Resorcinarene-mono-benzimidazolium salts as NHC ligands for Suzuki–Miyaura cross-couplings catalysts

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Abstract: Two mono-benzimidazolium salts of resorcinarene have been prepared and used as ligands in Suzuki–Miyaura cross-coupling reactions. They have been fully characterized by ^{1}H and ^{13}C NMR, MALDI, and FT-IR spectroscopic methods, and their structures were confirmed by X-ray diffraction analysis. These two new resorcinarene-based mono-benzimidazolium salts showed good catalytic activity for coupling reactions in DMF. The highest conversion was achieved for arylation of 4-bromotoluene using the resorcinarenyl mono-dimethylbenzimidazolium salt.

Key words: Suzuki–Miyaura reaction, resorcinarene, cavitand, N-heterocyclic carbene, benzimidazolium salt, catalyst

1. Introduction

Palladium-catalyzed Suzuki–Miyaura cross-couplings are among the most important and studied cross-coupling reactions.[1−4] Phosphine ligands are often used in palladium-catalyzed reactions, but most of these ligands are not air-stable.[5] The development of air-stable ligands is therefore crucial and N-heterocyclic carbenes (NHCs) have proved to be suitable ligands for Suzuki–Miyaura cross-coupling reactions. NHCs show a powerful σ-donating and weak π-accepting character, allowing for the generation of a stronger bond to the metal in transition metal catalysis. Metal–NHC complexes are air-stable, easy to handle, and highly active in several catalytic transformations.[6−10]

Transition metal complexes of resorcinarenes and their functionalized derivatives such as cavitands and capsules are widely investigated owing to their interesting properties in catalysis.[11−17] The bridging C2 carbon atoms of resorcinarene cavitands are easily functionalized to prepare ligands bearing phosphines and imidazolium salts for several cross-coupling reactions.[18−22] Functionalized structures such as calixarenes,[23−26] cyclodextrins,[29−39] and resorcinarene cavitands[40] have therefore been successfully employed in homogeneous catalysis. All these supramolecular ligands exhibited significant catalytic properties thanks to their hosting abilities toward the reaction substrates. In particular, resorcinarene cavitands have additional advantages thanks to their tailorable structural versatility.

A limited number of cavitands containing mono-imidazolium salts are described.[22,26] These precursors of NHC ligands are known to improve palladium-catalyzed cross-coupling between arylboronic acids and aryl

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halides.[22] As it is known that fine structural modifications in a ligand can affect the activity of a catalytic complex, we designed resorcinarenyl mono-benzimidazolium salts that have never been evoked as monodentate proligands in organometallic catalysis. Herein, we describe the synthesis of the resorcinarenyl mono-benzimidazolium salts and their use in Suzuki–Miyaura cross-coupling reactions between 3,5-dimethoxyphenylboronic acid and several aryl bromides and chlorides. To fully investigate the cavity effect of these new catalytic systems, analogous ligands without cavities have been prepared as well.

