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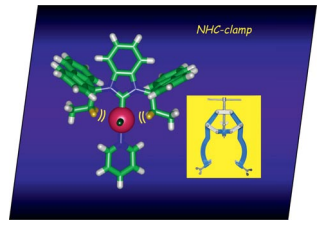
N-Heterocyclic Carbenes Functioning as Monoligating Clamps



COVER PICTURE

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Benzimidazolium salts N,N′-disubstituted with 9-alkylfluorenyl groups (**3a**–**e**, alkyl = methyl, ethyl, propyl, butyl, benzyl) have been synthesised in high yields in three steps from *o*-phenylenediamine. This amine was treated with fluorenone in the presence of $TiCl_4$ and tetramethylethylenediamine (TMEDA) to form *N*,*N*′-bis(9*H*-fluoren-9-ylidene)benzene-1,2-diamine (**1**) in 91 % yield. Diamines **2a**–**e** were then obtained in yields superior or equal to 77 % by reacting diimine **1** with the appropriate organolithium reagent. In the final step, diamines **2a**–**e** were treated with ethylorthoformate under acidic conditions to afford benzimidazolium salts **3a**–**e**. These were readily converted into the PEPPSI palladium complexes **4a**–**e** (PEPPSI = pyridine-enhanced precatalyst preparation stabilisation and initiation). NMR and X-ray diffraction studies revealed that the flat fluorenylidene moiety orientates the alkyl groups towards the metal centre and because of its restricted rotational freedom makes the ligand bulkiness time independent. Thus, the metal centre is permanently confined between the two alkyl groups, and thereby forms a monoligating clamp with the carbenic centre. The CH_2 groups close to the palladium ion give rise to anagostic C–H···Pd interactions. Catalytic tests revealed that the palladium complexes **4a**–**e** are highly efficient in Suzuki–Miyaura cross-coupling reactions; their activity is equal or superior to the best PEPPSI catalysts reported to date.

Introduction

N-Heterocyclic carbenes (NHCs) have attracted considerable interest in transition-metal chemistry since the isolation of the first stable compound of this family in 1991[1] and the discovery of the catalytic activity of their complexes.[2–6] Palladium-mediated cross-coupling reactions are among the catalytic reactions for which NHCs have been successfully applied.[3,7–13] In these transformations, electronic and steric ligand factors are crucial. Although their strong σ-donor properties make NHCs particularly efficient for promoting the oxidative addition step of the reaction, their steric encumbrance may facilitate the reductive elimination step as well as increase the stability of catalytic intermediates. As the carbenic centre of an NHC is part of a planar moiety, the steric properties of these ligands are mainly determined by the bulk of the *N*-substituents that may form a pocket about the metal centre. These are remote from the heterocyclic moiety, and therefore any modification of the ligand encumbrance has essentially no significant effect on the electronic properties. Thus, steric fine-tuning of NHCs can be achieved straightforwardly without changing the ligand donor properties.

Many authors have attested to the pivotal role of steric parameters in Suzuki–Miyaura cross-coupling reactions.[7,14,15] A general belief is that to be efficient, NHCs used in cross-coupling reactions must create strong hemispherical encumbrance about the catalytic centre.

It has also been widely contended that high catalytic activity requires that the sterically demanding *N*-substituents (typically *o*-substituted aryls[8,16,17] or spiroalkyl groups[7,18]) possess sufficient structural flexibility to adapt to the steric requirements of the individual steps of the whole catalytic cycle. In the present study, we describe highly active Suzuki–Miyaura catalysts based on NHCs, which unlike the usual expanded NHCs, generate only "planar" confinement in which encumbrance is created at two virtual, *trans*-located positions. These NHCs form complexes in which the metal centre is held within a clamp-like ligand characterised by its restricted conformational flexibility (Scheme 1). The new ligands, which were generated from benzimidazolium precursors, all have 9-alkylfluorenyl groups as *N*-substituents with such restricted rotational freedom that the steric congestion at the metal centre can undergo at most very minor fluctuations.

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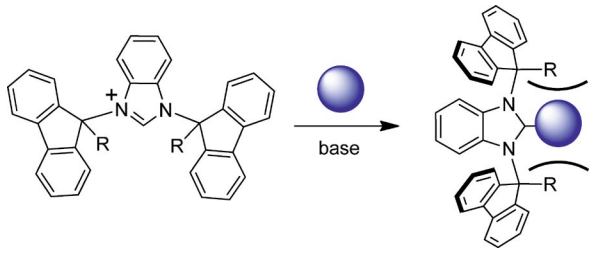
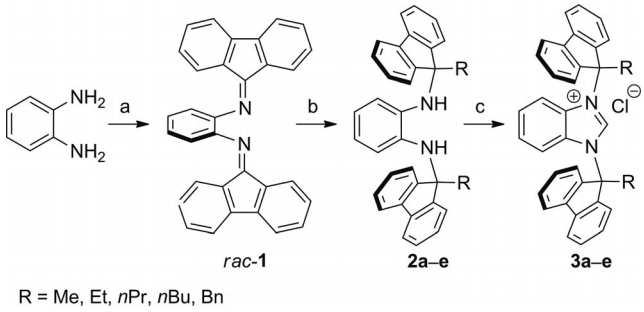


Scheme 1. Coordination of metal centres to clamp-like NHC ligands.

Results and Discussion

The alkylfluorenyl-substituted benzimidazolium salts **3a**–**e** were obtained in three steps according to Scheme 2. Their syntheses began with that of **1**,[19] which was obtained by condensation of 1,2-diaminobenzene with fluorenone in the presence of $TiCl_4$.



Scheme 2. Synthesis of benzimidazolium salts **3a**–**e**. Reagents and conditions: a) fluorenone, $TiCl_4$, tetramethylethylenediamine (TMEDA), toluene, reflux, 91%; b) RLi, tetrahydrofuran (THF), –78 °C to room temp., 77–85%; c) $HC(OEt)_3$, concd. HCl, 80 °C, 75–95%. Compound **1** has a C_2-symmetric structure.

Diimine **1** was then reacted with five different organolithium reagents RLi to afford the corresponding diamines **2a**–**e** in high yields. We observed that the use of Grignard reagents instead of alkyllithium compounds resulted in significantly lower yields (< 50%), and the reactions led to azophilic addition products. In the final step, the amines were treated with ethylorthoformate under acidic conditions to result in the benzimidazolium chlorides **3a**–**e**.[20,21] In each of the corresponding ^{1}H NMR spectra, the C-2 proton of the imidazolium ring appears as a singlet at $\delta \approx$ 11.2 ppm. 2D ^{1}H NMR ROESY experiments established a strong proximity between this proton and the NCCH_2 atoms, but not with the aromatic H atoms of the benzimidazolium moiety, and this is indicative of the fluorenyl planes folding back towards the central phenylene ring (see Supporting Information). This structural feature was confirmed by an X-ray diffraction study carried out for **3b** (Figure 1). Molecular modelling (Spartan)[22] further revealed that the alkylfluorenyl groups cannot rotate about the N–$C_{alkylfluorenyl}$ bond owing to the expanded structure of the fluorenyl plane. Back-folding of the fluorenyl moieties was also found in diamine **2a** in the solid state (see Supporting Information).

