the efficiency of our new developed Pd–NHC complexes **2b**–**4b** in Suzuki–Miyaura reactions, bromobenzene and 4-methoxyphenyl boronic acid were selected as substrates to optimize the reaction conditions (Table 1). Preliminary experiments demonstrated that the same results were obtained with NHC–Pd complexes and catalyst formed in situ. The activities observed with our calixarene palladium complexes are similar to those of the Matt complexes.[13a]



(a) 2b (b) 4b (c) 4b

Fig. 3. X-ray structures of **2b** and **4b**. Solvent of crystallization and counter anions were omitted for clarity. View of the dihedral angle $C_{Arcalix}$–N_{Im}–C_{Im}–C_{Im} of **4b** (a) and **2b** (b). Representation of the C–H…π interaction between the benzimidazole and the proximal aromatic ring of the calixarene (c).

Table 1
Condition screening and optimization[a]



Entry	Cat./mol %	Base	Solvent	Yield[b] (%)
1	**2b**/1	*t*-BuOK	Dioxane	57
2	**3b**/1	*t*-BuOK	Dioxane	43
3	**4b**/1	*t*-BuOK	Dioxane	65
4	**4b**/1	KOH	Dioxane	94
5	**4b**/1	K_2CO_3	Dioxane	95
6	**4b**/1	KF	Dioxane	93
7	**4b**/1	KOAc	Dioxane	95
8	**4b**/1	K_3PO_4	Dioxane	99
9	**4b**/0.1	K_3PO_4	Dioxane	98
10	**4b**/0.1	K_3PO_4	DMA	93
11	**4b**/0.1	K_3PO_4	DMF	94
12	**4b**/0.1	K_3PO_4	DME	52
13	**4b**/0.1	K_3PO_4	THF	91
14	**4b**/0.1	K_3PO_4	Toluene	61
15	**4b**/0.08	K_3PO_4	Dioxane	90
16	**4b**/0.05	K_3PO_4	Dioxane	82
17	\	\	Dioxane	NR

[a] 1 mmol scale at 100 °C for 24 h.
[b] Isolated yield.

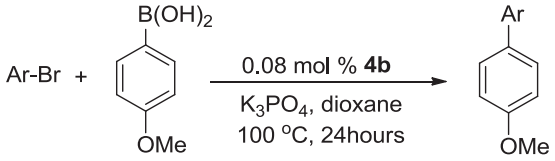
To our delight, a 65% isolated yield of the resulting product was observed when *t*-BuOK was applied as base (Table 1, entry 3); however, when catalysts **2b** and **3b** were applied, lower yields were observed, which may attribute to stronger σ-donor and weaker π-acceptor properties of **4b**. Simultaneously, other potassium bases were selected for further optimization. It is interesting that all selected weak potassium bases like K_2CO_3, KOAc, K_3PO_4 and another strong base KOH accelerated the transformation and resulted in similar satisfactory yields (90–99%, Table 1, entries 4–8). Further decreasing the catalyst loading to 0.1 mol %, a similar excellent isolated yield was afforded when K_3PO_4 and dioxane were used as base and solvent (98% vs 99% Table 1, entries 8 and 9). With other polar solvents, such as DMA, DMF and THF, instead of dioxane, the coupling processes still work well and similar yields beyond 90% were obtained (Table 1, entries 10, 11 and 13). However, the presence of DME and toluene as solvent obviously decreased the reaction activity (Table 1, entries 12 and 13). Additionally, no reactions occurred when selected organic bases were tested. In contrast to the blank test, upon decreasing the catalyst loading to 0.08 mol % or 0.05 mol %, 90% and 82% yields were still obtained when reactions were carried out in the presence of K_3PO_4 and dioxane (Table 1, entries 15 and 16), which further confirmed the catalyst efficiency.

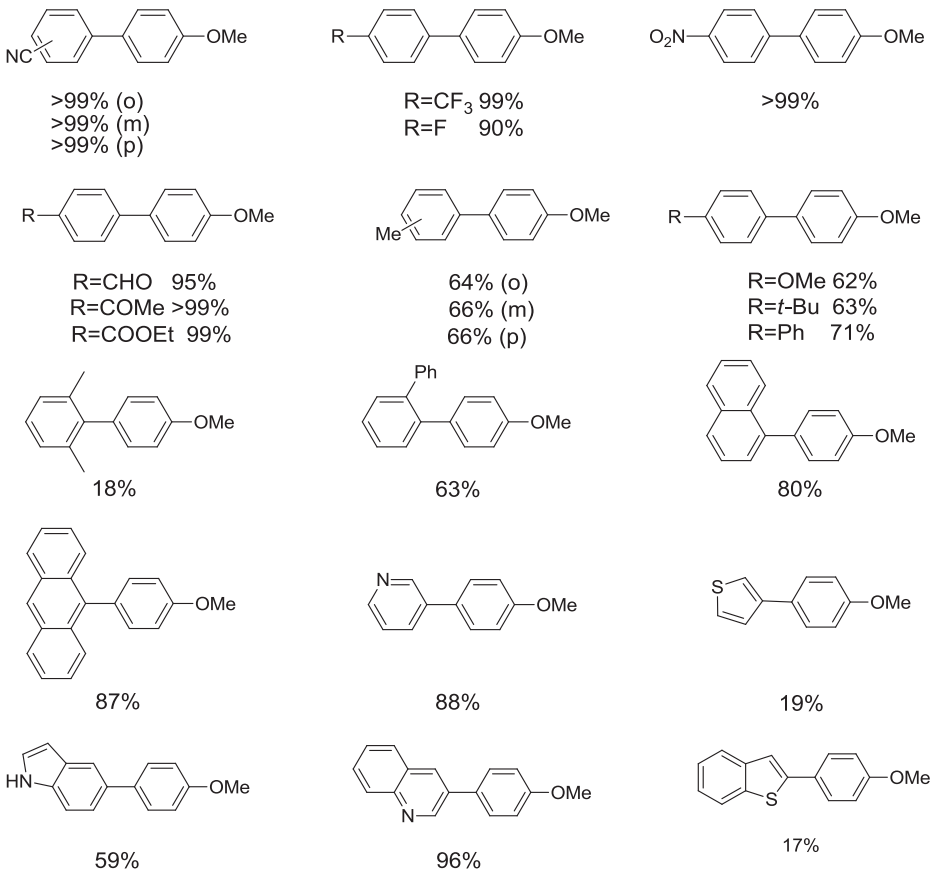
With the optimized reaction conditions in hand, the reaction scope with various aryl bromides was then explored. As shown in Table 2, the protocol well tolerates diverse electronic and steric substituents on one side of the reacting partners, as well as for heterocyclic substrates. To our delight, aryl bromides all gave out good to excellent isolated yields (>90%). Moreover, the relative position of electron-deficient substituents hardly hindered the coupling efficiency. Similar moderate yields were obtained with *o*-, *m*- and *p*-bromotoluene, which revealed that steric substituents on one side of the reacting partners did not influence the coupling efficiency and electronic properties of the electrophiles hampered the coupling process.

