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Nucleophilic Substitutions and Radical Reactions of Phenylazocarboxylates

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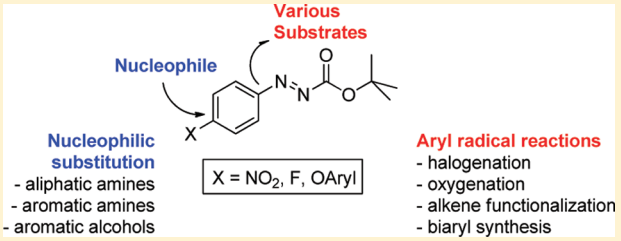
Supporting Information

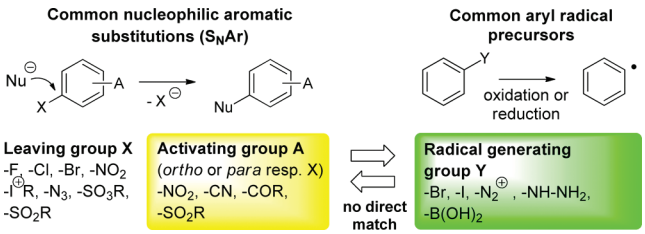
ABSTRACT: *tert*-Butyl phenylazocarboxylates are versatile building blocks for synthetic organic chemistry. Nucleophilic substitutions of the benzene ring proceed with aromatic amines and alcohols under mild conditions. The attack of aliphatic amines may be directed to the aromatic core as well as to the carbonyl unit leading to azocarboxamides. The benzene ring can further be modified through radical reactions, in which the *tert*-butyloxycarbonylazo group enables the generation of aryl radicals at either elevated temperatures or under acidic conditions. Radical reactions include oxygenation, halogenation, carbohalogenation, carbohydroxylation, and aryl−aryl coupling.



INTRODUCTION

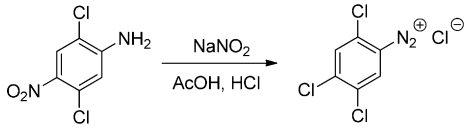
Nucleophilic aromatic substitutions usually require one or more electron-withdrawing substituents on the aromatic core to proceed under mild conditions.[1−3] Among the functional groups suitable for an activation of arenes toward an attack of nucleophiles, nitro, cyano, and acyl groups as well as sulfones are certainly the most prominent. Frequently used leaving groups include halogens, nitro, iodonium, and azido groups, sulfonates, and sulfones. Interestingly, none of the classical activating substituents shown below are also suitable for a generation of aryl radicals under mild conditions (Scheme 1).[4]

Scheme 1. Common Groups and Substituents in Nucleophilic Aromatic Substitutions and Aryl Radical Reactions



For this purpose, aryl iodides and bromides as well as aryl diazonium salts have a remarkable history in radical chemistry and are most commonly employed.[5] Aryl boronic acids[6] and aryl hydrazines[7] have so far not been used frequently, but they will probably gain more importance in the future. Among these "radical precursor substituents" enabling homolytic bond cleavage and aryl radical formation, only the diazonium group is known to activate arenes toward nucleophilic substitution.[8] Remarkably, the activation of arenes arising from the diazonium group is even stronger than that of any other classical activating group mentioned above.[1a,9] An early example for this reaction type, in which the aromatic core of an aryl diazonium ion is modified while the diazonium moiety remains unchanged, is shown in Scheme 2.[10] Such reactions frequently occur as

Scheme 2. Nucleophilic Substitution on an Aryl Diazonium Salt after Diazotization



undesired side reactions during diazotizations of anilines bearing suitable leaving groups in the ortho or para position of the amino substituent.[11] In that case, chloride ions from the solvent hydrochloric acid act as nucleophiles. The unwanted substitution step can be suppressed by employing sulfuric acid containing less nucleophilic hydrogensulfate ions.[10]

In general, nucleophilic aromatic substitutions of arenediazonium ions, in which the diazonium substituent remains unchanged, are not easy to conduct. The main reasons for complications are (1) the pronounced electrophilicity of the diazonium moiety itself,[8] which is essentially exploited in azo coupling reactions,[12] triazene[13] and azo ether formation,[14] and Japp−Klingemann reactions,[15] (2) the alternative ability of nucleophiles to replace the diazonium group,[16,17] and (3) the reducing character of many nucleophiles leading to a loss of nitrogen and aryl radical formation.[5a,14,18] By exchanging the positively charged diazonium group for a *tert*-butyl azocarboxylate, we recently found that the high degree of activation toward nucleophilic aromatic substitution remained, but these

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substitutions could be carried out far more selectively than with (unprotected) diazonium salts.[19]

Furthermore, the *tert*-butyl azocarboxylate moiety offered, comparable to the diazonium group, the possibility to conduct radical reactions under mild conditions. As a result, a new type of benzene-derived reagent (Figure 1) could be introduced,

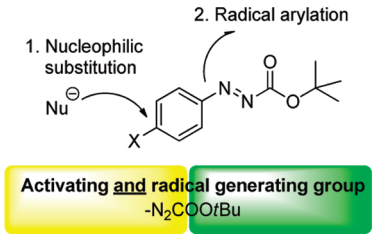


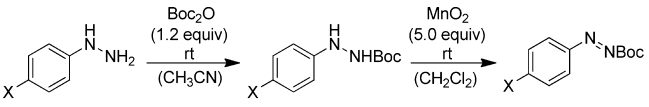
Figure 1. Reactions of *tert*-butyl phenylazocarboxylates.

which can be diversely modified by nucleophilic substitution *and* radical transformations.[19] In this article, we describe several new reaction types and conditions rendering phenyl azocarboxylates even more versatile and widely applicable building blocks in organic synthesis.

RESULTS AND DISCUSSION

The *tert*-butyl phenylazocarboxylates **1** and **2** are readily available in gram scales through a convenient two-step procedure from the commercially available aryl hydrazines. Reaction of the hydrazines **3** or **4** with di-*tert*-butyl dicarbonate to **5** or **6** followed by oxidation with manganese dioxide gave the target compounds **1** or **2** in good to high overall yields (Scheme 3).[20]

Scheme 3. Preparation of Phenylazocarboxylates 1 and 2



3 (X = F)
4 (X = NO_2)

5 (X = F): 82%
6 (X = NO_2): 74%

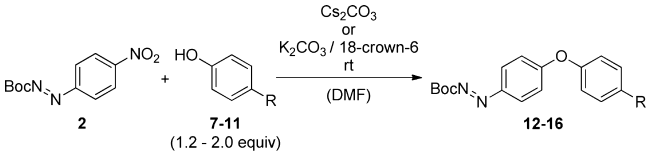
1 (X = F): 99%
2 (X = NO_2): 99%

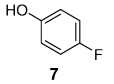
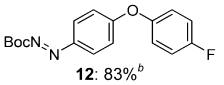
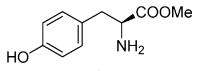
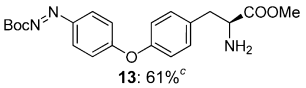
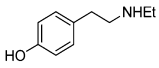
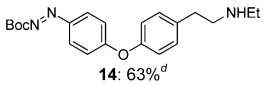
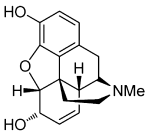
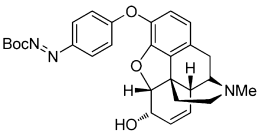
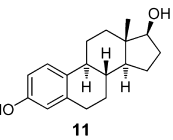
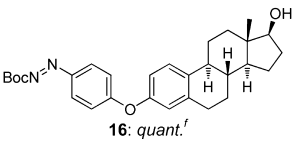
In contrast to their methyl derivatives, which we initially intended to prepare, the *tert*-butyl phenylazocarboxylates show a significantly higher stability that allows for purification by column chromatography. Compounds **1** and **2** are also stable toward air and moisture as well as under slightly acidic or basic conditions in solution.

For the synthesis of diphenyl ethers by nucleophilic substitution, the nitro derivative **2** was found to be most suitable. Under mild basic conditions, a variety of phenols underwent smooth reaction with **2**. Selected examples are shown in Table 1. Reactions that were found to proceed slowly with cesium carbonate could be accelerated by using potassium carbonate in combination with the crown ether 18-crown-6 (Table 1, entries 2 and 4).

In contrast to phenols, aliphatic amines react with *tert*-butyl 2-(4-fluorophenyl)azocarboxylate (**1**) (Table 2). Among these nucleophiles, primary amines were found to attack the aromatic core and the azocarboxylate unselectively, whereby the latter group is converted to an azocarboxamide (Table 2, entries 1 and 2). By increasing the sterical demand of the substituent attached to the amine, the regioselectivity can be improved toward the desired product, but the nucleophilic substitution

Table 1. Nucleophilic Substitution of 2 with Phenols



entry	phenol	diphenyl ether (%)[a]
1	 **7**	 **12**: 83%[b]
2	 **8**	 **13**: 61%[c]
3	 **9**	 **14**: 63%[d]
4	 **10**	 **15**: 81%[e]
5	 **11**	 **16**: *quant.*[f]

[a]Isolated yields. [b]Cs_2CO_3 (5.0 equiv), **7** (1.2 equiv). [c]K_2CO_3/18-crown-6 (4.2 equiv), **8** (0.83 equiv). [d]Cs_2CO_3 (5.0 equiv), **9** (1.5 equiv). [e]K_2CO_3/18-crown-6 (8.3 equiv), **10** (0.83 equiv). [f]Cs_2CO_3 (5.0 equiv), **11** (0.50 equiv).

now also proceeds signficantly slower (Table 2, entry 3). Better results than with any primary amine were obtained from reactions with a range of secondary amines (Table 2, entries 4–8).

With aromatic amines as nucleophiles, aromatic substitutions of phenylazocarboxylates can be achieved when the 4-fluorophenoxy-substituted derivative **12** is used (Table 3). Although phenoxy groups may not be known as common leaving groups in nucleophilic aromatic substitutions, several intramolecular examples have so far been described.[21] Comparable intermolecular reactions are limited so that a high activation such as by two nitro groups in 2,4-dinitrodiphenyl ethers is required.[22,23] Surprisingly for us, however, and in contrast to all aromatic substitutions shown above, the formation of the desired diarylamines **35** and **36** proceeded best under slightly acidic conditions, under which the aromatic amine can be considered to be largely protonated. A closer investigation revealed that the rate of formation of **35** and **36** is strongly dependent on the number of equivalents of trifluoroacetic acid per aromatic amine that are initially added to the reaction mixture. After 24 h at room temperature, full conversion of the azocarboxylate **12** can be reached by adding 1.0 equiv of acid, by 1.5 equiv the reaction proceeds even faster. The lower yield of **36** compared to **35** was hereby found to result from a lower stability of **36** under the chosen conditions.[24] With no trifluoroacetic acid present in the reaction mixture, both reactants remained unchanged over 24 h. The addition of 0.5 equiv of acid (per aromatic amine) led to only incomplete (ca. 50%) conversions in the same overall reaction time. At present, we assign the accelerating, catalytic effect of trifluoroacetic acid to an additional activation of the

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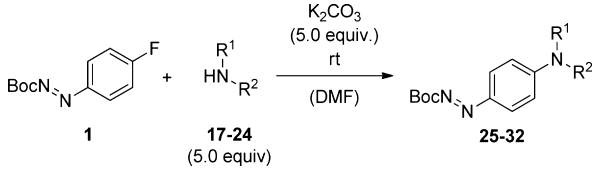
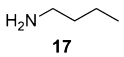
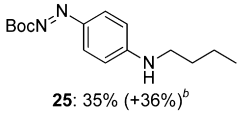
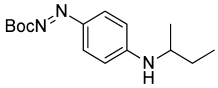
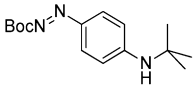
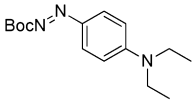
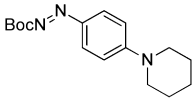
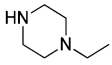
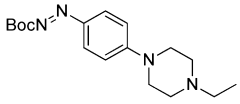
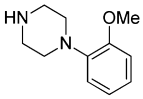
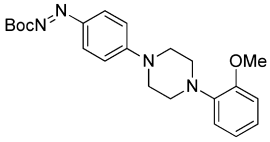
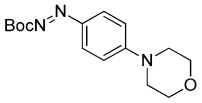
Table 2. Nucleophilic Substitution of 1 with Aliphatic Amines



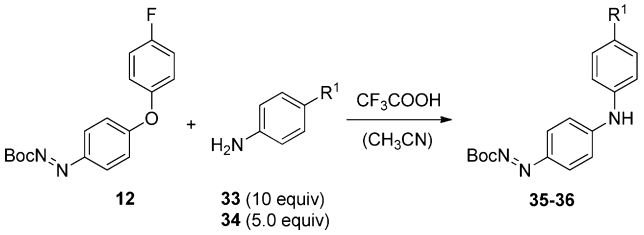
entry	amine	arylamine (%)[a]
1	 **17**	 **25**: 35% (+36%)[b]
2	 **18**	 **26**: 43% (+40%)[b]
3	 **19**	 **27**: 23%[c]
4	 **20**	 **28**: 74%
5	 **21**	 **29**: 92%
6	 **22**	 **30**: 80%
7	 **23**	 **31**: 88%
8	 **24**	 **32**: 90%

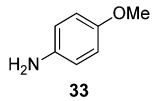
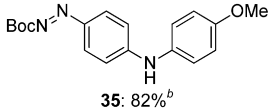
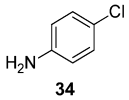
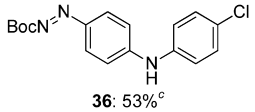
[a]Isolated yields. [b]Yield of azocarboxamide. [c]Yield based on recovered starting material **1**.

azo carboxylate **12** resulting from a partial protonation of the azo moiety (Scheme 4).[3b] In addition, the presence of the acid could also improve, again by protonation, the properties of 4-fluorophenol (**7**) to act as a leaving group. Apparently, these effects are able to overcompensate the decrease in concentration of the aromatic amine base caused by the acidic conditions.