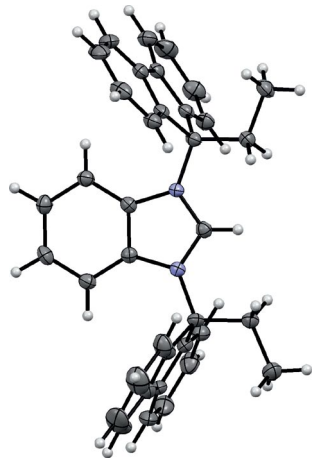
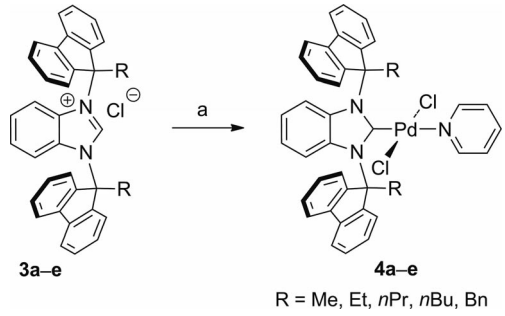


Figure 1. ORTEP representation of the benzimidazolium salt **3b**. The chloride counterion as well as the cocrystallising methanol molecule are not shown.

The benzimidazolium salts **3a**–**e** were readily converted into the PEPPSI Pd complexes **4a**–**e** by applying a standard procedure (Scheme 3, PEPPSI = pyridine-enhanced precatalyst preparation stabilisation and initiation).[23] PEPPSI complexes are regarded as belonging to the most efficient cross-coupling catalysts.[15,16,23–25]



Scheme 3. Synthesis of palladium complexes **4a**–**e** (conditions: $PdCl_2$, K_2CO_3, pyridine, 80 °C, 22–85%).

The ^{1}H NMR spectra of complexes **4a**–**e** revealed the presence of a pyridine/NHC ratio of 1:1. The most remarkable feature of these spectra concerns the NCCH_2 signals, which are remarkably downfield shifted with respect to those of the corresponding diamines ($\Delta\delta$ = 2.26–3.38 ppm). X-ray diffraction studies carried out for **4a**–**c** (R = Me, Et, *n*Pr) revealed that in the solid state the methylenic NCCH_2 atoms are very close to the metal d_{z^2} orbital, and the carbenic plane bisects the two CH_2 groups. The methylenic C*H* atom is located only ca. 2.55 Å from the metal centre, and the NHC ligand can thus be viewed as a clamp that meridionally confines the metal centre (Figure 2). This feature is obviously imposed by the directional properties of the fluorenyl planes that push the two methylenic NCCH_2 groups towards the d_{z^2} orbital. As for **3a**–**e**, there is no indication of alkyfluorenyl moieties freely rotating about the corresponding N–C_{quat} bonds.[26] Thus, to the best of our knowledge, among the bulky NHCs reported to date,[27] the above ligands constitute the most confining NHCs with

time-independent crowding. The downfield shift observed for the NCCH_2 protons as well as the $^1J(^{13}C,^1H)$ values (ca. 130 Hz) are typically those of anagostic C–H···Pd bonds in which the bonding interactions display highly electrostatic character.[28–30]

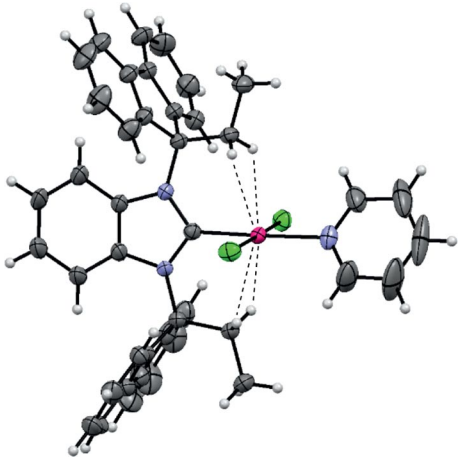
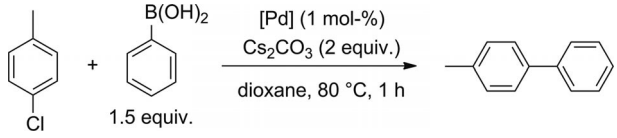


Figure 2. ORTEP representation of complex **4b**, which bears an NHC ligand that behaves as a clamp.

To assess their catalytic potential, complexes **4a**–**e** were used in a Suzuki–Miyaura test reaction, namely that between *p*-tolyl chloride and phenylboronic acid. The catalytic runs were carried out in dioxane at 80 °C with 1 mol-% of catalyst precursor in the presence of 2 equiv. of Cs_2CO_3. All complexes were remarkably active (Table 1). Under the above conditions, the conversions ranged from 19 to 70% after 1 h, and the highest reaction rates were observed with **4b** (R = Et). Interestingly, the activity of **4a** (R = Me) was twice that of *t*Bu-substituted complex **5** (Figure 3), despite the fact that the corresponding NHCs have nearly the same buried volume [36.9% (**4a**); 36.6% (**5**)].[31–33] This probably reflects the restricted rotational freedom of the *N*-substituents of **4a**, which permanently holds the NC*Me* groups close to the metal centre and, therefore, increases the metal protection. In other terms, the time-averaged steric crowding about the metal centre is lower in **5**, as the *t*Bu groups freely rotate around the corresponding N–C_{quat} bonds. Clearly, these observations show that the buried-volume parameter, although it is useful in catalytic studies, does not take into account molecular dynamics that may result in a transient modification of the real bulk of a given ligand. The significant activity increase observed on going from **4a** to the sterically more crowded complexes **4b** and **4c** is possibly due to a lowering of the activation barrier of the reductive elimination step. However, increasing the bulk of the R groups by using substituents larger than propyl (complexes **4d** and **4e**) led to somewhat lower activities; these groups probably restrict access of the substrate to the metal centre. We also found that the activity of clamp complex **4b** surpasses that of complexes **6**–**8** (Figure 3), which contain the most efficient NHCs used in Suzuki–Miyaura cross-coupling reactions.[8,9,11,15,17,23] Finally, preliminary tests showed that the above clamps can also efficiently be employed in more challenging cross-coupling reactions. For example, in the reaction of 2,6-dimethoxyphenylboronic acid with 4-chlorotoluene, **4b** was twice as active as complex **6** (see Supporting Information).

Table 1. Suzuki–Miyaura cross-coupling of phenylboronic acid with *p*-tolyl chloride using **4**–**8**.



Entry[a]	Complex	Yield[b]
1	$Pd(OAc)_2$	0
2	**4a**	40
3	**4b**	70
4	**4c**	60
5	**4d**	21
6	**4e**	19
7	**5**	20
8	**6**	63
9	**7**	38
10	**8**	37

[a] Reaction conditions: *p*-tolyl chloride (1 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (2 mmol), dioxane (3 mL). [b] Yields were determined by ^1H NMR spectroscopy with 1,4-dimethoxybenzene as internal standard. Averaged over two runs. No homocoupling products were detected.

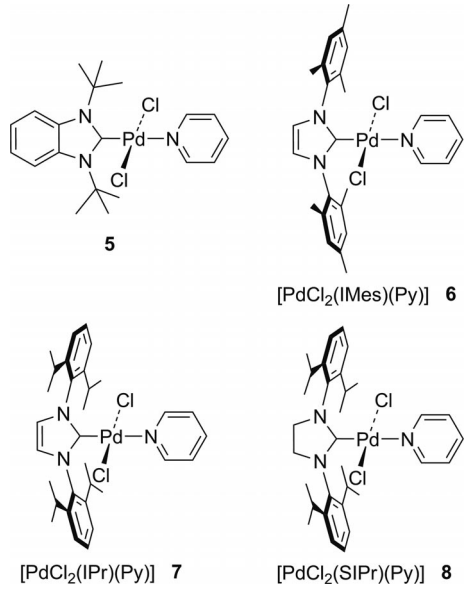


Figure 3. Palladium complexes with bulky NHC ligands used in cross-coupling reactions for comparison with **4a**–**e**.