2. Results and discussion

2.1. Synthesis and characterization of resorcinarenyl mono-benzimidazolium salts

Mono-benzimidazolium salts **6** and **7** were prepared, both in high yields, according to Scheme 1. Their successful preparation was evidenced by ^{1}H and ^{13}C NMR, MALDI, and FT-IR methods. The synthesis of **6** and **7** began with corresponding benzyl benzimidazoles, which were obtained in 90% yield for **3** and 92% yield for **4**. The benzimidazolium salts **6** and **7** were obtained in quantitative yields by a quaternization reaction of cavitand **5**[41] with N-substituted benzimidazoles **3** and **4** in chloroform under refluxing conditions.
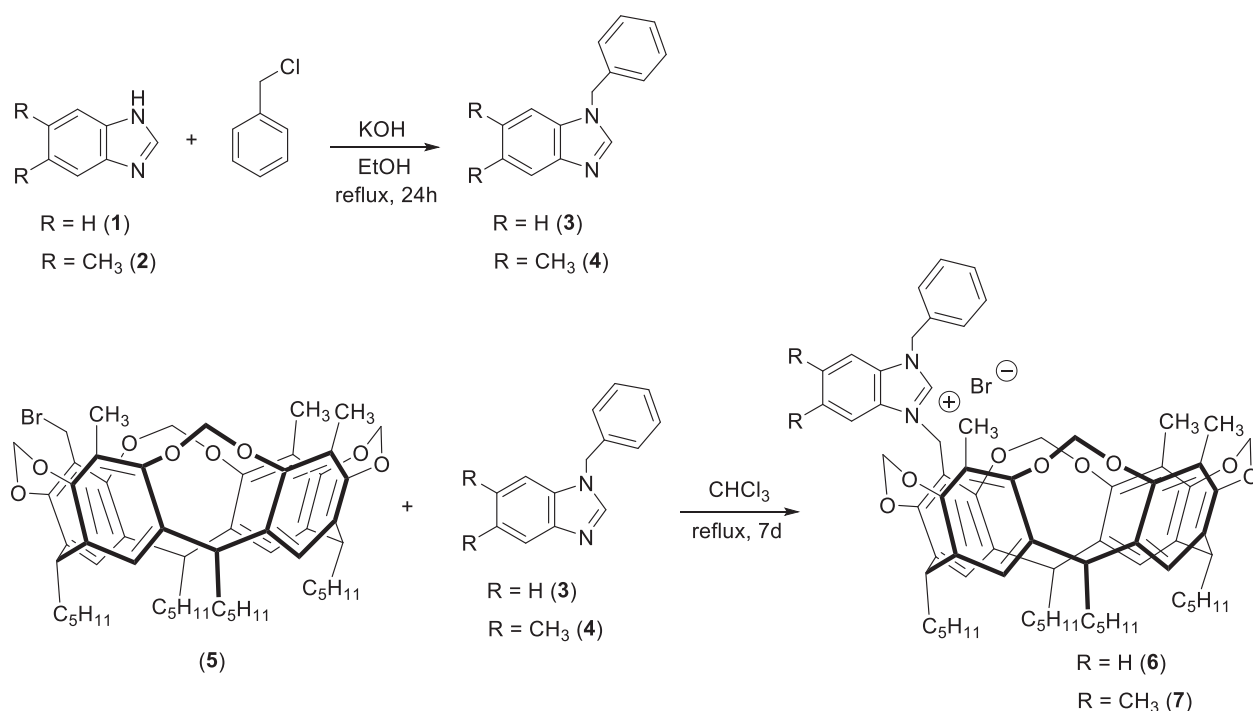
Scheme 1. Synthesis of resorcinarenyl mono-benzimidazolium salts **6** and **7**.

FT-IR data for mono-benzimidazolium salts **6** and **7** clearly showed the presence of the -C=N- group with a ν (C=N) vibration at 1466 and 1471 cm^{-1}, respectively. The ^{1}H NMR spectra of mono-benzimidazolium salts **6** and **7** are accordance with C$_s$-symmetrical cavitands, each of these cavitands displaying the presence of two distinct AB patterns for the OCH$_2$O protons and two methine triplets. The ^{1}H NMR spectra clearly exhibit a singlet at 11.32 ppm for mono-benzimidazolium salt **6** and at 11.14 ppm for **7** typical of the N=CH$-$N fragment. The ^{1}H NMR spectra of mono-benzimidazolium salts **6** and **7** show singlets at 5.73 ppm for **6** and at 5.64 ppm for **7**, characteristic for the benzyl protons (-CH$_2$Ph). ^{13}C NMR chemical shifts were consistent

with the proposed structure: the imino carbon appeared as a typical singlet at 143.5 ppm for **6** and at 142.3 ppm for **7**, respectively.

In order to evidence the supramolecular effect of the cavity likely to act as a receptor for the reaction substrate, it was necessary to have analogous NHC ligands without the cavity. This is why benzimidazolium salts **8** and **9** (Figure 1) were prepared according to a reported protocols.[42,43] These two compounds were used as references in Suzuki–Miyaura cross-coupling reactions to fully investigate the cavity effect of the resorcinarene mono-benzimidazolium ligands.
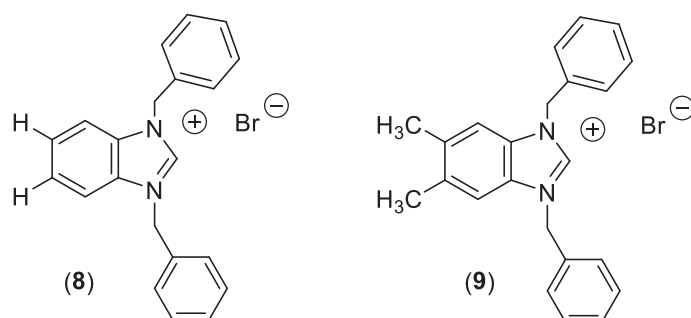

Figure 1. Reference benzimidazolium salts **8** and **9**.

