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FULL PAPER

The Suzuki-Miyaura cross coupling as the key step for the synthesis of 2-aminobiphenyls and 2,2'-diaminobiphenyls: applications for the synthesis of Schiff base complexes of zinc.

Knut Tormodssønn Hylland,*[a] Sigurd Øien-Ødegaard,[a] and Mats Tilset*[a]

Abstract: 2-nitrophenylboronic acids serve as interesting starting materials for the construction of biphenyl- and terphenyl-based amines, if subjected to the Suzuki-Miyaura reaction. Unfortunately, these boronic acids suffer from low reactivity in Suzuki reactions, alongside their low stability in the presence of Pd. Herein, a general method for the construction of 2-nitro substituted bi- and terphenyls is presented, with special emphasis on the synthesis of 2-amino-2'-nitrobi- and terphenyls. Comparisons are made with other boronic acids that have some of the aforementioned issues. Finally, the application of the obtained 2-amino-2'-nitrobi- and terphenyls as starting materials for the synthesis of bi- and terphenyl based di- and triamines is encountered for, with emphasis on the use of these amines as precursors for Schiff base ligands. In addition, the synthesis of some Zn complexes of these ligands is presented.

Introduction

The Suzuki-Miyaura cross coupling reaction utilizing boronic acids that quickly decompose under the reaction condition has been a challenge within the field for several years.[1] Polyfluorinated and heteroaromatic boronic acids have been given special focus.[2] Fewer studies have been conducted on the Suzuki-Miyaura reaction with 2-nitro-substituted arylboronic acids, which readily degrades in the presence of Pd and bases, especially at elevated temperatures.[3] 2-Nitro-substituted biphenyls are readily reduced to the corresponding amines (**I**, Figure 1). If the 2'-substituent is either another nitro group or an amino group, the 2,2'-diaminobiphenyl motif (**II**, Figure 1) is available through reduction. This motif serves as a direct precursor for ligands for metals,[4] organocatalysts,[5] and heterocycles.[6] In addition, amino-substituted bi- and terphenyl dicarboxylic acids may serve as possible ligands in Metal Organic Frameworks (MOFs), introducing functionality in these materials.[7] While symmetrically substituted 2,2'-dinitrobiphenyls (and hence 2,2'-diaminobiphenyls through reduction) are obtainable through the classical Ullmann coupling[8] and electrophilic aromatic nitration,[9] unsymmetrically substituted motifs are more difficult to obtain by these methods. Waldvogel and co-workers reported an electrochemical approach for the synthesis of unsymmetrical 2,2'-diaminobiphenyls *via* oxidative coupling of *N*-protected anilines.[10] Recently, the synthesis of unsymmetrical 2,2'-diaminobiphenyls, utilizing Rh-catalyzed C-H activation, was reported.[11] Methods utilizing the benzidine rearrangement have also been reported.[12] Apart from the aforementioned applications, 2,2'-diaminobiphenyls represent an interesting class of precursors for Schiff base complexes, *e.g.* of Zn (**III** and **IV**, Figure 1), as the amino groups are positioned in such a manner that a salen-like chelate can be constructed. Schiff base complexes of Zn finds application within catalysis,[13] supramolecular chemistry,[14] chemical sensing[15] and as precursors for the synthesis of other Schiff base metal complexes.[16] These applications take advantage of the Lewis acidic character of Zn.[17]

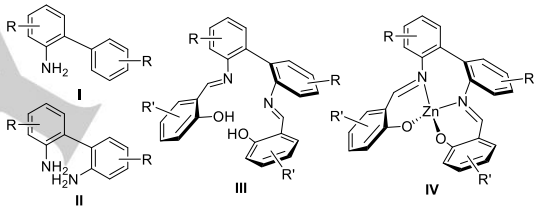

Figure 1. 2-aminobiphenyl **I**, 2,2'-diaminobiphenyl **II**, Schiff base ligand **III** and Zn complex **IV**.

The Suzuki-Miyaura reaction has over the last decades become a very important method for the construction of aryl-aryl bonds. [18] The reaction stands out for its general broad scope, as well as the large selection of commercially available starting materials. These factors have made the reaction heavily used in medicinal chemistry,[19] industrial processes[20] and material science,[21] amongst other fields. There exist a large number of literature for construction of 2-nitrobiphenyls through the Suzuki-Miyaura reaction, however the majority of this only cover the introduction of the 2-nitro substituent through the electrophilic coupling partner. We were interested in methods that utilize arylboronic acids with a 2-nitro substituent, and that could be applied in gram-scale, for serving as intermediate for the synthesis of Schiff base ligands and Zn complexes of these. Herein, we report a general method for the construction of various highly functionalized 2-nitrobiphenyls, -terphenyls and -quaterphenyls in gram-scale, with special focus on 2-amino-2'-nitrobi- and terphenyls.

Results and Discussion

The reaction between 4-methoxycarbonyl-2-nitrophenylboronic acid (1-B(OH)$_2$) and various aryl halides. Background, scope and limitations.

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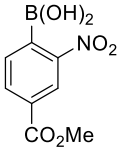
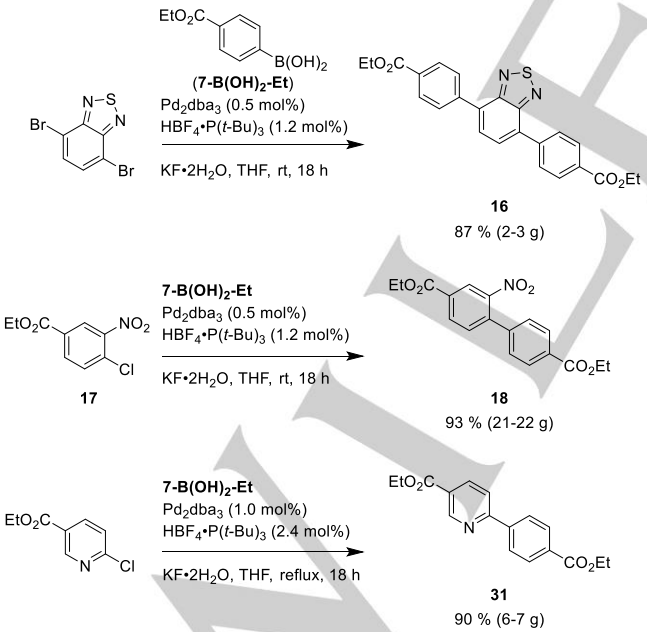
4-Methoxycarbonyl-2-nitrophenylboronic acid (**1-B(OH)$_2$**) (Figure 2) was an attractive starting point for the synthesis of 2-nitrobi- and terphenyls, as it is commercially available, and besides the nitro group, it also carries a methoxycarbonyl substituent. This open up for the synthesis of carboxylic acid-based ligands for various purposes, *e.g.* MOFs.



1-B(OH)$_2$

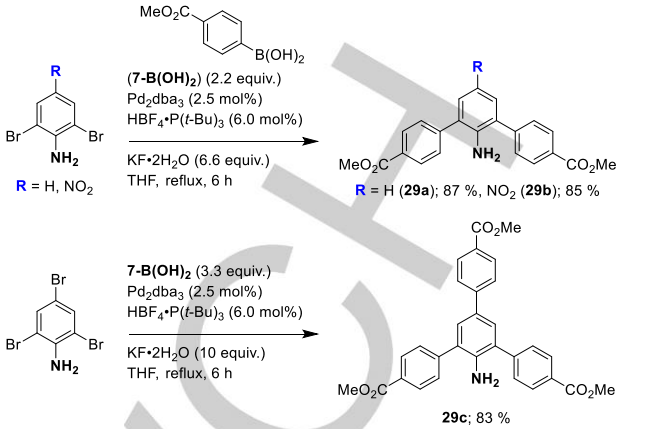
Figure 2. The *ortho*-NO_2 substituted arylboronic acid **1-B(OH)$_2$**.

The drawback of **1-B(OH)$_2$** is its low reactivity in the Suzuki-Miyaura reaction due to presence of the very electron-withdrawing nitro substituent.[22] This called for a highly efficient catalytic system. The method reported by Lou and Fu in 2010,[23] using a highly active *in situ* generated Pd/P(*t*-Bu)$_3$ catalyst from air stable Pd_2dba_3 and HBF_4·P(*t*-Bu)$_3$ [24] in the presence of KF·2H$_2$O in THF, had earlier proven to be a highly reliable and scalable method for performing Suzuki couplings for the synthesis of **31**[25] (Scheme 1). These reaction conditions could also be employed successfully for the synthesis of terphenyl **16** and biphenyl **18** (Scheme 1) which were both obtained in very good yields on a relatively large scale (2-22 g).



Scheme 1. Synthesis of biphenyls **16**, **17** and **31** using the protocol developed by Lou and Fu.[23]

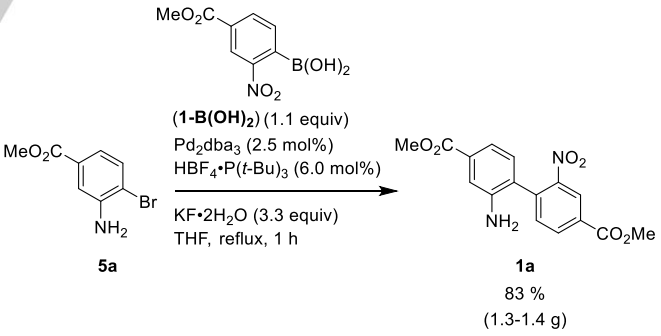
The method also proved useful for cross-coupling reactions utilizing bromoanilines (Scheme 2).



Scheme 2. Application of aniline derivatives in the cross-coupling reaction with 4-methoxycarbonylphenylboronic acid (**7-B(OH)$_2$**).

The protocol developed by Lou and Fu is especially attractive as it requires no air or moisture sensitive reagents, and by the deliberate introduction of water *via* KF·2H$_2$O, also circumvents some reproducibility issues, addressed by the same authors, associated with the original protocol employing anhydrous KF. [23] The use of HBF_4·P(*t*-Bu)$_3$ as an air stable source of P(*t*-Bu)$_3$, facilitates the employment of this phosphine ligand, which in combination with a suitable Pd precursor represents a highly active catalyst for Suzuki-Miyaura reactions[24] that may be needed for reactions with challenging arylboronic acids such as **1-B(OH)$_2$**.

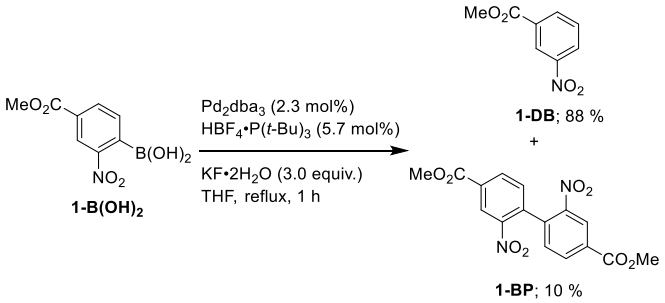
Hence, the reaction conditions were applied to the reaction between 2-bromoaniline **5a** and **1-B(OH)$_2$** for the synthesis of **1a** (Scheme 3). The reaction proceeded smoothly and gave biphenyl **1a** in good yields within one hour reaction time, and the reaction could be performed on a >1 g scale.



Scheme 3. Synthesis of 2-amino-2'-nitrobiphenyl **1a**.

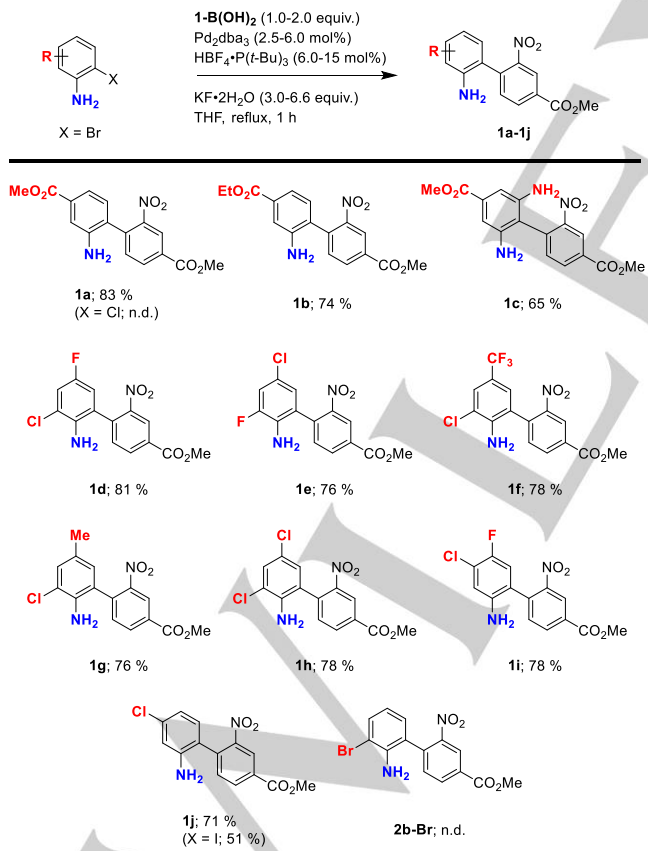
During the work, it was noticed that **1-B(OH)$_2$** could not be recovered after the reaction, even if a fairly large excess (1.5 equiv.) was employed. When subjected to the reaction conditions in the absence of an aryl halide, **1-B(OH)$_2$** was found to decompose to the parent arene **1-DB** and the homocoupling product **1-BP** (Scheme 4). Both decomposition pathways are well-known side reactions in the Suzuki-Miyaura reaction.[18, 22] It is not known *per se* whether the decomposition of **1-B(OH)$_2$** to **1-DB** is metal- or base-catalyzed (or both), but it has been

reported that metal-catalyzed protodeboronation is much faster than base-catalyzed protodeboronation.[26]

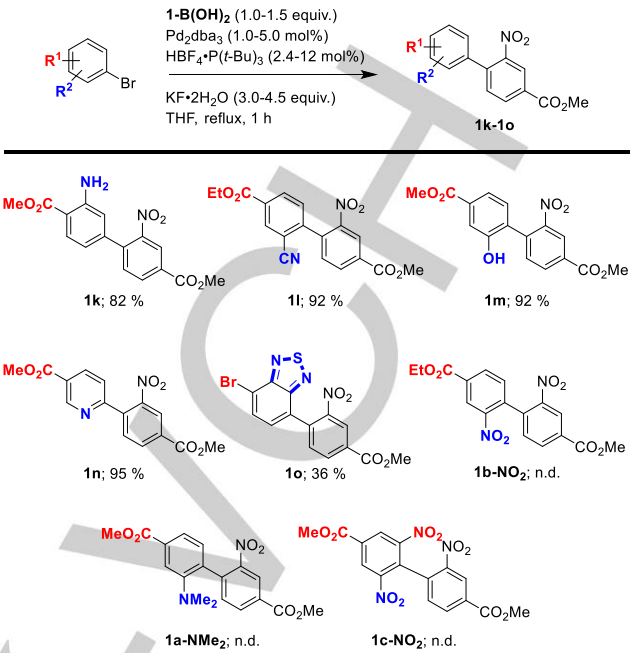


Scheme 4. Decomposition of **1-B(OH)₂** to **1-DB** and **1-BP**. Note that different ratios between **1-DB** and **1-BP** were encountered when an aryl halide was present, dependent on the exact conditions.

With the promising result for the synthesis of **1a**, the reaction was tested for a multitude of other aryl bromides, bearing functional groups in different positions relative to the bromide (Scheme 5 and Scheme 6). Both electron-donating (-NH_2, -OH) and electron-withdrawing (-CF_3, -CO_2Me, -F, -Cl, -CN and 2-pyridyl) functional groups were well tolerated, as well as combinations of these. The reactions proceeded with moderate to very good yields, and most of the products could be prepared in > 1 g-scale.



Scheme 5. Synthesis of 2-amino-2'-nitrobiphenyls **1a**—**1j**.



