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Directional properties of fluorenylidene moieties in unsymmetrically substituted N-heterocyclic carbenes. Unexpected CH activation of a methylfluorenyl group with palladium. Use in palladium catalysed Suzuki–Miyaura cross coupling of aryl chlorides†

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Benzimidazolium salts having their two nitrogen atoms substituted by different 9-alkylfluorenyl groups (**4a–e** and **4g**, alkyl[1]/alkyl[2] = Me/Et, Me/Pr, Me/*n*-Bu, Me/*i*-Pr, Me/Bn, Me/CH_2SMe have been synthesised in high yields in two or three steps from *N*,*N*′-bis(9*H*-fluoren-9-ylidene)benzene-1,2-diamine (**1**). The imidazolium salts **4a–e** were converted readily into the corresponding PEPPSI-type palladium complexes (PEPPSI = pyridine-enhanced precatalyst preparation stabilisation and initiation), while reaction of the methylthioether-substituted salt **4g** with $PdCl_2/K_2CO_3$/pyridine afforded the palladacycle **5g** resulting from metallation of the methyl group attached to the fluorenylidene moiety. NMR and X-ray diffraction studies revealed that the carbene ligands in **5a–5e** behave as clamp-like ligands, the resulting metal confinement arising from a combination of the orientational properties of the fluorenylidene moieties that push the alkyl groups towards the metal centre and attractive anagostic interactions involving CH_2(fluorenyl) groups. Complexes **5a–e** were assessed in Suzuki–Miyaura cross-coupling reactions. Like their symmetrical analogues they displayed high activity in the coupling of phenyl boronic acid with *p*-tolylchloride but their performance remained slightly inferior to that of the related, symmetrical Et/Et complex **5h**.

Introduction

A number of palladium complexes with a single N-heterocyclic carbene (NHC) ligand have proven to be useful catalysts in cross-coupling reactions of aryl halides (Fig. 1).[1–27] Among the most popular catalysts for such reactions are palladium complexes of the type $[PdX_2(NHC)L]$ (X = halide), in which L is an ancillary ligand that readily dissociates.[28–37] Several authors have identified pertinent criteria that may increase the effectiveness of the NHC ligand. Thus, optimised NHC's should

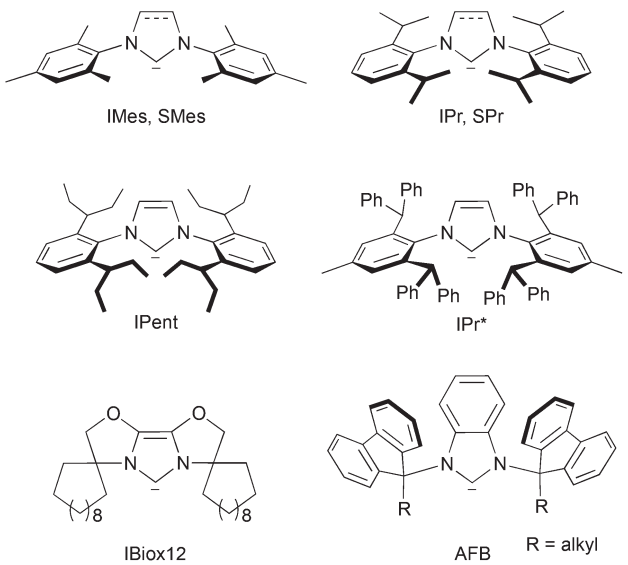

Fig. 1 Effective NHCs used as ligands in palladium-catalysed cross-coupling.

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contain N-substituents that are both bulky and flexible, bulkiness favouring the reductive elimination step and stabilisation of catalytic intermediates, the flexibility enabling an entering substrate to approach the metal centre after release of the product in the last step of the catalytic cycle.

We have recently reported a series of NHC–Pd complexes in which the two nitrogen atoms are substituted by (identical) alkylfluorenyl substituents.[27] The large fluorenylidene moiety was shown to orientate the alkyl groups towards the palladium centre while its restricted rotational freedom made the ligand bulkiness time independent. It is worthy of note that these ligands (termed AFB in Fig. 1) do not display hemispherical encumbrance such as do, *e.g.*, IPr, IPr*, or SIPr. Instead, the ligands give rise to meridional encumbrance, with two small, apically localised CH_2 (or CH_3) groups coming in close contact to the palladium centre. Despite their rather inflexible form, these NHCs resulted in catalysts that are among the fastest Suzuki–Miyaura cross-coupling catalysts reported to date. These results unambiguously establish the key role in cross-coupling reactions of NHCs that display essentially confining properties along with very limited flexibility.

As an extension of these studies, we now report the synthesis and catalytic performance in Suzuki–Miyaura coupling of related Pd-complexes containing unsymmetrically substituted NHCs. One of the NHCs contains a potentially coordinating $-CH_2SMe$ side group.

Results and discussion

Syntheses of benzimidazolium salts

The synthesis of the palladium complexes used for this study began with that of unsymmetrically substituted imidazolium ligand-precursors (**4a–e** and **4g**). These were obtained according to one of the routes displayed in Scheme 1. The one-pot synthesis of **4a–4d** was achieved by treatment of *rac*-**1** with one equiv. of MeLi and subsequent addition of a second, distinct alkyllithium reagent (2 equiv.). Workup resulted in the corresponding diamines (**3a–3d**) in over 78% yield. Ring closure to the imidazolium salts **4a–4d** was then performed with triethylorthoformate and HCl. Attempts to prepare an Et/*n*-Pr analogue of **3b** in a pure form (using EtLi and *n*-PrLi as reagents) were unsuccessful, as this product could not be separated from the Et/Et and *n*-Pr/*n*-Pr side products that formed during its synthesis.

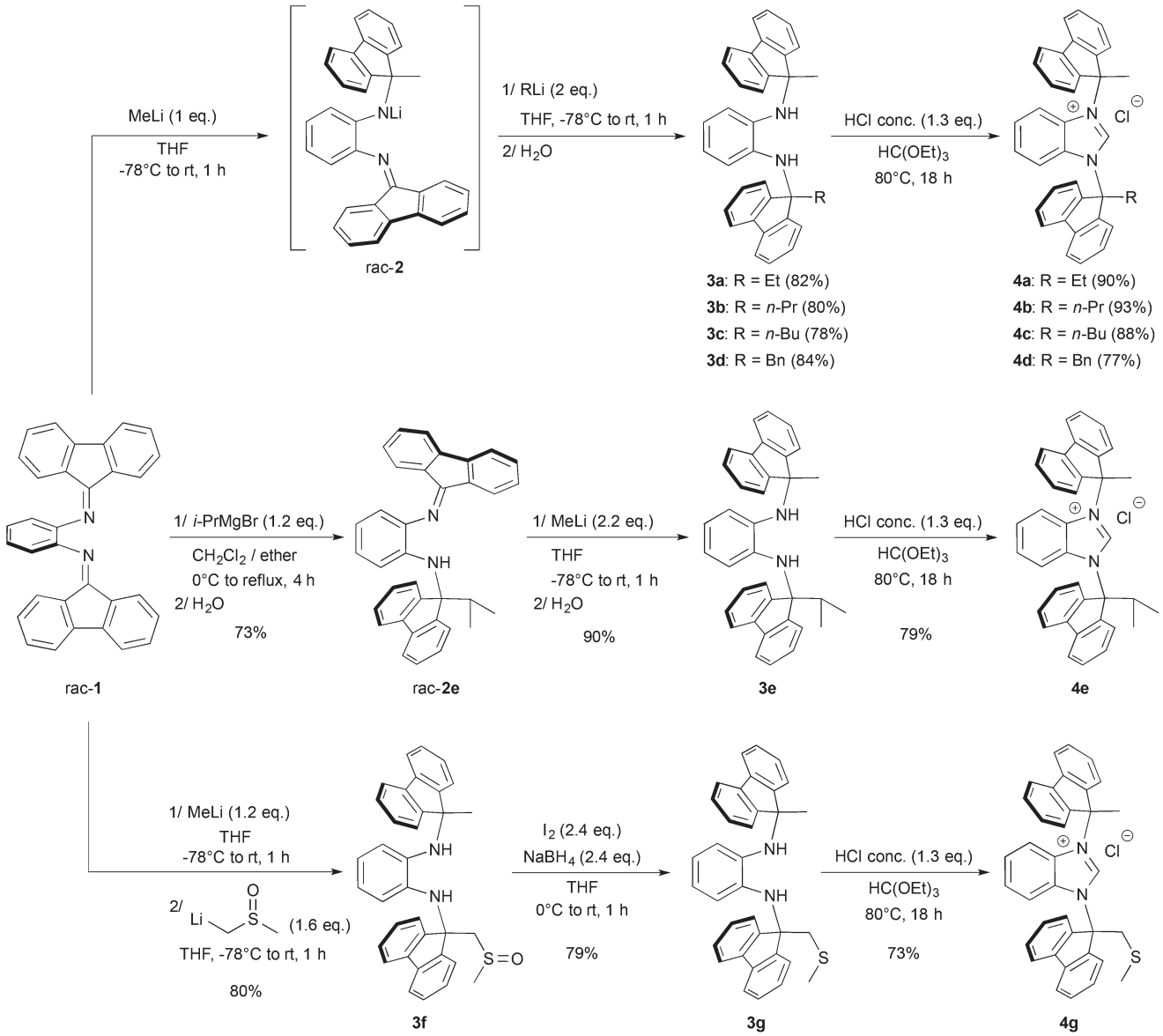
For the preparation of **4e**, the first alkylation was arbitrarily performed with a Grignard reagent, namely *i*-PrMgBr, this leading after hydrolysis to the mixed imine–amine **2e** in 73% yield. Alkylation of **2e** with MeLi and subsequent hydrolysis gave **3e** in 90% yield. Finally, diamine **3e** was reacted with $HC(OEt)_3$–HCl to yield the imidazolium salt **4e** in 79%.

