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Radical arylation of anilines and pyrroles via aryldiazotates

Josefa Hofmann,[a] Eva Gans,[a] Timothy Clark[b] and Markus R. Heinrich*[a]

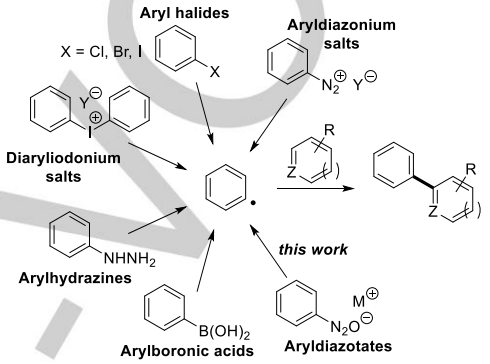
Dedication ((optional))

Abstract: The radical arylation of anilines and pyrroles can be achieved under transition metal- and catalyst-free conditions using aryldiazotates in strongly alkaline aqueous solutions. The aryl diazotates act as protected diazonium ions, which do not undergo azo coupling with electron-rich aromatic substrates, but are still able to serve as sources for aryl radicals at slightly elevated temperatures. Based on an improved preparation of aryldiazotates in aqueous solution, homolytic aromatic substitutions of anilines and pyrroles can now be conducted with good overall yields and with high regio-selectivity. Moreover, further mechanistic insights were obtained and could be supported through calculations.

Introduction

Homo- and heterobiaryls are present as substructures in many natural products, pharmaceuticals as well as in compounds for diverse other applications including optics and material chemistry.[1] Besides the widely used Suzuki cross-coupling approach,[2] a variety of aryl-aryl coupling reactions based on aromatic C-H activation have recently been developed.[3] A third option for the synthesis of biaryls are radical arylations,[4] which have raised much interest over the last years, especially through the manifold advances in the field of photoredox catalysis.[5] Although such radical arylations are formally comparable with C-H functionalizations, and relatively simple starting materials can thus be employed, the insufficient regioselectivity of the radical attack on most substituted benzenes represents a major drawback.[6] Notable exceptions are arylations of anilines, phenols and nitrobenzenes, which can be conducted with good to high regioselectivity.[7]

Heteroarenes, on the other hand, are in most cases more effective radical acceptors than substituted benzenes,[8] and high selectivities for particular positions on the aromatic core are often observed.[4c-e] However, the reaction conditions may need to be chosen more carefully, as rearomatization following the aryl radical attack is not as straightforward for heterocyclic aromatic systems as it is for benzene and its derivatives.[9] Scheme 1 gives a general overview over radical arylations of arenes and heteroarenes, mainly with regard to the precursors that have recently been used for the generation of the aryl radicals.



Scheme 1. Radical arylations of arenes and heteroarenes.

Among the radical precursors, aryldiazonium salts,[10] which may also be generated *in situ*,[11] as well as aryl chlorides, bromides and iodides[12] are the most commonly used. This variety has recently been complemented by arylhydrazines,[13] diaryliodonium salts[14] and arylboronic acids.[15] Regarding aryldiazonium salts in particular, a limitation exists in the way that arylations of strongly nucleophilic arenes (e.g. anilines, phenolates) cannot directly be carried out, as side reactions such as azo coupling or triazene formation would then prevail.[16],[17] A suitable strategy to circumvent this difficulty is the use of protected diazonium ions, which however need to retain the ability to serve as precursors for aryl radicals. Known examples are arylazo sulfides,[18] which even allow the radical arylation of strongly nucleophilic phenolates. The arylation of anilines had remained unknown under metal-free, basic Gomberg-Bachmann type conditions for a long time, but it could recently be achieved with aryldiazotates.[19,20] In comparison to aryldiazo anhydrides, which are the generally accepted intermediates in classical Gomberg-Bachmann reactions,[21] aryldiazotates show a much better stability towards an attack of nucleophiles.[22] Also very recently, an *ortho*-selective arylation of anilines proceeding via benzyne intermediates has been reported by Daugulis.[23]

In this article, we now give a comprehensive overview over the applicability of aryldiazotates in transition metal- and catalyst-free radical arylations of arenes and heteroarenes including results from computational studies.

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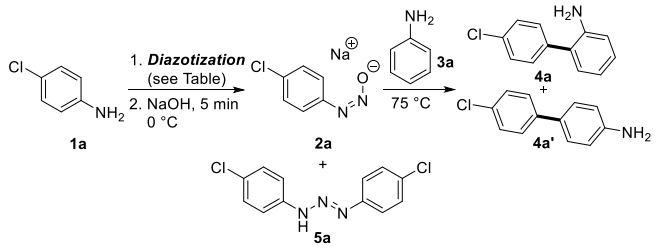
Results and Discussion

Our investigations started with a preliminary study on optimized conditions for the preparation of aryldiazotate **2a** from 4-chloroaniline (**1a**), which is conducted in two steps via the corresponding aryldiazonium chloride (Table 1). To monitor the effect of different conditions in the diazotization step, the diazotate **2a** was subsequently submitted to the known arylation of aniline (**3a**) to give 2-aminobiphenyl **4a** along with smaller amounts of its regioisomer **4a'**.[19] Through several variations, a procedure providing the aryldiazotate **2a** as a clear and almost colorless aqueous solution could be established.

Table 1. Optimization of reaction conditions for diazotization.



Entry	$NaNO_2$ (equiv.)	Variation of general reaction conditions[a]	Yield[b] **4a**/**4a'** (%/%)	Yield[b] **5a** (%)
1	1.05	-	50/16	< 5
2	1.10	-	43/17	15
3	1.30	-	33/11	15
4	1.30	Urea added (3 mmol)	42/16	10
5	1.05	3 N HCl (20 mL)	n.d.[d]	6
6	1.05	1 M H_2SO_4 (15 mL)	34/11	12
7	1.05	Reverse addition	34/12	10
8	2.00[c]	-	19/7	10

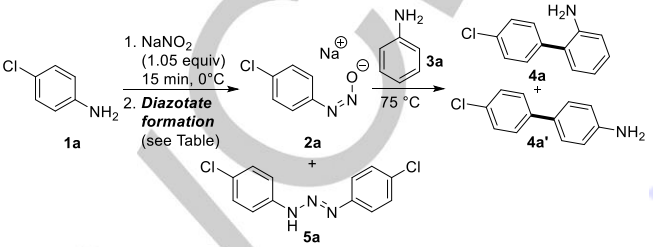
[a] A degassed solution of sodium nitrite (10.5-13.0 mmol, see Table) in water (5 mL) was added dropwise to an ice-cooled degassed solution of 4-chloroaniline (10.0 mmol) in hydrochloric acid (1.5 N, 20 mL) under nitrogen over a period of 15 min. The clear solution was stirred for 15 more minutes at 0 °C. [b] Yield determined by ^{1}H NMR spectroscopy using 1,4-dimethyl terephtalate and 1,3,5-trimethoxybenzene as internal standards. [c] Diazotization with NO (2 equiv.) under air in a 250 mL round bottom flask equipped with a balloon for pressure equilibration . [d] Complex product mixture formed.

Although one might assume that a larger excess of sodium nitrite should lead to a reliable and full diazotization of **1a** (entries 1-3), this variation was accompanied by an increased formation of the undesired triazene **5a**. It thus appears likely that an excess of nitrite ions can cause a reduction of the aromatic diazonium ions back to the aniline **1a** under the strongly basic conditions required for the consecutive diazotate formation.[24] Albeit the addition of urea,[25] the use of more concentrated hydrochloric acid and the change to sulfuric acid led to less triazene **5a**, these modifications were not able to increase the overall result concerning the biphenyls **4a** and **4a**' (entries 5-7). Further attempts using an inverse addition of the reagents (entry 8)[26] or a recently developed diazotization with nitrogen oxides (entry 8) were not successful either.[27]

Regarding other possible side-products of overall reaction sequence, it is remarkable that unsymmetrical triazenes, as they could be formed from diazotized 4-chloroaniline and aniline (**3**), were not detected. This indicates that the protective character of the diazotate **2a** is indeed strong enough to prevent the attack of nucleophiles such as aromatic amines.

In the series of experiments, the diazotate formation was investigated using the previously optimized conditions for diazotization (Table 2). In the diazotate forming step, the cooled aqueous solution of the diazonium salt is typically added dropwise to an as well cooled aqueous solution of a strong base.

Table 2. Optimization of reaction conditions for diazotate formation.



Entry	Atmos-phere	Variation of general reaction conditions[a]	Yield[b] **4a**/**4a'** (%/%)[b]	Yield[b] **5a** (%)
1	Ar	-	50/16	<5
2	N_2	-	48/13	<5
3	Air	-	44/15	10
4	Air	6 N NaOH (2 mL)[c]	48/15	11
5	N_2	Addition in one batch	30/13	12
6	N_2	0.5 min	38/12	10
7	Ar	6 N NaOH (3 mL)	45/11	9
8	Ar	4 N LiOH (3 mL)	39/12	13
9	Ar	4 N KOH (3 mL)	41/15	10
10	Ar	4 N CsOH (3 mL)	34/12	13

[a] An aliquot of the 0.4 M 4-chlorophenyldiazonium chloride solution (2.00 mmol 5.00 mL) was added to a pre-cooled and vigorously stirred aqueous solution of sodium hydroxide (4 N, 3 mL) under argon. The homogeneous solution was stirred for five minutes in total. [b] Yield determined by ^{1}H NMR spectroscopy using 1,4-dimethyl terephthalate and 1,3,5-trimethoxybenzene as internal standards. [c] CH_3CN (1 mL) added.

The best results considering desired biaryl and undesired triazene formation were obtained under argon (entries 1-3). Further attempts to improve the yields of **4a**/**4a**' under nitrogen or air through a variation of the reaction conditions remained unsuccessful (entries 4-6). The use of more concentrated sodium hydroxide (entry 7) or the change to other alkali metal bases (entries 8-10) did not lead to improvements either.

In general, an effective preparation of the diazotate **2a** can easily be monitored as a clear and colorless aqueous solution of **2a** is then typically obtained. In less successful attempts, the formation of precipitates and an emergence of yellow color indicate the formation of undesired side-products such as diazo anhydrides.[28]

With optimized conditions now available, we re-evaluated the synthesis of a number of 2-aminobiphenyls **4**. A comparison of the yields obtained from the previous protocol[19] and the newly developed procedure is summarized in Table 3. In this study, all 2-aminobiphenyls could be prepared in better yields than before. The most significant improvements were determined for biphenyls **4c** and **4e** (entries 3 and 5), which were isolated in yields increased by 21% and 24%, respectively. The smallest gain of 6% was observed for 4,5'-difluorobiphenyl-2-amine (**4d**).

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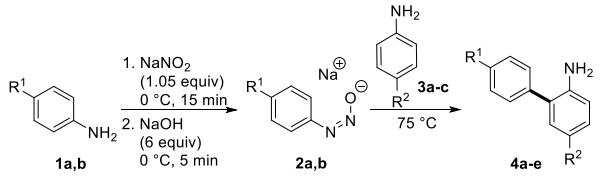
Table 3. Arylation of anilines with aryldiazotates under optimized conditions.