For the bulky substrates like 1,1′-biphenyl-2-bromide and 1-bromonaphthalene were applied, good to moderate yields were still obtained. Further investigation of di-*ortho*-substituted bromides afforded in a surprising outcome, in which anthracen-9-yl bromide resulted in a much better yield than 2,6-dimethyl analogue, which indicated that electronic properties influence is greater than steric effects during the transformation and further supported by the coupling outcomes of 1,1′-biphenyl and naphthalenyl bromides.

When other heterocyclic substrates were applied, good to excellent results were observed, which can be further extended to the coupling with heterocyclic substrates containing free NH group and a moderate yield was obtained without any additional protection procedure. Encouraged by the satisfactory results in the coupling of aryl bromides and 4-methoxyphenyl boronic acid, we turned our attention to explore the substrate scope of various arylboronic acids. As illustrated in Table 3, 4-methylphenyl boronic acid and 4-*tert*-butylphenyl boronic acid resulted in similar isolated yields, 96% and 97%, respectively, much higher than a 61% yield obtained with 4-cyanophenyl boronic acid, which demonstrated that electron-donating group does promote the coupling process. In

Table 2
Suzuki–Miyaura couplings with various aryl bromides[a]





[a] 1 mmol scale at 100 °C for 24 h. Isolated yield.

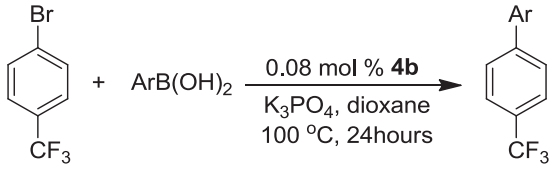
addition, with the same catalyst loading as previous aryl bromides, no reaction is observed. When the catalyst loading was increased up to 2 mol %, only 30–50% isolated yields were observed.

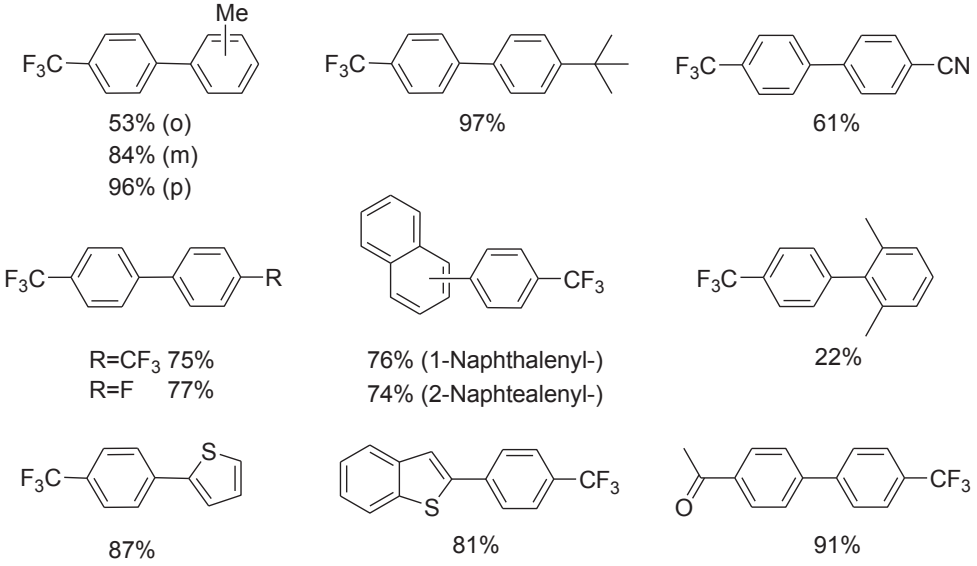
The relative position of substituents impacted the coupling efficiency; *p*-methylphenylboronic acid resulted in a higher yield than its *o*-analogue (96% vs 53%). A 22% yield resulted from 2,6-dimethylphenyl boronic acid suggested that steric substituents on both sides of the reacting partners could hinder the coupling process significantly. Besides, similar moderate yields were obtained with naphthalenylboronic acid and thiophenylboronic acid (74%, 76% and 87%).