The preparation of thioether-imidazolium salt **4g**, which we considered as a potential precursor (*vide infra*) of a chelating *carbene-thioether* ligand is basically similar to that of **4a–4d**, although this synthesis required an additional step to generate the thioether function. Thus, after sequential addition of MeLi (1.2 equiv.) and $LiCH_2S(O)Me$ (1.6 equiv.), diamine-sulfoxide **3f** was obtained in 80% yield. Reduction of the sulfoxide was carried out with $NaBH_4$ in the presence of iodide, leading to thioether **3g** in 79% yield. In the last step imidazolium salt **4g** was readily synthesised applying the above $HC(OEt)_3$–HCl procedure. All imidazolium salts are characterised by a methine signal in their ^1H NMR spectrum lying in the range 11.15–11.70 ppm.

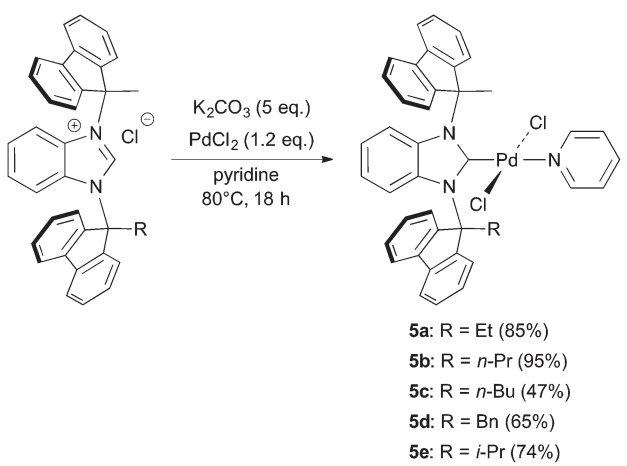
Syntheses of palladium complexes

The PEPPSI-type[28–31] palladium complexes **5a–e** were obtained in medium-to-good yields using the standard procedure initially developed by Organ (Scheme 2). As already observed for related palladium complexes having two *identical* alkylfluorenyl substituents, *e.g.* **5h** (Fig. 2), all the NCC*H* signals are markedly downfield shifted when compared to their analogues in the corresponding imidazolium precursor ($\Delta\delta$ = 1.0–1.7 ppm). This reflects anagostic CH interactions between these protons and the palladium centre, and means that the alkyl groups attached to the fluorenylidene moiety are pushed towards the metal d_{z^2} orbital, while the fluorenylidene plane itself is bent towards the NHC-fused aromatic ring. The particular orientation of the fluorenylidene plane is seemingly persistent in solution, as the only ROESY correlations involving the benzimidazolium unit are seen with aromatic protons of the fluorenylidene moieties, but with none of the alkyl groups.[38] A single crystal X-ray diffraction study carried out for **5d** confirmed the orientation of the methyl and benzyl moieties towards the metal d_{z^2} orbital, which results in a double apical encumbrance of the metal centre (Fig. 3). The unit cell of this structure contains two nearly identical molecules. Short CH···Pd separations consistent with anagostic interactions between CH atoms of the methyl and benzyl groups were found in both of them, the shortest CH···Pd distances being 2.457 Å (in molecule 1) and 2.455 Å (in molecule 2). The X-ray study further allowed evaluation of the percent buried volume of the carbene ligand of **5d** as 36.7% (using a $M–C_{carbene}$ bond fixed at 2.10 Å for the calculation), which actually is close to that of IMes.[39,40] It is worthy of mention here that, as inferred from ROESY experiments, a "folded-back" orientation of the fluorenylidene planes as in **5a–5e** (as well as **5h**, taken as reference compound), can also be seen in the corresponding amine and imidazolium precursors. This conclusion was corroborated by the observation that the H^a protons belonging to the C_6H_4-ring have significantly higher-field shifts (*ca.* 0.8 ppm) with respect to their analogues in *o*-phenylenediamine. This is a consequence of the fact that the H^a protons lie in the shielding region of the neighbouring fluorenylidene moieties.

Preliminary DFT calculations carried out on the reference complex **5h**, which has two ethyl substituents oriented towards the d_{z^2} orbital, indicate a rotational barrier of *ca.* 30 kcal mol^{-1} for a 180° rotation of the alkylfluorenylidene groups about the N–C(fluorenylidene) bond. In the following, an alkyl orientation as in **5h** will be termed an *exo*-orientation, while the opposite one will be called an *endo*-orientation. The theoretical study revealed that **5h** is more stable by about 16.4 kcal mol^{-1}

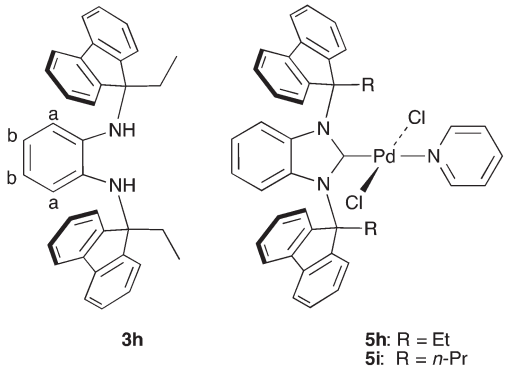


Scheme 1 Synthesis of benzimidazolium salts **4a–e**.



Scheme 2 Synthesis of palladium complexes **5a–e**.

than a hypothetical *endo*/*endo* rotamer, that is the one with the fluorenylidene plane inclined towards the metal ion. Interestingly, the calculated rotational barrier for an *endo–exo* alkyl orientational change was found to be lower by *ca.* 15 kcal mol^{-1} than the *exo–endo* conversion discussed above. This obviously reflects the presence of anagostic interactions in the *exo*/*exo* conformer, which significantly increase the stability of this rotamer *vs.* the opposite one. Overall these calculations lead us to refine somewhat our previous description of the clamp-like behaviour of the carbene ligand of complex **5h** and related ones. Clearly, the encumbrance of the d_{z^2} orbital in all the PEPPSI complexes discussed in this study is due to a combination of the orientational properties of the pre-oriented fluorenylidene plane and the attractive anagostic interactions that contribute to maintain the steric encumbrance on both sides of the coordination plane.



3h **5h**: R = Et; **5i**: R = *n*-Pr

Fig. 2 Diamine **3h** and palladium complexes **5h** and **5i**.

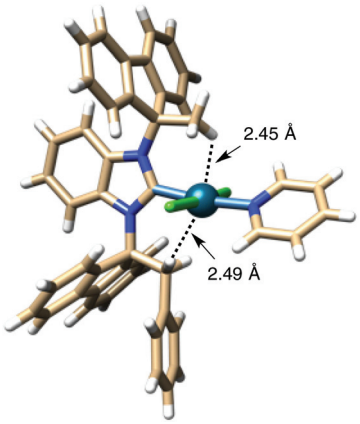
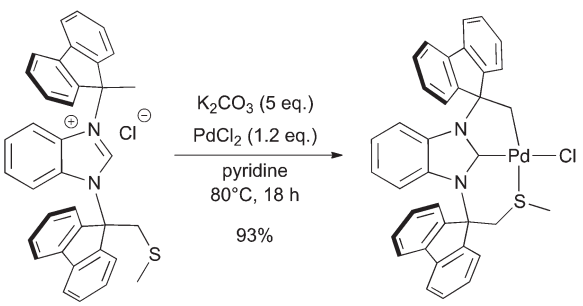


Fig. 3 Solid state structure of complex **5d** (only one of the two similar molecules in the unit cell is shown).

Attempts to form an analogue of **5a–5e** starting from the thioether imidazolium salt **4g** failed. Instead, the cyclometallated pincer-type complex **5g** formed quantitatively (Scheme 3), the structure of which was determined by a single crystal X-ray diffraction study (Fig. 4). In the ^{1}H NMR spectrum, the metalated CH_2 group appears as a sharp singlet at 3.70 ppm (*cf.* 2.31 ppm for the methyl group of precursor **4g**). In contrast, the CH_2S signal is broad, this reflecting some dynamics within the puckered Pd,$C_{carbene}$,S ring. Complex **5g** is the only known example of a palladium–NHC complex containing a metallated



4g **5g**

Scheme 3 High yield synthesis of the cyclometalated carbene complex **5g**.

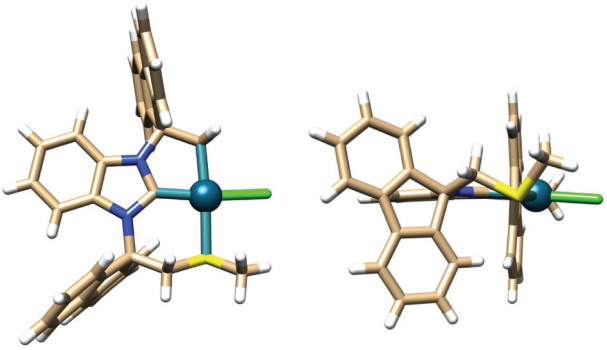


Fig. 4 Molecular structure of **5g** (top view, left: side view, right).

alkyl side group (It is noteworthy that CH activation of propane with NHC–Pd complexes has been reported recently).[41] As K_2CO_3 and pyridine are both relatively weak bases, metalation probably occurred through CH activation by the palladium centre after coordination of the thioether group. Molecular models clearly show that owing to the orientational properties of the fluorenyl moieties, *C*,*S*-chelation of an hypothetical thioether-carbene ligand positions the Me group of the methylfluorenyl substituent trans to the sulfur atom, thereby strongly facilitating a CH activation process.