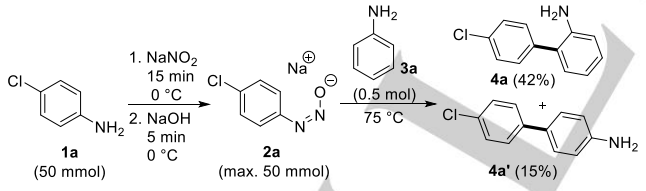


Entry	Diazotate[a] **2**: R^1 =	Aniline **3**: R^2 =	Yield (this work)[b] **4** (%)	Yield (ref. 19)[b] **4** (%)
1	**2a**: Cl	**3a**: H	**4a** [**4a'**]: 48 [8][c]	**4a** [**4a'**]: 35 [7][c]
2	**2a**: Cl	**3b**: F	**4b**: 53	**4b**: 41
3	**2a**: Cl	**3c**: Cl	**4c**: 60	**4c**: 39
4	**2b**: F	**3b**: F	**4d**: 48	**4d**: 42
5	**2b**: F	**3c**: Cl	**4e**: 58	**4e**: 34

[a] To a vigorously stirred aniline (20.0 mmol) at 75 °C under argon was added dropwise the previously prepared solution of the aryl diazotate (2.00 mmol, 8.00 mL) over a period of ten minutes. After the addition was complete, the mixture was left to stir for 20 more minutes. [b] Yield after purification by column chromatography. [c] **4a**': regioisomer of **4a** (see Table 3).

Moreover, and as a result of the optimization, triazenes could no longer be detected by ^{1}H NMR spectroscopy as by-products in the crude reaction mixtures, which indicates that they were formed in yields lower than 5%. As easily removable, volatile halobenzenes are now the only by-products from arylations with diazotate **2a** and **2b**, the final purification of the 2-aminobiphenyl **4** simplifies and just requires separation from the excess of aniline (see Supporting Information).

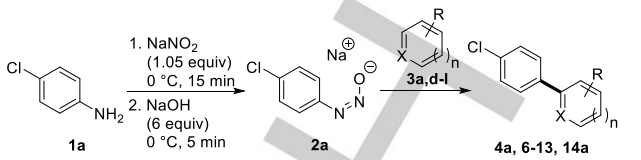
To further underline the usefulness of the diazotate-based arylation for preparative purposes, a reaction on a 50 mmol scale was conducted (Scheme 2). This experiment gave **4a** (4.31 g) and its regioisomer **4a'** (1.52 g) in a total yield of 57%, whereat we do not yet have an explanation for the slight change in product distribution (c.f. Table 3, entry 1). After work-up, 92% of the remaining excess of aniline (**3a**) could be recovered through distillation. 4'-Chlorobiphenyl-2-amine (**4a**), which is currently prepared on large industrial scale via a Suzuki aryl-aryl coupling reaction, represents an important building block for the synthesis of the fungizide Boscalid.[29]

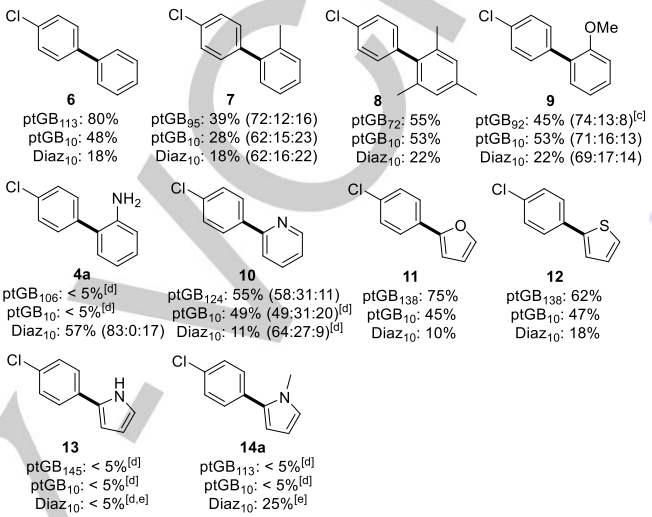


Scheme 2. Large scale experiment.

In the next stage, the diazotate-based radical arylation was evaluated in combination with other substituted benzenes and heterocycles (Table 4). In addition, the diazotate variant was compared to the established phase-transfer Gomberg-Bachmann conditions developed by Gokel (ptGB).[6b] As this method uses a large excess of radical acceptor of around 100 equivalents (excess given as subscript in Table 4), and to allow better comparison, the ptGB protocol was repeated with same excess of arene or heteroarene as it is typically used in diazotate method, namely 10 equivalents (labeled as $ptGB_{10}$). The diazotate method was conducted under conditions identical to those applied for the experiments of Table 3 (labeled as $Diaz_{10}$).

Table 4. Comparison of arylation with diazotates to phase-transfer Gomberg-Bachmann conditions.[a],[b]





[a] $ptGB_{72\text{-}138}$: Yields from phase-transfer Gomberg-Bachmann as reported by Gokel et al.[6b] Biaryls **4a**, **13** and **14a** (not reported in ref. [6b]) synthesized according to this reference. Subscript number indicates equivalents of radical acceptor **3a,d-l**. $ptGB_{10}$: Repetition of ptGB reaction under conditions of ref. [6b], but with 10 equivalents of radical acceptor. $Diaz_{10}$: Diazotate-based arylation according to conditions used in Table 3. Ratios given in brackets indicate the regioisomeric distribution (*ortho*:*meta*:*para*). [b] For $ptGB_{10}$ and $Diaz_{10}$: Yields determined after column chromatography. [c] Ratio does not sum up to 100 in ref. 6b. [d] Yields determined by ^{1}H NMR using 1,4-dimethyl terephthalate and 1,3,5-trimethoxybenzene as internal standards. [e] Diarylazo compound formed as main product.

An inspection of the results summarized in Table 4 reveals that the diazotate method is not beneficial for benzene (**3d**), toluene (**3e**), mesitylene (**3f**) and anisole (**3g**), which were converted to biaryls **6**-**9**. Interestingly, some ptGB reactions showed a strong dependence on the excess of radical acceptor (biphenyls **6** and **7**), but almost no difference was observed for mesitylene and anisole when lowering the excess of radical from 72 or 92 to 10 equivalents (biphenyls **8** and **9**). Starting from aniline (**3a**), only the diazotate method is able to give useful yield of biphenyl **4a**.

Among the heterocyclic substrates, the arylation of pyridine (**3h**) turned out as inefficient when following the diazotate protocol. Under ptGB conditions, biaryl **10** can be prepared in useful yields with an only small dependence on the excess of pyridine. Experiments with furan (**3i**) and thiophene (**3j**) gave slightly better yields of biaryls **11** and **12** under the diazotate conditions, which are however far from competitive to the ptGB protocol. In the case of pyrrole (**3k**), all methods failed to give the desired biaryl **13** in a detectable yield, which is most probably due to an insufficient stability of diazotate **2a** towards pyrrole as a nucleophile.

For 1-methylpyrrol (**3l**), the diazotate variant appears as superior to the ptGB conditions. However, the biaryl **14a** (25%) was

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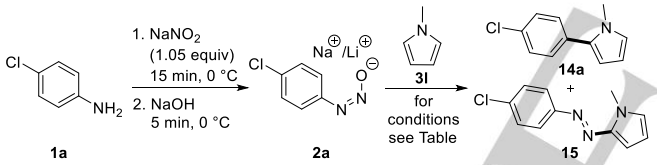
isolated along with 44% of the corresponding diarylazo compound in this initial experiment.

Based on these results and the assumption that 1-methylpyrrol (**3l**) could be suitable for a diazotate-based arylation, attempts to optimize the reaction conditions were made. The major aim thereby was to avoid the formation of azo compound **15** (Table 5). An previous examination of the existing radical transformations revealed that reactions using aryldiazonium ions as radical sources or intermediates, such as the methods developed by Felpin[11b], Carrillo[10b] and Maulide[10c] are limited to pyrroles bearing an electron-withdrawing group on the nitrogen atom due to competing azo coupling.[30] A related silver nitrite assisted arylation by Gowrisankar and Seayad,[11c] of which the mechanism is yet unknown, might not proceed via free diazonium ions as electron-rich pyrroles are tolerated. Alternatively, as shown by König,[12g] aryl bromides can be employed as radical sources which are insensitive towards azo coupling as side reaction.

In our study, the optimized conditions for the preparation of 4-chlorophenyldiazotate (**2a**) from 4-chloroaniline (**1a**) (see Tables 1 and 2) were also used as a basis for the arylation of 1-methylpyrrole (**3l**). An overview is shown in Table 5. Control experiments had confirmed that a pre-formation of diazotate **2a** is required for the successful synthesis of **14a** as the direct addition of the diazonium salt to a mixture of **3l** and base only provided the azo compound **15**.

Table 5. Arylation of 1-methylpyrrole (**3l**) with 4-chlorophenyldiazotate (**2a**): optimization of reaction conditions.



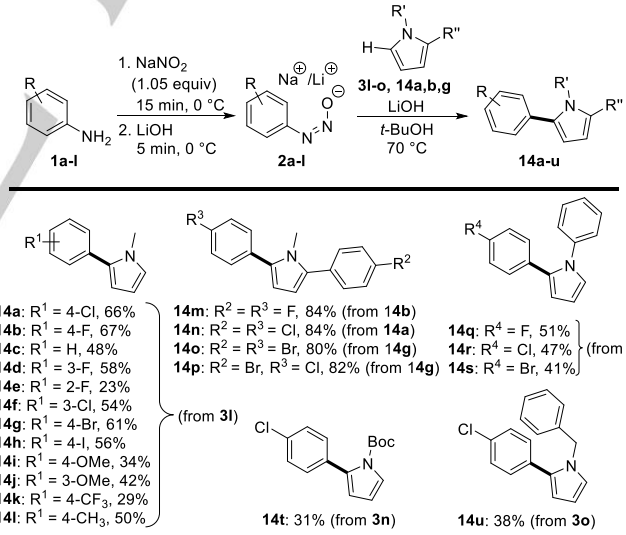
Entry	Temp (°C)	Variation of general reaction conditions[a]	Yield[b] **14a** (%)	Yield[b] **15** (%)
1	rt	--	25%	44%
2	rt	4N NaOH (3 mL)	21%	7%
3	50	4N NaOH (3 mL)	40%	34%
4	70	4N NaOH (3 mL)	50%	8%
5	80	4N NaOH (3 mL)	42%	6%
6	100	4N NaOH (3 mL)	34%	7%
7	70	4N NaOH (3 mL)[c]	50%	7%
8	70	8N NaOH (3 mL)	50%	8%
9	70	4N NaOH (3 mL), under air	42%	7%
10	70	1.5N TBAH (6 mL)	-	-
11	70	NaOH (12 mmol)[c,d]	54%	-
12	70	NaOH (12 mmol)[d,e]	55%	-
13	70	NaOtBu (12 mmol)[d]	52%	-
14	70	NaOtBu/NaOH (6/6 mmol)[d]	53%	-
15	70	LiOH (12 mmol)[d,f]	66%	-
16	70	KOH (12 mmol)[d,f]	58%	-
17	70	CsOH (12 mmol)[d,f]	59%	-

[a] General conditions: To 1-methylpyrrole (**3l**) (20.0 mmol) under argon was added dropwise the previously prepared solution of the aryldiazotate **2a** (max. 2.00 mmol, 8.00 mL) over a period of seven minutes. After the addition was complete, the mixture was left to stir for 23 more minutes. [b] Yield determined by ^{1}H NMR spectroscopy using 1,4-dimethyl terephthalate and 1,3,5-trimethoxy-benzene as internal standards. [c] 20 Equiv. of **3l**. [d] *t*BuOH (3 mL) added. [e] 18-Crown-6 (5 mol%) added. [f] Base also used in diazotate formation instead of NaOH.