The trifluoroacetic-acid-induced activation of azo carboxylate **12** (Scheme 4) did not provide sufficient reactivity to enable ring substitution with aliphatic alcohols (e.g., ethanol), which would have nicely completed the range of substrates from aliphatic amines, aromatic amines and aromatic alcohols to aliphatic alcohols. In the presence of acetic acid and trifluoroacetic acid, in constrast, **12** decomposed to form 4-fluorophenol (**7**). A number of carboxylic acids should therefore be able to liberate phenols from diphenyl ethers,

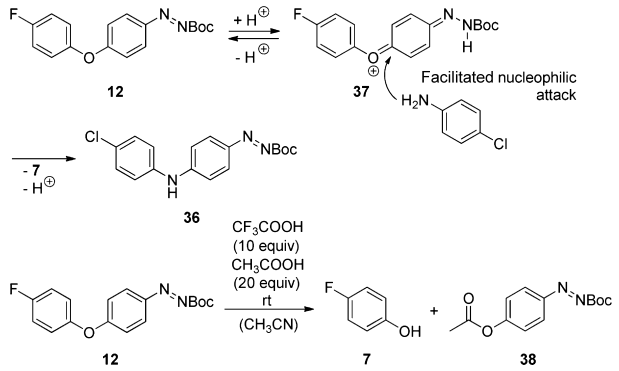
Table 3. Nucleophilic Substitution of 12 with Aromatic Amines



entry	amine	arylamine (%)[a]
1	 **33**	 **35**: 82%[b]
2	 **34**	 **36**: 53%[c]

[a]Isolated yields. [b]CF_3COOH (15 equiv/**12**, 1.5 equiv/**33**), 50 °C. [c]CF_3COOH (5.0 equiv/**12**, 1.0 equiv/**34**), rt.

Scheme 4. Proposed Activation of 12 toward Nucleophilic Substitution by Protonation



such as **12**, activated by an azocarboxylic acid ester. Given this option, **2** could in principle be used as a reagent to reversibly label or protect phenols as intensely colored and easily detectable diphenylethers (see below for optical properties of azocarboxylates). As a further consequence, a highly activated phenyl ester **38** has to arise from the nucleophilic aromatic substitution of **12**. Under the given reaction conditions, ester **38** did however not show sufficient stability to allow detection.

As already indicated in Table 2, nucleophilic substitutions by aliphatic amines can also occur at the carbonyl group of the phenylazocarboxylates **1** and **2**. High selectivities and yields have very recently been observed in reactions of amines with sterically less hindered ethyl phenylazocarboxylates to give azocarboxamides.[25] When *tert*-butyl phenylazocarboxylates are employed instead, the attack on the carbonyl group is sufficiently slowed down to allow nucleophilic ring substitution. By simply changing to solvents such as ethyl acetate, the reaction can however also be directed toward the carbonyl group (Table 4, entries 1–5). Although the resulting azocarboxamides **40**–**44** have not shown superior properties with regard to the desired generation of aryl radicals in later studies, the modification from ester to amide can be a useful option for those synthetic applications, in which the

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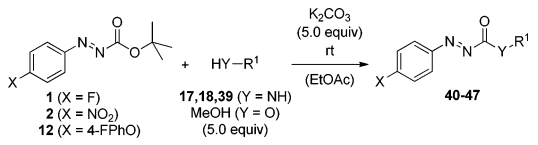
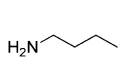
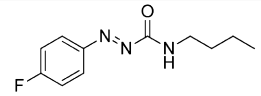
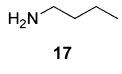
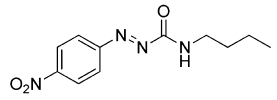
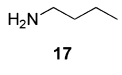
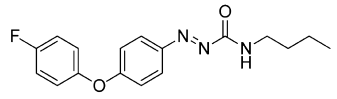
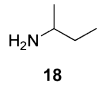
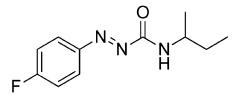
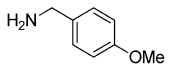
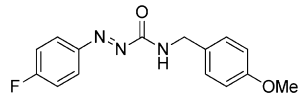
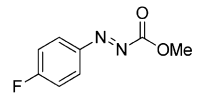
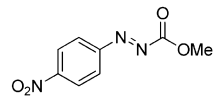
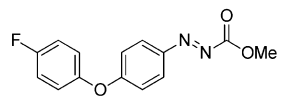
Table 4. Nucleophilic Substitutions with Aliphatic Amines and Methanol Directed Toward the Carbonyl Group



entry	amine / alcohol	product (%)[a]
1	 **17**	 **40**: 79%
2	 **17**	 **41**: 63%
3	 **17**	 **42**: *quant.*
4	 **18**	 **43**: 66%
5	 **39**	 **44**: 52%
6	MeOH	 **45**: 19%
7	MeOH	 **46**: 32%
8	MeOH	 **47**: 49%

[a]Isolated yields.

azo moiety remains as a part of the final product (see below, e.g., Scheme 5).

With methanol as nucleophile, substitution reactions also preferably occur at the carbonyl group (Table 4, entries 6–8). Because of the low stability of the methyl azocarboxylates, a fact that we had observed before during the preparation of the azo carboxylates (Scheme 3), the products **45**–**47** could only be isolated in moderate to low yields.[26] Attempts to employ the transesterification from *tert*-butyl to methyl and the ensuing degradation of the methyl esters for the generation of aryl radicals were successful but did not turn out as more efficient than those methods that are described in the following sections.

As pointed out in the introductory section, the desired key feature of the phenylazocarboxylates **1**, **2**, and **12** is to allow nucleophilic aromatic substitution *and* aryl radical generation under mild conditions (Figure 1). On the basis of our initial results,[19] a further evaluation of diverse reaction conditions for the second, radical reaction step revealed that acids such as trifluoroacetic acid and phosphoric acid remain the most efficient and versatile reagents for the envisaged reaction types. Under such acidic conditions, the cleavage of the *tert*-butyloxycarbonyl group[27] leads to the formation of an usually short-lived aryl diazene, which then acts as a precursor for the aryl radical.[28,29] This mechanistic idea is supported by the positive influence of air or oxygen on the reaction course.[30] In the absence of oxygen, the aryl diazene possesses a signficantly longer lifetime, and side-reactions such as azo coupling (by aryl radical addition to the diazene) are thus observed. In the presence of oxygen, on the other hand, the concentration of the aryl diazenes is kept very low at all times because they are readily converted to aryl radicals by hydrogen transfer and loss of nitrogen.[30]

Reductions and carbon–carbon bond formations with olefinic and aromatic substrates can be easily achieved by treating *tert*-butyl phenylazocarboxylates with trifluoroacetic acid in the presence of a suitable hydrogen donor (e.g., ethanol or 2-propanol) or the respective radical acceptor (e.g., arenes, alkenes) at slightly elevated temperatures (Table 5).[19] The reactions shown in entries 5 and 6 (Table 5) are examples for Meerwein-type olefin functionalizations, in which copper(II) chloride or TEMPO serve as trapping reagents. Manganese dioxide was found to be a useful additive to prevent the reduction of the azocarboxylates to the corresponding hydrazines (see also Table 8).

Inspired by a methodology recently reported by Taniguchi,[31] we also attempted the introduction of oxygen through a direct oxygenation as well as through carbohydroxylation reactions. An example for an oxygenation, which is able to produce phenols such as **55** from azocarboxylates, is reported in Table 6 (entry 1) along with typical halogenation reactions (Table 6, entries 2–5). The acid-induced radical generation from **2** therefore simply had to be conducted under oxygen atmosphere instead of under air. So far, only a few examples have been reported for this reaction type.[5a,32] With regard to the overall two-step strategy, this methodology offers a new way to transfer 4-hydroxyphenyl groups to nucleophilic agents via substitution of a phenylazocarboxylate and subsequent radical oxygenation. Phenols, in contrast, are usually unreactive toward nucleophiles.

To achieve carbohydroxylation reactions, the aryl radical addition to the alkene has to compete successfully with the direct trapping of the aryl radical by oxygen (Table 7).[33,34] Therefore not surprisingly, reactions of nonactivated alkenes such as **60** and **61** (Table 7, entries 1–3) produce comparatively larger quantities of phenols (yields reported in brackets) than reactions with activated alkenes such as the methyl methacrylate (**62**) (Table 7, entries 4–5).[35] For a more convenient isolation of the products, all initially formed hydroperoxides were converted to alcohols by treatment with triphenyl phosphine.[36] Only the hydroperoxide arising from the reaction of **2** and **61** already fragmented under the acidic conditions to finally give ketone **66** (Table 7, entry 3).[37]

Since the popular and widely used Boc-protecting group is known to be labile at elevated temperatures,[38] we also investigated thermally initiated reactions of phenylazocarboxylates with aromatic substrates (Table 8).[39] Preliminary experiments aimed at the determination of the thermal stability

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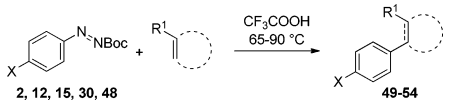
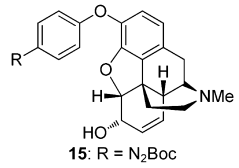
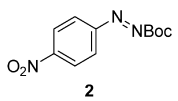
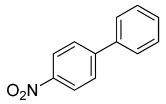
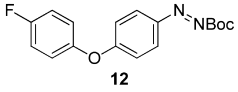
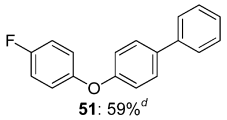
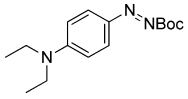
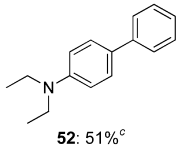
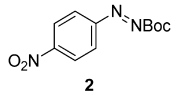
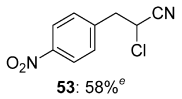
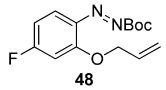
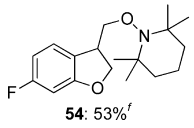
Table 5. Generation of Aryl Radicals: Reduction and C−C Coupling

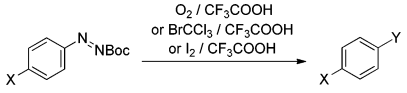


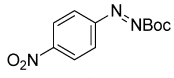
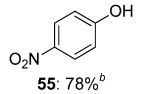
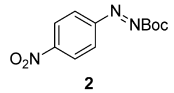
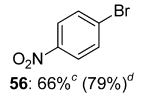
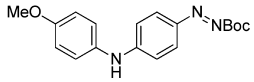
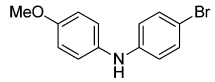
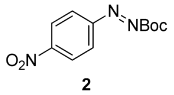
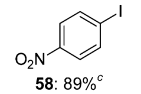
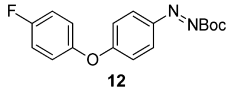
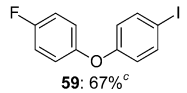
entry	azocarboxylate	product (%)[a]
1	 **15**: R = N_2Boc	**49**: R = H (73%)[b]
2	 **2**	 **50**: 64%[c]
3	 **12**	 **51**: 59%[d]
4	 **30**	 **52**: 51%[c]
5	 **2**	 **53**: 58%[e]
6	 **48**	 **54**: 53%[f]

[a]Isolated yields. [b]EtOH (5.0 equiv), CF_3COOH (30 equiv), CH_3CN/H_2O (1:1). [c]CF_3COOH (10 equiv), benzene. [d]CF_3COOH (1.0 equiv), benzene. [e]CF_3COOH (10 equiv), acrylonitrile (30 equiv), $CuCl_2$ (1.0 equiv), MnO_2 (1.0 equiv), CH_3CN. [f]CF_3COOH (10 equiv), TEMPO (2.0 equiv), CH_3CN.