Comparison with symmetrically-substituted carbenes

In our previous publication on clamp-like carbene ligands, we had assessed symmetrically substituted analogues of the above complexes in Suzuki–Miyaura cross coupling reactions. Thus for example, the meridionally encumbered complexes **5h** and **5i** were found to behave as fast catalytic systems in the coup-

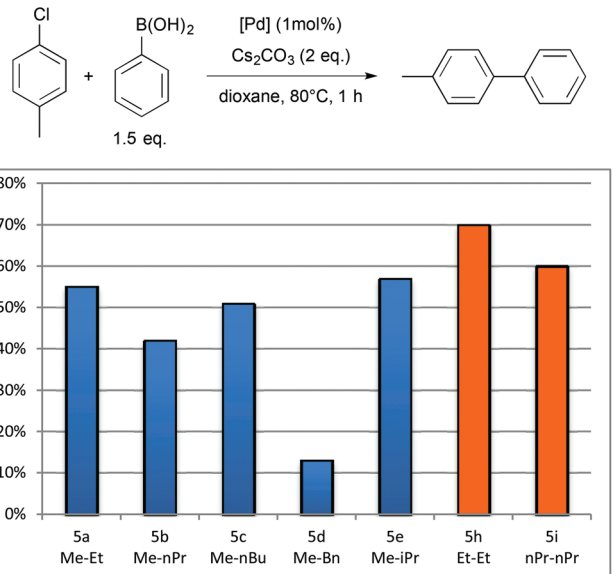


Fig. 5 Product yields in Suzuki–Miyaura cross-coupling of $PhB(OH)_2$ with *p*-Cl-C_6H_4Me using palladium complexes **5a–e** and **5h,i**. Reaction conditions: *p*-tolyl chloride (1 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (2 mmol), [Pd] (1 mol%), dioxane (3 mL). Yields were determined by ^{1}H NMR.

ling of phenylboronic acid with *p*-tolyl chloride, their activities being equal or superior to those of the fastest systems reported to date (IMes/Pd, IPr/Pd).[27] To answer the question whether an unsymmetrical ligand structure in a related complex would modify the catalytic outcome, tests were performed with **5a–5e** under conditions identical to those previously applied for **5h** and **5i**, namely by operating with 1 mol% of palladium complex and 2 equiv. of Cs_2CO_3 in dioxane at 80 °C. The reaction rates observed for the unsymmetrical complexes were of the same order of magnitude as those of **5h** and **5i**, although slightly inferior (see Fig. 5). The sole complex leading to a somewhat disappointing performance was the Me/Bn complex **5d**, this probably reflecting the bulkiness of the benzyl group that hinders substrate approach. A similar effect had previously been observed for the corresponding Bn/Bn complex.

Conclusions

We have described synthetic methodology that enables preparation in three or four steps of benzimidazolium salts having their two nitrogen atoms substituted by different alkylfluorenyl groups. With the exception of the thioether derivative **4g**, these salts readily form PEPPSI-type palladium complexes in which both fluorenylidene moieties orientate the corresponding alkyl group towards the d_{z^2} orbital of the palladium ion. Owing to a high rotational barrier about the N–C(fluorenyl) bond, time independent crowding is created about the metal in the most stable conformer, in which anagostic interactions significantly contribute to maintain the observed apical encumbrance. With imidazolium salt **4g**, and by applying conditions that normally lead to PEPPSI complexes, the cyclometallated pincer complex **5g** was obtained quantitatively. Its formation is likely to involve CH activation by the palladium centre after formation of a carbene ligand and binding of the thioether group. Like their symmetrical analogues, the complexes displayed high activities in the cross coupling of phenyl boronic acid with *p*-tolylchloride, but their performance did not surpass that of the symmetrical Et/Et complex **5h**.

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 on a FT Bruker AVANCE 300 (^1H: 300.1 MHz, ^{13}C: 75.5 MHz) instrument at 25 °C. ^1H NMR spectral data were referenced to residual protonated solvents ($CHCl_3$, δ 7.26; [D_6]DMSO, δ 2.50), ^{13}C chemical shifts are reported relative to deuterated solvents ($CDCl_3$, δ 77.16; [D_6]DMSO, δ 39.52). 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 data given hereafter, Cq denotes a quaternary carbon atom. Flash chromatography was performed as described by Still *et al.*,[42] employing Geduran SI (E. Merck, 0.040–0.063 mm) silica. Routine thin-layer chromatography 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) using CH_2Cl_2 or CH_3CN as solvent, or with a Bruker MaldiTOF spectrometer (MALDI-TOF) using 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 and are uncorrected. Diimine **1a** and complexes **5h** and **5i** were prepared following procedures described in the literature.[27]

Syntheses of amines

***N*-(2-((9*H*-Fluoren-9-ylidene)amino)phenyl)-9-isopropyl-9*H*-fluoren-9-amine (2e).** A solution of *i*-PrBr (0.598 g, 4.86 mmol) in Et_2O (5 mL) was added dropwise to a suspension of Mg (0.118 g, 4.86 mmol) in Et_2O (5 mL), at a rate to maintain a steady reflux (about 30 min). The suspension was maintained at reflux for 3 h and then allowed to reach room temperature. The *i*-PrMgBr solution ($C \approx 0.48$ M, 6 mL, 2.90 mmol) was added dropwise at 0 °C to a stirred solution of diimine **1** (1.05 g, 2.43 mmol) in CH_2Cl_2 (10 mL). The dark solution was heated at refluxed for 4 h and then allowed to reach room temperature. Water was slowly added (40 mL) 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, 10 : 90) to afford **2e** as a red solid (0.845 g, 73%). ^1H NMR ($CDCl_3$, 300 MHz), δ 8.11 (1H, d, ^3J = 7.4 Hz, ArH), 7.74 (2H, d, ^3J = 7.5 Hz, ArH), 7.67 (2H, d, ^3J = 7.5 Hz, ArH), 7.53 (1H, dd, ^3J = 7.5 Hz, ^4J = 1.2 Hz, ArH), 7.47–7.32 (4H, m, ArH), 7.31–7.24 (2H, m, ArH), 7.22–7.10 (3H, m, ArH), 7.01 (1H, dd, ^3J = 7.6 Hz, ^4J = 1.0 Hz, ArH), 6.82–6.76 (1H, m, ArH), 6.53–6.44 (2H, m, ArH), 5.54–5.47 (1H, m, ArH), 5.08 (1H, s, NH), 2.37–2.20 (1H, m, CH), 0.67 (6H, d, ^3J = 6.7 Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 163.9 (C=N), 147.6 (2 overlapped arom. Cq), 143.8 (arom. Cq), 141.9 (arom. Cq), 140.8 (2 overlapped arom. Cq), 138.1 (arom. Cq), 137.8 (arom. Cq), 136.9 (arom. Cq), 132.1 (arom. CH), 131.9 (arom. CH), 131.5 (arom. Cq), 128.6 (arom. CH), 128.0 (3 overlapped arom. CH), 127.3 (2 overlapped arom. CH), 127.1 (arom. CH), 125.9 (arom. CH), 124.2 (2 overlapped arom. CH), 123.3 (arom. CH), 120.3 (arom. CH), 119.9 (2 overlapped arom. CH), 119.8 (arom. CH), 118.1 (arom. CH), 116.8 (arom. CH), 113.4 (arom. CH), 71.4 (Cq), 65.5 (Cq), 39.1 (CH), 17.7 (CH_3). Found C, 87.85; H, 6.02; N, 6.12. Calc. for $C_{35}H_{28}N_2$ (M_r = 476.62): C, 88.20; H, 5.92; N, 5.88%.