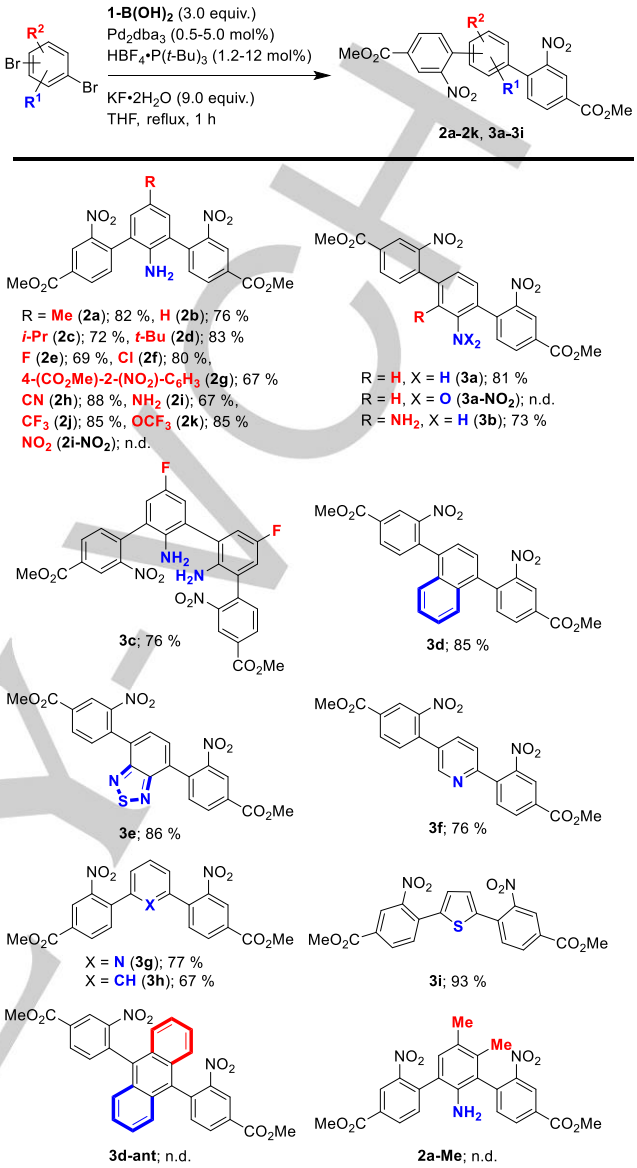
Scheme 6. Synthesis of 2-nitrobiphenyls **1k**—**1o**.

Interestingly, bromides carrying a nitro substituent failed to react under the reaction conditions, both for substrates where the nitro group was located *ortho* and *meta* to the leaving group (**1b-NO₂** and **1c-NO₂**, Scheme 6, and **2i-NO₂** and **3a-NO₂**, Scheme 7 (*vide infra*)). In the *ortho* positions, both the size and the electron withdrawing nature of the nitro group may interfere with the reaction, as well as potential coordination to Pd,[27] but in the *meta* position these factors should not be as important. However, Nakao and co-workers have shown that the nitro group is able to act as a leaving group in the Suzuki-Miyaura reaction,[28] clearly showing the non-innocence of this functional group. These observations show a striking difference with the general tolerance of the nitro group in the Pd-catalyzed Suzuki coupling[29] (*e.g.* the synthesis of **18**, Scheme 1 and **29b**, Scheme 2), and more specifically with the work of Bjørsvik and co-workers, which were able to synthesize 2,2'-dinitrobiphenyls from various nitro substituted aryl halides and different 2-nitrophenylboronic acids applying the microwave assisted Suzuki-Miyaura reaction.[30] In addition, **5a-NMe₂** failed to react with **1-B(OH)₂** under the conditions employed herein (**1a-NMe₂**, Scheme 6). Again, potential coordination to Pd might be the cause of the lack of reactivity,[31] but the failure might also be contributed to the added steric hindrance of **5a-NMe₂** compared with its primary analog **5a**. On the other hand, the electron rich bromide methyl 3,5-diamino-4-bromobenzoate (**6a**) with two NH_2 groups *ortho* to the leaving group, could successfully be employed as a substrate in the coupling reaction, giving biphenyl product **1c** in moderate to good yields (Scheme 5). This is to the best of the author's knowledge the first example of a Suzuki-Miyaura reaction yielding a tri-*ortho*-substituted biphenyl where two of these substituents are amines. Both 5-chloro-2-iodoaniline and 2-bromo-5-chloroaniline could be successfully employed as starting

materials for the synthesis of biphenyl **1j** (Scheme 5). Interestingly, the bromoaniline was found to be more reactive than the iodoaniline, which may be attributed to the inhibiting effect of KI (generated during the reaction), on Suzuki-Miyaura reactions in aqueous THF as previously reported by Milner and co-workers.[32] Whereas 2-bromo-5-chloroaniline reacted to give **1j** with full consumption of the starting material, a significant amount of starting material could be recovered when 5-chloro-2-iodoaniline was used, supporting the potential inhibiting effect of *in situ* generated KI.

Since the presence of a nitro group in the starting aryl bromide seemed to inhibit the reaction, one could assume that di- and tribromides would fail to yield nitro substituted ter- and quaterphenyls upon reaction with **1-B(OH)$_2$.** However, this was not the case and various di- and tribromides reacted in the presence of 2.2-4.5 equivalents of **1-B(OH)$_2$** to yield ter- and quaterphenyls in moderate to very good yields (Scheme 7). In fact, attempts to synthesize biphenyl **2b-Br** from 2,6-dibromoaniline and one equivalent of **1-B(OH)$_2$** failed (Scheme 5), and only the terphenyl product **2b** (Scheme 7) could be detected by ^{1}H NMR. On the contrary, biphenyl **1o** could be obtained in poor yields (36 %), alongside terphenyl **3e** and unreacted starting material, when 4,7-Dibromobenzo[c]-1,2,5-thiadiazole was reacted with one equivalent of **1-B(OH)$_2$** (Scheme 6). Higher selectivity towards the biphenyl product **1o** may be achievable by employing lower reaction temperatures, although this was not investigated. Full selectivity towards the terphenyl product **3e** was achieved by increasing the equivalents of **1-B(OH)$_2$** (Scheme 7).

Starting materials with potential Pd-chelating moieties[33] (**12** and **15**) (Figure 3) did not inhibit the reaction, and the products **3b** and **3c** were obtained in good yields (73 % and 76 % respectively).



Scheme 7. Synthesis of ter- and quaterphenyls **2a**—**2k** and **3a**—**3l**.

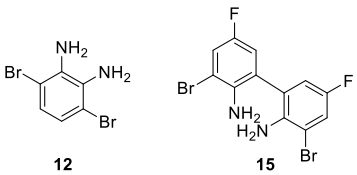
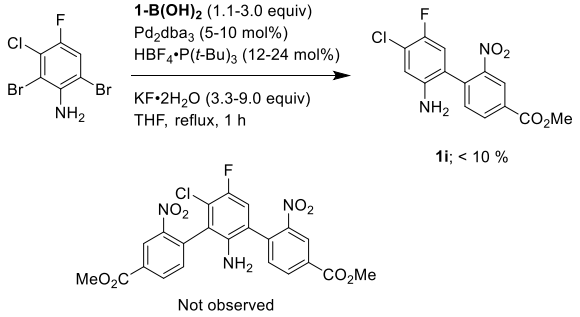


Figure 3. Substrates **12** and **15** containing potential Pd-chelating moieties.[33]

On the other hand, further problems with sterically hindered bromides were encountered. The very sterically hindered 9,10-dibromoanthracene failed to react under the conditions employed here (**3d-ant**, Scheme 7). More surprisingly was the lack of reactivity associated with dibromide 2,6-dibromo-3,4-dimethylaniline (**2a-Me**, Scheme 7). No selectivity for the less sterically hindered bromide was observed,

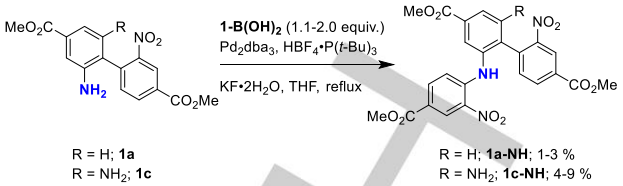
and only unreacted starting material could be recovered. The related 2,6-dibromo-3-chloro-4-fluoroaniline reacted in a different manner (Scheme 8).



Scheme 8. The attempted synthesis of an unsymmetrical dinitroterphenyl from 2,6-dibromo-3-chloro-4-fluoroanilne, leading only to the isolation of trace quantities of biphenyl **1i**.

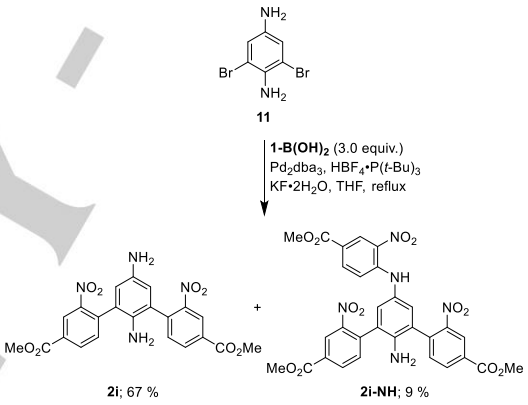
Most of the starting material could be recovered from the crude product, but small amounts of (impure) **1i** could be separated from the reaction mixture, as the only identifiable coupling product (Figure S113, ESI). The bromide with two *ortho*-substituents (one of them being electron withdrawing Cl) would seemingly undergo oxidative addition to the Pd catalyst faster than the other, less sterically hindered bromide.[34] Due to the steric bulk, coupling with **1-B(OH)$_2$** would be disfavored and hydrodehalogenation occurred instead. This reaction may be catalyzed by Pd as well,[35] in the presence of a suitable reducing agent, *e.g.* an aniline[36] or water.[37] The resulting monobromide would then undergo coupling and furnish **1i**. It may also be possible that the less sterically hindered bromide undergoes coupling with **1-B(OH)$_2$** first, but this seems less likely as only small amounts of **1i** was formed, and the major species in the crude product was unreacted 2,6-dibromo-3-chloro-4-fluoroaniline (Figure S112, ESI).

Although the reaction conditions proved to be fairly general and of a broad scope (with the exceptions already mentioned), it suffered from the relatively large excess of **1-B(OH)$_2$** needed in many cases, which created some issues in terms of purification. Since unreacted **1-B(OH)$_2$** was found to decompose during the course of reaction, purification became more cumbersome in some cases. Besides from forming deboronated species **1-DB** and biphenyl **1-BP** (Scheme 4), **1-B(OH)$_2$** would also react with some of the NH_2-containing products, to form small amounts of secondary amines. Amines are known to react with boronic acids in the Chan-Lam-Evans reaction, usually carried out with catalytic amounts of Cu(II) salts under oxidative conditions.[38] Trace amounts of oxygen or another oxidant together with Pd may also yield the same type of products, and the use of both Pd nanoparticles and $PdCl_2$ under aqueous conditions has been described as efficient catalysts for the reaction.[39] Small amounts of various *N*-arylated side products could be observed by ^{1}H NMR (and isolated and identified) as side products in the synthesis of **1a** and **1c** (Scheme 9).



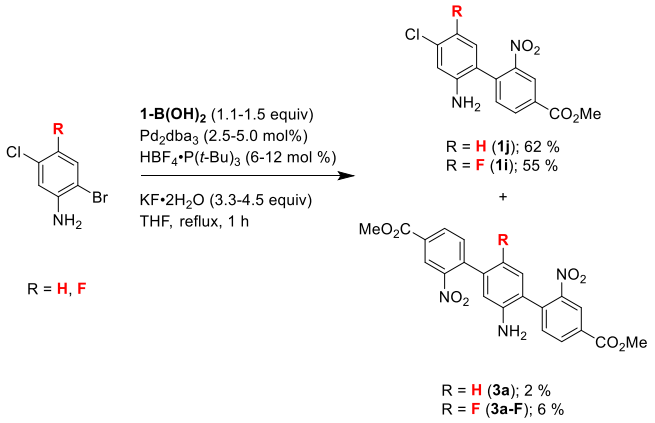
Scheme 9. Formation of side products **1a-NH** and **1c-NH** from the synthesis of **1a** and **1c**, respectively.

Interestingly, *N*-arylated side products could not be detected in cases where anilines with two *ortho*-substituents were employed. For diamine **11**, with one NH_2 group with two *ortho*-substituents and one NH_2 without any *ortho*-substituents, traces of one *N*-arylated side product could be detected from the reaction with **1-B(OH)$_2$** alongside terphenyl **2i** (Scheme 10). Although not structurally characterized, it seems reasonable that the less hindered NH_2 group undergo arylation, based on NMR and the observations made for other amines in this study.



Scheme 10. Formation of side products **2i-NH** from the synthesis of **2i**.

Aryl chlorides are generally more attractive halogenated substrates in the Suzuki-Miyaura reaction than the corresponding bromides (and iodides). However, employing chloroanilines rather than bromoanilines as substrates were mainly unsuccessful. When methyl 3-amino-4-chlorobenzoate was reacted with **1-B(OH)$_2$** under the conditions described herein, product **1a** could not be detected by ^{1}H NMR. Similar observations were made for chlorides **1d** and **1i** (*vide infra*). However, when 2-bromo-5-chloroaniline and 2-bromo-4-fluoro-5-chloroaniline each was reacted with an excess of **1-B(OH)$_2$**, small amounts of the corresponding terphenyls **3a** and **3a-F** could be isolated alongside the main products **1j** and **1i** as well as other side products (*vide infra*) (Scheme 11).



Scheme 11. Synthesis of biphenyls **1j** and **1i**. Using 1.1-1.5 equiv. of **1-B(OH)$_2$** lead to formation of small quantities of terphenyls **3a** and **3a-F** alongside the desired biphenyls.

The reactivity of chloroanilines 1d, 1e, 1g and 1i towards different arylboronic acids.

As the reaction between **1-B(OH)$_2$** and chloroanilines did not take place except for the cases mentioned above, the focus was turned to other boronic acids with some of the same issues as **1-B(OH)$_2$** in terms of stability, steric hindrance and low reactivity in the Suzuki-Miyaura reaction (Figure 4).

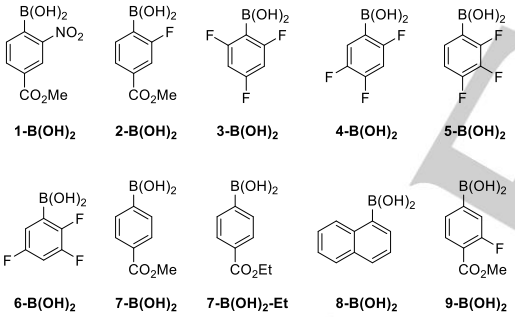
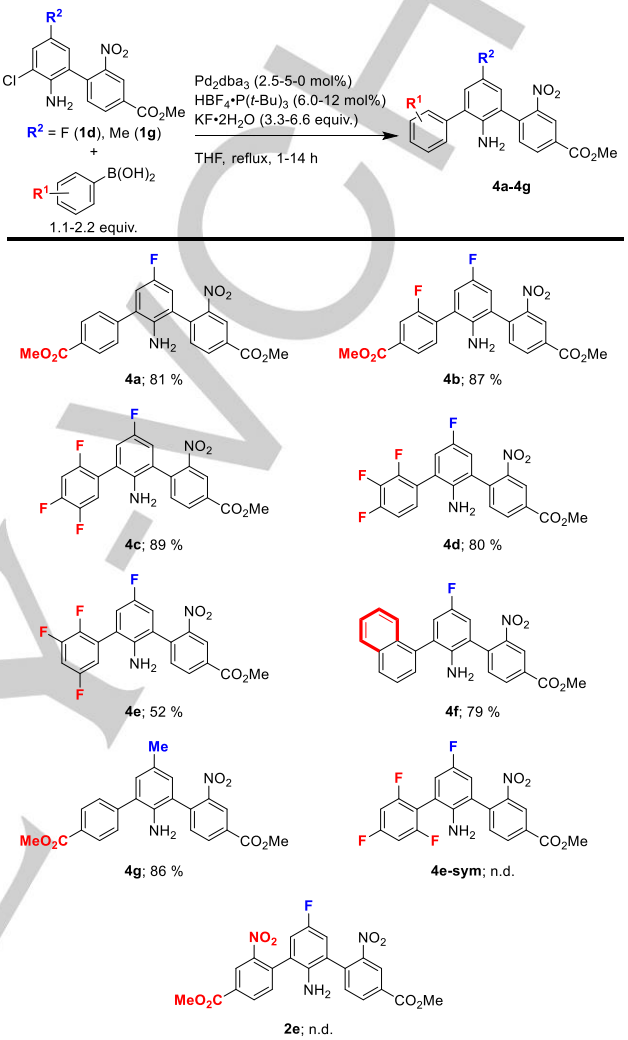


Figure 4. Various aromatic boronic acids studied herein.