In conclusion, we have shown that owing to its substituent-orienting properties, the 9-fluorenylidene moiety constitutes a valuable tool for the creation of NHC clamps with time-independent crowding. The palladium derivatives **4a**–**e**, which contain such monoligating NHC ligands, were shown to display activities superior or equal to those obtained with the fastest Pd–NHC Suzuki–Miyaura cross-coupling catalysts reported to date. Overall, the above results suggest that "meridional confinement"[34] may be an

interesting alternative to hemispherical encumbrance. Ligands of this type will be assessed in other catalytic reactions.

Experimental Section

General Procedures: All commercial reagents were used as supplied. The syntheses were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. Routine ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with an FT Bruker AVANCE 300 (^1H: 300.1 MHz, ^{13}C: 75.5 MHz) instrument at 25 °C. ^1H NMR spectroscopic data are referenced to residual protonated solvents ($CHCl_3$, δ = 7.26; DMSO, δ = 2.50 ppm), and ^{13}C chemical shifts are reported relative to deuterated solvents ($CDCl_3$, δ = 77.16; [D_6]DMSO, δ = 39.52 ppm). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (*J*) in Hertz (Hz), integration and assignment. In the NMR spectroscopic data given hereafter, Cq denotes a quaternary carbon atom. Flash chromatography was performed as described by Still et al.[35] by employing Geduran SI (E. Merck, 0.040–0.063 mm) silica. Routine TLC analyses were carried out by using plates coated with Merck Kieselgel 60 GF254. Mass spectra were recorded either with a Bruker MicroTOF spectrometer (ESI-TOF) with CH_2Cl_2 or CH_3CN as solvent or with a Bruker MaldiTOF spectrometer with dithranol as matrix. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie (CNRS), Strasbourg. Melting points were determined with a Büchi 535 capillary melting-point apparatus. Precursor salts of **5**,[20,36] **6**,[37,38] **7**[37,38] and **8**[37,38] were prepared by following procedures described in the literature.

***N*,*N*′-Bis(9*H*-fluoren-9-ylidene)benzene-1,2-diamine (1):** A solution of *ortho*-phenylenediamine (2.160 g, 20 mmol), fluorenone (7.630 g, 42.3 mmol) and TMEDA (36 mL, 240 mmol) in toluene (200 mL) was heated at 80 °C. $TiCl_4$ (6.7 mL, 60 mmol) was then added dropwise over 20 min before the temperature was increased to 110 °C. After 5 h, the reaction mixture was cooled to room temperature and filtered through Celite to remove insoluble materials. These were washed with AcOEt (100 mL), and the filtrate was concentrated to dryness. The residue was dissolved in AcOEt (ca. 20 mL), and the resulting solution was passed through a short pad of silica gel and eluted with AcOEt until the product was completely recovered. The dark orange filtrate was concentrated to afford a red solid, which was purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 60:40). Diimine **1** was obtained as an orange solid (7.85 g, 91%); m.p. > 250 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.72 (d, ^3J = 7.5 Hz, 2 H, ArH), 7.50–7.41 (m, 4 H, ArH), 7.35–7.10 (m, 12 H, ArH), 7.00 (ddd, ^3J = $^3J'$ = 7.5 Hz, ^4J = 0.9 Hz, 2 H, ArH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 162.9 (C=N), 143.6 (arom. Cq), 141.7 (arom. Cq), 140.9 (2×, arom. Cq), 137.6 (arom. Cq), 131.8 (arom. CH), 131.6 (arom. CH), 128.3 (arom. CH), 127.7 (arom. CH), 127.0 (arom. CH), 125.0 (arom. CH), 123.5 (arom. CH), 120.1 (arom. CH), 119.8 (arom. CH), 119.4 (arom. CH) ppm. The spectroscopic data are in full agreement with those of the literature.[19]

***N*,*N*′-Bis(9-methyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (2a):** To a stirred solution of diimine **1** (1.150 g, 2.67 mmol) in tetrahydrofuran (THF, 10 mL) cooled to –78 °C, was added dropwise MeLi (1.6 M in Et_2O, 4 mL, 6.40 mmol). The red solution quickly turned black. The reaction mixture was allowed to reach room temperature and was stirred for 30 min. After slow addition of water (30 mL), the mixture was extracted with AcOEt (3× 40 mL), the combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether, 0.5:99.5) to afford **2a** as a pale brown solid (1.030 g, 83%); m.p. 178 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.51 (d, ^3J = 7.1 Hz, 4 H, ArH), 7.41–7.35 (m, 8 H, ArH), 7.30–7.25 (m, 4 H, ArH), 6.10 (m, 2 H, ArH), 5.63 (m, 2 H, ArH), 4.38 (br. s, 2 H, NH), 1.76 (s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 150.0 (arom. Cq), 139.1 (arom. Cq), 135.8 (arom. Cq), 128.1 (arom. CH), 127.8 (arom. CH), 123.2 (arom. CH), 120.4 (arom. CH), 119.8 (arom. CH), 117.2 (arom. CH), 65.4 (*C*qCH$_3$), 30.8 (CH_3) ppm. $C_{34}H_{28}N_2$ (M_r = 464.60): calcd. C 87.90, H 6.07, N 6.03; found C 87.68, H 6.14, N 5.85.

***N*,*N*′-Bis(9-ethyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (2b):** A solution of ethyl bromide (1.850 g, 17 mmol) in pentane (15 mL) was added to a suspension of lithium powder (25 wt.-% in mineral oil, 0.940 g, 34 mmol) in pentane (15 mL) at a rate to maintain a steady reflux (about 1 h). The solution was maintained at reflux for 3 h and then allowed to reach room temperature. After decantation, the clear supernatant (25 mL, C ≈ 0.5 M,[39] 12.5 mmol) was removed and added dropwise by syringe to a stirred solution of **1** (2.17 g, 5 mmol) in THF (17 mL) at –78 °C. The dark solution was then allowed to reach room temperature. The mixture was stirred for 1 h, water (40 mL) was slowly added, and the product was extracted with AcOEt (3× 40 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether, 0.5:99.5) to afford **2b** as a pale brown solid (2.010 g, 82%); m.p. 130 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.76 (d, ^3J = 7.4 Hz, 4 H, ArH), 7.42–7.35 (m, 8 H, ArH), 7.31–7.26 (m, 4 H, ArH), 6.10–6.07 (m, 2 H, ArH), 5,66–5.63 (m, 2 H, ArH), 4.43 (br. s, 2 H, NH), 2.22 (q, ^3J = 7.4 Hz, 4 H, CH_2), 0.61 (t, ^3J = 7.4 Hz, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 148.3 (arom. Cq), 140.2 (arom. Cq), 135.8 (arom. Cq), 128.1 (arom. CH), 127.6 (arom. CH), 123.5 (arom. CH), 120.2 (arom. CH), 119.6 (arom. CH), 117.0 (arom. CH), 69.0 (*C*qCH$_2$), 36.4 (CH_2), 8.4 (CH_3) ppm. $C_{36}H_{32}N_2$ (492.65): calcd. C 87.77, H 6.55, N 5.69; found C 87.63, H 6.56, N 5.49.