***N*-(9-Ethyl-9*H*-fluoren-9-yl)-*N*′-(9-methyl-9*H*-fluoren-9-yl)-benzene-1,2-diamine (3a).** A solution of ethyl bromide (1.04 g, 9.72 mmol) in pentane (10 mL) was added to a suspension of lithium powder (25 wt% in mineral oil 0.551 g, 19.7 mmol) in pentane (9 mL) at a rate to maintain a steady reflux

(about 1 h). The suspension was maintained at reflux for 3 h and then allowed to reach room temperature. The EtLi solution ($C \approx 0.5$ M) was used without further purification. To a stirred solution of diimine **1** (1.06 g, 2.45 mmol) in THF (10 mL) cooled to −78 °C, was added dropwise MeLi (1.6 M in Et_2O, 1.8 mL, 2.88 mmol). The dark solution obtained was allowed to reach room temperature and was stirred for 1 h. The mixture was then cooled to −78 °C and the EtLi solution previously prepared (10 mL, 5 mmol), was added dropwise. The mixture was allowed to reach room temperature and was stirred 1 h. Water was slowly added (30 mL) and the product was extracted with AcOEt (3 × 30 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 **3a** as a pale red solid (0.962 g, 82%); mp 164 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.77–7.72 (4H, m, ArH), 7.41–7.34 (8H, m, ArH), 7.30–7.24 (4H, m, ArH), 6.11–6.08 (2H, m, ArH), 5.68–5.65 (1H, m, ArH), 5.63–5.60 (1H, m, ArH), 4.39 (2H, br s, NH), 2.20 (2H, q, ^3J = 7.4 Hz, CH_2), 1.76 (3H, s, CH_3), 0.57 (3H, t, ^3J = 7.4 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 149.9 (arom. Cq), 148.26 (arom. Cq), 140.12 (arom. Cq), 139.1 (arom. Cq), 136.3 (arom. Cq), 135.3 (arom. Cq), 128.1 (arom. CH), 128.0 (arom. CH), 127.7 (arom. CH), 127.6 (arom. CH), 123.4 (arom. CH), 123.2 (arom. CH), 120.3 (arom. CH), 120.1 (arom. CH), 119.3 (arom. CH), 117.7 (arom. CH), 116.8 (arom. CH), 68.8 (Cq), 65.4 (Cq), 36.4 (CH_2) 30.4 (CH_3), 8.31 (CH_2CH_3). Found C, 87.52; H, 6.46; N, 5.96. Calc. for $C_{35}H_{30}N_2$ (M_r = 478.63): C, 87.83; H, 6.32; N, 5.85%.

***N*-(9-Propyl-9*H*-fluoren-9-yl)-*N*′-(9-methyl-9*H*-fluoren-9-yl)-benzene-1,2-diamine (3b).** A solution of *n*-propyl bromide (0.950 g, 7.72 mmol) in pentane (10 mL) was added to a suspension of lithium powder (25 wt% in mineral oil 0.514 g, 18.3 mmol) in pentane (9 mL) at a rate to maintain a steady reflux (about 1 h). The suspension was maintained at reflux for 3 h and then allowed to reach room temperature. The *n*-PrLi solution ($C \approx 0.4$ M) was used without further purification. To a stirred solution of diimine **1** (0.950 g, 2.20 mmol) in THF (10 mL) cooled to −78 °C, was added dropwise MeLi (1.6 M in Et_2O, 1.7 mL, 2.72 mmol). The dark solution obtained was allowed to reach room temperature and was stirred for 1 h. The mixture was then cooled to −78 °C and the *n*-PrLi solution previously prepared (11 mL, 4.40 mmol), was added dropwise. Water was slowly added (30 mL) and the product was extracted with AcOEt (3 × 30 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 **3b** as a pale red solid (0.864 g, 80%); mp 148 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.67–7.61 (4H, m, ArH), 7.45–7.34 (8H, m, ArH), 7.34–7.24 (4H, m, ArH), 6.14–6.11 (2H, m, ArH), 5.71–5.69 (1H, m, ArH), 5.65–5.62 (1H, m, ArH), 4.42 (2H, br s, NH), 2.18–2.13 (2H, m, $CqCH_2$), 1.79 (3H, s, CH_3), 0.99–0.89 (2H, m, CH_2CH_3), 0.82 (3H, t, ^3J = 7.3 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 150.0 (arom. Cq), 148.7 (arom. Cq), 140.1 (arom. Cq), 139.1 (arom. Cq), 136.2 (arom. Cq), 135.5 (arom. Cq), 128.1 (arom. CH), 128.1 (arom. CH), 127.8 (arom. CH), 127.7 (arom. CH), 123.5 (arom. CH), 123.2 (arom. CH), 120.4 (arom. CH), 120.2 (arom. CH), 120.1 (arom. CH), 117.4 (arom. CH), 117.6 (arom. CH), 116.9 (arom. CH), 68.7 (Cq), 65.5 (Cq), 45.9 ($CqCH_2$) 30.6 (CH_3), 17.1 (CH_2CH_3), 14.3 (CH_2CH_3). Found C, 87.62; H, 6.66; N, 5.51. Calc. for $C_{36}H_{32}N_2$ (M_r = 492.67): C, 87.77; H, 6.55; N, 5.69%.

***N*-(9-Butyl-9*H*-fluoren-9-yl)-*N*′-(9-methyl-9*H*-fluoren-9-yl)-benzene-1,2-diamine (3c).** To a stirred solution of diimine **1** (1.04 g, 2.40 mmol) in THF (8 mL) cooled to −78 °C, was added dropwise MeLi (1.6 M in Et_2O, 1.7 mL, 2.72 mmol). The dark solution obtained was allowed to reach room temperature and was stirred for 1 h. The mixture was then cooled to −78 °C and *n*-BuLi, (1.6 M in hexanes, 2 mL, 3.20 mmol) was added dropwise. The mixture was allowed to reach room temperature and was stirred 1 h. Water was slowly added (30 mL) and the product was extracted with AcOEt (3 × 30 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 **3c** as a pale red solid (0.947 g, 78%); mp 90 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.78–7.74 (4H, m, ArH), 7.42–7.34 (8H, m, ArH), 7.31–7.24 (4H, m, ArH), 6.14–6.09 (2H, m, ArH), 5.72–5.69 (1H, m, ArH), 5.63–5.60 (1H, m, ArH), 4.39 (2H, br s, NH), 2.18–2.11 (2H, m, $CqCH_2$), 1.78 (3H, s, CH_3), 1.22 (2H, tq, ^3J = $^3J'$ = 7.5 Hz, CH_2CH_3), 0.95–0.86 (2H, m, $CqCH_2CH_2$), 0.80 (3H, t, ^3J = 7.5 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 150.0 (arom. Cq), 148.7 (arom. Cq), 140.0 (arom. Cq), 139.1 (arom. Cq), 136.3 (arom. Cq), 135.4 (arom. Cq), 128.1 (arom. CH), 128.0 (arom. CH), 127.8 (arom. CH), 127.6 (arom. CH), 123.5 (arom. CH), 123.2 (arom. CH), 120.4 (arom. CH), 120.2 (arom. CH), 120.1 (arom. CH), 119.3 (arom. CH), 117.7 (arom. CH), 116.9 (arom. CH), 68.6 (Cq), 65.5 (Cq), 43.4 ($CqCH_2$), 30.5 (CH_3), 25.9 ($CqCH_2CH_2$), 23.0 (CH_2CH_3), 14.1 (CH_2CH_3). Found C, 87.30; H, 6.83; N, 5.68. Calc. for $C_{37}H_{34}N_2$ (M_r = 506.69): C, 87.71; H, 6.76; N, 5.53%.

***N*-(9-Benzyl-9*H*-fluoren-9-yl)-*N*′-(9-methyl-9*H*-fluoren-9-yl)-benzene (3d).** *n*-BuLi (1.6 M in hexanes, 3.80 mL, 6.10 mmol) was added dropwise at −78 °C to a suspension of toluene (0.645 mL, 6.10 mmol) and *t*-BuOK (0.685 g, 6.10 mmol) in THF (5 mL). The red solution was allowed to reach room temperature and was stirred 1 h. The benzyl lithium solution obtained ($C \approx 0.7$ M) was used without further purification. To a stirred solution of diimine **1** (1.30 g, 3.00 mmol) in THF (12 mL) cooled to −78 °C, was added dropwise MeLi (1.6 M in Et_2O, 2.0 mL, 3.20 mmol). The dark solution obtained was allowed to reach room temperature and was stirred for 1 h. The mixture was then cooled to −78 °C and the benzyl lithium solution previously prepared (9 mL, 6.10 mmol), was added dropwise. The mixture was allowed to reach room temperature and stirred 1 h. Water was slowly added (30 mL) and the product was extracted with AcOEt (3 × 30 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 **3d** as a pale orange solid (1.36 g, 84%);

mp 110 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.80 (2H, d, ^3J = 7.5 Hz, ArH), 7.73 (2H, d, ^3J = 7.5 Hz ArH), 7.44–7.20 (15H, m, ArH), 7.05 (2H, dd, ^3J = 7.6 Hz, ^4J = 1.8 Hz, ArH), 6.05–6.01 (2H, m, ArH), 5.65–5.62 (1H, m, ArH), 5.48–5.45 (1H, m, ArH), 4.92–4.11 (2H, overlapped br s, NH), 3.30 (2H, s, $CH_2C_6H_5$), 1.86 (3H, s, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 150.0 (arom. Cq), 148.2 (arom. Cq), 139.6 (arom. Cq), 139.2 (arom. Cq), 136.1 (arom. Cq), 135.7 (arom. Cq), 135.2 (arom. Cq), 131.2 (arom. CH), 128.2 (arom. CH), 128.1 (arom. CH), 128.0 (arom. CH), 127.9 (arom. CH), 127.2 (arom. CH), 127.1 (arom. CH), 124.3 (arom. CH), 123.0 (arom. CH), 120.4 (arom. CH), 120.3 (arom. CH), 119.8 (arom. CH), 119.1 (arom. CH), 116.7 (arom. CH), 115.8 (arom. CH), 68.5 (Cq), 65.3 (Cq), 45.9 ($CH_2C_6H_5$) 31.1 (CH_3). Found C, 88.46; H, 5.99; N, 4.99. Calc. for $C_{40}H_{32}N_2$ (M_r = 540.71): C, 88.85; H, 5.97; N, 5.18%.