showed that the decomposition of the *tert*-butyl azocarboxylate **2** in high-boiling organic solvents such as diphenyl ether starts to occur at around 160 °C.[40] In the same study, no significant difference was observed between phenylazocarboxylates bearing electron-withdrawing substituents such as nitro or cyano[41] (compounds **2** and **63**) and those bearing donor groups such as an aryloxy or dialkyl amine (compounds **12** and **30**). Satisfactory synthetic results were later only obtained from experiments in which the acceptor-substituted phenylazocarboxylates **2** and **63** were reacted with electron-rich aromatic substrates. A gradual change to donor-substituents in the azocarboxylate (Table 8, entries 1−5) as well as the replacement of 1,4-dimethoxybenzene (**69**) (Table 8, entry 1) with 1,4-dichlorobenzene (**70**) (Table 8, entry 6) led to a remarkable decrease in yield. These results suggest that an alternative, nonradical decomposition pathway exists for donor-substituted phenylazocarboxylates, such as **12** and **30**, at elevated temperatures. In general, the reaction outcome is probably influenced by the nucleophilicity of the substrate, because aryl radicals can be considered more or less electrophilic,[42] as well as by the radical stabilizing effects of the substituents located on the substrate.[43] For syntheses that would require "thermally unfavorable" reactant combinations (Table 8, entries 3−6), we recommend the use of the trifluoroacetic-acid-mediated variant (Table 5).[44]

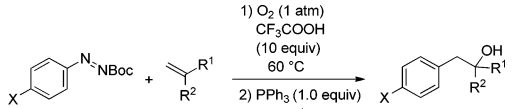
Table 6. Generation of Aryl Radicals: Introduction of Oxygen and Halogens

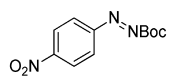
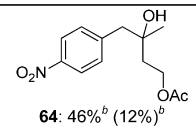
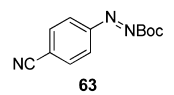
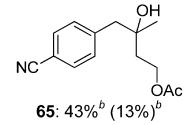
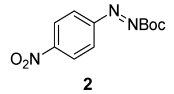
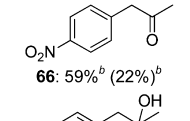
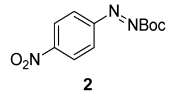
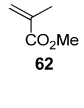
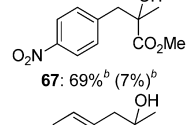
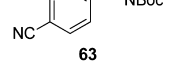
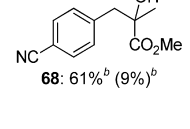


entry	azocarboxylate	product (%)[a]
1	 **2**	 **55**: 78%[b]
2	 **2**	 **56**: 66%[c] (79%)[d]
3	 **35**	 **57**: 42%[c]
4	 **2**	 **58**: 89%[c]
5	 **12**	 **59**: 67%[c]

[a]Isolated yields. [b]CF_3COOH (10 equiv), O_2 (1 atm), 60 °C, CH_3CN. [c]CF_3COOH (10 equiv), $BrCCl_3$ or I_2 (30 equiv), 80 °C, CH_3CN. [d]CF_3COOH (10 equiv), $BrCCl_3$ (30 equiv), rt, benzene.

Table 7. Generation of Aryl Radicals: Carbohydroxylation of Activated and Nonactivated Alkenes



entry	azocarboxylate	alkene	product (%)[a]
1	 **2**	 **60**	 **64**: 46%[b] (12%)[b]
2	 **63**	 **60**	 **65**: 43%[b] (13%)[b]
3	 **2**	 **61**	 **66**: 59%[b] (22%)[b]
4	 **2**	 **62**	 **67**: 69%[b] (7%)[b]
5	 **63**	 **62**	 **68**: 61%[b] (9%)[b]

[a]Isolated yields. [b]Yield of phenol derivative.

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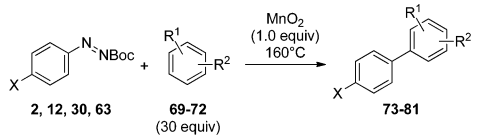
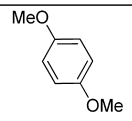
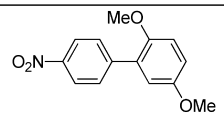
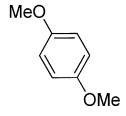
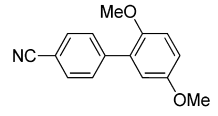
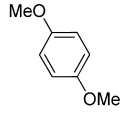
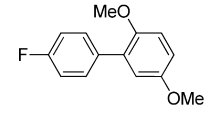
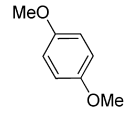
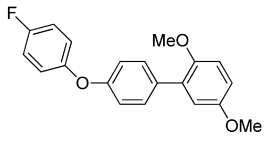
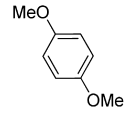
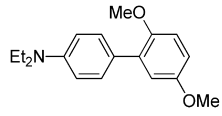
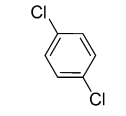
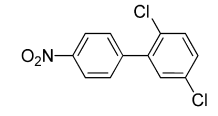
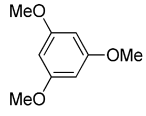
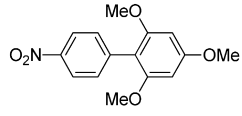
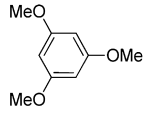
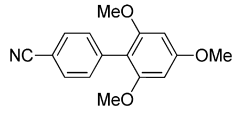
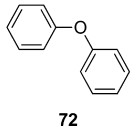
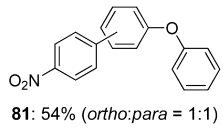
Table 8. Thermal Reactions of Azocarboxylates



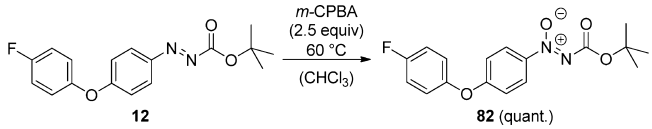
entry	aromatic substrate	product (%)[a]
1	 **69**	 **73**: 53%
2	 **69**	 **74**: 44%
3	 **69**	 **75**: 27%.
4	 **69**	 **76**: 32%
5	 **69**	 **77**: 12%
6	 **70**	 **78**: 36%
7	 **71**	 **79**: 59%
8	 **71**	 **80**: 50%
9	 **72**	 **81**: 54% (*ortho*:*para* = 1:1)

[a]Isolated yields.

In a series of photochemical experiments, the phenylazocarboxylates **2**, **12**, and **30** showed remarkable stability, although the related UV spectra had before indicated suitable absorption maxima.[45] Even under prolonged irradiation at wavelength around 300 nm, and in the presence of TEMPO, these attempts to generate aryl radicals remained unsuccessful.[46] In solution, a more intense color was observed for those azocarboxylates bearing an electron-donating substituent (see compounds reported in Tables 1−3), which is in agreement with the optical properties generally observed for donor−acceptor substituted benzenes.[47]

Besides the possibility to employ phenylazocarboxylates as precursors for aryl radicals (see above), a number of transformations have also been described, in which the azo moiety is not cleaved but remains as a part of the target molecule. Alkylations, arylations, and heteroarylations of the nitrogen−nitrogen double bond present in phenylazocarboxylates have recently been reported using such diverse reagents as organobismut compounds,[48] organolithium and Grignard reagents,[49] as well as arylboronic acids[50] and enamines.[51] Phenylazocarboxylates have further been employed as reactive diazenes for the ring expansion of cyclopropanes[52] and in cycloaddition reactions.[53] Another possible modification is the selective oxidation of the nitrogen−nitrogen double bond leading to azoxy compounds. This efficient reaction type has been described for some azocarboxylates[54] but not yet for the especially versatile *tert*-butyl derivatives. One representative example is depicted in Scheme 5. Given that the aromatic core

Scheme 5. Oxidation of Phenylazocarboxylates



of the azocarboxylate can now also be modified by nucleophilic substitution prior to the oxidation step, this provides a broader access to azoxy compounds of type **82**, which have recently been described as pesticidally and acaricidally active substances.[55]

CONCLUSIONS

In summary, we have shown that *tert*-butyl phenylazocarboxylates can serve as versatile building blocks for various synthetic purposes. Because of the strongly activating effect of the *tert*-butyloxycarbonylazo group, which is even further increased under acidic conditions, nucleophilic aromatic substitutions can be conducted under mild conditions. As a unique property of the *tert*-butyloxycarbonylazo group, it may additionally serve as a leaving group leading to the formation of aryl radicals. The aryl radicals generated in this way can be further reacted under an oxygen atmosphere to give oxygenation or carbohydroxylation products. Besides halogenations and Meerwein-type carbohalogenations, biaryls are accessible under either acidic or thermal conditions.

EXPERIMENTAL SECTION

General Methods. All commercially available solvents and chemicals were used without further purification. ^{1}H NMR were recorded on 360 and 600 MHz spectrometers using $CDCl_3$ as solvent referenced to TMS (0 ppm) or $CHCl_3$ (7.26 ppm). ^{13}C NMR were recorded at 91 and 151 MHz in $CDCl_3$ using $CDCl_3$ (77.0 ppm) as standard. ^{19}F NMR were recorded at 282 and 338 MHz in $CDCl_3$ using $CFCl_3$ (0 ppm) or C_6F_6 (−164.9 ppm) as standard. 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),

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q (quadruplet), m (multiplet). 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 to visualize components. Silica gel (Kieselgel 60, 40−63 μm, Merck) was used for flash column chromatography.

Starting material. *N*-Ethyl-tyramine (**9**),[56] 3-methyl-3-butenyl acetate (**60**),[57] and 2-methallyl acetate (**61**)[57] were prepared according to literature.

General Procedure for the Synthesis of Diphenylethers with Cs_2CO_3 (Table 1, Method A). To a solution of the phenol (0.50−1.5 equiv) in dry DMF (0.1 M) under argon, Cs_2CO_3 (5.0 equiv) was added, and the resulting mixture was stirred at rt for 1 h. Azo compound **2** (1.0 equiv) was added, and stirring was continued until **2** could no longer be detected by TLC. Under cooling with ice, the reaction was quenched with water, and the resulting mixture was extracted four times with ethyl acetate. The combined organic phases were washed with brine and dried over Na_2SO_4. Concentration in vacuo and purification by silica gel chromatography (as described with each compound) gave the desired products.

General Procedure for the Synthesis of Diphenylethers with K_2CO_3/18-crown-6 (Table 1, Method B). A mixture of K_2CO_3 (4.2−8.3 equiv) and 18-crown-6 (4.2−8.3 equiv) in dry DMF (0.1 M) was stirred under argon for 30 min at rt. The phenol (0.83 equiv) was added, and stirring was continued for 1 h. After the addition of azo compound **2** (1.0 equiv), the reaction course was monitored by TLC until total consumption of **2**. Under cooling with ice, the reaction was quenched with water, and the resulting mixture was extracted four times with ethyl acetate. The combined organic phases were washed with brine and dried over Na_2SO_4. Concentration in vacuo and purification by silica gel chromatography (as described with each compound) gave the desired products.

General Procedure for the Nucleophilic Substitution of Azo Compound 1 with Aliphatic Amines (Table 2, Method C). To a stirred solution of **1** (1.0 equiv) and K_2CO_3 (5.0 equiv) in dry DMF (0.1 M) under argon was added the amine (5.0 equiv), and the resulting mixture was stirred at rt until **1** could no longer be detected by TLC. The reaction mixture was diluted with saturated aqueous $NaHCO_3$ and extracted three times with ethyl acetate. The combined organic phases were washed with brine and dried over Na_2SO_4. Concentration in vacuo and purification by silica gel chromatography (as described with each compound) gave the desired products.

General Procedure for the Nucleophilic Substitution of Azocarboxylates Directed toward the Carbonyl Group (Table 4, Method D). To a stirred solution of the azocarboxylate (1.0 equiv) and K_2CO_3 (5.0 equiv) in ethyl acetate (0.2 M) under argon, the nucleophile was added, and the resulting mixture was stirred at rt. The reaction course was monitored by TLC until total consuption of the azocarboxylate. The reaction mixture was diluted with water and extracted three times with ethyl acetate. The combined organic phases were washed with brine and dried over Na_2SO_4. Concentration in vacuo and purification by silica gel chromatography (as described with each compound) gave the desired products.

General Procedure for the Nucleophilic Substitution with Aromatic Amines and Radical Reactions of Azocarboxylates (Tables 3, 5 and 6, Method E). To a stirred solution of the azocarboxylate (0.3 M) in acetonitrile, the substrate (30 equiv) was added, and the mixture was heated to 80 °C. At that temperature, the required amount of trifluoroacetic acid (see individual products) was added, and the reaction course was monitored by TLC until total consumption of the azocarboxylate. After the mixture was cooled to rt, saturated aqueous Na_2CO_3 was used to adjust the pH to a value of >7, and the resulting mixture was extracted three times with ethyl acetate. The combined organic phases were washed with brine and dried over Na_2SO_4. Concentration in vacuo and purification by silica gel chromatography (as described with each compound) gave the desired products.