3. Conclusion

In summary, a new series of NHC–palladium catalysts attached to the calixarene scaffold was developed. After the preparation of mono-substituted calixarene through conventional procedure, imidazolyl, 1,2,4-triazolyl and benzimidazolyl groups were directly attached to calixarene moiety as a precursor of *N*-heterocyclic carbenes. The series of NHCs was easily formed with the alkylation of *n*-butylbromide, which chelated with palladium to compose new series of catalyst of Suzuki–Miyaura cross-coupling reactions. Through the evaluation of catalytic activity, the calixarene supported *N*-heterocyclic carbenes palladium complexes showed good performance in Suzuki–Miyaura cross-coupling reactions. Unfortunately, the conformational study as well as the catalytic results in catalysis did not allow putting in evidence a supramolecular effect of the macrocycle cavity towards the coupling process. Among the screening of substrates, the electron-donating effect showed accelerating effect on boronic acid, in contrast to the neglectable influence on bromoarene substrates. The 'out' conformation adopted by our new class of *N*-heterocyclic carbene palladium complexes based on calix[4]arenes, let the metallic centre and the cavity far from each other. Constraining the active site to point towards the calixarene core could transfer a supramolecular effect from the calixarene cavity towards the active catalytic site. This researched 'in' conformation could induce a selectivity towards the all possible products of the reaction. With this goal in

Table 3
Suzuki–Miyaura couplings with various arylboronic acids[a]





[a] 1 mmol scale at 100 °C for 24 h. Isolated yield.

mind, new strategies, such as covalent constrain or steric hindrance are currently tested in our laboratory.

4. Experimental section

4.1. General procedure

All commercial reagents were used as received. Solvents were dried by conventional methods. All reactions were carried out under nitrogen. Column chromatography was performed using silica gel (0.040–0.063 nm). Reactions were monitored by TLC on silica gel plate and visualized by UV light. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz. Mass spectra were acquired on an LCQ Advantage ion trap instrument, detecting positive ions (+) or negative ions (−) in the ESI mode. Samples (in methanol/dichloromethane/water, 45:40:15, v/v/v) were infused directly into the source (5 L/min) using a syringe pump. The bromocalix[4]arene compound **1** was prepared according to the literature procedure.[13a]

*4.1.1. 5-(N-Imidazolyl)-25,26,27,28-tetrapropyloxycalix[4]arene (cone) (**2**).* Into an oven-dried resealable tube were added with 5-bromo-25,26,27,28-tetrapropyloxycalix[4]arene **1** (1.027 g, 1.53 mmol, 1.0 equiv), imidazole (0.125 g, 1.84 mmol, 1.2 equiv), CuI (0.154 g, 0.81 mmol, 0.53 equiv), Cs_2CO_3 (1.056 g, 3.24 mmol, 2.1 equiv), *N*,*N*′-dimethylethylenediamine (42 μL, 0.39 mmol, 0.26 equiv) and 5 mL of dry DMF. The mixture was stirred at 170 °C for 7 days. After cooling to room temperature, HCl (1 mol/L, 50 mL) was added followed by $CHCl_3$ (50 mL). The organic layer was separated and the aqueous phase was extracted with $CHCl_3$ (2×50 mL). The combined organic layer was washed with NaOH (2 mol/L, 2×50 mL), then with water (3×100 mL) until pH=5∼7. The organic phase was dried over $MgSO_4$, and evaporated under reduced pressure. The product was afforded by flash chromatography (SiO_2, DCM/MeOH, 100:1, v/v) as a light yellow solid. Yield: 0.736 g, 73%. Mp 163.5–166.7 °C. R_f=0.44 (SiO_2, DCM/MeOH, 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (br, 1H, NC*H*C), 7.26 (s, 1H, NC*H*N), 7.05–6.99 (m, 4H), 6.87 (t, *J*=8.0 Hz, 2H), 6.17 (d, *J*=8.0 Hz, 2H), 6.15 (s, 2H), 6.05 (t, *J*=8.0 Hz, 1H), 4.50 and 3.17 (AB spin system, $^2J_{AB}$=16.0 Hz, 4H; ArCH_2Ar), 4.44 and 3.16 (AB spin system, $^2J_{AB}$=16.0 Hz, 4H; ArCH_2Ar), 4.02–3.97 (m, 4H; OCH_2), 3.76–3.68 (m, 4H; OCH_2), 1.98–1.85 (m, 8H), 18.12–1.06 (m, 6H), 0.91 (t, *J*=8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.58, 155.51, 154.97, 136.87, 135.83, 135.64, 133.61, 129.26 (N*C*HN), 128.58 (N*C*H), 127.33 (N*C*H), 122.15, 121.94, 120.64, 77.08 (O*C*H$_2$), 76.90 (O*C*H$_2$), 76.58 (O*C*H$_2$), 31.06 (Ar*C*H$_2$Ar), 30.92 (Ar*C*H$_2$Ar), 23.44, 23.40, 23.00, 10.70, 10.68, 9.88. HRMS (ESI): calculated for $C_{43}H_{50}N_2O_4$ $[M+H]^+$: 659.3849; found: 659.3820.