The large amount of azo compound **15** (44%) obtained in the initial attempt revealed that the excess of base remaining from generation of the diazotate **2a** is not sufficient to maintain the protection of the diazonium ion in the aryl-aryl coupling step (entry 1). Subsequent experiments with additional sodium hydroxide gave lower amounts of **15** and led to an optimum temperature of 70 °C (entries 2-6), which is comparable to results from earlier studies on the arylation of aniline.[19] Increases in the amount of pyrrole **3l**, base and conduction of the reaction under air, which could facilitate rearomatization,[31] did not lead to improvements (entries 7-9). Whereas the use of tetra-*n*-butyl ammonium hydroxide resulted in a complete failure (entry 10), the change to sodium hydroxide in *tert*-butanol as main solvent led to increases in yield (entries 11-14) and a full suppression of **15**.[32] Finally, the yield of **14a** could be improved to 66% through a change of the base to lithium hydroxide in the diazotate formation and the aryl-aryl coupling step (entries 15-17). A control experiment, in which the diazotate formation was performed with sodium hydroxide and the arylation under addition of lithium hydroxide gave **14a** in a lower yield of 59%.

The optimized conditions (Table 5, entry 15) were next applied to determine scope and limitations of the arylation procedure (Table 6). Starting from 1-methylpyrrole (**3l**), synthetically useful yields (based on anilines **1a-l**) were obtained for most substitution patterns on the aryldiazotate with the exception of the 2-fluoro, 4-methoxy and 4-trifluoromethyl substituents (c.f. **14e**, **14i**, **14k**).

Table 6. Arylation of pyrroles with aryldiazotates: substrate scope.



A variation of the pyrrole unit showed that 2-aryl-1-methylpyrroles **14a,b,g** are excellent acceptors and thus making the new methodology a valuable tool for the preparation of symmetrical and unsymmetrical 2,5-diarylpyrroles such as **14m-p**.[33] The slightly lower yields of biaryls **14q-s** and **14t** obtained from 1-phenylpyrrol (**3m**) and 1-Boc-pyrrole (**3n**) can be explained by the fact that the aryl group, and even more the *tert*-butyloxycarbonyl group, act as electron acceptors. Beneficially, on the other hand, arylation of 1-phenylpyrrol selectively occurred on the pyrrole unit.[34] When using 1-benzylpyrrole (**3o**) as radical acceptor to

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give **14u**, the arylation is to some extent complicated by hydrogen abstraction from the benzylic position.[4c] Reactions with unsubstituted pyrrole or indole under comparable conditions furnished four azo compounds (c.f. compound **15**, Table 5) in 85% to quantitative yield, thus showing that diazotates –when combined with pyrrole or indole – may also be used for a yet unknown, highly efficient azo coupling reaction (see Supporting Information).[35]

Regarding radical arylation, Figure 1 depicts the dependency of the product distribution on the excess of 1-methylpyrrole (**3l**). With a lower excess of only 2.5 equivalents, biaryl **14a** could still be obtained in 49% yield. A 1:1 ratio of **2a**:**3l** provided almost equal amounts of **14a** (25%) and the diarylated pyrrole **14n** (26%).

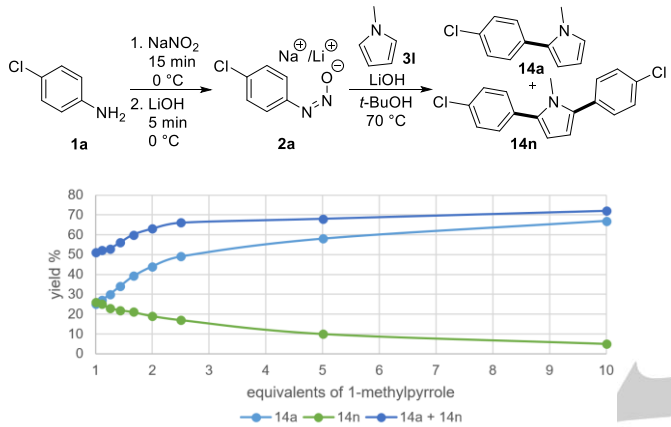
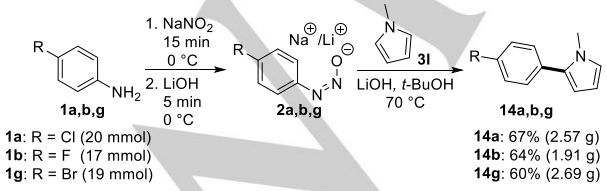


Figure 1. Variation of equivalents of 1-methylpyrrole (**3l**).

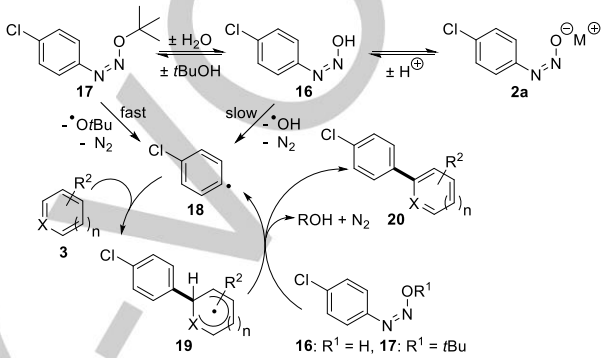
These results show that radical arylation reactions can so far not compete with modern Pd-catalyzed C-H functionalizations of heteroarenes, even if good radical acceptors such as anilines and pyrroles are employed. Related Pd-catalyzed transformations are able to provide good to high yields when the reactants are used in a 1:1 ratio.[36] For the arylation of anilines, which can be considered as slightly less efficient aryl radical acceptors than 1-methylpyrrole (**3l**), the results of Table 3 suggest that an excess of five to ten equivalents of aniline per diazonium salt is necessary to obtain aminobiphenyls in useful yields of around 50%.

Reactions on a larger, approximately 10-fold reaction scale were also conducted with 1-methylpyrrole (**3l**) to underline the usefulness of the methodology for preparative purposes (Scheme 3). The desired biaryls **14a,b,g** were obtained from these reactions in yields of 60-67%.



Scheme 3. Reactions on larger scale.

The positive effect of *tert*-butanol (Table 5, entries 11-17) on the arylation of 1-methylpyrrole can be rationalized by the mechanism depicted below (Scheme 4),[32] in which the generation of aryl radical **18** is facilitated through the occurrence of the diazo ether **17** as a more effective radical source than the diazohydroxide **16**.[37] The significant differences observed between the ptGB conditions and the diazotate method (Table 4) are indirectly also in agreement with the *tert*-butanol effect and can be explained as described below. Control experiments with the previously studied anilines **3a** and **3b** (c.f. Table 3) revealed that the arylation of anilines can not be further improved through the addition of *tert*-butanol, as similar yields for 2-aminobiphenyls **4a** and **4d** were obtained.



Scheme 4. Plausible reaction mechanism.

Basically, and in the absence of *tert*-butanol, the formation of aryl radicals **18** from diazohydroxides is slow. To nevertheless avoid long reaction times and higher concentrations of the diazotate, under which the diazotate may undergo undesired side-reactions, it would be helpful if the conversion of **16** to aryl radical **18** was not only dependent on the thermally induced homolytic bond cleavage of **16**. Regarding Scheme 4, this step could alternatively be induced, if it was coupled to the rearomatization of adduct **19** leading to the final biaryl product **20**.[38] Strongly reducing adducts **19** should then provide better product yields as the reductive cleavage of the diazohydroxide **16** to an aryl radical **18**, nitrogen and an hydroxide anion could smoothly occur as part of a chain process and thermal initiation would only be of minor importance. To gain further insight, this assumption was evaluated using quantum chemical calculations. All calculations used the B3LYP hybrid density functional[39] with the aug-cc-pVBDZ basis set[40] including the Grimme D3 dispersion correction.[41] Geometries were optimized without symmetry constraints and all structures reported were confirmed to be local minima by calculating their normal vibrations within the harmonic approximation. All calculations used the Gaussian 09 program.[42]

s **6***, **9***, **4a*** and **14a*** derived from benzene, anisole, aniline and 1-methylpyrrole, each for two possible reaction mechanisms (Scheme 5).[37] In the first, the general radical adduct **19** is deprotonated to give the radical anion **19**$^{\bullet-}$, which is then oxidized to give the product **20**. The second mechanism reverses the order of the deprotonation and oxidation steps to give first the adduct cation **19**$^{+}$, which deprotonates to give the biaryl **20**.

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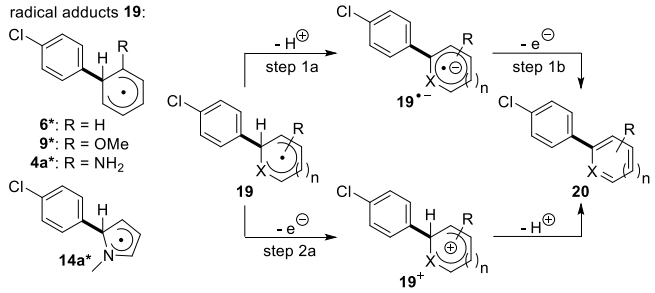

Scheme 5. Pathways for rearomatization of radical adduct **19**.

Table 7. Calculated reaction energies for the substeps in the rearomatization of radical adduct **19**.[a]

Radical adduct (from radical acceptor)	Proton affinity **19•-**→**19** (step 1a)	Ionization potential[b] **19•-**→**20** (step 1b)	Ionization potential **19**→**19+** (step 2a)
6* (from benzene)	-334	-0.03	6.66
9* (from anisole)	-342	-0.18	6.04
4a* (from aniline)	-342	-0.24	5.59
14a* (from 1-methylpyrrole)	-347	-0.27	5.43

[a] B3LYP-D3/aug-cc-pVDZ + zero-point energy, proton affinities in kcal mol^{-1}, electron affinities and ionization potentials in eV. [b] Ionization potential of **19•-** corresponds to negative electron affinity of **20**.

Table 7 shows the calculated gas phase proton affinity of **19•-**, and the ionization potentials of **19•-** and **19**. The first two govern the thermodynamics of the two steps of the deprotonation/oxidation mechanism **19**→**19•-**→**20** (Scheme 5, steps 1a and 1b), and the last the oxidation step **19**→**19+** of the oxidation/deprotonation mechanistic sequence shown below (Scheme 5, step 2a).
The calculated proton affinities (**19•-**→**19**) hardly distinguish between the different radical adducts suggesting that the deprotonation step 1a is not rate-determining. The oxidation step in the deprotonation/oxidation reaction sequence (step 1b), which is governed by the ionization potential of the radical anion **19•-** does distinguish the four reactants in correct order, although the difference is more distinct for the oxidation step 2a in the oxidation/deprotonation reaction sequence, suggesting that this step controls the outcome of the reaction sequence.
On the basis of the experimental and computational results, it is thus likely that diazotate-based arylations of anilines and pyrroles benefit from two distinct factors: Firstly, the aryldiazotate acts as a nucleophile-resistant diazonium salt with the ability to suppress azo coupling reactions and triazene formation, and secondly, the radical adducts **19** -derived from anilines and pyrroles- are able to serve as chain propagators as they are sufficiently strong reductants to generate new aryl radicals (Scheme 4, Table 7).