General Procedure for Carbohydroxylations (Table 7, Method F). To a stirred mixture of trifluoroacetic acid (10.0 mmol, 745 μL) and the alkene (10.0 mmol) in acetonitrile (0.25 M) at 60 °C, a solution of the azocarboxylate (1.00 mmol) in acetonitrile (0.20 M) was added dropwise over a period of 3 h. During the reaction, a constant flow of oxygen was passed through the mixture (ca. 50 mL/min), and stirring was continued at 60 °C until the azocarboxylate could no longer be detected by TLC. After the mixture was cooled to rt, triphenylphosphine (1.00 mmol, 262 mg) was added, and the solution was stirred overnight at rt. The reaction mixture was diluted with water and extracted three times with dichloromethane. The combined organic phases were washed with brine and dried over Na_2SO_4. Concentration in vacuo and purification by silica gel chromatography (as described with each compound) gave the desired products.

General Procedure for the Thermal Reactions of Azocarboxylates (Table 8, Method G). To the melted substrate (20 equiv) and MnO_2 (1.0 equiv), the azocarboxylate was added (1.0 equiv) in small portions at 160 °C. The mixture was stirred at that temperature until the azocarboxylate could no longer be detected by TLC. After the mixture was cooled to rt, the remaining substrate was removed by kugelrohr distillation, and the products were purified by silica gel chromatography (as described with each compound).

***tert*-Butyl 2-(4-Fluorophenyl)hydrazine Carboxylate (5).** To a stirred solution of 4-fluoro-phenyl hydrazine (**3**)[58] (15.2 mmol, 1.90 g) in dry CH_3CN (20 mL) under argon, di-*tert*-butyl dicarbonate (15.2 mmol, 3.30 g) was added. After complete consumption of the reactants, as monitored by TLC, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 4:1) to give **5** (12.4 mmol, 2.81 g, 82%) as a yellow solid: R_f = 0.3 (hexane/EtOAc = 4:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.45 (s, 9 H), 5.68 (s, 1 H), 6.38 (s, 1 H), 6.75−6.80 (m, 2 H), 6.90−6.96 (m, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 28.2 (3 × CH_3), 81.4 (C_q), 114.3 (d, J_{CF} = 7.7 Hz, 2 × CH), 115.7 (d, J_{CF} = 22.7 Hz, 2 × CH), 144.6 (d, J_{CF} = 1.1 Hz, C_q), 156.2 (C_q), 157.7 (d, J_{CF} = 238.0 Hz, C_q); ^{19}F-NMR (282 MHz, $CDCl_3$) δ −123.8; MS (EI) *m*/*z* (%) 226 (4) [M^+], 171 (9), 170 (100), 126 (35), 125 (13), 110 (32), 109 (14), 83 (14), 58 (61), 43 (15); HRMS (EI) calcd for $C_{11}H_{15}FN_2O_2$ [M^+] 226.1118, found 226.1118.

***tert*-Butyl 2-(4-Nitrophenyl)hydrazine Carboxylate (6).** To a stirred solution of 4-nitrophenyl hydrazine (**4**) (22.9 mmol, 3.50 g) in CH_3CN (35 mL) under argon, di-*tert*-butyl dicarbonate (27.4 mmol, 5.99 g) was added. After complete consumption of the reactants, as monitored by TLC, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 4:1) to give **6** (16.9 mmol, 4.28 g, 74%) as an orange solid: R_f = 0.6 (hexane/EtOAc = 1:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.47 (s, 9 H), 6.30 (s, 1 H), 6.48 (s, 1 H), 6.82 (d, *J* = 9.1 Hz, 2 H), 8.13 (d, *J* = 9.1 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 28.2 (3 × CH_3), 82.3 (C_q), 111.6 (2 × CH), 125.9 (2 × CH), 141.1 (C_q), 153.8 (C_q), 155.5 (C_q).

***tert*-Butyl 2-(4-Fluorophenyl)azocarboxylate (1).** To a stirred solution of **5** (12.4 mmol, 8.80 g) in dry CH_2Cl_2 (25 mL) under argon, MnO_2 (62.2 mmol, 5.41 g) was added. After completion of the reaction, as monitored by TLC, the reaction mixture was filtered over Celite, and the filter cake was further washed with CH_2Cl_2. Removal of the solvent under reduced pressure gave **1** (11.7 mmol, 2.61 g, 94%) as an orange oil: R_f = 0.6 (hexane/EtOAc = 19:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.66 (s, 9 H), 7.15−7.23 (m, 2 H), 7.91−7.97 (m, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 27.9 (3 × CH_3), 85.1 (C_q), 116.3 (d, J_{CF} = 23.2 Hz, 2 × CH), 126.0 (d, J_{CF} = 10.6 Hz, 2 × CH), 148.1 (d, J_{CF} = 3.0 Hz, C_q), 161.0 (C_q), 165.8 (d, J_{CF} = 256.6 Hz, C_q); ^{19}F-NMR (282 MHz, $CDCl_3$) δ −104.7; MS (EI) *m*/*z* (%) 152 (6) [$M^+ - OC(CH_3)_3 + H^+$], 151 (62), 124 (10), 123 (47), 96 (15), 95 (91), 82 (14), 75 (46), 59 (22), 58 (100), 45 (16), 43 (63), 41 (16).

***tert*-Butyl 2-(4-Nitrophenyl)azocarboxylate (2).** To a stirred solution of **6** (16.6 mmol, 4.20 g) in dry CH_2Cl_2 (30 mL) under argon, MnO_2 (83.0 mmol, 7.20 g) was added. After completion of the reaction, as monitored by TLC, the reaction mixture was filtered over Celite, and the filter cake was further washed with CH_2Cl_2. Removal of the solvent under reduced pressure gave **2** (16.0 mmol, 4.02 g, 96%) as an orange solid: R_f = 0.7 (hexane/EtOAc = 4:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.68 (s, 9 H), 8.02 (d, *J* = 9.2 Hz, 2 H), 8.38 (d, *J* = 9.2 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 27.9 (3 × CH_3), 86.1 (C_q), 124.1 (2 × CH), 124.8 (2 × CH), 150.1 (C_q), 154.4 (C_q), 160.5 (C_q).

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***tert*-Butyl 2-(4-(4-Fluorophenoxy)phenyl)azocarboxylate (12).** Title compound was prepared according to method A using 4-fluorophenol (**7**) (4.80 mmol, 538 mg) in DMF (30 mL), Cs_2CO_3 (20.0 mmol, 6.51 g), and **2** (4.00 mmol, 1.01 g). Purification by column chromatography (hexane/EtOAc = 19:1) gave **12** (3.33 mmol, 1.05 g, 83%) as an orange solid. For analytical data, see reference 19.

Methyl (*S*)-2-Amino-3-[4-(4-*tert*-butyl-azocarboxylatephenoxy)phenyl]propionate (13). Title compound was prepared according to method B as described in reference 19.

***tert*-Butyl 2-(4-(4-(2-(Ethylamino)ethyl)phenoxy)phenyl)azocarboxylate (14).** Title compound was prepared from *N*-ethyltyramine (**9**) (750 μmol, 124 mg) in DMF (5 mL), Cs_2CO_3 (2.50 mmol, 815 mg), and **2** (500 μmol, 126 mg) according to method A. Purification by column chromatography (CH_2Cl_2/MeOH = 75:1 → 10:1, desactivated with triethylamine) gave **14** (314 μmol, 113 mg, 63%) as a red oil: R_f = 0.3 (CH_2Cl_2/MeOH = 10:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.18 (t, *J* = 7.2 Hz, 3 H), 1.66 (s, 9 H), 2.67−2.70 (m, 3 H), 2.73−2.85 (m, 3 H), 7.01−7.04 (m, 4 H), 7.25 (d, *J* = 8.5 Hz, 2 H), 7.91 (d, *J* = 9.1 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 11.5 (CH_3), 27.9 (3 × CH_3), 32.6 (CH_2), 46.9 (CH_2), 54.7 (CH_2), 84.6 (C_q), 117.5 (2 × CH), 120.4 (2 × CH), 125.9 (2 × CH), 130.2 (2 × CH), 130.3 (C_q), 146.9 (C_q), 153.5 (C_q), 161.1 (C_q), 162.8 (C_q); MS (EI) *m*/*z* (%) 325 (4) [M^+ − C_2H_6N], 324 (15), 296 (8) [M^+ − C_4H_9O], 268 (8) [M^+ − Boc], 267 (10), 196 (15) [M^+ − N_2Boc − C_2H_6N], 130 (12), 87 (76), 86 (100), 76 (10), 72 (12), 58 (69), 57 (100).

Morphine Derivative 15. Title compound was prepared according to method B as described in reference 19.

Estradiol Derivative 16. Title compound was prepared according to method A as described in reference 19.

***tert*-Butyl 2-(4-Butylaminophenyl)azocarboxylate (25).** Title compound was prepared from **1** (446 μmol, 100 mg) and *n*-butylamine (**17**) (2.23 mmol, 220 μL) according to method C. Purification by column chromatography (hexane/EtOAc = 3:1, desactivated with triethylamine) gave **25** (157 μmol, 43.6 mg, 35%) as an orange solid: R_f = 0.4 (hexane/EtOAc = 4:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.3 Hz, 3 H), 1.44 (dd, *J* = 7.2 Hz, *J* = 15.3 Hz, 2 H), 1.60−1.69 (m, 11 H), 3.20−3.27 (m, 2 H), 4.49 (s, 1 H), 6.58 (d, *J* = 9.1 Hz, 2 H), 7.86 (d, *J* = 9.1 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 13.8 (CH_3), 20.2 (CH_2), 27.9 (3 × CH_3), 31.3 (CH_2), 43.1 (CH_2), 83.3 (C_q), 111.9 (2 × CH), 127.5 (C_q), 143.6 (2 × CH), 153.7 (C_q), 161.2 (C_q); MS (EI) *m*/*z* (%) 277 (1) [M^+], 177 (42), 176 (20) [M^+ − Boc], 149 (58), 148 (51) [M^+ − NNBoc], 140 (11), 135 (13), 134 (88), 122 (17), 121 (12), 120 (26), 118 (12), 107 (31), 106 (100), 105 (65), 104 (20), 93 (15), 92 (44), 91 (13), 83 (12), 79 (26), 78 (18), 77 (59), 76 (13), 65 (30), 64 (10), 57 (100), 56 (75), 55 (36), 53 (15), 52 (11), 51 (29), 50 (18), 44 (100), 41 (100), 40 (16), 39 (75), 38 (10).

***tert*-Butyl 2-(4-*sec*-Butylaminophenyl)azocarboxylate (26).** Title compound was prepared from **2** (890 μmol, 200 mg) and *sec*-butylamine (**18**) (4.46 mmol, 453 μL) according to method C. Purification by column chromatography (hexane/EtOAc = 9:1, desactivated with triethylamine) gave **26** (224 μmol, 62.2 mg, 25%) as an orange solid: R_f = 0.3 (hexane/EtOAc = 4:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.5 Hz, 3 H), 1.21 (d, *J* = 6.4 Hz, 3 H), 1.50−1.63 (m, 2 H), 1.64 (s, 9 H), 3.50−3.55 (m, 1 H), 4.46 (d, *J* = 7.7 Hz, 1 H), 6.55 (d, *J* = 9.1 Hz, 2 H), 7.84 (d, *J* = 9.1 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 10.3 (CH_3), 20.1 (CH_3), 27.9 (3 × CH_3), 29.6 (CH_2), 49.8 (CH), 83.2 (C_q), 112.2 (2 × CH), 127.6 (2 × CH), 143.4 (C_q), 153.1 (C_q), 161.3 (C_q); MS (EI) *m*/*z* (%) 277 (5) [M^+], 204 (15), 177 (48), 176 (53) [M^+ − Boc], 154 (27), 149 (50), 148 (100) [M^+ − NNBoc], 134 (36), 133 (15), 121 (19), 120 (100), 119 (100), 118 (31), 117 (11), 93 (18), 92 (46), 91 (20), 77 (28), 65 (26), 58 (15), 57 (100), 56 (70), 55 (29), 53 (10), 51 (18), 50 (12), 44 (82), 42 (11), 41 (100), 40 (12), 39 (50), 38 (12); HRMS (EI) calcd for: $C_{15}H_{23}N_3O_2$ [M^+] 277.1790, found 277.1788.