*4.1.2. 5-(1-1,2,4-Triazolyl)-25,26,27,28-tetrapropyloxycalix[4]arene (cone) (**3**).* Into an oven-dried resealable tube were added with 5-bromo-25,26,27,28-tetrapropyloxycalix[4]arene **1** (0.204 g, 0.30 mmol, 1.0 equiv), 1,2,4-triazole (0.033 g, 0.48 mmol, 1.6 equiv), CuI (0.030 g, 0.16 mmol, 0.53 equiv), Cs_2CO_3 (0.205 g, 0.63 mmol, 2.1 equiv), *N*,*N*′-dimethylethylenediamine (16 μL, 0.15 mmol, 0.50 equiv) and 1.5 mL of dry DMF. The mixture was stirred at 180 °C for 7 days. After cooling to room temperature, HCl (1 mol/L,

20 mL) was added followed by $CHCl_3$ (20 mL). The organic layer was separated and the aqueous phase was extracted with $CHCl_3$ (2×20 mL). The combined organic layer was washed with NaOH (2 mol/L, 2×20 mL), then with water (3×50 mL) until pH=5～7. The organic phase was dried over $MgSO_4$, and evaporated under reduced pressure. The product was afforded by flash chromatography (SiO_2, MeOH/CH_2Cl_2, 1:100, v/v) as a light yellow solid. Yield: 0.112 g, 57%. Mp 70.9–72.7 °C. R_f=0.35 (SiO_2, DCM/MeOH, 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (br, 2H, triazole), 6.95 (d, *J*=8.0 Hz, 4H), 6.82 (t, *J*=8.0 Hz, 2H), 6.50 (s, 2H), 6.25 (d, *J*=8.0 Hz, 2H), 5.99 (t, *J*=8.0 Hz, 1H), 4.52 and 3.21 (AB spin system, $^2J_{AB}$=18.0 Hz, 4H; ArC*H*$_2$Ar), 4.46 and 3.17 (AB spin system, $^2J_{AB}$=16.0 Hz, 4H; ArC*H*$_2$Ar), 4.03–3.90 (m, 4H, OC*H*$_2$), 3.82–3.72 (m, 4H, OC*H*$_2$), 2.00–1.85 (m, 8H), 1.12–1.05 (m, 6H), 0.95 (t, *J*=8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.31, 155.77, 136.43, 136.00, 135.43, 133.98, 129.05, 128.49, 127.41, 122.11, 121.55, 119.62, 76.93 (O*C*H$_2$), 76.77 (O*C*H$_2$), 76.57 (O*C*H$_2$), 31.04 (Ar*C*H$_2$Ar), 30.87 (Ar*C*H$_2$Ar), 23.34, 23.29, 23.01, 10.57, 10.55, 9.93. HRMS (ESI): calculated for $C_{42}H_{50}N_3O_4$: 660.3796 $[M+H]^+$, found: 660.3770.

*4.1.3. 5-(1-Benzimidazolyl)-25,26,27,28-tetrapropyloxycalix[4]arene (cone) (**4**).* Into an oven-dried resealable tube were added with 5-bromo-25,26,27,28-tetrapropyloxycalix[4]arene **1** (0.208 g, 0.31 mmol, 1.0 equiv), benzimidazole (0.056 g, 0.46 mmol, 1.5 equiv), CuI (0.034 g, 0.18 mmol, 0.58 equiv), Cs_2CO_3 (0.215 g, 0.66 mmol, 2.1 equiv), *N*,*N*′-dimethylethylenediamine (17 μL, 0.16 mmol, 0.5 equiv) and 1.5 mL of dry DMF. The mixture was stirred at 180 °C for 7 days. After cooling to room temperature, HCl (1 mol/L, 20 mL) was added followed by $CHCl_3$ (20 mL). The organic layer was separated and the aqueous phase was extracted with $CHCl_3$ (2×20 mL). The combined organic layer was washed with NaOH (2 mol/L, 2×20 mL), then with water (3×50 mL) until pH=5～7. The organic phase was dried over $MgSO_4$, and evaporated under reduced pressure. The product was afforded by flash chromatography (SiO_2, DCM/MeOH, 100:1, v/v) as a light yellow solid. Yield: 0.123 g, 56%. Mp 83.7–86.1 °C. R_f=0.41 (SiO_2, DCM/MeOH, 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (br, 1H, benzimidazole), 7.18–7.15 (m, 2H), 7.10 (t, *J*=8.0 Hz, 1H, benzimidazole), 7.03 (d, *J*=8.0 Hz, 2H), 6.96 (d, *J*=8.0 Hz, 2H), 6.82 (t, *J*=8.0 Hz, 2H), 6.29 (s, 2H), 6.14 (d, *J*=8.0 Hz, 2H), 5.81–5.78 (m, 1H), 4.48 and 3.14 (AB spin system, $^2J_{AB}$=14.0 Hz, 4H, ArC*H*$_2$Ar), 4.40 and 3.11 (AB spin system, $^2J_{AB}$=12.0 Hz, 4H, ArC*H*$_2$Ar), 4.05–3.91 (m, 4H, OC*H*$_2$) 3.72–3.60 (m, 4H, OC*H*$_2$), 1.97–1.79 (m, 8H), 1.08–1.00 (m, 6H), 0.86 (t, *J*=8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 155.25, 154.96, 136.98, 136.00, 135.56, 133.25, 129.25, 128.62, 127.57, 122.66, 122.32, 122.22, 119.88 (N*C*HN), 77.08 (O*C*H$_2$), 76.59 (O*C*H$_2$), 31.04 (Ar*C*H$_2$Ar), 30.89 (Ar*C*H$_2$Ar), 23.46, 22.97, 10.72, 9.84. HRMS (ESI): calculated for $C_{47}H_{53}N_2O_4$ $[M+H]^+$: 709.4000, found: 709.3997.