***N*-(9-Isopropyl-9*H*-fluoren-9-yl)-*N*′-(9-methyl-9*H*-fluoren-9-yl)-benzene-1,2-diamine (3e).** To a stirred solution of amine **2e** (0.829 g, 1.54 mmol) in THF (10 mL) cooled to −78 °C, was added MeLi (1.6 M in Et_2O, 2.1 mL, 3.40 mmol). The dark solution obtained was allowed to reach room temperature and was stirred for 1 h. Water was slowly added (30 mL) and the product was extracted with AcOEt (3 × 30 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 **3e** as a pale brown solid (0.777 g, 90%); mp 80 °C. ^{1}HNMR ($CDCl_3$, 300 MHz), δ 7.76 (2H, d, ^3J = 7.4 Hz, ArH), 7.73 (2H, d, ^3J = 7.4 Hz, ArH), 7.41–7.21 (12H, m, ArH), 6.08–6.06 (2H, m, ArH), 5.74–5.72 (1H, m, ArH), 5.51–5.48 (1H, m, ArH), 4.72 (1H, br s, NH), 4.20 (1H, br s, NH), 2.44 (1H, hept, ^3J = 6.8 Hz, $CH(CH_3)_2$), 1.78 (3H, s, CH_3), 0.84 (6H, d, ^3J = 6.8 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 150.0 (arom. Cq), 147.6 (arom. Cq), 140.8 (arom. Cq), 139.2 (arom. Cq), 137.1 (arom. Cq), 134.8 (arom. Cq), 128.1 (arom. CH), 128.0 (arom. CH), 127.8 (arom. CH), 127.3 (arom. CH), 124.0 (arom. CH), 123.2 (arom. CH), 120.6 (arom. CH), 120.4 (arom. CH), 119.9 (arom. CH), 118.7 (arom. CH), 118.2 (arom. CH), 115.7 (arom. CH), 71.4 (Cq), 65.5 (Cq), 39.7 ($CH(CH_3)_2$), 30.4 (CH_3), 17.7 ($CH(CH_3)_2$). Found C, 87.72; H, 6.65; N, 6.00. Calc. for $C_{36}H_{32}N_2$ (M_r = 492.67): C, 87.77; H, 6.55; N, 5.69%.

***N*-(9-Methyl-9*H*-fluoren-9-yl)-*N*′-(9-methylsulfinylmethyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (3f).** A solution of *n*-BuLi (1.6 M in hexanes, 4.6 mL, 7.40 mmol) was added dropwise at −78 °C to a solution of dimethylsulfoxide (DMSO, 526 μL, 0.578 g, 7.40 mmol) in THF (10 mL). The white suspension was allowed to reach room temperature and was stirred 1 h. The dimsyl lithium (LiDMSO) suspension ($C \approx 0.5$ M) was used without further purification. To a stirred solution of diimine **1** (2.05 g, 4.73 mmol) in THF (10 mL) cooled to −78 °C, was added a solution of MeLi (1.6 M in Et_2O, 3.5 mL, 5.67 mmol). The dark solution obtained was allowed to reach room temperature and was stirred for 1 h. The mixture was then cooled to −78 °C and the LiDMSO solution previously prepared (15 mL, 7.40 mmol), was then added dropwise. The mixture was allowed to reach room temperature and was stirred 1 h. Water was slowly added (30 mL) and the product was extracted with AcOEt (3 × 30 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, 70 : 30) to afford **3f** as a pale red solid (1.99 g, 80%); mp 185 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.87–7.78 (5H, m, ArH), 7.67–7.59 (3H, m, ArH), 7.54–7.29 (8H, m, ArH), 5.99 (1H, ddd, ^3J = $^3J'$ = 7.6 Hz, ^4J = 1.3 Hz, ArH), 5.90 (1H, ddd, ^3J = $^3J'$ = 7.6 Hz, ^4J = 1.3 Hz, ArH), 5.59 (1H, br s, NH), 5.40 (2H, d, ^3J = 7.6 Hz, ArH), 5.23 (1H, br s, NH), 3.76 (1H, d, ^2J = 13.5 Hz, CH_2SCH_3), 2.66 (1H, d, ^2J = 13.5 Hz, CH_2SCH_3), 2.63 (3H, s, CH_2SCH_3), 1.95 (3H, s, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 150.32 (arom. Cq), 150.19 (arom. Cq), 148.17 (arom. Cq), 146.03 (arom. Cq), 139.46 (arom. Cq), 139.14 (arom. Cq), 138.89 (arom. Cq), 138.49 (arom. Cq), 135.69 (arom. Cq), 132.71 (arom. Cq), 129.07 (2 overlapped arom. CH), 128.40 (arom. CH), 127.92 (arom. CH), 127.85 (arom. CH), 127.81 (3 arom. CH), 125.03 (arom. CH), 123.29 (arom. CH), 123.17 (arom. CH), 122.82 (arom. CH), 120.80 (arom. CH), 120.69 (arom. CH), 120.33 (arom. CH), 120.29 (arom. CH), 119.40 (arom. CH), 117.40 (arom. CH), 114.51 (arom. CH), 113.37 (arom. CH), 68.11 (Cq), 66.84 (CH_2SCH_3), 65.06 (Cq), 39.67 (CH_2SCH_3), 31.51 (CH_3). Found C, 79.57; H, 5.92; N, 5.11. Calc. for $C_{35}H_{30}N_2OS$ (M_r = 526.70): C, 79.82; H, 5.74; N, 5.32%.

***N*-(9-Methyl-9*H*-fluoren-9-yl)-*N*′-(9-methylthiomethyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (3g).** $NaBH_4$ (0.224 g, 5.92 mmol) was added under vigorous stirring at 0 °C to a solution of diamine **3f** (1.29 g, 2.45 mmol) and I_2 (1.50 g, 5.90 mmol) in THF (40 mL). Gas emission was observed. The reaction mixture was allowed to reach room temperature and was stirred 1 h. A 10% aqueous sodium hydroxide solution was slowly added (80 mL) and the product was extracted with AcOEt (3 × 60 mL). The combined organic layers were washed with a 10% aqueous sodium thiosulfate solution (2 × 80 mL), water (80 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt–petroleum ether, 10 : 90) to afford **3g** as a white solid (0.988 g, 79%); mp 84 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.83 (4H, d, ^3J = 7.5 Hz, ArH), 7.61 (2H, d, ^3J = 7.5 Hz, ArH), 7.54 (2H, d, ^3J = 7.3 Hz, ArH), 7.49–7.40 (4H, m, ArH), 7.40–7.30 (4H, m, ArH), 6.19–6.05 (2H, m, ArH), 5.17–5.60 (2H, m, ArH), 5.29–4.30 (2H, overlapped br s, NH), 3.21 (2H, s, CH_2SCH_3), 2.21 (3H, s, CH_2SCH_3), 1.88 (3H, s, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 149.9 (arom. Cq), 147.8 (arom. Cq), 139.6 (arom. Cq), 139.1 (arom. Cq), 135.9 (arom. Cq), 135.2 (arom. Cq), 128.6 (arom. CH), 128.1 (arom. CH), 127.8 (arom. CH), 127.6 (arom. CH), 124.0 (arom. CH), 123.1 (arom. CH), 120.4 (arom. CH), 120.3 (arom. CH), 119.8 (arom. CH), 119.4 (arom. CH), 116.6 (arom. CH), 116.4 (arom. CH), 68.0 (Cq), 65.3(Cq), 49.6 (CH_2SCH_3), 30.8 (CH_2SCH_3), 18.4 (CH_3). Found C, 82.60; H, 5.82; N, 5.23. Calc. for $C_{35}H_{30}N_2S$ (M_r = 510.70): C, 82.32; H, 5.92; N, 5.49%.

Syntheses of benzimidazolium salts

1-(9-Ethyl-9*H*-fluoren-9-yl)-3-(9-methyl-9*H*-fluoren-9-yl)-1*H*-benzimidazolium chloride (4a). Diamine **3a** (0.512 g,

1.07 mmol) was dissolved under magnetic stirring in HC(OEt)$_3$. HCl (12 M, 116 μL, 1.39 mmol) was added, and the mixture was heated at 80 °C for 15 h. The mixture was then 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 **4a** (0.507 g, 90%) was obtained as a hygroscopic white solid; mp 192 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 11.16 (1H, s, NCHN), 7.86–7.78 (8H, m, ArH), 7.51–7.43 (4H, m, ArH), 7.38–7.29 (4H, m, ArH), 6.78–6.72 (2H, m, ArH), 6.26–6.16 (2H, m, ArH), 3.70 (2H, q, ^3J = 7.0 Hz, CH_2CH$_3$), 2.91 (3H, s, CH$_3$), 0.51 (3H, t, ^3J = 7.0 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 145.1 (arom. Cq), 143.1 (arom. Cq), 142.4 (NCHN), 140.4 (arom. Cq), 139.0 (arom. Cq), 131.1 (arom. Cq), 130.7 (arom. Cq), 130.2 (2 overlapped arom. CH), 129.4 (2 overlapped arom. CH), 126.1 (2 overlapped arom. CH), 125.0 (arom. CH), 124.9 (arom. CH), 120.8 (arom. CH), 120.5 (arom. CH), 114.9 (arom. CH), 114.7 (arom. CH), 75.3 (Cq), 71.4 (Cq), 31.4 (*C*H$_2$CH$_3$), 27.3 (CH$_3$), 7.4 (CH$_2$*C*H$_3$). Found C, 80.30; H, 5.70; N, 5.34. Calc. for $C_{36}H_{29}ClN_2$·0.6H$_2$O (M_r = 525.09 + 10.81): C, 80.69; H, 5.68; N, 5.23%.