***tert*-Butyl 2-(4-*tert*-Butylaminophenyl)azocarboxylate (27).** Title compound was prepared from **1** (890 μmol, 200 mg) and *tert*-butylamine (**19**) (4.46 mmol, 473 μL) according to method C. After 22 h, further 19 and 26 h, **19** (4.46 mmol, 473 μL) was added again. Purification by column chromatography (hexane/EtOAc = 10:1 → 4:1, desactivated with triethylamine) gave **27** (134 μmol, 37.2 mg, 23% (brsm)) as an orange solid: R_f = 0.2 (hexane/EtOAc = 4:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.44 (s, 9 H), 1.64 (s, 9 H), 4.57 (s, 1 H), 6.66 (d, *J* = 9.1 Hz, 2 H), 7.82 (d, *J* = 9.1 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ = 27.9 (3 × CH_3), 29.6 (3 × CH_3), 51.7 (C_q), 83.2 (C_q), 113.9 (2 × CH), 127.3 (2 × CH), 143.1 (C_q), 152.6 (C_q), 161.2 (C_q); MS (EI) *m*/*z* (%) 277 (5) [M^+], 204 (11), 177 (29), 176 (40) [M^+ − Boc], 168 (12), 162 (22), 149 (21), 148 (55) [M^+ − NNBoc], 134 (61), 133 (33), 127 (14), 120 (11), 93 (52), 65 (25), 58 (16), 57 (100), 56 (45), 55 (19), 51 (10), 44 (58), 42 (12), 41 (100).

***tert*-Butyl 2-(4-(Diethylamino)phenyl)azocarboxylate (28).** Title compound was prepared from **1** (6.69 mmol, 1.50 g) and diethylamine (**20**) (33.5 mmol, 3.45 mL) according to method C. After 48 h, **20** (33.5 mmol, 3.45 mL) was added once again. Purification by column chromatography (hexane/EtOAc = 4:1, desactivated with triethylamine) gave **28** (4.93 mmol, 1.37 g, 74%) as an orange solid: R_f = 0.3 (hexane/EtOAc = 4:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.2 Hz, 6 H), 1.65 (s, 9 H), 3.47 (q, *J* = 7.2 Hz, 4 H), 6.67 (d, *J* = 9.4 Hz, 2 H), 7.91 (d, *J* = 9.4 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 12.6 (2 × CH_3), 27.9 (3 × CH_3), 44.9 (2 × CH_2), 82.9 (C_q), 110.9 (2 × CH), 127.7 (2 × CH), 142.2 (C_q), 152.7 (C_q), 161.2 (C_q); MS (EI) *m*/*z* (%) 277 (21) [M^+], 204 (23), 177 (90), 176 (87) [M^+ − Boc], 163 (15), 162 (100), 149 (64), 148 (100) [M^+ − NNBoc], 147 (20), 135 (15), 162 (100), 133 (94), 132 (13), 120 (33), 119 (36), 118 (26), 106 (57), 105 (40), 104 (33), 91 (37), 85 (40), 83 (63), 79 (25), 77 (49), 76 (14), 65 (17), 58 (24), 57 (100), 56 (54), 55 (22), 51 (21), 50 (12), 47 (12), 44 (63), 43 (14), 42 (100), 40 (42).

***tert*-Butyl 2-(4-(Piperidin-1-yl)phenyl)azocarboxylate (29).** Title compound was prepared from **1** (890 μmol, 200 mg) and piperidine (**21**) (4.46 mmol, 441 μL) according to method C. Purification by column chromatography (hexane/EtOAc = 4:1, desactivated with triethylamine) gave **29** (820 μmol, 236 mg, 92%) as an orange solid: R_f = 0.6 (hexane/EtOAc = 2:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.65 (s, 9 H), 1.69 (m, 6 H), 3.46 (t, *J* = 4.6 Hz, 4 H), 6.87 (d, *J* = 9.3 Hz, 2 H), 7.89 (d, *J* = 9.3 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 24.3 (CH_2), 25.4 (2 × CH_2), 27.9 (3 × CH_3), 48.4 (2 × CH_2), 83.3 (C_q), 113.1 (2 × CH), 127.1 (2 × CH), 143.2 (C_q), 155.1 (C_q), 161.2 (C_q); MS (EI) *m*/*z* (%) 289 (12) [M^+], 252 (10), 216 (19), 190 (12), 189 (86), 188 (92) [M^+ − Boc], 176 (19), 175 (11), 162 (11), 161 (100) [M^+ − NNBoc], 160 (100), 159 (30), 132 (37), 131 (13), 130 (15), 120 (21), 119 (14), 118 (16), 117 (14), 106 (13), 105 (46), 104 (56), 103 (11), 92 (20), 91 (23), 85 (16), 83 (25), 78 (17), 77 (63), 76 (15), 65 (14), 58 (22), 57 (100), 56 (54), 55 (41), 53 (41), 51 (25), 50 (13), 45 (69), 44 (13), 43 (12), 42 (100) 41 (11), 40 (51).

***tert*-Butyl 2-(4-(4-Ethylpiperazin-1-yl)phenyl)azocarboxylate (30).** Title compound was prepared from **1** (890 μmol, 200 mg) and *N*-ethylpiperazine (**22**) (4.46 mmol, 570 μL) according to method C. Purification by column chromatography (hexane/EtOAc = 4:1, desactivated with triethylamine) gave **30** (780 μmol, 227 mg, 80%) as an orange solid: R_f = 0.4 (hexane/EtOAc = 4:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.13 (t, *J* = 7.2 Hz, 3 H), 1.65 (s, 9 H), 2.48 (q, *J* = 7.2 Hz, 2 H), 2.57−2.60 (m, 4 H), 3.45−3.48 (m, 4 H), 6.90 (d, *J* = 9.3 Hz, 2 H), 7.90 (d, *J* = 9.3 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 11.9 (CH_3), 27.9 (3 × CH_3), 47.1 (2 × CH_2), 52.3 (CH_2), 52.4 (2 × CH_2), 83.5 (C_q), 113.4 (2 × CH), 126.7 (2 × CH), 143.8 (C_q), 154.8 (C_q), 161.2 (C_q); MS (EI) *m*/*z* (%) 318 (2) [M^+], 217 (12) [M^+ − Boc], 190 (25), 189 (26) [M^+ − NNBoc], 105 (13), 84 (16), 77 (11), 57 (100), 56 (24), 45 (21), 43 (20), 42 (38), 40 (13).

***tert*-Butyl 2-(4-(4-(2-Methoxyphenyl)piperazin-1-yl)phenyl)azocarboxylate (31).** Title compound was prepared from **1** (890 μmol, 200 mg) and *N*-(2-methoxyphenyl)piperazine (**23**) (4.46 mmol, 789 μL) according to method C. Purification by column chromatography (hexane/EtOAc = 1:1, desactivated with triethylamine) gave **31** (780 μmol, 311 mg, 88%) as an orange solid: R_f = 0.5 (hexane/EtOAc = 2:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.66 (s, 9 H), 3.18−3.26 (m, 4 H), 3.60−3.64 (m, 4 H), 3.90 (s, 3 H), 6.91 (d,

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J = 8.4 Hz, 2 H), 6.96 (dd, J = 2.1 Hz, J = 7.2 Hz, 2 H), 7.05 (ddd, J = 2.6 Hz, J = 6.4 Hz, J = 8.0 Hz, 2 H), 7.93 (d, J = 9.3 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 27.1 (3 × CH_3), 47.4 (2 × CH_2), 50.4 (2 × CH_2), 55.5 (CH_3), 83.6 (C_q), 111.4 (CH), 113.5 (2 × CH), 118.3 (CH), 121.1 (CH), 123.5 (CH), 126.7 (2 × CH), 140.7 (C_q), 143.9 (C_q), 152.3 (C_q), 155.0 (C_q), 161.2 (C_q); MS (EI) m/z (%) 396 (4) [M^+], 296 (11), 295 (14) [M^+ − Boc], 269 (13), 268 (62), 267 (38) [M^+ − NNBoc], 252 (13), 162 (29), 136 (16), 135 (37), 134 (20), 121 (15), 120 (28), 106 (12), 105 (38), 104 (22), 91 (11), 85 (20), 83 (31), 77 (26), 57 (100), 56 (29), 55 (14), 45 (41), 42 (61), 40 (28).

***tert*-Butyl (4-Morpholin-4-ylphenyl)azocarboxylate (32).** Title compound was prepared according to method C as described in reference 19.

4-(*tert*-Butyloxycarbonylazophenyl)-(4-methoxyphenyl)-amine (35). Title compound was prepared from **12** (790 μmol, 250 mg), *p*-anisidine (**33**) (7.90 mmol, 975 mg), and trifluoroacetic acid (11.9 mmol, 880 μL) according to method E. Purification by column chromatography (hexane/EtOAc = 6:1) gave **35** (647 μmol, 212 mg, 82%) as an orange solid. For analytical data, see reference 19.

4-(*tert*-Butyloxycarbonylazophenyl)-(4-chlorophenyl)-amine (36). Title compound was prepared according to method E as described in reference 19.

***N*-Butyl 2-(4-Fluorophenyl)azocarboxamide (40).** Title compound was prepared from **1** (3.00 mmol, 672 mg) and *n*-butylamine (**17**) (15.0 mmol, 1.48 mL) according to method D. After 72 h, **17** (30.0 mmol, 2.96 mL) was added once again. Purification by column chromatography (hexane/EtOAc = 9:1, desactivated with triethylamine) gave **40** (2.36 mmol, 528 mg, 79%) as an orange solid: R_f = 0.2 (hexane/EtOAc = 4:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.97 (t, J = 7.3 Hz, 3 H), 1.44 (qd, J = 7.3 Hz, J = 14.4 Hz, 2 H), 1.61−1.70 (m, 2 H), 3.49 (dt, J = 6.1 Hz, J = 7.2 Hz, 2 H), 6.42 (s, 1 H), 7.20 (dd, J_{HF} = 8.1 Hz, J = 9.0 Hz, 2 H), 7.97 (dd, J_{HF} = 5.2 Hz, J = 9.0 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 13.7 (CH_3), 20.0 (CH_2), 31.5 (CH_2), 40.5 (CH_2), 116.4 (d, J_{CF} = 23.1 Hz, 2 × CH), 126.3 (d, J_{CF} = 9.5 Hz, 2 × CH), 147.6 (d, J_{CF} = 3.0 Hz, C_q), 160.3 (C_q), 165.9 (d, J_{CF} = 256.2 Hz, C_q); ^{19}F-NMR (338 MHz, $CDCl_3$) δ −107.9; MS (EI) m/z (%) 269 (29), 267 (15), 235 (16), 233 (10), 123 (5), 100 (21), 96 (12), 95 (17), 87 (11), 85 (63), 83 (100), 71 (14), 70 (13), 57 (91), 55 (14), 47 (22), 44 (31), 43 (15), 41 (38).

***N*-Butyl 2-(4-Nitrophenyl)azocarboxamide (41).** Title compound was prepared from **2** (1.00 mmol, 251 mg), MnO_2 (1.00 mmol, 86.9 mg), and *n*-butylamine (**17**) (5.00 mmol, 494 μL) according to method D. After 12 h, **17** (5.00 mmol, 494 μL) was added once again. Purification by column chromatography (hexane/EtOAc = 3:1, desactivated with triethylamine) gave **41** (630 μmol, 159 mg, 63%) as an orange solid: R_f = 0.2 (hexane/EtOAc = 4:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.99 (t, J = 7.4 Hz, 3 H), 1.46 (qd, J = 7.4 Hz, J = 14.7 Hz, 2 H), 1.68 (td, J = 7.4 Hz, J = 14.7 Hz, 2 H), 3.54 (dt, J = 6.2 Hz, J = 7.2 Hz, 2 H), 6.45 (s, 1 H), 8.07 (d, J = 8.9 Hz, 2 H), 8.39 (d, J = 8.9 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 13.7 (CH_3), 20.0 (CH_2), 31.5 (CH_2), 40.7 (CH_2), 100.0 (C_q), 124.4 (2 × CH), 121.8 (2 × CH), 154.1 (C_q), 159.7 (C_q); MS (EI) m/z (%) 123 (13) [M^+ − $C_5H_{10}N_3O$], 122 (7), 100 (54), 76 (11), 75 (8), 58 (6), 57 (100), 50 (9).

***N*-Butyl 2-(4-(4-Fluorophenoxy)phenyl)azocarboxamide (42).** Title compound was prepared from **12** (630 μmol, 200 mg) and *n*-butylamine (**17**) (3.16 mmol, 312 μL) according to method D. After 14 h, further 8, 16, and 24 h, **17** (3.16 mmol, 312 μL) was added again. Purification by column chromatography (hexane/EtOAc = 4:1, desactivated with triethylamine) gave **42** (644 μmol, 203 mg, *quant.*) as an orange solid: R_f = 0.2 (hexane/EtOAc = 4:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.97 (t, J = 7.3 Hz, 3 H), 1.43 (qd, J = 7.3 Hz, J = 14.4 Hz, 2 H), 1.65 (td, J = 7.5 Hz, J = 14.7 Hz, 2 H), 3.49 (dt, J = 6.1 Hz, J = 7.2 Hz, 2 H), 6.44 (s, 1 H), 7.02 (d, J = 9.1 Hz, 2 H), 7.06−7.14 (m, 4 H), 7.94 (d, J = 9.1 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 13.7 (CH_3), 20.0 (CH_2), 31.6 (CH_2), 40.4 (CH_2), 116.8 (d, J_{CF} = 23.5 Hz, 2 × CH), 117.4 (2 × CH), 121.9 (d, J_{CF} = 8.4 Hz, 2 × CH), 126.2 (2 × CH), 146.4 (C_q), 151.0 (d, J_{CF} = 2.8 Hz, C_q), 159.7 (d, J_{CF} = 243.9 Hz, C_q), 160.6 (C_q), 162.8 (C_q); ^{19}F-NMR (338 MHz, $CDCl_3$) δ −120.8; MS (EI) m/z (%) 217 (12), 216 (91), 215 (58) [M^+ − $C_5H_{10}NO$], 188 (46), 187 (52) [M^+ − $C_5H_{10}N_3O$], 159 (36), 133 (19), 100 (26), 57 (100).