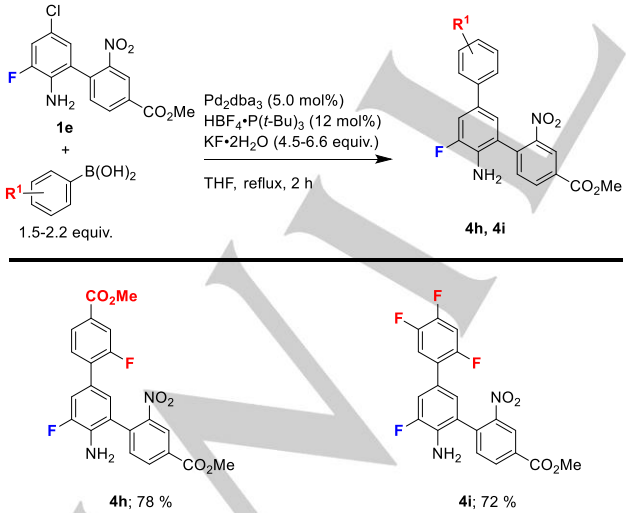
Many studies have been carried out on polyfluorinated arylboronic acids[1d, 40] and their sensitivity to the reaction conditions often encountered in Suzuki-Miyaura reactions. Although many of them are highly unstable towards aqueous base, especially those with fluorine substituent(s) *ortho* to the B(OH)$_2$ group,[2d] they are reported to undergo transmetalation more rapidly than *e.g.* phenylboronic acid.[1d] It was of interest to investigate the behaviour of the chloroanilines **1d**, **1e** and **1i** towards some of these highly fluorinated arylboronic acids (Figure 4), to get a perspective on the lack of reactivity of **1-B(OH)$_2$** with chloroanilines. As these fluorophenylboronic acids reacts relatively readily in Suzuki reactions, and impose little steric effect, it was also of interest to investigate the behaviour of **1d** and **1g** towards **7-B(OH)$_2$** and **8-B(OH)$_2$** (Figure 4). **7-B(OH)$_2$** is electron poor, but is anticipated to be much more stable to the reaction conditions than **1-B(OH)$_2$**. To evaluate the effect of steric hindrance, chloride **1d** was also reacted with **8-B(OH)$_2$**. The results are summarized in Scheme 12, Scheme 13 and Scheme 14.



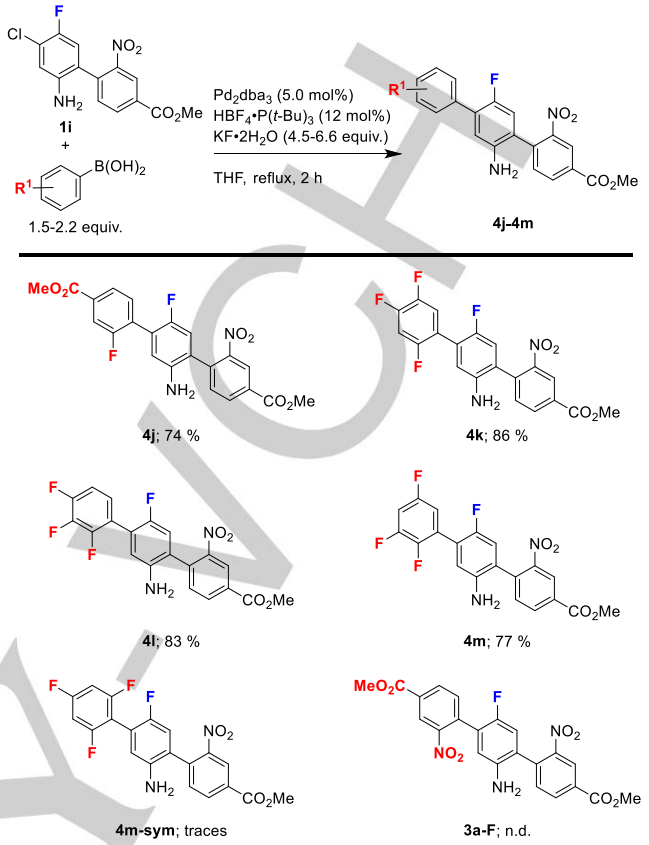
Scheme 12. Reactivity of chlorides **1d** and **1g** to the arylboronic acids depicted in Figure 4.

The reaction between **1c** and **7-B(OH)$_2$**, and the reaction between slightly more electron rich **1g** and **7-B(OH)$_2$**, gave terphenyls **4a** and **4g** in good yields (Scheme 12). The reaction between **1d** and **2-B(OH)$_2$** proceeded with full consumption of starting material within two hours, yielding **4b** (Scheme 12). The successful synthesis of **4b** illustrates the retarding effect of the relatively large NO$_2$ group in **1-B(OH)$_2$** compared to the accelerating effect of the small F substituent. Whether this is strictly an electronic phenomenon or a combination of steric and electronic factors are not known *per se*, but the fact that **1d** and **8-B(OH)$_2$** reacted readily to give **4f** (Scheme 12) should rule out that there are strictly steric reasons for the lack of reactivity of **1d** towards **1-B(OH)$_2$**. **1d** reacted with the three isomeric trifluorophenylboronic acids **4-B(OH)$_2$**, **5-B(OH)$_2$** and **6-B(OH)$_2$** to give the corresponding tetrafluoroterphenyl products **4c**, **4d** and **4e** in moderate to very good yields (Scheme 12). Rather large

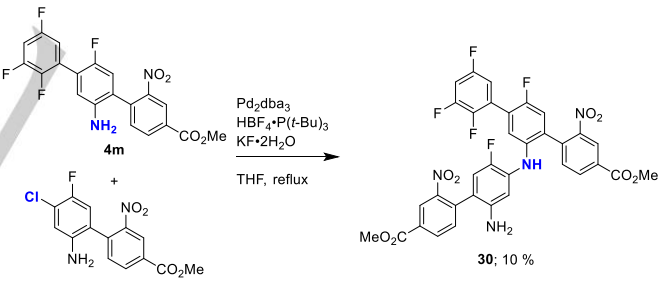
differences between the three trifluorophenylboronic acids with respect to reactivity were found. **1d** and **4-B(OH)$_2$** reacted readily to give terphenyl **4c** in high yields (89-92 %). The reaction of **1d** with **5-B(OH)$_2$** or **6-B(OH)$_2$** was less straightforward. Terphenyl **4d** was mostly obtained in good yields (77-82 %), but occasionally significantly lower yields were encountered (59-63 %; see ESI). Terphenyl **4e** could only be isolated in moderate yields. The low yields obtained for **4e** and occasionally for **4d** were caused by incomplete conversion of **1d**, and **1d** could only be removed efficiently with moderate recovery of the corresponding product. The results obtained for the reactions of **1d** with the three aforementioned boronic acids, closely correlate with the reported half-lives of these three boronic acids under similar conditions (pH 12, aqueous dioxane, 70 °C) as those reported here, where $t_{1/2}$(**4-B(OH)$_2$**) = 1 h > $t_{1/2}$(**5-B(OH)$_2$**) = 39 min > $t_{1/2}$(**6-B(OH)$_2$**) = 10 min.[2c] Unsurprisingly the reaction between **1d** and **3-B(OH)$_2$** failed to yield any detectable product **4e-sym** (Scheme 12). Lloyd-Jones and co-workers estimated the half-life of **3-B(OH)$_2$** to be 1 sec under the conditions mentioned above.[2c] The same group also estimated the half-life of 2-nitrophenylboronic acid to be < 5 min under these reaction conditions.[41] The reactivity of **1e** towards **2-B(OH)$_2$** and **4-B(OH)$_2$** was investigated. For both these boronic acids, **1e** gave lower yields of terphenyl products (**4h** and **4i**, Scheme 13) compared to **1d**. On the other hand, **1i** was found to more reactive than **1d**, which can be explained by the different position of the Cl substituent relative to the NH_2 group for the two chloroanilines (**4j**—**4m**, Scheme 14). Biphenyl **1i** reacted readily with **2-B(OH)$_2$**, **4-B(OH)$_2$** and **5-B(OH)$_2$** (**4j**, **4k** and **4l,** Scheme ***14***) whereas the reaction with **6-B(OH)$_2$** was less straightforward. The terphenyl product **4m** could only be obtained in highly variating yields (42-72 %) as the synthesis was hampered by side product formation (Figure S218, ESI). The low stability of boronic acid **6-B(OH)$_2$** caused a significant amount of **1i** to be left unreacted allowing it to further react with the product of the reaction, terphenyl **4m**, yielding the secondary amine **30** (Scheme 15).



Scheme 13. Reactivity of chloride **1e** to arylboronic acids **2-B(OH)$_2$** and **4-B(OH)$_2$** (Figure 4).



Scheme 14. Reactivity of chloride **1i** to the boronic acids depicted in Figure 4.

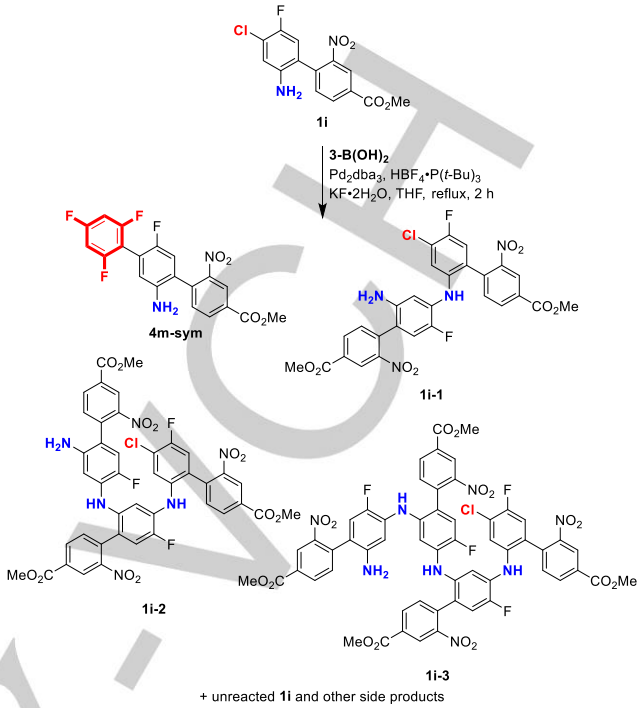


Scheme 15. Formation of side product **30** during the synthesis of terphenyl **4m**.

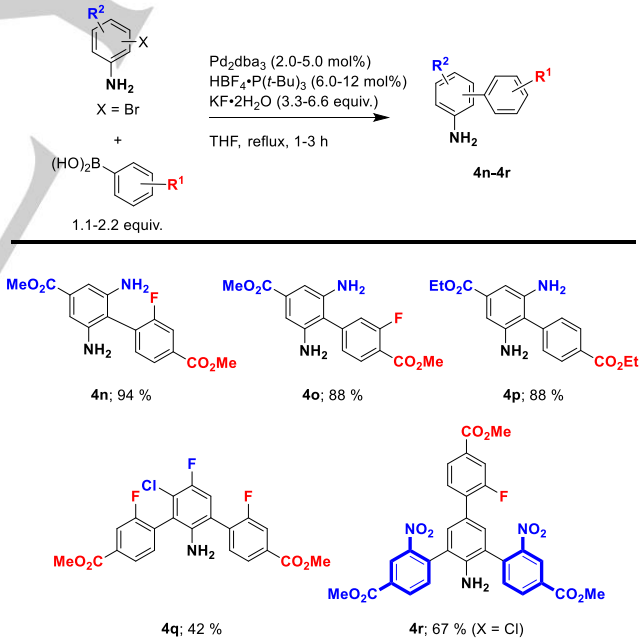
The side product is assumed to be generated through a Buchwald-Hartwig amination. The result is interesting as Buchwald-Hartwig aminations in general requires anhydrous conditions, although there exists reports of carrying out these reactions in the presence of water.[36, 42] Furthermore, fluoride bases are not among the typically used bases in the Buchwald-Hartwig reaction,[36] although Lee and co-workers observed exclusive *N*-arylation under Suzuki-Miyaura reaction conditions using KF as the base, for the reaction between the pinacol ester of 4-aminophenylboronic acid and a chlorobenzothiophene derivative.[43] On increasing the concentration of reactants in the synthesis of **4m**, the side product formation was minimized, and better and more consistent yields of **4m** were obtained (74-79 %).

Whereas **1d** was left virtually unreacted on attempted reaction with the very unstable **3-B(OH)$_2$** (Figure S194, ESI), different results were obtained for **1i** (Scheme 16). Traces of the desired terphenyl product could be detected (by ^{1}H NMR and MS), but could not be isolated in pure form. Based on ^{1}H NMR and MS data, the secondary amines **1i-1**, **1i-2** and **1i-3** have tentatively been assigned to be the main products of the reaction. However, none of the compounds were isolated in pure form, and the number of different products may very well exceed those shown in Scheme 16. Interestingly, the attempted synthesis of **3a-F** from the reaction between **1i** and **1-B(OH)$_2$** resulted primarily in the recovery of unreacted **1i** (Scheme 14); none of the secondary amines observed in the attempted synthesis of **4m-sym** could be detected by ^{1}H NMR of the crude product. This indicates that **1-B(OH)$_2$** does not follow the same decomposition profile as *e.g.* **3-B(OH)$_2$**. While the latter decompose very fast due to the alkaline reaction conditions, the decomposition of **1-B(OH)$_2$** seems to be mainly Pd-mediated, thus consuming the catalyst and to a large extent inhibiting potential Pd-catalyzed side reactions **1i** could undergo with itself.

From studying the reaction profile between different chloroanilines and arylboronic acids with various substituents, it is reasonable to conclude that the reactivity of **1-B(OH)$_2$** seems to be strongly limited by a low tendency to undergo Suzuki reactions accompanied by a relative rapid Pd-induced decomposition profile. In the synthesis of **1c** it was noted that even when employing relatively generous amounts of Pd (6-10 mol% Pd_2dba_3) not much was gained with respect to conversion of diamine **6a** (Table S1, ESI) indicating that other processes may have consumed significant amount of Pd, *i.e.* the decomposition of **1-B(OH)$_2$**. Furthermore, the amine-specific side products arising from Chan-Lam-Evans couplings with **1-B(OH)$_2$** limited the excess of boronic acid that was synthetically viable to employ. Interestingly, the fluorosubstituted boronic acid **2-B(OH)$_2$** was inert towards the *N*-arylation side reaction, thus a large excess (2.0 equiv.) could be employed in the reaction between **6a** and **2-B(OH)$_2$** without having any cumbersome purification issues to deal with (**4n**, Scheme 17). The very low reactivity of **1-B(OH)$_2$** compared to e.g. **2-B(OH)$_2$** was further demonstrated by reacting 2,6-dibromo-3-chloro-4-fluoroaniline with one equivalent of **2-B(OH)$_2$** (**4q**, Scheme 17). No biphenyl product was observed, and only the terphenyl product **4q** together with unreacted starting material could be isolated, similar to the observation made for the attempted synthesis of **2b-Br** (*vide supra*).Although **4q** only could be obtained in poor yields using these reaction conditions, it would be anticipated that good yields could be obtained by increasing the equivalents of **2-B(OH)$_2$**.



Scheme 16. Tentatively assigned products from the reaction of **1i** and **3-B(OH)$_2$**. Note that none of the products were isolated in pure form.



Scheme 17. Synthesis of amines **4n—4r.**

Crystallographic structure determination of cross coupling products.

Some of the cross coupling products, **2b** (Figure 5), **3a** (Figure 6), **4a** (Figure 7) were characterized by single crystal X-ray diffraction (XRD), in addition to **30** (Figure 8). **2b** had a crystallographically imposed C_2 symmetry axis, and the biphenyl dihedral angle of **2b**

was found to be 66.459(5)° which is similar to what has been reported for other 2-nitro-substituted biphenyls,[44] as well as *m*-terphenyls.[45] The corresponding angle in **3a** was found to be −46.630(5)°. Interestingly, the apparently unsymmetrical terphenyl **3a** was found to possess a crystallographically imposed inversion center. The NH_2 group was found to be disordered by this inversion symmetry over two positions, C2 and C5, with 50 % occupancy at each position (see ESI for more details). The appearance of the ^{1}H NMR and ^{13}C NMR spectra of **3a**, however, was consistent with a terphenyl with three non-equivalent phenyl rings.

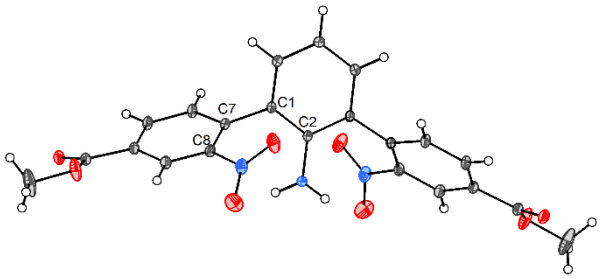


Figure 5. ORTEP plot of **2b** with 50 % ellipsoids. Selected angles [°]: C2-C2-C7-C8 = 66.459(5)°.