The solid-state structures of **6** and **7** were further confirmed by X-ray diffraction analysis. Suitable crystals of **6** and **7** were grown by slow evaporation in EtOH at room temperature. The crystallographic analysis revealed that both compounds crystallize in the monoclinic space group $P2_1/c$. As expected, the resorcinarene moiety kept its conical shape (Figures 2 and 3). When compared with cavitand **6**, the cone conformation of cavitand **7** is distorted, as the dihedral angles between pairs of opposite aromatic rings (A/B and C/D) are 58.29° and 59.36° in **6** and 61.30° and 56.35° in **7**. The top rim diameters are 7.935 Å (C16–C42) and 8.060 Å (C27–C52) in **6** and 7.829 Å (C1–C15) and 8.124 Å (C9–C25) in **7.**
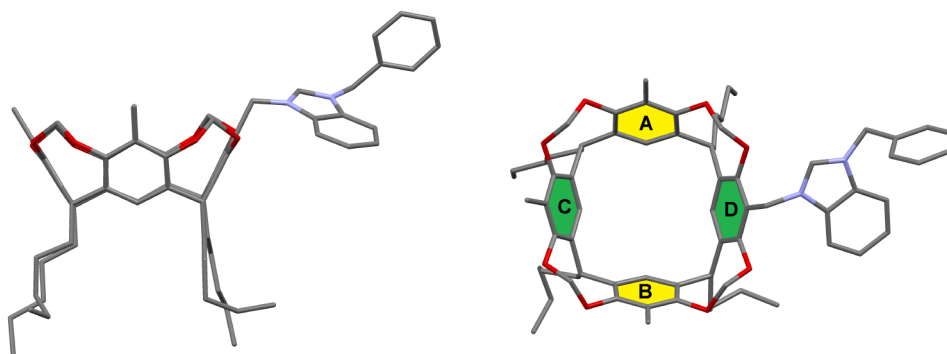

Figure 2. Side view (left) and top view (right) of the crystal structure of **6**. The H atoms and bromine ion were omitted for clarity.
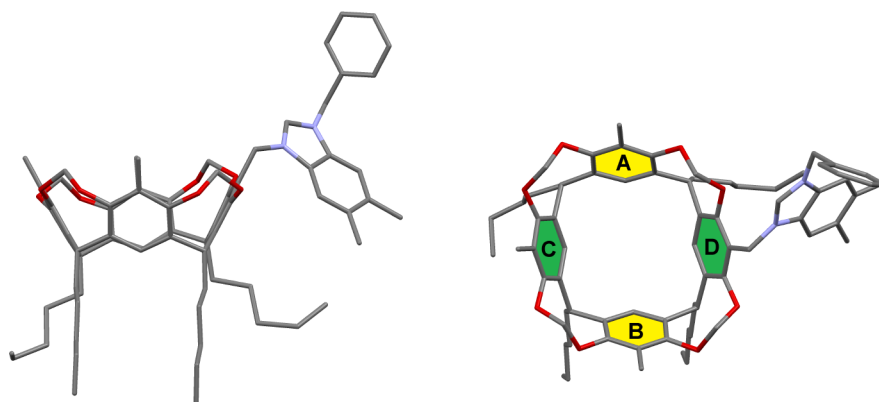
Figure 3. Side view (left) and top view (right) of the crystal structure of **7**. The H atoms, bromine ion, and solvent molecule (EtOH) were omitted for clarity.

2.2. Suzuki–Miyaura cross-couplings

Mono-benzimidazolium salts were used in Suzuki-Miyaura cross-coupling reactions between 3,5-dimethoxyphenylboronic acid and aryl halides in the presence of a base (Scheme 2). The catalysts were prepared in situ from mono-benzimidazolium (5×10^{-5} mmol, 1 equiv./Pd) salts and $[Pd(OAc)_2]$ (5×10^{-5} mmol, 1×10^{-2} mol%).
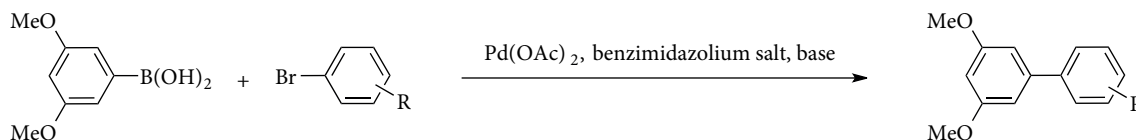
Scheme 2. Suzuki–Miyaura cross-coupling reaction.