*4.1.4. 5-(3-Butyl-1-imidazolylium)-25,26,27,28-tetrapropyloxycalix[4] arene bromide (cone) (**2a**).* The stirred mixture of **2** (0.157 g, 0.24 mmol, 1.0 equiv) and bromobutane (2 mL) was heated at reflux for 24 h. The precipitate formed was collected by filtration and washed with petroleum ether. The white solid was dried under vacuum and used without further purification. Yield: 0.136 g, 72%. Mp 152.7–155.4 °C. R_f=0.42 (SiO_2, DCM/MeOH, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.47 (br, 1H, NC*H*N), 7.31 (s, 1H, NC*H*), 7.05 (d, *J*=8.0 Hz, 2H), 6.99 (d, *J*=8.0 Hz, 2H), 6.86 (t, *J*=8.0 Hz, 2H), 6.73 (s, 1H, NC*H*), 6.41 (s, 2H), 6.24 (d, *J*=8.0 Hz, 2H), 6.06 (t, *J*=8.0 Hz, 1H), 4.58–4.55 (m, 2H, C*H*$_2$N$^+$), 4.49 and 3.25 (AB spin system, $^2J_{AB}$=14.0 Hz, 4H, ArC*H*$_2$Ar), 4.44 and 3.16 (AB spin system, $^2J_{AB}$=14.0 Hz, 4H, ArC*H*$_2$Ar), 4.04–3.90 (m, 4H, OC*H*$_2$), 3.79–3.69 (m, 4H, OC*H*$_2$), 1.97–1.86 (m, 10H), 1.43–1.37 (m, 2H), 1.10–1.04 (m, 6H), 0.97–0.90 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.36, 157.28, 155.97, 137.01, 136.45, 135.88, 135.40, 134.21, 129.20, 128.93, 128.37, 127.26, 122.46, 121.49, 121.33, 121.09, 120.52, 77.32 (O*C*H$_2$), 77.20 (O*C*H$_2$), 76.68 (O*C*H$_2$), 50.07 (*C*H$_2$N$^+$), 32.30 (Ar*C*H$_2$Ar), 30.97 (Ar*C*H$_2$Ar), 30.91 (Ar*C*H$_2$Ar), 23.40, 23.32, 22.97, 19.47, 10.63, 10.56, 9.89. HRMS (ESI): calculated for $C_{47}H_{59}N_2O_4$ $[M-Br]^+$: 715.4469, found: 715.4448.

*4.1.5. 5-(4-Butyl-1-triazolylium)-25,26,27,28-tetrapropyloxycalix[4] arene bromide (cone) (**3a**).* The stirred mixture of **3** (0.113 g, 0.17 mmol, 1.0 equiv) and bromobutane (1 mL) was heated at reflux for 24 h. After cooling down to room temperature, the mixture was evaporated to dryness. The product was afforded through flash chromatography (SiO_2, DCM/MeOH, 20:1, v/v). Yield: 0.054 g, 40%. Mp 145.2–147.5 °C. R_f=0.38 (SiO_2, DCM/MeOH, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.86 (s, 1H, NC*H*N), 9.17 (s, 1H, NC*H*N), 7.14 (s, 2H), 6.73 (d, *J*=8.0 Hz, 2H), 6.68–6.60 (m, 4H), 6.45 (d, *J*=8.0 Hz, 2H), 6.17 (t, *J*=8.0 Hz, 1H), 4.67–4.64 (m, 2H, C*H*$_2$N$^+$), 4.46 and 3.25 (AB spin system, $^2J_{AB}$=16.0 Hz, 4H, ArC*H*$_2$Ar), 4.41 and 3.12 (AB spin system, $^2J_{AB}$=14.0 Hz, 4H, ArC*H*$_2$Ar), 3.87–3.76 (m, 8H, OC*H*$_2$), 2.01–1.98 (m, 2H), 1.93–1.84 (m, 8H), 1.01–0.91 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 156.44, 156.36, 143.69 (NCHN), 139.71 (NCHN), 137.52, 135.31, 134.84, 133.84, 128.72, 128.67, 128.28, 127.83, 122.34, 121.30, 119.83, 48.52 (*C*H$_2$N$^+$), 32.14 (Ar*C*H$_2$Ar), 30.90 (Ar*C*H$_2$Ar), 30.83 (Ar*C*H$_2$Ar), 23.15, 23.11, 23.06, 19.32, 13.34, 10.26, 10.20, 10.11. HRMS (ESI): calculated for $C_{46}H_{58}N_3O_4$ $[M-Br]^+$: 716.4422, found: 716.4392.

