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A general approach to substituted diphenyldiazenes

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Dedicated to Professor Dr. Eberhard Reimann with warmest wishes on the occasion of his 80th birthday

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ABSTRACT

A general and practical synthetic method for the construction of unsymmetrically substituted diphenyldiazenes based on classical azo coupling reaction has been developed. A key feature of this method is the use of *N,N*-diallyl protected aniline derivatives as coupling components. The *N,N*-diallyl moiety of the coupling component warrants sufficient reactivity and allows to avoid formation of constitutional isomers resulting from intermediate triazene formation. Furthermore, subsequent to the coupling reaction, the *N,N*-diallyl aminofunction, can be replaced by other substituents including hydrogen via diazonium ion intermediates. In general, following this approach target compounds can be obtained in reasonable to good yields.

1. Introduction

Aromatic azo compounds have found widespread application in chemical and pharmaceutical industry. They are classically used for instance as dyes and pigments,[1] food additives, indicators for pH-measurements,[2] initiators for radical reactions,[3] as therapeutic agents[4,5] or as part of drug delivery systems.[6] Meanwhile a major focus of azobenzenes is on their use as light sensitive molecular switches,[7–9] as for example, for photoresponsive liquid crystals.[10–12] But in recent time, many papers appeared in particular on the use of photoswitchable ligands for photopharmacology, e.g., for the optical control of epithelial sodium channels,[13] insulin receptors,[14] the acetylcholinesterase,[15] μ-opioid receptors,[16] TRPV1-channels,[17] glutamate receptors,[18] NMDA receptors,[19] AMPA receptors,[20] local anesthetics[21] and cell division.[22] We recently described the use of this method to control the activity of a neurotransmitter transporter, the GABA transporter GAT1, employing a photoswitchable ligand.[23]

Because of the broad interest in azo compounds, several methods have been developed for their synthesis in the past.[24] Classical approaches comprise azo coupling reaction,[25] the Mills reaction,[26] and the Wallach reaction.[27] Recently, additional preparative methods have been reported such as the reductive coupling of aromatic nitro derivatives[28] or the oxidative coupling of aniline derivatives.[29] However, the substitution pattern of the aromatic azo compounds accessible by these methods is in general quite limited. Thus, when dimerization reactions such as the reductive coupling of nitro compounds are applied to establish the respective phenyl azo derivatives, homo and hetero coupling will inevitably lead to symmetrically and unsymmetrically substituted azo compounds and as a consequence thereof to poor yields. Clearly, the well known azo coupling reactions in which diazonium salts are reacted with aromatic systems give access to a broad array of differently substituted target compounds. But this approach suffers from distinct limitations as well. In this case the coupling component to be reacted with the diazonium salt must display a sufficiently high electron density, typically achieved by the presence of a hydroxy- or an amino group to undergo the desired conversion.

In the context with the development of new photoswitchable ligands for GABA transporters, we sought for a very specific substitution pattern of the diphenyldiazene unit, that is, exhibiting two main features (Scheme 1): There should be a halogen function at one of the two phenyl moieties allowing the assembly of the final photosensitive target compounds or precursors by cross coupling reactions like Suzuki, Sonogashira or Heck reactions. The second phenyl moiety should exhibit substituents such as halogens or alkyl groups preferentially in the *ortho* or the *para* position or in both

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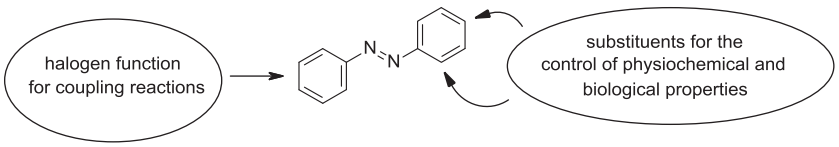


Scheme 1. Design of the desired target compounds.

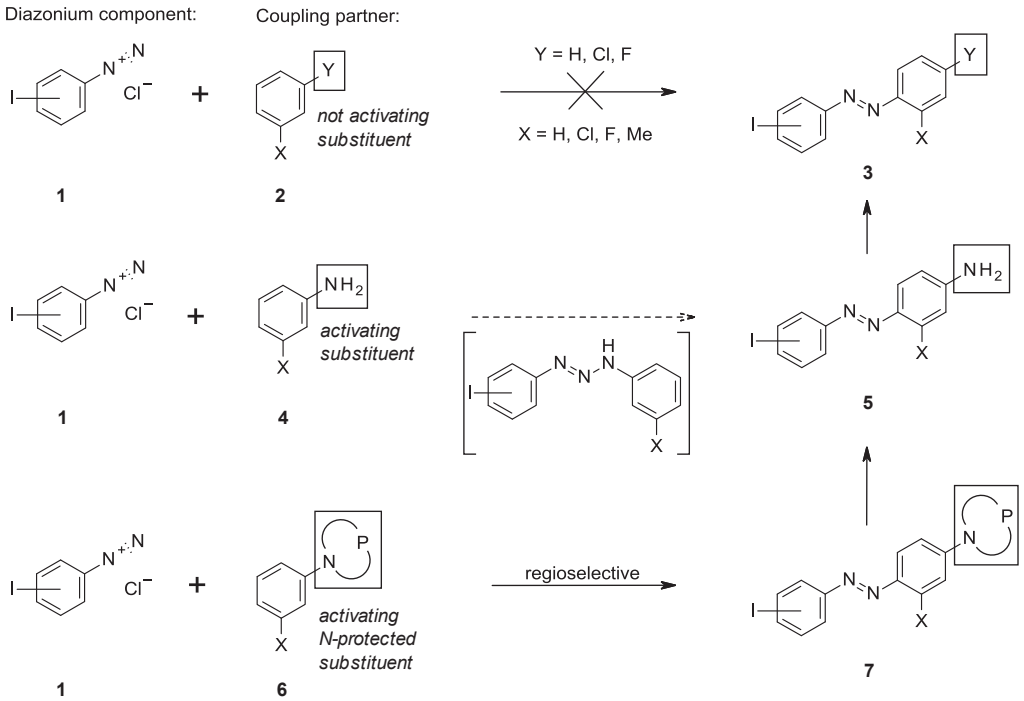
since due to former results substituents in these positions were expected to improve binding affinities to GABA transporters.[30] Moreover, particularly substituents in the *ortho* or *para* position might also allow to tune the kinetics of the *E*/*Z*-isomerization of the photosensitive compounds as well as the wavelength of the necessary light used for isomerization which is often a decisive factor for the use of photoswitchable compounds in organic tissues.

We considered azo coupling reactions as the most efficient and versatile synthetic approach to the desired azo compounds **3** (Scheme 2). For such coupling reactions, the diazonium salt **1** should be used exhibiting an iodine substituent that should allow to use the target compound for Palladium catalyzed coupling reactions. The main problem, however, to solve was the question which reactant might be employed as nucleophile in the azo coupling reaction. Benzene derivatives with halogen function but devoid of any activating groups such as an OH or an NH_2 group increasing electron density of the aromatic system like **2** do not come into consideration as they are known to fail in azo coupling reactions. Given the fact that primary aromatic amino groups can be efficiently exchanged by e.g., halogene substituents by Sandmeyer or Schiemann reactions, the use of aniline derivatives **4**, the electron density of which should be high enough to undergo the desired coupling reaction, appears quite tempting. But in that case, an exchange of the azo and the amino group may occur between the coupling reagents via triazenes as intermediates which would ultimately result in a variety of structurally isomeric azo compounds.

It appeared to us that this problem could be easily solved, if the aniline derivatives **4** displaying a primary amino function were replaced by benzene derivatives **6** exhibiting a tertiary amino function carrying suitable protecting groups. Due to the protecting groups, triazene formation and side reactions resulting therefrom could be ruled out whereas compounds **6** should be still amenable to azo coupling reactions owing to the positive mesomeric effect of the amino group. Given its easy introduction and efficient removal without a significant effect on the electron donor ability of amino groups, we considered allyl residues as the most appropriate protecting groups for the purpose of this study. In the present paper, we wish to report on the results of our study utilizing *N,N*-diallyl protected aniline derivatives **6** for azo coupling reactions and the subsequent transformation of the primary coupling products **7** into azo benzene derivatives **5** exhibiting a primary amino group by N-deprotection and further on the replacement of the primary amino group by various substituents (→**3**). To the best of our knowledge, the above outlined synthetic concept has not been reported before.

2. Results and discussions

The primary step of our synthetic sequence that should give access to a broad variety of differently substituted azo benzenes **3** and **5,** the coupling reaction between a diazonium salt and *N,N*-diallyl substituted aniline derivative was in general performed as follows. The diazonium salts of anilines **1**, i.e., **1a** and **1b**, were generated right before their use by treating the respective iodo



Scheme 2. Synthesis of substituted diphenyldiazenes by azo coupling.

aniline in a mixture of EtOH and 2 M HCl (3 equiv) with $NaNO_2$ (1.1 equiv in H_2O; excess $NaNO_2$ destroyed by addition of H_2NSO_3H). For the azo coupling reactions, the resulting solution was then added to a solution of the respective *N,N*-diallylaniline (in $EtOH/H_2O$) at 0 °C, in which, where indicated, also NaOAc or a further amount of 2 M HCl was present. The reaction mixture, the pH of which was estimated by means of indication paper, was finally stirred at 0 °C for the time given, before the product was isolated by extraction and purified by flash chromatography.

When diazonium salt **1** was reacted with *N,N*-diallylaniline (**8a**) under weak acidic pH conditions (pH ≈ 4), the reaction was complete within 4 h providing **9a** in 94% yield (Table 1, entry 1). For the coupling reaction of **1a** with the *m*-chloro substituted aniline derivative **8b**, longer reaction times were required. After 4 h as in the aforementioned reaction with **8a**, only 53% of **9b** were obtained which could be raised to 61% and 64% upon extension of the reaction time to 16 and 36 h, respectively (Table 1, entries 2–4).

When the compounds were allowed to react for 36 h but at a higher pH (≈5–6, adjusted by extra NaOAc), the yield lowered to 32% whereas 71% of **9b** could be isolated by running the reaction at a lower pH (Table 1, entry 6, pH ≈ 2–3, adjusted by omission of NaOAc). But when the pH was further reduced (to ≈1–2 by addition of 2 equiv of 2 M HCl) instead of an additional increase in yield a slight reduction occurred (Table 1, entry 7) indicating the pH optimum for the reaction to be ≈2–3. In case of the coupling reaction of **1a** with the *m*-fluoro substituted aniline derivative **8c** yields amounted to 55% (Table 1, entry 8) and 56% (Table 1, entry 9) only performed at the pH values of ≈4 and ≈2–3 that had so far appeared to be the most rewarding. For the more electron-rich 3-methyl substituted aniline derivative **8d**, the coupling reaction proceeded again quite smoothly. At both pH values, ≈4 and ≈2–3, the reaction was complete within 4 h yielding the coupling product in 92% and 85%, respectively (Table 1, entries 10–11).