A series of experiments were performed to find optimum reaction conditions using 3,5-dimethoxyphenylboronic acid and 4-bromoanisole in dimethylformamide (DMF) or dioxane in the presence of NaH or Cs_2CO_3 as a base (Table 1). $Pd(OAc)_2$ salt alone was tested in the employed conditions and showed negligible activity in similar conditions.

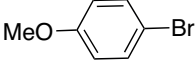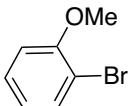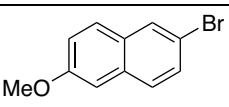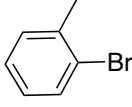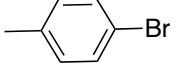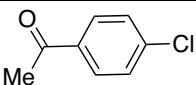**Table 1.** The search for optimal catalytic conditions of Suzuki–Miyaura cross-coupling of 4-bromoanisole with 3,5-dimethoxyphenylboronic acid using **6**. [a]

Entry	Solvent	Base	$T/$ °C	Conversion (%)
1	Dioxane	NaH	100	40.1
2	Dioxane	Cs_2CO_3	100	29.6
3	DMF	NaH	130	63.4
4	DMF	Cs_2CO_3	130	49.2

[a] Conditions: $[Pd(OAc)_2]$ (5×10^{-5} mmol, 1×10^{-2} mol%), benzimidazolium salt **6** (5×10^{-5} mmol, 1 equiv./Pd), ArBr (0.5 mmol), $(CH_3O)_2C_6H_3B(OH)_2$ (0.091 g, 0.75 mmol), NaH (60% dispersion in mineral oil) (0.030 g, 0.75 mmol), DMF (1.5 mL), 130 °C, 1 h. The conversions were determined by GC-MS. Averaged over two runs.

The highest conversion was observed in the presence of NaH in DMF at 130 °C (Table 1, entry 3). After the reaction conditions were optimized, the scope of the reaction with different aryl halides was investigated. The results are given in Table 2.

Table 2. Suzuki–Miyaura cross-coupling of aryl halides catalyzed by $[Pd(OAc)_2]$/benzimidazolium salts.[a]

Entry	ArBr	Conversion (%)	
		6	**7**
1	MeO—⬡—Br	63.4	57.2
2	⬡ OMe, Br	40.6	49.8
3	MeO—⬡⬡—Br	68.5	61.6
4	⬡ Me, Br	59.1	54.0
5	—⬡—Br	70.5	78.7
6	Me(C=O)—⬡—Cl	40.2	44.0

[a] Conditions: $[Pd(OAc)_2]$ (5×10^{-5} mmol, 1×10^{-2} mol%), benzimidazolium salt (5×10^{-5} mmol), ArBr (0.5 mmol), $(CH_3O)_2C_6H_3B(OH)_2$ (0.091 g, 0.75 mmol), NaH (60% dispersion in mineral oil) (0.030 g, 0.75 mmol), DMF (1.5 mL), 130 °C, 1 h. The conversions were determined by GC-MS and averaged over two runs.
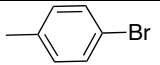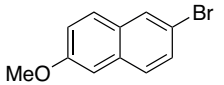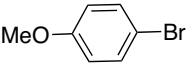
As shown in Table 2, mono-benzimidazolium salts **6** and **7** exhibited good activities with aryl bromides (entries 1–5). This shows that the activity of the catalytic systems depends on the bulkiness of the substrates. The conversion of 4-bromotoluene, which has a linear shape, was higher than those of the more bulky 2-bromotoluene, independently of the mono-benzimidazolium used (Table 2, entries 4 and 5 for **6**, and Table 2, entries 4 and 5 for **7**). Additionally, the benzimidazolium salts **6** and **7** were efficient ligands for arylation of bulky substrate like 2-bromo-6-methoxynaphthalene (Table 2, entry 3). The benzimidazolium salts **6** and **7** exhibited good activities in the coupling reactions with 4-chloroacetophenone (Table 2, entry 6). It is evident that there are not enormous changes of the efficiencies of ligands in Suzuki–Miyaura cross-coupling reactions.