*4.1.6. 5-(3-Butyl-1-benzimidazolylium)-25,26,27,28-tetrapropyloxy calix[4]arene bromide (cone) (**4a**).* The stirred mixture of **4** (0.250 g, 0.35 mmol, 1.0 equiv) and bromobutane (2 mL) was heated at reflux for 24 h. After cooling down to room temperature, the mixture was evaporated to dryness. The product was afforded through flash chromatography (SiO_2, DCM/MeOH, 20:1, v/v). Yield: 0.239 g, 81%. Mp 145.2–147.5 °C. R_f=0.50 (SiO_2, DCM/MeOH, 10:1, v/v). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.16 (s, 1H, NC*H*N), 7.63–7.55 (m, 2H), 7.45–7.39 (m, 1H), 7.20–7.12 (m, 4H), 6.95–6.90 (m, 2H), 6.62 (s, 2H), 6.36 (d, *J*=9.0 Hz, 1H), 6.23 (d, *J*=9.0 Hz, 2H), 5.69–5.63 (m, 1H), 4.86–4.81 (m, 2H, C*H*$_2$N$^+$), 4.53 and 3.31 (AB spin system, $^2J_{AB}$=12.5 Hz, 4H, ArC*H*$_2$Ar), 4.48 and 3.18 (AB spin system, $^2J_{AB}$=12.0 Hz, 4H, ArC*H*$_2$Ar), 4.16–3.98 (m, 4H, OC*H*$_2$), 3.80–3.75 (m, 2H, OC*H*$_2$), 3.70–3.65 (m, 2H, OC*H*$_2$), 2.08–1.86 (m, 10H), 1.49–1.42 (m, 2H), 1.15–1.06 (m, 6H), 0.98–0.90 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.39, 156.96, 155.31, 141.24 (N*C*HN), 136.87, 136.57, 136.07, 133.45, 131.16, 130.64, 129.18, 129.08, 127.47, 127.04, 126.45, 126.33, 123.39, 122.54, 121.84, 114.92, 112.47, 77.68, 77.33 (O*C*H$_2$), 76.64 (O*C*H$_2$), 47.38 (*C*H$_2$N$^+$), 31.63 (Ar*C*H$_2$Ar), 30.91 (Ar*C*H$_2$Ar), 30.87 (Ar*C*H$_2$Ar), 23.46, 23.39, 22.94, 19.78, 13.56, 10.71, 10.63, 9.79. HRMS (ESI): calculated for $C_{51}H_{61}N_2O_4$ $[M-Br]^+$: 765.4626, found: 765.4591.

4.2. Palladium complexes

*4.2.1. [5-(3-Butylimidazol-2-yliden-1-yl)-25,26,27,28-tetrapropyloxy calix[4]arene] (pyridine) palladium(II) dibromide (cone) (**2b**).* A mixture of bromide **2a** (0.050 g, 0.063 mmol, 1.0 equiv), $PdCl_2$ (0.013 g, 0.073 mmol, 1.2 equiv), K_2CO_3 (0.067 g, 0.49 mmol, 7.8 equiv), KBr (0.152 g, 1.27 mmol, 20.0 equiv) in pyridine (5 mL) was stirred at 80 °C for 22 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was evaporated to dryness. The crude mixture was purified by flash chromatography (SiO_2, DCM/MeOH, 50:1, v/v) to afford aspect product. Yield: 0.065 g, 97%. Mp 120.1–123.0 °C. R_f=0.55 (SiO_2, DCM/MeOH, 100:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82–8.80 (m, 2H, *o*-*N* in pyridine), 7.60–7.57 (m, 1H, *p*-*N* in pyridine), 7.18 (s, 1H, NC*H* in imidazole), 7.15–7.12 (m, 2H, *m*-*N* in pyridine), 6.90 (d, 1H, NC*H* in imidazole), 6.74–6.68 (m, 5H), 6.55–6.52 (m, 1H), 6.39–6.37 (m, 2H), 6.27–6.24 (m, 2H), 4.51 (t, *J*=8.0 Hz, 2H, C*H*$_2$N$^+$), 4.50 and 3.28 (AB spin system, $^2J_{AB}$=14.0 Hz, 4H, ArC*H*$_2$Ar), 4.47 and 3.16 (AB spin

system, $^2J_{AB}$=16.0 Hz, 4H, ArCH_2Ar), 3.93–3.80 (m, 4H, OCH_2), 3.76–3.72 (m, 4H, OCH_2), 2.06–2.03 (m, 2H), 1.95–1.83 (m, 8H), 1.49–1.43 (m, 6H), 1.00–0.88 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.09, 156.97, 155.93, 152.55 (*o-N* in pyridine), 147.41 (NCN), 137.48, 136.25, 135.72, 134.29, 133.91, 133.24, 128.72 (*p-N* in pyridine), 128.19, 127.94, 126.47, 124.28 (*m-N* in pyridine), 123.40, 122.24, 121.64, 121.23, 77.20 (OCH_2), 76.87 (OCH_2), 76.65 (OCH_2), 51.13 (CH_2N$^+$), 32.01 (ArCH_2Ar), 30.91 (ArCH_2Ar), 29.65 (ArCH_2Ar), 23.27, 23.23, 23.14, 20.02, 13.79, 10.41, 10.20, 10.16. MS (ESI): calculated for $C_{52}H_{63}N_3O_4Pd^{2+}$ [M−2Br]$^{2+}$: 899.4, found: 899.3. Found: C, 59.62; H, 6.03; N, 4.01%. Calculated for $C_{52}H_{67}Br_2N_3O_6Pd$ [M+2H_2O] (M_r=1096.33): C, 56.97; H, 6.16; N, 3.83%.