The reaction conditions that had turned out best for the preparation of the diazobenzenes **9a**–**d** were finally also applied to the synthesis of regioisomers **10a**–**d** exhibiting the iodo substituent in *meta* position. That way, by coupling **8a**–**d** with *meta* iodo substituted diazonium salt **1b**, the corresponding diazobenzenes **10a**–**d** could be obtained in reasonable to good yields (51–84%, Table 2, entries 1–4).

The next step aimed at the deprotection of the tertiary amino function in **9a**–**d** and **10a**–**d** which should be accomplished by isomerization of the two allyl residues and subsequent hydrolysis of the thus formed aminovinyl units.

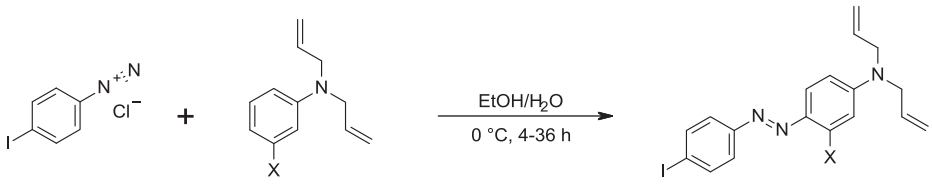
First attempts were performed with **9a** employing Pd/C, $Rh(PPh_3)_3Cl_2$ or $Ru(PPh_3)_3Cl_2$ in EtOH or THF also in presence of additives such as ethanolamine or trimethylamine, or the use of potassium *tert*-butoxide in DMSO or toluene remained unsuccessfully as either no reaction occurred or a complex mixture of products was formed. Finally, the transition metal catalyst $RuClH(CO)(PPh_3)_3$ reported by Krompiec et al.[31] to effect C–C double bond isomerization in *N*-allylamines was found to be well suited for our purposes, i.e., the isomerization of **9a** to **11a**. Thus when **9a** was heated with 1 Mol % of $RuClH(CO)(PPh_3)_3$ in CH_2Cl_2 to 60 °C in a microwave reactor, a clean reaction to the divinylamine **11a** occurred, which was complete within 2 h. Product **11a** was found to be labile. Therefore, neither **11a** nor the related products **11b**–**d** and **12a**–**d** were isolated, instead the solutions from the isomerization containing these compounds directly used for the next step.

The conditions required for the hydrolysis of the divinylamine function to liberate the primary amino group were exemplarily examined for **11a** to which end the solution of this compound resulting from the isomerization reaction was used without any purification. Treatment of **11a** with HCl, HOAc, NH_4Cl or water did not provide the desired amine or only as part of a complex reaction mixture. However, upon treatment of the CH_2Cl_2 solution of **11a**, obtained from the isomerization reaction, with $NH_3^+OHCl^-$ (10 equiv) and NEt_3 (5 equiv) at 60 °C for 3 h, a procedure developed for the cleavage of pyrrols,[32] a clear conversion to the free amino derivative occurred delivering **13a** in 96% yield.

The same procedure for the removal of the allyl protecting groups comprising isomerization and hydrolysis worked also well for **9b**–**9d** and the regioisomers regarding the iodo substituted **10a**–**d**, for the latter of which the reaction times for both steps had, however, to be extended to 4 h and 6 h, respectively, providing the target compounds **13b**–**d** and **14a**–**d** in yields from 87 to 95%.

The respective results that could be achieved for the cleavage of the *N,N*-diallylaniline protection group in these cases are shown in Table 3.

Table 1
Formation of diphenyldiazenes **9a**–**d** from diazotized 4-iodoaniline **1a** and *N,N*-diallylanilines **8a**–**d**[a]



1a **8a-d** **9a-d**

Entry	Educt	X	Additives[b]	pH range[c]	Reaction time [h]	Product	Yield:
1	**8a**	H	NaOAc, 2 equiv	≈4	4	**9a**	94%
2	**8b**	Cl	NaOAc, 2 equiv	≈4	4	**9b**	53%
3	**8b**	Cl	NaOAc, 2 equiv	≈4	16	**9b**	61%
4	**8b**	Cl	NaOAc, 2 equiv	≈4	36	**9b**	64%
5	**8b**	Cl	NaOAc, 4 equiv	≈5–6	36	**9b**	32%
6	**8b**	Cl	—	≈2–3	36	**9b**	71%
7	**8b**	Cl	2M HCl, 2 equiv	≈1–2	36	**9b**	68%
8	**8c**	F	NaOAc, 2 equiv	≈4	36	**9c**	55%
9	**8c**	F	—	≈2–3	36	**9c**	56%
10	**8d**	Me	NaOAc, 2 equiv	≈4	4	**9d**	92%
11	**8d**	Me	—	≈2–3	4	**9d**	85%

[a] A solution of **1a** was freshly generated from 4-iodoaniline by addition of $NaNO_2$ (1.1 equiv) and 2M HCl (3.0 equiv) in $EtOH/H_2O$ (2:1). This solution was then added to a separate solution of **8a**–**d** in $EtOH/H_2O$ (2:1).
[b] Further additives added to the solution of the coupling component **8a**–**d** where indicated.
[c] Determined from the reaction mixture directly after the addition of the solution of **1a** to the solution of **8a**–**d**.

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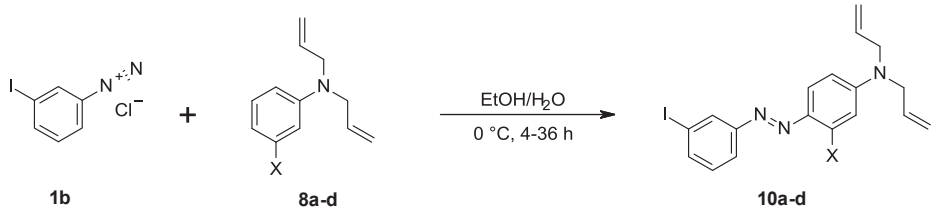
Table 2
Formation of diphenyldiazenes **10a**–**d** from diazotated 3-iodoaniline **1b** and *N,N*-diallylanilines **8a**–**d**[a]



1b **8a-d** **10a-d**

Entry	Educt	X	Additives[b]	pH range[c]	Reaction time [h]	Product	Yield:
1	**8a**	H	NaOAc, 2 equiv	≈4	4	**10a**	80%
2	**8b**	Cl	—	≈2–3	36	**10b**	63%
3	**8c**	F	—	≈2–3	36	**10c**	51%
4	**8d**	Me	NaOAc, 2 equiv	≈4	4	**10d**	84%

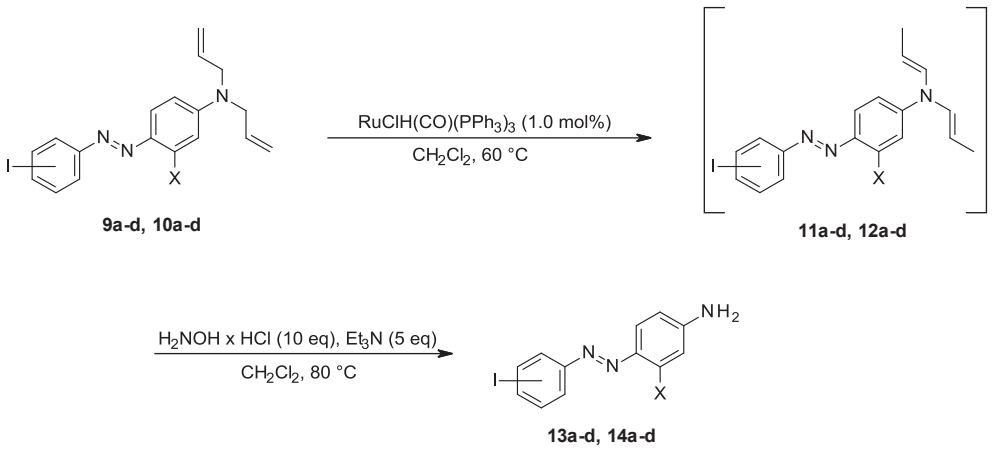
[a] A solution of **1b** was freshly generated from 4-iodoaniline by addition of $NaNO_2$ (1.1 equiv) and 2M HCl (3.0 equiv) in EtOH/H_2O (2:1). This solution was then added to a separate solution of **8a**–**d** in EtOH/H_2O (2:1).
[b] Further additives added to the solution of the coupling component **8a**–**d** where indicated.
[c] Determined from the reaction mixture directly after the addition of the solution of **1b** to the solution of **8a**–**d**.

To demonstrate the synthetic utility of the thus obtained diphenyldiazenes, prototypic reactions for the replacement of the amino group in **13a**–**d** by hydrogen, chlorine, and fluorine have been performed.

Reductive removal of the amino group in **13a**–**d** could be accomplished following a standard procedure. Treatment with $NaNO_2$ (3 equiv) and H_3PO_2 (20 equiv) of **13a**–**d** in THF provided the desired desamino derivatives **15a**–**d** in reasonable to good yields (Table 4, 66–75%).

Substitution of the amino group in the aniline derivatives obtained in this study by chlorine or fluorine in a Sandmeyer and Schiemann reaction is feasible as well, as shown for **13a**. Treatment of **13a** with *tert*-BuONO and 4-dodecylbenzenesulfonic acid in tetrachloromethane and subsequent heating with triethylamine following a literature procedure[33] provided the chloroderivative **16** in 52%. For this transformation, it occurred crucial that CCl_4 was employed as solvent as with other organic solvent which were required because of the poor solubility of **13a** in water, partial

Table 3
Deallylation of diphenyldiazenes **9** and **10** via isomerization and subsequent hydrolysis



9a-d, 10a-d **11a-d, 12a-d** **13a-d, 14a-d**

Entry	Educt	X	Isomerization time [h]	Hydrolysis time [h]	Product	Yield:
1	**9a**	H	2	3	**13a**	96%
2	**9b**	Cl	2	3	**13b**	93%
3	**9c**	F	2	3	**13c**	91%
4	**9d**	Me	2	3	**13d**	95%
5	**10a**	H	4	6	**14a**	92%
6	**10b**	Cl	4	6	**14b**	88%
7	**10c**	F	4	6	**14c**	87%
8	**10d**	Me	4	6	**14d**	90%

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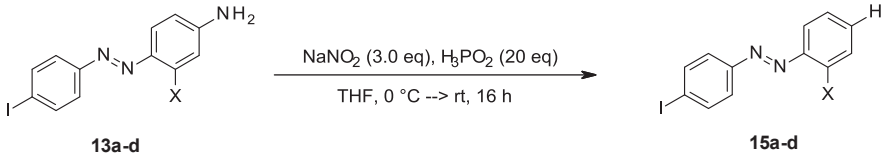
Table 4
Reductive removal of the amino group in aniline derivatives **13a**–**d**



13a-d **15a-d**

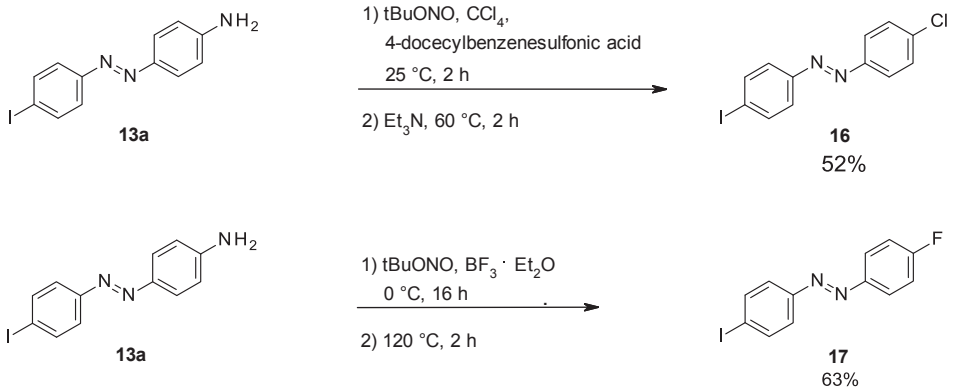
Entry	Educt	X	Product	Yield:
1	**13a**	H	**15a**	75%
2	**13b**	Cl	**15b**	66%
3	**13c**	F	**15c**	68%
4	**13d**	Me	**15d**	71%

replacement of the amino substituent by hydrogen occurred leading to diminished yields.