Even if the investigated substrates are not identical to those employed during previous studies using ligands based on related imidazolium salts, the catalytic activities reported here are in the same range of catalytic systems considered as efficient.

Resorcinarene-free benzimidazolium salts **8** and **9** (Figure 1) were prepared and used in the coupling reactions to investigate any potential resorcinarene cavity effect. Comparisons were made for the arylation of 4-bromotoluene, 2-bromo-6-methoxynaphthalene, and 4-bromoanisole (Table 3). For each of these reactions, conversions are in the same order respectively for the cavitand ligands **6** and **7** and for resorcinarene-free benzimidazolium salts **8** and **9**. Significantly lower conversions are consistently observed when using resorcinarene-free benzimidazolium salts **8** and **9** compared to the similar use of cavitand ligands. All of these results confirm that

the superior activity of resorcinarene mono-benzimidazolium salts **6** and **7** in the arylation reactions is due to the cavity effect of the resorcinarene cavitand, acting as a receptor for the reaction substrates. Another factor likely to have an effect on these results is the greater bulkiness of the ligands of **6** and **7** compared to **8** and **9**.

Table 3. Comparison of imidazolium salts in Suzuki–Miyaura cross-coupling of aryl bromides. [a]

Entry	ArBr	Conversion (%)			
		6	**7**	**8**	**9**
1	—⟨⟩—Br	70.5	78.7	37.8	34.3
2	MeO⟨⟩⟨⟩—Br	68.5	61.6	8.2	10.6
3	MeO—⟨⟩—Br	63.4	57.2	6.6	8.9

[a] Conditions: $[Pd(OAc)_2]$ (5×10^{-5} mmol, 1×10^{-2} mol%), benzimidazolium salt (5×10^{-5} mmol), ArBr (0.5 mmol), $(CH_3O)_2C_6H_3B(OH)_2$ (0.091 g, 0.75 mmol), NaH (60% dispersion in mineral oil) (0.030 g, 0.75 mmol), DMF (1.5 mL), 130 °C, 1 h. The conversions were determined by GC-MS and averaged over two runs.

In conclusion, we have prepared two novel resorcinarene based mono-benzimidazolium salts designed for Suzuki–Miyaura cross-coupling reactions. These two new resorcinarene-based mono-benzimidazolium salts exhibited good catalytic activity for coupling reactions in DMF. The importance of the cavity effect in which the cavitand acts as a receptor was demonstrated by comparing these activities with those of resorcinarene-free analogous ligands. On the other hand, the fact that **6** and **7** are bulkier than **8** and **9** is likely to play a role in the better catalytic activities observed. These new and efficient catalytic systems are currently being investigated in other cross-coupling reactions such as Negishi and Kumada–Tamao–Corriu.

3. Experimental

3.1. Materials

Mass spectra were recorded on a MALDI BRUKER Microflex LT using 2,5-dihydroxybenzoic acid as the matrix. NMR spectra were recorded in $CDCl_3$ solutions on a Varian 500 MHz spectrometer. IR spectra were recorded between 4000 and 600 cm^{-1} using a PerkinElmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection accessory featuring a zinc selenide (ZnSe) crystal. The catalytic solutions were analyzed by using an Agilent 5975C GC/MSD.

3.2. X-ray data collection and structure refinement

Data for compounds **6** and **7** were obtained with a Bruker APEX II QUAZAR three-circle diffractometer and Agilent XCalibur diffractometer (Eos CCD detector). For **6**, on the Bruker diffractometer, indexing was performed using APEX2. [44] Data integration and reduction were carried out with SAINT. [45] Absorption correction was performed by multiscan method implemented in SADABS. [46] Space groups were determined using XPREP implemented in APEX2. For **7**, the CrysAlisPro software program was used for data collection and cell refinement and data reduction. [47] Absorption correction was performed by analytical method based

on expressions derived by Clark and Reid.[47] The structures were solved using SIR-2004.[48] The least-square refinement on F^2 was achieved with CRYSTALS software.[49] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C-H in the range of 0.93–0.98 Å) and U_{iso}(H) (in the range of 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints. In refinement of **6**, Br1 and Br2 were refined with occupancy factor 0.5:0.5. The crystals available for X-ray structural analysis were of quite poor quality and weak scatterers at high resolution, thus resulting in comparatively high R values. Crystallographic data and refinement details of the data collection for **6** and **7** are given in Table S1 (on the journal's website). The final geometrical calculations and the molecular drawings were carried out with the Platon[50] and Mercury[51] programs.