***N*,*N*′-Bis(9-propyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (2c):** Propyl bromide (0.516 g, 4.20 mmol) dissolved in pentane (7 mL) was added to a suspension of lithium powder (25 wt.-% in mineral oil, 0.234 g, 8.4 mmol) in pentane (7 mL) at a rate to maintain a steady reflux (about 1 h). The solution was maintained at reflux for 3 h. After decantation at room temperature, the clear supernatant (6.7 mL, C ≈ 0.5 M,[6] 3.30 mmol) was removed and added dropwise by syringe to a stirred solution of **1** (0.562 g, 1.30 mmol) in THF (6 mL) at –78 °C under nitrogen. The dark solution was allowed to reach room temperature. The solution was stirred for a further 1 h, water (20 mL) was slowly added, and the reaction mixture was extracted with AcOEt (3× 20 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether, 0.5:99.5) to afford **2c** as a pale brown solid (0.521 g, 77%); m.p. 80 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.77 (d, ^3J = 7.4 Hz, 4 H, ArH), 7.43–7.37 (m, 8 H, ArH), 7.31–7.27 (m, 4 H, ArH), 6.12–6.09 (m, 2 H, ArH), 5,68–5.65 (m, 2 H, ArH), 4.44 (br. s, 2 H, NH), 2.18–2.13 (m, 4 H, CqCH_2), 1.01–0.90 (m, 4 H, CH_2CH$_3$), 0.86 (t, ^3J = 7.4 Hz, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 148.7 (arom. Cq), 140.0 (arom. Cq), 135.8 (arom. Cq), 128.0 (arom. CH), 127.6 (arom. CH), 123.5 (arom. CH), 120.1 (arom. CH), 119.6 (arom. CH), 117.1 (arom. CH), 68.7 (*C*qCH$_2$), 45.8 (CqCH_2), 17.2

(CH_2CH_3), 14.4 (CH_3) ppm. $C_{38}H_{36}N_2$ (520.71): calcd. C 87.65, H 6.97, N 5.38; found C 87.53, H 6.93, N 5.28.

***N*,*N*′-Bis(9-butyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (2d):** To a stirred solution of diimine **1** (1.020 g, 2.35 mmol) in THF (10 mL) cooled to –78 °C was added BuLi (1.6 M in hexanes, 4.4 mL, 7.04 mmol). The red solution quickly turned black. The reaction mixture was allowed to reach room temperature and was stirred for 30 min. Water (30 mL) was slowly added, the reaction mixture was extracted with AcOEt (3 × 40 mL), the combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether, 0.5:99.5) to afford **2d** as a pale brown solid (1.010 g, 78%); m.p. 79 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.77 (d, ^3J = 7.4 Hz, 4 H, ArH), 7.43–7.36 (m, 8 H, ArH), 7.32–7.27 (m, 4 H, ArH), 6.14–6.11 (m, 2 H, ArH), 5.67–5.66 (m, 2 H, ArH), 4.43 (br. s, 2 H, NH), 2.19–2.14 (m, 4 H, CqCH_2), 1.26 (tq, ^3J = $^3J'$ = 7.3 Hz, 4 H, CH_2CH$_3$), 1.03–0.92 (m, 4 H, CqCH$_2$CH_2), 0.84 (t, ^3J = 7.3 Hz, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 148.8 (arom. Cq), 140.1 (arom. Cq), 135.8 (arom. Cq), 128.0 (arom. CH), 127.6 (arom. CH), 123.5 (arom. CH), 120.2 (arom. CH), 119.6 (arom. CH), 117.2 (arom. CH), 68.6 (*C*qCH$_2$), 43.3 (Cq*C*H$_2$), 26.0 (CqCH$_2$*C*H$_2$), 23.0 (*C*H$_2$CH$_3$), 14.1 (CH$_3$) ppm. $C_{40}H_{40}N_2$ (548.76): calcd. C 87.55, H 7.35, N 5.10; found C 87.21, H 7.39, N 5.39.

***N*,*N*′-Bis(9-benzyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (2e):** To a mixture of *t*BuOK (0.151 g, 1.34 mmol) and toluene (143 μL, 1.31 mmol) in THF (10 mL) cooled to –78 °C was added BuLi (1.6 M in hexanes, 760 μL, 1.22 mmol). The suspension quickly turned red and was kept at –78 °C for 20 min. Diimine **1** (0.200 g, 0.46 mmol) was then added portionwise, and the mixture quickly turned black. The reaction mixture was allowed to reach room temperature and was stirred for 30 min. Water (20 mL) was slowly added, and the reaction mixture was extracted with AcOEt (3 × 20 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether, 0.5:99.5) to afford **2e** as a pale brown solid (0.241 g, 85%); m.p. 103 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.64 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.39–7.33 (m, 4 H, ArH), 7.28 (m, 8 H, ArH), 7.23–7.14 (m, 6 H, ArH), 6.89 (dd, ^3J = 7.7 Hz, ^4J = 1.5 Hz, 4 H, ArH), 6.04–6.00 (m, 2 H, ArH), 5.58–5.55 (m, 2 H, ArH), 4.68 (br. s, 2 H, NH), 3.42 (s, 4 H, CH$_2$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 147.9 (arom. Cq), 139.9 (arom. Cq), 135.7 (arom. Cq), 135.5 (arom. Cq), 130.9 (arom. CH), 128.2 (arom. CH), 127.6 (arom. CH), 127.3 (arom. CH), 126.8 (arom. CH), 124.1 (arom. CH), 120.2 (arom. CH), 119.5 (arom. CH), 116.5 (arom. CH), 69.0 (*C*qCH$_2$), 50.1 (CH$_2$) ppm. $C_{46}H_{36}N_2$ (616.79): calcd. C 89.58, H 5.88, N 4.54; found C 89.09, H 6.10, N 4.52. Despite several recrystallisations the carbon content remained below the expected value.

1,3-Bis(9-methyl-9*H*-fluoren-9-yl)benzimidazolium Chloride (3a): Diamine **2a** (0.502 g, 1.08 mmol) was dissolved under magnetic stirring in HC(OEt)$_3$ (3 mL). HCl (12 M, 120 μL, 1.40 mmol) was then added, and the mixture was heated at 80 °C for 15 h. The mixture was cooled to room temperature, and petroleum ether was added (ca. 20 mL). The precipitate was collected by filtration and washed with petroleum ether (3 × 15 mL). Compound **3a** (0.553 g, 86%) was obtained as a white solid; m.p. 210 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 11.24 (s, 1 H, NCHN), 7.89 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.85 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.50 (ddd, ^3J = $^3J'$ = 7.6 Hz, ^4J = 0.9 Hz, 4 H, ArH), 7.35 (ddd, ^3J = $^3J'$ = 7.6 Hz, ^4J = 0.9 Hz, 4 H, ArH), 6.82–6.78 (m, 2 H, ArH), 6.25–6.21 (m, 2 H, ArH), 2.96 (s, 6 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 145.1 (arom. Cq), 142.6 (NCHN), 139.0 (arom. Cq), 130.9 (arom. Cq), 130.3 (arom. CH), 129.4 (arom. CH), 126.3 (arom. CH), 124.9 (arom. CH), 120.8 (arom. CH), 114.8 (arom. CH), 71.4 (*C*qCH$_3$), 27.3 (CH$_3$) ppm. $C_{35}H_{27}ClN_2$·1.4H_2O (511.06 + 25.22): calcd. C 78.39, H 5.60, N 5.22; found C 78.61, H 5.55, N 4.98.