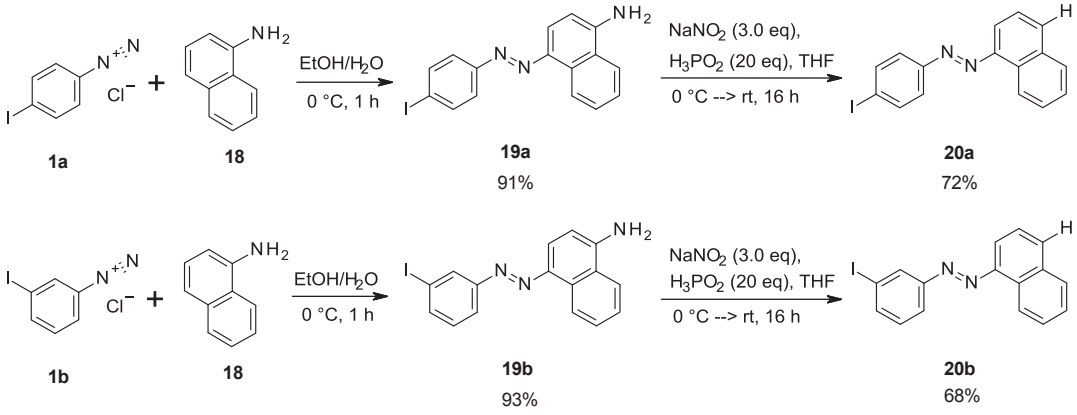
Similarly, the fluorine derivative **17** could be prepared in a Schiemann reaction treating **13a** with *tert*-BuONO and $BF_3 \cdot Et_2O$ (followed by heating to 120 °C) the yield amounting to 63% (Scheme 3). According to these results, the synthetic sequence of azo coupling with *N,N*-diallyl protected aniline derivatives, subsequent deprotection and substitution of the amino group represents a highly efficient and versatile access to differently substituted diphenyldiazene derivatives (see Scheme 4).

Having successfully accomplished the formation of amino substituted diphenyldiazenes by azo coupling reactions with N-protected aniline derivatives, we wondered whether an analogous reaction could possibly also be performed with 1-aminonaphthalene in either N-protected or even unprotected form.

Interestingly, in this case a protection of the primary amino group was not required. When the diazonium salts **1a** and **1b** derived from 4-iodoaniline and 3-iodoaniline were reacted with 1-aminonaphtalene (**18**) the corresponding azo coupling products **19a** and **19b** were formed without any sign of isomeric products that could have resulted from intermediate triazene formation. Also the yields for the products amounting to 91% and 93% for **19a** and **19b**, respectively, were very high. As in the case of the amino substituted diphenyldiazenes the reductive elimination of the amino group in **19a**–**b** employing $NaNO_2$ and H_3PO_2 worked here well, too, providing the desaminated phenylnaphtyl diazenes **20a**–**b** in good yields (**20a**: 72%; **20b**: 68%).



Scheme 3. Replacement of the amino group in **13a** by a chlorine and fluorine substituent.



Scheme 4. Azo coupling of diazotated iodoaniline **1a**–**b** with 1-aminonaphthaline (**18**).

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Of these compounds, the naphtylphenyl diazene derivative **20b** has already successfully been used as a building block for the construction of a valuable photoswitchable ligand of the GABA transporter GAT1.[23]

3. Conclusion

Based on diazonium chemistry, a highly versatile synthetic route to substituted diphenyldiazenes exhibiting an iodo substituent on one of the two aromatic rings and additional substituents on the other has been established.

The method comprises the coupling of diazonium salts derived from iodo substituted aniline derivatives on the one with *N,N*-diallyl protected anilines on the other side. The key feature of this approach is to be seen in the use of the temporary protection of the amino group of the aniline derivative with two *N*-allyl residues. The *N,N*-diallyl residue warrants sufficient reactivity of the benzene derivatives for azo coupling reactions whereas the N-protection of the amino group rules out side reaction that would otherwise arise from intermediate triazene formation. Further, the primary amino group accessible by deprotection of the *N,N*-diallyl moiety after the azo coupling reaction has the advantage to provide the opportunity for a broad array of transformation reactions as exemplified by its replacement by hydrogen, chlorine or fluorine substituents employing common methods. Overall the synthetic method outlined in this paper provides a broadly applicable and flexible approach to differently substituted diphenyl diazenens derivatives which equipped with a suitable functional group, such as an iodine substituent for metal catalyzed coupling reactions, can be rewarding building blocks for the construction of photoswitchable bioactive compounds.

4. Experimental section

4.1. General methods

For all reactions only distilled solvents were used. THF and NEt_3 were dried over sodium and distilled under nitrogen. CH_2Cl_2 was distilled from CaH_2 under nitrogen. Commercial available reagents were used without further purification. Flash column chromatography was performed using silica gel (40–60 μm). NMR spectra were measured with a Jeol Eclipse +400 (400 MHz) and a Jeol Eclipse +500 (500 MHz) spectrometer or an Avance III HD 400 MHz Bruker BioSpin and an Avance III HD 500 MHz Bruker BioSpin spectrometer. ^1H NMR chemical shifts were referenced to TMS and ^{13}C NMR chemical shifts were referenced to $CHCl_3$. The coupling constants were stated with an accuracy of 0.5 Hz. MestreNova software was used for further analysis of the spectra. IR spectra were recorded with an FT-IR spectrometer Paragon 1000 (PerkinElmer). Samples were measured either as KBr pellets or as films on NaCl plates. Spectrum v2.00 software (PerkinElmer) was used for analysis. Mass spectra were measured with a mass spectrometer 59827A with 59980 particle beam LC/MS interface (Hewlett–Packard). High resolution mass spectrometry was carried out with an LTQ FT (ThermoFinnigan), FAB (Xenon, 6 kV, MBA, reference PEG), or a JMS GCmate II (Jeol).

4.2. General procedure for the allylation of aniline derivatives (GP1)

The corresponding aniline was dissolved in EtOH (2 mL/mmol) and H_2O (0.5 mL/mmol) was added. Ally bromide (2.4 equiv) and Na_2CO_3 (1.2 equiv) were added and the mixture was heated to reflux for the indicated time. After the end of the reaction, the main part of the alcohol was removed by distillation. CH_2Cl_2 (5 mL/mmol) and H_2O (5 mL/mmol) were added and the product was extracted with CH_2Cl_2 (3×). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (eluting with pentane) to give the diallylated derivatives.

4.3. General procedure for the azo coupling (GP2)

The corresponding iodo aniline (1.0 equiv) was dissolved in of EtOH (3 mL/mmol) und 2N HCl (1.5 mL/mmol, 3.0 equiv) was added. The mixture was cooled to 0 °C and a pre-cooled solution of $NaNO_2$ (1.1 equiv) in H_2O (1.5 mL/mmol) was added dropwise over a period of 10 min. After the end of the addition, the solution was stirred for further 10 min at 0 °C. Then the excess of $NaNO_2$ was removed by the addition of amidosulfuric acid (0.2 equiv) once again followed by stirring for 10 min at 0 °C (suspension A).

The corresponding *N,N*-diallyl aniline derivative (1.0 equiv) was dissolved in EtOH (20 mL/mmol) and 10 mL/mmol water was added (solution B). If indicated, to this solution is also added either NaOAc (2.0 equiv) or a further amount of 2N HCl (1 mL/mmol, 2.0 equiv) additionally.

Suspension A was then added to solution B at 0 °C, the pH was determined of the resulting mixture (indicator paper) and it was stirred for the indicated time at 0 °C. Afterwards it was allowed to warm up to rt slowly followed by the addition of both CH_2Cl_2 (20 mL/mmol) and H_2O (20 mL/mmol). The aqueous phase was made alkaline (pH 10–12) by the addition of NaOH and the product was extracted with CH_2Cl_2 (3×). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (eluting with pentane/CH_2Cl_2=8/2) to give the clean azo compound.

4.4. General procedure for the deallylation of the diallylamines (GP3)

Under nitrogen the corresponding *N,N*-diallyl amine (1.0 equiv) and $RuClH(CO)(PPh_3)_3$ (0.01 equiv) were introduced in a pressure tube and dissolved in of CH_2Cl_2 (5 mL/mmol). The tube was sealed air tightly and the solution was heated to 60 °C for the indicated time. After cooling to rt both $H_2NOH{\times}HCl$ (10 equiv) and Et_3N (5 equiv) were added and the mixture was heated to 80 °C for the indicated time. After cooling to rt, once again H_2O (5 mL/mmol) was added and the product was extracted with CH_2Cl_2 (3×). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (eluting with pentane/dichloromethane=1/1) to give the corresponding primary aromatic amine.

4.5. General procedure for the reductive dediazoniation of the aromatic amines (GP4)

The corresponding primary aromatic amine derivative (1.0 equiv) was dissolved in THF (20 mL/mmol), cooled to 0 °C and hypophosphorous acid (50% solution in water, 20 equiv) was added. Sodium nitrite (3.0 equiv) was added and the mixture was stirred for 4 h at 0 °C and then at rt for further 12 h. Afterwards there were added CH_2CL_2 (20 mL/mmol) and water (20 mL/mmol) and the aqueous phase was made alkaline (pH 10–12) with 2N NaOH. The product was extracted with CH_2Cl_2 (3×). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (eluting with pentane) to give the corresponding reduced species.