Conclusions

In conclusion, aryldiazotates have been found to be useful reactants for the radical arylation of anilines and 1-substituted pyrroles. Based on a significantly optimized preparation of aryldiazotates from anilines, a variety of biaryls could be obtained, even on larger reaction scales. The key feature of diazotate-based arylations is that these intermediates can serve as protected diazonium ions so that common ionic side reactions, such as azo coupling or triazene formation, are suppressed. Beneficially, aryldiazotates are nevertheless able to act as precursors for aryl radicals at slightly elevated temperatures. Computational studies gave further insight and supported the experimentally derived assumption that the reduction potential in the rearomatization step plays a critical role in the overall reaction course. In this way, the comparably narrow substrate scope of radical arylations with diazotates, which basically comprises anilines and 1-substituted pyrroles, can be explained. An interesting challenge for future research is to reduce the required excess of aromatic radical acceptor, as this is yet a significant drawback of intermolecular radical aryl-aryl coupling reactions.

Experimental Section

Experimental Details: Solvents and reagents were used as received. ^{1}H NMR spectra were recorded on 360 and 600 MHz spectrometers using $CDCl_3$ as solvents referenced to TMS (0 ppm) and $CHCl_3$ (7.26 ppm). Chemical shifts are reported in parts per million (ppm). Coupling constants are in Hertz (*J* Hz). The following abbreviations are used for the description of signals: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quadruplet) m (multiplet). ^{13}C NMR spectra were recorded at 90.6 and 150.9 MHz in $CDCl_3$ using $CHCl_3$ (77.0 ppm) as standard. Chemical shifts are given in parts per million (ppm). ^{19}F NMR spectra were recorded at 338.8 MHz using $CFCl_3$ (0 ppm) or C_6F_6 (-164.9 ppm) as standard. Mass spectra were recorded using electron impact (EI). Analytical TLC was carried out on Merck silica gel plates using short wave (254 nm) UV light and ninhydrin to visualize components. Silica gel (Kieselgel 60, 40-63 µm, Merck) was used for flash column chromatography.

General procedure for Table 1: For preparation of the diazonium salt, see Table 1. An aliquot of this 0.4 M 4-chlorophenyldiazonium chloride solution (max. 2.00 mmol, 5.00 mL) was added to a pre-cooled and vigorously stirred aqueous solution of sodium hydroxide (4 N, 3 mL) under argon. The homogeneous solution was stirred for five minutes in total. To vigorously stirred aniline (**3a**) (20.0 mmol, 1.82 mL) at 70 °C was added dropwise the previously prepared solution of the aryl diazotate (max. 2.00 mmol, 8.00 mL) under argon over a period of ten minutes. After the addition was complete, the mixture was left to stir for 20 more minutes. The resulting reaction mixture was then extracted with dichloromethane (3 × 75 mL). The combined organic phases were washed with saturated aqueous sodium chloride and dried over sodium sulfate. The solvent was removed under reduced pressure. Further purification was carried out by Kugelrohr distillation and column chromatography on silica gel.

4'-Chlorobiphenyl-2-amine (4a) and **4'-chlorobiphenyl-4-amine (4a`):** The crude products were purified by Kugelrohr distillation under reduced pressure at 80 °C and flash chromatography on silica gel (hexane / EtOAc = 10 : 1) to give the two isomers as brown oils: 4'-Chlorobiphenyl-2-amine (**4a**): R_f: 0.6 (hexane / EtOAc = 4 : 1) [UV]; ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 6.76 (dd, *J* = 1.2 Hz, *J* = 8.6 Hz, 1 H), 6.86 (dt, *J* = 1.2 Hz, *J* = 7.5 Hz, 1 H), 7.08 (dd, *J* = 1.6 Hz, *J* = 7.6 Hz, 1 H), 7.16 (ddd, *J* = 1.6 Hz, *J* = 7.4 Hz, *J* = 8.0 Hz, 1 H), 7.38 - 7.42 (m, 4 H); ^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 115.6 (CH), 118.4

(CH), 126.3 (C_q), 128.7 (CH), 129.1 (2 × CH), 130.3 (CH), 130.5 (2 × CH), 133.6 (C_q), 136.9 (C_q), 143.2 (C_q). 4'-Chlorobiphenyl-4-amine (**4a`**): R_f: 0.3 (hexane / EtOAc = 4 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 6.76 (d, J = 8.6 Hz, 2 H), 7.35 (d, J = 8.6 Hz, 2 H), 7.38 (d, J = 8.6 Hz, 2 H), 7.46 (d, J = 8.5 Hz, 2 H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 115.4 (2 × CH), 127.4 (2 × CH), 127.9 (2 × CH), 128.7 (2 × CH), 130.2 (C_q), 132.5 (C_q), 139.8 (C_q), 146.7 (C_q). The analytical data obtained is in agreement with those reported in literature.[19]

General procedure for Table 2: A degassed solution of sodium nitrite (10.5 mmol, 714 mg) in water (5 mL) was added dropwise to an ice-cooled degassed solution of 4-chloroaniline (**1a**) (10.0 mmol, 1.27 g) in hydrochloric acid (1.5 N, 20 mL) over a period of 15 min. The clear solution was stirred for 15 more minutes at 0 °C. For preparation of the 4-chlorophenyldiazotate (**2a**), see Table 2. To vigorously stirred aniline (**3a**) (20.0 mmol, 1.82 mL) at 70 °C was added dropwise the previously prepared solution of the aryl diazotate (max. 2.00 mmol, 8.00 mL) under argon over a period of ten minutes. After the addition was complete, the mixture was left to stir for 20 more minutes. The resulting reaction mixture was then extracted with dichloromethane (3 × 75 mL). The combined organic phases were washed with saturated aqueous sodium chloride and dried over sodium sulfate. The solvent was removed under reduced pressure. Further purification was carried out by Kugelrohr distillation and column chromatography on silica gel to give 4'-chlorobiphenyl-2-amine (**4a**) and 4'-chlorobiphenyl-4-amine (**4a'**). For analytical data, see general procedure for Table 1.

General procedure for Table 3: A degassed solution of sodium nitrite (10.5 mmol, 714 mg) in water (5 mL) was added dropwise to an ice-cooled degassed solution of aniline **1a** or **1b** (10.0 mmol, 1.27 g) in hydrochloric acid (1.5 N, 20 mL) over a period of 15 min. The clear solution was stirred for 15 more minutes at 0 °C. An aliquot of this 0.4 M aryldiazonium chloride solution (max. 2.00 mmol, 5.00 mL) was added to a pre-cooled and vigorously stirred aqueous solution of sodium hydroxide (4 N, 3 mL) under argon. The homogeneous solution of the diazotate **2a** or **2b** was stirred for five minutes in total. To the vigorously stirred aniline **3a,b** or **c** (20.0 mmol) at 70 °C was added dropwise the previously prepared solution of the aryl diazotate **2a** or **2b** (max. 2.00 mmol, 8.00 mL) under argon over a period of ten minutes. After the addition was complete, the mixture was left to stir for 20 more minutes. The resulting reaction mixture was then extracted with dichloromethane (3 × 75 mL). The combined organic phases were washed with saturated aqueous sodium chloride and dried over sodium sulfate. The solvent was removed under reduced pressure. Further purification was carried out by Kugelrohr distillation and column chromatography on silica gel.

4'-Chlorobiphenyl-2-amine (4a) and **4'-chlorobiphenyl-4-amine (4a`):** The crude products were purified by Kugelrohr distillation under reduced pressure at 80 °C and flash chromatography on silica gel (hexane / EtOAc = 10 : 1) to give the two isomers as brown oils (4a = 195 mg, 0.96 mmol, 48%; 4a` = 30 mg, 0.16 mmol, 8%). For analytical data, see general procedure for Table 1.

4'-Chloro-5-fluorobiphenyl-2-amine (4b): The crude product was purified by Kugelrohr distillation under reduced pressure at 80 °C and flash chromatography on silica gel (hexane / EtOAc = 10 : 1) to give the product as a dark brown oil (233 mg, 1.06 mmol, 53%). R_f: 0.4 (hexane / EtOAc = 4 : 1) [UV]. ^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 6.70 (dd, J_{HF} = 4.8 Hz, J = 8.7 Hz, 1 H), 6.83 (dd, J = 3.0 Hz, J_{HF} = 9.2 Hz, 1 H), 6.85 (ddd, J = 3.0 Hz, J_{HF} = 8.2 Hz, J = 8.3 Hz, 1 H), 7.38 (d, J = 8.8 Hz, 2 H), 7.43 (d, J = 8.8 Hz, 2 H). ^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 115.2 (d, J_{CF} = 22.2 Hz, CH), 116.5 (d, J_{CF} = 22.6 Hz, CH), 116.8 (d, J_{CF} = 7.8 Hz, CH), 127.5 (d, J_{CF} = 7.3 Hz, C_q), 129.1 (2 × CH), 130.3 (2 × CH), 133.6 (C_q) 136.9 (d, J_{CF} = 1.7 Hz, C_q), 139.2 (d, J_{CF} = 2.2 Hz, C_q), 155.1 (d, J_{CF} = 243.9 Hz, C_q). The analytical data obtained is in agreement with those reported in literature.[19]

4',5-Dichlorobiphenyl-2-amine (4c): The crude product was purified by Kugelrohr distillation under reduced pressure at 85 °C and flash chromatography on silica gel (hexane / EtOAc = 10 : 1) to give the product as a dark brown oil (284 mg, 1.20 mmol, 60%). R_f: 0.5 (hexane / EtOAc = 4:1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 6.69 (d, J = 8.2 Hz, 1 H), 7.07 (d, J = 2.5 Hz, 1 H), 7.11 (dd, J = 2.5 Hz, J = 8.5 Hz, 1 H), 7.36 (d, J = 8.7 Hz, 2 H), 7.41 (d, J = 8.6 Hz, 2 H). ^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 116.9 (CH), 124.0 (C_q), 128.3 (CH), 129.1 (2 × CH), 130.0 (2 × CH), 130.6 (CH), 131.6 (C_q), 133.5 (C_q), 136.1 (C_q), 141.8 (C_q). The analytical data obtained is in agreement with those reported in literature.[19]