1,3-Bis(9-ethyl-9*H*-fluoren-9-yl)benzimidazolium Chloride (3b): Diamine **2b** (0.400 g, 0.81 mmol) was dissolved under magnetic stirring in HC(OEt)$_3$ (3 mL). After the addition of HCl (12 M, 89 μL, 1.07 mmol), the mixture was heated at 80 °C for 15 h. The mixture was cooled to room temperature, petroleum ether was added (ca. 20 mL). The precipitate was collected by filtration and washed with petroleum ether (3 × 15 mL). Compound **3b** (0.414 g, 95%) was obtained as a white solid; m.p. 205 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 11.11 (s, 1 H, NCHN), 7.81 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.79 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.48 (ddd, ^3J = $^3J'$ = 7.5 Hz, ^4J = 0.9 Hz, 4 H, ArH), 7.34 (ddd, ^3J = $^3J'$ = 7.5 Hz, ^4J = 0.9 Hz, 4 H, ArH), 6.76–6.73 (m, 2 H, ArH), 6.25–6.21 (m, 2 H, ArH), 3.68 (q, ^3J = 7.0 Hz, 4 H, CH$_2$), 0.51 (t, ^3J = 7.0 Hz, 6 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 143.2 (arom. Cq), 142.2 (NCHN), 140.6 (arom. Cq), 131.6 (arom. Cq), 130.4 (arom. CH), 129.6 (arom. CH), 126.3 (arom. CH), 125.1 (arom. CH), 120.6 (arom. CH), 115.0 (arom. CH), 75.4 (*C*qCH$_2$), 31.7 (CH$_2$), 7.6 (CH$_3$) ppm. $C_{37}H_{33}ClN_2O$ (**3b**·H_2O, 557.13): calcd. C 79.77, H 5.97, N 5.03; found C 79.94, H 6.20, N 4.80.

1,3-Bis(9-propyl-9*H*-fluoren-9-yl)benzimidazolium Chloride (3c): Diamine **2c** (0.422 g, 0.81 mmol) was dissolved under magnetic stirring in HC(OEt)$_3$ (3 mL). After the addition of HCl (12 M, 89 μL, 1.07 mmol), the mixture was heated at 80 °C for 15 h. The solution was cooled to room temperature, and petroleum ether was added (ca. 20 mL). The resulting precipitate was collected by filtration and washed with petroleum ether (3 × 15 mL). Compound **3c** (0.358 g, 78%) was obtained as a white solid; m.p. 195 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 11.03 (s, 1 H, NCHN), 7.82 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.80 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.47 (ddd, ^3J = $^3J'$ = 7.5 Hz, ^4J = 0.9 Hz, 4 H, ArH), 7.34 (ddd, ^3J = $^3J'$ = 7.5 Hz, ^4J = 0.9 Hz, 4 H, ArH), 6.74–6.71 (m, 2 H, ArH), 6.23–6.19 (m, 2 H, ArH), 3.62–3.57 (m, 4 H, CqCH_2), 0.92 (t, ^3J = 7.1 Hz, 6 H, CH$_3$), 0.85–0.72 (m, 4 H, CH_2CH$_3$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 143.6 (arom. Cq), 141.9 (NCHN), 140.3 (arom. Cq), 131.0 (arom. Cq), 130.3 (arom. CH), 129.5 (arom. CH), 126.1 (arom. CH), 125.1 (arom. CH), 120.5 (arom. CH), 114.9 (arom. CH), 74.8 (*C*qCH$_2$), 39.9 (Cq*C*H$_2$), 16.6 (*C*H$_2$CH$_3$), 14.1 (CH$_3$) ppm. $C_{39}H_{35}ClN_2$·0.7H_2O (567.16 + 12.61): calcd. C 80.79, H 6.33, N 4.83; found C 80.91, H 6.27, N 4.77.

1,3-Bis(9-butyl-9*H*-fluoren-9-yl)benzimidazolium Chloride (3d): Diamine **2d** (0.912 g, 1.66 mmol) was dissolved under magnetic stirring in HC(OEt)$_3$ (5 mL). After the addition of HCl (12 M, 183 μL, 2.19 mmol), the mixture was heated at 80 °C for 15 h. The solution was then cooled to room temperature, and petroleum ether was added (ca. 20 mL). The precipitate was collected by filtration, washed with petroleum ether (3 × 15 mL) and dried in vacuo. Compound **3d** (0.878 g, 89%) was obtained as a white solid; m.p. 170 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 11.10 (s, 1 H, NCHN), 7.83 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.82 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.49 (dd, ^3J = $^3J'$ = 7.5 Hz, 4 H, ArH), 7.35 (dd, ^3J = $^3J'$ = 7.5 Hz, 4 H, ArH), 6.75–6.70 (m, 2 H, ArH), 6.23–6.19 (m, 2 H, ArH), 3.67–3.62 (m, 4 H, CqCH_2), 1.40 (tq, ^3J = $^3J'$ = 7.3 Hz, 4 H, CH_2CH$_3$), 0.77–0.67 (m, 10 H, CqCH$_2$CH_2 and CH$_3$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 143.7 (arom. Cq), 142.1 (N*C*HN), 140.4 (arom. Cq), 131.0 (arom. Cq), 130.3 (arom. CH), 129.5 (arom. CH), 126.1 (arom. CH), 125.1 (arom. CH), 120.5

(arom. CH), 114.9 (arom. CH), 74.8 (*C*qCH$_2$), 37.7 (Cq*C*H$_2$), 25.34 (CqCH$_2$*C*H$_2$), 22.59 (*C*H$_2$CH$_3$), 14.28 (CH$_3$) ppm. $C_{41}H_{39}ClN_2$·0.8H$_2$O (595.21 + 14.41): calcd. C 80.78, H 6.71, N 4.60; found C 80.59, H 6.62, N 4.71.

1,3-Bis(9-benzyl-9*H*-fluoren-9-yl)benzimidazolium Chloride (3e): Diamine **2e** (0.450 g, 0.73 mmol) was dissolved under magnetic stirring in HC(OEt)$_3$ (3 mL) and then HCl 12 M (81 μL, 0.97 mmol) was added. The mixture was heated at 80 °C for 15 h. The solution was cooled to room temperature, petroleum ether was added (ca. 20 mL), and the resulting precipitate was collected by filtration and washed with petroleum ether (3 × 15 mL). Compound **3e** (0.362 g, 75%) was obtained as a white solid; m.p. 225 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 11.49 (s, 1 H, NCHN), 8.01–8.07 (m, 4 H, ArH), 7.52–7.50 (m, 4 H, ArH), 7.42–7.35 (m, 8 H, ArH), 6.93 (t, ^3J = 7.5 Hz, 2 H, ArH), 6.83–6.76 (m, 6 H, ArH), 6.61 (d, ^3J = 7.5 Hz, 4 H, ArH), 6.25–6.22 (m, 2 H, ArH), 5.06 (s, 4 H, CH$_2$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ = 143.9 (arom. Cq), 142.9 (NCHN), 142.2 (arom. Cq), 132.0 (arom. Cq), 131.1 (arom. Cq), 131.0 (arom. CH), 130.3 (arom. CH), 128.9 (arom. CH), 127.0 (arom. CH), 126.6 (arom. CH), 126.3 (arom. CH), 125.6 (arom. CH), 120.4 (arom. CH), 115.2 (arom. CH), 75.1 (*C*qCH$_2$), 44.2 (CH$_2$) ppm. $C_{47}H_{39}ClN_2O$ (**3e**·2H$_2$O, 699.28): calcd. C 80.73, H 5.62, N 4.01; found C 80.43, H 5.34, N 4.11.