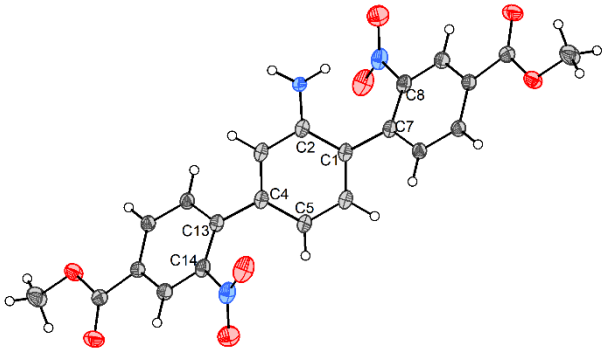


Figure 6. ORTEP plot of **3a** with 50 % ellipsoids. The NH_2 group is disordered over two positions, C2 and C5, with 50 % occupancy at each position. Selected angles [°]: C2-C1-C7-C8 = −46.630(5).

The appearance of the ^{1}H NMR and ^{13}C NMR spectra of **2b** was only partially consistent with its solid state C_2 symmetry, and two different rotamers were observed at room temperature. As expected for rotamers,[46] the ratio between the resonances belonging to each rotamer was found to vary in different solvents (Figure 9). Rotamers were observed in the ^{1}H, ^{13}C and ^{19}F NMR spectra for several of the ter- and quaterphenyls described in this work. This behaviour complicated assessment of purity by ^{1}H NMR. Because of this, elemental analysis was carried out for a representative selection of the products in order to confirm their purity (see experimental section and ESI). The unsymmetrical terphenyl **4a** crystallized with two molecules in its asymmetric unit. The biphenyl dihedral angles of **4a** were found to be 58.633(16)° (C2-C1-C7-C8) and 62.292(15)° (C2-C3-C13-C14), which is somewhat smaller than the corresponding angle in terphenyl **2b**. Unlike what was seen for **2b**, different rotamers of **4a** could not be detected by ^{1}H NMR spectroscopy at room temperature, indicating the need for relatively large substituents *ortho* to the phenyl-phenyl bonds of the *m*-terphenyl moiety in order to create a significant rotational barrier at ambient temperature.

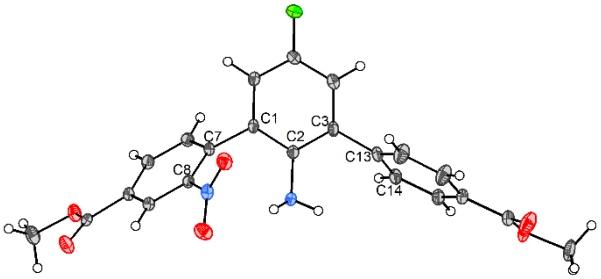


Figure 7. ORTEP plot of **4a** with 50 % ellipsoids. Only one of the two molecules of the asymmetric unit is shown. Selected angles [°]: C2-C1-C7-C8 = 58.633(16)°; C2-C3-C13-C14 = 62.292(15)°.

In addition, the secondary amine **30**, obtained as a side product in the synthesis of **4m** (Scheme 15), was structurally characterized (Figure 8). The compound is interesting as it contains 3 different sets of 2,2'-disubstituted biphenyls. As expected, the dihedral angle of the biphenyl moiety with 2,2'-difluorosubstituents is smaller than the corresponding angles of the 2-amino-2'-nitrobiphenyl moieties.

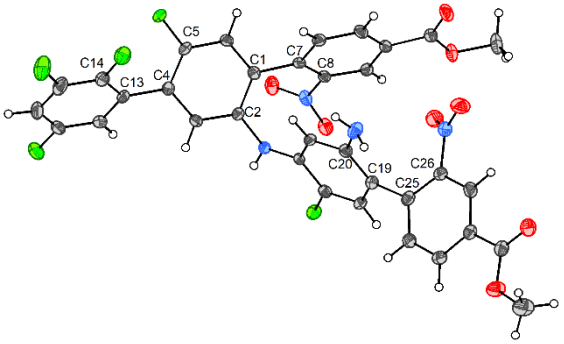


Figure 8. ORTEP plot of side product **30** with 50 % ellipsoids. Benzene (solvent of crystallization) has been removed for clarity. Selected angles [°]: C5-C4-C13-C14 = −45.858(3); C2-C1-C7-C8 = 50.751(3); C20-C19-C25-C26 = −53.685(3).

The presence of multiple 2,2'-substituents in **30** gave rise to broadened resonances in ^{1}H and ^{19}F NMR, most likely caused by hindered rotation around the phenyl-phenyl bonds.

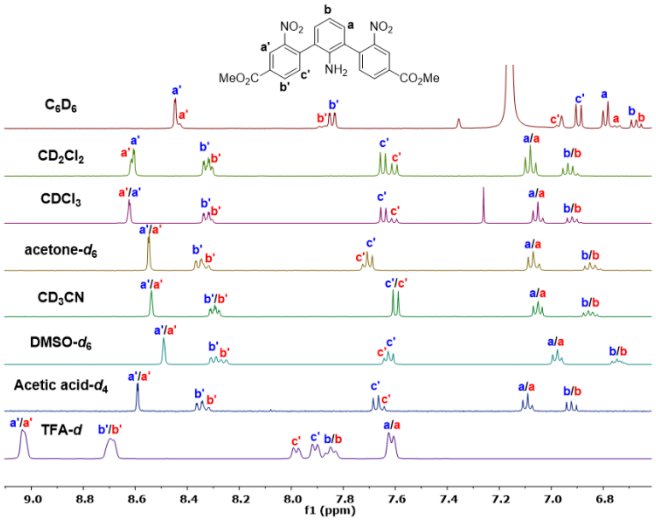
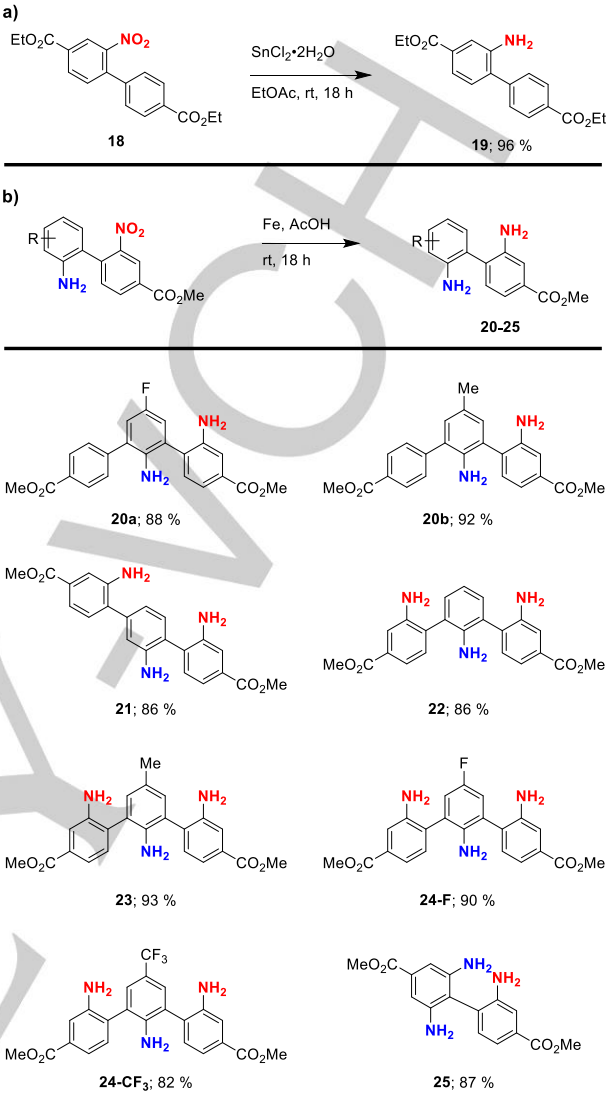


Figure 9. Stacked ^{1}H NMR (400 MHz) spectra of **2b** in different solvents, showing the aromatic region. Notation: blue = major rotamer, red = minor rotamer.

Synthesis of mono-, di- and triaminobiphenyls and –terphenyls.

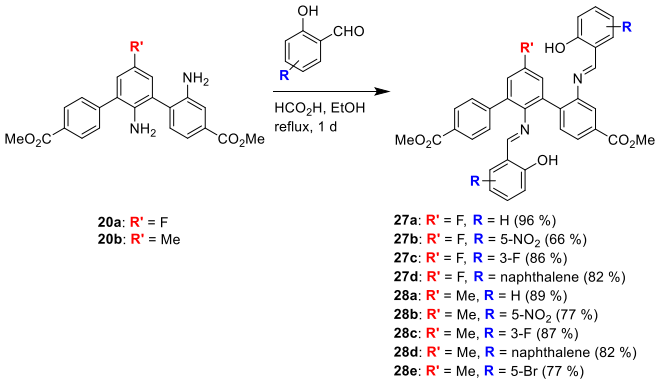
As mentioned in the introduction, the main motivation for developing these methods was to get access to mono-, di- and triaminobiphenyls and –terphenyls. To demonstrate this, several of the aforementioned products was subjected to reductions (iron in acetic acid for **20**—**25** and $SnCl_2{\cdot}2H_2O$ for **19**) (Scheme 18). The reductions proceeded smoothly and the resulting amines were obtained in very good to excellent yields. The products could be purified by recrystallization, and the reactions could be performed on a relatively large scale; product **19** could be obtained in 15 g scale. The reduction protocol gave access to gram-quantities of 2,6,2'-triaminobiphenyl **25**. Although 2,6,2'-triaminobiphenyls are relatively small molecules, they are scarcely described in the literature. The synthesis of 2,6,2'-triaminobiphenyl or one its non-6'-substituted derivatives has to the best of the author's knowledge only been described once before, in low yields.[47] Only a selection of the cross coupling products were subjected to reduction, but it is anticipated that the reaction conditions will be applicable for the majority of nitro compounds presented herein.



Scheme 18. Reduction of nitro containing cross-coupling products to the corresponding amines **19**—**25**.

Synthesis of Schiff base ligands and Zn complexes.

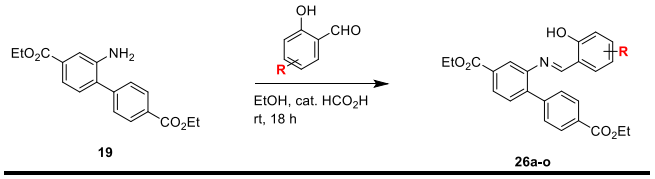
As 2-aminobiphenyls and 2,2'-diaminobiphenyls are suitable starting materials for the synthesis of Schiff base ligands, some of the amines presented in Scheme 18 were studied for this purpose. Amines **19**, **20a** and **20b** were reacted with different salicylaldehydes according to Scheme 19 and Scheme 20, yielding the corresponding Schiff bases (**26a**—**26o**, **27a**—**27d** and **28a**—**28e**). In general, the reactions proceed with good to very good yield, with no other requirements for purification of the products than filtration of the reaction mixture and subsequent recrystallization. As many salicylaldehyde derivatives are commercially available, a large selection of Schiff base ligands with different electronic and steric properties, could be obtained in a relatively straight-forward manner.



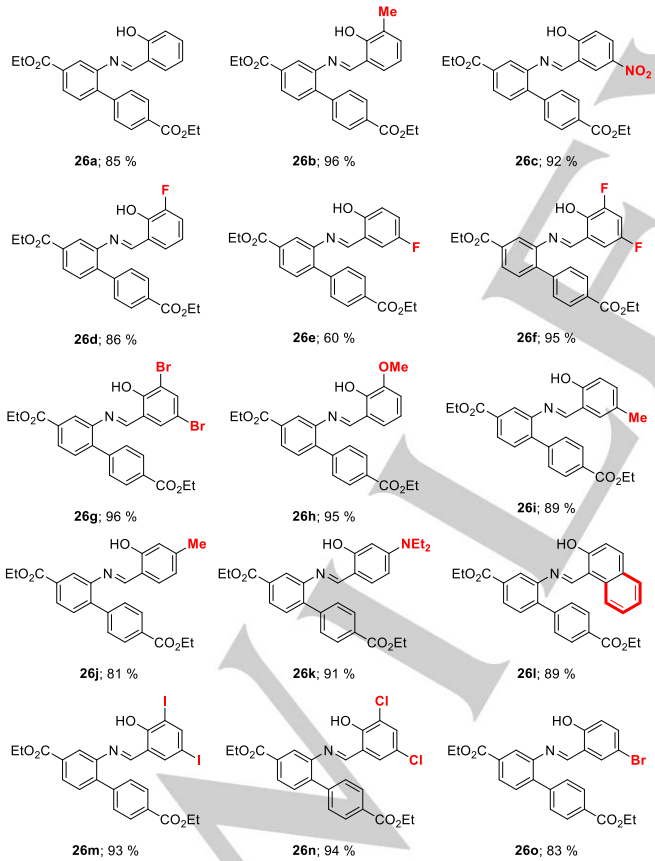
20a: R' = F
20b: R' = Me

27a: R' = F, R = H (96 %)
27b: R' = F, R = 5-NO_2 (66 %)
27c: R' = F, R = 3-F (86 %)
27d: R' = F, R = naphthalene (82 %)
28a: R' = Me, R = H (89 %)
28b: R' = Me, R = 5-NO_2 (77 %)
28c: R' = Me, R = 3-F (87 %)
28d: R' = Me, R = naphthalene (82 %)
28e: R' = Me, R = 5-Br (77 %)

Scheme 19. Synthesis of Schiff base ligands **27a**—**27d** and **28a**—**27e** from diamines **20a** and **20b**.



19 **26a-o**

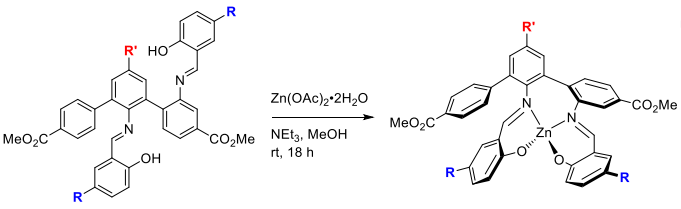


26a; 85 % **26b**; 96 % **26c**; 92 %
26d; 86 % **26e**; 60 % **26f**; 95 %
26g; 96 % **26h**; 95 % **26i**; 89 %
26j; 81 % **26k**; 91 % **26l**; 89 %
26m; 93 % **26n**; 94 % **26o**; 83 %

Scheme 20. Synthesis of Schiff base ligands **20a**—**20o** from amine **19**.

Finally, Zn complexes of some of these ligand were synthesized (Scheme 21, Scheme 23 and Scheme 22), to demonstrate the method's overall usefulness for the construction of metal complexes of biphenyl- and terphenyl-based Schiff base ligands. The complexes were obtained in moderate to very good yields, using reaction conditions that are similar to those reported in the literature for the synthesis of related Zn complexes.[48] The Zn complexes obtained from the tetradentate ligands in Scheme 19 can be categorized as salen-like complexes[49] ("Zn(salen)") (**27a-Zn**, **28a-Zn** and **28e-Zn**), while the Zn complexes derived from the bidentate ligands **26a**—**26o** (Scheme 20) can be described as homoleptic bis(salicylaldiminato) complexes[50] ("Zn(sal)$_2$"). During the synthesis of complex **26b-Zn**, it was noticed that the choice of base in the reaction had a large impact on the nature of the product (Scheme 22 and Scheme 23). When NEt_3 was used, tetracoordinated complex **26b-Zn** was obtained (Scheme 22), while the use of DBU furnished the pentacoordinated complex **26b-Zn-DBU** (*vide infra*) (Scheme 23).