4',5-Difluorobiphenyl-2-amine (4d): The crude product was purified by Kugelrohr distillation under reduced pressure at 80 °C and flash chromatography on silica gel (hexane / EtOAc = 10 : 1) to give the product as a dark brown oil (199 mg, 0.96 mmol, 48%). R_f: 0.4 (hexane / EtOAc = 4 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 6.69 (dd, J_{HF} = 4.8 Hz, J = 8.7 Hz, 1 H), 6.83 (dd, J = 3.0 Hz, J_{HF} = 9.2 Hz, 1 H), 6.84 - 6.89 (m, 1 H), 7.13 (t, J = 8.7 Hz, J_{HF} = 8.7 Hz, 2 H), 7.40 (dd, J_{HF} = 5.4 Hz, J = 8.8 Hz, 2 H). ^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 115.0 (d, J_{CF} = 22.3 Hz, CH), 115.8 (d, J_{CF} = 21.4 Hz, 2 × CH), 116.6 (d, J_{CF} = 7.7 Hz, CH), 116.7 (d, J_{CF} = 22.5 Hz, CH), 127.7 (d, J_{CF} = 7.2 Hz, C_q), 130.6 (d, J_{CF} = 8.0 Hz, 2 × CH), 134.4 (dd, J_{CF} = 1.6 Hz, J_{CF} = 3.3 Hz, C_q), 139.4 (d, J_{CF} = 2.3 Hz, C_q), 156.3 (d, J_{CF} = 237.5 Hz, C_q), 162.3 (d, J_{CF} = 247.2 Hz, C_q). The analytical data obtained is in agreement with those reported in literature.[19]

5-Chloro-4'-fluorobiphenyl-2-amine (4e): The crude product was purified by Kugelrohr distillation under reduced pressure at 85 °C and flash chromatography on silica gel (hexane / EtOAc = 10 : 1) to give the product as a dark brown oil (255 mg, 1.16 mmol, 58%). R_f: 0.4 (hexane / EtOAc = 4:1) [UV]. ^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 6.69 (d, J = 8.4 Hz, 1 H), 7.07 (d, J = 2.2 Hz, 1 H), 7.08-7.16 (m, 3 H), 7.39 (dd, J_{HF} = 5.3 Hz, J = 8.8 Hz, 2 H). ^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 115.9 (d, J_{CF} = 21.4 Hz, 2 × CH), 116.7 (CH), 123.2 (CH), 127.9 (C_q), 128.3 (CH), 130.0 (d, J_{CF} = 0.7 Hz, C_q), 130.7 (d, J_{CF} = 8.1 Hz, 2 × CH), 134.2 (d, J_{CF} = 3.5 Hz, C_q), 142.2 (C_q), 162.3 (d, J_{CF} = 247.2 Hz, C_q). The analytical data obtained is in agreement with those reported in literature.[19]

General procedure for Scheme 2: A degassed solution of sodium nitrite (52.5 mmol, 3.57 g) in water (25 mL) was added dropwise to an ice-cooled degassed solution of 4-chloroaniline (**1a**) (50.0 mmol, 6.38 g) in hydrochloric acid (1.5 N, 100 mL) over a period of 15 min. The clear solution was stirred for 15 more minutes at 0 °C. This 0.4 M aryldiazonium chloride solution (max. 50.0 mmol, 125 mL) was added to a pre-cooled and vigorously stirred aqueous solution of sodium hydroxide (4 N, 75 mL) under argon. The homogeneous solution of diazotate **2a** was stirred for five minutes in total. To vigorously stirred aniline (**3a**) (100 mmol, 9.11 mL) at 70 °C was added dropwise the previously prepared

solution of the aryl diazotate **2a** (max. 50.0 mmol, 200 mL) under argon over a period of ten minutes. After the addition was complete, the mixture was left to stir for 20 more minutes. The resulting reaction mixture was then extracted with dichloromethane (3 × 100 mL). The combined organic phases were washed with saturated aqueous sodium chloride and dried over sodium sulfate. The solvent was removed under reduced pressure. Further purification was carried out by distillation and column chromatography on silica gel to give 4'-chlorobiphenyl-2-amine (**4a**) (4.26 g, 21.0 mmol, 42%) and 4'-chlorobiphenyl-4-amine (**4a`**) (1.50 g, 7.50 mmol, 15%). For analytical data, see general procedure for Table 1.

General procedures for Table 4:

a) Procedure "ptGB$_{106\text{-}145}$" for biaryls 4a, 13 and 14a: To a mixture of 4-chlorphenyldiazonium tetrafluoroborate (2.00 mmol, 452 mg) and 18-crown-6 (5 mol %, 26 mg) in 10 mL of radical acceptor (**3a**, **3k** or **3l**) at ambient temperature was added KOAc (4.00 mmol, 393 mg). Stirring was continued for 90 minutes. The red coloured mixture was filtered and the filtrate washed with saturated aqueous sodium chloride and water. The organic layer was dried over sodium sulfate. The solvent was removed under reduced pressure and evaporated to dryness. Depending on the product, further purification was carried out by eventual distillation and column chromatography on silica gel.

b) Procedure "ptGB$_{10}$" for biaryls 4a, 6-13, 14a: To a mixture of the 4-chlorophenyldiazonium tetrafluoroborate (2.00 mmol, 452 mg), 18-crown-6 (5 mol %, 26 mg) and the radical acceptor (**3a, 3d-l**) (20.0 mmol) at ambient temperature was added KOAc (4.00 mmol, 393 mg). Stirring was continued for 90 minutes. The red coloured mixture was filtered and the filtrate washed with saturated aqueous sodium chloride and water. The organic layer was dried over sodium sulfate. The solvent was removed under reduced pressure. Depending on the product, further purification was carried out by eventual distillation and column chromatography on silica gel.

c) Procedure "Diaz$_{10}$" for biaryls 4a, 6-13, 14a: A degassed solution of sodium nitrite (10.5 mmol, 714 mg) in water (5 mL) was added dropwise to an ice-cooled degassed solution of 4-chloroaniline (**1a**) (10.0 mmol, 1.27 g) in hydrochloric acid (1.5 N, 20 mL) over a period of 15 min. The clear solution was stirred for 15 more minutes at 0 °C. An aliquot of this 0.4 M 4-chlorophenyldiazonium chloride solution (max. 2.00 mmol, 5.00 mL) was added to a pre-cooled and vigorously stirred aqueous solution of sodium hydroxide (4 N, 3 mL) under argon. The homogeneous solution of the diazotate **2a** was stirred for five minutes in total. To vigorously stirred radical acceptor (**3a,d-l**) (20.0 mmol) at 70 °C was added dropwise the previously prepared solution of the aryl diazotate **2a** (max. 2.00 mmol, 8.00 mL) under argon over a period of ten minutes. After the addition was complete, the mixture was left to stir for 20 more minutes. The resulting reaction mixture was then extracted with dichloromethane (3 × 75 mL). The combined organic phases were washed with saturated aqueous sodium chloride and dried over sodium sulfate. The solvent was removed under reduced pressure. Further purification was carried out by Kugelrohr distillation and column chromatography on silica gel.

4'-Chlorobiphenyl (6): The crude product was purified by flash chromatography on silica gel (hexane 100%) to give **6** as a dark red oil. R_f: 0.7 (hexane / EtOAc = 19 : 1) [UV]. ^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 7.32-7.35 (m, 1 H), 7.37 (d, J = 8.8 Hz, 2 H), 7.40-7.43 (m, 2 H), 7.48 (d, J = 8.8 Hz, 2 H), 7.50-7.54 (m, 2 H). ^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 127.0 (2 × CH), 127.6 (2 × CH), 128.4 (2 × CH), 128.8 (CH), 128.9 (2 × CH), 133.3 (C_q), 139.7 (C_q), 140.0 (C_q). The analytical data obtained is in agreement with those reported in literature.[19]

4'-Chloro-2-methylbiphenyl (7a), 4'-chloro-3-methylbiphenyl (7a`) and **4'-chloro-4-methylbiphenyl (7a``):** The crude products were purified by flash chromatography on silica gel (hexane 100%) to give a mixture of the three isomers: 4'-Chloro-2-methylbiphenyl (**7a**): R_f: 0.6 (hexane 100%) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 2.28 (s, 3 H), 7.23-7.29 (m, 6 H), 7.41 (m, 2 H). 4'-Chloro-3-methylbiphenyl (**7a`**): R_f: 0.6 (hexane 100%) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 2.45 (s, 3 H), 7.20 (d, J = 8.8 Hz, 2 H), 7.35-7.43 (m, 5 H), 7.53 (m, 1 H). 4'-Chloro-4-methylbiphenyl (**7a``**): R_f: 0.6 (hexane 100%) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 2.39 (s, 3 H), 7.24 (d, J = 7.4 Hz, 2 H), 7.38 (d, J = 7.8 Hz, 2 H), 7.45 (d, J = 7.6 Hz, 2 H), 7.49 (d, J = 8.0 Hz, 2 H). The analytical data obtained is in agreement with those reported in literature.[43]

4'-Chloro-2,4,6-trimethylbiphenyl (8): The crude product was purified by flash chromatography on silica gel (hexane 100%) to give **8** as a yellow oil. R_f: 0.7 (hexane 100%) [UV]. ^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 1.99 (s, 6 H), 2.32 (s, 3 H), 6.93 (s, 2 H), 7.07 (d, J = 8.6 Hz, 2 H), 7.38 (d, J = 8.6 Hz, 2 H). ^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 20.7 (2 × CH_3), 21.0 (CH_3), 128.1 (2 × CH), 128.6 (2 × CH), 130.7 (2 × CH), 132.5 (C_q), 135.9 (C_q), 136.9 (C_q), 137.7 (C_q), 139.5 (C_q). The analytical data obtained is in agreement with those reported in literature.[44]

4'-Chloro-2-methoxybiphenyl (9), 4'-chloro-3-methoxybiphenyl (9`) and **4'-chloro-4-methoxybiphenyl (9``):** The crude products were purified by flash chromatography on silica gel (hexane 100%) to give a mixture of the three isomers: 4'-chloro-2-methoxybiphenyl (**9**): R_f: 0.2 (hexane 100%) [UV]. ^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 3.81 (s, 3 H), 6.98 (dd, J = 0.9 Hz, J = 8.3 Hz, 1 H), 7.02 (dt, J = 1.1 Hz, J = 7.5 Hz, 1 H), 7.28 (dd, J = 1.8 Hz, J = 7.6 Hz, 1 H), 7.30-7.34 (m, 1 H), 7.36 (d, J = 8.8 Hz, 2 H), 7.46 (d, J = 8.8 Hz, 2 H). 4'-Chloro-3-methoxybiphenyl (**9`**): R_f: 0.2 (hexane 100%) [UV]. ^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 3.86 (s, 3 H), 6.91 (ddd, J = 0.9 Hz, J = 2.4 Hz, J = 8.2 Hz, 1 H), 7.08 (dd, J = 1.9 Hz, J = 2.4 Hz, 1 H), 7.14 (ddd, J = 0.9 Hz, J = 1.9 Hz, J = 7.6 Hz, 1 H), 7.35 (d, J = 7.9 Hz, 1 H), 7.40 (d, J = 8.7 Hz, 2 H), 7.51 (d, J = 8.7 Hz, 2 H). **4**'-Chloro-4-methoxybiphenyl (**9``**): R_f: 0.2 (hexane 100%) [UV]. ^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 3.85 (s, 3 H), 6.97 (d, J = 8.9 Hz, 2 H), 7.37 (d, J = 8.7 Hz, 2 H), 7.45-7.50 (m, 4 H). The analytical data obtained is in agreement with those reported in literature.[45]

4'-Chlorobiphenyl-2-amine (4a) and **4'-chlorobiphenyl-4-amine (4a`):** The crude products were purified by Kugelrohr distillation under reduced pressure at 80 °C and flash chromatography on silica gel (hexane / EtOAc = 10 : 1) to give the two isomers as brown oils. For analytical data, see general procedure for Table 1.