***trans*-[1,3-Bis(9-methyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene]-(pyridine)palladium(II) Dichloride (4a):** Nitrogen was passed (2 min) through a suspension of benzimidazolium salt **3a** (0.260 g, 0.51 mmol), K$_2$CO$_3$ (0.356 g, 2.58 mmol) and PdCl$_2$ (0.110 g, 0.62 mmol) in pyridine (3 mL). The suspension was then heated at 80 °C for 15 h under vigorous stirring. The mixture was cooled to room temperature, the mixture was filtered through Celite, and the solid was washed with CH$_2$Cl$_2$ (ca. 20 mL). The solvent was removed in vacuo, and the residue was purified by flash chromatography (SiO$_2$; CH$_2$Cl$_2$/petroleum ether, 50:50) to afford **4a** as a yellow solid (0.316 g, 85%); m.p. > 240 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 9.19–9.12 (m, 2 H, *o*-NC$_5H_5$), 7.85–7.78 (m, 9 H, 8H ArH and 1 H, *p*-NC$_5H_5$), 7.47–7.37 (m, 6 H, 4H ArH and 2H *m*-NC$_5H_5$), 7.29 (dd, ^3J = $^3J'$ = 7.5 Hz, 4 H, ArH), 6.40–6.37 (m, 2 H, ArH), 6.08–6.05 (m, 2 H, ArH), 4.02 (s, 6 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ = 161.5 (NCN), 151.8 (arom. CH), 149.2 (arom. Cq), 138.4 (arom. Cq), 138.2 (arom. CH), 134.4 (arom. Cq), 129.1 (2×, arom. CH), 124.9 (arom. CH), 124.7 (arom. CH), 122.5 (arom. CH), 120.7 (arom. CH), 113.1 (arom. CH), 72.2 (*C*qCH$_3$), 33.8 (CH$_3$) ppm. $C_{40}H_{31}Cl_2N_3Pd$·0.2CH$_2$Cl$_2$ (731.02 + 16.99): calcd. C 64.55, H 4.23, N 5.62; found C 64.39, H 4.31, N 5.56.

***trans*-[1,3-Bis(9-ethyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene]-(pyridine)palladium(II) Dichloride (4b):** Nitrogen was passed (2 min) through a stirred suspension of benzimidazolium salt **3b** (0.103 g, 0.19 mmol), K$_2$CO$_3$ (0.132 g, 0.96 mmol) and PdCl$_2$ (0.041 g, 0.23 mmol) in pyridine (2.5 mL). The suspension was then heated at 80 °C for 15 h under vigorous stirring. The solution was cooled to room temperature, the mixture was filtered through Celite, and the solid was washed with CH$_2$Cl$_2$ (ca. 20 mL). The filtrate was concentrated under vacuum and purified by flash chromatography (SiO$_2$; CH$_2$Cl$_2$/petroleum ether, 50:50) to afford **4b** as a yellow solid (0.113 g, 78%); m.p. > 240 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 9.13–9.10 (m, 2 H, *o*-NC$_5H_5$), 7.84–7.76 (m, 5 H, 4H ArH and 1 H, *p*-NC$_5H_5$), 7.72 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.45–7.35 (m, 6 H, 4H ArH and 2H *m*-NC$_5H_5$), 7.28 (ddd, ^3J = $^3J'$ = 7.5 Hz, ^4J = 0.9 Hz, 4 H, ArH), 6.37–6.34 (m, 2 H, ArH), 6.18–6.15 (m, 2 H, ArH), 5.45 (q, ^3J = 7.3 Hz, 4 H, CH$_2$), 0.42 (t, ^3J = 7.3 Hz, 6 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ = 160.4 (NCN), 151.8 (arom. CH), 146.4 (arom. Cq), 140.3 (arom. Cq), 138.2 (arom. CH), 134.6 (arom. Cq), 129.1 (2×, arom. CH), 125.0 (arom. CH), 124.8 (arom. CH), 122.1 (arom. CH), 120.0 (arom. CH), 113.5 (arom. CH), 76.7 (*C*qCH$_2$), 36.8 (CH$_2$), 8.7 (CH$_3$) ppm. $C_{42}H_{35}Cl_2N_3Pd$ (759.07): calcd. C 66.46, H 4.65, N 5.54; found C 66.73, H 4.99, N 5.16.

***trans*-[1,3-Bis(9-propyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene]-(pyridine)palladium(II) Dichloride (4c):** Nitrogen was passed (2 min) through a suspension of benzimidazolium salt **3c** (0.352 g, 0.62 mmol), K$_2$CO$_3$ (0.427 g, 3.09 mmol) and PdCl$_2$ (0.132 g, 0.74 mmol) in pyridine (3 mL). The suspension was then heated at 80 °C for 24 h under vigorous stirring. The solution was cooled to room temperature, the mixture was filtered through Celite, and the solid was washed with CH$_2$Cl$_2$ (ca. 20 mL). The solvent was removed in vacuo, and the residue was purified by flash chromatography (SiO$_2$; CH$_2$Cl$_2$/petroleum ether, 50:50) to afford **4c** as a yellow solid (0.108 g, 22%); m.p. > 240 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 9.16–9.14 (m, 2 H, *o*-NC$_5H_5$), 7.87–7.72 (m, 9 H, 8H ArH and 1 H, *p*-NC$_5H_5$), 7.43–7.38 (m, 6 H, 4H ArH and 2H *m*-NC$_5H_5$), 7.30–7.26 (m, 4 H, ArH), 6.35–6.32 (m, 2 H, ArH), 6.15–6.11 (m, 2 H, ArH), 5.46–5.41 (m, 4 H, CqCH_2), 0.92 (t, ^3J = 7.2 Hz, 6 H, CH$_3$), 0.62 (tq, ^3J = $^3J'$ = 7.2 Hz, 4 H, CH_2CH$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ = 160.7 (NCN), 151.9 (arom. CH), 147.0 (arom. Cq), 140.0 (arom. Cq), 138.2 (arom. CH), 134.5 (arom. Cq), 129.1 (arom. CH), 129.1 (arom. CH), 124.9 (arom. CH), 124.8 (arom. CH), 122.4 (arom. CH), 120.0 (arom. CH), 113.4 (arom. CH), 76.0 (*C*qCH$_2$), 46.0 (Cq*C*H$_2$), 17.6 (*C*H$_2$CH$_3$), 14.5 (CH$_3$) ppm. $C_{44}H_{39}Cl_2N_3Pd$·0.2CH$_2$Cl$_2$ (787.13 + 16.99): calcd. C 66.02, H 4.94, N 5.23; found C 66.06, H 4.96, N 5.14.