1-(9-Methyl-9*H*-fluoren-9-yl)-3-(9-propyl-9*H*-fluoren-9-yl)-1*H*-benzimidazolium chloride (4b). Diamine **3b** (0.271 g, 0.550 mmol) was dissolved under magnetic stirring in HC(OEt)$_3$ (2 mL) and then HCl 12 M (58 μL, 0.70 mmol) was added. The mixture was heated at 80 °C for 15 h. The mixture was then 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 **4b** (0.274 g, 93%) was obtained as a hygroscopic white solid; mp 192 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 11.15 (1H, s, NCHN), 7.87–7.81 (8H, m, ArH), 7.48 (4H, t, ^3J = 7.5 Hz, ArH), 7.38–7.31 (4H, m, ArH), 6.79–6.73 (2H, m, ArH), 6.24–6.19 (2H, m, ArH), 3.67–3.62 (2H, m, CqCH$_2$), 2.93 (3H, s, CH$_3$), 0.91 (3H, t, ^3J = 7.5 Hz, CH$_2$CH_3), 0.85–0.75 (2H, m, CH_2CH$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 145.1 (arom. Cq), 143.6 (arom. Cq), 142.3 (NCHN), 140.3 (arom. Cq), 139.0 (arom. Cq), 131.0 (arom. Cq), 130.8 (arom. Cq), 130.3 (2 overlapped arom. CH), 129.5 (arom. CH), 129.4 (arom. CH), 126.2 (arom. CH), 126.2 (arom. CH), 125.0 (arom. CH), 124.9 (arom. CH), 120.8 (arom. CH), 120.5 (arom. CH), 115.0 (arom. CH), 114.7 (arom. CH), 74.8 (Cq), 71.4 (Cq), 39.9 (Cq*C*H$_2$) 27.3 (CH$_3$), 16.5 (*C*H$_2$CH$_3$), 13.9 (CH$_2$*C*H$_3$). Found C, 79.73; H, 5.90; N, 4.80. Calc. for $C_{37}H_{31}ClN_2$·0.9H$_2$O (M_r = 539.12 + 16.21): C, 80.03; H, 5.95; N, 5.04%.

1-(9-Butyl-9*H*-fluoren-9-yl)-3-(9-methyl-9*H*-fluoren-9-yl)-1*H*-benzimidazolium chloride (4c). Diamine **3c** (0.902 g, 1.78 mmol) was dissolved under magnetic stirring in HC(OEt)$_3$ (8 mL) and then HCl 12 M (195 μL, 2.34 mmol) was added. The mixture was heated at 80 °C for 15 h. The mixture was then cooled to room temperature and petroleum ether was added (*ca.* 20 mL). The precipitate was collected by filtration and washed with petroleum ether (3 × 25 mL). Compound **4c** (0.865 g, 88%) was obtained as a hygroscopic white solid; mp 163 °C.

^{1}H NMR ($CDCl_3$, 300 MHz), δ 11.15 (1H, s, NCHN), 7.89–7.82 (8H, m, ArH), 7.52–7.41 (4H, m, ArH), 7.38–7.30 (4H, m, ArH), 6.80–6.73 (2H, m, ArH), 6.25–6.19 (2H, m, ArH), 3.71–3.66 (2H, m, CqCH$_2$), 2.94 (3H, s, CH$_3$), 1.38 (2H, tq, ^3J = $^3J'$ = 7.5 Hz, CH_2CH$_3$), 0.79–0.67 (5H, m, overlapped signals, CqCH$_2$CH_2 and CH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 145.1 (arom. Cq), 143.5 (arom. Cq), 142.2 (NCHN), 140.3 (arom. Cq), 139.0 (arom. Cq), 131.0 (arom. Cq), 130.8 (arom. Cq), 130.2 (2 overlapped arom. CH), 129.4 (arom. CH), 129.4 (arom. CH), 126.2 (arom. CH), 126.2 (arom. CH), 125.0 (arom. CH), 124.9 (arom. CH), 120.8 (arom. CH), 120.5 (arom. CH), 115.0 (arom. CH), 114.7 (arom. CH), 74.8 (Cq), 71.4 (Cq), 37.7 (Cq*C*H$_2$), 27.3 (CH$_3$), 25.2 (CqCH$_2$*C*H$_2$), 22.5 (CH_2CH$_3$), 14.2 (CH$_2$*C*H$_3$). Found C, 80.80; H, 6.03; N, 5.10. Calc. for $C_{38}H_{33}ClN_2$·0.5H$_2$O (M_r = 553.15 + 9.01): C, 81.19; H, 6.10; N, 4.98%.

1-(9-Benzyl-9*H*-fluoren-9-yl)-3-(9-methyl-9*H*-fluoren-9-yl)-1*H*-benzimidazolium chloride (4d). Diamine **3d** (0.612 g, 1.13 mmol) was dissolved under magnetic stirring in HC(OEt)$_3$ (4 mL) and then HCl 12 M (122 μL, 1.47 mmol) was added. The mixture was heated at 120 °C for 15 h. After cooling 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 **4d** (0.510 g, 77%) was obtained as a hygroscopic white solid; mp 209 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz), δ 10.70 (1H, s, NCHN), 8.12 (4H, dd, ^3J = $^3J'$ = 8.8 Hz, ArH), 7.99 (2H, d, ^3J = 7.4 Hz, ArH), 7.72 (2H, d, ^3J = 7.2 Hz, ArH), 7.56 (2H, dd, ^3J = $^3J'$ = 7.4 Hz, ArH), 7.46–7.35 (6H, m, ArH), 7.00–6.80 (5H, m, ArH), 6.45 (2H, d, ^3J = 7.4 Hz, ArH), 6.14–6.05 (2H, m, ArH), 4.88 (2H, CH_2(C$_6$H$_5$), 2.70 (3H, s, CH$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 145.2 (arom. Cq), 143.6 (NCHN), 142.6 (arom. Cq), 140.0 (arom. Cq), 138.6 (arom. Cq), 132.5 (arom. Cq), 130.3 (arom. CH), 130.2 (arom. CH), 130.1 (arom. CH), 130.0 (arom. Cq), 129.8 (arom. Cq), 129.0 (arom. CH), 128.4 (arom. CH), 127.1 (arom. CH), 126.6 (arom. CH), 126.3 (arom. CH), 126.2 (arom. CH), 125.3 (arom. CH), 124.6 (arom. CH), 121.5 (arom. CH), 120.8 (arom. CH), 114.2 (arom. CH), 113.9 (arom. CH), 73.9 (Cq), 70.3 (Cq), 42.4 (*C*H$_2$(C$_6$H$_5$)), 26.2 (CH$_3$). Found C, 79.72; H, 5.50; N, 4.20. Calc. for $C_{41}H_{31}ClN_2$·1.7H$_2$O (M_r = 587.16 + 30.63): C, 79.71; H, 5.61; N, 4.53%.

1-(9-Methyl-9*H*-fluoren-9-yl)-3-(9-iso-propyl-9*H*-fluoren-9-yl)-1*H*-benzimidazolium chloride (4e). Diamine **3e** (0.455 g, 0.92 mmol) was dissolved under magnetic stirring in HC(OEt)$_3$ (3 mL) and then HCl 12 M (110 μL, 1.32 mmol) was added. 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 and washed with petroleum ether (3 × 15 mL). Compound **4e** (0.391 g, 79%) was obtained as a hygroscopic white solid; mp 175 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 11.67 (1H, s, NCHN), 7.90 (2H, d, ^3J = 7.5 Hz, ArH), 7.82 (4H, dd, ^3J = $^3J'$ = 7.3 Hz, ArH), 7.77 (2H, d, ^3J = 7.5 Hz, ArH), 7.49 (4H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 7.34 (4H, dd, ^3J = $^3J'$ = 7.3 Hz, ArH), 6.79–6.71 (2H, m, ArH), 6.19–6.13 (1H, m, ArH), 5.99–5.93 (1H, m, ArH), 4.88 (1H, hept, ^3J = 6.5 Hz, C*H*(CH$_3$)$_2$), 2.97 (3H, s, CH$_3$), 1.05 (6H, d, ^3J = 6.5 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 145.0 (arom. Cq), 144.2 (NCHN), 142.8 (arom. Cq),

140.6 (arom. Cq), 139.1 (arom. Cq), 131.4 (arom. Cq), 130.7 (arom. Cq), 130.4 (arom. CH), 130.3 (arom. CH), 129.4 (arom. CH), 129.0 (arom. CH), 126.2 (arom. CH), 126.2 (arom. CH), 126.1 (arom. CH), 124.7 (arom. CH), 120.9 (arom. CH), 120.5 (arom. CH), 115.4 (arom. CH), 114.8 (arom. CH), 78.8 (Cq), 71.7 (Cq), 33.7 ($CH(CH_3)_2$) 27.8 (CH_3), 17.9 ($CH(CH_3)_2$). Found C, 79.46; H, 6.15; N, 4.77. Calc. for $C_{37}H_{31}ClN_2 \cdot 1.2H_2O$ (M_r = 539.12 + 21.62): C, 79.25; H, 6.00; N, 5.00%.