2-(4'-Chlorophenyl)pyridine (10), 3-(4'-chlorophenyl)pyridine (10`) and **4-(4'-chlorophenyl)pyridine (10``):** The crude products were purified by flash chromatography on silica gel (hexane 100%) to give a mixture of the three isomers: 2-(4'-chlorophenyl)pyridine (**10**): R_f: 0.2 (hexane 100%) [UV]. ^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 7.03 (m, 1 H), 7.28 (d, J = 8.3 Hz, 2 H), 7.48-7.50 (m, 5 H), 7.81 (d, J = 8.3 Hz, 2 H). 3-(4'-

chlorophenyl)pyridine (**10`**): R_f: 0.2 (hexane 100%) [UV]. ^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 7.37-7.41 (m, 1 H), 7.45 (d, *J* = 8.5 Hz, 2 H), 7.50 (d, *J* = 8.5 Hz, 2 H), 7.86 (dt, *J* = 1.7 Hz, *J* = 7.8 Hz, 1 H), 8.61 (d, *J* = 2.7 Hz, 1 H) 8.83 (s, 1 H). 4-(4'-chlorphenyl)pyridine (**10``**): R_f: 0.2 (hexane 100%) [UV]. ^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 7.45-7.52 (m, 4 H), 7.58 (d, *J* = 8.9 Hz, 2 H), 8.68 (bs, 2 H). The analytical data obtained is in agreement with those reported in literature.[46]

2-(4'-Chlorophenyl)furan (11): The crude product was purified by flash chromatography on silica gel (hexane 100%) to give **11** as a light brown oil. R_f: 0.7 (hexane 100%) [UV]. ^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 6.47 (dd, *J* = 1.8 Hz, *J* = 3.4 Hz, 1 H), 6.64 (dd, *J* = 0.8 Hz, *J* = 3.4 Hz, 1 H), 7.35 (d, *J* = 8.8 Hz, 2 H), 7.46 (dd, *J* = 0.8 Hz, *J* = 1.8 Hz, 1 H), 7.59 (d, *J* = 8.8 Hz, 2 H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 105.4 (CH), 111.7 (CH), 125.0 (2 × CH), 128.8 (2 × CH), 129.4 (CH), 132.9 (C_q), 142.3 (C_q), 152.9 (C_q). The analytical data obtained is in agreement with those reported in literature.[47]

2-(4'-Chlorophenyl)thiophene (12): The crude product was purified by flash chromatography on silica gel (hexane 100%) to give **12** as a yellow oil. R_f: 0.7 (hexane 100%) [UV]. ^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 7.07 (dd, *J* = 3.8 Hz, *J* = 4.9 Hz, 1 H), 7.28 (m, 1 H), 7.29 (dd, *J* = 1.2 Hz, *J* = 2.9 Hz, 1 H), 7.34 (d, *J* = 8.8 Hz, 2 H), 7.53 (d, *J* = 8.8 Hz, 2 H). The analytical data obtained is in agreement with those reported in literature.[43a]

2-(4'-Chlorophenyl)pyrrole (13): The crude product was purified by flash chromatography on silica gel (hexane / EtOAc = 10 : 1) to give **13** as a brown oil. R_f: 0.6 (hexane / EtOAc = 4 : 1) [UV]. ^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm= 6.30 (m, 1 H), 6.50 (ddd, *J* = 1.5 Hz, *J* = 2.7 Hz, *J* = 3.6 Hz, 1 H), 6.86 (dt, *J* = 1.5 Hz, *J* = 2.7 Hz, *J* = 2.7 Hz, 1 H), 7.32 (d, *J* = 8.9 Hz, 2 H) 7.39 (d, *J* = 8.9 Hz, 2 H) 8.32 (bs, 1 H). ^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 106.4 (CH), 110.4 (CH), 119.2 (CH), 125.0 (2 × CH), 129.0 (2 × CH), 131.0 (C_q), 131.3 (C_q), 131.8 (C_q). HRMS (EI) calcd. for $C_{10}H_7ClN^-$ [-H^+]: 176.0273, found: 176.0281.

1-Methyl-2-(4-chlorophenyl)pyrrole (14a): The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 / 1) to give **14a** as light brown crystals. R_f: 0.6 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.65 (s, 3 H), 6.18-6.23 (m, 2 H), 6.72 (m, 1 H), 7.32 (d, *J* = 8.6 Hz, 2 H), 7.36 (d, *J* = 8.6 Hz, 2 H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 35.0 (CH_3), 107.9 (CH), 109.0 (CH), 124.0 (CH), 128.7 (2 × CH), 129.8 (2 × CH), 131.8 (C_q), 132.7 (C_q), 133.3 (C_q). HRMS (EI) calcd. for $C_{11}H_{11}ClN$ [H^+]: 192.0578, found: 192.0576. The analytical data obtained is in agreement with those reported in literature. [48]

General procedure for Table 5: A degassed solution of sodium nitrite (10.5 mmol, 714 mg) in water (5 mL) was added dropwise to an ice-cooled degassed solution of 4-chloroaniline (**1a**) (10.0 mmol, 1.27 mg) in hydrochloric acid (1.5 N, 20 mL) over a period of 15 min. The clear solution was stirred for 15 more minutes at 0 °C. An aliquot of this 0.4 M aryldiazonium chloride solution (max. 2.00 mmol, 5.00 mL) was added to a pre-cooled and vigorously stirred aqueous solution of sodium hydroxide (4 N, 3 mL) under argon. The homogeneous solution of the diazotate **2a** was stirred for five minutes in total. For the conditions used in the radical arylation of 1-methylpyrrole (**3l**), see Table 5. The resulting reaction mixture was extracted with dichloromethane (3 × 75 mL). The combined organic phases were washed with saturated aqueous sodium chloride and dried over sodium sulfate. The solvent was removed under reduced pressure. The yields of biaryl **14a** and azo compound **15** were determined by ^{1}H-NMR using 1,4-dimethyl terephthalate and 1,3,5-trimethoxybenzene as internal standards. 1-Methyl-2-(4-chlorophenyl)pyrrole (**14a**): For analytical data, see general procedure for Table 4.

General procedure for Table 6: A degassed solution of sodium nitrite (10.5 mmol, 714 mg) in water (5 mL) was added dropwise to an ice-cooled degassed solution of the aniline **1a-l** (10.0 mmol) in hydrochloric acid (1.5 N, 20 mL) over a period of 15 min. The clear solution was stirred for 15 more minutes at 0 °C. An aliquot of this 0.4 M aryldiazonium chloride solution (max. 2.00 mmol, 5.00 mL) was added to a pre-cooled and vigorously stirred aqueous solution of lithium hydroxide (4 N, 3 mL) under argon. The homogeneous solution of the diazotate **2a-l** was stirred for five minutes in total. To a mixture of the pyrrole derivative (20.0 mmol) and lithium hydroxide (12.0 mmol, 288 mg) in *tert*-butanol (3.0 mL) at 70 °C under argon was added dropwise the previously prepared solution of the aryl diazotate **2a-l** (max. 2.00 mmol, 8.00 mL) over a period of seven minutes. After the addition was complete, the mixture was left to stir for 23 more minutes. The resulting reaction mixture was then extracted with dichloromethane (3 × 75 mL). The combined organic phases were washed with saturated aqueous sodium chloride and dried over sodium sulfate. The solvent was removed under reduced pressure. Depending on the product, further purification was carried out by eventual distillation and column chromatography on silica gel.

1-Methyl-2-(4-chlorophenyl)pyrrole (14a): The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 / 1) to give **14a** as a dark red oil (251 mg, 1.32 mmol, 66%). For analytical data, see general procedure for Table 4.

1-Methyl-2-(4-fluorophenyl)pyrrole (14b): The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14b** as light brown solid (233 mg, 1.34 mmol, 67%). R_f: 0.5 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.62 (s, 3 H), 6.17-6.20 (m, 2 H), 6.73 (t, *J* = 4.5 Hz, 1 H), 7.11 (dd, J_{HF} = 8.7 Hz, *J* = 8.7 Hz, 2 H), 7.38 (dd, J_{HF} = 5.4 Hz, *J* = 8.8 Hz, 2 H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 34.9 (CH_3), 107.7 (CH), 108.6 (CH), 115.3 (d, J_{CF} = 21.3 Hz, 2 × CH), 123.5 (CH), 129.4 (d, J_{CF} = 3.4 Hz, C_q), 130.3 (d, J_{CF} = 7.8 Hz, 2 × CH), 133.5 (C_q), 161.9 (d, J_{CF} = 246.4 Hz, C_q). HRMS (EI) calcd. for $C_{11}H_{11}FN$ [H^+]: 176.0970, found: 176.0973. The analytical data obtained is in agreement with those reported in literature.[48]

1-Methyl-2-phenylpyrrole (14c): The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14c** as light brown crystals (151 mg, 0.96 mmol, 48%). R_f: 0.6 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.03 (s, 3 H), 6.18 (dd, *J* = 2.7 Hz, *J* = 3.6 Hz, 1 H), 6.24 (dd, *J* = 1.8 Hz, *J* = 3.6 Hz, 1 H), 6.73 (t, *J* = 4.5 Hz, 1 H), 7.26-7.32 (m, 1 H), 7.36-7.42 (m, 4 H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 35.0 (CH_3), 107.7 (CH), 108.6 (CH), 123.6 (CH), 126.7 (CH), 128.3 (2 × CH), 128.6 (2 × CH), 133.3 (C_q), 134.6 (C_q). HRMS (EI) calcd. for $C_{11}H_{12}N$ [H^+]: 158.0964, found: 158.0965. The analytical data obtained is in agreement with those reported in literature.[48]

1-Methyl-2-(3-fluorophenyl)pyrrole (14d): The crude product was purified by flash chromatography on silica gel

(hexane / dichloromethane = 30 : 1) to give **14d** as a dark red oil (200 mg, 1.16 mmol, 58%). R_f: 0.5 (hexane / EtOAc = 10:1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.67 (s, 3 H), 6.19 (dd, *J* = 2.7 Hz, *J* = 3.6 Hz, 1 H), 6.25 (dd, *J* = 1.8 Hz, *J* = 3.6 Hz, 1 H), 6.72 (dd, *J* = 1.8 Hz, *J* = 2.7 Hz, 1 H), 6.98 (dt, J_{HF} = 3.1 Hz, *J* = 8.7 Hz, 1 H), 7.09 (ddd, J_{HF} = 0.8 Hz, *J* = 3.1 Hz, *J* = 10.1 Hz, 1 H), 7.16 (ddd, J_{HF} = 1.0 Hz, *J* = 1.6 Hz, *J* = 7.7 Hz, 1 H), 7.33 (dt, J_{HF} = 6.3 Hz, *J* = 8.0 Hz, *J* = 8.2 Hz, 1 H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 35.1 (CH_3), 107.9 (CH), 109.3 (CH), 113.4 (d, J_{CF} = 21.2 Hz, CH), 115.2 (d, J_{CF} = 21.7 Hz, CH), 124.1 (d, J_{CF} = 3.0 Hz, CH), 124.2 (CH), 129.8 (d, J_{CF} = 8.8 Hz, CH), 133.3 (C_q), 135.4 (d, J_{CF} = 8.7 Hz, C_q), 162,7 (d, J_{CF} = 245.6 Hz, C_q). ^{19}F-NMR (235 MHz, $CDCl_3$): δ(ppm) = −113.6. HRMS (EI) calcd. for $C_{11}H_{11}FN$: 176.0870, found: 176.0877. The analytical data obtained is in agreement with those reported in literature.[48]