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4.6. Characterization data of new products

*4.6.1. N,N-Diallylaniline (**8a**).* According to GP1 from aniline (4.7 g, 50 mmol), allylbromide (14.8 g, 120 mmol) and K_2CO_3 (6.4 g, 60 mmol). The reaction time was 3 h **8a** was obtained as colorless oil (8.20 g, 95%). TLC: $R_f \approx 0.3$ (pentane). IR (NaCl): $\tilde{\nu}$=3084, 3062, 2979, 2912, 2858, 1642, 1599, 1574, 1505, 1388, 1357, 1233, 1181, 988, 918, 746, 691 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 21 °C, TMS): δ=3.90 (dt, J=4.6/1.6 Hz, 4H), 5.10–5.21 (m, 4H), 5.84 (ddt, J=17.2/10.1/4.9 Hz, 2H), 6.63–6.72 (m, 3H), 7.14–7.23 (m, 2H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 21 °C, TMS): δ=52.81 (2C), 112.41 (2C), 116.06 (2C), 116.38, 129.16 (2C), 134.12 (2C), 148.78 ppm. M ($C_{12}H_{15}N$)=173.25. MS (EI+): *m/z*: 173.1 (M^+). HRMS (EI+): M^+ calcd for $C_{12}H_{15}N$: 173.1204; found 173.1205.

*4.6.2. N,N-Diallyl-3-chloroaniline (**8b**).* According to GP1 from 3-chloro-aniline (6.4 g, 50 mmol), allylbromide (14.8 g, 120 mmol) and K_2CO_3 (6.4 g, 60 mmol). The reaction time was 4 h **8b** was obtained as colorless oil (9.60 g, 92%). TLC: $R_f \approx 0.3$ (pentane). IR (NaCl): $\tilde{\nu}$=3083, 3008, 2981, 2910, 2865, 1642, 1594, 1560, 1493, 1417, 1385, 1357, 1235, 1180, 1101, 985, 920, 830, 759, 681 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 21 °C, TMS): δ=3.89 (dt, J=4.0/1.7 Hz, 4H), 5.14 (dq, J=8.8/1.7 Hz, 2H), 5.17 (m, 2H), 5.82 (ddt, J=16.8/10.7/4.8 Hz, 2H), 6.54 (ddd, J=8.4/2.4/0.9 Hz, 1H), 6.63 (m, 2H), 7.07 (t, J=8.0 Hz, 1H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 21 °C, TMS): δ=52.81 (2C), 110.48, 112.19, 116.20, 116.36 (2C), 130.08, 133.36 (2C), 135.07, 149.85 ppm. M ($C_{12}H_{14}ClN$)=207.7. MS (EI+): *m/z*: 207.1 (M^+). HRMS (EI+): M^+ calcd for $C_{12}H_{14}ClN$ 207.0815; found 207.0808.

*4.6.3. N,N-Diallyl-3-fluoroaniline (**8c**).* According to GP1 from 3-fluoro-aniline (5.6 g, 50 mmol), allylbromide (14.8 g, 120 mmol) and K_2CO_3 (6.4 g, 60 mmol). The reaction time was 4 h **8c** was obtained as colorless oil (9.01 g, 94%). TLC: $R_f \approx 0.3$ (pentane). IR (NaCl): $\tilde{\nu}$=3083, 3008, 2981, 2912, 2866, 1642, 1619, 1578, 1500, 1418, 1389, 1357, 1333, 1257, 1184, 1158, 991, 960, 922, 822, 753, 681 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 21 °C, TMS): δ=3.89 (dt, J=3.8/1.7 Hz, 4H), 5.14 (dq, J=5.1/1.7 Hz, 2H), 5.16–5.18 (m, 2H), 5.82 (ddt, J=17.7/9.8/4.8 Hz, 2H), 6.32–6.38 (m, 2H), 6.43 (ddd, J=8.4/2.3/0.9 Hz, 1H), 7.04–7.14 (m, 1H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 21 °C, TMS): δ=52.93 (2C), 99.34 (d, $^2J_{CF}$=26.1 Hz), 102.77 (d, $^2J_{CF}$=21.6 Hz), 107.91 (d, $^4J_{CF}$=2.0 Hz), 116.32 (2C), 130.13 (d, $^3J_{CF}$=10.4 Hz), 133.49 (2C), 150.54 (d, $^3J_{CF}$=10.7 Hz), 164.24 (d, $^1J_{CF}$=241.5 Hz) ppm. M ($C_{12}H_{14}FN$)=191.2. MS (EI+): *m/z*: 191.1 (M^+). HRMS (EI+): M^+ calcd for $C_{12}H_{14}FN$ 191.1110; found 191.1108.

*4.6.4. N,N-Diallyl-3-methylaniline (**8d**).* According to GP1 from 3-methyl-aniline (5.4 g, 50 mmol), allylbromide (14.8 g, 120 mmol) and K_2CO_3 (6.4 g, 60 mmol). The reaction time was 4 h **8d** was obtained as colorless oil (8.12 g, 87%). TLC: $R_f \approx 0.3$ (pentane). IR (NaCl): $\tilde{\nu}$=3079, 3042, 3006, 2978, 2916, 2861, 1641, 1601, 1581, 1497, 1417, 1385, 1357, 1333, 1249, 1179, 990, 954, 917, 837, 764, 691 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 21 °C, TMS): δ=2.28 (s, 3H), 3.89 (dt, J=4.5/1.6 Hz, 4H), 5.12–5.19 (m, 4H), 5.84 (ddt, J=17.2/10.0/4.9 Hz, 2H), 6.46–6.55 (m, 3H), 7.03–7.12 (m, 1H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 21 °C, TMS): δ=22.05, 52.75 (2C), 109.66, 113.11, 116.00 (2C), 117.36, 129.05, 134.21 (2C), 138.82, 148.89 ppm. M ($C_{13}H_{17}N$)=187.28. MS (EI+): *m/z*: 187.1 (M^+). HRMS (EI+): M^+ calcd for $C_{13}H_{17}N$ 187.1361; found 187.1355.

*4.6.5. N,N-Diallyl-4-[(E)-(4-iodophenyl)azo]aniline (**9a**).* According to GP2 solution A was made of 4-iodoaniline (2.24 g, 10.0 mmol) in EtOH (30 mL) and 2 N HCl (15 ml, 30 mmol), sodium nitrite (0.76 g, 11.0 mmol) in H_2O (10 mL) and amidosulfuric acid (0.20 g, 2.0 mmol). Solution B was obtained from **8a** (1.77 g, 10.0 mmol) in EtOH (200 mL) and H_2O (100 mL) and an addition of sodium acetate (1.70 g, 20.0 mmol). The resulting pH was about 4. The reaction time was 4 h at 0 °C. **9a** was obtained as red solid (3.80 g, 94%). TLC: $R_f \approx 0.4$ (pentane/CH_2Cl_2=8/2). Mp: 41 °C. IR (KBr): $\tilde{\nu}$=3075, 3006, 2974, 2864, 1596, 1512, 1401, 1383, 1350, 1310, 1234, 1158, 1137, 1001, 938, 919, 829 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 21 °C, TMS): δ=3.98 (dt, J=4.0/1.6 Hz, 4H), 5.13–5.22 (m, 4H), 5.84 (ddt, J=17.1/10.1/4.7 Hz, 2H), 6.70–6.74 (m, 2H), 7.53–7.58 (m, 2H), 7.75–7.79 (m, 2H), 7.79–7.84 (m, 2H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 21 °C, TMS): δ=52.89 (2C), 95.36, 111.87 (2C), 116.65 (2C), 124.05 (2C), 125.30 (2C), 132.83 (2C), 138.15 (2C), 143.76, 151.41, 152.64 ppm. M ($C_{18}H_{18}IN_3$)=403.26. MS (ESI+): *m/z*: 404.1 ($[M+H]^+$). HRMS (ESI+): M^+ calcd for $C_{18}H_{19}IN_3$ 404.0545; found 404.0617.

*4.6.6. N,N-Diallyl-3-chloro-4-[(E)-(4-iodophenyl)azo]aniline (**9b**).* According to GP2 solution A was made of 4-iodoaniline (2.24 g, 10.0 mmol) in EtOH (30 mL) and 2 N HCl (15 mL, 30 mmol), sodium nitrite (0.76 g, 11.0 mmol) in H_2O (10 mL) and amidosulfuric acid (0.20 g, 2.0 mmol). Solution B was obtained from **8b** (2.12 g, 10.0 mmol) in EtOH (200 mL) and H_2O (100 mL) without any further additions. The resulting pH was between 2 and 3. The reaction time was 36 h at 0 °C. **9b** was obtained as red solid (3.12 g, 71%). TLC: $R_f \approx 0.4$ (pentane/CH_2Cl_2=8/2). Mp: 81 °C. IR (KBr): $\tilde{\nu}$=3429, 3078, 3004, 2975, 2885, 1590, 1503, 1381, 1344, 1322, 1300, 1229, 1191, 1176, 1126, 1043, 1002, 925, 835, 802 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 21 °C, TMS): δ=3.97 (dt, J=4.7/1.8 Hz, 4H), 5.16 (dq, J=17.1/1.6 Hz, 2H), 5.21 (dq, J=10.3/1.4 Hz, 2H), 5.83 (ddt, J=17.1/10.2/4.7 Hz, 2H), 6.58 (dd, J=9.3/2.8 Hz, 1H), 6.77 (d, J=2.8 Hz, 1H), 7.59–7.62 (m, 2H), 7.74 (d, J=9.2 Hz, 1H), 7.77–7.81 (m, 2H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 21 °C, TMS): δ=52.92 (2C), 96.09, 111.01, 112.30, 116.95 (2C), 118.59, 124.45 (2C), 132.28 (2C), 138.25 (2C), 138.87, 139.21, 151.82, 152.70 ppm. M ($C_{18}H_{17}ICl N_3$)=437.70. MS (EI+): *m/z*: 437.0 (M^+). HRMS (EI+): M^+ calcd for $C_{18}H_{17}ICl N_3$ 437.0156; found 437.0146.

*4.6.7. N,N-Diallyl-3-fluoro-4-[(E)-(4-iodophenyl)azo]aniline (**9c**).* According to GP2 solution A was made of 4-iodoaniline (2.24 g, 10.0 mmol) in EtOH (30 mL) and 2 N HCl (15 mL, 30 mmol), sodium nitrite (0.76 g, 11.0 mmol) in H_2O (10 mL) and amidosulfuric acid (0.20 g, 2.0 mmol). Solution B was obtained from **8c** (1.95 g, 10.0 mmol) in EtOH (200 mL) and H_2O (100 mL) without any further additions. The resulting pH was between 2 and 3. The reaction time was 36 h at 0 °C. **9c** was obtained as red solid (2.36 g, 56%). TLC: $R_f \approx 0.4$ (pentane/CH_2Cl_2=8/2). Mp: 72 °C. IR (KBr): $\tilde{\nu}$=3078, 3003, 2976, 2923, 1610, 1560, 1511, 1395, 1381, 1350, 1330, 1232, 1184, 1108, 1001, 919, 828 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 21 °C, TMS): δ=3.94–3.98 (m, 4H), 5.16 (dq, J=17.2/1.6 Hz, 2H), 5.21 (dq, J=10.4/1.6 Hz, 2H), 5.82 (ddt, J=17.0/10.0/4.7 Hz, 2H), 6.41–6.48 (m, 2H), 7.55–7.60 (m, 2H), 7.70–7.75 (m, 1H), 7.75–7.80 (m, 2H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 21 °C, TMS): δ=53.00 (2C), 95.83, 98.85 (d, J=24.9 Hz), 108.22 (d, J=1.5 Hz), 116.94 (2C), 118.71 (d, J=2.2 Hz), 124.23 (2C), 131.64 (d, J=7.1 Hz), 132.27 (2C), 138.18 (2C), 152.72, 153.00 (d, J=11.6 Hz), 162.49 (d, J=255.5 Hz) ppm. M ($C_{18}H_{17}IFN_3$)=421.25. MS (EI+): *m/z*: 421.0 (M^+). HRMS (EI+): M^+ calcd for $C_{18}H_{17}IFN_3$ 421.0451; found 421.0450.