***trans*-[1,3-Bis(9-butyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene]-(pyridine)palladium(II) Dichloride (4d):** Nitrogen was passed (2 min) through a suspension of benzimidazolium salt **3d** (0.503 g, 0.84 mmol), K$_2$CO$_3$ (0.590 g, 4.27 mmol) and PdCl$_2$ (0.179 g, 1.01 mmol) in pyridine (3 mL). The mixture was then heated at 80 °C for 15 h under vigorous stirring. The mixture was cooled to room temperature and filtered through Celite, and the filtered solid was washed with CH$_2$Cl$_2$ (ca. 20 mL). The solvent was removed in vacuo, and the residue was purified by flash chromatography (SiO$_2$; CH$_2$Cl$_2$/petroleum ether, 50:50) to afford **4d** as a yellow solid (0.279 g, 41%); m.p. > 240 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 9.19–9.17 (m, 2 H, *o*-NC$_5H_5$), 7.83–7.72 (m, 9 H, 8H ArH and 1 H, *p*-NC$_5H_5$), 7.43–7.38 (m, 6 H, 4H ArH and 2H *m*-NC$_5H_5$), 7.30–7.25 (m, 4 H, ArH), 6.34–6.31 (m, 2 H, ArH), 6.15–6.11 (m, 2 H, ArH), 5.47–5.41 (m, 4 H, CqCH_2), 1.34 (tq, ^3J = $^3J'$ = 7.3 Hz, 4 H, CH_2CH$_3$), 0.69 (t, ^3J = 7.3 Hz, 6 H, CH$_3$), 0.55 (tt, ^3J = $^3J'$ = 7.3 Hz, 4 H, CqCH$_2$CH_2) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ = 160.5 (NCN), 151.9 (arom. CH), 147.0 (arom. Cq), 140.1 (arom. Cq), 138.2 (arom. CH), 134.6 (arom. Cq), 129.1 (arom. CH), 129.0 (arom. CH), 124.9 (arom. CH), 124.7 (arom. CH), 122.3 (arom. CH), 120.0 (arom. CH), 113.4 (arom. CH), 76.1 (*C*qCH$_2$), 43.6 (Cq*C*H$_2$), 26.1 (CqCH$_2$*C*H$_2$), 23.0 (*C*H$_2$CH$_3$), 14.1 (CH$_3$) ppm. $C_{46}H_{43}Cl_2N_3Pd$·0.1CH$_2$Cl$_2$ (815.18 + 8.49): calcd. C 67.22, H 5.29, N 5.10; found C 67.37, H 5.39, N 4.99.

***trans*-[1,3-Bis(9-benzyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene]-(pyridine)palladium(II) Dichloride (4e):** Nitrogen was passed (2 min) through a suspension of benzimidazolium salt **3e** (0.200 g, 0.30 mmol), K$_2$CO$_3$ (0.207 g, 1.5 mmol) and PdCl$_2$ (0.065 g, 0.36 mmol) in pyridine (3 mL). The suspension was then heated at 80 °C for 15 h under vigorous stirring. The mixture was cooled to room temperature and filtered through Celite, and the filtered solid was washed with CH$_2$Cl$_2$ (ca. 20 mL). The solvent was removed in

vacuo, and the residue was purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50:50) to afford **4e** as a yellow solid (0.177 g, 67%); m.p. > 240 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 9.01–8.98 (m, 2 H, *o*-NC_5H_5), 8.02–7.97 (m, 4 H, ArH), 7.66 (tt, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 1 H, *p*-NC_5H_5), 7.44–7.22 (m, 14 H, 12H ArH and 2H *m*-NC_5H_5), 6.94 (tt, ^3J = 7.4 Hz, ^4J = 1.1 Hz, 2 H, ArH), 6.83–6.74 (m, 8 H, 4H ArH and 4H CH_2), 6.41 (d, ^3J = 7.4 Hz, 4 H, ArH), 6.38–6.35 (m, 2 H, ArH), 6.16–6.12 (m, 2 H, ArH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 161.3 (NCN), 151.6 (arom. CH), 146.2 (arom. Cq), 140.1 (arom. Cq), 138.0 (arom. CH), 134.6 (arom. Cq), 134.5 (arom. Cq), 131.2 (arom. CH) 129.2 (arom. CH), 128.6 (arom. CH), 126.6 (arom. CH), 125.9 (arom. CH), 125.4 (arom. CH), 125.0 (arom. CH) 122.5 (arom. CH), 119.9 (arom. CH), 113.8 (arom. CH), 76.3 (*C*qCH$_2$), 50.0 (Cq*C*H$_2$) ppm. $C_{52}H_{39}Cl_2N_3Pd$ (883.21): calcd. C 70.71, H 4.45, N 4.76; found C 70.72, H 4.56, N 4.82.

***trans*-[1,3-Bis(*tert*-butyl)benzimidazol-2-ylidene](pyridine)palladium(II) Dichloride (5):** Nitrogen was passed (2 min) through a suspension of 1,3-bis(*tert*-butyl)benzimidazolium chloride (0.630 g, 2.36 mmol), K_2CO_3 (1.63 g, 11.8 mmol) and $PdCl_2$ (0.415 g, 2.34 mmol) in pyridine (5 mL). The suspension was then heated at 80 °C for 15 h under vigorous stirring. The mixture was cooled to room temperature and filtered through Celite, and the filtered solid was washed with CH_2Cl_2 (ca. 20 mL). The combined washings and the filtrate were evaporated to dryness. The residue was then purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50:50) to afford **5** as a yellow solid (0.921 g, 80%); m.p. 229 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 9.03–8.98 (m, 2 H, *o*-NC_5H_5), 7.83–7.79 (m, 2 H, ArH), 7.78 (tt, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1 H, *p*-NC_5H_5), 7.38–7.33 (m, 2 H, *m*-NC_5H_5), 7.24–7.18 (m, 2H ArH), 2.52 (s, 18 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 157.2 (NCN), 151.6 (arom. CH), 137.9 (arom. CH), 135.1 (arom. Cq), 124.7 (arom. CH), 121.6 (arom. CH), 115.3 (arom. CH), 61.3 (*C*qCH$_3$), 31.9 (CH_3) ppm. $C_{20}H_{27}Cl_2N_3Pd$ (486.77): calcd. C 49.35, H 5.59, N 8.63; found C 48.81, H 5.64, N 8.43.

***trans*-[1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene](pyridine)palladium(II) Dichloride (6):** Nitrogen was passed (2 min) through a suspension of bis(2,4,6-trimethylphenyl)imidazolium chloride (0.511 g, 1.50 mmol), K_2CO_3 (1.04 g, 7.50 mmol) and $PdCl_2$ (0.320 g, 1.80 mmol) in pyridine (5 mL). The suspension was then heated at 80 °C for 15 h under vigorous stirring. The mixture was cooled to room temperature and filtered through Celite, and the collected solid washed with CH_2Cl_2 (ca. 20 mL). The filtrate was evaporated to dryness, and the resulting residue was purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50:50) to afford **6** as a yellow solid (0.689 g, 82%); m.p. > 240 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.54–8.48 (m, 2 H, *o*-NC_5H_5), 7.54 (tt, ^3J = 7.6 Hz, ^4J = 1.5 Hz, 1 H, *p*-NC_5H_5), 7.12–7.07 (m, 2 H, *m*-NC_5H_5), 7.06 (s, 2 H, ArH), 7.05 (s, 4 H, ArH), 2.37 (s, 6 H, *p*-CH_3), 2.36 (s, 12 H, *o*-CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 152.9 (NCN), 151.6 (arom. CH), 139.2 (arom. Cq), 137.5 (arom. CH), 136.4 (arom. Cq), 135.2 (arom. Cq), 129.3 (arom. CH), 124.2 (arom. CH), 124.0 (arom. CH), 21.3 (*p*-CH_3) 19.2 (*o*-CH_3) ppm. $C_{26}H_{29}Cl_2N_3Pd$ (560.85): calcd. C 55.68, H 5.21, N 7.49.f; found C 55.68, H 5.51, N 7.23.