1-Methyl-2-(2-fluorophenyl)pyrrole (14e): The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14e** as a dark red oil (81 mg, 0.56 mmol, 23%). R_f: 0.5 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.56 (s, 3 H), 6.20-6.24 (m, 2 H), 6.25 (dd, *J* = 1.8 Hz, *J* = 3.6 Hz, 2 H), 6.75 (t, *J* = 2.2 Hz, 2 H), 7.08-7.7.15 (m, 1 H), 7.17 (dd, J_{HF} = 0.6 Hz, *J* = 2.8 Hz, 1 H), 7.28-7.37 (m, 2 H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 34.6 (CH_3), 107.9 (CH), 110.0 (CH), 115.7 (d, J_{CF} = 22.2 Hz, CH), 115.7 (d, J_{CF} = 22.2 Hz, C_q), 124.0 (d, J_{CF} = 3.6 Hz, CH), 124.1 (d, J_{CF} = 3.3 Hz, CH), 128.2 (C_q), 129.2 (d, J_{CF} = 7.8 Hz, CH), 132.5 (d, J_{CF} = 7.8 Hz, CH), 159.9 (d, J_{CF} = 246.7 Hz, C_q). HRMS (EI) calcd. for $C_{11}H_{11}FN$ [H^+]: 176.0870, found: 176.0870. The analytical data obtained is in agreement with those reported in literature.[48]

1-Methyl-2-(3-chlorophenyl)pyrrole (14f): The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14f** as a dark red oil (202 mg, 1.08 mmol, 54%). R_f: 0.5 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.69 (s, 3 H), 6.23 (dd, *J* = 2.7 Hz, *J* = 3.6 Hz, 1 H), 6.27 (dd, *J* = 1.8 Hz, *J* = 3.6 Hz, 1 H), 6.75 (t, *J* = 4.5 Hz, 1 H), 7.26 (m, *3* H), 7.421 (t, *J* = 1.8 Hz, 1 H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 35.1 (CH_3), 108.0 (CH), 109.3 (CH), 124.3 (CH), 126.6 (CH), 126.7 (CH), 128.4 (CH), 129.6 (CH), 133.1 (C_q), 134.2 (C_q), 135.1 (C_q). HRMS (EI) calcd. for $C_{11}H_{11}ClN$ [H^+]: 192.0574, found: 192.0579.

1-Methyl-2-(4-bromophenyl)pyrrole (14g): The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14g** as orange crystals (288 mg, 1.22 mmol, 61%). R_f: 0.5 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.64 (s, 3 H), 6.19 (dd, *J* = 2.7 Hz, *J* = 3.6 Hz, 1 H), 6.22 (dd, *J* = 1.8 Hz, *J* = 3.6 Hz, 1 H), 6.72 (dd, *J* = 1.9 Hz, *J* = 2.5 Hz, 1 H), 7.26 (d, *J* = 8.6 Hz, 2 H), 7.51 (d, *J* = 8.6 Hz, 2 H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 35.0 (CH_3), 107.9 (CH), 109.0 (CH), 120.7 (C_q), 124.1 (CH), 130.0 (2 × CH), 131.5 (2 × CH), 132.2 (C_q), 133.3 (C_q). HRMS (EI) calcd. for $C_{11}H_{11}BrN$ [H^+]: 236.0069, found: 236.0063. The analytical data obtained is in agreement with those reported in literature.[48]

1-Methyl-2-(4-iodophenyl)pyrrole (14h): The crude product was puriThe crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14h** as a brownish solid (318 mg, 1.12 mmol, 56%). R_f: 0.5 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.67 (s, 3 H), 6.21 (m, 1 H), 6.25 (dd, *J* = 1.5 Hz, *J* = 3.6 Hz, 1 H), 6.75 (dd, *J* = 1.9 Hz, *J* = 2.5 Hz, 1 H), 7.16 (d, *J* = 8.5 Hz, 2 H), 7.73 (d, *J* = 8.5 Hz, 2 H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 35.1 (CH_3), 92.1 (C_q), 108.0 (CH), 109.0 (CH), 124.2 (CH), 130.2 (2 × CH), 132.8 (C_q), 133.4 (C_q), 137.4 (2 × CH). The analytical data obtained is in agreement with those reported in literature.[49]

1-Methyl-2-(4-methoxyphenyl)pyrrole (14i): The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14i** as dark brown crystals (142 mg, 0.68 mmol, 34%). R_f: 0.7 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.62 (s, 3 H), 3.83 (s, 3 H), 6.12-6.20 (m, 2 H), 6.68 (m, 1 H), 6.93 (d, *J* = 8.8 Hz 2 H) 7.31 (d, *J* = 8.8 Hz, 2 H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 34.8 (CH_3), 55.3 (CH_3), 107.5 (CH), 108.0 (CH), 113.8 (2 × CH), 122.9 (CH), 125.9 (C_q), 130.0 (2 × CH), 134.3 (C_q), 158.6 (C_q). HRMS (EI) calcd. for $C_{12}H_{14}NO$ [H^+]: 188.1070, found: 188.1070. The analytical data obtained is in agreement with those reported in literature.[48]

1-Methyl-2-(3-methoxyphenyl)pyrrole (14j): The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14j** as a brown oil (158 mg, 0.84 mmol, 42%). R_f: 0.7 (hexane / EtOAc = 10 : 1) [UV] ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.66 (s, 3 H), 3.83 (s, 3 H), 6.19 (d, *J* = 3.4 Hz, 1 H), 6.22 (d, *J* = 3.6 Hz, 1 H), 6.70 (t, *J* = 4.5 Hz, 1 H), 6.84 (ddd, *J* = 1.0 Hz, *J* = 2.6 Hz, *J* = 8.3 Hz, 1 H), 6.94 (dd, *J* = 1.5 Hz, *J* = 2.5 Hz, 1 H), 6.98 (ddd, *J* = 1.0 Hz, *J* = 1.6 Hz, *J* = 7.6 Hz, 1 H) 7.30 (m, 1 H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 35.0 (CH_3), 55.2 (CH_3), 107.7 (CH), 108.7 (CH), 112.2 (CH), 114.3 (CH), 121.1 (CH), 123.7 (CH), 128.4 (CH), 134.4 (C_q), 134.7 (C_q), 159.5 (C_q). HRMS (EI) calcd. for $C_{12}H_{14}NO$ [H^+]: 188.1067, found: 188.1070.

1-Methyl-2-(4-trifluoromethylphenyl)pyrrole (14k): The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14k** as a brown solid (130 mg, 0.58 mmol, 29%). R_f: 0.4 (hexane / EtOAc = 10:1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.72 (s, 3 H), 6.24 (dd, *J* = 2.7 Hz, *J* = 3.6 Hz, 1 H), 6.33 (dd, *J* = 1.7 Hz, *J* = 3.6 Hz, 1 H) 6.78 (t, *J* = 4.4 Hz, 1 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.66 (d, *J* = 8.2 Hz, 2 H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 35.2 (CH_3), 108.2 (CH), 109.9 (CH), 124.3 (q, J_{CF} = 273.3 Hz, C_q), 124.9 (2 × CH), 125.4 (q, J_{CF} = 273.3 Hz, 2 × CH), 128.3 (2 × CH) 128.3 (q, J_{CF} = 65.2 Hz, C_q), 133.1 (C_q), 136.8 (C_q). ^{19}F-NMR (235 MHz, $CFCl_3$): δ(ppm) = −62.9. HRMS (EI) calcd. for $C_{12}H_{11}F_3N$ [H^+]: 226.0838, found: 226.0840. The analytical data obtained is in agreement with those reported in literature.[48]

1-Methyl-2-(4-methylphenyl)pyrrole (14l): The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14l** as dark red crystals (172 mg, 1.00 mmol, 50%). R_f: 0.7 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 2.38 (s, 3 H), 3.64 (s, 3 H), 6.18 (d, *J* = 2.2 Hz, 2 H), 6.69 (t, *J* = 2.25 Hz, 1 H), 7.20 (d, *J* = 8.6 Hz, 2 H), 7.29 (d, *J* = 8.6 Hz, 2 H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 21.1 (CH_3), 35.0 (CH_3), 107.6 (CH), 108.3 (CH), 123.3 (CH), 128.3 (2 × CH), 129.0 (2 × CH), 130.5 (C_q), 134.6 (C_q), 136.5 (C_q). HRMS (EI) calcd. for $C_{12}H_{14}N$ [H^+]: 172.1121, found: 172.1121. The analytical data obtained is in agreement with those reported in literature.[48]

1-Methyl-2,5-bis(4-fluorophenyl)pyrrole (14m): Due to the required amount of the heteroaryl substrate the reaction scale

was reduced to 0.5 mmol of **4c**. The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14m** as red crystals (113 mg,0.42 mmol, 84%). R_f: 0.8 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.54 (s, 3 H), 6.26 (s, 2 H), 7.11 (t, J_{HF} = 8.7 Hz, J = 8.7 Hz, 4 H), 7.41 (dd, J_{HF} = 5.4 Hz, J = 8.8 Hz, 4 H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 33.9 (CH_3), 108.6 (2 × CH), 125.7 (d, J_{CF} = 21.4 Hz, 4 × CH), 129.5 (d, J_{CF} = 3.2 Hz, 2 × C_q), 130.4 (d, J_{CF} = 7.9 Hz, 4 × CH), 135.6 (2 × C_q), 140.2 (d, J_{CF} = 246.7 Hz, 2 × C_q). HRMS (EI) calcd. for $C_{17}H_{14}F_2N$ [H^+]: 270.1088, found: 270.1082.

1-Methyl-2,5-bis(4-chlorophenyl)pyrrole (14n): Due to the required amount of the heteroaryl substrate the reaction scale was reduced to 0.5 mmol of **4a**. The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14n** as red crystals (127 mg, 0.42 mmol, 84%). R_f: 0.8 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.57 (s, 3 H), 6.30 (s, 2 H), 7.39 (s, 8 H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 34.2 (CH_3), 109.1 (2 × CH), 128.7 (4 × CH), 129.8 (4 × CH), 131.7 (2 × C_q), 132.9 (2 × C_q), 136.0 (2 × C_q). HRMS (EI) calcd. for $C_{17}H_{14}Cl_2N$: 303.0397, found: 303.0392.