*4.6.8. N,N-Diallyl-3-methyl-4-[(E)-(4-iodophenyl)azo]aniline (**9d**).* According to GP2 solution A was made of 4-iodoaniline (2.24 g, 10.0 mmol) in EtOH (30 mL) and 2 N HCl (15 ml, 30 mmol), sodium nitrite (0.76 g, 11.0 mmol) in H_2O (10 mL) and amidosulfuric acid (0.20 g, 2.0 mmol). Solution B was obtained from **8d** (1.91 g, 10.0 mmol) in EtOH (200 mL) and H_2O (100 mL) and an addition of sodium acetate (1.70 g, 20.0 mmol). The resulting pH was about 4. The reaction time was 4 h at 0 °C. **9d** was obtained as red solid (3.84 g, 92%). TLC: $R_f \approx 0.4$ (pentane/CH_2Cl_2=8/2). Mp: 68 °C. IR (KBr): $\tilde{\nu}$=3075, 3002, 2974, 2920, 2886, 1596, 1565, 1503, 1378, 1347, 1324, 1298, 1232, 1190, 1102, 1001, 957, 920, 835, 821, 802 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 21 °C, TMS): δ=2.66 (s, 3H),

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3.94–3.99 (m, 4H), 5.13–5.20 (m, 4H), 5.84 (ddt, *J*=17.0/9.9/4.7 Hz, 2H), 6.51–6.56 (m, 2H), 7.53–7.57 (m, 2H), 7.68–7.73 (m, 1H), 7.74–7.78 (m, 2H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 21 °C, TMS): δ=18.36, 52.70 (2C), 94.99, 110.39, 112.84, 116.54 (2C), 117.11, 124.14 (2C), 132.96 (2C), 138.09 (2C), 141.58, 141.94, 151.39, 153.03 ppm. M ($C_{19}H_{20}IN_3$)=417.29. MS (EI+): *m/z*: 417.1 (M^+). HRMS (EI+): M^+ calcd for $C_{19}H_{20}IN_3$ 417.0702; found 417.0694.

*4.6.9. N,N-Diallyl-4-[(E)-(3-iodophenyl)azo]aniline (**10a**).* According to GP2 solution A was made of 3-iodoaniline (2.24 g, 10.0 mmol) in EtOH (30 mL) and 2 N HCl (15 ml, 30 mmol), sodium nitrite (0.76 g, 11.0 mmol) in H_2O (10 mL) and amidosulfuric acid (0.20 g, 2.0 mmol). Solution B was obtained from **8a** (1.77 g, 10.0 mmol) in EtOH (200 mL) and H_2O (100 mL) and an addition of sodium acetate (1.70 g, 20.0 mmol). The resulting pH was about 4. The reaction time was 4 h at 0 °C. **10a** was obtained as red high vicious oil (3.22 g, 80%). TLC: $R_f \approx 0.4$ (pentane/CH_2Cl_2=8/2). IR (KBr): $\tilde{\nu}$=3070, 3060, 3006, 2980, 2920, 1642, 1599, 1565, 1512, 1420, 1387, 1354, 1334, 1312, 1233, 1177, 1156, 1138, 1052, 991, 921, 820, 783, 701 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 21 °C, TMS): δ=3.97–4.04 (m, 4H), 5.13–5.24 (m, 4H), 5.86 (ddt, *J*=16.9/9.8/4.7 Hz, 2H), 6.74 (d, *J*=9.1 Hz, 2H), 7.19 (t, *J*=7.9 Hz, 1H), 7.67 (d, *J*=7.8 Hz, 1H), 7.78–7.81 (m, 1H), 7.82 (d, *J*=9.1 Hz, 2H), 8.16 (t, *J*=1.6 Hz, 1H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 21 °C, TMS): δ=52.78 (2C), 94.60, 111.73 (2C), 116.55 (2C), 122.85, 125.27 (2C), 129.95, 130.43, 132.68 (2C), 137.78, 143.59, 151.41, 154.08 ppm. M ($C_{18}H_{18}IN_3$)=403.3. MS (EI+): *m/z*: 403.1 (M^+). HRMS (EI+): M^+ calcd for $C_{18}H_{18}IN_3$ 403.0545; found 403.0546.

*4.6.10. N,N-Diallyl-3-chloro-4-[(E)-(3-iodophenyl)azo]aniline (**10b**).* According to GP2 solution A was made of 3-iodoaniline (2.24 g, 10.0 mmol) in EtOH (30 mL) and 2 N HCl (15 ml, 30 mmol), sodium nitrite (0.76 g, 11.0 mmol) in H_2O (10 mL) and amidosulfuric acid (0.20 g, 2.0 mmol). Solution B was obtained from **8b** (2.12 g, 10.0 mmol) in EtOH (200 mL) and H_2O (100 mL) without any further additions. The resulting pH was between 2 and 3. The reaction time was 36 h at 0 °C. **10b** was obtained as red solid (2.75 g, 63%). TLC: $R_f \approx 0.4$ (pentane/CH_2Cl_2=8/2). Mp: 74 °C. IR (KBr): $\tilde{\nu}$=3070, 3062, 3006, 2980, 2922, 1591, 1501, 1438, 1382, 1353, 1225, 1173, 1133, 1040, 991, 923, 782 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 22 °C, TMS): δ=3.93–4.00 (m, 4H), 5.16 (d, *J*=17.2 Hz, 2H), 5.21 (d, *J*=10.3 Hz, 2H), 5.82 (ddt, *J*=18.7/9.4/4.4 Hz, 2H), 6.57 (dd, *J*=9.2/2.1 Hz, 1H), 6.77 (d, *J*=2.6 Hz, 1H), 7.18 (t, *J*=7.9 Hz, 1H), 7.68 (d, *J*=7.8 Hz, 1H), 7.72 (d, *J*=9.2 Hz, 1H), 7.84 (d, *J*=8.0 Hz, 1H), 8.19 (t, *J*=1.7 Hz, 1H). ppm ^{13}C NMR (126 MHz, $CDCl_3$, 22 °C, TMS): δ=52.75 (2C), 94.58, 110.80, 112.10, 116.80 (2C), 118.45, 122.86, 130.45, 130.71, 132.08 (2C), 138.23, 138.88, 138.97, 151.74, 154.02 ppm. M ($C_{18}H_{17}IN_3Cl$)=437.7. MS (EI+): *m/z*: 437.0 (M^+). HRMS (EI+): M^+ calcd for $C_{18}H_{17}IN_3Cl$ 437.0156; found 437.0150.

*4.6.11. N,N-Diallyl-3-fluoro-4-[(E)-(3-iodophenyl)azo]aniline (**10c**).* According to GP2 solution A was made of 3-iodoaniline (2.24 g, 10.0 mmol) in EtOH (30 mL) and 2 N HCl (15 ml, 30 mmol), sodium nitrite (0.76 g, 11.0 mmol) in H_2O (10 mL) and amidosulfuric acid (0.20 g, 2.0 mmol). Solution B was obtained from **8c** (1.95 g, 10.0 mmol) in EtOH (200 mL) and H_2O (100 mL) without any further additions. The resulting pH was between 2 and 3. The reaction time was 36 h at 0 °C. **10c** was obtained as red solid (2.16 g, 51%). TLC: $R_f \approx 0.4$ (pentane/CH_2Cl_2=8/2). Mp: 65 °C. IR (KBr): $\tilde{\nu}$=3082, 3062, 3007, 2981, 2922, 1613, 1566, 1510, 1387, 1355, 1331, 1235, 1182, 1112, 991, 921, 821, 783 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 22 °C, TMS): δ=3.95–4.00 (m, 4H), 5.17 (dd, *J*=17.2/1.4 Hz, 2H), 5.22 (dd, *J*=10.4/1.3 Hz, 2H), 5.83 (ddt, *J*=17.1/9.9/4.7 Hz, 2H), 6.41–6.50 (m, 2H), 7.18 (t, *J*=7.9 Hz, 1H), 7.68 (dt, *J*=7.7/1.1 Hz, 1H), 7.72 (m, 1H), 7.81 (dt, *J*=8.0/1.3 Hz, 1H), 8.17 (t, *J*=1.7 Hz, 1H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 22 °C, TMS): δ=52.87 (2C), 94.56, 98.69 (d, $^2J_{CF}$=24.9 Hz), 108.07 (d, $^4J_{CF}$=1.5 Hz), 116.82 (2C), 117.07, 118.63 (d, $^3J_{CF}$=2.2 Hz), 122.82, 130.28, 130.43, 131.45 (d, $^3J_{CF}$=7.2 Hz), 132.09 (2C), 138.10, 152.98 (d, $^2J_{CF}$=11.6 Hz), 154.10, 162.42 (d, $^1J_{CF}$=255.9 Hz) ppm. M ($C_{18}H_{17}IN_3F$)=421.3. MS (EI+): *m/z*: 421.0 (M^+). HRMS (EI+): M^+ calcd for $C_{18}H_{17}IN_3F$ 421.0451; found 421.0450.

*4.6.12. N,N-Diallyl-3-methyl-4-[(E)-(3-iodophenyl)azo]aniline (**10d**).* According to GP2 solution A was made of 3-iodoaniline (2.24 g, 10.0 mmol) in EtOH (30 mL) and 2 N HCl (15 ml, 30 mmol), sodium nitrite (0.76 g, 11.0 mmol) in H_2O (10 mL) and amidosulfuric acid (0.20 g, 2.0 mmol). Solution B was obtained from **8d** (1.91 g, 10.0 mmol) in EtOH (200 mL) and H_2O (100 mL) and an addition of sodium acetate (1.70 g, 20.0 mmol). The resulting pH was about 4. The reaction time was 4 h at 0 °C. **10d** was obtained as red solid (3.52 g, 84%). TLC: $R_f \approx 0.4$ (pentane/CH_2Cl_2=8/2). Mp: 65 °C. IR (KBr): $\tilde{\nu}$=3070, 3061, 3006, 2979, 2920, 1598, 1503, 1381, 1354, 1228, 1177, 1107, 991, 915, 804, 782 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 22 °C, TMS): δ=2.68 (s, 3H), 3.97–4.01 (m, 4H), 5.14–5.22 (m, 4H), 5.86 (ddt, *J*=17.0/9.8/4.7 Hz, 2H), 6.52–6.57 (m, 2H), 7.18 (t, *J*=7.9 Hz, 1H), 7.66 (d, *J*=7.8 Hz, 1H), 7.68–7.71 (m, 1H), 7.79 (d, *J*=8.0 Hz, 1H), 8.14 (t, *J*=1.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, 22 °C, TMS): δ=18.27, 52.60 (2C), 110.25, 112.72, 116.45 (2C) 117.07, 122.79, 130.23, 130.41, 132.82 (2C), 137.51, 141.66 ppm. M ($C_{19}H_{20}IN_3$)=417.3. MS (EI+): *m/z*: 417.1 (M^+). HRMS (EI+): M^+ calcd for $C_{19}H_{20}IN_3$ 417.0702; found 417.0704.