Complexes **26a-Zn**, **26c-Zn**, **26b-Zn-DBU**, **27a-Zn** and **28a-Zn** were characterized by single crystal X-ray diffraction analysis (Figure 10-Figure 15). The coordination geometries of the complexes were assigned using geometrical descriptors, τ_5 for pentacoordinated complexes,[51] and τ_4' for tetracoordinated complexes.[52] Complex **28a-Zn** crystallized a pentacoordinated monomer, with an additional DMSO-ligand. The geometry around zinc was found to be distorted square pyramidal (τ_5 = 0.28) (Figure 10). Complex **27a-Zn** crystallized as a dimer with two pentacoordinated square pyramidal zinc nuclei (τ_5 = 0.01) (Figure 11). Complexes **26a-Zn** and **26c-Zn** crystallized as monomers with distorted tetrahedral geometry around zinc (τ_4' = 0.67 and 0.70 respectively) (Figure 12, Figure 13 and Figure 14), whereas **26b-Zn-DBU** crystallized as monomer with a pentacoordinated zinc nucleus (Figure 15). The geometry around zinc was found to be intermediate between square pyramidal and trigonal bipyramidal (τ_5 = 0.49).



27a: R' = F, R = H
28a: R' = Me, R = H
28e: R' = Me, R = Br

27a-Zn: R' = F, R = H (68 %)
28a-Zn: R' = Me, R = H (46 %)
28e-Zn: R' = Me, R = Br (61 %)

Scheme 21. Synthesis of Zn complexes **27a-Zn**, **28a-Zn** and **28e-Zn**.

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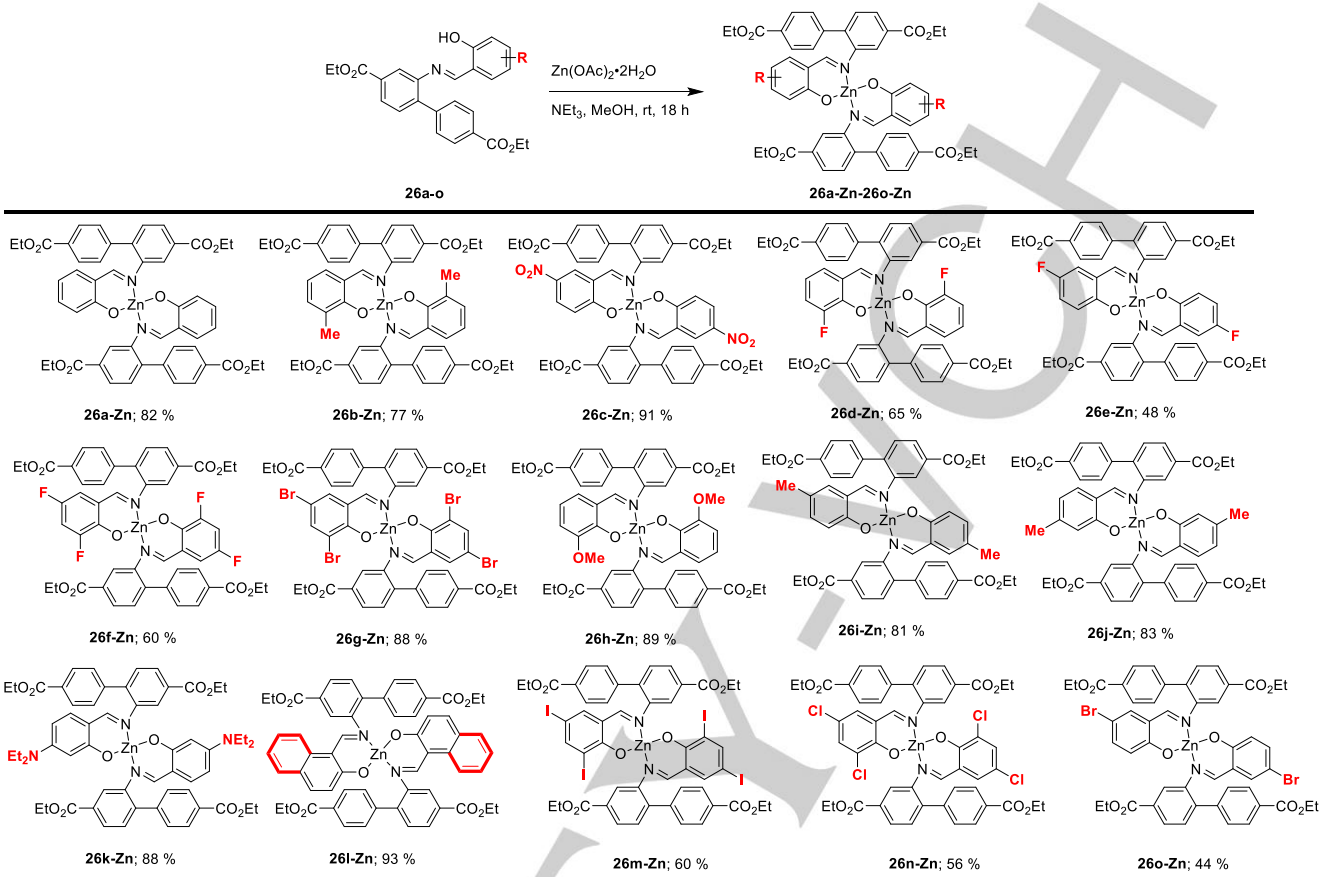
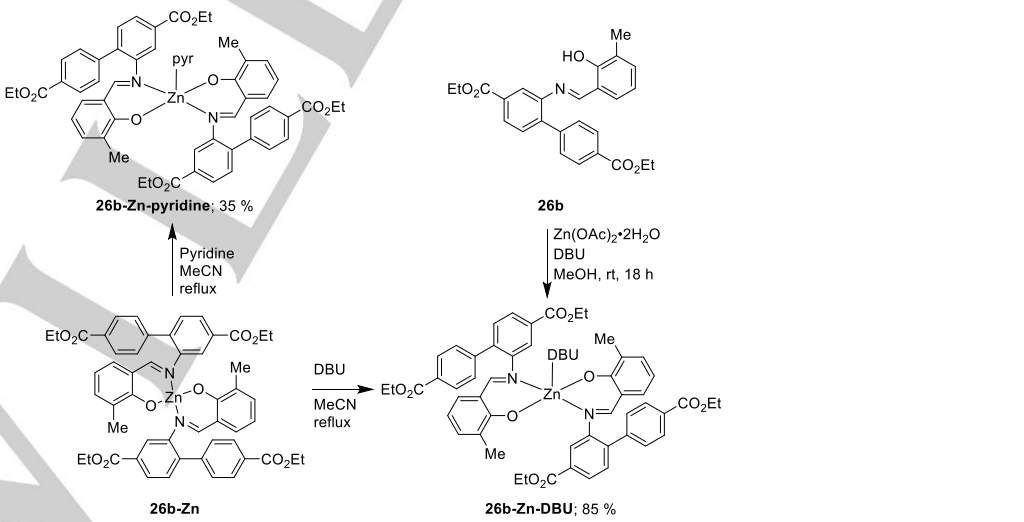


Scheme 22. Synthesis of Zn complexes **26a-Zn**—**26o-Zn**.



Scheme 23. Synthesis of Zn complexes **26b-Zn-pyridine** and **26b-Zn-DBU**.

10.1002/ejoc.202000599

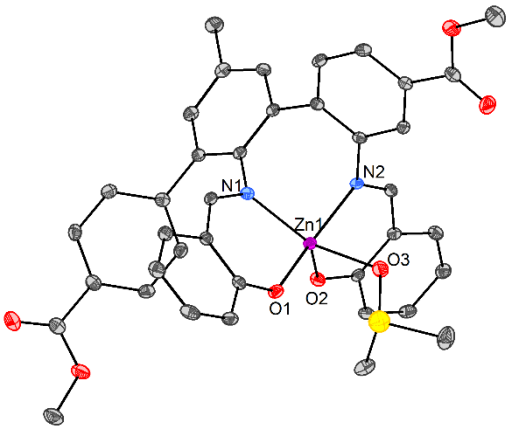


Figure 10. ORTEP plot of **28a-Zn-DMSO** with 50 % ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1-N1 = 2.0955(1); Zn1-N2 = 2.0728(1); Zn1-O1 = 1.9589(1); Zn1-O2 = 1.9505(1); Zn1-O3 = 2.2023(1); N1-Zn1-N2 = 90.552(3); N1-Zn1-O1 = 89.519(3); N1-Zn1-O2 = 116.346(3); N1-Zn1-O3 = 142.514(3); N2-Zn1-O1 = 159.240(4); N2-Zn1-O2 = 91.751(3); N2-Zn1-O3 = 83.912(3); O1-Zn1-O2 = 106.772(3); O1-Zn1-O3 = 83.443(3); O2-Zn1-O3 = 100.897(3).

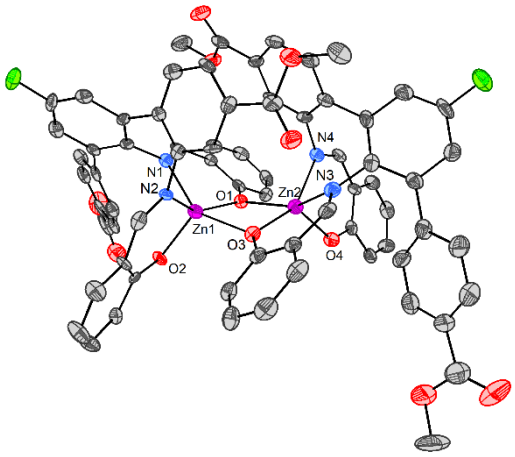


Figure 11. ORTEP plot of **27a-Zn** with 50 % ellipsoids Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1-N1 = 2.1495(1); Zn1-N2 = 2.0171(1); Zn1-O1 = 1.9579(0); Zn1-O2 = 1.9279(0); Zn1-O3 = 2.1988(1); Zn2-N3 = 2.1699(1); Zn2-N4 = 2.0426(1); Zn2-O1 = 2.1405(1); Zn2-O3 = 1.9636(1); Zn2-O4 = 1.9329(1); N1-Zn1-N2 = 86.687(1); N1-Zn1-O1 = 88.530(2); N1-Zn1-O2 = 106.858(1); N1-Zn1-O3 = 145.037(2); N2-Zn1-O1 = 144.678(2); N2-Zn1-O2 = 93.790(1); N2-Zn1-O3 = 93.790(1); O1-Zn1-O2 = 121.008(1); O1-Zn1-O3 = 73.797(1); O2-Zn1-O3 = 108.104(2); N3-Zn2-N4 = 86.921(1); N3-Zn2-O1 = 146.810(2); N3-Zn2-O3 = 88.438(1); N3-Zn2-O4 = 104.874(2); N4-Zn2-O1 = 91.699(1); N4-Zn2-O3 = 147.157(1); N4-Zn2-O4 = 92.927(1); O1-Zn2-O3 = 75.026(1); O1-Zn2-O4 = 108.314(2); O3-Zn2-O4 = 119.644(2); Zn1-O1-Zn2 = 104.685(2); Zn1-O3-Zn2 = 102.367(2).

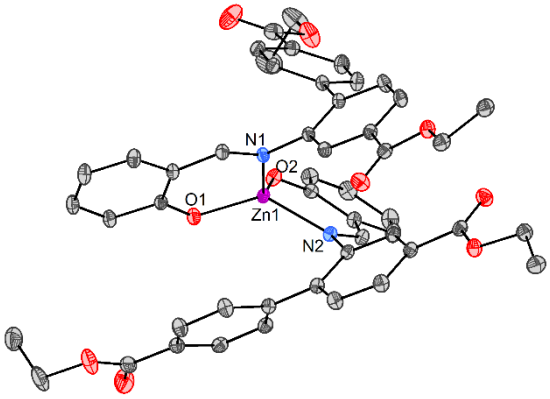


Figure 12. ORTEP plot of **26a-Zn** with 50 % ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1-N1 = 2.0334(1); Zn1-O1 = 1.9155(1); N1-Zn1-N2 = 101.172(2); N1-Zn1-O1 = 94.931(3); N1-Zn1-O2 = 132.728(3); O1-Zn1-O2 = 105.971(5).

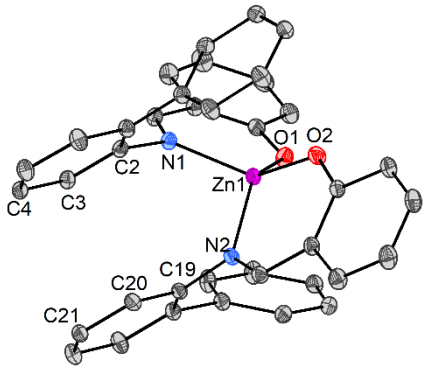


Figure 13. ORTEP plot of **26a-Zn** with 50 % ellipsoids. Hydrogen atoms and ethoxycarbonyl groups have been omitted for clarity. Selected distances [Å]: C2---C19 = 3.3707(3) Å; C3---C20 = 3.2775(3); C4---C21 = 3.3912(3); N1---N2 = 3.1419(2).

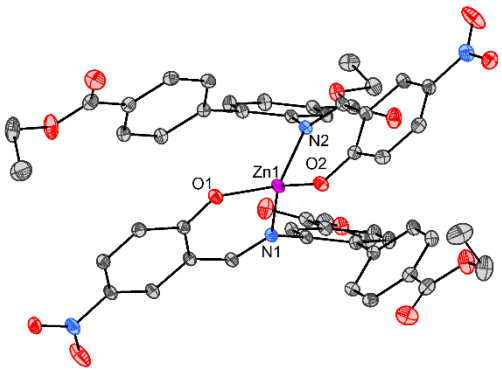


Figure 14. ORTEP plot of **26c-Zn** with 50 % ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1-N1 = 2.0179(1); Zn1-O1 = 1.9137(1); N1-Zn1-N2 = 103.997(1); N1-Zn1-O1 = 95.721(2); N1-Zn1-O2 = 130.669(2); O1-Zn1-O2 = 104.792(3).

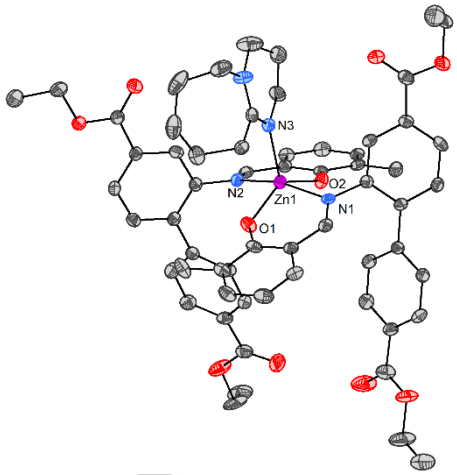


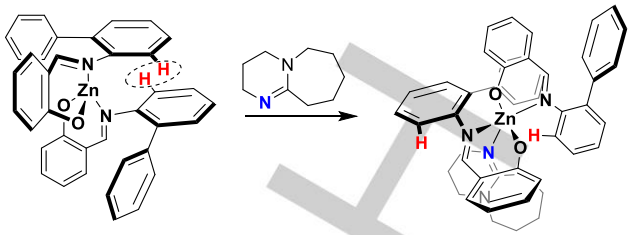
Figure 15. ORTEP plot of **26b-Zn-DBU** with 50 % ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1-N1 = 2.1496(1); Zn1-N2 = 2.1754(1); Zn1-N3 = 2.0563(1); Zn1-O1 = 1.9609(1); Zn1-O2 = 1.9758(1); N1-Zn1-N2 = 163.405(3); N1-Zn1-N3 = 100.812(3); N1-Zn1-O1 = 87.852(3); N1-Zn1-O2 = 84.543(2); N2-Zn1-N3 = 95.287(3); N2-Zn1-O1 = 88.681(2); N2-Zn1-O2 = 86.1791(3); N3-Zn1-O1 = 116.079(3); N3-Zn1-O2 = 110.109(3); O1-Zn1-O2 = 133.801(3).