*4.2.2. [5-(3-Butylimidazol-2-yliden-1-yl)-25,26,27,28-tetrapropyl oxycalix[4]arene] (N-quinoline) palladium(II) dibromide (cone) (**2c**).* A mixture of bromide **2a** (0.051 g, 0.064 mmol, 1.0 equiv), $PdCl_2$ (0.014 g, 0.077 mmol, 1.2 equiv), K_2CO_3 (0.044 g, 0.32 mmol, 5.0 equiv), KBr (0.155 g, 1.28 mmol, 20.0 equiv) and quinoline (380 μL, 3.2 mmol, 50.0 equiv) in dioxane (1 mL) was stirred at 80 °C for 24 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was evaporated to dryness. The crude mixture was purified by flash chromatography (SiO_2, DCM) to afford aspect product. Yield: 0.029 g, 41%. Mp 160.0–162.5 °C. R_f=0.64 (SiO_2, DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J*=8.0 Hz, 1H, *o-N* in quinoline), 7.75 (d, *J*=8.0 Hz, 1H), 7.57–7.42 (m, 3H), 7.30–7.28 (m, 1H), 7.18–7.12 (m, 2H), 6.87–6.77 (m, 3H), 6.68–6.36 (m, 5H), 4.66 (t, *J*=8.0 Hz, 2H, CH_2N$^+$), 4.61 and 3.37 (AB spin system, $^2J_{AB}$=12.0 Hz, 4H, ArCH_2Ar), 4.51 and 3.19 (AB spin system, $^2J_{AB}$=14.0 Hz, 4H, ArCH_2Ar), 4.06–3.77 (m, 8H, OCH_2), 2.27–2.20 (m, 2H), 2.09–1.89 (m, 8H), 1.63–1.57 (m, 2H), 1.14–0.98 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.97, 146.55 (NCN), 137.91, 135.52, 133.57, 130.26, 129.24, 129.11, 128.59, 127.87, 127.72, 127.27, 126.31, 123.39, 122.56, 121.80, 121.20, 121.08, 76.83 (OCH_2), 51.24 (CH_2N$^+$), 32.07 (ArCH_2Ar), 31.07 (ArCH_2Ar), 30.93 (ArCH_2Ar), 23.42, 23.31, 23.17, 20.16, 13.82, 10.18. HRMS (ESI): calculated for $C_{47}H_{59}N_2O_4^+$ [M−2Br−Pd+H]$^+$: 715.4469, found: 715.4434.

*4.2.3. [5-(3-Butylimidazol-2-yliden-1-yl)-25,26,27,28-tetrapropyloxy calix[4]arene] (N-isoquinoline) palladium (II)dibromide (cone) (**2d**).* A mixture of bromide **2a** (0.050 g, 0.063 mmol, 1.0 equiv), $PdCl_2$ (0.014 g, 0.076 mmol, 1.2 equiv), K_2CO_3 (0.044 g, 0.32 mmol, 5.0 equiv), KBr (0.153 g, 1.26 mmol, 20.0 equiv) and isoquinoline (380 μL, 3.2 mmol, 50.0 equiv) in dioxane (1 mL) was stirred at 80 °C for 24 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was evaporated to dryness. The crude mixture was purified by flash chromatography (SiO_2, DCM) to afford aspect product. Yield: 0.052 g, 74%. Mp 104.9–106.6 °C. R_f=0.72 (SiO_2, DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33 (s, 1H, *o-N* in isoquinoline), 8.71 (d, 1H, *J*=8.0 Hz, *o-N* in isoquinoline), 7.76–7.55 (m, 3H), 7.57–7.56 (m, 2H), 7.39 (s, 1H), 7.26 (s, 1H), 7.00 (s, 1H), 6.93–6.81 (m, 5H), 6.70–6.67 (m, 1H), 6.44 (d, *J*=4.0 Hz, 2H), 6.26 (t, *J*=8.0 Hz, 2H), 4.64 (t, *J*=8.0 Hz, 2H, CH_2N$^+$), 4.54 and 3.31 (AB spin system, $^2J_{AB}$=14.0 Hz, 4H, ArCH_2Ar), 4.48 and 3.17 (AB spin system, $^2J_{AB}$=12.0 Hz, 4H, ArCH_2Ar), 4.05–3.79 (m, 8H, OCH_2), 2.16–2.14 (m, 2H), 2.07–1.91 (m, 8H), 1.60–1.54 (m, 2H), 1.10–0.97 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.19, 157.00, 155.99, 155.83, 148.36 (NCN), 144.14, 136.35, 135.86, 134.12, 133.80, 131.92, 128.88, 128.45, 128.30, 128.27, 127.97, 127.83, 126.86, 126.16, 123.47, 122.49, 121.72, 121.34, 121.16, 76.88 (OCH_2), 76.62 (OCH_2), 51.15 (CH_2N$^+$), 32.04 (ArCH_2Ar), 30.92 (ArCH_2Ar), 29.66 (ArCH_2Ar), 23.79, 23.30, 23.24, 23.12, 20.07, 13.82, 10.45, 10.19, 10.14. HRMS (ESI): calculated for $C_{47}H_{59}N_2O_4$ [M−2Br−Pd+H]$^+$: 715.4475, found: 715.4436.