***sec*-Butyl 2-(4-Fluorophenyl)azocarboxamide (43).** Title compound was prepared from **1** (1.00 mmol, 224 mg) and *sec*-butylamine (**18**) (5.00 mmol, 508 μL) according to method D. After 3 h, further 24 and 48 h, **18** (10.0 mmol, 1.02 mL) was added again. Purification by column chromatography (hexane/EtOAc = 9:1 → 4:1, desactivated with triethylamine) gave **43** (663 μmol, 148 mg, 66%) as an orange solid: R_f = 0.2 (hexane/EtOAc = 4:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.99 (t, J = 7.5 Hz, 3 H), 1.29 (d, J = 6.6 Hz, 3 H), 1.59−1.68 (m, 2 H), 4.02 (ddd, J = 6.6 Hz, J = 8.7 Hz, J = 13.3 Hz, 1 H), 6.20 (s, 1 H), 7.20 (dd, J_{HF} = 8.1 Hz, J = 9.2 Hz, 2 H), 7.98 (dd, J_{HF} = 5.2 Hz J = 9.2 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 10.3 (CH_3), 20.3 (CH_3), 29.6 (CH_2), 48.3 (CH), 116.4 (d, J_{CF} = 23.1 Hz, 2 × CH), 126.3 (d, J_{CF} = 9.5 Hz, 2 × CH), 147.7 (d, J_{CF} = 3.0 Hz, C_q), 159.7 (C_q), 165.9 (d, J_{CF} = 256.1 Hz, C_q); ^{19}F-NMR (338 MHz, $CDCl_3$) δ −108.0; MS (EI) m/z (%) 123 (41) [M^+ − $C_5H_{10}NO$], 101 (6), 100 (93), 96 (34), 95 (74) [M^+ − $C_5H_{10}N_3O$], 85 (7), 83 (10), 75 (19), 58 (11), 57 (100), 55 (8); HRMS (EI) calcd for $C_{11}H_{14}FN_3O$ [M^+] 223.1121, found 223.1121.

2-(4-Fluorophenyl)-*N*-(4-methoxybenzyl)azocarboxamide (44). Title compound was prepared from **12** (1.00 mmol, 224 mg) and methoxybenzylamine (**39**) (5.00 mmol, 653 μL) according to method B. After 48 h, **39** (5.00 mmol, 653 μL) was added once again. Purification by column chromatography (hexane/EtOAc = 4:1 → 2:1, desactivated with triethylamine) gave **44** (520 mmol, 149 mg, 52%) as an orange solid: R_f = 0.4 (hexane/EtOAc = 2:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.80 (s, 3 H), 4.60 (d, J = 5.9 Hz, 2 H), 6.71 (s, 1 H), 6.89 (d, J = 8.7 Hz, 2 H), 7.19 (dd, J_{HF} = 8.2 Hz, J = 8.9 Hz, 2 H), 7.30 (d, J = 8.7 Hz, 2 H), 7.95 (dd, J_{HF} = 5.2 Hz, J = 8.9 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 44.3 (CH_3), 55.3 (CH_2), 114.3 (2 × CH), 116.5 (d, J_{CF} = 23.1 Hz, 2 × CH), 126.4 (d, J_{CF} = 9.5 Hz, 2 × CH), 129.2 (C_q), 129.4 (2 × CH), 147.6 (d, J_{CF} = 3.0 Hz, C_q), 159.4 (C_q), 160.1 (C_q), 166.0 (d, J_{CF} = 256.5 Hz, C_q); ^{19}F-NMR (338 MHz, $CDCl_3$) δ −107.6; MS (EI) m/z (%) 163 (22), 134 (10), 123 (11) [M^+ − $C_9H_{10}NO_2$], 122 (100), 121 (100), 95 (55) [M^+ − $C_9H_{10}N_3O_2$], 91 (28), 90 (10), 78 (39), 77 (47), 75 (18), 65 (13), 51 (11).

Methyl 2-(4-Fluorophenyl)azocarboxylate (45). Title compound was prepared from **1** (446 μmol, 100 mg) and dry methanol (2.23 mmol, 90.0 μL) according to method D. After 6 h, further 24 and 3 h, methanol (2.23 mmol, 90.0 μL) was added again. Purification by column chromatography (hexane/EtOAc = 6:1) gave **45** (85.1 μmol, 15.5 mg, 19%) as a colorless solid: R_f = 0.6 (hexane/EtOAc = 6:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.08 (s, 3 H), 7.22 (dd, J_{HF} = 8.1 Hz, J = 8.9 Hz, 2 H), 7.98 (dd, J_{HF} = 5.2 Hz, J = 8.9 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 54.9 (CH_3), 116.5 (d, J_{CF} = 23.2 Hz, 2 × CH), 126.3 (d, J_{CF} = 9.6 Hz, 2 × CH), 148.2 (d, J_{CF} = 3.0 Hz, C_q), 162.4 (C_q), 166.2 (d, J_{CF} = 256.9 Hz, C_q); ^{19}F-NMR (338 MHz, $CDCl_3$) δ −107.0; MS (EI) m/z (%) 95 (9) [M^+ − $C_2H_3N_2O_2$] 85 (15), 83 (25).

Methyl 2-(4-Nitrophenyl)azocarboxylate (46). Title compound was prepared from **2** (397 μmol, 100 mg) and dry methanol (1.99 mmol, 81.0 μL) according to method D. After 6 h, methanol (1.99 mmol, 81.0 μL) was added once again. Purification by column chromatography (hexane/EtOAc = 9:1) gave **46** (232 μmol, 48.5 mg, 58%) as a colorless solid: R_f = 0.4 (hexane/EtOAc = 4:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.12 (s, 3 H), 8.05 (d, J = 8.8 Hz, 2 H), 8.40 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 55.2 (CH_3), 124.3 (2 × CH), 124.9 (2 × CH), 150.4 (C_q), 154.3 (C_q), 162.0 (C_q); MS (EI) m/z (%) 209 (1) [M^+], 150 (57) [M^+ − $C_2H_3O_2$], 122 (70) [M^+ − $C_2H_3N_2O_2$], 92 (18), 83 (11), 76 (31), 75 (33), 64 (11), 59 (100), 50 (31); HRMS (EI) calcd for $C_8H_7N_3O_4$ [M^+] 209.0437, found 209.0436.

Methyl 2-(4-(4-Fluorophenoxy)phenyl)azocarboxylate (47). Title compound was prepared from **12** (158 μmol, 50 mg) and dry methanol (791 μmol, 32.0 μL) according to method D. After 16 h, methanol (791 μmol, 32.0 μL) was added once again. Purification by column chromatography (hexane/EtOAc = 19:1 → 9:1) gave **47** (78.0 μmol, 21.3 mg, 49%) as a colorless solid: R_f = 0.3 (hexane/EtOAc = 10:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 4.07 (s, 3 H),

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7.03 (d, J = 9.2 Hz, 2 H), 7.07−7.14 (m, 4 H), 7.94 (d, J = 9.2 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 54.8 (CH_3), 116.8 (d, J_{CF} = 23.5 Hz, 2 × CH), 117.4 (2 × CH), 122.0 (d, J_{CF} = 8.4 Hz, 2 × CH), 126.3 (2 × CH), 147.1 (C_q), 150.9 (d, J_{CF} = 2.7 Hz, C_q), 159.8 (d, J_{CF} = 244.0 Hz, C_q), 162.5 (C_q), 163.3 (d, J_{CF} = 0.8 Hz, C_q); ^{19}F-NMR (338 MHz, $CDCl_3$) δ −120.7; MS (EI) m/z (%) 274 (2) [M^+], 216 (23), 215 (100) [$M^+ - C_2H_3O_2$], 188 (19), 187 (100) [$M^+ - C_2H_3N_2O_2$], 186 (10), 160 (18), 159 (100), 139 (10), 133 (58), 95 (11), 75 (11), 59 (25), 50 (10); HRMS (EI) calcd for $C_{14}H_{11}FN_2O_3$ [M^+] 274.0754, found 274.0753.

***tert*-Butyl (2-Allyloxy-4-fluorophenyl)azocarboxylate (48).** Title compound was prepared as described in reference 19.

3-Phenylmorphine (49). Title compound was prepared as described in reference 19.

4-Nitrobiphenyl (50). Title compound was prepared from **2** (2.00 mmol, 503 mg) and trifluoroacetic acid (20.0 mmol, 1.49 mL) in benzene (8.5 mL) according to method E. Purification by column chromatography (hexane/CH_2Cl_2 = 3:2) gave **50** (1.28 mmol, 152 mg, 64%) as a colorless solid. For analytical data, see reference 19.

4-(4-Fluorophenoxy)biphenyl (51). Title compound was prepared according to method E as described in reference 19.

4-(*N*,*N*-Diethylamino)biphenyl (52). Title compound was prepared from **30** (1.00 mmol, 277 mg) and trifluoroacetic acid (10.0 mmol, 740 μL) in benzene (5 mL) according to method E. Purification by column chromatography (hexane/EtOAc = 39:1, desactivated with triethylamine) gave **52** (514 μmol, 116 mg, 51%) as a colorless solid: R_f = 0.3 (hexane/EtOAc = 39:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.20 (t, J = 7.1 Hz, 6 H), 3.40 (q, J = 7.1 Hz, 4 H), 6.76 (d, J = 8.9 Hz, 2 H), 7.23−7.26 (m, 1 H), 7.39 (dd, J = 8.2 Hz, J = 7.5 Hz, 2 H), 7.49 (d, J = 8.9 Hz, 2 H), 7.55 (d, J = 8.2 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 12.7 (2 × CH_3), 44.4 (2 × CH_2), 112.0 (2 × CH), 125.8 (CH), 126.1 (2 × CH), 127.9 (2 × CH), 128.1 (C_q), 128.6 (2 × CH), 141.3 (C_q), 147.2 (C_q); MS (EI) m/z (%) 226 (16) [M^+ + H], 225 (85) [M^+], 211 (33), 210 (100), 182 (37), 181 (21), 180 (17), 154 (17), 153 (24), 152 (34), 44 (23); HRMS (EI) calcd for $C_{16}H_{19}N$ [M^+] 225.1517, found 225.1517.[59]

2-Chloro-3-(4-nitrophenyl)propionitrile (53). Title compound was prepared according to method E as described in reference 19.

1-((6-Fluoro-2,3-dihydrobenzofuran-3-yl)methoxy)-2,2,6,6-tetramethylpiperidine (54). Title compound was prepared according to method E as described in reference 19.

4-Nitrophenol (55). To a stirred mixture of trifluoroacetic acid (10.0 mmol, 745 μL) in CH_3CN (6 mL) at 60 °C, a solution of **2** (1.00 mmol, 251 mg) in CH_3CN (5 mL) was added dropwise over a period of 3 h. During the reaction, a constant flow of oxygen was passed through the mixture (ca. 50 mL/min), and stirring was continued at 60 °C until the azocarboxylate could no longer be detected by TLC. After cooling to rt, the reaction mixture was diluted with water and extracted three times with CH_2Cl_2. The combined organic phases were washed with brine and dried over Na_2SO_4. Purification by column chromatography (100% CH_2Cl_2) gave **55** (782 μmol, 109 mg, 78%) as a colorless solid: R_f = 0.1 (100% CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.82 (br s, 1 H), 6.91 (d, J = 9.3 Hz, 2 H), 8.18 (d, J = 9.2 Hz, 2 H).[60]

4-Bromo-nitrobenzene (56). Title compound was prepared according to method E as described in reference 19.

4-Bromo-*N*-(4-methoxyphenyl)aniline (57). Title compound was prepared according to method E as described in reference 19.

4-Iodo-nitrobenzene (58). Title compound was prepared according to method E as described in reference 19.

1-Fluoro-4-(4-iodophenoxy)benzene (59). Title compound was prepared according to method E as described in reference 19.