*4.6.13. 4-[(E)-(4-Iodophenyl)azo]aniline (**13a**).* According to GP3 with *N,N*-diallyl-4-[(*E*)-(4-iodophenyl)azo]aniline (**9a**, 2.02 g, 5.00 mmol) in CH_2Cl_2 (25 mL) the double bond isomerization was caused by RuClH(CO) (PPh_3)$_3$ (48 mg, 50 μmol) and heating for 2 h. The subsequent hydrolysis was induced by adding of hydroxylamine hydrochloride (3.47 g, 50.0 mmol) and triethylamine (2.53 g, 25.0 mmol) and heating for 3 h **13a** was obtained as orange solid (1.55 g, 96%). TLC: $R_f \approx 0.3$ (pentane/CH_2Cl_2=1/1). Mp: 164 °C. IR (KBr): $\tilde{\nu}$=3440, 3359, 1612, 1593, 1561, 1501, 1422, 1387, 1279, 1142, 1131, 1051, 997, 842 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 21 °C, TMS): δ=4.08 (s, 2H), 6.68–6.77 (m, 2H), 7.53–7.62 (m, 2H), 7.75–7.85 (m, 4H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 21 °C, TMS): δ=96.02, 114.74 (2C), 124.18 (2C), 125.46 (2C), 138.27 (2C), 145.45, 150.03, 152.41 ppm. M ($C_{12}H_{10}IN_3$)=323.1. MS (EI+): *m/z*: 323.1 (M^+). HRMS (EI+): M^+ calcd for $C_{12}H_{10}IN_3$ 322.9919; found 322.9919.

*4.6.14. 3-Chloro-4-[(E)-(4-iodophenyl)azo]aniline (**13b**).* According to GP3 with *N,N*-diallyl-3-chloro-4-[(*E*)-(4-iodophenyl)azo]aniline (**9b**, 2.19 g, 5.00 mmol) in CH_2Cl_2 (25 mL) the double bond isomerization was caused by RuClH(CO) (PPh_3)$_3$ (48 mg, 50 μmol) and heating for 2 h. The subsequent hydrolysis was induced by adding of hydroxylamine hydrochloride (3.47 g, 50.0 mmol) and triethylamine (2.53 g, 25.0 mmol) and heating for 3 h **13b** was obtained as orange solid (1.66 g, 93%). TLC: $R_f \approx 0.3$ (pentane/CH_2Cl_2=1/1). Mp: 175 °C. IR (KBr): $\tilde{\nu}$=3415, 3328, 3212, 1627, 1595, 1489, 1413, 1301, 1242, 1187, 1043, 1001, 899, 859, 837 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ=4.13 (s, 2H), 6.57 (dd, *J*=8.9/2.4 Hz, 1H), 6.81 (d, *J*=2.6 Hz, 1H), 7.60–7.65 (m, 2H), 7.71 (d, *J*=8.9 Hz, 1H), 7.79–7.84 (m, 2H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): δ=96.57, 113.57, 114.97, 118.87, 124.44 (2C), 138.23 (2C), 138.49, 140.81, 150.37, 152.39 ppm. M ($C_{12}H_9ClIN_3$)=357.6. MS (EI+): *m/z*: 357.0 (M^+). HRMS (EI+): M^+ calcd for $C_{12}H_9ClIN_3$ 356.9530; found 356.9523.

*4.6.15. 3-Fluoro-4-[(E)-(4-iodophenyl)azo]aniline (**13c**).* According to GP3 with *N,N*-diallyl-3-fluoro-4-[(*E*)-(4-iodophenyl)azo]aniline (**9c**, 2.11 g, 5.00 mmol) in CH_2Cl_2 (25 mL) the double bond isomerization was caused by RuClH(CO) (PPh_3)$_3$ (48 mg, 50 μmol) and heating for 2 h. The subsequent hydrolysis was induced by adding

of hydroxylamine hydrochloride (3.47 g, 50.0 mmol) and triethylamine (2.53 g, 25.0 mmol) and heating for 3 h **13c** was obtained as orange solid (1.55 g, 91%). TLC: $R_f \approx 0.3$ (pentane/CH_2Cl_2=1/1). Mp: 167 °C. IR (KBr): $\tilde{\nu}$=3438, 1635, 1615, 1587, 1498, 1429, 1245, 1119, 1004, 828 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ=4.19 (s, 2H), 6.42–6.51 (m, 2H), 7.56–7.62 (m, 2H), 7.71 (t, J=8.8 Hz, 1H), 7.77–7.83 (m, 2H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): δ=96.34, 101.49 (d, $^2J_{CF}$=23.2 Hz), 110.76, 119.05, 124.23 (2C), 133.12 (d, $^3J_{CF}$=6.8 Hz), 138.18 (2C), 151.57 (d, $^2J_{CF}$=11.8 Hz), 152.42, 162.21 (d, $^1J_{CF}$=257.0 Hz) ppm. M ($C_{12}H_9FIN_3$)=341.1. MS (EI+): m/z: 341.0 (M^+). HRMS (EI+): M^+ calcd for $C_{12}H_9FIN_3$ 340.9825; found 340.9820.

*4.6.16. 3-Methyl-4-[(E)-(4-iodophenyl)azo]aniline (**13d**).* According to GP3 with *N,N*-diallyl-3-methyl-4-[(*E*)-(4-iodophenyl)azo]aniline (**9d**, 2.09 g, 5.00 mmol) in CH_2Cl_2 (25 mL) the double bond isomerization was caused by RuClH(CO) $(PPh_3)_3$ (48 mg, 50 μmol) and heating for 2 h. The subsequent hydrolysis was induced by adding of hydroxylamine hydrochloride (3.47 g, 50.0 mmol) and triethylamine (2.53 g, 25.0 mmol) and heating for 3 h **13d** was obtained as orange solid (1.60 g, 95%). TLC: $R_f \approx 0.3$ (pentane/CH_2Cl_2=1/1). Mp: 118 °C. IR (KBr): $\tilde{\nu}$=3457, 3424, 3388, 3331, 3210, 2923, 1616, 1593, 1491, 1417, 1385, 1322, 1255, 1227, 1185, 1111, 1001, 826 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ=2.63 (s, 3H), 3.99 (s, 2H), 6.51 (dd, J=8.7/2.9 Hz, 1H), 6.56 (d, J=3.1 Hz, 1H), 7.54–7.58 (m, 2H), 7.65 (d, J=8.7 Hz, 1H), 7.76–7.81 (m, 2H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): δ=17.68, 95.48, 112.92, 115.78, 117.24, 124.12 (2C), 138.06 (2C), 141.67, 143.38, 149.85, 152.67 ppm. M ($C_{13}H_{12}IN_3$)=337.2. MS (EI+): m/z: 337.0 (M^+). HRMS (EI+): M^+ calcd for $C_{13}H_{12}IN_3$ 337.0076; found 337.0081.

*4.6.17. 4-[(E)-(3-Iodophenyl)azo]aniline (**14a**).* According to GP3 with *N,N*-diallyl-4-[(*E*)-(3-iodophenyl)azo]aniline (**10a**, 2.02 g, 5.00 mmol) in CH_2Cl_2 (25 mL) the double bond isomerization was caused by RuClH(CO) $(PPh_3)_3$ (48 mg, 50 μmol) and heating for 4 h. The subsequent hydrolysis was induced by adding of hydroxylamine hydrochloride (3.47 g, 50.0 mmol) and triethylamine (2.53 g, 25.0 mmol) and heating for 6 h **14a** was obtained as orange solid (1.48 g, 92%). TLC: $R_f \approx 0.3$ (pentane/CH_2Cl_2=1/1). Mp: 88 °C. IR (KBr): $\tilde{\nu}$=3447, 3365, 1618, 1597, 1503, 1459, 1427, 1397, 1287, 1218, 1138, 832 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ=4.08 (s, 2H), 6.70–6.74 (m, 2H), 7.21 (t, J=7.9 Hz, 1H), 7.69–7.72 (m, 1H), 7.77–7.83 (m, 3H), 8.17 (t, J=1.8 Hz, 1H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): δ=94.62, 114.60 (2C), 123.06, 125.46 (2C), 130.14, 130.54, 138.29, 145.28, 150.05, 153.84 ppm. M ($C_{12}H_{10}IN_3$)=323.1. MS (EI+): m/z: 323.0 (M^+). HRMS (EI+): M^+ calcd for $C_{12}H_{10}IN_3$ 322.9920; found 322.9920.

*4.6.18. 3-Chloro-4-[(E)-(3-iodophenyl)azo]aniline (**14b**).* According to GP3 with *N,N*-diallyl-3-chloro-4-[(*E*)-(4-iodophenyl)azo]aniline (**10b**, 2.19 g, 5.00 mmol) in CH_2Cl_2 (25 mL) the double bond isomerization was caused by RuClH(CO) $(PPh_3)_3$ (48 mg, 50 μmol) and heating for 4 h. The subsequent hydrolysis was induced by adding of hydroxylamine hydrochloride (3.47 g, 50.0 mmol) and triethylamine (2.53 g, 25.0 mmol) and heating for 6 h **14b** was obtained as orange solid (1.58 g, 88%). TLC: $R_f \approx 0.3$ (pentane/CH_2Cl_2=1/1). Mp: 112 °C. IR (KBr): $\tilde{\nu}$=3448, 3434, 3343, 1615, 1593, 1488, 1419, 1407, 1301, 1289, 1238, 1131, 1044, 899, 864, 818, 782, 672 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ=4.14 (s, 2H), 6.56 (dd, J=8.9/3.1 Hz, 1H), 6.80 (d, J=2.9 Hz, 1H), 7.21 (t, J=7.9 Hz, 1H), 7.69 (d, J=8.7 Hz, 1H), 7.73 (d, J=7.9 Hz, 1H), 7.86 (d, J=7.9 Hz, 1H), 8.21 (t, J=1.6 Hz, 1H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): δ=94.55, 113.51, 114.91, 118.88, 123.00, 130.53, 130.94, 138.65, 138.74, 140.70, 150.49, 153.84 ppm. M ($C_{12}H_9ClIN_3$)=357.6. MS (EI+): m/z: 357.0 (M^+). HRMS (EI+): M^+ calcd for $C_{12}H_9ClIN_3$ 356.9530; found 356.9521.