*4.2.4. [5-(4-Butyltriazol-2-yliden-1-yl)-25,26,27,28-tetrapropyloxy calix[4]arene] (pyridine) palladium(II) dibromide (cone) (**3b**).* A mixture of bromide **3a** (0.054 g, 0.068 mmol, 1.0 equiv), $PdCl_2$ (0.015 g, 0.086 mmol, 1.2 equiv), K_2CO_3 (0.118 g, 0.86 mmol, 12.6 equiv), KBr (0.184 g, 1.54 mmol, 23.0 equiv) in pyridine (1 mL) was stirred at 80 °C for 22 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was evaporated to dryness. The crude mixture was purified by flash chromatography (SiO_2, DCM) to afford aspect product as a yellow solid. Yield: 0.040 g, 56%. Mp 115.3–116.9 °C. R_f=0.50 (SiO_2, DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88–8.86 (m, 2H, *o-N* in pyridine), 8.03 (s, 1H), 7.80 (s, 2H), 7.65–7.61 (m, 1H, *p-N* in pyridine), 7.20–7.16 (m, 2H, *m-N* in pyridine), 6.91–6.88 (m, 2H), 6.73–6.70 (m, 1H), 6.50–6.48 (m, 2H), 6.12–6.06 (m, 4H), 4.59 (t, *J*=8.0 Hz, 2H, CH_2N$^+$), 4.45 and 3.22 (AB spin system, $^2J_{AB}$=12.0 Hz, 4H, ArCH_2Ar), 4.38 and 3.07 (AB spin system, $^2J_{AB}$=14.0 Hz, 4H, ArCH_2Ar), 4.02–3.89 (m, 4H, OCH_2), 3.65–3.62 (m, 4H, OCH_2), 2.21–2.13 (m, 2H), 1.95–1.86 (m, 4H), 1.84–1.77 (m, 4H), 1.51–1.46 (m, 2H), 1.03–0.98 (m, 9H), 0.90–0.83 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.42, 157.61, 155.53, 155.34, 152.69, 142.40, 137.83, 137.12, 136.61, 133.50, 132.84, 132.79, 128.70, 128.27, 127.58, 125.86, 124.52, 122.22, 121.77, 76.86 (OCH_2), 76.75 (OCH_2), 76.42 (OCH_2), 49.33 (CH_2N$^+$), 31.64 (ArCH_2Ar), 30.95 (ArCH_2Ar), 23.42, 23.12, 23.01, 19.90, 13.66, 10.68, 9.98, 9.92. MS (ESI): calculated for $C_{51}H_{64}N_4O_4Pd$ [M−2Br]$^+$: 902.4, found: 902.3. Found: C, 57.57; H, 5.97; N, 5.13%. Calculated for $C_{51}H_{62}Br_2N_4O_4Pd$ (M_r=1058.22): C, 57.72; H, 5.89; N, 5.28%.

*4.2.5. [5-(3-Butylbenzimidazol-2-yliden-1-yl)-25,26,27,28-tetrapropyloxy calix[4]arene] (pyridine) palladium(II) dibromide (cone) (**4b**).* A mixture of bromide **4a** (0.233 g, 0.28 mmol, 1.0 equiv), $PdCl_2$ (0.059 g, 0.33 mmol, 1.2 equiv), K_2CO_3 (0.318 g, 2.30 mmol, 8.3 equiv), KBr (0.662 g, 5.56 mmol, 20 equiv) in pyridine (5 mL) was stirred at 80 °C for 22 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was evaporated to dryness. The crude mixture was purified by flash chromatography (SiO_2, DCM) to afford product as a yellow solid. Yield: 0.248 g, 81%. Mp 141.8–142.8 °C. R_f=0.48 (SiO_2, DCM). ^{1}H NMR (400 MHz, toluene-d_8): δ 8.87 (br, 2H, *o-N* in pyridine), 7.48 (s, 2H), 6.89–6.72 (m, 6H), 6.60 (d, *J*=8.0 Hz, 2H), 6.54 (d, *J*=8.0 Hz, 1H), 6.39–6.37 (m, 3H), 6.28–6.26 (m, 2H), 6.13 (t, 2H, *J*=8.0 Hz), 4.64–4.61 (m, 2H, CH_2N$^+$), 4.38 and 3.09 (AB spin system, $^2J_{AB}$=12.0 Hz, 4H, ArCH_2Ar), 4.32 and 2.92 (AB spin system, $^2J_{AB}$=14.0 Hz, 4H, ArCH_2Ar), 3.85–3.82 (m, 2H, OCH_2), 3.73 (t, *J*=8.0 Hz, 2H, OCH_2), 3.58 (t, *J*=8.0 Hz, 4H, OCH_2), 2.13–2.09 (m, 2H), 1.81–1.65 (m, 8H), 1.32–1.26 (m, 2H), 0.81–0.70 (m, 15H). ^{13}C NMR (100 MHz, toluene-d_8): δ 165.97, 158.22, 157.78, 156.65, 153.46 (*o-N* in pyridine), 137.80, 129.99, 129.59, 129.32, 129.28, 129.08, 128.82, 128.45, 128.21, 127.97, 125.36, 124.17, 123.40, 123.32, 112.23, 110.60, 77.50 (OCH_2), 77.37 (OCH_2), 77.24 (OCH_2), 49.42 (CH_2N$^+$), 31.92 (ArCH_2Ar), 31.63 (ArCH_2Ar), 23.99, 23.97, 23.84, 14.07, 10.91, 10.70, 10.67. HRMS (ESI): calculated for $C_{56}H_{65}N_3O_4Pd$ [M−2Br]$^{2+}$: 949.4010, found: 949.2720.

4.2.6. General procedure for Pd-catalysed Suzuki–Miyaura coupling. In air, potassium phosphate (3 mmol, 0.636 g), catalyst **1** (0.08 mol %, 0.0009 g) and arylboronic acid (2 mmol) were weighed into a 50 mL glass vial that was sealed with a septum and purged with N_2 (3×). Dioxane (1 mL) was then injected via syringe followed by the aryl bromide (1 mmol) (if liquid). If the aryl bromide was a solid, it was introduced into the vial prior to purging with N_2. At this time, the reaction stirred for 24 h at 100 °C. The reaction mixture was concentrated in vacuo and directly purified via silica gel flash chromatography.

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Supplementary data

NMR spectra and mass analyses of all new compounds and complexes (Figs. S1–S54); X-ray data for compounds **2b** and **4b** (Tables 1 and 2 and Figs. S55 and S56) and in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.02.051.

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