***tert*-Butyl 2-(4-Cyanophenyl)azocarboxylate (63).** Starting from 4-cyanophenylhydrazine,[58] (15.6 mmol, 2.08 g) *tert*-butyl 2-(4-cyanophenyl)hydrazine carboxylate was prepared with di-*tert*-butyldicarbonate (17.2 mmol, 3.75 g) in CH_3CN (20 mL) as described for **5**. Purification by column chromatography (hexane/EtOAc = 3:1) gave the hydrazine carboxylate (13.8 mmol, 3.52 g, 89%) as a yellow solid: R_f = 0.3 (hexane/EtOAc = 2:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.47 (s, 9 H), 6.05 (s, 1 H), 6.40 (s, 1 H), 6.83 (d, J = 8.8 Hz, 2 H), 7.50 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 28.2 (3 × CH_3), 82.1 (C_q), 103.1 (C_q), 112.6 (2 × CH), 119.6 (C_q), 133.7 (2 × CH), 151.9 (C_q), 155.6 (C_q).[61] In a second step, the hydrazine carboxylate (13.8 mmol, 3.52 g) was dissolved in dry CH_2Cl_2 (25 mL) under argon, and MnO_2 (69.0 mmol, 6.00 g) was added. After completion of the reaction, as monitored by TLC, the reaction mixture was filtered over Celite. The filter cake was further washed with CH_2Cl_2. Removal of the solvent under reduced pressure gave **2** (10.7 mmol, 2.49 g, 78%) as an orange solid: R_f = 0.5 (hexane/EtOAc = 4:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.67 (s, 9 H), 7.83 (d, J = 8.8 Hz, 2 H), 7.97 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 27.8 (3 × CH_3), 86.0 (C_q), 116.3 (C_q), 117.8 (C_q), 123.8 (2 × CH), 133.3 (2 × CH), 153.3 (C_q), 160.6 (C_q); MS (EI) m/z (%) 216 (21), 158 (48) [M^+−$OC(CH_3)_3$], 131 (32), 130 (72) [M^+ − Boc], 103 (58), 102 (100) [M^+ − NNBoc], 85 (16), 83 (25), 76 (42), 75 (44), 58 (20), 57 (100), 56 (29), 55 (16), 51 (32), 50 (22), 44 (36), 43 (24), 41 (100), 39 (34).

3-Hydroxy-3-methyl-4-(4′-nitrophenyl)butylacetate (64). Title compound was prepared from **2** (1.00 mmol, 251 mg) and 3-methyl-3-butenyl acetate (**60**) (10.0 mmol, 1.28 g) according to method F. Purification by column chromatography (hexane/EtOAc = 1:1) gave **64** (462 μmol, 123 mg, 46%) as a yellow solid: R_f = 0.6 (hexane/EtOAc = 1:2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.21 (s, 3 H), 1.79 (br s, 1 H), 1.85 (t, J = 6.8 Hz, 2 H), 2.06 (s, 3 H), 2.85 (d, J = 13.3 Hz, 1 H), 2.93 (d, J = 13.3 Hz, 1 H), 4.25−4.33 (m, 2 H), 7.42 (d, J = 8.8 Hz, 2 H), 8.17 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 21.0 (CH_3), 26.9 (CH_3), 40.1 (CH_2), 48.3 (CH_2), 60.9 (CH_2), 71.7 (C_q), 123.2 (2 × CH), 131.4 (2 × CH), 145.0 (C_q), 146.9 (C_q), 170.9 (C_q); MS(EI) m/z (%) 270 (12), 268 (100) [M^+ + H], 267 (30) [M^+], 235 (44), 233 (22), 219 (15), 217 (7), 85 (27), 83 (39), 47 (8); HRMS (EI) calcd for $C_{13}H_{17}NO_5$ [M^+] 267.1107, found 267.1107.

3-Hydroxy-3-methyl-4-(4′-cyanophenyl)butylacetate (65). Title compound was prepared from **63** (1.00 mmol, 231 mg) and 3-methyl-3-butenyl acetate (**60**) (10.0 mmol, 1.28 g) according to method F. Purification by column chromatography (hexane/EtOAc = 2:1) gave **65** (433 μmol, 107 mg, 43%) as an orange oil: R_f = 0.6 (hexane/EtOAc = 1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.19 (s, 3 H), 1.71 (br s, 1 H), 1.84 (dt, J = 1.1 Hz, J = 6.9 Hz, 2 H), 2.05 (s, 3 H), 2.81 (d, J = 13.3 Hz, 1 H), 2.88 (d, J = 13.3 Hz, 1 H), 4.28 (dt, J = 3.1 Hz, J = 7.0 Hz, 2 H), 7.37 (d, J = 8.2 Hz, 2 H), 7.60 (d, J = 8.3 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 20.9 (CH_3), 26.7 (CH_3), 39.9 (CH_2), 48.6 (CH_2), 60.8 (CH_2), 71.6 (C_q), 110.4 (C_q), 118.8 (C_q), 131.3 (2 × CH), 131.7 (2 × CH), 142.9 (C_q), 170.9 (C_q); MS (EI) m/z (%) 160 (18), 154 (13), 131 (50), 118 (12), 117 (99), 116 (36), 90 (16), 89 (51), 72 (12), 71 (100).

1-(4-Nitrophenyl)propan-2-one (66). Title compound was prepared from **2** (1.00 mmol, 231 mg) and 2-methylallyl acetate (**61**) (10.0 mmol, 1.14 g) according to method F. Purification by column chromatography (100% CH_2Cl_2) gave **66** (587 μmol, 105 mg, 59%) as a colorless oil: R_f = 0.4 (hexane/EtOAc = 2:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.24 (s, 3 H), 3.85 (s, 2 H), 7.36 (d, J = 8.8 Hz, 2 H), 8.20 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 29.8 (CH_3), 50.1 (CH_2), 123.8 (2 × CH), 130.4 (2 × CH), 141.4 (C_q), 147.2 (C_q), 204.0 (C_q).[62]

Methyl (2-Hydroxy-2-methyl-3-(4′-nitrophenyl))propionate (67). Title compound was prepared from **2** (1.00 mmol, 251 mg) and methyl methacrylate (**62**) (10.0 mmol, 1.08 mL) according to method F. Purification by column chromatography (hexane/EtOAc = 2:1) gave **67** (690 μmol, 165 mg, 69%) as a yellow solid: R_f = 0.4 (hexane/EtOAc = 2:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.51 (s, 3 H), 3.04 (d, J = 8.4 Hz, 1 H), 3.14 (br s, 1 H), 3.15 (d, J = 8.4 Hz, 1 H), 3.76 (s, 3 H), 7.37 (d, J = 8.8 Hz, 2 H), 8.14 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 26.3 (CH_3), 45.6 (CH_2), 52.6 (CH_3), 74.9 (C_q), 123.3 (2 × CH), 131.0 (2 × CH), 143.8 (C_q), 147.1 (C_q), 176.2 (C_q); MS (EI) m/z (%) 180 (35) [$M^+ - CO_2Me$], 138 (13), 137 (100), 121 (6), 120 (12), 107 (20), 103 (7), 91 (10), 90 (15), 89 (7); HRMS (EI) calcd for $C_{11}H_{13}NO_5$ [M^+] 239.0794, found 239.0794.

Methyl (2-Hydroxy-2-methyl-3-(4′-cyanophenyl))-propionate (68). Title compound was prepared from **63** (1.00 mmol,

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231 mg) and methyl methacrylate (**62**) (10.0 mmol, 1.08 mL) according to method F. Purification by column chromatography (hexane/EtOAc = 2:1) gave **68** (608 μmol, 133 mg, 61%) as a yellow solid: R_f = 0.4 (hexane/EtOAc = 2:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.49 (s, 3 H), 2.98 (d, J = 13.5 Hz, 1 H), 3.10 (d, J = 13.5 Hz, 1 H), 3.75 (s, 3 H), 7.31 (d, J = 8.5 Hz, 2 H), 7.57 (d, J = 8.5 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 26.2 (CH_3), 45.9 (CH_2), 52.9 (CH_3), 74.9 (C_q), 110.9 (C_q), 118.8 (C_q), 130.9 (2 × CH), 131.8 (2 × CH), 141.7 (C_q), 176.2 (C_q); MS (EI) m/z (%) 219 (7) [M^+],160 (78) [M^+ − CO_2Me], 118 (41), 117 (100), 116 (31), 103 (14), 91 (10), 90 (31), 89 (29), 83 (15), 63 (11); HRMS (EI) calcd for $C_{12}H_{13}NO_3$ [M^+] 219.0895, found 219.0895.

2,5-Dimethoxy-4′-nitrobiphenyl (73). Title compound was prepared from **2** (797 μmol, 200 mg), MnO_2 (797 μmol, 69.3 mg), and 1,4-dimethoxybenzene (**69**) (23.9 mmol, 3.30 g) according to method G. Purification by column chromatography (hexane/EtOAc = 19:1 → 4:1) gave **73** (420 μmol, 109 mg, 53%) as a colorless solid: R_f = 0.4 (hexane/EtOAc = 4:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.78 (s, 3 H), 3.82 (s, 3 H), 6.90 (dd, J = 0.5 Hz, J = 2.9 Hz, 1 H), 6.92–6.97 (m, 2 H), 7.69 (d, J = 9.0 Hz, 2 H), 8.26 (d, J = 9.0 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 55.9 (CH_3), 56.2 (CH_3), 112.8 (CH), 114.6 (CH), 116.6 (CH), 123.2 (2 × CH), 129.2 (C_q), 130.3 (2 × CH), 145.2 (C_q), 150.7 (C_q), 153.9 (C_q), one C_q-signal is missing because of overlapping; MS (EI) m/z (%) 260 (17) [M^+ + H], 259 (100) [M^+], 244 (15), 227 (16), 199 (10), 198 (67), 197 (17), 183 (31), 155 (22), 127 (17), 83 (10), 44 (10); HRMS (EI) calcd for $C_{14}H_{13}NO_4$ [M^+] 259.0845, found 259.0845.

2,5-Dimethoxybiphenyl-4′-carbonitrile (74). Title compound was prepared from **63** (1.00 mmol, 233 mg), MnO_2 (1.00 mmol, 86.9 mg), and 1,4-dimethoxybenzene (**69**) (10.0 mmol, 1.38 g) according to method G. Purification by column chromatography (hexane/EtOAc = 4:1) gave **74** (440 μmol, 105 mg, 44%) as a yellowish solid: R_f = 0.4 (hexane/EtOAc = 4:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.76 (s, 3 H), 3.81 (s, 3 H), 6.87 (dd, J = 0.5 Hz, J = 3.0 Hz, 1 H), 6.92 (td, J = 5.9 Hz, J = 8.9 Hz, 2 H), 7.64 (d, J = 8.7 Hz, 2 H), 7.68 (d, J = 8.7 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 55.8 (CH_3), 56.2 (CH_3), 110.6 (C_q), 112.7 (CH), 114.3 (CH), 116.5 (CH), 119.1 (C_q), 129.5 (C_q), 130.2 (2 × CH), 131.8 (2 × CH), 143.2 (C_q), 150.6 (C_q), 153.9 (C_q); MS (EI) m/z (%) 240 (17) [M^+ + H], 239 (100) [M^+], 225 (14), 224 (98), 209 (50), 196 (16), 193 (15), 181 (16), 164 (12), 153 (33), 127 (19), 54 (11), 44 (19); HRMS (EI) calcd for $C_{15}H_{13}NO_2$ [M^+] 239.0946, found 239.0947.

4′-Fluoro-2,5-dimethoxybiphenyl (75). Title compound was prepared from **1** (1.00 mmol, 224 mg), MnO_2 (1.00 mmol, 86.9 mg), and 1,4-dimethoxybenzene (**69**) (30.0 mmol, 4.14 g) according to method G. Purification by column chromatography (hexane/EtOAc = 29:1 → 19:1) gave **75** (230 μmol, 53.5 mg, 23%) as a colorless solid: R_f = 0.4 (hexane/EtOAc = 19:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.75 (s, 3 H), 3.81 (s, 3 H), 6.84–6.94 (m, 3 H), 7.09 (t, J_{HF} = 8.9 Hz, J = 8.9 Hz, 2 H), 7.50 (dd, J_{HF} = 5.5 Hz, J = 8.9 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 55.8 (CH_3), 56.3 (CH_3), 112.7 (CH), 113.1 (CH), 114.9 (d, J_{CF} = 21.3 Hz, 2 × CH), 116.7 (CH), 130.6 (C_q), 131.0 (d, J_{CF} = 8.0 Hz, 2 × CH), 134.3 (d, J_{CF} = 3.4 Hz, C_q), 150.7 (C_q), 153.8 (C_q), 162.1 (d, J = 246.1 Hz, C_q); ^{19}F-NMR (338 MHz, $CDCl_3$) δ −118.8; MS (EI) m/z (%) 233 (16) [M^+ + H], 232 (100) [M^+], 219 (11), 218 (12), 217 (84), 202 (42), 189 (19), 186 (19), 174 (13), 146 (24), 120 (10), 83 (12), 44 (24); HRMS (EI) calcd for $C_{14}H_{13}FO_2$ [M^+] 232.0900, found 232.0901.