1-Methyl-2,5-bis(4-bromophenyl)pyrrole (14o): Due to the required amount of the heteroaryl substrate the reaction scale was reduced to 0.5 mmol of **4g**. The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14o** as red crystals (156 mg, 0.40 mmol, 80%). R_f: 0.7 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.57 (s, 3 H), 6.30 (s, 2 H), 7.32 (d, J = 8.6 Hz, 4 H), 7.55 (d, J = 8.6 Hz, 4 H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 34.2 (CH_3), 109.2 (2 × CH), 121.0 (2 × C_q), 130.1 (4 × CH), 131.6 (4 × CH), 132.1 (2 × C_q), 136.1 (2 × C_q). HRMS (EI) calcd. for $C_{17}H_{14}Br_2N$ [H^+]: 389.9445, found: 389.9442. The analytical data obtained is in agreement with those reported in literature.[49]

1-Methyl-2-(4-bromophenyl)-5-(4-chlorophenyl)pyrrole (14p): Due to the required amount of the heteroaryl substrate the reaction scale was reduced to 0.5 mmol of **4g**. The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14p** as red crystals (142 mg, 0.41 mmol, 82%). R_f: 0.7 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.57 (s, 3 H), 6.29-6.31 (m, 2 H), 7.32 (d, J = 8.0 Hz, 2 H), 7.36-4.41 (m, 4 H), 7.54 (d, J = 8.4 Hz, 2 H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 34.2 (CH_3), 109.1 (CH), 109.2 (CH), 120.9 (C_q), 121.0 (C_q), 128.7 (2 × CH), 129.8 (2 × CH), 130.1 (2 × CH), 131.6 (2 × CH), 131.7 (C_q), 132.2 (C_q), 132.9 (C_q), 136.1 (C_q). HRMS (EI) calcd. for $C_{17}H_{14}BrClN$ [H^+]: 345.9993, found: 345.9984.

1-Phenyl-2-(4-fluorophenyl)pyrrole (14q): The excess of 1-phenylpyrrole (**3m**) was removed by Kugelrohr distillation in vacuo at 85 °C. The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14q** as light brown crytals (240 mg, 1.02 mmol, 51%). R_f: 0.5 (Hexan / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 6.35 (dd, J = 2.8 Hz, J = 3.6 Hz,1 H), 6.39 (dd, J = 1.8 Hz, J = 3.6 Hz, 1 H), 6.89 (t, J = 8.8 Hz, J_{HF} = 8.8 Hz, 2 H) 6.93 (dd, J = 1.8 Hz, J = 2.8 Hz, 1 H), 7.08 (dd, J_{HF} = 5.4 Hz, J = 9.0 Hz, 2 H), 7.12-7.17 (m, 2 H), 7.25-7.35 (m, 3 H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 109.2 (CH), 110.5 (CH), 114.9 (CH), 124.2 (CH), 125.7 (2 × CH), 126.7 (d, J_{CF} = 5.7 Hz, 2 × CH), 129.1 (2 × CH), 129.1 (d, J_{CF} = 3.4 Hz, C_q), 129.9 (d, J_{CF} = 7.9 Hz, 2 × CH), 132.8 (C_q), 140.3 (C_q), 161.5 (d, J_{CF} = 245.9 Hz, C_q). HRMS (EI) calcd. for $C_{17}H_{15}FN$ [H^+]: 238.1027, found: 238.1024. The analytical data obtained is in agreement with those reported in literature.[50]

1-Phenyl-2-(4-chlorophenyl)pyrrole (14r): The excess of 1-phenylpyrrole (**3m**) was removed by Kugelrohr distillation in vacuo at 85 °C. The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14r** as light brown crytals (240 mg, 0.94 mmol, 47%). R_f: 0.5 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 6.35 (dd, J = 2.9 Hz, J = 3.5 Hz,1 H), 6.43 (dd, J = 1.8 Hz, J = 3.6 Hz, 1 H), 6.94 (dd, J = 1.8 Hz, J = 2.9 Hz, 1 H) 7.04 (d, J = 8.7 Hz, 2 H), 7.12-7.18 (m, 4 H), 7.28 (t, J = 7.4 Hz, 1 H), 7.33 (dt, J = 3.2 Hz, J = 7.4 Hz, 2 H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 109.3 (CH), 109.9 (CH), 124.7 (CH), 125.7 (2 × CH), 126.8 (CH), 128.2 (2 × CH), 129.1 (2 × CH), 129.3 (2 × CH), 131.4 (C_q), 132.1 (C_q), 132.5 (C_q), 140.2 (C_q). HRMS (EI) calcd. for $C_{16}H_{13}ClN$ [H^+]: 254.0731, found: 254.0734. The analytical data obtained is in agreement with those reported in literature.[50]

1-Phenyl-2-(4-bromophenyl)pyrrole (14s): The excess of 1-phenylpyrrole (**3m**) was removed by Kugelrohr distillation in vacuo at 85 °C. The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14s** as light brown crytals (193 mg, 0.82 mmol, 41%). R_f: 0.5 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 6.35 (dd, J = 2.8 Hz, J = 3.5 Hz, 1 H), 6.43 (dd, J = 1.7 Hz, J = 3.6 Hz, 1 H), 6.94 (dd, J = 1.7 Hz, J = 2.8 Hz, 1 H) 6.98 (d, J = 8.7 Hz, 2 H), 7.13-7.18 (m, 2 H), 7.28 (t, J = 7.4 Hz, 1 H), 7.30-7.36 (m, 4 H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 109.4 (CH), 111.0 (CH), 120.2 (C_q), 124.8 (CH), 125.7 (2 × CH), 126.8 (CH), 129.1 (2 × CH), 129.6 (2 × CH), 131.2 (2 × CH), 131.9 (C_q), 132.5 (C_q), 140.2 (C_q). HRMS (EI) calcd. for $C_{16}H_{13}BrN$ [H^+]: 298.0226, found: 298.0229.

1-*tert*-Butoxycarbonyl-2-(4-chlorophenyl)pyrrole (14t): The excess of 1-*tert*-butoxycarbonylpyrrole (**3n**) was removed by Kugelrohr distillation under reduced pressure at 80 °C. The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14t** as a dark red oil (171 mg,0.61 mmol, 31%). R_f:0.7 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.41 (s, 9 H), 6.20 (dd, J = 1.8 Hz, J = 3.2 Hz, 1 H), 6.23 (t J = 3.3 Hz, 1 H), 7.29 (d, J = 8.7 Hz, 2 H), 7.33 (d, J = 8.7 Hz, 2 H), 7.33 (dd, J = 1.8 Hz, J = 2.8 Hz, 1 H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 27.6 (3 × CH_3), 83.8 (C_q), 110.6 (CH), 114.7 (CH), 122.8 (CH), 127.7 (2 × CH), 130.4 (2 × CH), 132.8 (C_q), 133.1 (C_q), 133.7 (C_q), 149.1 (C_q). HRMS (EI) calcd. for $C_{15}H_{16}ClNNaO_2$ [M+H^+]: 300.0762, found: 300.0760. The analytical data obtained is in agreement with those reported in literature. [11b]

1-Benzyl-2-(4-chlorophenyl)pyrrole (14u): The excess of 1-benzylpyrrole (**3o**) was removed by Kugelrohr distillation in vacuo at 80 °C. The crude product was purified by flash chromatography on silica gel (hexane / dichloromethane = 30 : 1) to give **14u** as an orange oil (201 mg, 0.76 mmol, 38%). R_f: 0.5 (hexane / EtOAc = 10 : 1) [UV]. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 5.14 (s, 2 H), 6.27-6.31 (m, 2 H), 6.79 (t, J = 4.5 Hz, 1 H), 7.01 (d, J = 7.4 Hz, 2 H), 7.22-7.36 (m, 7 H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 50.7 (CH_2), 108.6 (CH), 109.3 (CH), 123.4 (CH), 126.3 (2 × CH), 127.8 (CH), 128.5 (2 × CH), 128.7 (2 × CH), 130.0

(2 × CH), 131.7 (C_q), 132.9 (C_q), 133.6 (C_q), 138.5 (C_q). HRMS (EI) calcd. for $C_{17}H_{15}ClN$ [H^+]: 268.0889, found: 268.0888.

General procedure for Figure 1: A degassed solution of sodium nitrite (21.0 mmol, 1.43 g) in water (10 mL) was added dropwise to an ice-cooled degassed solution of the 4-chloroaniline (**1a**) (20.0 mmol, 2.54 mg) in hydrochloric acid (1.5 N, 40 mL) over a period of 15 min. The clear solution was stirred for 15 more minutes at 0 °C. An aliquot of this 0.4 M aryldiazonium chloride solution (max. 2.00 mmol, 5.00 mL) was added to a pre-cooled and vigorously stirred aqueous solution of lithium hydroxide (4 N, 3 mL) under argon. To a mixture of 1-methylpyrrole (**3l**) (20.0 mmol) and lithium hydroxide (1-10 × 12.0 mmol, 288 mg) in *tert*-butanol (1-10 × 3.0 mL) at 70 °C under argon was added dropwise the previously prepared solution of the aryl diazotate (stepwise 1-10 × 2.00 mmol, 8.00 mL) over a period of seven minutes. After the addition was complete, the mixture was left to stir for 23 more minutes. The resulting reaction mixture was then extracted with dichloromethane (3 × 75 mL). The combined organic phases were washed with saturated aqueous sodium chloride and dried over sodium sulfate. The solvent was removed under reduced pressure. The yields of biaryls **14a** and azo compound **14n** were determined by ^{1}H NMR using 1,4-dimethyl terephthalate and 1,3,5-trimethoxybenzene as internal standards. 1-Methyl-2-(4-chlorophenyl)pyrrole (**14a**): For analytical data, see general procedure for Table 4. 1-Methyl-2,5-bis(4-chlorophenyl)pyrrole (**14n**): For analytical data, see general procedure for Table 6.

General procedure for Scheme 3: A degassed solution of sodium nitrite (21.0 mmol, 1.43 g) in water (10 mL) was added dropwise to an ice-cooled degassed solution of the aniline **1a,b** or **g** (20.0 mmol) in hydrochloric acid (1.5 N, 40 mL) over a period of 15 min. The clear solution was stirred for 15 more minutes at 0 °C. An aliquot of this 0.4 M aryldiazonium chloride solution (17-20 mmol) was added to a pre-cooled and vigorously stirred aqueous solution of lithium hydroxide (4 N) under argon to give the aryldiazotate **2a,b** or **g**. To a mixture of 1-methylpyrrole (10.0 equiv. per diazotate) and lithium hydroxide (6.0 equiv.) in *tert*-butanol at 70 °C under argon was added dropwise the previously prepared solution of the aryl diazotate over a period of seven minutes. After the addition was complete, the mixture was left to stir for 23 more minutes. The resulting reaction mixture was then extracted with dichloromethane (3 × 75 mL). The combined organic phases were washed with saturated aqueous sodium chloride and dried over sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel. 1-Methyl-2-(4-chlorophenyl)pyrrole (**14a**): For analytical data, see general procedure for Table 4. 1-Methyl-2-(4-fluorophenyl)pyrrole (**14b**) and 1-methyl-2-(4-bromophenyl)pyrrole (**14g**): For analytical data, see general procedure for Table 6.

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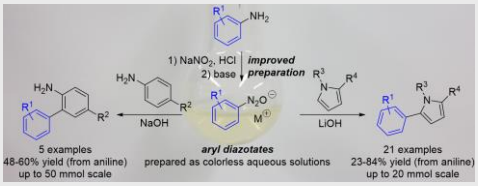

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Radical arylation of anilines and pyrroles via aryldiazotates

Based on an improved preparation of aryldiazotates, the arylation of anilines and 1-substituted pyrroles could be achieved under transition metal- and catalyst-free conditions. Combining manifold experimental and computational results, this study gives insights into the particular features of the underlying reaction mechanism.