The dimeric structure obtained for **27a-Zn** is not surprising, and there are several reports of dimeric structures of related Zn complexes with tetradentate ligands in the literature.[53] As expected for square pyramidal d^{10} complex, the bond length between the apical substituent (O2) and Zn was found to be shorter than the corresponding bond length between the basal substituents and Zn.[54] The bonds between Zn and the coordinating oxygens and nitrogens within each tetradentate ligand are of similar lengths as reported earlier for related pentacoordinated Zn complexes in the literature.[55] On the other hand, the bonds between the two Zn nuclei and the bridging oxygen atoms are significantly longer than what was reported by Reek and co-workers for a related Zn salphen complex (2.027(2) Å).[53a] This may be attributed to the high Lewis acidity of Zn salphen complexes.[13d] Accommodation of a fifth ligand to Zn is highly favoured as the salphen ligand forces Zn into a disfavoured, nearly square planar geometry,[56] whereas Schiff base ligands of derivatives of 2,2'-diaminobiphenyls are more in favour of a tetrahedral geometry around Zn.[55, 57] This is also evident from the crystal structure of **28a-Zn**. The DMSO-ligation observed for **28a-Zn** was expected based on literature reports,[58] however the Zn-O(DMSO) bond is significantly longer than Zn-O(DMSO) bonds reported for Zn salen and Zn salphen complexes. Kleij and co-workers reported Zn-O bond lengths between 2.039(3) Å and 2.086(1) Å for four Zn complexes derived either from salen[58a-b] or salphen[58c] ligands, whereas the corresponding bond length was found to be 2.2023(1) Å for **28a-Zn**. Although slightly distorted from the ideal square pyramidal geometry, the bond between the apically oriented substituent and Zn (Zn1-O2) is still shorter than the bonds between the basally oriented substituents and Zn, which is in accordance with the assignment of square pyramidal geometry around Zn.[54] The bond lengths between Zn and the two nitrogens of the ligand are more similar to each other than what was observed for **27a-Zn** (2.0955(1) Å and 2.0728(1) Å for **28a-Zn**,

and 2.1495(1) Å and 2.0171(1) Å for **27a-Zn**). These differences in bond lengths may be attributed to the degree of distortion of each complex from ideal square pyramidal geometry.

The monomeric structures of **26a-Zn** and **26c-Zn** are in accordance with earlier reports in the literature, with respect to coordination number and geometry around zinc, as well as bond lengths and bond angles[50, 59] The pentacoordination obtained for **26b-Zn-DBU** is more unusual. The DBU ligand was found to coordinate Zn through the sp^2-hybridized nitrogen, rather than the sp^3-hybridized nitrogen, which is in accordance with the coordination mode observed for DBU in pentacoordinated Zn complexes in the literature.[60] The Zn-N(DBU) bond in **26b-Zn-DBU** is noticeably shorter than the bonds between Zn and the two nitrogens of ligand **26b**.

Di Bella and co-workers used calculations to show that $Zn(sal)_2$ complexes are electronically saturated species, and remains tetracoordinated even in the presence of donating solvents, unlike Zn(salen) complexes which readily forms pentacoordinated species in the presence of donors.[17b] The structural studies of complex **26b-Zn-DBU** show that $Zn(sal)_2$ complexes also form pentacoordinated adducts. However, from the studies of **26b-Zn** in the presence of weaker donors such as DMSO or pyridine there are no indications that pentacoordination takes place (see ESI), and related complex **26c-Zn** crystallized with tetracoordination around Zn even in the presence of DMSO (*vide supra*). This is especially evident when evaluating some of the chemical shifts of the complexes in DMSO-d_6. From the crystal structures of **26a-Zn** and **26c-Zn** it was observed that the aromatic rings connected to each of the *N*-termini of the imines had a displaced parallel orientation to each other, with an aryl-aryl distance of 3.991 Å for **26a-Zn** (Figure 13). This displaced parallel orientation could lead to substantial shielding of some of protons in the ring, most notably the protons associated with carbon atoms C3 and C20. From studies of **26b-Zn** in DMSO-d_6, the chemical shift of these protons was found to be remarkable upfield (7.16 ppm) on comparison with the chemical shift of the corresponding proton in ligand **26b** (8.00 ppm). This may indicate that the tetracoordinated geometry around zinc is preserved in this strongly donating solvent. This is further illustrated on comparison with the chemical shift of the same protons of **26b-Zn** in poorly donating CD_2Cl_2, which was found to be 7.07 ppm, *i.e.* not very different. From NMR-studies of **26b-Zn-DBU** however, the chemical shift of these protons was found to appear significantly more downfield (ca. 7.65 ppm, see supporting information) in DMSO-d_6. Upon inspection of the crystal structure of **26b-Zn-DBU**, it was observed that the aforementioned aromatic rings no longer are oriented displaced parallel to each other, which should result in smaller shielding effects (Scheme 24). These observations suggest that the pentacoordinated complex **26b-Zn-DBU** may be present as a defined species in solution, but that preservation of tetrahedral geometry for **26b-Zn** is dominant in the presence of donating solvents such as DMSO-d_6.



Scheme 24. Coordination of DBU to complex **26b-Zn**. Ethoxycarbonyl and methyl substituents have been omitted for clarity.

Recrystallization of **26b-Zn** from a mixture of MeCN and pyridine furnished the tentative complex **26b-Zn-pyridine**. Although the obtained crystalline material contained one equivalent pyridine by ^{1}H NMR integration, the complex appeared essentially the same way as **26b-Zn** with respect to chemical shifts in DMSO-d_6 (Figure S367, ESI) and in CD_2Cl_2. The complex may be pentacoordinated in the solid state, but there are no indications of this in solution. The ^{1}H NMR spectrum of complex **26b-Zn-DBU** appeared substantially different from that of **26b-Zn** not only with respect to the chemical shifts. All of the resonances in the ^{1}H NMR spectrum of the former were significantly broadened in DMSO-d_6 at room temperature. This may be indicative of a reversible coordination/decoordination of the DBU ligand, or a relatively rapid interconversion between species with different geometries,[61] commonly seen for pentacoordinated metal complexes.[62] Unfortunately it was not possible to conduct any in-depth NMR studies of the complex to investigate its potential dynamic behaviour, as it was found to be unstable in solution.

Conclusions

This paper has disclosed a general method for performing Suzuki-Miyaura reactions between various aryl bromides and 4-Methoxycarbonyl-2-nitrophenylboronic acid (**1-B(OH)$_2$**), which to a large extent overcomes the boronic acid's low reactivity in the Suzuki-Miyaura-reaction and the low stability of **1-B(OH)$_2$** in the presence of Pd. A variety of different products were synthesized and the functional group tolerance was in general high. Within the work, there has been a special emphasis on the reactions between different 2-bromoanilines and **1-B(OH)$_2$** for the synthesis of precursors for unsymmetrical substituted 2,2'-diaminobi- and terphenyls. Unfortunately, chloroanilines proved to be unreactive towards **1-B(OH)$_2$** under the reaction conditions described here. The lack of reactivity of **1-B(OH)$_2$** towards chloroanilines were put in perspective by comparison with the corresponding reactions between a series of chloroanilines and some other arylboronic acids, with issues concerning low reactivity, steric hindrance and low stability under the reaction conditions employed here. Of the different boronic acids studied, it was shown that the lack of reactivity for **1-B(OH)$_2$** only could be matched by the very base sensitive 2,4,6-trifluorophenylboronic acid (**3-B(OH)$_2$**). From the outcome of the experiments with **1-B(OH)$_2$** compared to **3-B(OH)$_2$** there are some indications that the decomposition of **1-B(OH)$_2$** is mainly Pd-mediated, and that base-catalyzed decomposition is less important. Furthermore, some of the cross coupling products synthesized with the methods described within this text, were

reduced to the corresponding di- and triamines, giving access to compounds which are difficult to obtain by other methods. Finally, some of the amines were further reacted with salicylaldehyde derivatives to yield the corresponding Schiff bases, which accordingly were used to synthesize some new Zn complexes, showing the potential of the compounds described herein to serve as starting materials for the synthesis of advanced metal complexes.

Experimental Section

General considerations. Pd_2dba_3 and $HBF_4{\cdot}P(t\text{-}Bu)_4$ were purchased from Sigma Aldrich and handled in air. $KF{\cdot}2H_2O$ was ground with a mortar and pestle immediately before use. All other chemicals were used as received. THF (unstabilized) was dried using a MB SPS-800 solvent purifier system from MBraun. Hexanes were distilled before use. Other solvents were used as received. TLC was performed using Merck 60 F254-plates. Flash chromatography was performed using silica gel from Merck (60, 0.040-0.063 mm). NMR spectroscopy was performed using Bruker Avance AVII400, Bruker Avance AVIIIHD400, Bruker Avance AVI600, Bruker Avance AVII600 or Bruker Avance AVIIHD800 operating at 400 MHz (^{1}H NMR), 376 MHz (^{19}F NMR), 101 MHz (^{13}C NMR), or 600 MHz (^{1}H NMR) and 151 MHz (^{13}C NMR), or 800 MHz (^{1}H NMR) and 201 MHz (^{13}C NMR) respectively. All spectra were recorded at 300 K. ^{1}H NMR and ^{13}C NMR spectra have been referenced relative to the residual solvent signals, and the peaks are numbered according to Figure 16 Chemical shifts in ^{19}F NMR have been referenced to $CFCl_3$ by using C_6F_6 (−164.9 ppm with respect to $CFCl_3$ at 0 ppm) as an internal standard (−164.9 ppm), and are proton decoupled. Chemical shifts in ^{15}N NMR have been calibrated against CH_3NO_2 as external standard (0.0 ppm). All ^{15}N NMR chemical shifts were obtained and assigned using ^{1}H-^{15}N HMBC experiments. The peaks in the ^{1}H NMR and ^{13}C NMR spectra were assigned using various 2D experiments (NOESY, COSY, TOCSY, HSQC, HMBC and HETCOR). MS (ESI) was recorded on a Bruker maXis II ETD spectrometer by Osamu Sekiguchi. All melting points are uncorrected and were obtained with a Stuart SMP10 melting point apparatus. Elemental analysis was performed by Microanalytisches Laboratorium Kolbe, Oberhausen, Germany.

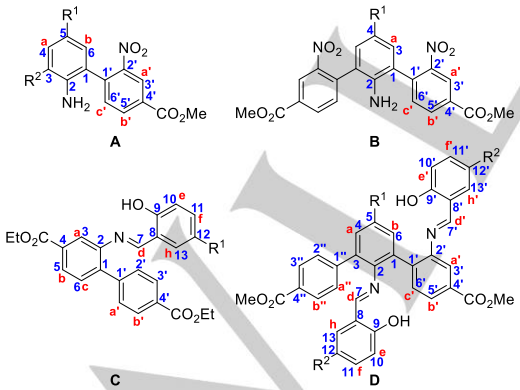


Figure 16. Numbering scheme used for reporting the NMR data. Letters = protons, numbers = carbons.

Experimental and analytical data for a selection of the compounds described within the text are presented here, data for all compounds can be found in ESI.

General procedure for synthesis of biphenyls 1a—1o (GP1). Aryl halide (2.50-5.00 mmol, 1.0 equiv.), **1-B(OH)$_2$** (1.0-2.0 equiv.) and freshly powdered $KF{\cdot}2H_2O$ (3.0-6-0 equiv.) were mixed in THF (0.5 M with respect to aryl halide) in a 50 mL Schlenk flask. Ar was bubbled The suspension was bubbled with Ar for 10 min. before Pd_2dba_3 (0.5-6.0 mol %) and $HBF_4{\cdot}P(t\text{-}Bu)_3$ (1.2-14 mol%) was added. The bubbling was continued for 1-2 minutes after which a magnetic stirrer was added and a reflux condenser was attached to the flask. The reaction mixture was then heated at reflux temperature for one hour under Ar. After cooling to room temperature, the reaction was worked up according to **method a)**: the reaction mixture was extracted with CH_2Cl_2 (50-100 mL) and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (hexane/CH_2Cl_2/EtOAc). The obtained product could be further purified by recrystallization if required. **Example (1d)** (numbering scheme A, Figure 16): 2-Bromo-6-chloro-4-fluoroaniline (1.13 g, 5.01 mmol, 1.0 equiv.), **1-B(OH)$_2$** (1.24 g, 5.52 mmol, 1.1 equiv.) and freshly powdered $KF{\cdot}2H_2O$ (1.56 g, 16.5 mmol, 3.3 equiv.) were mixed in THF (10 mL) in a 50 mL Schlenk flask. The resulting suspension was bubbled with Ar for 10 min before Pd_2dba_3 (0.113 g, 0.123 mmol, 2.5 mol%) and $HBF_4{\cdot}P(t\text{-}Bu)_3$ (0.0870 g, 0.302 mmol, 6.0 mol%) were added. The bubbling was continued for 1-2 minutes after which a magnetic stirrer was added and a reflux condenser was attached to the flask. The reaction mixture was then heated at reflux temperature for one hour under Ar. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2 (50 mL) and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (silica gel, 15 % EtOAc/85 % hexanes), yielding a yellow solid. Recrystallization from EtOH yielded **1d** as orange crystals (1.32 g, 4.05 mmol, 81 %). M.p. 145-146 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.66 (d, $^4J_{H,H}$ = 1.3 Hz, 1H, **H^a**), 8.34 (dd, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.4 Hz, 1H, **H^b**), 7.55 (d, $^3J_{H,H}$ = 7.9 Hz, 1H, **H^c**), 7.13 (dd, $^3J_{H,F}$ = 8.0 Hz, $^4J_{H,H}$ = 2.8 Hz, 1H, **H^a**), 6.70 (dd, $^3J_{H,F}$ = 8.2 Hz, $^4J_{H,H}$ = 2.8 Hz, 1H, **H^b**), 4.01 (s, 3H, CO_2CH_3), 3.74 ppm (broadened s, 2H, NH_2); ^{13}C NMR (151 MHz, $CDCl_3$): δ 164.5 (**C**O_2CH_3), 154.8 (d, $^1J_{C,F}$ = 241.3 Hz, **C^5**), 149.2 (**C$^{2'}$**), 136.9 (d, $^4J_{C,F}$ = 2.1 Hz, **C^2**), 136.1 (d, $^4J_{C,F}$ = 1.6 Hz, **C$^{1'}$**), 133.9 (**C$^{5'}$**), 132.8 (**C$^{6'}$**), 131.8 (**C$^{4'}$**), 125.8 (**C$^{3'}$**), 123.9 (d, $^3J_{C,F}$ = 8.1 Hz, **C^1**), 120.3 (d, $^3J_{C,F}$ = 10.5 Hz, **C^3**), 117.0 (d, $^2J_{C,F}$ = 25.4 Hz, **C^4**), 114.5 (d, $^2J_{C,F}$ = 23.3 Hz, **C^6**), 52.9 ppm (CO_2**C**H_3); ^{19}F NMR (376 MHz, $CDCl_3$): δ –127.8 ppm; LRMS (ESI): *m/z* (%): 347.020 (100) $[M+Na]^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{10}ClFN_2O_4$+Na: 347.0205 $[M+Na]^+$; found: 347.0205.

General procedure for synthesis of ter- and quaterphenyls 2a—2k and 3a—3i (GP2). Aryl halide (2.50-10.0 mmol, 1.0 equiv.), **1-B(OH)$_2$** (2.2-4.5 equiv.) and freshly powdered $KF{\cdot}2H_2O$ (6.6-13.5 equiv.) were mixed in THF (0.25-0.5 M with respect to aryl halide) in a Schlenk flask. The suspension was bubbled with Ar for 10-20 min. before Pd_2dba_3 (0.5-10.0 mol%) and $HBF_4{\cdot}P(t\text{-}Bu)_3$ (1.2-24 mol%) was added. The bubbling was continued for 1-2 minutes after which a magnetic stirrer was added and a reflux condenser was attached to the flask. The reaction mixture was then heated at reflux temperature for one hour under Ar. After cooling to room temperature, the reaction was worked up either as described above (**method a)**) or by **method b)**: After cooling to room temperature, MeOH (5-6x the initial volume of THF) was added with stirring. After stirring for 30 min at rt, the reaction flask was cooled in a refrigerator for one day, followed by filtration. The solids were washed with MeOH, air dried, dissolved in CH_2Cl_2 and filtered through a short silica column (CH_2Cl_2). CH_2Cl_2 was removed under reduced pressure, and the residue was recrystallized to yield the pure product. **Example (2a)** (numbering scheme B, Figure 16): 2,6-Dibromo-4-methylaniline (2.65 g, 10.0 mmol, 1.0 equiv.), **1-B(OH)$_2$** (6.75 g, 30.0 mmol, 3.0 equiv.) and freshly powdered $KF{\cdot}2H_2O$ (8.47 g, 90.0 mmol, 9.0 equiv.) were mixed in THF (30 mL) in a 250 mL Schlenk flask. The suspension was bubbled with Ar for 15 min. before Pd_2dba_3 (0.462 g, 0.50 mmol, 5.0 mol%) and $HBF_4{\cdot}P(t\text{-}Bu)_3$ (0.352 g, 1.21 mmol, 12 mol%) was added. The bubbling was continued for 2 minutes after which a magnetic stirrer was added and a reflux condenser was

attached to the flask. The reaction mixture was then heated at reflux temperature for one hour under Ar. After cooling to room temperature, MeOH (180 mL) was added with stirring. After 30 min stirring at rt, the reaction flask was cooled in a refrigerator for one day, followed by filtration. The solids were washed with MeOH, air dried, dissolved in CH_2Cl_2 and filtered through a short silica column (CH_2Cl_2). CH_2Cl_2 was removed under reduced pressure, and recrystallization of the residue from THF/MeOH yielded **2a** as a red-orange crystals (3.83 g, 8.23 mmol, 82 %). M.p. 201-202 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.62 (s, minor) + 8.61 (d, $^4J_{H,H}$ = 1.4 Hz, major) (2H, **H$^{a'}$**), 8.31 (dd, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.4 Hz, major) + 8.30 (s, minor) (2H, **H$^{b'}$**), 7.63 (d, $^3J_{H,H}$ = 7.9 Hz, major) + 7.59 (d, $^3J_{H,H}$ = 7.9 Hz, minor) (2H, **H$^{c'}$**), 6.87 (s, major) + 6.85 (s, minor) (2H, **H^{a}**), 4.00 (s, 6H, CO_2CH_3), 3.26 (broadened s, minor) + 3.20 (broadened s, major), (2H, NH_2), 2.28 (s, major) + 2.26 ppm (s, minor) (3H, CH_3); ^{13}C NMR (151 MHz, $CDCl_3$): δ 164.7 (**C**O_2CH_3), 149.8 (minor) + 149.5 (major) (**C$^{2'}$**), 138.5 (minor) + 138.2 (major) **C^{2}**), 137.7 (major) + 137.6 (minor) (**C$^{1'}$**), 133.6 (major) + 133.3 (minor) (**C$^{5'}$**), 133.5 (major) + 133.0 (minor) (**C$^{6'}$**), 131.1 (minor) + 131.0 (major) (**C$^{4'}$**), 130.1 (major) + 130.0 (minor) (**C^{3}**), 128.5 (major) + 128.4 (minor) (**C^{4}**), 125.6 (**C$^{3'}$**), 123.6 (minor) + 123.5 (major) (**C^{1}**), 52.8 (CO_2CH_3), 20.3 ppm (CH_3); ^{15}N{^{1}H} NMR (600 MHz, $CDCl_3$): δ – 10.3 (***N***O_2), – 329.4 ppm (***N***H_2); LRMS (ESI): *m/z* (%): 488.106 (100) [*M*+Na]$^+$; HRMS (ESI): *m/z* calcd for $C_{23}H_{19}N_3O_8$+Na: 488.1064 [*M*+Na]$^+$; found: 488.1064; elemental analysis calcd (%) for $C_{23}H_{19}N_3O_8$: C 59.36, H 4.12, N 9.03; found: C 59.31, H 4.20, N 8.93.