***trans*-[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene](pyridine)palladium(II) Dichloride (7):** Nitrogen was passed (2 min) through a suspension of bis(2,6-diisopropylphenyl)imidazolium chloride (0.301 g, 0.71 mmol), K_2CO_3 (0.493 g, 3.55 mmol) and $PdCl_2$ (0.151 g, 0.85 mmol) in pyridine (5 mL). The suspension was then heated at 80 °C for 15 h under vigorous stirring. The mixture was cooled to room temperature and filtered through Celite, and the collected solid was washed with CH_2Cl_2 (ca. 20 mL). The filtrate and the washings were evaporated to dryness, and the resulting residue was purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50:50) to afford **7** as a yellow solid (0.322 g, 70%); m.p. 235 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.58–8.51 (m, 2 H, *o*-NC_5H_5), 7.57–7.44 (m, 3 H, 2H ArH and 1 H, *p*-NC_5H_5), 7.35 (d, ^3J = 7.6 Hz, 4 H, ArH), 7.14–7.05 (m, 4 H, 2H ArH and 2 H, *m*-NC_5H_5), 3.18 (qq, $^3J = {}^3J'$ = 6.7 Hz, 4 H, C*H*Me$_2$), 1.49 (d, ^3J = 6.7 Hz, 12 H, CHC*H*$_3$), 1.12 (d, ^3J = 6.7 Hz, 12 H, CHC*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 155.0 (NCN), 151.5 (arom. CH), 146.7 (arom. Cq), 137.5 (arom. CH), 135.2 (arom. Cq), 130.3 (arom. CH), 125.1 (arom. CH), 124.1 (2×, arom. CH), 28.8 (*C*HMe$_2$) 26.4 (CH_3) 23.4 (CH_3) ppm. $C_{32}H_{41}Cl_2N_3Pd$ (645.01): calcd. C 59.59, H 6.41, N 6.51; found C 59.53, H 6.63, N 6.29. The spectroscopic data are in full agreement with those of the literature.[15]

***trans*-[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene](pyridine)palladium(II) Dichloride (8):** Nitrogen was passed (2 min) through a suspension of bis(2,6-diisopropylphenyl)imidazolinium chloride (0.303 g, 0.71 mmol), K_2CO_3 (0.496 g, 3.55 mmol) and $PdCl_2$ (0.152 g, 0.85 mmol) in pyridine (5 mL). The suspension was then heated at 80 °C for 15 h under vigorous stirring. The mixture was cooled to room temperature and filtered through Celite, and the collected solid washed with CH_2Cl_2 (ca. 20 mL). The filtrate was evaporated to dryness, and the resulting residue was purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50:50) to afford **8** as a yellow solid (270 mg, 58%); m.p. 227 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.54–8.47 (m, 2 H, *o*-NC_5H_5), 7.52 (tt, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1 H, *p*-NC_5H_5), 7.44–7.37 (m, 2 H, ArH), 7.32–7.27 (m, 4 H, ArH), 7.10–7.04 (m, 2 H, *m*-NC_5H_5), 4.06 (s, 4 H, CH_2), 3.60 (qq, $^3J = {}^3J'$ = 6.7 Hz, 4 H, C*H*Me$_2$), 1.57 (d, ^3J = 6.7 Hz, 12 H, CHC*H*$_3$), 1.27 (d, ^3J = 6.7 Hz, 12 H, CHC*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 186.2 (NCN), 151.3 (arom. CH), 147.6 (arom. Cq), 137.4 (arom. CH), 135.5 (arom. Cq), 129.5 (arom. CH), 125.5 (arom. CH), 124.0 (arom. CH), 58.9 (CH_2), 28.8 (*C*HMe$_2$) 26.9 (CH_3) 24.3 (CH_3) ppm. $C_{32}H_{43}Cl_2N_3Pd$ (647,03): calcd. C 59.40, H 6.70, N 6.49; found C 59.15, H 6.98, N 6.01.

General Procedure for Palladium-Catalysed Suzuki–Miyaura Cross-Coupling Reactions: A mixture of the palladium complex (0.01 mmol), phenylboronic acid (0.183 g, 1.50 mmol) and base (2 mmol) was suspended in an appropriate solvent (3 mL). After the addition of *p*-tolyl chloride (0.126 g, 1 mmol), the mixture was vigorously stirred at 80 °C for a given period of time. The hot mixture was filtered through Celite. 1,4-Dimethoxybenzene (0.069 g, 0.5 mmol; internal standard) was then added to the filtrate. The solvent was removed under reduced pressure, and the crude mixture was analysed by ^1H NMR spectroscopy. The yields were determined by comparing the intensity of the methyl signal of the product [δ(Me) = 2.41 ppm] with that of the internal reference [δ(Me) = 3.78 ppm]. In some experiments the product was isolated chromatographically. The isolated yield turned out to be very close (deviation less than 5%) to that determined by using the internal reference.

Crystal Data for Benzimidazolium Salt 3b·MeOH: Crystals suitable for X-ray diffraction were obtained by slow evaporation of a deuterated chloroform solution of the complex: $C_{38}H_{35}ClN_2O$, M = 571.13, monoclinic, space group $P2_1/c$, a = 13.2006(3), b = 16.0741(4), c = 14.5915(4) Å, β = 102.141(3), V = 3026.89(13) Å^3, Z = 4, μ = 0.160 mm^{-1}, F(000) = 1208. Crystals of the compound were mounted on an Oxford Diffraction CCD Sapphire 3 Xcalibur diffractometer. Data collection with Mo-K_α radiation (λ = 0.71073 Å) was carried out at 140 K. 23233 reflections were col-

lected ($2.66 < \theta < 27.00°$), 6590 were found to be unique and 3594 were observed (merging $R = 0.0549$). The structure was solved with SHELXS-97.[40] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.0957, 0.0394, 0.0889, 0.0811, 0.819. Residual electron density minimum/maximum: –0.237/0.254 e Å^{-3}.

Crystal Data for Complex 4b: Crystals suitable for X-ray diffraction were obtained by slow diffusion of THF into a deuterated chloroform solution of the complex: $C_{42}H_{35}Cl_2N_3Pd$, $M = 759.03$, monoclinic, space group $P2_1/n$, $a = 11.27110(10)$, $b = 22.3694(3)$, $c = 17.3400(2)$ Å, $\beta = 93.3090(10)$, $V = 4364.61(9)$ Å^3, $Z = 4$, $\mu = 0.576$ mm^{-1}, $F(000) = 1552$. Crystals of the compound were mounted on an Oxford Diffraction CCD Sapphire 3 Xcalibur diffractometer. Data collection with Mo-K_a radiation ($\lambda = 0.71073$ Å) was carried out at 150 K. 61105 reflections were collected ($2.78 < \theta < 27.00°$), 9522 were found to be unique and 6814 were observed (merging $R = 0.0462$). The structure was solved with SHELXS-97.[40] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.0579, 0.0341, 0.1380, 0.1203, 0.559. Residual electron density minimum/maximum: –0.324/0.365 e Å^{-3}.

CCDC-811568 (for **3b**·MeOH) and -811477 (for **4b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): 2D ^{1}H–^{1}H ROESY NMR spectra for **3a** and **4b**, base and solvent screening for 4-methylbiphenyl synthesis with palladium complex **4b**, general procedure for the cross-coupling of (2,6-dimethoxyphenyl)boronic acid with 4-chlorotoluene, ORTEP representation of the molecular structure of **2a** and the crystal data for **2a**.

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