4′-(4-Fluorophenoxy)-2,5-dimethoxybiphenyl (76). Title compound was prepared from **12** (1.00 mmol, 316 mg), MnO_2 (1.00 mmol, 86.9 mg), and 1,4-dimethoxybenzene (**69**) (30.0 mmol, 4.14 g) according to method G. Purification by column chromatography (hexane/EtOAc = 6:1) gave **76** (304 μmol, 98.6 mg, 32%) as a yellowish solid: R_f = 0.5 (hexane/EtOAc = 4:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.77 (s, 3 H), 3.81 (s, 3 H), 6.85 (dd, J = 3.1 Hz, J = 8.9 Hz, 1 H), 6.89 (d, J = 3.1 Hz, 1 H), 6.91 (d, J = 8.9 Hz, 1 H), 7.00 (d, J = 8.7 Hz, 2 H), 7.04–7.05 (m, 4 H), 7.50 (d, J = 8.7 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 55.8 (CH_3), 56.3 (CH_3), 112.8 (d, J_{CF} = 22.6 Hz, 2 × CH), 116.2 (CH), 116.4 (CH), 116.7 (CH), 117.6 (2 × CH), 120.8 (d, J_{CF} = 8.3 Hz, 2 × CH), 130.8 (2 × CH), 130.9 (C_q), 132.0 (C_q), 133.2 (C_q), 150.8 (C_q), 152.7 (d, J_{CF} = 2.6 Hz, C_q), 156.9 (d, J_{CF} = 0.7 Hz, C_q), 158.9 (d, J_{CF} = 241.7 Hz, C_q); ^{19}F-NMR (338 MHz, $CDCl_3$) δ −123.1; MS (EI) m/z (%) 325 (15) [M^+ + H], 324 (70) [M^+], 199 (15), 198 (100), 183 (28), 155 (15), 83 (13), 44 (25); HRMS (EI) calcd for $C_{20}H_{17}FO_3$ [M^+] 324.1162, found 324.1161.

***N,N*-Diethyl-2′,5′-dimethoxybiphenyl-4-amine (77).** Title compound was prepared from **30** (1.00 mmol, 277 mg), MnO_2 (1.00 mmol, 86.9 mg), and 1,4-dimethoxybenzene (**69**) (30.0 mmol, 4.14 g) according to method G. Purification by column chromatography (hexane/EtOAc = 9:1, desactivated with triethylamine) gave **77** (119 μmol, 34.0 mg, 12%) as a colorless solid: R_f = 0.3 (hexane/EtOAc = 9:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.19 (t, J = 7.1 Hz, 6 H), 3.39 (q, J = 7.1 Hz, 4 H), 3.75 (s, 3 H), 3.80 (s, 3 H), 6.72 (d, J = 9.0 Hz, 2 H), 6.77 (dd, J = 3.1 Hz, J = 8.9 Hz, 1 H), 6.90 (dd, J = 6.9 Hz, J = 10.2 Hz, 2 H), 7.43 (d, J = 9.0 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 12.7 (2 × CH_3), 44.3 (2 × CH_2), 55.8 (CH_3), 56.3 (CH_3), 111.1 (2 × CH), 111.8 (CH), 112.6 (CH), 116.2 (CH), 125.0 (C_q), 130.3 (2 × CH), 132.0 (C_q), 146.9 (C_q), 150.9 (C_q), 153.8 (C_q); MS (EI) m/z (%) 286 (11) [M^+ + H], 285 (52) [M^+], 271 (22), 270 (100), 255 (11), 241 (12), 240 (22), 198 (14), 151 (10), 135 (15), 44 (17); HRMS (EI) calcd for $C_{18}H_{23}NO_2$ [M^+] 285.1729, found 285.1729.

2,5-Dichloro-4′-nitrobiphenyl (78). Title compound was prepared from **2** (797 μmol, 200 mg), MnO_2 (797 μmol, 69.3 mg), and 1,4-dichlorobenzene (**70**) (23.9 mmol, 3.51 g) according to method G. Purification by column chromatography (hexane/EtOAc = 10:1) gave **78** (287 μmol, 76.5 mg, 36%) as a yellowish solid: R_f = 0.6 (hexane/EtOAc = 10:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33–7.36 (m, 2 H), 7.45 (d, J = 9.0 Hz, 1 H), 7.60 (d, J = 8.9 Hz, 2 H), 8.31 (d, J = 8.9 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 123.3 (2 × CH), 129.4 (CH), 130.4 (2 × CH), 130.6 (C_q), 130.8 (CH), 131.4 (CH), 133.1 (C_q), 139.7 (C_q), 144.5 (C_q), 147.6 (C_q); MS (EI) m/z (%) 271 (11), 270 (14), 269 (71), 268 (16) [M^+ + H], 267 (100) [M^+], 237 (15), 211 (14), 209 (19), 188 (31), 187 (14), 186 (99), 151 (32), 150 (31), 93 (18), 83 (12), 75 (16); HRMS (EI) calcd for $C_{12}H_7Cl_2NO_2$ [M^+] 266.9854, found 266.9856.

2,4,6-Trimethoxy-4′-nitrobiphenyl (79). Title compound was prepared from **2** (1.00 mmol, 251 mg), MnO_2 (2.00 mmol, 174 mg), and 1,3,5-trimethoxybenzene (**71**) (30.0 mmol, 5.05 g) according to method G. Purification by column chromatography (hexane/EtOAc = 4:1) gave **79** (595 μmol, 172 mg, 59%) as a colorless solid: R_f = 0.4 (hexane/EtOAc = 4:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.74 (s, 6 H), 3.88 (s, 3 H), 6.23 (s, 2 H), 7.51 (d, J = 8.9 Hz, 2 H), 8.22 (d, J = 8.9 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 55.4 (CH_3), 55.8 (2 × CH_3), 90.9 (2 × CH), 110.2 (C_q), 122.7 (2 × CH), 132.2 (2 × CH), 141.8 (C_q), 146.3 (C_q), 158.2 (2 × C_q), 161.6 (C_q); MS (EI) m/z (%) 290 (17) [M^+ + H], 289 (100) [M^+], 288 (6), 260 (7), 259 (6), 228 (17), 213 (13), 185 (9), 170 (7), 126 (6), 114 (7); HRMS (EI) calcd for $C_{15}H_{15}NO_5$ [M^+] 289.0950, found 289.0950.

2,4,6-Trimethoxybiphenyl-4′-carbonitrile (80). Title compound was prepared from **63** (1.00 mmol, 233 mg), MnO_2 (2.00 mmol, 174 mg), and 1,3,5-trimethoxybenzene (**71**) (15.0 mmol, 2.52 g) according to method G. Purification by column chromatography (hexane/EtOAc = 4:1 → 3:1) gave **80** (504 μmol, 136 mg, 50%) as a yellowish solid: R_f = 0.4 (hexane/EtOAc = 4:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.73 (s, 6 H), 3.87 (s, 3 H), 6.23 (s, 2 H), 7.44 (d, J = 8.6 Hz, 2 H), 7.64 (d, J = 8.6 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 55.4 (CH_3), 55.8 (2 × CH_3), 90.9 (2 × CH), 109.8 (C_q), 110.5 (C_q), 119.4 (C_q), 131.3 (2 × CH), 132.1 (2 × CH), 139.5 (C_q), 158.1 (2 × C_q), 161.4 (C_q); MS (EI) m/z (%) 270 (18) [M^+ + H], 269 (100) [M^+], 240 (12), 153 (14), 140 (13), 116 (17), 85 (11), 83 (15), 44 (16); HRMS (EI) calcd for $C_{16}H_{15}NO_3$ [M^+] 269.1052, found 269.1053.[63]

4-Nitro-4′-phenoxybiphenyl and 4-Nitro-2′-phenoxybiphenyl (81). Compound **81** was prepared from **2** (1.00 mmol, 251 mg), MnO_2 (2.00 mmol, 174 mg), and diphenylether (**72**) (15.0 mmol, 2.55 g, 2.38 mL) according to method G. Purification by column chromatography (hexane/EtOAc = 19:1 → 4:1) gave **81** (540 μmol, 157 mg, 54%) as a mixture of ortho and para as colorless liquids. **4-Nitro-4′-phenoxybiphenyl**: R_f = 0.4 (hexane/EtOAc = 19:1); ^{1}H

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NMR (360 MHz, $CDCl_3$) δ 7.05–7.13 (m, 3 H), 7.13–7.20 (m, 1 H), 7.26–7.31 (m, 1 H), 7.33–7.48 (m, 3 H), 7.60 (d, J = 9.0 Hz, 1 H), 7.71 (dd, J = 2.2 Hz, J = 9.0 Hz, 2 H), 8.29 (dd, J = 2.2 Hz, J = 9.0 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 118.9 (2 × CH), 119.0 (CH), 119.1 (2 × CH), 124.2 (2 × CH), 127.4 (2 × CH), 128.8 (2 × CH), 129.8 (2 × CH), 133.4 (C_q), 146.8 (C_q), 146.9 (C_q), 156.4 (C_q), 158.5 (C_q); MS (EI) m/z (%) 292 (20) [M^+ + H], 291 (100) [M^+], 261 (4), 215 (4), 153 (4), 152 (29), 151 (5), 139 (6), 77 (6), 51 (3); HRMS (EI) calcd for $C_{18}H_{13}NO_3$ [M^+] 291.0895, found 291.0895.[64]

4-Nitro-2′-phenoxybiphenyl: R_f = 0.4 (hexane/EtOAc = 19:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.92 (dd, J = 1.1 Hz, J = 8.7 Hz, 2 H), 7.02–7.09 (m, 2 H), 7.23–7.32 (m, 3 H), 7.35–7.41 (m, 1 H), 7.45–7.48 (m, 1 H), 7.72 (d, J = 9.0 Hz, 2 H), 8.22 (d, J = 9.0 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 118.2 (2 × CH), 120.0 (CH), 123.3 (CH), 123.4 (2 × CH), 124.2 (CH), 129.8 (2 × CH), 129.9 (C_q), 130.1 (2 × CH), 130.2 (CH), 131.0 (CH), 131.2 (C_q), 144.6 (C_q), 153.8 (C_q), 157.1 (C_q); MS (EI) m/z (%) 292 (18) [M^+ + H], 291 (100) [M^+], 244 (13), 218 (9), 215 (14), 202 (9), 152 (15), 151 (10), 139 (10), 83 (9), 77 (9); HRMS (EI) calcd for $C_{18}H_{13}NO_3$ [M^+] 291.0895, found 291.0895.

***tert*-Butyl 2-(4-(4-Fluorophenoxy)phenyl)azoxycarboxylate (82).** To a stirred solution of **12** (63 μmol, 20 mg) in chloroform (0.10 mL), a solution of *m*-CPBA (158 μmol, 27 mg) in chloroform (0.30 mL) was added dropwise, and the mixture was heated to 60 °C for 1 h. After cooling to rt, the reaction mixture was washed with aqueous Na_2SO_3 (2 M) and dried over Na_2SO_4. Compound **82** (63 μmol, 22 mg, *quant.*) was obtained as a red solid: R_f = 0.7 (hexane/EtOAc = 4:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.62 (s, 9 H), 6.97 (d, J = 9.4 Hz, 2 H), 7.03–7.13 (m, 4 H), 8.16 (d, J = 9.4 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 27.9 (3 × CH_3), 85.3 (C_q), 116.8 (d, J_{CF} = 24.1 Hz, 2 × CH), 116.9 (2 × CH), 121.9 (d, J_{CF} = 8.5 Hz, 2 × CH), 124.6 (2 × CH), 140.5 (C_q), 151.0 (d, J_{CF} = 3.7 Hz, C_q), 156,6 (C_q), 159.7 (d, J_{CF} = 242.9 Hz, C_q), 162.2 (C_q); MS (EI) m/z (%) 332 (17) [M^+], 276 (12), 259 (52) [$M^+ - C_4H_9O$], 217 (21) [M^+ − NBoc], 204 (33), 203 (53), 188 (24), 187 (81) [M^+ − NONBoc], 160 (14), 159 (91), 133 (36), 95 (10), 75 (13), 58 (16), 57 (100), 56 (13), 55 (10), 50 (10); HRMS (EI) calcd for $C_{17}H_{17}FN_2O_4$ [M^+] 332.1172, found 332.1172.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(41) Compound **63** was prepared from 4-cyanophenylhydrazine according to the general procedure reported above (cf. Scheme 3).
(42) Aryl radicals are considered as electrophilic when compared to other carbon-centered radicals. On a general scale including strongly electrophilic radicals such as fluorine, they have been classified as moderate to weak nucleophiles: De Vleeschouwer, F.; van Speybroeck, V.; Waroquier, M.; Geerlings, P.; de Proft, F. *Org. Lett.* **2007**, *9*, 2721.
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(45) **2**: λ_{max} = 284 nm; **12**: λ_{max} = 236 nm, 321 nm; **30**: λ_{max} = 267 nm, 434 nm.
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