Crystallographic data for these structures have been deposited with the Cambridge Crystallographic Data Centre under deposition numbers 1027354 for **6** and 1027355 for **7**.

3.3. Synthesis

The bromomethylated resorcinarene cavitand **5**[41] was prepared following reported procedures. All reaction solvents were dried and purified as described by Perrin and Armarego.[52]

3.4. Preparation of 1-benzyl benzimidazoles 3 and 4

1-Benzylbenzimidazoles **3** and **4** were prepared according to a slightly modified procedure.[53] Potassium hydroxide (1 mmol) was added to a solution of corresponding benzimidazole (1 mmol) in ethanol (20 mL), the mixture was stirred for 1 h at room temperature, and benzyl chloride was added dropwise. This reaction mixture was then heated for 8 h at 80 °C. The mixture was diluted with water (50 mL) and extracted with dichloromethane (3 × 25 mL), and the combined extracts were washed with water and dried over Na_2SO_4. The benzyl benzimidazole was isolated by chromatography on silica gel using CH_2Cl_2. The NMR spectra of the products were identical to those reported previously for **3** and **4**.

3.5. Preparation of mono benzyl benzimidazole resorcinarene cavitand 6

A chloroform solution of the bromomethylated resorcinarene cavitand **5** (0.5 g, 0.525 mmol) and benzimidazole **3** (0.109 g, 0.525 mmol) was refluxed for 5 days. The reaction mixture was evaporated to dryness and the solid residue was washed with Et_2O (2 × 25 mL) to afford the benzimidazolium-resorcinarene cavitand **6** as a white solid. Yield: 98%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 11.32$ (s, 1H, NCHN), 7.81 (d, 1H, arom. CH), 7.52–7.35 (m, 7H, arom. CH), 7.16 (s, 1H, arom. CH of resorcinarene), 6.96 (s, 3H, arom. CH of resorcinarene), 6.28 and 4.53 (AB spin system, 4H, OCH_2O, $^2J = 7.4$Hz), 5.97 (s, 2H, $ArCH_2N$), 5.88 and 4.31 (AB spin system, 4H, OCH_2O, $^2J = 7.3$ Hz), 5.73 (s, 2H, $ArCH_2$), 4.77 (t, 2H, $CHCH_2$, $^3J = 7.9$ Hz), 4.69 (t, 2H, $CHCH_2$, $^3J = 7.7$ Hz), 2.27–2.16 (m, 8H, $CHCH_2$), 1.42–1.20 (m, 24H, $CH_2CH_2CH_2CH_3$), 0.90 (t, 6H, CH_2CH_3, $^3J = 6.2$ Hz), 0.85 (t, 6H, CH_2CH_3, $^3J = 6.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 153.73, 153.32, 153.20$ (arom. C_{quat}), 143.57 (s, NCHN), 139.06, 138.35, 137.69, 136.45, 132.25, 131.52, 130.76, 129.50, 129.41, 127.98, 127.11, 126.84, 124.19, 123.90, 122.57, 118.75, 117.17, 117.04, 114.12, 113.09, 100.15, 98.59, 51.47, 42.26, 36.97, 36.83, 32.05, 31.86, 30.14, 29.85, 27.63, 27.45, 22.66, 22.59, 14.07, 14.02, 10.37, 10.35.

MALDI-TOF: m/z = 1081.74 $[M + H]^+$.