General procedure for synthesis of bi-, ter- and quaterphenyls 4a—4r (GP3). Aryl halide (2.00-2.50 mmol, 1.0 equiv.), boronic acid (1.1-2.2 equiv.) and freshly powdered KF·2H_2O (3.3-6.6 equiv.) were mixed in THF (0.25-0.5 M with respect to aryl halide) in a 50 mL Schlenk flask. The suspension was bubbled with Ar for 10 min. before Pd_2dba_3 (2.0-5.0 mol %) and HBF_4·P(*t*-Bu)$_3$ (4.8-12 mol%) was added. The bubbling was continued for 1-2 minutes after which a magnetic stirrer was added and a reflux condenser was attached to the flask. The reaction mixture was then heated at reflux temperature under Ar (1-14 h). After cooling to room temperature, the reaction was worked up either according to **method a)** or **method b)**. **Example (4a)** (numbering scheme D, Figure 16): **1d** (0.813 g, 2.50 mmol, 1.0 equiv.), **7-B(OH)$_2$** (0.495 g, 2.75 mmol, 1.1 equiv.), and freshly powdered KF·2H_2O (0.778 g, 8.27 mmol, 3.3 equiv.) were mixed in THF (5 mL) in a 50 mL Schlenk flask. The suspension was bubbled with Ar for 10 min. before Pd_2dba_3 (0.0573 g, 0.0625 mmol, 2.5 mol%) and HBF_4·P(*t*-Bu)$_3$ (0.0430 g, 0.148 mmol, 5.9 mol%) was added. The bubbling was continued for 1-2 minutes after which a magnetic stirrer was added and a reflux condenser was attached to the flask. The reaction mixture was then heated at reflux temperature for 14 h under Ar. After cooling to room temperature, the reaction was worked up according to **method b)**. Recrystallization from MeCN yielded **4a** as dark red crystals (0.859 g, 2.02 mmol, 81 %). M.p. 190-191 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.65 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, **H$^{a'}$**), 8.34 (dd, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.6 Hz, 1H, **H$^{b'}$**), 8.13 (d, $^3J_{H,H}$ = 8.3 Hz, 2H, **H$^{b''}$**), 7.62 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, **H$^{c'}$**), 7.56 Hz (d, $^3J_{H,H}$ = 8.3 Hz, 2H, **H$^{a''}$**), 6.95 (dd, $^3J_{H,F}$ = 8.8 Hz, $^4J_{H,H}$ = 2.9 Hz, 1H, **H^{a}**), 6.80 (dd, $^3J_{H,F}$ = 8.3 Hz, $^4J_{H,H}$ = 2.9 Hz, 1H, **H^{b}**), 4.01 (s, 3H, $CO_2CH'_3$), 3.95 (s, 3H, $CO_2CH''_3$), 3.43 (broadened s, 2H, NH_2); ^{13}C NMR (151 MHz, $CDCl_3$): δ 166.6 (**C**$''O_2CH_3$), 164.6 (**C**$'O_2CH_3$), 155.8 (d, $^1J_{C,F}$ = 238.9 Hz, **C^{5}**), 149.4 (**C$^{2'}$**), 142.7 (**C$^{1''}$**), 136.9 (**C$^{1'}$**), 136.8 ($^4J_{C,F}$ = 1.9 Hz, **C^{2}**), 133.8 (**C$^{5'}$**), 133.1 (**C$^{6'}$**), 131.5 (**C$^{4'}$**), 130.3 (**C$^{3''}$**), 129.7 (**C$^{4''}$**), 129.2 (**C$^{2''}$**), 128.5 (d, $^3J_{C,F}$ = 7.1 Hz, **C^{3}**), 125.8 (**C$^{3'}$**), 124.1 (d, $^3J_{C,F}$ = 7.8 Hz, **C^{1}**), 117.3 (d, $^2J_{C,F}$ = 22.7 Hz, **C^{4}**), 115.4 (d, $^2J_{C,F}$ = 23.3 Hz, **C^{6}**), 52.9 ($CO_2C'H_3$), 52.2 ($CO_2C''H_3$); ^{19}F NMR (376 MHz, $CDCl_3$): δ – 129.3 ppm; LRMS (ESI): *m/z* (%): 447.096 (100) [*M*+Na]$^+$; HRMS (ESI): *m/z* calcd for $C_{22}H_{17}FN_2O_6$+Na: 447.0963 [*M*+Na]$^+$; found: 447.0963.

Synthesis of 17: 4-Chloro-3-nitrobenzoic acid (103 g, 513 mmol, 1.0 equiv.) was mixed with EtOH (750 mL). Conc. H_2SO_4 (50 mL) was added to the mixture dropwise over 30 min. When all sulfuric acid had been added, the reaction mixture was heated at reflux temperature for 18 h. After cooling to rt, the solution was poured in to ice/water (ca. 4 L), precipitating a pale yellow solid, which was filtered off, washed with water (3x 500 mL) and dried under suction for 30 min. The solid was dissolved in CH_2Cl_2 (1.2 L). The CH_2Cl_2 solution was washed with sat. $NaHCO_3$ (aq) (500 mL) and sat. NaCl (aq) (500 mL), dried with Na_2SO_4, filtered and evaporated to yield a yellow solid. Recrystallization from EtOH gave **17** as pale yellow crystals in two crops (108 g, 471 mmol, 92 %). M.p. 61-62 °C (Lit.[63]: 60-61 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, $^4J_{H,H}$ = 2.0 Hz, 1H), 8.17 (dd, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 2.0 Hz, 1H), 7.64 (d, $^3J_{H,H}$ = 8.4 Hz, 1H), 4.43 (q, $^3J_{H,H}$ = 7.1 Hz, 2H), 1.42 ppm (t, $^3J_{H,H}$ = 7.1 Hz); ^{13}C NMR (151 MHz, $CDCl_3$): δ 163.7, 147.9, 133.5, 132.1, 131.5, 130.4, 126.5, 62.1, 14.2 ppm; LRMS (ESI): *m/z* (%): 252.003 [*M*+Na]$^+$ (100 %); HRMS (ESI): *m/z* calcd for $C_9H_8ClNO_4$+Na: 252.0034 [*M*+Na]$^+$; found: 252.0034. The spectroscopic data are in accordance with those reported in the literature.[64]

Synthesis of 18: The reaction conditions reported by Lou and Fu were used.[23] **17** (15.2 g, 66.3 mmol, 1.0 equiv.), **7-B(OH)$_2$-Et** (14.1 g, 73.0 mmol, 1.1 equiv.), KF·2H_2O (20.6 g, 218 mmol, 3.3 equiv.), Pd_2dba_3 (0.296 g, 0.323 mmol, 0.5 mol%), HBF_4·P(*t*-Bu)$_3$ (0.212 g, 0.731 mmol, 1.2 mol%) and THF (100 mL) were used. **18** was obtained as pale yellow crystals after filtration through a silica column (CH_2Cl_2) and recrystallization from EtOH (21.1 g, 61.6 mmol, 93 %). M.p. 66-67 °C (Lit.[65]: 64-66 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, $^4J_{H,H}$ = 1.5 Hz, 1H), 8.30 (dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H), 8.13 (d, $^3J_{H,H}$ = 8.4 Hz, 2H), 7.54 (d, $^3J_{H,H}$ = 8.0 Hz, 1H), 7.40 (d, $^3J_{H,H}$ = 8.4 Hz, 2H), 4.38-4.49 (m, 4H), 1.39-1.46 ppm (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.0, 164.2, 149.0, 141.0, 139.4, 133.1, 132.0, 131.3, 130.8, 130.0, 127.8, 125.4, 62.0, 61.2, 14.3, 14.2; LRMS (ESI): *m/z* (%): 366.095 [*M*+Na]$^+$ (100 %); HRMS (ESI): *m/z* calcd for $C_{18}H_{17}NO_6$+Na: 366.0948 [*M*+Na]$^+$; found: 366.0948. The spectroscopic data are in accordance with those reported in the literature.[65]

Synthesis of 19: **18** (17.4 g, 50.6 mmol, 1.0 equiv.) and $SnCl_2$·2H_2O (58.0 g, 257 mmol, 5.1 equiv.) was stirred in EtOAc (500 mL) at rt for 24 h. The solution was transferred to a 2 L separation funnel, and sat. $NaHCO_3$ (aq) (500 mL) was added in portions over 30 min. EtOAc was separated off, and the aqueous phase was extracted with EtOAc (4x 100 mL). The combined organic phases were washed with water (2x 500 mL), sat. NaCl (aq) (500 mL), dried with Na_2SO_4 and filtered. The solvent was removed under reduced pressure, and the residue was recrystallized from EtOH, yielding **19** as pale yellow crystals (15.2 g, 48.5 mmol, 96 %). M.p. 83-84 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, $^3J_{H,H}$ = 8.4 Hz, 2H), 7.55 (d, $^3J_{H,H}$ = 8.4 Hz, 2H), 7.50 (dd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.6 Hz, 1H), 7.45 (d, $^4J_{H,H}$ = 1.6 Hz, 1H), 7.18 (d, $^3J_{H,H}$ = 7.8 Hz, 1H), 4.35-4.44 (m, 4H), 3.86 (broadened s, 2H), 1.38-1.44 ppm (m, 6H);^{13}C NMR (101 MHz, $CDCl_3$): δ 166.5, 166.2, 143.4, 143.3, 131.1, 130.4, 130.3, 130.2, 129.8, 128.8, 119.7, 119.6, 61.1, 60.9, 14.3 ppm; LRMS (ESI): *m/z* (%): 336.121 (100) [*M*+Na]$^+$; HRMS (ESI): *m/z* calcd for $C_{18}H_{19}NO_4$+Na: 336.1206 [*M*+Na]$^+$; found: 336.1206.

General procedure for reduction of nitroanilines (GP4). Nitroaniline (1.00-10.0 mmol, 1.0 equiv.) was suspended in AcOH (0.1 M with respect to nitroaniline) in a round bottom flask. Fe (15 equiv.) was added, and the reaction mixture was flushed with Ar under stirring. When hydrogen gas had ceased to evolve (typically within 1 h), the reaction mixture was stirred at rt under Ar for 20-24 h. The contents of the reaction flask were transferred to a beaker with ice, and concentrated ammonia (2x the initial volume of AcOH) was added. The suspension was then stirred for few minutes, and filtered. The solids were washed with water, air dried, dissolved in EtOAc and filtered through Celite. The Celite was washed with EtOAc. The combined filtrate and washings were dried with Na_2SO_4 and filtered, before the solvent was removed under reduced pressure. The

residue was then recrystallized to yield the pure product. **Example (25)** (numbering scheme A, Figure 16): **1c** (3.464g, 10.0 mmol, 1.0 equiv.) was suspended in AcOH (100 mL). Fe (8.46 g, 151 mmol, 15 equiv.) was added and the reaction mixture was flushed with Argon under stirring for one hour, before it was stirred at rt under Ar for 24 h. The contents of the reaction flask were transferred to a beaker with ice (ca. 600 mL), and concentrated ammonia (200 mL) was added in portions, with stirring. When all the ammonia had been added, the suspension was filtered, and the solids were washed with water and dried in air for 18 h. The solids were suspended in EtOAc (400 mL) and filtered through Celite. The Celite was washed with several portions of EtOAc (100 mL). The combined filtrate and washings were dried with Na_2SO_4, filtered and the solvent was removed under reduced pressure. The obtained residue was recrystallized from EtOH, yielding **25** as pale brown crystals (2.75 g, 8.72 mmol, 87 %). M.p. 200-201 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50-7.52 (m, 2H, **H$^{a'}$** + **H$^{b'}$**), 7.19 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, **H$^{c'}$**), 6.89 (s, 2H, **H^{a}**), 3.92 (s, 3H, $CO_2CH'_3$), 3.88 (s, 3H, CO_2CH_3), 3.85 (s, broadened, 2H, NH'_2), 3.60 ppm (s, broadened, 4H, NH_2); ^{13}C NMR (151 MHz, $CDCl_3$): δ 167.2 (**C**O_2CH_3), 167.0 (**C**$'O_2CH_3$), 145.0 (**C^2**), 144.8 (**C$^{2'}$**), 131.4 (**C^4**), 131.3 (**C$^{4'}$**), 131.2 (**C$^{6'}$**), 123.3 (**C$^{1'}$**), 120.2 (**C$^{5'}$** or **C$^{3'}$**), 116.8 (**C$^{3'}$** or **C$^{5'}$**), 112.3 (**C^1**), 106.4 (**C^3**), 52.1 (CO_2**C**$'H_3$), 52.1 ppm (CO_2**C**H_3); LRMS (ESI): *m/z* (%): 316.129 (100) [*M*+H]$^+$; HRMS (ESI): *m/z* calcd for $C_{16}H_{18}N_3O_4$+H: 316.1292 [*M*+Na]$^+$; found: 316.1290; elemental analysis calcd (%) for $C_{16}H_{18}N_3O_4$: C 60.94, H 5.40, N 13.34; found: C 60.80, H 5.40, N 13.34.