1-(9-Methyl-9*H*-fluoren-9-yl)-3-(9-methylthiomethyl-9*H*-fluoren-9-yl)-1*H*-benzimidazolium chloride (4g). Diamine **3g** (0.292 g, 0.57 mmol) was dissolved under magnetic stirring in $HC(OEt)_3$ (2 mL) and then HCl 12 M (65 μL, 0.78 mmol) was added. 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 and washed with petroleum ether (3 × 15 mL). Compound **4g** (0.235 g, 73%) was obtained as a hygroscopic white solid; mp 178 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 11.61 (1H, s, NCHN), 8.03 (2H, d, ^3J = 7.7 Hz, ArH), 7.84 (6H, d, ^3J = 7.7 Hz, ArH), 7.55–7.46 (4H, m, ArH), 7.39–7.31 (4H, m, ArH), 6.80–6.76 (2H, m, ArH), 6.21–6.17 (1H, m, ArH), 6.10–6.06 (1H, m, ArH), 4.74 (2H, s, CH_2SCH_3), 2.94 (3H, s, CH_2SCH_3), 2.31 (3H, s, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 145.0 (arom. Cq), 144.4 (NCHN), 143.2 (arom. Cq), 139.9 (arom. Cq), 139.0 (arom. Cq), 130.8 (arom. Cq), 130.6 (arom. CH), 130.5 (arom. Cq), 130.3 (arom. CH), 129.4 (arom. CH), 129.1 (arom. CH), 126.2 (arom. CH), 126.1 (2 overlapped arom. CH), 124.9 (arom. CH), 120.8 (arom. CH), 120.7 (arom. CH), 114.8 (arom. CH), 114.7 (arom. CH), 73.7 (Cq), 71.3 (Cq), 42.6 (CH_2SCH_3), 27.2 (CH_2SCH_3), 17.4 (CH_3). Found C, 77.86; H, 5.30; N, 4.78. Calc. for $C_{36}H_{29}ClN_2S$ (M_r = 557.15): C, 77.61; H, 5.25; N, 5.03%.

Palladium complexes

***trans*-[1-(9-Ethyl-9*H*-fluoren-9-yl)-3-(9-methyl-9*H*-fluoren-9-yl)-1*H*-benzimidazol-2-ylidene](pyridine)palladium(II) dichloride (5a).** A suspension of benzimidazolium salt **4a** (0.310 g, 0.59 mmol), finely crushed K_2CO_3 (0.407 g, 2.95 mmol), and $PdCl_2$ (0.126 g, 0.71 mmol) in pyridine (2 mL) was heated at 80 °C for 15 h under vigorous stirring. The mixture was cooled to room temperature, 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 **5a** as a yellow solid (0.373 g, 85%); mp > 240 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 9.17–9.12 (2H, m, *o*-NC_5H_5), 7.89–7.73 (9H, m, 8H ArH and 1H *p*-NC_5H_5), 7.48–7.37 (6H, m, 4H ArH and 2H *m*-NC_5H_5), 7.35–7.26 (4H, m, ArH), 6.41–6.35 (2H, m, ArH), 6.22–6.17 (1H, m, ArH), 6.11–6.05 (1H, m, ArH), 5.45 (2H, q, ^3J = 7.1 Hz, CH_2CH_3), 4.06 (3H, s, CH_3), 0.46 (3H, t, ^3J = 7.1 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 161.0 (NCN), 151.7 (arom. CH), 149.3 (arom. Cq), 146.3 (arom. Cq), 140.3 (arom. Cq), 138.3 (arom. Cq), 138.2 (arom. CH), 134.6 (arom. Cq), 134.2 (arom. Cq), 129.2 (arom. CH), 129.1 (arom. CH), 129.0 (arom. CH), 124.9 (arom. CH), 124.8 (arom. CH), 124.7 (arom. CH), 122.5 (arom. CH), 120.7 (arom. CH), 120.0 (arom. CH), 113.4 (arom. CH), 113.1 (arom. CH), 76.7 (Cq), 72.3 (Cq), 36.7 (CH_2CH_3) 33.9 (CH_3), 6.7 (CH_2CH_3). Found C, 65.91; H, 4.80; N, 5.51. Calc. for $C_{41}H_{33}Cl_2N_3Pd$ (M_r = 745.06): C, 66.10; H, 4.46; N, 5.64%.

***trans*-[1-(9-Methyl-9*H*-fluoren-9-yl)-3-(9-propyl-9*H*-fluoren-9-yl)-1*H*-benzimidazol-2-ylidene](pyridine)palladium(II) dichloride (5b).** A suspension of benzimidazolium salt **4b** (0.307 g, 0.57 mmol), finely crushed K_2CO_3 (0.407 g, 2.95 mmol), and $PdCl_2$ (0.120 g, 0.67 mmol) in pyridine (2 mL) was heated at 80 °C for 15 h under vigorous stirring. The mixture was cooled to room temperature, 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 **5b** as a yellow solid (0.412 g, 95%); mp > 240 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 9.19–9.14 (2H, m, *o*-NC_5H_5), 7.88–7.76 (9H, m, 8H ArH and 1H *p*-NC_5H_5), 7.48–7.37 (6H, m, 4H ArH and 2H *m*-NC_5H_5), 7.35–7.27 (4H, m, ArH), 6.41–6.35 (2H, m, ArH), 6.21–6.14 (1H, m, ArH), 6.11–6.05 (1H, m, ArH), 5.47–5.41 (2H, m, $CqCH_2$), 4.07 (3H, s, CH_3), 0.95 (3H, t, ^3J = 7.1 Hz, CH_2CH_3), 0.76–0.50 (2H, m, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 161.1 (NCN), 151.8 (arom. CH), 149.3 (arom. Cq), 146.9 (arom. Cq), 140.1 (arom. Cq), 138.3 (arom. Cq), 138.2 (arom. CH), 134.5 (arom. Cq), 134.3 (arom. Cq), 129.1 (arom. CH), 129.0 (arom. CH), 124.8 (arom. CH), 124.7 (arom. CH), 124.6 (arom. CH), 122.4 (arom. CH), 120.7 (arom. CH), 120.0 (arom. CH), 113.4 (arom. CH), 113.1 (arom. CH), 75.9 (Cq), 72.3 (Cq), 46.0 ($CqCH_2$) 33.9 (CH_3), 17.5 (CH_2CH_3), 14.5 (CH_2CH_3). Found C, 66.17; H, 4.86; N, 5.17. Calc. for $C_{42}H_{35}Cl_2N_3Pd$ (M_r = 759.08): C, 66.46; H, 4.65; N, 5.54%.

***trans*-[1-(9-Butyl-9*H*-fluoren-9-yl)-3-(9-methyl-9*H*-fluoren-9-yl)-1*H*-benzimidazol-2-ylidene](pyridine)palladium(II) dichloride (5c).** A suspension of benzimidazolium salt **4c** (0.498 g, 0.90 mmol), finely crushed K_2CO_3 (0.622 g, 4.50 mmol), and $PdCl_2$ (0.191 g, 1.08 mmol) in pyridine (2 mL) was heated at 80 °C for 15 h under vigorous stirring. The mixture was cooled to room temperature, 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 **5c** as a yellow solid (0.330 g, 47%); mp > 240 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 9.19–9.14 (2H, m, *o*-NC_5H_5), 7.87–7.70 (9H, m, 8H ArH and 1H *p*-NC_5H_5), 7.46–7.36 (6H, m, 4H ArH and 2H *m*-NC_5H_5), 7.33–7.24 (4H, m, ArH), 6.39–6.33 (2H, m, ArH), 6.18–6.12 (1H, m, ArH), 6.09–6.03 (1H, m, ArH), 5.45–5.39 (2H, m, $CqCH_2$), 4.04 (3H, s, CH_3), 1.37 (2H, tq, ^3J = $^3J'$ = 7.4 Hz, CH_2CH_3), 0.71 (3H, t, ^3J = 7.4 Hz, CH_2CH_3), 0.64–0.51 (2H, m, $CqCH_2CH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 161.0 (NCN), 151.8 (arom. CH), 149.4 (arom. Cq), 146.9 (arom. Cq), 140.2 (arom. Cq), 138.3 (arom. Cq), 138.2 (arom. CH), 134.6 (arom. Cq), 134.3 (arom. Cq), 129.1 (arom. CH), 129.0 (arom. CH), 128.6 (arom. CH), 124.8 (arom. CH), 124.7 (arom. CH), 122.4 (arom. CH), 120.7 (arom. CH), 120.1 (arom. CH), 113.4 (arom. CH), 113.1 (arom. CH), 75.9 (Cq), 72.3 (Cq), 43.6 ($CqCH_2$) 34.0 (CH_3), 26.1

(CqCH$_2$*C*H$_2$), 23.0 (*C*H$_2$CH$_3$), 15.1 (CH$_2$*C*H$_3$). Found C, 65.51; H, 4.93; N, 5.42. Calc. for $C_{43}H_{37}Cl_2N_3Pd$ (M_r = 773.11): C, 66.80; H, 4.82; N, 5.44%.