3.6. Preparation of mono benzyl benzimidazole resorcinarene cavitand 7

A chloroform solution of the bromomethylated resorcinarene cavitand **5** (0.5 g, 0.525 mmol) and benzimidazole **4** (0.124 g, 0.525 mmol) was refluxed for 5 days. The reaction mixture was evaporated to dryness and the solid residue was washed with Et_2O (2 × 25 mL) to afford the benzimidazolium-resorcinarene cavitand **7** as a white solid. Yield: 97%. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 11.14 (s, 1H, NCHN), 7.44 (s, 1H, arom. CH), 7.42–7.35 (m, 4H, arom. CH), 7.19 (s, 1H, arom. CH of resorcinarene), 7.15 (s, 1H, arom. CH of resorcinarene), 6.95 (s, 3H, arom. CH of resorcinarene), 6.24 and 4.51 (AB spin system, 4H, OCH$_2$O, ^{2}J = 7.4 Hz), 5.95 (s, 2H, ArCH$_2$N), 5.88 and 4.32 (AB spin system, 4H, OCH$_2$O, ^{2}J = 7.3 Hz), 5.64 (s, 2H, ArCH$_2$), 4.77 (t, 2H, CHCH$_2$, ^{3}J = 7.9 Hz), 4.69 (t, 2H, CHCH$_2$, ^{3}J = 7.7 Hz), 2.33 (s, 3H, ArCH$_3$), 2.31 (s, 3H, ArCH$_3$), 2.27–2.16 (m, 8H, CHCH$_2$), 1.44–1.20 (m, 24H, CH$_2$CH$_2$CH$_2$CH$_3$), 0.90 (t, 6H, CH$_2$CH$_3$, ^{3}J = 6.2 Hz), 0.85 (t, 6H, CH$_2$CH$_3$, ^{3}J = 6.2 Hz); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 153.70, 153.41, 153.31, 153,15 (arom. C$_{quat}$), 142.31 (s, NCHN), 138.87, 138.33, 137.66, 137.17, 136.93, 136.57, 132.51, 130.01, 129.46, 129.32, 129.27, 127.70, 124.19, 123.91, 122.34, 118.95, 117.16, 117.04, 113.70, 112.65, 100.15, 98.60, 51.15, 42.11, 36.97, 36.76, 32.05, 31.82, 30.14, 29.82, 27.63, 27.44, 22.66, 22.59, 20.64, 20.63, 15.22, 14.07, 13.99, 10.37, 10.34, 0.98, 0.04.

MALDI-TOF: m/z = 1109.26 $[M + H]^+$.

3.7. General procedure for palladium-catalyzed Suzuki–Miyaura cross-coupling reactions and GC analyses

The solution of Pd(OAc)$_2$ in DMF, the solution of the ligand in DMF, aryl bromide (0.5 mmol), 3,5-dimethoxyphenylboronic acid (0.091 g, 0.75 mmol), NaH (0.030 g, 0.75 mmol), and an additional amount of DMF (to have a final reaction volume of 1.5 mL) were put into a 10 mL reaction flask. The reaction mixture was then heated for 1 h at 130 °C. After cooling to room temperature, 1 mL of the reaction mixture was passed through a Millipore filter and analyzed by GC-MS.

The runs were carried out using an ArBr/Pd ratio of 10,000. The calibration was based on diethylene glycol monobuthyl ether. Conversions given in Tables 1–3 were averaged over two runs and have been calculated relatively to the aryl bromide.

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Table S1. Crystal data and refinement parameters for **6** and **7**.

Crystal parameters	6	7
CCDC	1027354	1027355
Empirical formula	$C_{70}H_{83}BrN_2O_8$	$C_{74}H_{93}BrN_2O_9$
Formula weight (g mol^{-1})	1160.34	1234.46
Temperature (K)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	27.039(5)	25.1170(15)
b (Å)	12.042(5)	11.4920(4)
c (Å)	20.321(5)	24.9090(14)
α (°)	90	90
β (°)	97.206(5)	110.942(7)
γ (°)	90	90
Crystal size (mm)	$0.135 \times 0.176 \times 0.207$	$0.309 \times 0.558 \times 0.699$
V (Å^3)	6564(3)	6714.9(7)
Z	4	4
ρ_{calcd} (g cm^{-3})	1.174	1.221
μ (mm^{-1})	0.680	0.669
$F(000)$	2464	2632
θ range for data collection (°)	1.52–25.68	3.12–26.38
$h/k/l$	–32/32, 0/14, 0/24	–31/29, 0/14, 0/31
Measured reflections	49,016	29,757
Independent reflections (R_{int})	12,440 [R(int) = 0.0710]	13,724 [R(int) = 0.0300]
Absorption correction	Multiscan	Analytical
Data / restraints / parameters	12440 / 65 / 739	13724 / 90 / 775
Goodness-of-fit on F^2 (S)	1.078	0.926
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1163$, $wR_2 = 0.2759$	$R_1 = 0.0820$, $wR_2 = 0.1869$
R indices (all data)	$R_1 = 0.1903$, $wR_2 = 0.3146$	$R_1 = 0.1362$, $wR_2 = 0.2167$
Largest diff. peak and hole (e Å^{-3})	1.48 and –0.97	0.680 and –0.780