*4.6.19. 3-Fluoro-4-[(E)-(3-iodophenyl)azo]aniline (**14c**).* According to GP3 with *N,N*-diallyl-3-fluoro-4-[(*E*)-(4-iodophenyl)azo]aniline (**10c**, 2.11 g, 5.00 mmol) in CH_2Cl_2 (25 mL) the double bond isomerization was caused by RuClH(CO) $(PPh_3)_3$ (48 mg, 50 μmol) and heating for 4 h. The subsequent hydrolysis was induced by adding of hydroxylamine hydrochloride (3.47 g, 50.0 mmol) and triethylamine (2.53 g, 25.0 mmol) and heating for 6 h **14c** was obtained as orange solid (1.49 g, 87%). TLC: $R_f \approx 0.3$ (pentane/CH_2Cl_2=1/1). Mp: 107 °C. IR (KBr): $\tilde{\nu}$=3471, 3379, 1621, 1575, 1497, 1427, 1318, 1245, 1161, 1118, 957, 836, 782 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ=4.21 (s, 2H), 6.39–6.51 (m, 2H), 7.21 (t, J=7.9 Hz, 1H), 7.63–7.76 (m, 2H), 7.79–7.87 (m, 1H), 8.18 (t, J=1.7 Hz, 1H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): δ=94.58, 101.46 (d, $^2J_{CF}$=23.4 Hz), 110.77 (d, $^4J_{CF}$=2.2 Hz), 119.13 (d, $^3J_{CF}$=1.9 Hz), 123.00, 130.55, 133.05 (d, $^3J_{CF}$=6.9 Hz), 138.63, 151.77 (d, $^2J_{CF}$=11.9 Hz), 153.94, 162.31 (d, $^1J_{CF}$=257.5 Hz) ppm. M ($C_{12}H_9FIN_3$)=341.1. MS (EI+): m/z: 341.0 (M^+). HRMS (EI+): M^+ calcd for $C_{12}H_9FIN_3$ 340.9825; found 340.9828.

*4.6.20. 3-Methyl-4-[(E)-(4-iodophenyl)azo]aniline (**14d**).* According to GP3 with *N,N*-diallyl-3-methyl-4-[(*E*)-(3-iodophenyl)azo]aniline (**10d**, 2.09 g, 5.00 mmol) in CH_2Cl_2 (25 mL) the double bond isomerization was caused by RuClH(CO) $(PPh_3)_3$ (48 mg, 50 μmol) and heating for 4 h. The subsequent hydrolysis was induced by adding of hydroxylamine hydrochloride (3.47 g, 50.0 mmol) and triethylamine (2.53 g, 25.0 mmol) and heating for 6 h **14d** was obtained as orange solid (1.52 g, 90%). TLC: $R_f \approx 0.3$ (pentane/CH_2Cl_2=1/1). Mp: 106 °C. IR (KBr): $\tilde{\nu}$=3454, 3369, 3051, 1616, 1598, 1591, 1461, 1402, 1308, 1255, 1218, 1104, 885, 858, 758 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ=2.65 (s, 3H), 4.01 (s, 2H), 6.51 (dd, J=8.6/2.7 Hz, 1H), 6.57 (d, J=2.8 Hz, 1H), 7.20 (t, J=7.9 Hz, 1H), 7.64 (d, J=8.8 Hz, 1H), 7.67–7.72 (m, 1H), 7.77–7.85 (m, 1H), 8.15 (t, J=1.8 Hz, 1H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): δ=17.73, 94.55, 112.89, 115.75, 117.34, 122.92, 130.40, 130.47, 137.99, 141.86, 143.34, 149.97, 154.19 ppm. M ($C_{13}H_{12}IN_3$)=337.2. MS (EI+): m/z: 337.0 (M^+). HRMS (EI+): M^+ calcd for $C_{13}H_{12}IN_3$ 337.0076; found 337.0072.

*4.6.21. (E)-(4-Iodophenyl)phenyldiazene (**15a**).* According to GP4 starting from 4-[(*E*)-(4-iodophenyl)azo]aniline (**13a**, 162 mg, 0.50 mmol) in THF (10 mL), 50% wt solution of hypophosphorous acid (1.32 g, 10.0 mmol) and sodium nitrite (105 mg, 1.00 mmol) **15a** was obtained as orange solid (115 mg, 75%). TLC: $R_f \approx 0.3$ (pentane). Mp: 105 °C. IR (KBr): $\tilde{\nu}$=3055, 1636, 1561, 1459, 1441, 1403, 1204, 1148, 1051, 992, 914, 880, 793, 768, 761, 685 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.46–7.55 (m, 3H), 7.65 (d, J=8.5 Hz, 2H), 7.86 (d, J=8.5 Hz, 2H), 7.89–7.94 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ=97.69, 122.99 (2C), 124.49 (2C), 129.16 (2C), 131.36, 138.36 (2C), 151.94, 152.46 ppm. M ($C_{12}H_9IN_2$)=308.1. MS (EI+) m/z (%): 308.0 (57, M^+), 230.0 (11), 203.0 (40), 152.1 (15), 105.0 (52), 77.0 (100), 76.0 (36). HRMS (EI+): M^+ calcd for $C_{12}H_9IN_2$ 307.9810; found 307.9798.

*4.6.22. (E)-(2-Chlorophenyl)-(4-iodophenyl)diazene (**15b**).* According to GP4 starting from 3-chloro-4-[(*E*)-(4-iodophenyl)azo]aniline (**13b**, 180 mg, 0.50 mmol) in THF (10 mL), 50% wt solution of hypophosphorous acid (1.32 g, 10.0 mmol) and sodium nitrite (105 mg, 1.00 mmol) **15b** was obtained as orange solid (112 mg, 66%). TLC: $R_f \approx 0.25$ (pentane). Mp: 101 °C. IR (KBr): $\tilde{\nu}$=3063, 1636, 1577, 1568, 1480, 1469, 1390, 1149, 1050, 1004, 830, 760, 717 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ=7.32 (t, J=7.6 Hz, 1H), 7.39 (t, J=7.6 Hz, 1H), 7.55 (d, J=7.9 Hz, 1H), 7.65–7.71

(m, 3H), 7.86 (d, J=8.2 Hz, 2H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): δ=98.48, 117.46, 124.83 (2C), 127.25, 130.74, 131.98, 135.59, 138.39 (2C), 148.42, 151.96 ppm. M ($C_{12}H_8ClIN_2$)=342.6. MS (EI+) m/z (%): 344.0 (22, M^+), 343.0 (10, M^+), 342.0 (66, M^+), 231.0 (69), 203.0 (100), 152.1 (13), 139.0 (24) 111.0 (56), 76.0 (50), 75.0 (21). HRMS (EI+): M^+ calcd for $C_{12}H_8ClIN_2$ 341.9421; found 341.9413.

*4.6.23. (E)-(2-Fluorophenyl)-(4-iodophenyl)diazene (**15c**).* According to GP4 starting from 3-fluoro-4-[(*E*)-(4-iodophenyl)azo]aniline (**13c**, 171 mg, 0.50 mmol) in THF (10 mL), 50% wt solution of hypophosphorous acid (1.32 g, 10.0 mmol) and sodium nitrite (105 mg, 1.00 mmol) **15c** was obtained as orange solid (111 mg, 68%). TLC: R_f≈0.25 (pentane). Mp: 115 °C. IR (KBr): $\tilde{\nu}$=3063, 1628, 1605, 1586, 1576, 1567, 1480, 1389, 1264, 1213, 1151, 1103, 1049, 1005, 827, 756 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ=7.20 (t, J=7.7 Hz, 1H), 7.23–7.29 (m, 1H), 7.42–7.48 (m, 1H), 7.66 (d, J=8.5 Hz, 2H), 7.74 (td, J=7.9/1.6 Hz, 1H), 7.85 (d, J=8.4 Hz, 2H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): δ=98.30, 117.12 (d, $^2J_{CF}$=19.5 Hz), 117.64, 124.29 (d, $^3J_{CF}$=3.1 Hz), 124.66 (2C), 132.85 (d, $^3J_{CF}$=8.6 Hz), 138.36 (2C), 140.42 (d, $^2J_{CF}$=7.3 Hz), 152.01, 160.19 (d, $^1J_{CF}$=258.4 Hz) ppm. M ($C_{12}H_8FIN_2$)=326.1. MS (EI+) m/z (%): 326.0 (65, M^+), 231.0 (73), 203.0 (100), 123.0 (14), 95.1 (30), 76.1 (53), 75.0 (17). HRMS (EI+): M^+ calcd for $C_{12}H_8FIN_2$ 325.9716; found 325.9716.

*4.6.24. (E)-(2-Methylphenyl)-(4-iodophenyl)diazene (**15d**).* According to GP4 starting from 3-methyl-4-[(*E*)-(4-iodophenyl)azo]aniline (**13d**, 168 mg, 0.50 mmol) in THF (10 mL), 50% wt solution of hypophosphorous acid (1.32 g, 10.0 mmol) and sodium nitrite (105 mg, 1.00 mmol) **15d** was obtained as orange solid (116 mg, 72%). TLC: R_f≈0.25 (pentane). Mp: 105 °C. IR (KBr): $\tilde{\nu}$=3063, 2923, 1576, 1564, 1477, 1459, 1427, 1390, 1058, 1052, 1003, 832, 764, 721 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=2.70 (s, 3H), 7.22–7.28 (m, 1H), 7.29–7.39 (m, 2H), 7.59–7.66 (m, 3H), 7.79–7.87 (m, 2H) ppm ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ=17.52, 97.34, 115.36, 124.51 (2C), 126.42, 131.30 (2C), 138.27 (2C), 138.41, 150.46, 152.24 ppm. M ($C_{13}H_{11}IN_2$)=322.1. MS (EI+) m/z (%): 322.0 (59, M^+), 231.0 (11), 203.0 (42), 195.1 (15), 119.1 (19), 91.1 (100), 76.0 (21), 65.0 (16). HRMS (EI+): M^+ calcd for $C_{13}H_{11}IN_2$ 321.9967; found 321.9957.