***trans*-[1-(9-Benzyl-9*H*-fluoren-9-yl)-3-(9-methyl-9*H*-fluoren-9-yl)-1*H*-benzimidazol-2-ylidene](pyridine)palladium(II) dichloride (5d).** A suspension of benzimidazolium salt **4d** (0.211 g, 0.39 mmol), finely crushed K_2CO_3 (0.282 g, 2.04 mmol), and $PdCl_2$ (0.085 g, 0.48 mmol) in pyridine (2 mL) was heated at 80 °C for 15 h under vigorous stirring. The mixture was cooled to room temperature, 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 **5d** as a yellow solid (0.205 g, 65%); mp > 212 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 9.11–9.05 (2H, m, *o*-NC_5H_5), 7.97–7.93 (2H, m, ArH), 7.87 (4H, d, ^3J = 7.9 Hz, ArH), 7.73 (1H, m, 8H, *p*-NC_5H_5), 7.51–7.26 (12H, m, 10H ArH and 2H *m*-NC_5H_5), 6.94 (1H, t, ^3J = 7.5 Hz, ArH), 6.80 (2H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 6.73 (2H, s, C*H*$_2$C$_6$H$_5$), 6.43–6.33 (4H, m, ArH), 6.14–6.09 (2H, m, ArH), 4.09 (3H, s, CH$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 161.5 (NCN), 151.6 (arom. CH), 149.3 (arom. Cq), 146.2 (arom. Cq), 140.1 (arom. Cq), 138.4 (arom. Cq), 138.1 (arom. CH), 134.6 (arom. Cq), 134.5 (arom. Cq), 134.3 (arom. Cq), 131.1 (arom. CH), 129.2 (arom. CH), 129.1 (arom. CH), 129.0 (2 overlapped arom. CH), 128.5 (arom. CH), 126.6 (arom. CH), 125.9 (arom. CH), 125.3 (arom. CH), 125.0 (arom. CH), 124.7 (arom. CH), 122.5 (arom. CH), 120.7 (arom. CH), 120.0 (arom. CH), 113.7 (arom. CH), 113.2 (arom. CH), 76.0 (Cq), 72.4 (Cq), 49.9 (*C*H$_2$C$_6$H$_5$), 34.0 (CH$_3$). Found C, 68.33; H, 4.59; N, 4.89. Calc. for $C_{46}H_{35}Cl_2N_3Pd$ (M_r = 807.13): C, 68.45; H, 4.37; N, 5.21%.

***trans*-[1-(9-Methyl-9*H*-fluoren-9-yl)-3-(9-iso-propyl-9*H*-fluoren-9-yl)-1*H*-benzimidazol-2-ylidene](pyridine)palladium(II) dichloride (5e).** A suspension of benzimidazolium salt **4e** (0.518 g, 0.96 mmol), finely crushed K_2CO_3 (0.656 g, 4.75 mmol), and $PdCl_2$ (0.199 g, 1.12 mmol) in pyridine (3 mL) was heated at 80 °C for 15 h under vigorous stirring. The mixture was cooled to room temperature, 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 **5e** as a yellow solid (0.539 g, 74%); mp > 203 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 9.14–9.09 (2H, m, *o*-NC_5H_5), 7.86–7.76 (9H, m, 8H ArH and 1H *p*-NC_5H_5), 7.46–7.38 (6H, m, 4H ArH and 2H *m*-NC_5H_5), 7.32–7.22 (4H, m, ArH), 7.00 (1H, hept, ^3J = 6.6 Hz, C*H*(CH$_3$)$_2$), 6.39–6.23 (2H, m, ArH), 6.11–6.05 (1H, m, ArH), 5.86–5.80 (1H, m, ArH), 4.13 (3H, s, CH$_3$), 1.32 (6H, d, ^3J = 7.1 Hz, C*H*(CH$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 161.7 (NCN), 151.7 (arom. CH), 149.7 (arom. Cq), 146.1 (arom. Cq), 140.2 (arom. Cq), 138.2 (overlapped arom. CH and arom. Cq), 135.8 (arom. Cq), 134.6 (arom. Cq), 129.1 (2 overlapped arom. CH), 128.9 (arom. CH), 128.0 (arom. CH), 126.4 (arom. CH), 125.0 (arom. CH), 124.7 (arom. CH), 122.5 (arom. CH), 122.3 (arom. CH), 120.7 (arom. CH), 120.0 (arom. CH), 113.9 (arom. CH), 113.3 (arom. CH), 82.1 (Cq), 73.1 (Cq), 34.2 (*C*H(CH$_3$)$_2$) 33.7 (CH$_3$), 22.4 (CH(*C*H$_3$)$_2$). Found C, 66.13; H, 4.85; N, 5.17. Calc. for $C_{42}H_{35}Cl_2N_3Pd$ (M_r = 759.02): C, 66.46; H, 4.65; N, 5.54%.

Palladium complex 5g

A suspension of benzimidazolium salt **4g** (0.234 g, 0.42 mmol, finely crushed K_2CO_3 (0.291 g, 2.10 mmol), and $PdCl_2$ (0.089 g, 0.50 mmol) in pyridine (3 mL) was heated at 80 °C for 15 h under vigorous stirring. The mixture was cooled to room temperature, 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–MeOH ether, 92 : 8) to afford **5g** as a yellow solid (0.260 g, 93%); mp > 240 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.90 (2H, d, ^3J = 7.5 Hz, ArH), 7.78 (2H, d, ^3J = 7.5 Hz, ArH), 7.72 (2H, d, ^3J = 7.5 Hz, ArH), 7.60–7.52 (4H, m, ArH), 7.45–7.24 (6H, m, ArH), 6.65–6.42 (2H, m, ArH), 5.96–5.90 (1H, m, ArH), 5.77–5.71 (1H, m, ArH), 3.70 (2H, s, CH$_2$Pd), 3.33 (2H, br s, C*H*$_2$SCH$_3$), 2.70 (3H, s, CH$_2$SC*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 176.5 (NCN), 147.3 (arom. CH), 144.2 (arom. Cq), 139.2 (arom. Cq), 138.9 (arom. Cq), 132.0 (arom. Cq), 131.7 (arom. Cq), 130.6 (arom. CH), 129.1 (arom. Cq), 128.7 (arom. CH), 128.5 (arom. CH), 124.8 (arom. CH), 123.8 (2 overlapped arom. CH), 123.2 (arom. CH), 121.3 (arom. CH), 120.4 (arom. CH), 113.4 (arom. CH), 111.3 (arom. CH), 77.3 (Cq), 72.1 (Cq), 47.4 (CH$_2$Pd) 38.8 (*C*H$_2$SCH$_3$), 19.4 (CH$_2$S*C*H$_3$). Found C, 65.61; H, 4.32; N, 4.51. Calc. for $C_{36}H_{27}ClN_2PdS$ (M_r = 661.56): C, 65.36; H, 4.11; N, 4.23%.

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 Cs_2CO_3 (0.652 g, 2 mmol) was suspended in dioxane (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 ^{1}H 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.

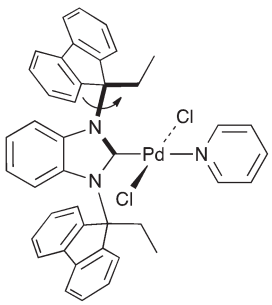
X-ray crystallography

Crystal data for complex 5d. Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a dichloromethane solution of the complex: $C_{98}H_{75}Cl_9N_6Pd_2$, M = 1868.49, monoclinic, space group $P2_1/c$, a = 20.5938(5), b = 18.5018(4), c = 24.0322(7) Å, β = 103.048(3), V = 8920.4(4) Å^3, Z = 4, μ = 0.723 mm^{-1}, F(000) = 3800. Crystals of the compound were mounted on a Oxford Diffraction CCD Saphire 3 Xcalibur diffractometer. Data collection with Mo-Kα radiation

(λ = 0.71073 Å) was carried out at 150 K. 67 669 reflections were collected (2.60 < θ< 27.00°), 19 447 were found to be unique and 9064 were observed (merging R = 0.0689). The structure was solved with SHELXS-97.[43] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.1384, 0.0673, 0.2091, 0.1883, 0.717. Residual electron density minimum/maximum = −1.070/2.021 e Å^{-3}.

Computational details

Calculations were performed using the ADF 2013 package.[44] All electrons Slater type orbital were used with all-electron triple-ζ quality basis sets at DFT level with PBE functional.[45,46] Dispersive interactions were taken into account through Grimme corrections.[47] Scalar relativistic effects were included through ZORA Hamiltonian.[48] Full geometry optimization was performed on the complex. Then the barrier was computed through the calculation of the relaxed potential energy surface. The C–C–N–C dihedral angle (below in bold) was varied from 0° to 180°.



Crystal data for complex 5g. Crystals suitable for X-ray diffraction were obtained by slow diffusion of ether into a dichloromethane solution of the complex: $C_{36}H_{27}ClN_2PdS$, M = 661.51, orthorhombic, space group *Pbca*, a = 14.5752(3), b = 19.1704(4), c = 22.6020(5) Å, β = 90.00, V = 6315.3(2) Å^3, Z = 8, μ = 0.765 mm^{-1}, F(000) = 2688. Crystals of the compound were mounted on a Oxford Diffraction CCD Saphire 3 Xcalibur diffractometer. Data collection with Mo-Kα radiation (λ = 0.71073 Å) was carried out at 100 K. 84 941 reflections were collected (2.70 < θ< 27.00°), 6894 were found to be unique and 4643 were observed (merging R = 0.0799). The structure was solved with SHELXS-97.[43] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.0703, 0.0365, 0.1002, 0.0916, 0.866. Residual electron density minimum/maximum = −0.271/1.737 e Å^{-3}.

CCDC 970760 (for **5d**) and 862359 (for **5g**) contain the supplementary crystallographic data for this paper.

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