General procedure for synthesis of Schiff base ligands 26a—26o (GP5). **19** (1.00-10.0 mmol, 1.00 equiv.) and salicylaldehyde derivative (1.05 equiv.) were mixed in EtOH (5-10 mL pr. mmol **19**). Formic acid (5-10 drops) was added and the reaction mixture was stirred at rt for 20-24 h. The precipitated solids were filtered. The solid was washed with EtOH, air dried and recrystallized from EtOH if required. **Example (26c)** (numbering scheme C, Figure 16): **19** (3.140 g, 10.03 mmol, 1.00 equiv.) and 5-nitrosalicylaldehyde (1.757 g, 10.51 mmol, 1.05 equiv.) were mixed in EtOH (100 mL). Formic acid (10 drops) was added and the reaction mixture was stirred at rt for 23 h. The precipitated solids were filtered. The solid was washed with EtOH and air dried, yielding **26c** as a pale yellow solid (4.285 g, 9.27 mmol, 92 %). M.p. 124-125 °C; ^{1}H NMR (400 MHz, C_6D_6): δ 13.30 (s, 1H, O**H**), 8.25 (d, $^3J_{H,H}$ = 8.4 Hz, 2H, **H$^{b'}$**), 8.08 (dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.6 Hz, 1H, **H^{b}**), 7.92 (d, $^4J_{H,H}$ = 1.5 Hz, 1H, **H^{a}**), 7.69 (dd, $^3J_{H,H}$ = 9.1 Hz, $^4J_{H,H}$ = 2.7 Hz, 1H, **H^{f}**), 7.58-7.59 (m, 2H, **H^{d}** + **H^{h}**), 7.16-7.18 (m, 2H, **H$^{a'}$**), 7.09 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, **H^{c}**), 6.41 (d, $^3J_{H,H}$ = 9.1 Hz, 1H, **H^{e}**), 4.25 (q, $^3J_{H,H}$ = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 4.10 (q, $^3J_{H,H}$ = 7.1 Hz, 2H, $CO_2CH'_2CH_3$), 1.13 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 0.99 ppm (t, $^3J_{H,H}$ = 7.1 Hz, 3H, $CO_2CH_2CH'_3$); ^{13}C NMR (101 MHz, C_6D_6): δ 166.1 (**C^9**), 165.8 (**C**$'O_2CH_2CH_3$), 165.6 (**C**$O_2CH_2CH_3$), 162.2 (**C^7**), 145.3 (**C^2**), 142.7 (**C$^{1'}$**), 141.0 (**C^1**), 140.3 (**C^{12}**), 131.9 (**C^4**), 131.1 (**C^6**), 130.9 (**C$^{4'}$**), 130.0 (**C$^{2'}$** or **C$^{3'}$**), 129.9 (**C$^{2'}$** or **C$^{3'}$**), 129.0 (**C^{13}**), 128.8 (**C^5**), 128.6 (**C^{11}**), 120.2 (**C^3**), 118.0 (**C^8**), 117.9 (**C^{10}**), 61.6 (CO_2**C**H_2CH_3), 61.1 (CO_2**C**$'H_2CH_3$), 14.4 (CO_2CH_2**C**H_3), 14.2 ppm (CO_2CH_2**C**$'H_3$); ^{15}N{^{1}H} NMR (600 MHz, C_6D_6): δ – 12.8 (**N**O_2), – 86.6 ppm (CH=**N**); LRMS (ESI): *m/z* (%): 485.132 (100) [*M*+Na]$^+$; HRMS (ESI): *m/z* calcd for $C_{25}H_{22}N_2O_7$+Na: 485.1319 [*M*+Na]$^+$; found: 485.1319.

General procedure for synthesis of Zn complexes 26a-Zn—26o-Zn (GP6). Schiff base ligand (0.50-1.00 mmol, 1.0 equiv.) was suspended in MeOH (10 mL pr. mmol ligand). NEt_3 (2.0 equiv.), followed by $Zn(OAc)_2{\cdot}2H_2O$ (0.5 equiv.), was added. The reaction mixture was stirred at room temperature for 20-24 h, after which it was filtered. The solid was washed with MeOH, air dried and recrystallized (if required) to yield the Zn complex. **Example (26c-Zn)** (numbering scheme C, Figure 16): **26c** (0.464 g, 1.00 mmol, 1.0 equiv.) was suspended in MeOH (10 mL). NEt_3 (0.28 mL, 2.00 mmol, 2.0 equiv.) and then $Zn(OAc)_2{\cdot}2H_2O$ (0.111 g, 0.50 mmol, 0.5 equiv.) were added. The reaction mixture was stirred at room temperature for 24 h, after which it was filtered. The solid was washed with MeOH and air dried to yield **26c-Zn** as a pale yellow solid (0.450 g, 0.455 mmol, 91 %). M.p. 258-259 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.56 (broadened s, 2H, **H^{d}**), 8.27 (d, $^4J_{H,H}$ = 2.5 Hz, 2H, **H^{h}**), 7.83 (dd, $^3J_{H,H}$ = 9.5 Hz, $^4J_{H,H}$ = 2.9 Hz, 2H, **H^{f}**), 7.80 (d, $^3J_{H,H}$ = 8.2 Hz, 4H, **H$^{b'}$**), 7.74 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, **H^{b}**), 7.44-7.46 (m, 6H, **H^{c}** + **H$^{a'}$**), 7.40 (s, 2H, **H^{a}**), 6.09 (d, $^3J_{H,H}$ = 9.3 Hz, 2H, **H^{e}**), 4.24-4.28 (m, 8H, $CO_2CH_2CH_3$ + $CO_2CH'_2CH_3$), 1.26-1.31 ppm (m, 12H, $CO_2CH_2CH_3$ + $CO_2CH_2CH'_3$); ^{13}C NMR (151 MHz, DMSO-d_6): δ 175.7 (**C^9**), 172.1 (**C^7**), 165.3 (**C**$'O_2CH_2CH_3$), 164.6 (**C**$O_2CH_2CH_3$), 148.1 (**C^2**), 141.7 (**C$^{1'}$**), 137.6 (**C^1**), 134.0 (**C^{12}**), 133.6 (**C^{13}**), 130.5 (**C^6**), 130.0 (**C$^{2'}$**), 129.9 (**C^4**), 129.0 (**C$^{3'}$**), 128.8 (**C^{11}**), 127.0 (**C^5**), 124.1 (**C^3**), 122.8 (**C^{10}**), 117.7 (**C^8**), 60.9 (CO_2**C**H_2CH_3 or CO_2**C**$'H_2CH_3$), 60.7 (CO_2**C**H_2CH_3 or CO_2**C**$'H_2CH_3$), 14.0 (CO_2CH_2**C**H_3 or CO_2CH_2**C**$'H_3$), 13.9 ppm (CO_2CH_2**C**H_3 or CO_2CH_2**C**$'H_3$). One of the resonances (**C$^{4'}$**) could not be observed in DMSO-d_6. Several of the resonances were broadened. ^{15}N{^{1}H} NMR (600 MHz, DMSO-d_6): δ – 10.2 (***N***O_2), – 120.9 ppm (***N***-Zn); ^{15}N{^{1}H} NMR (600 MHz, C_6D_6): δ – 13.1 (**N**O_2), – 145.1 ppm (**N**-Zn). For more NMR data in other solvents, see ESI. LRMS (ESI): *m/z* (%): 485.132 (100) [*L*+Na]$^+$, 1009.188 (66) [*M*+Na]$^+$; HRMS (ESI): *m/z* calcd for $C_{50}H_{42}N_4O_{14}Zn$+Na: 1009.1881 [*M*+Na]$^+$; found: 1009.1886; elemental analysis calcd (%) for $C_{50}H_{42}N_4O_{14}Zn$: C 60.77, H 4.28, N 5.67; found: C 60.54, H 4.26, N 5.62.

General procedure for synthesis of Schiff base ligands 27a—27d and 28a—28e (GP7): Amine **20a** or **20b** (1.00 mmol, 1.0 eq.) and salicylaldehyde derivative (2.2 equiv.) were mixed in EtOH (5 mL pr. mmol amine). Formic acid (5 drops) was added and the suspension was refluxed for 24h. After cooling to rt, the suspension was filtered. The solids were washed with EtOH, air dried and recrystallized if required, yielding the Schiff base ligand. **Example (28e)** (numbering scheme D, Figure 16): **20b** (0.391 g, 1.00 mmol, 1.0 eq.) and 5-bromosalicylaldehyde (0.444 g, 2.21 mmol, 2.2 equiv.) were mixed in EtOH (5 mL). Formic acid (5 drops) was added and the suspension was refluxed for 24h. After cooling to rt, the suspension was filtered. The solids were washed with EtOH, air dried and recrystallized from MeCN, yielding **28e** as orange crystals (0.585 g, 0.774 mmol, 77 %). M.p: 175-176 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 12.44 (broadened s, 1H, O**H**), 12.08 (broadened s, 1H, O**H**), 8.39 (s, 1H, **H$^{d'}$**), 8.04 (dd, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.6 Hz, 1H, **H$^{b'}$**), 7.97 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, **H$^{b''}$**), 7.84 (d, $^4J_{H,H}$ = 1.5 Hz, 1H, **H$^{a'}$**), 7.64 (s, 1H, **H^{c}**), 7.53 (d, $^3J_{H,H}$ = 7.9 Hz, **H$^{c'}$**), 7.41-7.44 (m, 3H, **H$^{f'}$** + **H$^{a''}$**), 7.31 (d, $^4J_{H,H}$ = 2.5 Hz, 1H, **H$^{g'}$**), 7.26-7.28 (m, 2H, **H^{a}** + **H^{e}**), 7.19 (d, $^4J_{H,H}$ = 1.3 Hz, 1H, **H^{b}**), 6.82 (d, $^3J_{H,H}$ = 8.8 Hz, 1H, **H$^{e'}$**), 6.64 (d, $^3J_{H,H}$ = 8.8 Hz, 1H, **H^{d}**), 6.62 (d, $^4J_{H,H}$ = 2.4 Hz, 1H, **H^{f}**), 3.96 (s, 3H, $CO_2CH'_3$), 3.89 (s, 3H, $CO_2CH''_3$), 2.46 ppm (s, 3H, CH_3); ^{13}C NMR (201 MHz, $CDCl_3$): δ 166.8 (**C**$''O_2CH_3$), 166.5 (**C^7**), 166.2 (**C**$'O_2CH_3$), 162.0 (**C$^{7'}$**), 159.8 (**C$^{9'}$**), 159.6 (**C^9**), 146.1 (**C$^{2'}$**), 144.0 (**C$^{1''}$**), 142.8 (**C^2**), 138.8 (**C$^{1'}$**), 136.2 (**C^5**), 136.2 (**C$^{11'}$**), 135.7 (**C^{11}**), 134.4 (**C$^{13'}$**), 133.7 (**C^{13}**), 133.5 (**C^3**), 132.0 (**C^1**), 132.0 (**C^4**), 131.3 (**C$^{6'}$**), 131.1 (**C$^{4'}$**), 131.0 (**C^6**), 129.7 (**C$^{3''}$**), 129.6 (**C$^{2''}$**), 128.7 (**C$^{4''}$**), 128.3 (**C$^{5'}$**), 120.4 (**C$^{12'}$**), 119.6 (**C^{12}**), 119.1 (**C$^{10'}$**), 119.0 (**C^{10}** or **C$^{3'}$**), 118.9 (**C^{10}** or **C$^{3'}$**), 110.7 (**C$^{8'}$**), 110.3 (**C^8**), 52.4 (CO_2**C**$'H_3$), 52.1 (CO_2**C**$''H_3$), 20.9 ppm (**C**H_3); LRMS (ESI): *m/z* (%): 777.021 (50) [*M*+Na]$^+$; HRMS (ESI): *m/z* calcd for $C_{37}H_{28}Br_2N_2O_6$+Na: 777.0206 [*M*+Na]$^+$; found: 777.0207.

General procedure for synthesis of Zn complexes 27a-Zn, 28a-Zn and 28e-Zn (GP8): Schiff base ligand (0.50 mmol, 1.0 eq.) was suspended in MeOH (10 mL pr. mmol Schiff base). NEt_3 (3.6 equiv.), followed by $Zn(OAc)_2{\cdot}2H_2O$ (1.1 equiv.), was added. The resulting suspension was stirred at rt for 20 h. The solids were filtered, washed with MeOH and dried at 100 °C, yielding the Zn complex. **Example (28e-Zn)** (numbering scheme D, Figure 16): **28e** (0.376 g, 0.49 mmol, 1.0 eq.) was suspended in MeOH (5 mL). NEt_3 (0.25 mL, 1.8 mmol, 3.6 equiv.) and then $Zn(OAc)_2{\cdot}2H_2O$ (0.120 g, 0.55 mmol, 1.1 equiv.) were added. The resulting suspension was stirred at rt for 20 h. The solids were filtered, washed with MeOH and dried at 100 °C, yielding **28e-Zn** as a pale yellow solid (0.248 g, 0.302 mmol, 61 %). M.p: 295-296 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.32 (s,

1H, **H$^{d'}$**), 7.92 (dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.7 Hz, 1H, **H$^{b'}$**), 7.88 (s, 1H, **H^{d}**), 7.84 (d, $^3J_{H,H}$ = 8.4 Hz, 2H, **H$^{b''}$**), 7.61 (d, $^3J_{H,H}$ = 8.4 Hz, 2H, **H$^{a''}$**), 7.60 (d, $^4J_{H,H}$ = 1.7 Hz, 1H, **H$^{a'}$**), 7.55 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, **H$^{c'}$**), 7.43 (d, $^4J_{H,H}$ = 2.8 Hz, 1H, **H$^{h'}$**), 7.29 (dd, $^3J_{H,H}$ = 9.1 Hz, $^4J_{H,H}$ = 2.8 Hz, 1H, **H$^{f'}$**), 7.27 (d, $^4J_{H,H}$ = 1.4 Hz, 1H, **H^{a}**), 7.14 (dd, $^3J_{H,H}$ = 9.1 Hz, $^4J_{H,H}$ = 2.8 Hz, 1H, **H^{f}**), 7.12 (d, $^4J_{H,H}$ = 1.4 Hz, 1H, **H^{b}**), 7.00 (d, $^4J_{H,H}$ = 2.8 Hz, 1H, **H^{h}**), 6.72 (d, $^3J_{H,H}$ = 9.1 Hz, 1H, **H$^{e'}$**), 6.47 (d, $^3J_{H,H}$ = 9.1 Hz, 1H, **H^{e}**), 3.87 (s, 3H, $CO_2C\mathbf{H'}_3$), 3.80 (s, 3H, $CO_2C\mathbf{H''}_3$), 2.34 ppm (s, 3H, $C\mathbf{H}_3$); ^{13}C NMR (151 MHz, DMSO-d_6): δ 174.0 (**C^{7}**), 170.3 (**C$^{9'}$**), 170.1 (**C^{9}**), 167.7 (**C$^{7'}$**), 165.9 (**C''**O_2CH_3), 165.6 (**C'**O_2CH_3), 147.7 (**C$^{2'}$**), 143.6 (**C$^{1''}$**), 143.5 (**C^{2}**), 137.6 (**C$^{1'}$**), 137.3 (**C$^{13'}$**), 137.1 (**C^{11}**), 136.9 (**C$^{11'}$** + **C^{13}**), 136.2 (**C^{5}**), 135.3 (**C^{3}**), 132.2 (**C^{1}**), 131.9 (**C^{4}**), 131.4 (**C^{6}**), 130.8 (**C$^{6'}$**), 130.3 (**C$^{2''}$**), 130.0 (**C$^{4'}$**), 129.0 (**C$^{3''}$**), 127.8 (**C$^{4''}$**), 126.9 (**C$^{5'}$**), 125.4 (**C$^{10'}$**), 124.7 (**C^{10}**), 123.3 (**C$^{3'}$**), 120.7 (**C^{8}**), 119.8 (**C$^{8'}$**), 103.0 (**C$^{12'}$**), 102.5 (**C^{12}**), 52.4 ($CO_2\mathbf{C'}H_3$), 52.1 ($CO_2\mathbf{C''}H_3$), 20.2 ppm ($C\mathbf{H}_3$); LRMS (ESI): *m/z* (%): 838.934 (39) [*M*+Na]$^+$; HRMS (ESI): *m/z* calcd for $C_{37}H_{26}Br_2N_2O_6Zn$+Na: 838.9341 [*M*+Na]$^+$; found: 838.9340; elemental analysis calcd (%) for $C_{37}H_{26}Br_2N_2O_6Zn$: C 54.21, H 3.20, N 3.42; found: C 53.95, H 3.18, N 3.39.

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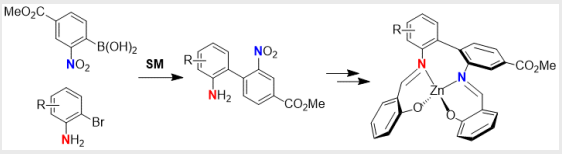

The Suzuki-Miyaura (SM) reaction is used as a key step for the synthesis of 2-aminobiphenyls and 2,2'-diaminobiphenyls, which in turn can be utilized to make Schiff base complexes of Zn. Special emphasis is on the cross coupling between 2-bromoanilines and a 2-nitro substituted arylboronic acid, for which there are little existing precedence for.

Suzuki-Miyaura reaction, Zn complexes

K. T. Hylland, S. Øien-Ødegaard, M. Tilset**

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The Suzuki-Miyaura cross coupling as the key step for the synthesis of 2-aminobiphenyls and 2,2'-diaminobiphenyls: applications for the synthesis of Schiff base complexes of Zn.