*4.6.25. (E)-(4-Chlorophenyl)-(4-iodophenyl)diazene (**16**).* 4-[(*E*)-(4-Iodophenyl)azo]aniline (**13a**, 162 mg, 0.50 mmol, 1.00 equiv) was dissolved in CCl_4 (10 mL). 4-dodecylbenzenesulfonic acid (163 mg, 0.50 mmol, 1.00 equiv) was added and the mixture was stirred for 5 min at room temperature. Then *tert*-butyl nitrite (310 mg, 3.00 mmol, 6.00 equiv) was added and the reaction mixture was stirred at room temperature until the initial aromatic amine disappeared (TLC, pentane/ethyl acetate=8/2; the reaction was complete after about 2 h). Triethylamine (51 mg, 0.50 mmol, 1.00 equiv) was added and the reaction mixture was heated to 80 °C for 2 h resulting in an instant nitrogen evolving. After cooling to room temperature again, H_2O (10 mL) was added and the product was extracted with CH_2Cl_2 (3×). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane) to give 14 as orange solid (90 mg, 52%). TLC: R_f≈0.2 (pentane). Mp: 178 °C. IR (KBr): $\tilde{\nu}$=3064, 1575, 1565, 1472, 1389, 1088, 1050, 1003, 835 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C, TMS): δ=7.46–7.51 (m, 2H), 7.61–7.67 (m, 2H), 7.82–7.90 (m, 4H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 21 °C, TMS): δ=98.20, 124.36 (2C), 124.63 (2C), 129.55 (2C), 137.43, 138.54 (2C), 150.87, 151.83 ppm. M ($C_{12}H_8ClIN_2$)=342.6. MS (EI+) m/z (%): 344 (33), 342.0 (100, M^+), 231.0 (42), 203.0 (90), 139.1 (32), 113 (20), 111.1 (65), 76.1 (45). HRMS (EI+): M^+ calcd for $C_{12}H_8ClIN_2$ 341.9421; found 341.9421.

*4.6.26. (E)-(4-Fluorophenyl)-(4-iodophenyl)diazene (**17**).* 4-[(*E*)-(4-Iodophenyl)azo]aniline (**13a**, 162 mg, 0.50 mmol, 1.00 equiv) was dissolved in CH_2Cl_2 (5 mL) and the mixture was cooled to 0 °C. Boron trifluoride etherate (106 mg, 0.75 mmol, 1.50 equiv) was added and the mixture was stirred for 5 min at 0 °C. Then *tert*-butyl nitrite (103 mg, 1.00 mmol, 2.00 equiv) was added dropwise and the mixture was stirred for 16 h (0 °C to rt). Afterwards pentane (10 mL) was added and the precipitated diazonium salt was filtered off and washed with pentane. The residue was heated to 120 °C for 2 h and the obtained product was directly purified by flash chromatography (eluting with pentane) to give **15** as orange solid (102 mg, 63%). TLC: R_f≈0.2 (pentane). Mp: 128 °C. IR (KBr): $\tilde{\nu}$=3059, 1595, 1569, 1498, 1473, 1389, 1229, 1127, 1005, 840 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C, TMS): δ=7.15–7.22 (m, 2H), 7.59–7.65 (m, 2H), 7.82–7.87 (m, 2H), 7.92 (dd, J=8.2/5.5 Hz, 2H) ppm ^{13}C NMR (126 MHz, $CDCl_3$, 21 °C, TMS): δ=97.85, 116.25 (d, $^2J_{CF}$=22.9 Hz, 2C), 124.54 (2C), 125.14 (d, $^3J_{CF}$=9.0 Hz, 2C), 138.47 (2C), 149.03 (d, $^4J_{CF}$=3.0 Hz), 151.81, 164.66 (d, $^1J_{CF}$=252.6 Hz) ppm. M ($C_{12}H_8FIN_2$)=326.1. MS (EI+) m/z (%): 326.1 (100, M^+), 231.0 (24), 203.0 (63), 123.1 (34), 95 (75), 76.1 (44). HRMS (EI+): M^+ calcd for $C_{12}H_8FIN_2$ 325.9716; found 325.9716.

*4.6.27. 4-[(E)-(4-Iodophenyl)azo]naphthalen-1-amine (**19a**).* According to GP2 solution A was made of 4-iodoaniline (1.12 g, 5.00 mmol) in EtOH (15 mL) and 2 N HCl (7.5 mL, 15.0 mmol), sodium nitrite (0.38 g, 5.50 mmol) in water (5 mL) and amidosulfuric acid (0.10 g, 1.0 mmol). Solution B was obtained from 1-naphthylamine (0.73 g, 5.0 mmol) in EtOH (100 mL) and H_2O (50 mL) and an addition of 2 N HCl (5.0 ml, 10 mmol). The resulting pH was between 1 and 2. The reaction time was 1 h at 0 °C. **19a** was obtained as dark red solid (1.78 g, 95%). TLC: R_f≈0.4 (pentane/CH_2Cl_2=1/1). Mp: 204 °C. IR (KBr): $\tilde{\nu}$=3416, 3298, 3186, 3012, 1638, 1571, 1514, 1464, 1385, 1336, 1191, 1142, 1052, 999, 826, 755 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C, TMS): δ=4.66 (s, 2H), 6.82 (d, J=8.3 Hz, 1H), 7.56 (ddd, J=8.3/6.8/1.3 Hz, 1H), 7.66 (ddd, J=8.4/6.8/1.2 Hz, 1H), 7.70–7.73 (m, 2H), 7.82 (d, J=8.5 Hz, 1H), 7.84–7.87 (m, 2H), 7.94 (d, J=8.3 Hz, 1H), 9.02 (d, J=8.5 Hz, 1H) ppm ^{13}C NMR (101 MHz, $CDCl_3$, 21 °C, TMS): δ=95.90, 109.26, 114.31, 120.73, 122.53, 124.17, 124.44 (2C), 125.59, 127.41, 133.38, 138.35 (2C), 140.37, 146.81, 153.04 ppm. M ($C_{16}H_{12}IN_3$)=373.2. MS (ESI$^+$) m/z: 374.1 ([M+H]$^+$). HRMS (EI+): calcd for $C_{16}H_{12}IN_3$, 373.0076; found 373.0069.

*4.6.28. 4-[(E)-(3-Iodophenyl)azo]naphthalen-1-amine (**19b**).* According to GP2 solution A was made of 3-iodoaniline (1.12 g, 5.00 mmol) in EtOH (15 mL) and 2 N HCl (7.5 mL, 15.0 mmol), sodium nitrite (0.38 g, 5.50 mmol) in water (5 mL) and amidosulfuric acid (0.10 g, 1.0 mmol). Solution B was obtained from 1-naphthylamine (0.73 g, 5.0 mmol) in EtOH (100 mL) and H_2O (50 mL) and an addition of 2 N HCl (5.0 mL, 10 mmol). The resulting pH was between 1 and 2. The reaction time was 1 h at 0 °C. **19b** was obtained as dark red solid (1.76 g, 94%). TLC: R_f≈0.4 (pentane/CH_2Cl_2=1/1). Mp: 123 °C. IR (KBr): $\tilde{\nu}$=3396, 3328, 3235, 3054, 1647, 1619, 1574, 1515, 1466, 1400, 1339, 1213, 1159, 992, 880, 845, 832, 790, 756 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C, TMS): δ=4.66 (s, 2H), 6.79 (d, J=8.4 Hz, 1H), 7.25 (t, J=7.9 Hz, 1H), 7.52–7.58 (m, 1H), 7.63–7.69 (m, 1H), 7.73 (dt, J=8.0/1.3 Hz, 1H), 7.80 (d, J=8.5 Hz, 1H), 7.90–7.97 (m, 2H), 8.30 (t, J=1.7 Hz, 1H), 9.03 (d, J=8.4 Hz, 1H) ppm ^{13}C NMR (101 MHz, $CDCl_3$, 21 °C, TMS): δ=94.67 (s, 1C), 109.02 (d, 1C), 114.29 (d, 1C), 120.56 (d, 1C), 122.27 (s, 1C), 123.28 (d, 1C), 124.01 (d, 1C), 125.44 (d, 1C), 127.35 (d, 1C), 130.35 (d, 1C), 130.56 (d, 1C), 133.24 (s, 1C), 138.16 (d, 1C), 140.06 (s, 1C), 146.82 (s, 1C), 154.32 (s, 1C) ppm. M ($C_{16}H_{12}IN_3$)=373.19. MS (ESI$^+$) m/z: 374.1 ([M+H]$^+$). HRMS (EI+): calcd for $C_{16}H_{12}IN_3$, 373.0076; found 373.0069.

*4.6.29. (E)-(4-Iodophenyl)-(1-naphthyl)diazene (**20a**).* According to GP4 starting from **16a** (1.50 g, 4.00 mmol) in THF (80 mL), 50% wt solution of hypophosphorous acid (10.6 g, 80.0 mmol) and sodium

nitrite (0.56 g, 8.00 mmol) **20a** was obtained as red solid (1.03 g, 72%). TLC: $R_f \approx 0.2$ (pentane). Mp: 116 °C. IR (KBr): $\tilde{\nu}$=3045, 2999, 1577, 1564, 1508, 1473, 1391, 1343, 1297, 1213, 1094, 1054, 1002, 862, 823, 797, 768 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 21 °C, TMS): δ=7.52–7.60 (m, 2H), 7.64 (ddd, J=8.4/6.8/1.3 Hz, 1H), 7.72–7.77 (m, 2H), 7.81 (dd, J=7.5/1.0 Hz, 1H), 7.85–7.89 (m, 2H), 7.91 (d, J=8.2 Hz, 1H), 7.98 (d, J=8.1 Hz, 1H), 8.89 (d, J=8.4 Hz, 1H) ppm ^{13}C NMR (101 MHz, $CDCl_3$, 21 °C, TMS): δ=97.89, 112.09, 123.46, 124.84 (2C), 125.72, 126.66, 127.10, 128.10, 131.47, 131.89, 134.43, 138.52 (2C), 147.60, 152.55 ppm. M ($C_{16}H_{11}IN_2$)=358.18. MS (ESI^+) *m/z*: 359.0 ($[M+H]^+$). HRMS (EI+): calcd for $C_{16}H_{11}IN_2$, 357.9967; found 357.9963.

*4.6.30. (E)-(3-Iodophenyl)-(1-naphthyl)diazene (**20b**).* According to GP4 starting from **16b** (1.50 g, 4.00 mmol) in THF (80 mL), 50% wt solution of hypophosphorous acid (10.6 g, 80.0 mmol) and sodium nitrite (0.56 g, 8.00 mmol) **20b** was obtained as red solid (0.98 g, 68%). TLC: $R_f \approx 0.2$ (pentane). Mp: 95 °C. IR (KBr): $\tilde{\nu}$=3048, 1562, 1508, 1454, 1403, 1386, 1344, 1206, 990, 909, 888, 800, 789, 768, 682 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 21 °C, TMS): δ=7.29 (t, J=7.9 Hz, 1H), 7.53–7.61 (m, 2H), 7.64–7.69 (m, 1H), 7.79–7.83 (m, 2H), 7.93 (d, J=8.2 Hz, 1H), 7.98–8.03 (m, J=10.8/5.4/4.5 Hz, 2H), 8.36 (t, J=1.8 Hz, 1H), 8.91 (d, J=8.4 Hz, 1H) ppm ^{13}C NMR (101 MHz, $CDCl_3$, 21 °C, TMS): δ=97.89, 112.09, 123.46, 124.84, 125.72, 126.66, 127.10, 128.10, 131.47, 131.89, 134.43, 138.52, 147.60, 152.55 ppm. M ($C_{16}H_{11}IN_2$)=358.18. MS (ESI^+) *m/z*: 359.0 ($[M+H]^+$). HRMS (EI+): calcd for $C_{16}H_{11}IN_2$, 357.9967; found 357.9963.

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